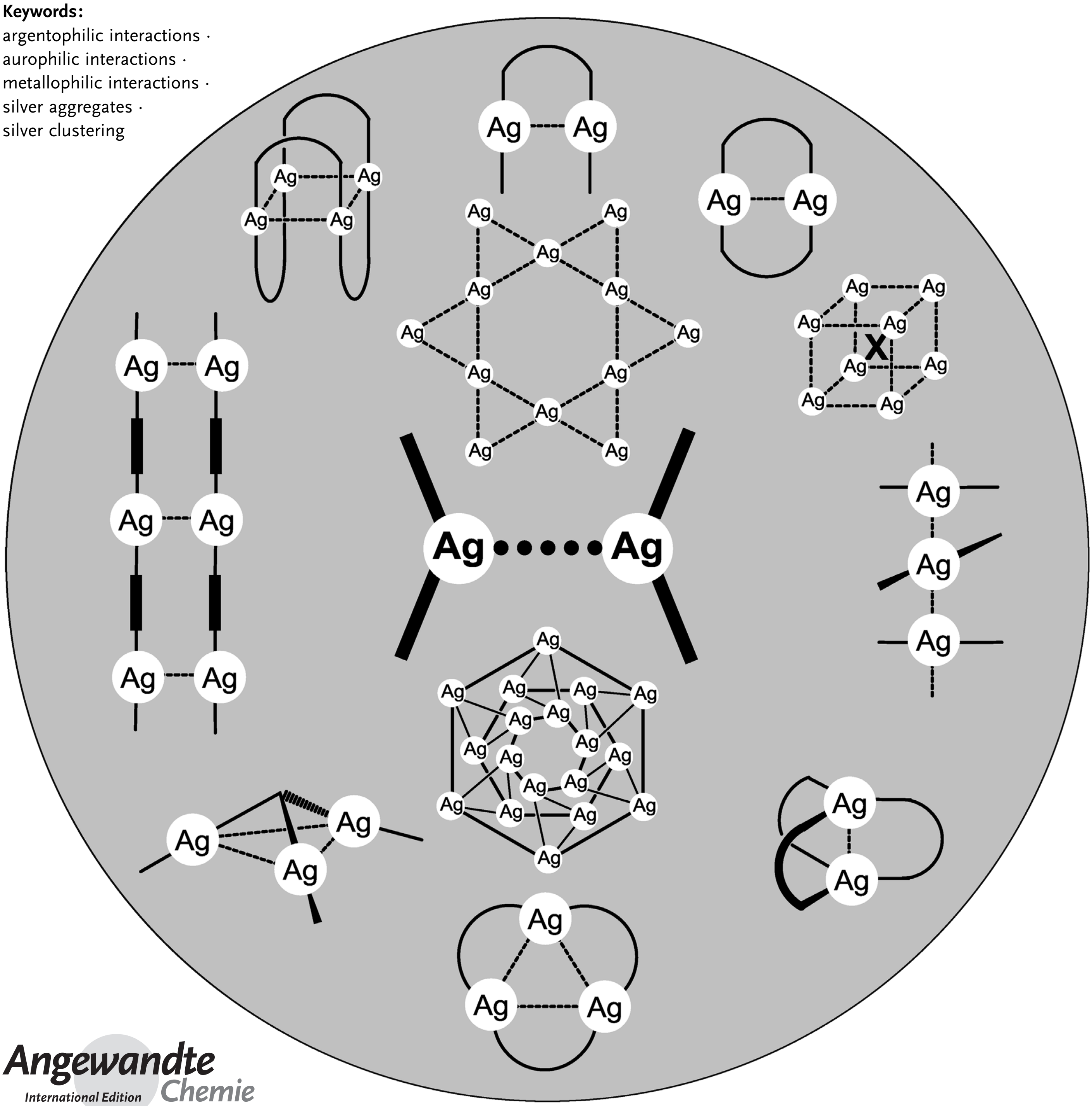
DOI: 10.1002/anie.201405936

Argentophilicity

Argentophilic Interactions

Hubert Schmidbaur and Annette Schier*

Keywords:
argentophilic interactions ·
aurophilic interactions ·
metallophilic interactions ·
silver aggregates ·
silver clustering



Angewandte International Edition Chemie

The decade 1990–2000 saw a growing interest in aurophilic interactions in gold chemistry. These interactions were found to influence significantly a variety of structural and other physical characteristics of gold(I) compounds. The attention paid to this unusual and counterintuitive type of intra- and intermolecular bonding between seemingly closed-shell metal centers has rapidly been extended to also include silver chemistry. Hundreds of experimental and computational studies have since been dedicated to the argentophilicity phenomenon. The results of this development are reviewed herein focusing on molecular systems where two or more silver(I) centers are in close contact leading to specific structural characteristics and a variety of novel physical properties. These include strongly modified ligand-to-metal charge-transfer processes observed in absorption and emission spectroscopy, but also colossal positive and negative thermal expansion on the one hand and unprecedented negative linear compressibility of crystal parameters on the other.

From the Contents

1. Introduction

A Review published in 1987 by Martin Jansen with the title "*Homoatomic d^{10}–d^{10} interactions and their influence on the structure and properties of matter*" summarized for the first time the experimental evidence for possible bonding interactions between metal cations with a "closed-shell" electronic configuration.[1] These observations had previously gone largely unnoticed even though a large number of unexplained pertinent phenomena had called for greater attention. The majority of the cases compiled in Jansen's Review of the mid-1980s with about 150 references were taken from solid-state silver(I) chemistry. Many binary and ternary solid phases containing silver(I) as a major component, but also simple silver(I) salts, had been shown to exhibit a strange aggregation of the silver cations in various structural domains leading not only to light absorption in the visible region—and therefore to color (yellow Ag_3PO_4) and photosensitivity (AgBr)—but also to electronic conductivity and other properties unexpected for simple metal salts. The determination of the crystal structure of the most common silver salt, $AgNO_3$, had shown that the silver cations are arranged in pairs with an Ag–Ag distance of only 3.22 Å,[2] and zigzag chains of silver cations with short Ag–Ag spacings of 3.032 Å were found, for example, in the silver trisulfimide, $Ag_3(S_3N_3O_6)\cdot(H_2O)_3$.[3]

In contrast, only very few examples of comparable phenomena had been observed and discussed in molecular silver(I) chemistry. Therefore most of the early models used for a theoretical description of the unexpected interactions between metal cations with a d^{10} "closed-shell" configuration were based on the situation in three-dimensional lattices.[1] Molecular systems were treated first by Hoffmann et al.[4,5] in extended Hückel molecular orbital (EHMO) analyses which suggested that even at this then still crude level of theory a hybridization of sets of s, p, and d atomic orbitals appears to lead to significant bonding interactions between coinage metal cations Cu^+, Ag^+, and Au^+. This concept was also shown to be valid for extended multidimensional systems.[6,7]

The 1980s also saw a rapid expansion of the chemistry of gold in general, and of gold(I) coordination chemistry in particular, and this development provided a plethora of structural data of new mono- and polynuclear gold(I) complexes.[8] Owing to the notoriously low coordination number of gold(I) in its complexes (generally linear two-coordination),[9–11] the configurations and conformations of polynuclear complexes, as well as the modes of aggregation of mononuclear units in crystals, allow for many close intra- and intermolecular contacts between Au^+ centers.[12] For Ag^+ ions, the preference for two-coordination is less pronounced and limited to complexes either with bulky or with particularly strong and soft ligands, which reduces the number of examples with a wide-open coordination sphere quite considerably compared to the gold analogues.[11]

This progress in gold coordination chemistry prompted the introduction of an illustrative terminology for the Au^+–Au^+ interactions, and in 1988 the terms "aurophilicity", "aurophilic bonding", and "aurophilic interactions" were therefore proposed and have been met with rapid acceptance.[13–18] The combination of *aurum* (Latin for gold, used also in its symbol as an element) and *philein* (Greek) for a "distinct preference" or "affinity" (love) makes its meaning (in chemistry) immediately obvious. For that reason, the linguistically more logical combination with the Greek *chrysos* for gold, to give "*chrysophilic* interactions", was not the alternative of choice. Shortly thereafter, the related phenomena observed in silver chemistry were addressed as

---

[*] Prof. Dr. H. Schmidbaur, Dr. A. Schier
Department Chemie, Technische Universität München
85747 Garching (Germany)
Prof. Dr. H. Schmidbaur
Chemistry Department, King Abdulaziz University
Jeddah 21589 (Saudi Arabia)

"*argentophilicity*", "*argentophilic* bonding", or "*argentophilic* interactions", using again the Latin "*argentum*" and not the Greek "*argyros*". To indicate the general validity of the concept in coinage metal chemistry, the term "*numismophilicity*" was proposed (from the Latin word *numisma* for a coin) by Vicente et al. in 1993,[19] but this was not used much because an even more general notion was needed to include closed-shell cations of metals outside the coinage-metal group. When the term "*metallophilicity*" was introduced by Pyykkö et al. in 1994,[20] this move has also found broad acceptance, and the term is now used as a unifying label in a rapidly growing number of texts.[21–27] A literature search for the term now meets hundreds of publications particularly in gold, silver, and copper chemistry.

1.1. A Note on Conflicting Terminologies

Surprisingly, the serious conflict in terminology that arose with the introduction of the term "argentophilic" into chemistry after 1990 went almost unnoticed. None of the chemistry authors has since ever mentioned that this term had already been introduced half a century earlier for a quite different matter. This observation is a good illustration of the broad gaps or high border walls between disciplines, in this case between chemistry and medicine: Silver salts, and in particular silver nitrate, have been used as analytical reagents in histology throughout the 20th century and up to the present time.[28] Distinct components of human and animal tissues show a staining after treatment with silver salts either directly or after reduction with formalin or other reductants, and these components are called "argentophilic" proteins,[29] bodies, plaques,[30] granules, globules,[31] fibers, papillar patterns,[32] inclusions, reticulae, deposits, materials etc. The analytical targets ("argentophilia") are identified by their reaction with silver salts used in various histochemical techniques to detect "argentophilic" structures and characteristics.[33] The analytical methods based on this reaction are currently highly relevant in the research and diagnosis of tumor tissues, leukemia, Alzheimer, and Creutzfeld–Jakob and other diseases.[32,34,35] A good part of the earlier pertinent publications have used the fully Greek alternative, namely, "*argyrophilic*",[28] which clearly did not lead to any confusion for those educated in both ancient languages. In addition, in publications in German, the term "argentaffin" has appeared,[36] but has not been used widely.

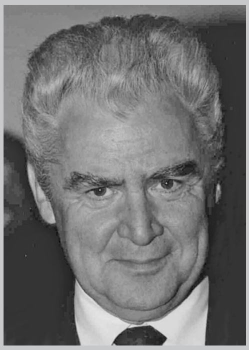
A similar development has taken place, on an as yet smaller scale, for the term "metallophilic". In medicine, current literature now refers, for example, to "metallophilic macrophages",[34] "selective metallophilicity of microorganisms",[35] "metallophiles with specific receptors",[36] "metallophilic zones" of tissues etc. However, these notions do not include the specific silver reactions mentioned above, but refer to biological substrates which generally accumulate certain metals.

Clearly, because researchers in chemistry and medicine live in largely separated worlds, no confusions or conflicts have yet been reported. Fortunately, there has not been a similar overlap in the use of the term "aurophilic". Even though solutions of gold salts were also used as reagents in histology and pathology to mark specific tissues,[28] the response has not been called "aurophilic".

In summary, scientists describing interactions between metal atoms or ions with closed-shell electronic configuration in chemistry can avoid nomenclature or terminology conflicts by using the terms "metallophilic bonding" or "metallophilic interactions", which are generally not used in the medical literature. In the present article, any close mutual approach of silver centers in molecular silver compounds is addressed as an "argentophilic contact" which is associated with an "argentophilic interaction" that may be weakly bonding and affect the structural and electronic characteristics in a way that can be recognized by standard analytical techniques.

1.2. Scope of the Review

In this Review of argentophilic interactions, the literature on the homoatomic metallophilic contacts between silver atoms is critically presented, excluding heteroatomic combinations of silver atoms with other metals. There is a wealth of information on mixed-metal systems including, not only the coinage congeners Cu and Au,[19] but also many of the other neighboring elements of silver in the periodic table. It is unfortunate that by this limitation, set to keep the article within an acceptable frame, some of the important new directions in this area of research cannot be accounted for. Fortunately, some key developments have recently been



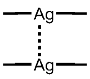
Hubert Schmidbaur is Professor Emeritus at the Department Chemie of Technische Universität München. He has published several books on topics in inorganic, organometallic and coordination chemistry of main-group and transition metals based on work carried out at the universities in Munich, Marburg, and Würzburg. For almost 50 years, the chemistry of gold and silver has been his favorite area of research. Several memberships in academies and learned societies and a list of national and international honors reflect his achievements in research and his profile as an academic teacher.

Annette Schier is Academic Director at the Department Chemie of Technische Universität München. For more than two decades she was involved in the crystallographic investigations of metallophilic interactions particularly in gold and silver compounds. She was in charge of the organization of several major chemistry conferences and is engaged in advanced teaching assignments at Technische Universität München.

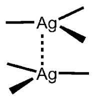
reviewed by Sculfort and Braunstein, and their article reflects the highlights of the art in this area.[37] In all the papers cited and discussed herein, the authors themselves have explicitly used the argentophilicity terminology to rationalize structural, spectroscopic, or other physical phenomena. In fact, the publications can easily be found by following just this lead.

In a first part (Section 2), we introduce some generally valid criteria that support the concept of argentophilic bonding based on structural and other physical data of simple, representative classes of compounds. The results obtained in computational studies of related model systems are also briefly introduced. The second part (Section 3) presents a selection of classical and more recent results on prominent groups of compounds which have been organized according to the following structural principles:

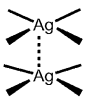
For about two decades already, argentophilic interactions have been differentiated in the literature as unsupported or supported, depending on the absence (**1a**–**c**) or presence (**2a**–**g**) of any ligand connectivity between the silver cations concerned. In the unsupported, the Ag–Ag contact often represents the closest approach between independent molecular units and therefore its effect is easier to evaluate. In contrast, for the ligand-supported cases the assessment of the significance of any argentophilic interactions only on the basis of, for example, the distance criterion (see Section 2.1) is more difficult because clearly the structural requirements of the ligand bridges may enforce either shortened or elongated Ag^+–Ag^+ contacts. By definition, single and multiple unsupported interactions are observed mainly between independent mono- or polynuclear units (i.e. intermolecular), supported argentophilic contacts are found within di- or polynuclear units (i.e. intramolecular). With only one ligand bridge, the contact is called mono- or semi-supported (**2a**, **2b**), while two or three bridges make it double- or triple-supported (**2c**–**g**). The units involved can be simple oligonuclear molecules in the form of short or long chains, small and large rings or cages, as well as layers.



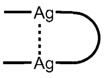
1a



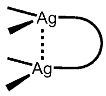
1b



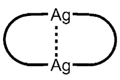
1c



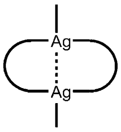
2a



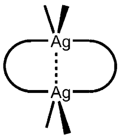
2b



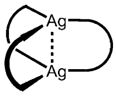
2c



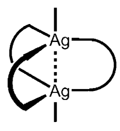
2d



2e



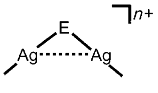
2f



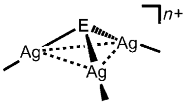
2g

As already indicated in the formulae **1** and **2**, the silver atoms may have coordination numbers of up to four, but for tri- or tetracoordination the distances to the donor atoms are generally very different suggesting that the third or fourth donor is only loosely attached in a non-standard distorted coordination geometry (not strictly trigonal planar or tetrahedral). This borderline situation arises mainly with chelating or other polydentate ligands which place extra donor sites close to the silver centers following their conformational preferences. In exceptional cases the coordination number of the silver cations may even exceed four.

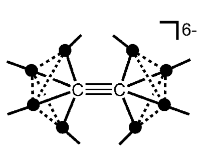
The recent work on the clustering of silver cations at a common central mono- or diatomic unit, such as in onium cations of the types **3a**, **3b** with E representing a halide or a chalcogenide anion, or in multi-cation clusters around a sulfide or an acetylide anion for which the symbols $[S@(Ag)_8]^{6+}$ or $[C_2@Ag_8]^{6+}$ (**3c**) have been introduced, deserves special consideration (Section 3.4). In these cases, the close mutual approach of the cations leads to particularly intimate argentophilic contacts.



3a



3b



3c

Throughout this article, all silver atoms are in the "closed-shell" +1 oxidation state, which excludes, in particular, the vast area of silver clusters in which mixed oxidation states of the silver atoms (between 0 and +1) lead to an entirely different bonding situation not to be addressed as argentophilic interactions.

2. Experimental and Computational Evidence for Argentophilic Bonding

2.1. The Ag–Ag Distance Criterion

For more than two decades, assessments of argentophilic interactions have been made mainly on the basis of short Ag–Ag distances in and between a large variety of molecules, and in multidimensional systems. For comparison, the 1984 edition of the standard treatise on "*Structural Inorganic Chemistry*" mentioned less than half a dozen structures where surprisingly close Ag–Ag contacts had been observed, suggesting "some metal–metal interaction".[38] In the discussion of the results of the structure determination of a compound $[Me_3PAgPMe_3]^+$ $[Ph\text{-}C{\equiv}CAgC{\equiv}CPh]^-$ by Corfield and Shearer in 1966 the distance of 3.033 Å between the silver atoms in an alternating chain of cations and anions was still listed under "non-bonding contacts".[39] Similarly, even the short Ag–Ag distance of 2.756 Å in the dinuclear 1:1 complex of 1,8-naphthyridine and $AgClO_4$ (type **2c**) went without any notice of its possible significance.[40] In the late 1980s,[41] following a structural study of dinuclear silver(I) formamidato complexes (also of type **2c**, see Section 3.7.3), Cotton et al. refuted explicitly the assignment of any Ag–Ag bonding in these and related examples based only on the presence of short intramolecular contacts. Even though the Ag–Ag distance was found to be as short as 2.705(1) Å, calculations on the SCF X_α SW level seemed to indicate that neither π nor δ bonding can make a significant bonding contribution, while the σ interactions are largely compensated by σ* interactions leaving little or no net Ag–Ag bonding. More recent detailed theoretical analyses of metallophilic bonding between coinage-metal cations have provided a deeper and more balanced insight into the specific correlations that can help to rationalize the interactions.[20–27,42]

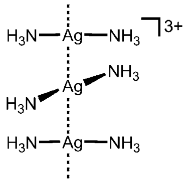
In the current literature there appears to be general agreement that argentophilic interactions must be considered to be present in all molecular and crystal structures where two or more low-coordinated silver cations with a $[Kr]4d^{10}$ electronic configuration appear in pairs or groups with sub-van der Waals contacts between the metal atoms (shorter than ca. 3.44 Å).[43] The lower end of the range of distances to be considered is marked by the length of the covalent bond observed in the diatomic molecule Ag^0_2 or in silver(II) compounds with a $[Ag^{2+}_2]^{4+}$ core, where the open shells $[Kr]d^{10}s^1$ and $[Kr]d^9s^0$ allow for standard Ag–Ag single bonds. For $[Kr]d^{10}s^1$, the gas-phase value of 2.5335(5) Å in the Ag_2 molecule is available,[44] but for $[Kr]d^9s^0$, there are no simple representative examples. The midway between the border regions is roughly set by the shortest interatomic distance in the ccp crystals of silver metal (2.89 Å).[38] The overall range is about the same as the one previously accepted for aurophilic interactions, mainly because Ag^+ and Au^+ have almost the same cationic radius, with Au^+ being only slightly smaller.[45]

It should be noted that the metallophilicity phenomenon is counterintuitive not only because of the closed electronic shell $[Kr]4d^{10}$ for Ag^+, but also because the interaction between metal cations is expected to be Coulomb repulsive, even though there may be some charge delocalization onto the ligands. Moreover, and surprisingly, there is ample experimental evidence that argentophilic interactions are not limited to pairs of silver atoms. Multinuclear units (Ag_3^{3+}... Ag_n^{n+}) and finally chains, rings, or even layers of silver atoms were also found to be held together by these contacts. A silver cation may entertain these multi-argentophilic interactions without a significant shortening or lengthening of the standard distances (ca. 3.0 Å), and with no specific directionality.

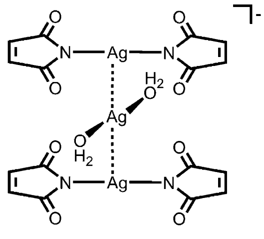
Wherever possible, most experimental or theoretical attempts to estimate the structure and energy characteristics of argentophilic interactions have tried to rely on cases or models of unsupported contacts (**1a–c**). These unsupported interactions are particularly relevant in supramolecular chemistry where in the absence of other functionalities the aggregation of the components may seem at a first glance to be solely determined by intermolecular Ag^+–Ag^+ contacts.

2.1.1. *Simple Silver(I) Complexes with Ammonia, Water, and other Small Ligands*

Simple formally unsupported examples are found, for example, in the classical crystal chemistry of di(ammino)silver salts $[H_3N\text{-}Ag\text{-}NH_3]^+X^-$. In all cases known to date, with half a dozen of different anions X^-, the cations are aggregated to form chains by argentophilic contacts with Ag–Ag distances in the narrow range of 2.9–3.1 Å and linearity for the Ag–Ag–Ag assembly, including cases where polymorphism occurs (**4**).[46–50] The N-Ag-N axes of neighboring cations are generally close to orthogonal (staggered with regard to the Ag–Ag axis), but with an exchange of the anions the dihedral angles N-Ag-Ag-N nevertheless may deviate from the 90° standard very considerably. In all comparable cases (with the same anions, investigated at about the same temperature), the distances are only slightly larger (by ca. 0.03 Å) than in the corresponding gold(I) complexes. For gold(I) complexes, a Mayer bond order[51,52] of 0.168 has been calculated for the unsupported Au–Au interaction, which accordingly is expected to be only slightly less for Ag–Ag.[53] In another theoretical study, the interaction of a di(aquo)gold cation $[H_2O\text{-}Ag\text{-}OH_2]^+$ with two bis(imido)gold cations (**5**) has been calculated as a model for the units found in the complex structure with bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxydiimide ligands (drawn as maleinimide in model **5**). This is a very rare case in which a homoleptically two-coordinate aquo complex of silver has been observed. An equilibrium Ag–Ag distance of 3.11 Å and a bond order of 0.15 have been obtained for the model system. The former compares well with the experimental data (3.087 and 3.114 Å).[54]



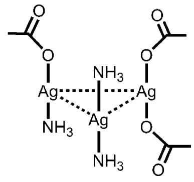
4



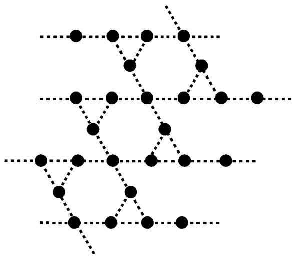
5

$[H_3N\text{-}Ag\text{-}NH_3]^+$ cations have also been found attached by argentophilic contacts to silver atoms engaged with other sets of ligands. One of the examples has the composition $[Ag_4(NH_3)_4(npt)_2(H_2O)]$ with npt = 3-nitrophthalate. In the crystals three silver atoms are associated into a triangle with Ag–Ag contact edges of 3.0191(1), 3.128(1), and 3.301(1) Å. These three silver atoms have their N-Ag-N, N-Ag-O, and O-Ag-O axes roughly perpendicular to the plane of the triangle (O = phthalate oxygen atoms, N = ammonia nitrogen atoms, **6a**). Further Ag–Ag contacts are extending from each corner of the triangle to neighbouring silver atoms to give the planar network shown schematically in **6b**. This structure is an illustrative example of infinite argentophilic bonding in two dimensions. It should be noted that all Ag atoms are strictly two-coordinate (close to perpendicular to the plane of the sheet) and all Ag–Ag contacts thus unsupported. The silver atoms can have two, three, or four nearest silver neighbors.[55]

To give an example for cases with unsupported Ag–Ag interactions between silver atoms with higher coordination numbers, short Ag–Ag distances are also found between the metal atoms of the dications $[Ag_2(NH_3)_8]^{2+}$ in the isotypical $[ZrF_6]^{2-}$ and $[HfF_6]^{2-}$ salts, where the two quasi-tetrahedral $[Ag(NH_3)_4]^+$ units are strongly flattened and some of the ammonia molecules more distant than others (Ag–N distances in the range 2.422(3)–3.142(4) Å) such that a mutual approach to give Ag–Ag distances of 3.1221(5)/3.1414(9) Å is possible (**7**). (For comparison, the Ag–N distances in the

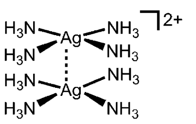


6a



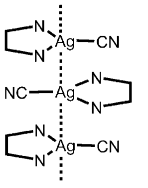
6b

cation $[H_3N\text{-}Ag\text{-}NH_3]^+$ are much shorter at an average of 2.12 Å). However, owing to the presence of so many of ammonia molecules, the Ag–Ag contacts in both cases—and in many others—may be taken as at least weakly supported by the extensive network of hydrogen bonds in the crystals.[56]



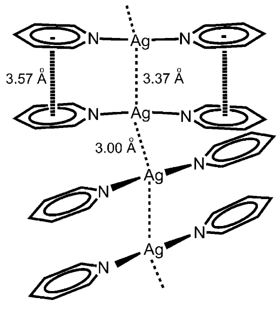
7

This observation can also be made with the 1:1 complexes of AgCN with ligands such as ethylenediamine, in which the silver atoms in the monomeric units are three coordinate. The monomers are organized in stacks with Ag–Ag contacts of 3.18 Å, supported by external hydrogen bonds (**8**, all hydrogen atoms omitted).[57] An even more obvious case has been presented for a compound with silver atoms bound to oxime functions linked by strong hydrogen bonds (Ag–Ag 3.187(1) Å).[58]



8

As another alternative, Ag–Ag interactions may be supported by π–π stacking interactions: the organization of di(pyridine)silver cations follows the same pattern as in **4** with a slightly puckered chain of silver atoms (in the presence of three different non-coordinating anions). In a dinuclear unit, the two N-Ag-N axes are staggered (**9**), and these dimers are eclipsed relative to the subsequent dimers in both directions along the string of silver atoms. Depending only slightly on the nature of the anion, the Ag–Ag distances are in the range 2.9642(2)–3.001(5) Å for the dimers, but 3.34–3.37 Å for the inter-dimer packing. Interestingly, the average distance between the pyridine rings is about 3.57 Å, indicating that the silver atoms are drawn closer together, even though the π–π stacking of the pyridine rings is already optimized at a longer distance. Accordingly, the N-Ag-N axes are bent (to an average of 175°).[59]



9

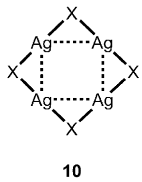
Considering all these results, it has recently been pointed out that even in the absence of ligand bridging by conventional electron-pair bonding (**1a–c**), the Ag^+–Ag^+ interaction may not really be "unsupported" in any condensed phase: Many of the ubiquitous weak forces, such as hydrogen bonding, π–π stacking, ion–ion, ion–dipole, and dipole–dipole attraction, and last but not least, van der Waals interactions, established between the ligands can influence markedly the mode of aggregation and thus co-determine the Ag^+–Ag^+ distance between the mononuclear components.[21,60]

Therefore, any estimation of the strength of the Ag–Ag bonding based only on relative distances should be taken with some reservation. There is generally a better correlation between M–M bond strength and the vibrational force constants of bonds in dinuclear homometallic compounds,[21] but as shown below (in Section 2.2), presently very few studies have been documented.[61]

It has further been demonstrated in extensive theoretical studies by Pyykkö et al. that the nature of the ligands has a significant influence on the distance and the strength of metallophilic interactions. This effect is due to both the symmetry ($C_{\infty v}$, C_{nv}, C_s etc.) and the electronic structure of the donor molecules which give rise to different mutual dispersion, induction, and dipole and multipole electrostatic interactions. Any comparison of data of complexes with different metals should therefore refer to comparable ligand systems.[62]

2.1.2. *Simple Hypothetical Model Systems $(AgX)_4$*

Several different hypothetical model systems which may best shed light on the role of argentophilic interactions owing to their simplicity have been subjected to theoretical studies, but for many of these cases there are no experimentally characterized counterparts. This is true, for example, for the series of the hypothetical tetranuclear model compounds $(AgX)_4$ with $X = H, CH_3, SiH_3, GeH_3, NH_2, PH_2, OH, F, Cl, Br$, and I recently investigated by DFT calculations. In the square-planar silver metallacycles which are the ground-state geometries (**10**), the Ag–Ag distances vary in the range 2.690–2.822 Å for electron-deficient systems (with $X = H, CH_3, SiH_3$, and GeH_3), while they are found near 3.010 Å for electron-pair donor–acceptor bonding (with X = halide, OH, NH_2), and up to as much as 3.851 Å (for $X = PH_2$). There is significant long-range diatropicity (aromaticity for $X = H, CH_3$) and paratropicity (anti-aromaticity for X = halide etc.) above/below and in the ring plane, respectively.[63] Note that in this model (**10**) there are only supported Ag–Ag contacts, which may make only very minor contributions to the overall bonding and influence the ground state geometry of the molecules very little. In the following two Sections therefore two classes of silver compounds (LAgX with L = tertiary phosphine or N-heterocyclic carbene) are highlighted, where unsupported interactions are the focus, and where theoretical and experimental data are more complementary.

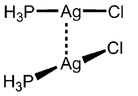


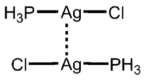
10

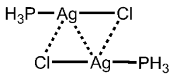
2.1.3. Phosphine Complexes [(R_3P)AgX]

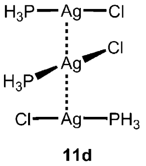
The theoretical work in this area focused first mainly on the dimerization of the phosphine complex [H_3PAgCl],[42] because the corresponding gold compounds of the type [R_3PAuX] are experimentally and theoretically well-documented reference systems.[15–26] In studies by the group of Stoll, the structure of the monomer was optimized, and for the dimer [{H_3PAgCl}$_2$] a model with a crossed (staggered) conformation (**11a**) was selected for DFT and ab initio calculations (MP2, MP2(CP), LMP2, LMP2(CP)). The results gave Ag–Ag distances in the range 2.866–2.921 Å. For any of the methods of calculation, these distances are much larger than those for the copper analogue (2.637–2.809 Å), and slightly shorter than those of the gold analogue (2.949–3.025 Å). The Ag–Ag interaction energies are in the range -30.70 to -38.90 kJ mol^{-1} indicating significant bonding. The values calculated for the Cu (-22.09 to -36.70) and Au (-34.82 to -47.79 kJ mol^{-1}) compounds have broader ranges, making a comparison difficult. The interaction is based on both dispersive and non-dispersive forces.[42]

The studies on the triad [H_3PMCl] with M = Cu, Ag, Au were refined in frequently cited work by O'Grady and Kaltsoyannis who employed methods beyond MP2 using QCISD and coupled cluster approaches. DFT calculations were also conducted, realizing though that this approach may not be reliable for van der Waals-like attractions (dispersion forces).[27] The staggered dimer was again selected as potentially the most informative model regarding the influences and the energy of the potential M–M interactions, even though the calculations indicate that the antiparallel and "shifted" (slipped) models (**11b**, **11c**) are both lower in energy. Surprisingly, the results have suggested that even though there is generally a substantial interaction energy, it rises from Cu to Ag, but then decreases from Ag to Au (and to element 111), while in MP2 calculations a steady increase had been found. The interaction energy in the dimer [{H_3PAgCl}$_2$] was determined to be approximately -15 kJ mol^{-1} which is the largest in the [{H_3PMCl}$_2$] series.


11a

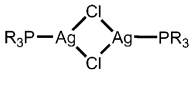

11b

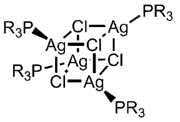

11c


11d

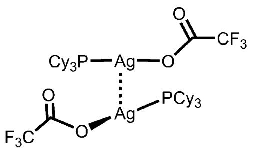
In another subsequent study, the group of Schwerdtfeger has confirmed this trend for the [{H_3PMCl}$_2$] dimers by DFT and MP2 calculations with energy-consistent small-core scalar-relativistic pseudopotentials and the corresponding large-sized valence basis sets, arriving at roughly the same value for the interaction energy. In this work, the staggered trimers (dihedral angles constrained to 90°, **11d**) have also been considered and found to exhibit even slightly larger interaction energies per Ag–Ag contact.[64]

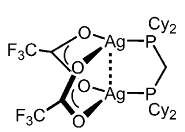
It should be noted, however, that a) no complex [(H_3P)AgX] is known, and that b) most complexes of tertiary phosphines with silver halides, [R_3PAgX], appear as monomers only if very bulky phosphines are present which preclude any aggregation. With less-bulky phosphines, oligomerization occurs either to four-membered ring dimers of the type **12a** or cubane-type tetramers **12b**, the structural variety being complemented by units with incomplete cubes or stair-type arrangements. Therefore the [{H_3PMCl}$_2$] models are not the best examples to trace metallophilic bonding.


12a


12b

The situation is different with anions other than halides: The complex [$Cy_3PAuOC(O)CF_3$] (Cy = cyclohexyl) indeed forms the expected "crossed" dimer with a monodentate ligation of the trifluoroacetate group at linearly two-coordinate silver atoms. The Ag–Ag contact of 3.095(1) Å is in the theoretically predicted range (**13a**).[65] However, already with the bidentate bis(dicyclophexylphosphino)methane, a triply supported Ag–Ag contact of 2.8892(9) Å is established (type **2f**; **13b**). The trifluoroacetate groups are bridging three-coordinate silver atoms. Other examples of this type are described below.


13a

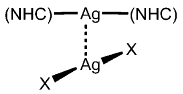

13b

2.1.4. N-Heterocyclic Carbene Complexes [(NHC)AgX] and Their Isomers

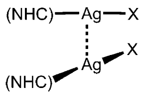
The situation is quite different for complexes [(NHC)AgX] where NHC is an N-heterocyclic carbene ligand and X a halogen. Because of the rapidly growing importance of these compounds as catalyst precursors, there is a much greater wealth of both experimental and theoretical data. The extremely complex structural chemistry was summarized early on in three Review articles.[66–68] As shown therein, with very bulky NHCs the molecules are heteroleptically substituted monomers with a linear C-Ag-X axis, but in several cases ligand redistribution has led also to ionic isomers made up of homoleptically substituted cations and anions [$Ag(NHC)_2$]$^+$[AuX_2]$^-$. These ions have linear C-Ag-C and X-Ag-X axes, respectively. In crystal structures, these ions may be either separated, or associated through argentophilic contacts with only minor distortions of this geometry, depending on the nature of the NHC ligand (**14a**).

With smaller NHCs, [(NHC)AgX] complexes are aggregated in virtually all cases known to date, but the structural pattern of the aggregates may be very different depending on the distribution of the substituents at the NHC and their electronic influence. Without ligand redistribution, two monomers may form a dimer by establishing an Ag–Ag contact retaining the C-Ag-X linearity at different torsional angles (**14b**, **14c**). However, the vectors of the two monomers may be shifted in opposite directions lengthening the Ag–Ag distances and shortening the Ag–X distances to reach finally a four-membered ring (Ag_2X_2) and induce a bending of the C-Ag-X axes (**14d**). It should be noted that the dimers thus reach an arrangement where the Ag_2X_2 ring resembles that in complexes **12a**, or one face of the cube $[\{(R_3P)AgX\}_4]$ formed by the complexes with tertiary phosphines (**12b**).

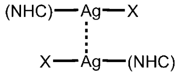
Moreover, with small NHCs ionic isomers are also observed which have their ions arranged in ion pairs (**14a**) or in alternating chains built through argentophilic bonding without major bending of the molecular axes (**14e**). Finally, in a third structural alternative for the same 1:1:1 stoichiometry (for L:Ag:X), the anions may be paired up in cyclic dimers $[(XAgX)_2]^{2-}$ which have the two cations attached again through Ag–Ag contacts (**14f**).



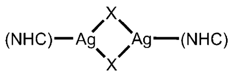
14a



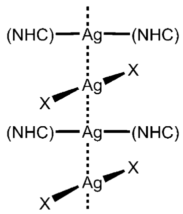
14b



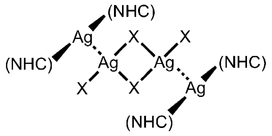
14c



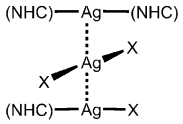
14d



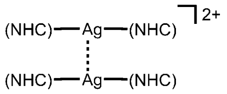
14e



14f



14g



14h

As shown by the groups of Nolan and Ghosh, various types of complexes indeed appear consistently as dimers (**14b**, **14c**) in the solid state and their structures and bonding characteristics have been investigated in great detail.[69,70] In crystals of complexes [(NHC)AgCl] with NHC = 1,3,4,5-tetramethyl-, 1,3-diisopropyl-, and 1,3-dicyclohexylimidazol-2-ylidene, for example, the dimeric units have Ag–Ag distances of 3.0673(3), 3.0181(6), and 3.124(2) Å, respectively. The gold analogue of the 1,3-dicyclohexylimidazol-2-ylidene was also investigated and shown to have a slightly longer Au–Au contact of 3.1566(6) Å. For certain NHCs only a partial ligand redistribution has been observed which leads to trinuclear aggregates (**14g**) comprising an $[(NHC)_2Ag]^+$ cation, an $[AgCl_2]^-$ anion, and an [(NHC)AgCl] molecule associated by two Ag–Ag contacts (3.0242(2) and 3.0752(2) Å). With very bulky NHCs, the molecules are monomers in the crystal structures, no doubt for steric reasons.[70] Similar results have been obtained with imidazol-based NHCs bearing a dangling ω-aminoalkyl substituent. The Ag–Ag contacts between $[AgCl_2]^-$ anions and $[(NHC)_2Ag]^+$ cations along the chain of silver atoms are near 3.20 Å for a set of different substitution patterns.[71]

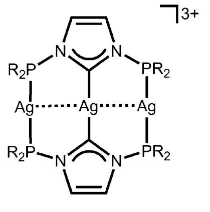
Crystals of the complexes of 1-benzyl-3-(*N*-*tert*-butylacetamido)imidazol-2-ylidene with AgCl and AuCl are isomorphous and contain dimers in staggered conformation (**14b**) with very similar dimensions, including contacts Ag–Ag 3.1970(12) and Au–Au 3.2042(2) Å. The C-Ag-Cl axis is more strongly bent (to 167.3(2)°) than the C-Au-Cl axis (to 172.38(8)°) allowing a particularly close Ag–Ag contact. The bonding in the dimers has been analyzed by DFT methods, and interaction energies of 12.8 (Ag) and 8.6 (Au) kcal mol^{-1} have been calculated.[69] These findings indicate that for this type of compound argentophilic interactions are indeed stronger than aurophilic interactions, and that bond length and bond energy are correlated.[21] Between cations and anions of compounds $[Ag(NHC)_2]^+{}_2[Ag_2X_4]^{2-}$ with X = Cl, I (**14f**) short Ag–Ag contacts of 2.984(1) and 3.135(4) Å have been observed. This situation is remarkable since in this combination the silver atoms have different coordination numbers (2 in the cations, 3 in the anions), illustrating again the versatility of this type of interactions.[72]

The most recent theoretical investigation by Pinter et al. of [(NHC)MX] complexes and their dimers $[\{(NHC)MX\}_2]$ with M = Cu, Ag, Au and X = F, Cl, Br, I used ab initio interaction energies, Ziegler–Rauk-type energy decomposition analysis, the natural orbital for chemical valence (NOCV) framework, and non-covalent interaction (NCI) indices to further characterize the metallophilic interactions.[73] The dimers were found to predominantly adopt the head-to-tail arrangement (**14c**) with interaction energies of -25 kcal mol^{-1} for M = Ag, Au and of -19.7 kcal mol^{-1} for M = Cu. However, the inclusion of solvation effects and thermal motions leads to a destabilization of the dimers by about 15 (Ag, Au) and 8 kcal mol^{-1} (Cu) suggesting monomer–dimer equilibria in solution. The major contribution to the energy associated with the dimerization arises from electrostatic interactions $[(NHC)^{\delta+}\text{-}X^{\delta-}]$, followed by dispersion and orbital interactions. The results have confirmed the similarity of argentophilic and aurophilic interactions and that the cuprophilic interaction is significantly weaker. The study of the influence of the four halide anions (F, Cl, Br, I) on the gas-phase dimers has shown that iodide leads to the shortest Ag–Ag contact (3.04 Å) and fluoride to the longest (3.64 Å), but to higher interaction energies for fluoride (F -26.3, Cl -22.6, Br -22.3, I -23.0 kcal mol^{-1}), mainly owing to electrostatic interactions $[(NHC)^{\delta+}\text{-}X^{\delta-}]$ and possibly hydrogen bonding.

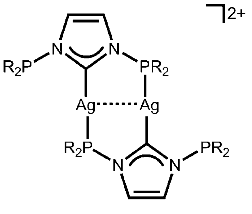
It has been pointed out that these results[73] deviate from those of previous studies of the $[\{H_3PMX\}_2]$ analogues,[22,42,74] mainly owing to the consideration of different conformers: the parallel head-to-tail conformation (**14c**) as opposed to the crossed conformation (**14b**), where the $[(\mathrm{NHC})^{\delta+}\text{-}\mathrm{X}^{\delta-}]$ interactions play a less-prominent role.

The cations $[(\mathrm{NHC})_2\mathrm{Ag}]^+$ with NHC = 1,3-bis(pyridinylmethyl)imidazol-2-ylidene and Cl^- or $\mathrm{PF_6}^-$ as the counterions form dimers **14h**, but therein the Ag–Ag contact is as long as 3.650(2) Å, and it is likely that the (Coulomb-repulsive) dimerization is only supported by π–π stacking of the imidazol rings.[75]

In a very recent experimental study by the group of Braunstein, *N*- and *N,N'*-diphosphanyl substituted NHCs have been employed as ligands for silver triflate. Dinuclear complexes have the two silver atoms in a heteroleptic bonding (phosphine/carbene), while for the trinuclear complexes the homoleptic bonding (phosphine/phosphine or carbene/carbene) is enforced (**15**, **16**). The Ag–Ag contacts in the trinuclear complex trication, 2.7599(3) Å, are among the shortest found for (supported) argentophilic interactions.[76]



15



16

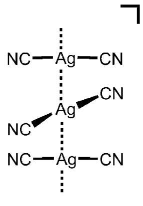
The reactions of silver(I) thiolates $(\mathrm{AgSR})_n$ with $\mathrm{PR_3}$ or NHC ligands (L) afford tetranuclear complexes $[\mathrm{Ag_4(SR)_4(L)_2}]$. The structures are based on an eight-membered ring of alternating Ag and S atoms with transannular Ag–Ag contacts and Ag–Ag edges bridged by S atoms. This multinuclear type of strongly supported argentophilic contacts is considered in Section 3.4.1.[77] It is generally true that Ag–S interactions overrule Ag–Ag interactions owing to the pronounced affinity of silver for sulfur.[78] Similar observations were made with gold(I) thiolate or thiophosphate complexes.[15–18]

Carbene carbon atoms bridging two silver atoms have been discovered in the trinuclear cation $[\mathrm{Ag_3(NHC)_3}]^{3+}$ with NHC = 1,3-dipicolylbenzylimidazol-2-ylidene. In the tetrafluoroborate salt the C_3-symmetrical triangle of gold atoms has short Ag–Ag distances of 2.777(1) Å (Section 2.4).[79]

2.2. Vibrational Spectroscopy Criteria

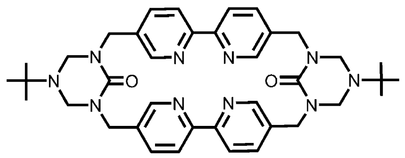
Since argentophilic interactions must have consequences for the internal molecular motions of molecules or aggregates of molecules, a few detailed investigations have been dedicated to the vibrational spectra of the silver compounds under consideration. However, owing to the complexity of most IR and Raman spectra of compounds with a variety of ligands, and the low frequencies of Ag–Ag vibrations, few studies have so far provided convincing evidence for significant bonding interactions.

Examples for unsupported interactions are found in crystals of various dicyanoargentates(I), $\mathrm{M[Ag(CN)_2]}$, where the anions are either paired or organized in linear or zigzag chains through Ag–Ag contacts (Section 3.5). The chains of $\mathrm{Ag(CN)_2}^-$ ions found in crystals of the prominent example $\mathrm{Tl[Ag(CN)_2]}$ are illustrated schematically in formula **17**. A detailed Raman study of this compound has shown that lines for the ν(Ag–Ag) vibrations can be detected in the range $\tilde{\nu} = 75$–$125\ \mathrm{cm^{-1}}$ (at 80 K) suggesting weak, but significant bonding between the silver atoms. The result was supported by extended Hückel calculations employing relativistic parameters for all atoms for the dimer, trimer, and pentamer $\{[\mathrm{Ag(CN)_2}]_n\}^{n-}$ ($n = 2, 3, 5$) which resemble segments of the chains of anions in the crystal. For the appropriate conformations, binding energies of 0.13, 0.6, and 0.7 eV were found for the depths of the corresponding potential wells.[80]

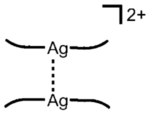


17

According to the results of a crystal-structure determination, silver atoms accommodated in the macrocycles **18a** are exposed on one side of the bowl-shaped ligand which allows Ag–Ag contacts (3.126(1) Å) between the bottoms of two bowls shown schematically in **18b**. Raman studies of the complex (with triflate counterions) in the solid state with laser excitation at $\lambda_{\mathrm{ex}} = 514.5$ nm showed new bands in the range $\lambda_{\mathrm{em}} = 55$–$174$ nm which have been assigned to Ag–Ag stretching modes. Detailed assignments were not possible owing to the complexity of the structure in which there are three different sites for tetracoordinate silver atoms. The support by the counterions is uncertain. The compound is luminescent ($\lambda_{\mathrm{ex}} = 355$ nm, $\lambda_{\mathrm{em}} = 410$, 460, and 485 nm).[81] Similar contacts have also been discussed for the dimers formed with other flat macrocycles, but there also the role of the anions is a point of concern.[60]

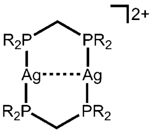


18a



18b

A Raman study of a supported argentophilic interaction has been carried out for the cyclic dications, shown in formula **19**, formed with 1,3-ditertiary phosphine ligands. In crystals of the salt with the non-coordinating hexafluorophosphate anion and R = Me, the Ag–Ag distances are 2.936(1) and 2.960(1) Å (for two independent molecules), suggesting significant bonding. Accordingly, a ν(Ag–Ag) stretching frequency was found at $\tilde{\nu} = 75\ \mathrm{cm^{-1}}$ (force constant $F = 0.18$ mdyn Å^{-1}) which again indicates argentophilic interactions. By contrast, with bromide as a coordinating anion, the Ag–Ag distance is lengthened to 3.605(2) Å and the Raman line is shifted to $\nu(\mathrm{Ag{-}Ag}) = 49\ \mathrm{cm^{-1}}$ (estimated force constant $F = 0.030$ mdyn Å^{-1}).[82] In later work by Che et al. on the cations **19** with R = cyclohexyl and associated with trifluoromethanesulfonate or hexafluorophosphate anions, very similar results were obtained by resonance Raman spectroscopy (in acetonitrile solution using the $\lambda_{ex} = 273.9$ nm excitation): d(Ag–Ag) = 2.948 Å; $\tilde{\nu}$(Ag-Ag) = 80 cm^{-1}; force constant $F = 0.203$ mdyn Å^{-1}). This work has confirmed the earlier conclusion that there is a good correlation between the distance d and the force constant F. Since for the corresponding gold complex the force constant is significantly higher ($\tilde{\nu}$(Au–Au) = 88 cm^{-1}; $F = 0.449$ mdyn Å^{-1}) for a comparable distance (2.987 Å), it has been concluded that in these specific cases the aurophilic interactions are stronger than the argentophilic interactions.[65,83]



19

2.3. Thermal Contraction and Negative Linear Compressibility

Thermal expansion of crystalline materials is a common physical property. Through the inherent anharmonicity of bond vibrations, the average distance between bonded pairs of atoms increases with temperature, and this increase is reflected in the expansion on the macroscopic scale (positive thermal expansion, PTE). Typical expansion coefficients α are on the order of 10^{-6} to 10^{-5} K^{-1}. Exceptional, but technically widely exploited cases of near-zero thermal expansion are rare and have been found mainly among specific alloys where thermal expansion is balanced by magnetorestiction effects. Other examples are lattices with flat energy profiles for the bending of valence angles, such as for Si-O-Si in quartz and silicates. A shrinking or contraction of the dimensions of matter upon heating (also called "negative thermal expansion", NTE) is an even rarer phenomenon.[84]

Extreme cases of thermal expansion (TE) and also of "NTE" have recently been detected for a group of tri-silver(I) hexacyanometallates(III) by Goodwin et al.[84,85] The effect was so pronounced that the terms "colossal TE and colossal NTE" have been created for cases where α is larger by about an order of magnitude (10^{-4} K^{-1}), and the effect has been traced to strong argentophilic interactions. Crystals of [Ag_3{Co(CN)$_6$}] are trigonal, space group $P\bar{3}1m$ (α-Po type), and are built of alternating layers of silver cations and [Co(CN)$_6$]$^{3-}$ anions. The silver atoms of a given layer form a Kagomé net with Ag–Ag distances of approximately 3.4 Å (**20**), and the cobalt-centered octahedra are positioned above and below the biggest "holes" in the Kagomé nets. Each cyano ligand is a linear connector for a silver and a cobalt atom: Ag-C≡N-Co (Figure 1, top). Upon heating (20–300 K), the crystals undergo drastic changes in the lattice parameters a (PTE) and c (NTE) as shown in Figure 1, bottom, as found by both X-ray and neutron diffraction studies. DFT calculations including a modest additional dispersive term (r^{-6}) have shown that argentophilic interactions contribute significantly to the bonding in the Kagomé nets of the silver atoms assisting in the shrinkage and resisting the expansion along the relevant crystal axes. The isostructural crystals of [Ag_3{Fe(CN)$_6$}] show the same behavior. In contrast, the parent structure with deuterium cations replacing the silver cations, [D_3{Co(CN)$_6$}], exhibits perfectly normal PTE. This finding has corroborated the significance of metallophilic bonding.[85,86]

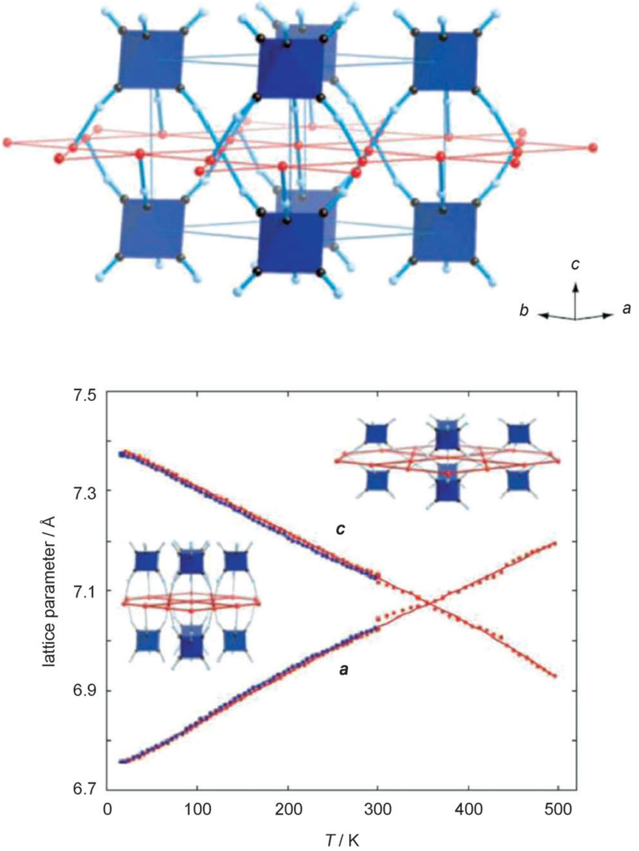
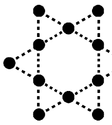


Figure 1. The trigonal lattice of the framework material [Ag_3{Co(CN)$_6$}]. The [CoN_6] octahedra are shown in blue, the silver atoms of the Kagomé-type lattice in red (top). Positive and negative thermal expansion along the axes a and c, respectively, with the deformations accentuated (bottom, Ref. [84]).



20

The reciprocal phenomenon, large "negative linear compressibility" (NLC), has also been observed for [Ag_3{Co(CN)$_6$}] at room temperature for the pressure range up to 7.65 GPa, which also includes a phase transition. Extremely large compressibility constants $K_a = +115$ TPa^{-1} and $K_c = -76$ TPa^{-1} for the a and c axis, respectively, have been measured (Figure 2). In a summary of this work it has been stated that the NTE and NTC effects observed in [Ag_3{Co(CN)$_6$}] are the strongest yet reported and comparable to those found for solid Xenon (+130 TPa^{-1} at 100 K). This parallel supports the significance of strong dispersion forces in metallophilic interactions.[87]

A similar connectivity pattern is found in the dicyanoargentates(I) of some rare-earth-metal cations. Well investigated examples have the general formula [M{Ag(CN)$_2$}$_3$-(H$_2$O)$_3$] with M = Eu^{III}[88,89] and Tb^{III}.[90] The only major difference arises from the higher coordination number of the rare-earth cations (9 for Eu, instead of 6 for Co) which is established by the addition of three water molecules. In the overall layer structure the silver atoms are again assembled in

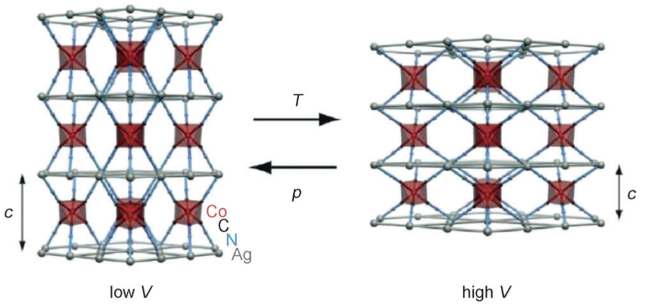


Figure 2. Large “negative compressibility” of $[Ag_3\{Co(CN)_6\}]$ (V = volume per formula unit, c = trigonal axis, p = pressure, T = temperature, Ref. [87]).

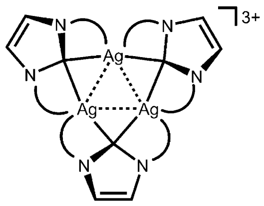
planar Kagomé nets in which each silver atom is in argentophilic contacts (e.g. Ag–Ag 3.3346(5) Å for the Tb compound) with four other silver atoms. Each silver atom is also the center of a linear NC-Ag-CN unit connecting the Eu/Tb atoms of the layers above and below. The corresponding gold compound is isostructural (Au–Au 3.31(1) Å), and mixed-metal systems Ag/Au have also been studied.[91] All the compounds of this series are luminescent, and the emission can be tuned by altering the composition.[92,93] To our knowledge, the temperature- and pressure-dependence of the crystal structure parameters and of the photophysical properties have not been investigated in detail.

Unusual thermal expansion properties have also been found for crystals of silver(I) pyrophosphonates, such as $[Ag_3(pcp)(pcpH)]$ with pcp = pyrocyclohexylphosphonate(2−) and $[Ag_3(ptp)CN]$ with ptp = pyro-3-thienylphosphonate(2−). In the network structures of these compounds there are sets of Ag–Ag contacts in the range 3.113–3.344 Å which are held responsible for the anisotropic temperature dependence (50–298 K) of the lattice constants and for the large expansion coefficients similar to those of $[Ag_3\{Co(CN)_6\}]$.[94]

It is yet unclear if argentophilic contacts play a role in the unusual “breathing ” behavior of porous metal–organic frameworks (MOFs) such as the one based on silver(I) 3,5-bis(trifluoromethyl)-1,2,4-triazolate (tz; “fluorous” MOFs). The structure contains $Ag_4(tz)_4$ clusters and shows positive and negative expansion for different crystal axes. Moreover, significant expansion is observed upon the absorption of gases such as N_2.[95] Like these compounds, silver(I) 3,5-bis(trifluoromethyl)pyrazolate also shows an extensive network of Ag–Ag contacts with other ligands (Section 2.5.3).[96]

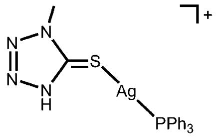
2.4. NMR and ESR Spectroscopy

The inconvenient nuclear properties of the only stable gold isotope, ^{197}Au, $s = {}^3/_2$, make ^{197}Au NMR spectroscopy a very tedious and ineffective technique. Aurophilic bonding has therefore never been traced by this technique.[97] By contrast, silver has two isotopes ($^{107/109}$Ag) with $s = {}^1/_2$ in high abundance. This prerequisite should offer chances to characterize any Ag–Ag bonding at least through spin–spin coupling phenomena, but surprisingly so far very few pertinent studies have been carried out. A very detailed analysis has been presented by Catalano and Malwitz for the trinuclear carbene complex **21** with its three short Ag–Ag distances (av. 2.724 Å). The NHC ligand bears two 2-pyridylmethyl substituents in the N,N' positions, drawn as linkers to Ag atoms. The ^{13}C NMR signal for the carbene carbon atoms shows all the expected $^1J(^{107,109}Ag,^{13}C)$ couplings which are compatible with significant interactions between the silver atoms.[75]

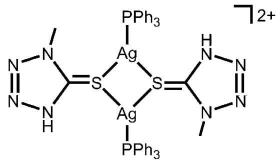


21

^{31}P NMR spectroscopy has been used by Karaghiosoff et al. to follow the monomer–dimer equilibrium of the complex $[Ph_3PAg(L)]^+[OSO_2CF_3]^-$ with L = tetrazole-5-thione in CH_2Cl_2 (**22a**, **22b**). Depending on concentration and temperature of the solution, the compound is associated to dimers. Separate signals are observed for monomers and dimers at −85 °C with different ^{107}Ag–^{31}P coupling constants of $^1J = 417.5$ versus 318.5 Hz, respectively, which indicate a change in the coordination number of the silver atoms. As already mentioned above, the structure of the dimers in the crystal has been elucidated and shown to have a head-to-tail parallel alignment of the bent P-Ag-S axes with a slippage that leads to an Ag–Ag distance of 3.0287(6) Å.[78] (Compare **12a** with SR for Cl.)

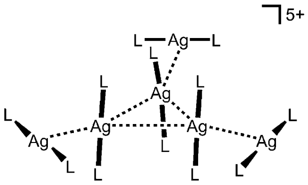


22a



22b

ESR studies were carried out by Eastland et al. on crystals of bis(imidazole)silver perchlorate (**23**, L = imidazole) after exposure to ^{60}Co X-rays (at 77 K). The hexanuclear cations of this compound have a unique structure of D_3 symmetry: Three silver atoms form an equilateral triangle with Ag–Ag edges of 3.493(1) Å and with the three N-Ag-N axes almost perpendicular to the plane of the triangle. The three remaining two-coordinate silver atoms are attached to the triangle by short Ag–Ag contacts of 3.051(1) Å and with their N-Ag-N axes staggered relative to those of the triangle. It should be noted that all six Ag–Ag contacts are unsupported, and that the silver atoms are engaged in two (peripheral) and three argentophilic bonds (central). At the time of its publication, it was an unprecedented case of metallophilic bonding. Note, however, the close similarity to the structure **6a** for a compound with a very different set of ligands.[98] The radical generated upon irradiation of the compound **23** shows an ESR signal with hyperfine coupling to three ^{107}Ag/^{109}Ag and six ^{14}N nuclei suggesting a delocalization of the extra electron over the Ag_3 core in an orbital mainly of 5s character.



23

2.5. Electronic Spectra

2.5.1. ESCA Criteria

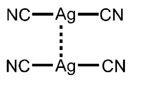
When X-ray diffraction studies of the two crystalline forms of $AgNO_3$ had shown that the orthorhombic phase, stable at room temperature, has the silver cations arranged in pairs,[2] an ESCA analysis was carried out to find evidence for Ag–Ag interactions.[99] An anomaly was found for the 4d states, but no detailed assignments could be made at that stage. It appears that work in this area has since not been resumed.

2.5.2. UV/Vis Absorption

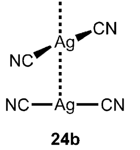
The electronic spectra of silver(I) compounds in the UV/Vis region have been investigated extensively owing to the associated photoluminescence phenomena. For a large number of mono- and polynuclear complexes the excitation spectra have been recorded as a basis for an interpretation of the intriguing emission properties of the compounds. Only few examples are selected herein which have given a deeper insight into the nature of the Ag–Ag interactions in the ground and excited state. Where ligands have suitably positioned HOMOs, the absorption spectra are largely determined by the individual electronic states of these ligands and the related ligand-to-metal charge transfer (LMCT) processes, but these appear to be modified significantly by the presence of the Ag–Ag (M–M) interactions, designated as ligand-to-metal-metal charge transfer (LMMCT).

In the absence of such suitable ligands, the absorption and emission properties are based on metal-to-metal transfer (MMCT): As already mentioned in Section 2.1.1, in crystals of salts containing $[H_3N\text{-}Ag\text{-}NH_3]^+$ cations associated with various anions (ClO_4^-, NO_3^-), the cations are aggregated into chains by short argentophilic contacts (**4**). These materials show strong luminescence upon irradiation at $\lambda_{ex} = 355$ nm. In the emission spectra, the bands are very broad and strongly red-shifted to a range of $\lambda_{em} = 450$–600 nm. With only ligands NH_3 present, these characteristics cannot have their origin in the excited state of the mononuclear complex of the cation Ag^+ ($4d^9 5s^1$), for which narrow bands at higher energies would be expected. The phenomenon is therefore attributed to the formation of excimers $[(H_3N)_2Ag\text{-}Ag^*(NH_3)_2]^{2+}$ or $[(H_3N)_2Ag\text{-}Ag^*(NH_3)_2\text{-}Ag(NH_3)_2]^{3+}$ in which the bonding is increased significantly over that of the original argentophilic contact(s).[53]

The most convincing evidence for unsupported argentophilic bonding between mononuclear units on the basis of UV/Vis and luminescence spectroscopy has been presented by the group of Patterson in the year of 2000.[100] They investigated the concentration dependence of aqueous and methanol solutions of $K[Ag(CN)_2]$. From previous work by Mason it had been known that dilute aqueous solutions of this compound show UV absorptions that can be assigned to the LMCT transitions of the monomeric anion.[101,102] Similar results are obtained for solid films of $[(n\text{-}C_4H_9)_4N]^+[Ag(CN)_2]^-$ (at 40 K) where the anions are separated by the bulky and branched cations ruling out any anion association.[102] These transitions are the same for both water and methanol as a solvent at low concentrations (5×10^{-4} M). The resolution is much lower than that observed for $[Au(CN)_2]^-$, owing to the lower spin-orbit couplings for Ag originating from smaller relativistic effects (Ag < Au).[100–102] Patterson et al. have found that the absorptions are extremely concentration-dependent. At higher concentrations (up to the saturation limit of 0.80 M), several new peak maxima appear, and these maxima are shifted from $\lambda_{max} = 200$ to as much as $\lambda_{max} = 270$ nm. Moreover, the intensities show a non-Beer's Law behavior, indicating the presence of far more than just one species. These results are corroborated by the luminescence properties of the solutions. At low concentrations, aqueous solutions of $K[Au(CN)_2]$ (and their frozen glasses at low temperature) are not luminescent, but with increasing concentration emission maxima grow in the spectra which are shifted up to $\lambda_{max} = 300$ nm (at 70 K). Clearly, both phenomena are associated with the formation of oligomers $[\{Ag(CN)_2\}_n]^{n-}$. For the dimer and trimer ($n = 2, 3$; **24a**,**b**) the equilibrium constants and the ΔG values of the association have been calculated. The results show that the dimerization, and even more so the trimerization, are exergonic processes. EH calculations of various model dimers and trimers (linear or angular, staggered or eclipsed) gave Ag—Ag bond energies of 21.0 and 29.5 kJ mol^{-1}, both lower than for the corresponding values for gold oligomers $[\{Au(CN)_2\}_n]^{n-}$ of 28.8 and 34.1 kJ mol^{-1}. Notably, each bond in the trimer is stronger than the bond in the dimer for both the silver and gold species. The results are confirmation of ground-state metallophilic bonding in agreement with the various current descriptions calling for higher participation of Ag/Au s orbitals in the bonding owing to relativistic effects.[103,104]



24a



24b

Although there is not yet support from the corresponding spectroscopic data, it should be noted that there is convincing evidence that $[Ag(CN)_2]^-$ anions are also associated in ionic liquids, such as the 1-ethyl-3-methyl-imidazolium salt. The crystallized melt (m.p. 73 °C) features slightly puckered chains of anions with argentophilic contacts of Ag–Ag 3.226(1) Å in length. Neighboring anions have an almost perpendicular orientation (**17**).[105]

Similar structural situations, but with much smaller aggregates, arise upon doping of alkali halide crystals with $[Ag(CN)_2]^-$ anions. In a KCl host lattice, the guest anions can form pairs and triples in various assemblies which are bonded through argentophilic contacts. These units give rise to various UV/Vis absorption characteristics, and upon excitation in different parts of the spectral range of absorptions, an equally broad range of emission spectra can be generated. This can be taken as an "exciplex tuning" of the luminescence of this material extending over a range of more than $\tilde{\nu} = 18000\,\mathrm{cm}^{-1}$. The energy characteristics have been interpreted through ab initio calculations, the results of which account for the broadness of the peaks, the absence of fine structure, and the large Stokes shifts by assuming various $[Ag(CN)_2]_n^{n+*}$ excimer and exciplex geometries.[106]

Solutions in alcohols of the [(NHC)AgCl] complexes mentioned above,[70] which are dimers in the solid state (**14b**), show UV/Vis absorptions in the $\lambda_{max} = 240$–250 nm region assigned to MLCT processes on the basis of calculated HOMO–LUMO gaps. Since it has not yet been demonstrated that the dimerization is retained in solution, it remains unclear if metallophilic interactions are involved. Glassy solutions (EtOH/MeOH at 77 K) are also luminescent ($\lambda_{max} =$ 483, 527, 580 nm for Ag, 427, 529, 575 nm for Au, upon excitation at $\lambda_{ex} = 244$ nm).

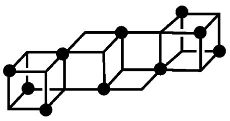
UV/Vis spectroscopy has also been employed for the characterization of ligand-supported argentophilic interactions in the dimetallacyclic complex dications **19** (R = cyclohexyl).[65] The absorption maxima of the PF_6^- and $CF_3SO_3^-$ salts (in CH_2Cl_2) appearing at $\lambda_{max} = 266$ nm are assigned to the 4dσ*→5pσ transition producing an Ag–Ag bonded excimer. A slight shift to $\lambda_{max} = 261$ nm is attributed to coordination of solvent molecules at the Ag atoms. The corresponding value $\lambda_{max} = 277$ nm for the gold analogue again indicates a significant difference in Au–Au and Ag–Ag bonding.

2.5.3. *Photoluminescence*

It has long been known that some silver salts show strong luminescence upon UV excitation in the solid state, in particular at low temperature.[107] Over several decades evidence has accumulated that this phenomenon is particularly common and pronounced for solid-state structures with short contacts between the silver cations (see Section 2.1). This does not mean, however, that all luminescence phenomena observed for silver compounds are necessarily due to this structural detail. Specific geometries and suitable ligand combinations may also lead to strong luminescence of a very different type.

In contrast, luminescence of discrete molecular silver complexes in the gas or solution state is far less common. The first example to be reported was probably the tetranuclear cluster built of four molecules of chloro(trimethylphosphite)silver(I), $[\{(MeO)_3PAgCl\}_4]$, investigated by Vogler and Kunkely.[108] Upon excitation at $\lambda_{ex} = 320$ nm, frozen toluene solutions (7.63×10^{-4} M, 77 K) of the compound show a strong emission at $\lambda_{em} = 483$ nm, which has been assigned to intramolecular transitions following the excitation $Ag_4 \rightarrow Ag^*$-(Ag_3) in the tetrahedral cluster of the metal atoms (**12b**, R = OMe). A simple MO diagram can be used to account qualitatively for the energy levels responsible for the strongly red-shifted emission.[109]

A large number of structures of tetranuclear complexes $[\{R_3PAgX\}_4]$ are known. The aggregation mode of the Ag_4X_4 core varies between an almost regular cube and a "stella quadrangular" type, both composed of interpenetrating Ag_4 and X_4 tetrahedra of the same or a different size, respectively. It appears that in all these variations the argentophilic interactions in the silver tetrahedra are maintained and contribute significantly to the stability of the tetramers.[110,111] Ag_nX_n cores are also present in more complex aggregates and held responsible for the intense luminescence of such systems. An example is shown in **25** representing the anion of $(Bu_4N)_4$-$[Ag_{10}Br_{12}(CN)_2]$. Its strong blue luminescence ($\lambda_{em} = 450$ nm upon excitation at $\lambda_{ex} = 397$ nm) is ascribed to the manifold of Ag–Ag contacts with distances in the range of 3.190–3.591 Å.[112]


25

The literature on the luminescence of silver compounds in the solid state is extremely large and growing rapidly because this research may lead the way to interesting applications in sensor or phosphor technology. The majority of studies have been dedicated to coordination polymers of silver(I) complexes which show strong luminescence upon irradiation in the spectral region where an extended ligand system has its maximum absorption. In bi- or polynuclear silver complexes of these ligands with short Ag–Ag contacts the emissions are found strongly red-shifted, and the effect is plausibly assigned to LMCT processes "perturbed by Ag–Ag interactions" (LMMCT).[113–117] The strong temperature dependence of the emission maximum and intensity of a complex with multiple argentophilic contacts is shown in Figure 3. The

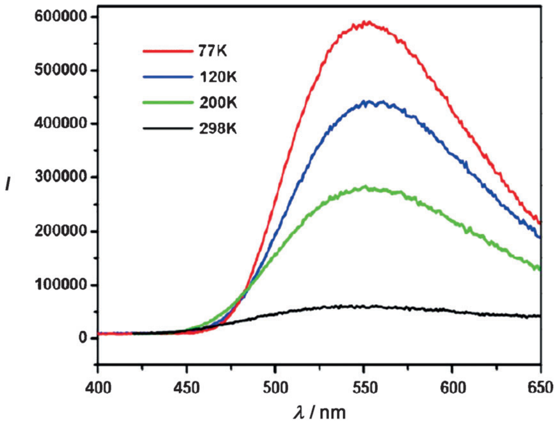
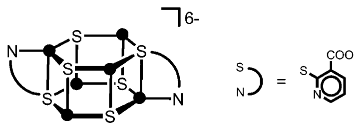


Figure 3. Temperature dependence of the emission spectra of $[Ag_3$-(BTC)(pyz)$(H_2O)]$ with BTC = benzene-1,3,5-tricarboxylate and pyr = pyrazole (excitation at 363 nm) (Ref. [113]).

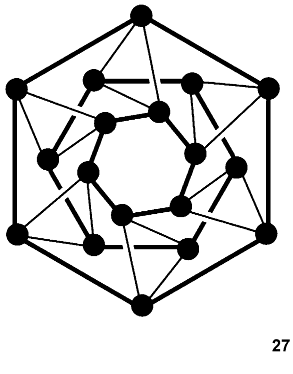
effect has been ascribed to enhanced argentophilic interactions at low temperatures.[113]

Similar results were obtained for the silver(I) 2-mercaptonicotinate anion $[(mna)Ag]^-$, which forms a hexamer $[(mna)_6Ag)_6]^{6-}$ in the solid state of the ammonium salt with six intramolecular Ag–Ag contacts. The connectivity is shown schematically in formula **26**. These contacts are modified upon addition of $[Zn(phen)]^{2+}$ cations (phen = phemanthroline)—which become attached to the hexanuclear cluster through the terminal carboxylate groups—leading to significant changes in the emission characteristics. The emission maxima are strongly temperature dependent ($\lambda_{ex} = 365$ nm: $\lambda_{em} = 551$ nm at 298 K → 571 nm at 77 K for $[\{(L)Ag\}_6]^{6-}$; $\lambda_{em} =$ 544 nm at 298 K → 565 nm at 77 K for $[\{(L)Ag\}_6\{Zn_2(phen)_2\}]^{2-}$) and gain in intensity as the temperature is lowered. The effect is assigned to the gradual shortening of the Ag–Ag contacts at low temperatures.[118–120]

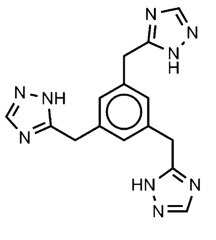


26

A particularly interesting octadecanuclear silver(I) complex $[Ag_{18}(TMTTB)_{12}][NO_3]_{18}\cdot(H_2O)_{30}$ was obtained in a hydrothermal reaction of $AgNO_3$ with 1,3,5-trimethyl-2,4,6-tris(triazol-1-ylmethyl)benzene (TMTTB) (assisted by phthalic acid). The 18 silver atoms are all homoleptically two-coordinated by triazol nitrogen atoms and assembled in the form of three hexagons stapled together by the trifunctional benzene units above and below the layer of silver atoms. The sandwich (ligands)-(silver atoms)-(ligands) has six-fold symmetry (**27**). The multiple Ag–Ag contacts between the six-membered rings are 3.403(6) Å long. The compound is strongly luminescent, and the emission increases in intensity as the temperature is lowered from 298 to 50 K ($\lambda_{ex} = 310$ nm, $\lambda_{em} = 500$ nm, at 50 K). The effect has been ascribed to the decrease in Ag–Ag contacts at low temperature.[116]

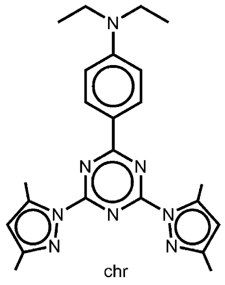


27

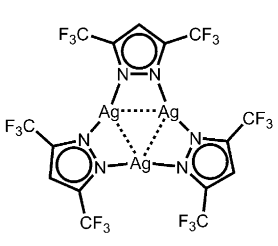


TMTTB

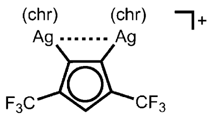
Concentration-dependent emission was observed for a compound prepared from a chromophore (chr) **28a** and the trinuclear silver 3,5-bis(trifluoromethyl)pyrazolide $[Ag_3(pyr)_3]$ (**28b**). Crystals of this product show a dinuclear cation where the two (chr)Ag silver units are bridged by a pyr ligand, and the counterion is a pentanuclear cluster $[Ag_5(pyr)_6]^-$ with a quasi-square pyramidal configuration. In the cation **28c** there is a semi-bridged Ag–Ag contact with a distance of 3.089(9) Å, and in the anion (not shown) the shortest such distance is 3.222(3) Å. Solutions in acetonitrile are strongly luminescent ($\lambda_{ex} = 330$ nm) with an emission maximum at $\lambda_{em} = 550$ nm at high concentration, but at $\lambda_{em} = 460$ nm at high dilution. At intermediate concentrations, both maxima are present. The luminescence of the crystals is temperature-dependent with a dramatic increase in intensity from 180 to 4 K, and with a significant bathochromic from $\lambda_{em} = 590$ to 565 nm. Because of strongly different lifetimes of the emitting states (0.4 s versus 96 ms at 77 K), both the green and orange emission can be observed with the naked eye upon shutting off of the UV irradiation (green afterglow after the bright orange emission has subsided). The results have been explained by a loosening of the Ag–Ag contacts by solvation at high dilution in the solvent, and their tightening at low temperature in the crystal.[96]



28a



28b

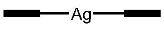


28c

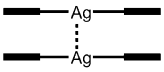
3. Selected Modes of Argentophilic Interactions

3.1. Unsupported Ag–Ag Contacts between Short and Long Chains of Silver(I) Coordination Compounds

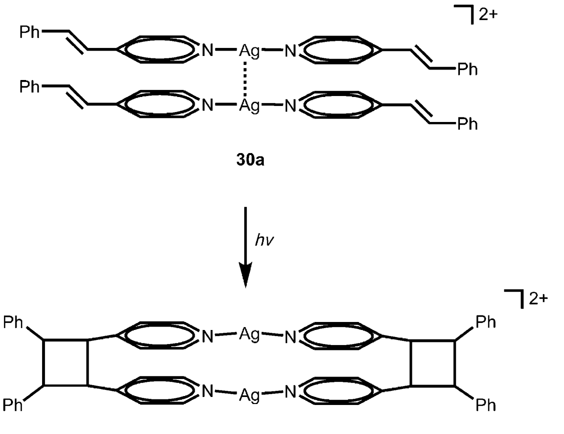
As already shown in Section 2.1.1, mononuclear complexes (cations or anions) with chainlike ligands (**29a**) are often found in an alignment as shown in **29b**, where the Ag–Ag contact is directing the relative placement of the neighboring components. This influence also offers the chance to use this arrangement for regioselective coupling reactions, mainly in the solid state. Thus the short-chain cations present in crystals of the 2:1 complex of 4-stilbazene and silver triflate aggregate in a parallel orientation to give pairs (**30a**) with Ag–Ag contacts of 3.41 Å. This distance is the shortest between any atoms of the two cations. Such an argentophilicity-induced dimerization supports the [2+2] photodimerizations of the olefinic units in the ligands: Upon UV irradiation of the crystals (!) the ligands dimerize to the corresponding cyclobutanes (**30b**). Interestingly, this rearrangement forces the silver atoms further apart because the flat olefin spacers (sp^2 carbon atoms) are converted into angular cyclobutane spacers (with sp^3 carbon atoms).[121]



29a

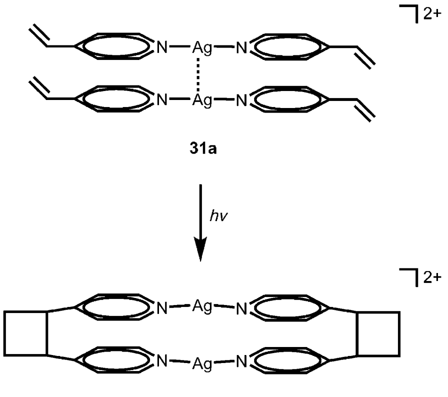


29b



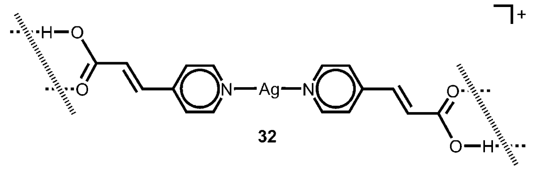
30a

30b

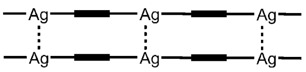


31a

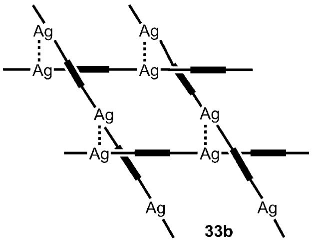
31b



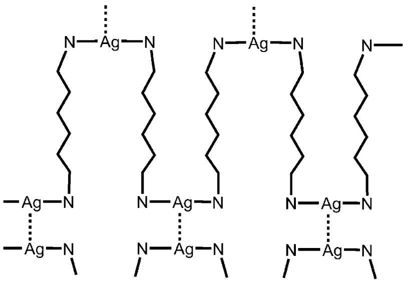
32



33a



33b



33c

In a further attempt to develop this concept, 4-vinylpyridine was shown to afford a 2:1 complex with $AgClO_4$ (**31a**). In the crystal, the cations are again aligned into dimers by Ag–Ag contacts, and this arrangement brings the free vinyl groups into close proximity. UV irradiation leads to a [2+2] cycloaddition reaction (**31b**).[122] In two different studies, 4-pyridyl acrylic acid and its methyl ester and amide were used to form 2:1 complexes with $AgNO_3$. The crystal structures of the products showed that the cations (**32**; only one chain is shown) are also aligned and connected by Ag–Ag contacts (3.46 Å). UV irradiation leads to the expected [2+2] cycloaddition reactions in nearly 100% yield.[123] With 3-pyridyl acrylic acid as a ligand, and with $AgBF_4$ or $AgClO_4$, the structures of the cations follow the same principle and form zigzag chains with strong hydrogen bonding between the terminal carboxyl groups (Ag–Ag contacts are in the range 3.32–3.44 Å). The photochemical [2+2] cycloaddition has been demonstrated by NMR spectroscopy investigations of the products.[124]

Silver atoms separated in a chain by α,ω-difunctional spacers are often found to establish argentophilic contacts with neighboring chains to form ladder-type aggregates. Depending on the structure and flexibility of the spacer, the chains may run roughly parallel (**33a**), cross each other (**33b**), or become intertwined in helical assemblies. For example, the polycationic chains formed of $AgNO_3$ and ethylenediamine are interwoven in networks with a rhombic pattern where each chain crossing leads to an Ag–Ag contact, with average distances of 3.1 Å.[125] With longer alkanediyl chains, as in 1,6-diaminohexane, the chains are meandering with Ag–Ag contacts pointing alternatingly to different neighboring chains (**33c**; cationic charge and anions omitted).[126]

For a large group of compounds these principles of organization are roughly the same. Therefore, in the formulae **34a–o** only the ligands are shown with the relevant donor atoms marked in color. This selection of compounds shows the enormous structural diversity in these systems, which as yet are always based to some extent on argentophilic contacts.

1,3-Bis(4-pyridyl)propane (**34a**) reacts with silver salts to give products with snake-like cationic chains. These chains are associated into undulated sheets through Ag–Ag contacts (3.06 Å), but depending on the nature of the anions and of the solvate molecules the neighboring N-Ag-N units may also show a "slippage" which brings the Ag atoms closer to the nitrogen atoms and lengthens the Ag–Ag distances (to 3.5 Å). The compounds are strongly luminescent in the solid state ($\lambda_{ex} = 230$ nm, $\lambda_{em} = 382$ nm).[127] Interconversion experiments with perchlorate and hexafluorophosphate, of which the perchlorate shows fewer Ag–Ag contacts, have been taken as evidence for the strong influence of these contacts on the intermolecular assembly.[128] Analogous phenomena were observed for ligands in which two imidazoles are connected by the butanediyl chain (**34b**). Helical chains with alternating ligand–metal units are formed with $AgClO_4$, and these chains are paired up by short Ag–Ag contacts of 2.966(1) Å.[129] With the less-flexible di(2-methylimidazol-1-yl)methane ligand (**34c**, R = Me) and silver nitrite, zigzag chains are formed with short inter-chain Ag–Ag contacts (2.9187(9) Å), and the chains are further linked into corrugated layers. The corresponding compound with the unsubstituted di(imidazol-1-yl)methane ligand (**34c**, R = H) and triflate anions features similar zigzag chains, but these are interwoven "one-over/one-under" (type **33b**), and at the cross-points the Ag-Ag distances are 3.121(1) Å long. Both compounds are only weakly luminescent.[130]

The chains formed with 4,4′-bipyridyl (**34d**) and silver cations in the presence of carboxylate and sulfonate anions are arranged as ladders (**33a**) or even double-ladders in which the rungs are Ag–Ag contacts of 3.299(1) Å.[131] The alignment of the shorter chains generated by using both 4,4′-bipyridyl (**34d**) and 4-(4-pyridyl)benzoic acid (**34e**) in 1:2 ratio is similar, with Ag–Ag contacts of 3.376(2) Å.[132] Bis-terminal pyridine ligands were further extended into flexible examples, such as 2,2′-bis(4-pyridylmethyleneoxy)1,1′-biphenyl (**34f**). The resulting polycationic zigzag chains show similar interstrand argentophilic interactions.[133] Dimers established by hydrogen bonding between the terminal carboxamide groups of isonicotinamide molecules (**34g**) can also function as *N,N*′-functional ligands, and chains are formed accordingly. The Ag–Ag contacts between these chains are 3.47(1) Å long, but it must be assumed that they are influenced by the sulfonate groups of the 2,6-naphthalene disulfonate anions.[134]

1,4-Di-3-pyridyl-2,3-diazabuta-1,3-diene (**34h**) has been used as a more rigid α,ω- linker for silver cations with methylsulfonate or hexafluorophosphate anions. The polycationic zigzag chains are fused periodically through Ag–Ag contacts of 3.1402(8) and 3.259(1) Å.[135,136]

The 1D multi-cationic, double-stranded coordination polymer formed from $AgPF_6$ and the thiophene-based bisamide ligand **34i** has inter-chain Ag–Ag contacts of 3.176(2) Å. In contrast, the reaction of the same ligand containing 4-pyridyl instead of 3-pyridyl end groups with $AgNO_3$ affords dicationic dimetallamacrocycles with transannular Ag–Ag contacts of 3.140(1)/3.038(1) Å (two independent heterocycles in the crystal). These macrocycles are further aggregated into chains through Ag–Ag contacts of 3.48 Å. In the corresponding trifluoroacetate and triflate compounds, the anions have Ag–O contacts which lengthen the transannular Ag–Ag distances to 3.3265(6) and even 3.42/3.60 Å, respectively (two independent molecules).[137]

Chains formed with the rigid V-shaped ligand **34j** (R = OMe) and $AgOSO_2CF_3$ are also linked through short Ag–Ag contacts of 3.1500(8) Å, but with other anions (BF_4, PF_6, NO_3) the organization of the chains is different, and short contacts are not always maintained.[138] Ag–Ag distances of 3.084(3) Å have further been observed at the crossing points of polynuclear chains formed in the complex of $AgNO_3$ with the multifunctional 4-(2-pyridyl)-6-(4-pyridyl)-2-aminopyrimidine (**34k**).[139]

Silver 2-pyrimidinolate (**34l**) forms ribbons with the silver atoms far apart. However, these ribbons are stacked in the crystal to establish Ag–Ag contacts of 3.302(1) Å to the ribbons above and below. The stacks are further connected by hydrogen bonds including hydrate water molecules.[140] A similar stacking has been found in crystals of the complex of 3-aminomethylpyridine (**34m**) with silver(I) triflate and two bipyridines as auxiliary ligands (two Ag–Ag contacts of 3.0846(3) Å).[141]

Chain-like coordination polymers may adopt a helical structure through intra-chain Ag–Ag interactions which draw the silver centers close together. An example was found in crystals of $[(L)Ag]OSO_2CF_3$ with L = 2-pyridinyl-3-pyridinylmethanone (**34n**). In two polymorphs the cations are associated into *P*- and *M*-helical chains with intrahelical Ag–Ag distances of 2.998 Å between every second silver atom of the chain. The anions are embedded between the helices.[142] In contrast, when L = di(3-pyridinyl)methanone (**34o**) was employed as a ligand for $AgNO_3$, the crystals of $[(L)Ag]NO_3$ feature helices with inter-helical instead of intra-helical Ag–Ag contacts (3.201 Å).[143] In an extension of these studies, the reactions of **34o** with silver perfluorocarboxylates $AgOC(O)C_nF_{2n+1}$ ($n = 1, 2, 3$) have been shown to produce metallamacrocyclic cations $[Ag(L)]_6^{6+}$ with hexagonal symmetry. These macrocycles associate by Ag–Ag contacts (3.07–3.31 Å) into tubes filled with the anions and solvent molecules.[144] Inter-helical Ag–Ag interactions (2.9996(8) and 3.3595(8) Å, with every other silver atom of a chain interacting with a different neighboring chain to generate a layer structure) were detected in crystals of silver tetrazol-1-yl-acetate (**34p**), which show a strong green luminescence (λ_{ex} = 372 nm, λ_{em} = 540 nm).[145] Helical structures with intra-chain Ag–Ag contacts (2.889(1) and 3.040(1) Å) are also found for the silver complexes with the 2,6-bis(5-pyrazolyl)pyridine ligand (**34q** R = ^{i}Pr and R' = Me). The pyridine nitrogen atom is not silver-coordinated.[146]

A particularly intriguing "triple helix of double helicates" has been discovered in a study with the ligand **34r** (L). In a repeating unit $[(L)_2Ag_2]^{2+}$—the two silver atoms are *N,N*′-chelated at the ends of the two ligands to become four-coordinate in a double helicate structure. These units are connected at both ends by Ag–Ag contacts (2.99 Å, type **1c** or **17**) to give helical chains. Finally, three of these chains wrap around a central spine of anions to give a triple helical braid. Taken strictly, the array can also be addressed as a representative of type **35b** with tetracoordinate silver atoms.[147] Complex helical arrays have also been discovered for 3,3′-di(4-pyridyl)-1,1′-biphenyl ligands exhibiting various torsions of the central bonds of the bipyridyl core (**34s**). Their 1:1 combination with $AgNO_3$, $AgClO_4$, or $AgPF_6$ leads to homochiral coordination polymers which are folded into two-, three- and fourfold helices, respectively. The twofold helices are cross-linked by two different types of Ag–Ag contacts of 3.211(1) and 3.488(1) Å to give sixfold helices in a chiral 3D network, while the three- and fourfold helices associate with each other in pairs to generate tubular architectures that are also induced by argentophilic cross-linking. Owing to the complexity of the system, the reader is directed to the original publications for details.[148]

Argentophilic interactions between layered coordination polymers are present in silver(I) complexes with melamine (ma, **34t**) which is a trifunctional spacer. These layers are established in crystals of the compound $[NH_4Ag_3(ma)_2(suc)_2]$ with succinate (suc) as the counterion (Ag–Ag 3.184(1) Å).[149] A similar distance (3.28 Å) has been found between layers of the compound $[Ag_2(tr_2ad)_2][ClO_4]_2$ where tr_2ad designates 1,3-bis(1,2,4-triazol-4-yl)adamantane. The rhombohedral grid with (4,4)-topology is tightly packed to establish these contacts.[150]

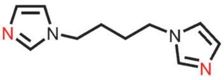
A case of "distantly supported", but particularly tight argentophilic contacts (2.88 and 2.93 Å) has been discovered using the 3,5-bis(2-bipyridyl)pyrazole ligand LH (**34u**). In a mixed-metal compound of the stoichiometry $[Fe_2Ag_4(L)_4]$-$[BF_4]_6$ the iron(III) cations are chelated by two bipyridyl groups of two different ligands (green N atoms), while the other bipyridyl group of each ligand chelates a silver(I) cation (red N atoms).[151]

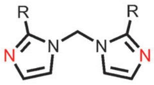
3.2. Unsupported Ag–Ag Contacts between Macrocyclic Units

In macrocycles with two or more silver atoms, the metal atoms may be engaged in transannular interactions provided that the ring is either sufficiently small, or large and flexible. The X-Ag-Y axes may then be parallel or twisted with various dihedral angles X-Ag-AgY (**35a**). Alternatively, more rigid metallacycles can be found associated through Ag–Ag contacts between rings (**35b**).[152] (There is also the isomeric alternative **35c** which allows for intra-chain Ag–Ag contacts, but these contacts are ligand-supported.) This Section gives examples for cases of the types **35a**,**b** which can appear as isomers or polymorphs. There are also examples where an extra silver atom becomes inserted between the two ring silver atoms to generate a triatomic transannular metal bridging arrangement (**35d**). In the formulae **36a–f** again only the ligands are shown which form the metallacycles.

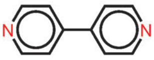
Schiff base ligands of the type **36a** ($n = 2$, 3) offer two terminal coordination sites which take on silver cations upon treatment with $AgClO_4$ or $AgOSO_2CF_3$. The 2:2 complexes have macrocyclic structures that allow for transannular Ag–Ag contacts (3.0680(2)–3.3348(5) Å for three different sol-


34a

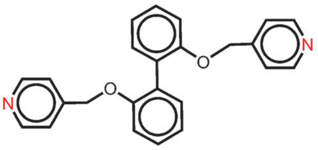

34b



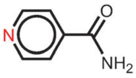
34c


34d

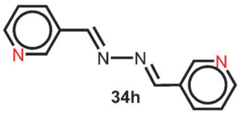
34e

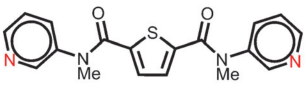


34f

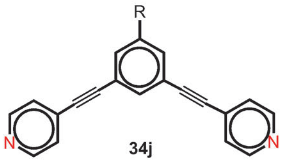


34g

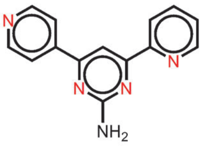

34h



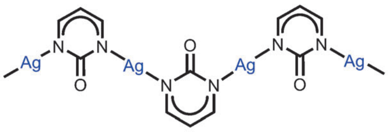
34i



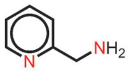
34j



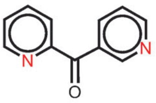
34k



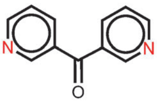
34l



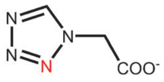
34m



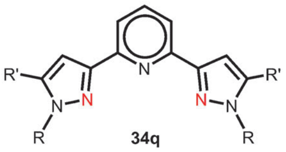
34n



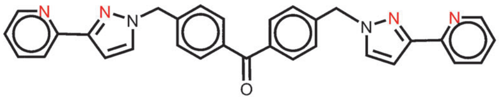
34o



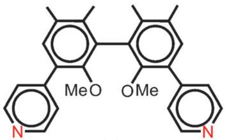
34p



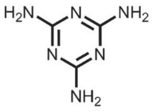
34q



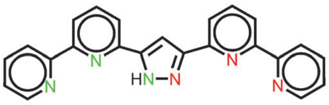
34r



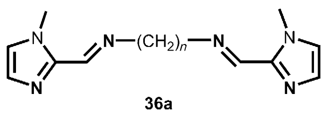
34s



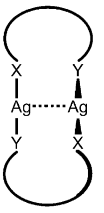
34t



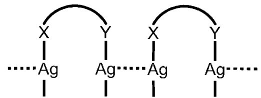
34u



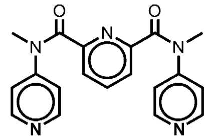
36a



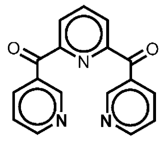
35a



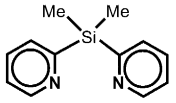
35b



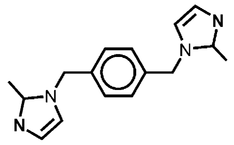
36b



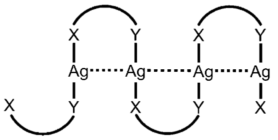
36c



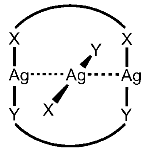
36d



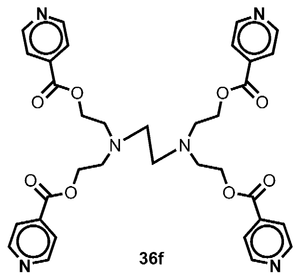
36e



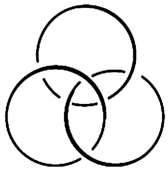
35c



35d



36f



36e'

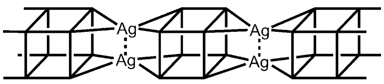
vates, type **35a**), because both the inner and outer donor atoms draw the metal atoms to the core of the large ring. A 2:3 complex has three silver atoms integrated between two ligands with Ag–Ag distances of 2.7842(2) and 3.1100(7) Å. The third silver atom is accommodated in the center sharing the N-atoms with two flanking ones (**35d**).[152,153] Between the silver atoms in the dicationic 2:2 complex with the large-span bis-amide **36b** (in crystals of the dinitrate) the Ag–Ag distance of 3.3629(8) Å is at the long side, probably owing to an interference of the counterions.[154] The situation is different with complexes of the smaller and thus less-flexible ligand **36c**. In the crystals of the perchlorate salt, the macrocyclic dications have no transannular Ag–Ag contacts, but associate to give chains because of external contacts (3.344(5) Å, type **35b**). This pattern of interactions varies very little with other anions (nitrate or $C_2F_5CO_2$).[155] In the nitrite, two silver atoms are located in a 28-membered ring. Instead of a direct transannular argentophilic interaction, an additional silver atom (with two nitrite ligands) becomes the central element of an Ag–Ag–Ag bridge with distances of 3.014(1) and 3.043(1) Å (type **35d**).[156] In the 2:2 complex of di(2-pyridyl)dimethylsilane (**36d**) with $AgClO_4$, two 16-membered ring dications associate to give dimers establishing only one inter-dimer Ag–Ag contact (3.145(1) Å; **35b**, but limited to a dimer instead of a chain). It has been pointed out that the N-Ag-N axis at the Ag atoms concerned is bent outwards to allow this contact (168.9(2)°), while the axis at the Ag atoms not engaged in argentophilic bonding is close to linear (178.0(2)°).[157]

A particularly fascinating structure has finally been discovered in crystals of the compound prepared from 1,4-bis(2-methylimidazol-1-yl)benzene (L, **36e**) and $AgBF_4$. The compound $[Ag_2(L)_3][BF_4]_2$ contains sheets with hexagonal arrays $[(L)Ag]_6^{6+}$ with the silver atoms as triply connected nodes in a trigonal-planar coordination. These units are interwoven to give a Borromean sheet pattern (**36e′**). At the crossing points of the rings, Ag–Ag contacts of 3.0619(4) Å are established which appear to direct the self-assembly of the structure.[158]

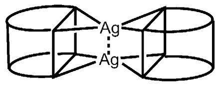
In the silver complexes of the multifunctional ligand **36f** with their chain-like organizations a manifold of coordination interactions is established, including Ag–Ag contacts, which are co-determined by the nature of the anion. The individual contributions to the organization and stability of the parallel or interwoven chains are difficult to assess.[159] Pyridine oxide functions are the donor sites offered to coordination with $AgClO_4$ in reactions with the calixarene-like tris(isonicotinoyl-*N*-oxide)cyclotriguaiacyclene. In complexes with *N*-methylpyrrolidone as an auxiliary ligand, the silver atoms are connecting nodes for the NO functions of the ligands and appear as linear trinuclear units with two equivalent distances of 3.2753(9) Å in an exceedingly complex structure.[160]

3.3. Unsupported and Supported Ag–Ag Contacts between Polyoxometalate Clusters

Polyoxometalate anions (POMs) have been shown to have a distinct preference for silver cations as linkers for their assembly into larger aggregates. Among other peripheral faces, octamolybdate anions $[Mo_8O_{26}]^{4-}$ offer two squares of terminal oxygen atoms in *trans* positions, and between these faces of neighboring clusters two Ag^+ cations can be accommodated which link the POMs into chains, thereby establishing Ag–Ag contacts (**37a**, POMs drawn as cubes to show the square faces). These columns are wrapped by the flexible nBu_4N^+ cations in the corresponding salts. The crystals may contain various solvent molecules (DMF, DMSO, MeCN). In the solvate-free crystals of the formula $[nBu_4N]_2[Ag_2Mo_8O_{26}]$ the Ag–Ag distance is 2.870(1)/2.853(4) Å (from two independent studies),[161,162] while in the solvates it varies between 2.853(4) and 3.4543(6) Å. The results of DFT calculations have indicated a significant bonding interaction.[161] The reaction of the nitrosylpolyoxomolybdate $[nBu_4N]_2[Mo_5O_{13}(OCH_3)_4(NO)Na(CH_3OH)]$ with $AgNO_3$ in methanol afforded a product of the formula $[nBu_4N]_4[Ag_2\{Mo_5O_{13}(OCH_3)_4(NO)\}_2]$. In the crystals, two polyoxometalate clusters are connected by a pair of silver atoms with an Ag–Ag distance of only 2.873(2) Å (**37b**; the single square face of each POM is shown as the contact area).[163]

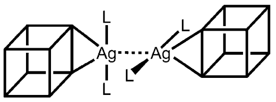


37a

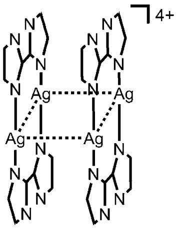


37b

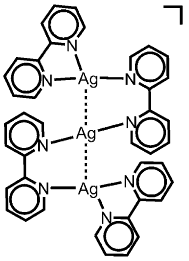
Similar results were obtained for the combination of $[H_3W_{12}O_{40}]^{5-}$ anions with $[Ag(NCCH_3)_2]^+$ and $[Ag(NCCH_3)_4]^+$ cations in the ratio 1:4:1. Two $[(MeCN)Ag(NCMe)]^+$ units form a pair through an Ag–Ag contact of 2.9075(2) Å which links the POMs. Each of the two silver atoms is positioned over an edge of a POM. The connectivity through four edges of each anion produces a three-dimensional porous framework (**38a**, the POMs shown as cubes, L = MeCN; only one linkage is shown.). The tetrahedral cation $[Ag(NCCH_3)_4]^+$ fills voids of the network. The results of DFT calculations carried out on a model composition suggest significant bonding Ag–Ag interactions.[164] Keggin polyoxometalate cluster units $[PW_{11}O_{39}]^{7-}$ and $[PW_{12}O_{40}]^{3-}$ have been found associated with silver cations and 2,2′-diimidazole (diim) in various combinations which include tetranuclear $[Ag_4(diim)_4]^{4+}$ cations (shown schematically in **38b**) and larger pentanuclear silver aggregates (not shown) that act as "cushions" between the POM units. The Ag–Ag contacts (2.864(3)–3.247(4) Å) in the two aggregates appear to be essential for the flexible structures that can easily adapt to structural preferences. The compounds are strongly luminescent (λ_{ex} = 336/370, λ_{em} = 415/493 nm for the crystals at room temperature).[165]



38a



38b



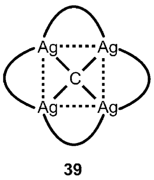
38c

Trinuclear units $[Ag_3(bipy)_4]^{3+}$ with a linear array of the three silver atoms (Ag–Ag 2.927(1) Å) have been found as linkers between Keggin anions $[PMo_{12}O_{40}]^{3-}$ in crystals of a dihydrate. The two terminal silver atoms are chelated by a bipy ligand, while the remaining two bipy ligands are bridging between the central silver atom and the two terminal ones (**38c**). A similar chain of four silver atoms is present in tetracations $[Ag_4(bipy)_6]^{4+}$ with Ag–Ag distances of 2.9363(3) (outer) and 3.131(2) Å (inner) which connect the anions $[PMo_{11}VO_{40}]^{4-}$. In both cases, the connectivity is established by the vertices of the POMs. The results of DFT calculations of the bonding in semi-bridged Ag–Ag contacts using model systems support the proposal of significant argentophilic interactions. The compounds show strong luminescence (λ_{ex} = 302, λ_{em} = 415 and 406 nm, respectively). See also Section 3.6.2, **94**).[166]

3.4. Multi-Argentation of Atoms

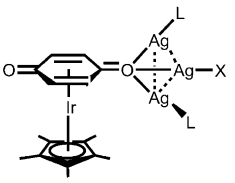
One of the most striking phenomena associated with aurophilic interactions has been the multiauration of main-group element atoms to give species of the type $[E\{Au(L)\}_n]^{m+}$ with E = B, C, N, P, As, O, S, Se, Te, Cl, and Br, with n in the range 2–6, the charge m depending on the nature of E, and with L as a supporting donor ligand.[15–18] The composition and structure, for example, of molecules or cations with the formula $[C\{Au(PR_3)\}_n]^{n-4}$ (n = 4–6) have been confirmed, and their bonding was the subject of several detailed theoretical analyses.[13–18] Surprisingly, to date no analogous molecular compounds with more than two silver atoms at a single bridging carbon atom have been reported. It is unclear if there were unsuccessful preparative attempts of polyargentation, or if the synthesis has so far not seriously been tried. The same is true for N- and O-centered analogues. As mentioned in the Introduction, solid-state chemistry provides many examples in which the combinations of silver cations and oxo- or imino-anions lead to a multicontact pattern, but the role of argentophilic interactions in these systems is far from clear. Recent examples also include silver sulfonylamides, cyanoximates, or triazine complexes in which Ag–Ag contacts are supported by multiple Ag–O or Ag–N coordination.[167–169] While in earlier work these aspects had not been considered, any such arrangement shows up prominently now in the discussions of the bonding characteristics in the current literature.

There have been several computational approaches to species with di- and poly-argentated atoms. One DFT study has considered model compounds with central CAg_4 units surrounded by bidentate auxiliary ligands, in a search for, among other things, a square-planar configuration of the carbon atom (**39**). It was found that argentophilic bonding should support this arrangement, but there is as yet no corroborating experimental evidence.[170]



39

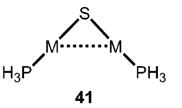
Molecules of the type $[E\{Ag(PR_3)\}_2]$ and the corresponding onium cations $[E\{Ag(PR_3)\}_3]^+$ with E = O, S, Se, Te are still unknown, while most of their gold analogues have long been prepared and structurally characterized.[15–18] Given the importance of trigoldoxonium salts $[\{(L)Au\}_3O]^+X^-$ in preparative gold chemistry, it is very noteworthy that no silver analogues have ever been introduced or considered. However, in a study of the reaction between silver triflate and a [(Cp*)Ir(benzoquinone)] complex (Cp* = C_5Me_5), a product has been isolated in which a quinone oxygen atom is capping a triangle of silver atoms with Ag–Ag edges of 3.37 Å ascribed to significant argentophilic interactions (**40**, L = MeCN, X = triflate).[171] Oxygen bridging between silver atoms has appeared in the complex array of silver cyanoximate (2-cyano-2-isonitrosamide) units $[\{Ag[NC\text{-}C(N{=}O)\text{-}C(O)NH_2]\}_n]$ with Ag–Ag distances of 3.1934(8) Å between hexacoordinate silver atoms, which in the present context is an extreme case regarding the connectivity of the silver atoms.[168]



40

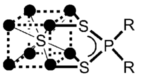
3.4.1. *Silver Clustering at Sulfur and Selenium*

As a model of the sulfur series, $[S(AgPH_3)_2]$ has been the target of recent theoretical studies.[172,173] In several variants of MP2 and DFT calculations its structure and those of the Cu and Au congeners have been optimized and found to feature narrow M-S-M angles with values in the range 76.4–80.0° for all three cases. The M–M distances in the "A-frame" (**41**, M = Cu, Ag, Au) are short for Cu (ca. 2.63 Å), but comparable for Ag and Au (ca. 2.9 and 3.0 Å) with variations ±0.1 Å depending on the level of theory. In an attempt to separate dispersion and ionic terms for the attraction between the metal atoms, it was found that for Cu the role of the ionic terms is exceptionally large, while for Ag and Au dispersion is the dominant effect.[172] With a move to single- and multi-reference range-separated DF perturbation theory, this trend—and the unique position of Cu—has been confirmed.[173] It should be noted that for $[S(MPH_3)_2]$ molecules an aggregation into dimers by intermolecular metallophilic interactions is to be anticipated, which is well known in gold chemistry.

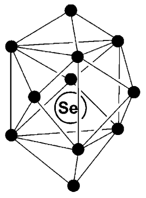


41

While examples of clusters with small numbers of silver atoms attached to a chalcogen atom are therefore still missing (**3a**, **3b**, **41**), the exhaustive clustering of silver cations at sulfide and selenide anions has been accomplished by introducing dithio- and diselenophosphate anions as multidentate peripheral ligands. In molecules of the composition $[Ag_8(S/Se)\{S/Se_2P(OR)_2\}_6]$ the central sulfur or selenium atoms are located in a cube of silver atoms with short Ag–Ag edges of average length 3.05 Å. $[(RO)_2PS_2]^-$ anions are attached to all six faces of the cube with each sulfur atom bridging two silver atoms (**42**, only one face shown covered with the dithiophosphonate ligand).[174–176] In the series $[Ag_{11}(S/Se)\{(S/Se)_2P(OR)_2\}_6X_3]$ with X = halogen and R = alkyl the environment of the nona-coordinate chalcogenide anion is a tricapped trigonal prism, and the edges of this polyhedron are within the same range of Ag–Ag distances. The two silver atoms capping the trigonal faces are not close to the sulfur/selenium center (**43**). This mode of clustering has also been found with halide anions as coordination centers (see Section 3.4.2).[177]



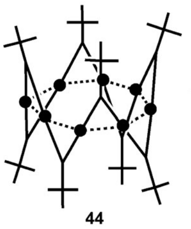
42

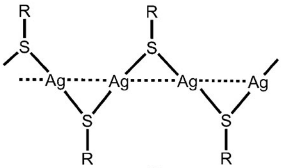


43

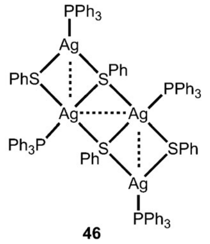
Thiolato instead of sulfido bridging of silver atoms is more common, and examples have been described for a variety of thiol precursors. In early work it was shown that the general formula $[\{RSAg\}_n]$ applies for both ring and chain structures. For primary alkyl groups R, polymers with $n = \infty$ are common, but for secondary and tertiary alkyl groups cyclic structures are formed: for example, $n = 12$ for cyclohexyl and $n = 8$ for *tert*-butyl (**44**). The 3-methyl-3-pentanethiolate, however, also has a chain structure.[178–180] The connectivities in the zigzag chains (**45**) are close to linear at the silver atoms and bent at the sulfur atoms with angles Ag-S-Ag in the range 88°–100°. This gives rise to intra-chain Ag–Ag contacts of around 3.10–3.30 Å. Shorter distances have been found between neighboring chains, the shortest being as short as 2.886(4) Å. These contacts were originally interpreted as just signaling the limit of repulsion,[179] but meanwhile—as shown in Section 2.1—there is generally more confidence in an Ag–Ag bonding contribution in these contacts. Structures of silver(I) thiophenolates have been determined for anions $[Ag_6(SPh)_8]^{2-}$ which are aggregated into a tubular framework through close Ag–S and Ag–Ag interactions (the shortest at 2.959(1) Å) with sulfur atoms bridging two or three silver atoms.[181] In the presence of auxiliary ligands, as in $[Ag_4(SPh)_4(PPh_3)_4]$, the silver atoms are also bridged by two thiolate groups with small Ag-S-Ag angles and an Ag–Ag contacts near 3.13 Å (**46**).[182]

A similar case of thiolate bridging has recently been discovered in a hexanuclear anion of the type $[Ag_6(L)_6]^{6-}$, with L = 3-(4-methoxyphenyl)-2-sulfanyl-propenoate (**47a**), and studied in great detail also by theoretical calculations of a model system.[183] The silver atoms form a planar hexagon the edges of which are alternately bridged by the thiolate sulfur atoms above and below the ring plane. Each silver atom is further coordinated by a carboxylate oxygen atom in


44

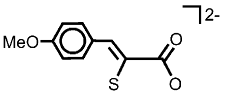


45

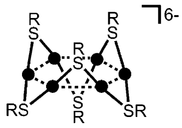


46

a chelate ring (chelation of the silver atoms by the carboxylate group not shown in **47b** for clarity). The Ag–Ag distances are very short at 2.8036(6) Å. Calculations of the model system $[Ag_6(SH)_6]$ (**47b** with R = H) at the HF and MP2 level have shown that inclusion of correlation effects is essential for reproducing the structure of the molecule. This is evidence that argentophilic bonding is indeed contributing significantly to the bonding in and between the $HSAg_2$ units. Energy differences of up to 300 kJ mol^{-1} between the HF and MP2 results have been found.[183]

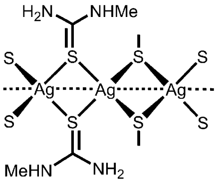


47a



47b

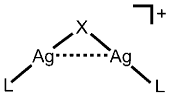
Methylthiourea (mtu) forms a 2:1 complex with $AgNO_3$ in which the cations are associated in chains with the silver atoms tetracoordinated by four bridging sulfur atoms. The Ag–Ag distances are 3.105(3) Å (**48**, +1 charge for each $[Ag(mtu)_2]^+$ unit not shown).[184] Sulfur-bridging of silver atoms by the thiolate groups of 2-mercaptonicotinic acid leads to the formation of hexanuclear units in which all the silver atoms are also coordinated by the pyridine N-atoms (type **47b**, RS for mercaptonicotinate, but pyridine coordination not shown). The carboxylate groups are not involved in Ag coordination but can be loaded with other metal complexes to give heterometallic aggregates which show thermochromic luminescence.[185] Tri-argentation of a sulfur atom has also been observed in an adduct of Ph_3PS at hexanuclear silver(I) trifluoroacetate (see Section 3.6.1).[186]



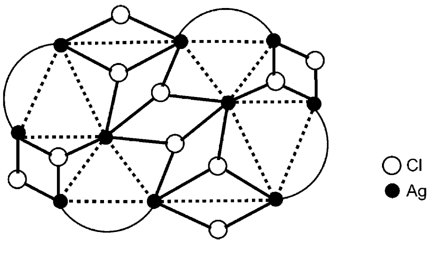
48

3.4.2. *Silver clustering at halogens*

There is no example of single halogen bridging in simple dinuclear silver complexes $[(L)AgXAg(L)]^+$ (**49**), but double bridging is present in molecules $(AgCl)_2$ and in anions $[\{[AgX_2\}_2]^{2-}$. These units appear di- or tetracoordinated by donor ligands (**12a**, **14d**, **14f**) with three- and four-coordinate silver atoms.[72,187] Because the transannular Ag–Ag distances (ca. 3.266 and 3.133 Å for Cl and I, respectively)[72] are largely determined by the halogen bridges, the role of argentophilic bonding cannot be reliably estimated. Tetramers of silver halides AgX are present in the cubane structures of the classical tetramers $[\{(Ph_3P)AgX\}_4]$ with X = Cl, Br, I already introduced in Section 2.1.3 (**12b**). There is now a large number of such cubane- or chair-type structures known in the literature which have doubly or triply argentated halogen atoms with Ag–Ag distances of approximately 3.00 Å.[110,188,189] From this wealth of data it has been concluded that conservation of the Ag–Ag interactions while minimizing the halide–halide repulsions are the determining effects in the formation of the clusters (cubane or distorted arrays as "stella quadrangular patterns").[110] Interestingly, a decamer has recently also been discovered in a cluster complex of the formula $[(NHC)_4Ag_{10}Cl_{10}]$ where NHC is 1-methyl-3-(2-dimethylaminoethyl)imidazol-2-ylidene. The large aggregate with its multiple Ag–Cl and Ag–Ag contacts is protected from further aggregation by the NHC ligands (**50**; carbene bridgings shown as bows).[71]

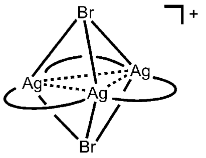


49

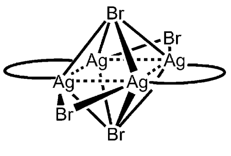


50

Capping of a triangle of silver atoms by bromine atoms above and below the plane of metal atoms is present in the structure of the cationic complex $[(Ag_3(dppm)_3Br_2]^+ Br^-$ (**51**; dppm = bis(diphenylphosphanyl)methane). Owing to the large atomic radius of the bromine atom, the Ag–Ag distances are on average 3.30 Å suggesting only weak bonding.[190] μ_2 and μ_4 bridging of silver atoms by bromine atoms has been observed with bis(diphenylphosphino)amine (dppa) ligands as in $[Ag_4(dppa)_2Br_4]$. The Ag–Ag distances are 2.964(3) and 3.081(2) Å (**52**).[191]



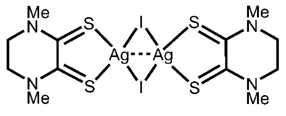
51



52

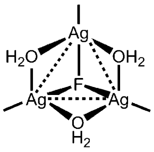
Silver atoms bridged by iodine atoms have been found in the 1:2 complex of *N,N'*-dimethylpiperazine-2,3-dithione (L) with AgI. In crystals of $[Ag_2(L)I_2]$ pairs of silver atoms with distances Ag–Ag as short as 2.8139(9) and 3.1460(9) Å (two different structural units) are double-bridged by iodine atoms with acute angles Ag-I-Ag of only 58.27(1)° (**53**). The bonding in the Ag_2I_2 rings contained therein has been analyzed by DFT, MP2, and atoms-in-molecules calculations. Considering bond and ring critical points, significant Ag–Ag bonding has been proposed. Argentophilic interactions appear to gain in importance rapidly as the distance is lowered to below 3.2 Å.[192]

In a double salt $(AgCN)(AgF)_2(H_2O)_3$ a μ_3-fluoride-bridge has been detected, and this bridge is further supported

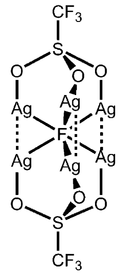


53

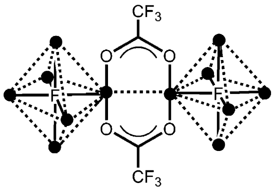
by a water molecule. This structural unit is unknown in gold chemistry. The water oxygen atoms, one fluoride anion, and the three silver cations form a pseudo-cube (missing one corner; **54**).[193] However, with a different ratio of the components, in $(AgCN)_3(AgF)(H_2O)_3$, one of the cyanide anions is di-argentated at both C and N, while the other two cyanide anions have diargentated N and mono-argentated C atoms, but the fluoride anion is in a terminal position Ag–F and is only involved in hydrogen bonding.[193] In the ternary system of the composition $4\,CF_3COOAg{\cdot}Ag_2C_2{\cdot}AgF{\cdot}2\,RCN$ (R = Me, Et) the fluoride anion is accommodated in a "lantern-type" (quasi-trigonal prismatic) cavity formed by six silver atoms and two tridentate triflate oxygen atoms (**55**). The side edges of the prism (Ag–Ag av. 2.95 Å) are also part of the silver cages around the acetylide dianion (see also Section 3.4.3).[194] Finally, in a compound $AgCN{\cdot}AgF{\cdot}4\,AgOC(O)CF_3{\cdot}2\,H_2O$ the single fluoride anion is in an octahedral coordination of six silver cations (**56**). This environment is the same as in the rock-salt structure of AgF, with Ag–Ag distances in the range 3.463–3.562 Å and therefore at the upper end of the range where argentophilic bonding could be involved. However, the silver atoms are also part of double-bridged eight-membered rings $[\{CF_3COOAg\}_2]$ with typical short transannular Ag–Ag contacts of 2.8835(8) Å (see Section 3.7.1).[195]



54

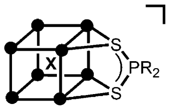


55



56

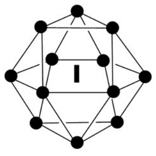
The situation is very different in halide-centered silver clusters stabilized by dithiophosphate ligands. In a compound $[Ag_8(F)\{S_2P(OR)_2\}_6]PF_6$ (R = Et, Pr), the fluoride anion resides at the center of a cube of silver cations with Ag–Ag edges in the range 3.04(1)–3.26(1) Å (**57**, X = F, the ligation is only shown for one of the six faces), similar to the structure of the corresponding sulfur-and selenium-centered clusters (**42**). It is important to point out that the Ag–Ag edges of the F-centered cube are shorter that those of the F-centered octahedra (in **56**). The bonding situation in these clusters has been analyzed by DFT calculations which suggest a high electrostatic character, but also significant Ag–Ag interactions.[175,196] Similar results have been obtained with dithiophosphinite ligands $[(PhCH_2CH_2)_2PS_2]^-$.[197]



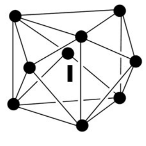
57

This chemistry has been extended to include interstitial chloride and bromide anions. For the same stoichiometry of the compounds, the two larger anions are also found in a cubic environment (**57**, X = Cl, Br) but the Ag–Ag edges in these larger polyhedra are in the ranges 3.22–3.42 and 3.32–3.41 Å, respectively, indicating much weaker interactions.[197] The results are similar for Cl- and Br-centered cubes with the corresponding diselenophosphate $[Se_2P(OR)_2]^-$ ligands.[198]

However, with iodide the octacoordination is no longer stable, and the polyhedron is enlarged to a cuboctahedral structure making the halide anion dodeca-coordinated: $[Ag_{12}I(S_2PR_2)_6]I_4$. This polyhedron has six square faces for the dithiophosphate ligands, and its Ag–Ag edges are again shorter with an average of 3.11 Å (**58**). The compound shows a strong yellow luminescence both in solution and in the solid state ($\lambda_{ex} = 444$, $\lambda_{em} = 560$ nm for the solid at 77 K). The effect was explored by computational studies which have shown the HOMO of the cluster to be largely composed of 4d(Ag) orbitals.[197] With a slightly different stoichiometry of reactants ($[Ag(MeCN)_4]PF_6$ and $[Bu_4N]I$ with ammonium dialkyl dithio- and ammonium dialkyl diselenophosphates), products were obtained which have the iodide anion in the center of a pentacapped trigonal prism of silver atoms. Ignoring the two silver atoms capping the triangles of the prism which are further apart, the iodide anion is nona-coordinate in the trigonal prism tricapped at its square faces (**59**). The lengths of the Ag–Ag edges cover a broad range, but are all within limits which allow for argentophilic interactions. The compounds are strongly luminescent both in solution and as solids ($\lambda_{ex} = 379$, $\lambda_{em} = 598$ nm at 77 K for the crystals of the diisopropyl dithiophosphate).[199]



58



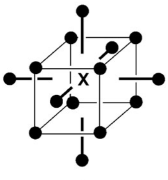
59

Halide anions encapsulated in even larger clusters of silver cations are present in compounds $[Ag_{14}(C{\equiv}C\mathit{t}Bu)_{12}(X)]BF_4$ with X = F, Cl, Br. A rhombohedral cage is established best described as an interpenetration of a cube and an octahedron, or as a cube of silver atoms with its six square faces capped by a silver atom (**60**). Two alkynyl ligands are coordinated linearly to each of the apical silver atoms. The Ag–Ag edges are in the ranges 2.90–2.92 (F), 2.95–2.99 (Cl), and 2.97–3.01 (Br) and indicate metallophilic interactions.[200]

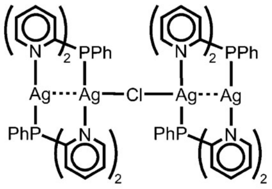
An almost linear Ag-Cl-Ag bridge has recently been discovered in chains of dinuclear complexes with di(2-pyridyl)phenylphosphine ligands (**61**). Short Ag–Ag contacts are observed only within the dimetallacycles (see Section 3.7.3).[201]

3.4.3. *Silver Clustering at the Acetylide Dianion*

The structural chemistry of silver(I) acetylides ("carbides", "acetylenediides", "ethynediides", "ethynides") has recently been summarized by the group of Mak which has



60

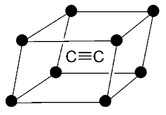


61

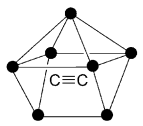
developed this field very extensively over the last two decades.[202] Therefore, this material is not duplicated here, and only the relevant aspects are highlighted.

It has been known for about two centuries that silver salts yield a dark, explosive precipitate of "silver carbide" Ag_2C_2 if acetylene gas is bubbled into their aqueous solutions. The structure is not known, but assumed to be a coordination polymer based not only on -Ag-C$\equiv$C-Ag- coordinative bonding in chains, but also on side-on π-bonding of the metal cations to the acetylide units, and on argentophilic interactions between these chains. In 1946 it was observed[203] that the precipitate is readily dissolved in an aqueous solution of an excess of $AgNO_3$ to yield a "double salt" $(Ag_2C_2)(AgNO_3)_6$, and subsequently several other products of this type were found with silver salts having anions other than nitrate. These results have shown that there is a pronounced affinity of the $[C\equiv C]^{2-}$ dianion for silver cations, and in later research it has been demonstrated that its poly-argentation leads to a fascinating variety of C_2-centered silver clusters in current literature represented by formulae such as $[C_2@Ag_n]^{(n-2)+}$ ($n = 6$–10).

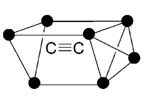
In early structural work is had already been demonstrated that in crystals of the classical example $(Ag_2C_2)(AgNO_3)_6$ the C_2 dumbbell is surrounded by a rhombohedral Ag_8 cage ($[C_2@Ag_8]^{6+}$, **62a**).[203] In $(Ag_2C_2)(AgNO_3)_5$, isolated from the same lot of crystals, the C_2 unit is accommodated in a trigonal prism monocapped at a square face or at a trigonal face ($[C_2@Ag_7]^{5+}$, **62b**, **62c**).[194,204] Dissolving Ag_2C_2 in a concentrated aqueous solution of AgF produces a complex of the composition $Ag_2C_2{\cdot}8\,AgF$ in which the C_2 dumbbells are located in the center of a capped square antiprism (**62d**) with one external silver atom on the fourfold axis (described as $[\{C_2@Ag_9\}Ag]^{8+}$.[205] The mixed product $Ag_2C_2{\cdot}AgF{\cdot}4\,CF_3COOAg{\cdot}CH_3CN$ also has $[C_2@Ag_7]^{5+}$ clusters with one silver atom capping a trigonal face of a trigonal prism (**62 c**).[206]



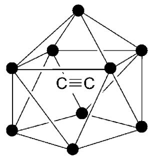
62a



62b



62c



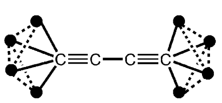
62d

This set of representative examples has further grown enormously to include a number of larger C_2-centered polyhedra which then can share edges or faces to form extended structures. The work published up to 2006 has been reviewed.[202] Later work has provided additional systems following the same pattern of clustering of silver atoms around the acetylide dianion. Extensive work has recently been dedicated to compounds with silver phenyl- and benzylphosphonates, which can only be obtained by hydrothermal methods. In the products, the C_2 units have been found in a manifold of discrete silver clusters of the types $C_2@Ag_9$, $(C_2)_2@Ag_{14}$, and $C_2@Ag_{18}$, but also in chains of such clusters and in layered aggregates.[207] Similar architectures had already been observed in fluorocarboxylates, such as $2\,Ag_2C_2{\cdot}12\,CF_3COOAg{\cdot}5\,H_2O$.[208]

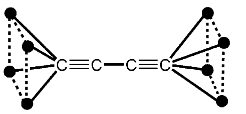
The bonding along the edges of the silver polyhedra (2.7–3.4 Å in length) has been ascribed to significant contributions from argentophilic interactions. It is true that the stoichiometry and structure of the $C_2@Ag_n$ units is mainly determined by the nature of the counterions and can also be influenced by auxiliary ligands. It is remarkable, however, that in virtually all variations multiple Ag–Ag contacts are maintained suggesting an essential stabilization of the clusters around one or more C_2 units.[202] With this background it is the more remarkable that no related phenomena have been observed for methanides $C@Ag_n$ with a single carbon atom embedded in a molecular silver matrix.

3.4.4. *Silver Clustering at Alkynyl Anions $[(C\equiv C)_n]^{2-}$, $[R\text{-}C\equiv C]^-$, and $[C\equiv C\text{-}X\text{-}C\equiv C]^{2-}$*

A similar structural chemistry has emerged from studies with the explosive "silver diacetylide" (butadiynide) Ag_2C_4 as a rod-like nucleation unit for the aggregation of silver cations at its ends. The work published up to 2007 has been summarized also in a Review by Mak and Zhao.[209] In standard cases, the linear $[C\equiv C\text{-}C\equiv C]^{2-}$ unit was found accommodated between up to four or even five silver cations in square or butterfly arrangements at either terminal carbon atom. Representative compounds, such as $Ag_2C_4{\cdot}16\,C_2F_5COOAg{\cdot}6\,CH_3CN{\cdot}8\,H_2O$ (**63a**) and $Ag_2C_4{\cdot}6\,CF_3COOAg$ (**63b**) serve to illustrate the small structural variations at the CAg_4 terminals.



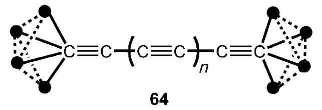
63a



63b

Very recently,[210] this work has been extended to include the tri- and tetraacetylides (hexatriynide and octatetraynides). The highly explosive compounds Ag_2C_6 and Ag_2C_8 can be protected by the addition of silver(I) triflate $AgOSO_2CF_3$ in compounds of the stoichiometry $Ag_2C_6{\cdot}8\,AgOSO_2CF_3$, crystallizing as a hexahydrate or as a DMSO solvate, and $5\,Ag_2C_8{\cdot}20\,AgOSO_2CF_3$ also as a DMSO solvate. The carbide rods being arranged parallel in different connectivity patterns, both ends of the rods are embedded in a group of three or four silver cations (**64**, $n = 1$, 2) which are interconnected by Ag–

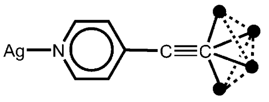
Ag contacts in the range 2.75–3.57 Å and further surrounded by the counterions and solvate molecules (not shown).



64

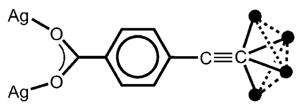
Similar arrangements are encountered at terminal alkynes like R-C≡CH (R = alkyl, aryl) and dialkynyls like HC≡C-L-C≡CH (L = difunctional linker). Through corner-, edge-, or face-sharing of the clusters built around the terminal alkynyl anions, multidimensional aggregates are formed, and multidimensionality is also achieved by using multifunctional terminal alkynes as also shown in very recent work.[209,211–213] In several Review articles, the variety of bonding modes has been summarized.[214–217] It is important to note that alkene and non-terminal alkyne units can become engaged in bonding with silver atoms through η^2 side-on complexation.[214] If only arene units are available for silver coordination in addition to the terminal alkynyl groups, and if there is a deficit in anion coordination, then the silver atoms entertain η^2-bonding to the edges of phenyl rings to assist in their coordinative saturation.[203]

Butterfly-type Ag_4 units have also been detected in the supramolecular aggregates produced from 4-pyridylethyne and CF_3COOAg (1:6) or $AgNO_3$ (2:4) with structural patterns as shown in **65**. The compounds are strongly luminescent in the solid state ($\lambda_{em} = 564$ and 610/556 and 620, $\lambda_{ex=}$362/380 nm, respectively).[218] 3,5-Diethynylpyridine affords a more extended framework, but each of the two ethynyl functions is also embedded in butterfly-type $C_2@Ag_4$ units.[219]



65

The reactions of 4-ethynyl benzoic acid and its esters with $AgNO_3$ yield products with the C_2 units anchored in polysilver aggregates with stoichiometries such as $(AgC_2\text{-}C_6H_4\text{-}COOAg)\cdot3\,AgNO_3$ featuring $C_2@Ag_4$ groups (**66**). The compounds are luminescent in the solid state at room temperature with $\lambda_{em} = 527$ nm ($\lambda_{ex} = 370$ nm, life time 0.20 ms) for the quoted example.[220]



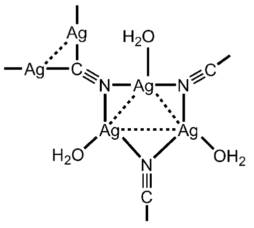
66

With simple alkynes shielded by bulky substituents, as in *t*Bu-C≡CH, smaller units are preserved in the crystals, as for example, in *t*Bu-C≡CAg·3 $CF_3COOAg\cdot H_2O$. Ag–Ag distances are again found in the range 2.873(1)–3.351(2) Å.[209] *t*Bu-C≡CH has also recently been used to cover polyoxometalate anions with a layer of silver cations assembled with the acetylide anions as peripheral integrating units. The compositions of the vanadates, molybdates, and tungstates studied by crystallography are, among others, $[Ag_{40}(t\mathrm{BuC}{\equiv}\mathrm{C})_{22}(CF_3COO)_{12}(V_{10}O_{28})]$,
$[Ag_{40}(t\mathrm{BuC}{\equiv}\mathrm{C})_{20}(CF_3COO)_{12}(Mo_6O_{22})]$,
$[Ag_{60}(t\mathrm{BuC}{\equiv}\mathrm{C})_{38}(Mo_6O_{22})_2]^{6+}$
$[Ag_{70}(t\mathrm{BuC}{\equiv}\mathrm{C})_{44}(PW_9O_{34})_2(H_2O)_2]^{8+}$,
$[(V_2O_7)_2@Ag_{44}(t\mathrm{BuC}{\equiv}\mathrm{C})_{14}@(V_{32}O_{96})]^{10-}$, and
$[(NO_3)_2@Ag_{16}(\mathrm{PhC}{\equiv}\mathrm{C})_{14}(t\mathrm{BuPO_3})_4V_4O_8]_2(NO_3)_2]$.

As indicated by @ in the latter two formulae, anions may be found encapsulated in multicentered silver alkynylide or arylynide frameworks which are again wrapped by an outer shell. An extensive network of argentophilic interactions and the steric protection by the *tert*-butyl groups stabilize the aggregates.[221–224] The core unit may also be a "single molecule magnet (SMM)" as in $[Ag_{42}(t\mathrm{BuC}{\equiv}\mathrm{C})_{28}Ho(W_5O_{18})_2Cl_4(OH)]$.[225] POMs have also been found organized around polysilver acetylide clusters $C_2@Ag_n$ with $n = 6$, 7. Owing to the complexity of the structures, the reader is directed to the original papers for details.[226,227]

3.5. Supramolecular Aggregates Based on Cyanoargentate(I) Anions $[Ag_m(CN)_n]^{(n-m)-}$

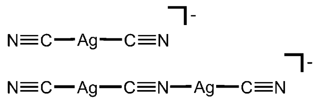
Multi-argentation of cyanide anions is not as common as for acetylide anions. Representative cases are found in the quaternary compound $2\,Ag_2C_2\cdot3\,AgCN\cdot15\,CF_3COOAg\cdot2\,AgBF_4\cdot9\,H_2O$, in which the cyanide anions are tri- and tetra-argentated (**67**),[228] and in the ternary system AgCN·Ag**F**·4 $AgOC(O)CF_3\cdot2\,H_2O$ already mentioned in Section 3.4.2.[195] Apart from these rare cases, silver(I) cyanide chemistry is dominated by the compositions with the cyanide anions terminally coordinated by one silver atom at either one or both ends, as in the solid-state structure of silver cyanide: -Ag-C≡N-Ag-C≡N-.



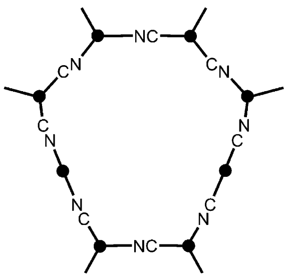
67

Extensive work in gold chemistry has shown that dicyanoaurates(I) with the anion $[Au(CN)_2]^-$ show a rich supramolecular chemistry.[229] The structures of many crystalline systems are (co-)determined by aurophilic interactions. Similar advances were recently achieved in silver chemistry, where the anions $[(N{\equiv}C)Ag(C{\equiv}N)]^-$ also appear as parts of equally linear dinuclear units $[(N{\equiv}C)Ag(C{\equiv}N)Ag(C{\equiv}N)]^-$ found much less often in gold chemistry. In short, the two anions (**68a**) can function as unique linear five-atom and seven-atom linkers between metal atoms, but through their argentophilic affinity they can also cross-link the resulting structures to give them a higher dimensionality.

The close approach of $[Ag(CN)_2]^-$ anions in the lattices of simple salts such as $K[Ag(CN)_2]$ or $Ca[\{Ag(CN)_2\}_2](H_2O)_2$ establishing short Ag–Ag contacts has been documented already in some very early literature.[230] This work has later been extended to include the heavy main-group metals, as in $Tl[Ag(CN)_2]$ mentioned in Section 2.2,[80,231] which exhibit strong luminescence owing to the presence of $[\{Ag(CN)_2\}_n]^{n-}$ chains (Ag–Ag distances 3.110(3) and 3.528(3) Å) with trinuclear repeating units (**17**). Similar aggregation has been found in organic onium dicyanoargentates(I) (Ref. [105], see Section 2.5.2).

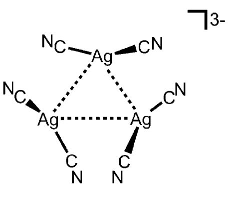


68a



68b

A unique assembly of anions through argentophilic interactions between both linearly two- and trigonally three-coordinate silver atoms (Ag–Ag 3.0731(5) and 3.1495(5) Å) has been detected in the compound $[NMe_4][Ag_3(CN)_4]$. The structure consists of threefold interpenetrated three-connected (10,3)-g nets. The grid of each single layer is composed of hexagons with silver atoms at their corners and two long (NCAgCNAgCN) and four short (NCAgCN) edges (**68b**), and these grids form interlayer Ag–Ag contacts. The compound emits a green luminescence ($\lambda_{max} = 510$ nm, life time 1.36 ns) upon excitation at $\lambda_{ex} = 398$ nm.[232] In contrast, in a compound of the composition $[NMe_4]_2[KAg_3(CN)_6]$ the silver atoms are associated in triangular units of C_3 symmetry (**69**). The C-Ag-C axes are bent to 166.8° allowing for Ag–Ag contacts of 3.2008(9) Å. The complex shows a green luminescence in the solid state ($\lambda_{ex} = 267$, $\lambda_{em} = 490$ nm) which has been assigned to LMCT processes by DFT calculations.[233]

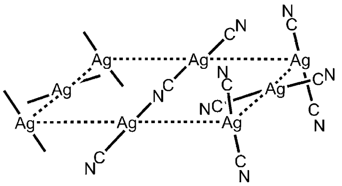


69

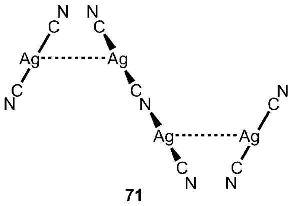
If coordinatively saturated metal cations are present instead of quaternary ammonium cations, the dicyanoargentate(I) anions also form separate aggregates. In the three isostructural Co^{III}, Cr^{III}, and Ru^{III} compounds of the type $[M(NH_3)_6\{Ag(CN)_2\}(H_2O)_2]$ (M = Co, Cr, Ru), the anions are organized in centrosymmetrical triples (**24b**) with a staggered conformation and with Ag–Ag distances of approximately 3.15 Å.[234]

Recent work has largely focused on compounds with coordinatively unsaturated transition-metal complex cations where the cyano groups therefore function as connectors or spacers establishing Ag-C≡N-M linkages (M = Zn, Cu, Ni, Co, Fe, Mn, Ru, Pt, Cd etc.). The reaction between Cu^{II}, Ni^{II}, Zn^{II}, and Cd^{II} salts with two equivalents each of ethylenediamine and $K[Ag(CN)_2]$ thus yields complexes $[M(en)_2\{Ag(CN)_2\}_2]$ which all feature Ag–Ag contacts in chains of anions (**17**).[235] Replacing en by 1,2-diaminopropane (pn) leads to similar results: $[Cu(pn)_2\{Ag(CN)_2\}]$.[236]

A representative example for the structural variability is the copper(II) complex with diethylenetriamine ligands (dien) of the formula $[Cu_2(dien)_2Ag_5(CN)_9]$ containing the $[Ag(CN)_2]^-$ and the $[Ag_2(CN)_3]^-$ anions in a ratio 3:1. Both anions link the Cu centers through their terminal nitrogen atoms and establish argentophilic Ag–Ag contacts as shown schematically in **70**.[237] In parallel studies a different ratio of mono- and dinuclear anions (1:1) was found in $[Cu(en)_2Ag_3(CN)_5]$. In the chains of silver atoms, the two anions alternate establishing Ag–Ag contacts of 3.102(1) Å length (**71**). With dien as a ligand, the stoichiometry can change to $[Cu(dien)\{Ag(CN)_2\}_2\{Ag_2(CN)_3\}]$ in which the dinuclear anion forms only Ag–Ag contacts while the mononuclear anions function as ligands to five-coordinate copper atoms.[238]



70

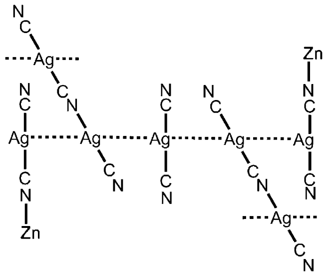


71

Independent 4-methylpyridine ligands (Mepyr) also build five-coordinate copper(II) complexes with end-on coordinating $[Ag(CN)_2]^-$ anions in the complex $[Cu(Mepyr)_2\{Ag(CN)_2\}_2]$. The anions are stacked to maintain Ag–Ag contacts (3.232(1) Å).[239] With an additional equivalent of Mepyr, one of the two silver atoms becomes tricoordinate, but its Ag–Ag contacts are even shorter (2.9264(5) Å) than that between the dicoordinated silver atoms (3.2463(6) Å). The compounds may contain traces of copper(I).[240] With copper(II) complexed by both phenanthroline and acetylacetonate $[Cu(phen)(acac)]^+$, the $[Ag(CN)_2]^-$ anions are arranged as pairs with orthogonal C-Ag-C axes and an Ag–Ag contact of 3.2144(7) Å (**24a**).[241]

Through a stacking of layers formed in crystals of a complex between dinuclear copper(II) 3-aminopropanolate cations and $[Ag(CN)_2]^-$ anions (**17**) the silver atoms become arranged in an almost straight line perpendicular to the sheet structure (Ag–Ag 3.015(1) Å). The corresponding gold(I) compound is isomorphous.[242] The copper(II) complex with a Schiff base ligand at the copper(II) center, $[\{(L)Cu\}Ag(CN)_2]$ with L = 3-(*E*)-[(2-aminoethyl)imino]methylphenolate, forms a coordination polymer with zigzag chains -Cu(L)-NC-Ag-CN-Cu(L)-NC- which are interconnected by argentophilic interactions (Ag–Ag 3.015(1) Å), again in a straight line of equidistant silver atoms (**17**). With a branched ligand side chain (L′ = 2-aminopropanolate), the complex [{(L′)Cu}Ag(CN)$_2$] exists as a monomer, but there are intermolecular Ag–Ag contacts of 3.0563(6) Å in pairs of molecules.[243]

The structural chemistry of the analogous zinc(II) dicyanoargentates(I) follows similar patterns. With the tris(2-aminoethyl)amine ligand (tren), a compound of the formula [(tren)Zn{Ag$_5$(CN)$_9$}] has been crystallized. It contains a sequence of [Ag(CN)$_2$]$^-$ and [Ag$_2$(CN)$_3$]$^-$ anions and (tren)Zn-NCAgCN units in chains formed exclusively through argentophilic contacts (**72**).[244,245]



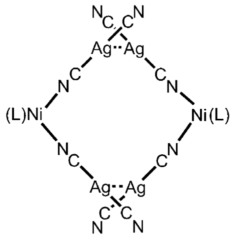
72

The complex [Ni(en)$_2${Ag(CN)$_2$}$_2$] already mentioned above has the anions arranged in chains in a staggered conformation with the silver atoms on a straight line with Ag–Ag distances of 3.221(2) Å (**17**). In contrast, with an extra en ligand and the nickel atoms thus coordinatively saturated, the anions appear in pairs (**24b**) with the Ag–Ag distance not very different, at 3.293(2) Å.[235]

The structure of [Ni(en)$_2${Ag$_3$(CN)$_5$}] has been determined by two groups.[238,246] It also contains [Ag(CN)$_2$]$^-$ and [Ag$_2$(CN)$_3$]$^-$ anions associating with each other at Ag–Ag distances of 3.2627(3) Å. Surprisingly, in the complex [(tren)Ni{Ag(CN)$_2$}]$_2$] the (tren)Ni units are linked by one half of the anions into zigzag chains, while the other half is filling the voids between these chains. The closest Ag–Ag contacts are as long as 3.5607(6) Å and therefore not indicative of any significant bonding contribution. No explanation could be offered for this unusual absence of metallophilic contacts.

The introduction of chiral macrocyclic ligands at the nickel atom leads to a rich complexity for the dicyanoargentate(I) complexes. The ligand employed in the studies was 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane in its racemic and enantiopure forms. Helical chains of complexes [(L)Ni{Ag(CN)$_2$}$_2$] with defined right-handed and left-handed helicity have been obtained and structurally characterized. The nickel atoms are surrounded by the multifunctional ligand L and bear the two terminally N-bonded [Ag(CN)$_2$] units in a *cis* arrangement. The complex molecules are linked by argentophilic contacts with Ag–Ag distances in the range 2.9956(7)–3.353(3) Å into dimers (**73**) or 1D polymers depending on the configuration of the (L)Ni components. The chirality has been traced by circular dichroism (CD) measurements of two stereoisomers. The compounds are strongly luminescent in the solid state with emission maxima near $\lambda_{em} = 425$ nm ($\lambda_{ex} = 310$ nm). The effect is ascribed to LMCT processes (see Section 2.5.2).[247]

Iron(II) dicyanoaurates(I) have been prepared with substituted pyridines as auxiliary ligands. Compounds of the type [Fe(3-Xpyr)$_2${Ag(CN)$_2$}$_2$] with 3-Xpyr representing a 3-halogeno-pyridine (X = F, Cl, Br, I) form corrugated layer structures in which the iron center is octahedrally coordinated including four [Ag(CN)$_2$] connectors. These layers form pairs (double layers) through Ag–Ag contacts (3.0–3.3 Å depending on X).[248] With 3,5-dimethylpyridine (dmp), the compound [Fe(dmp){Ag$_3$(CN)$_5$}] was obtained in which the equally hexacoordinated iron(II) centers are connected by both [Ag(CN)$_2$] and [Ag$_2$(CN)$_3$] spacers in *trans* positions. Corrugated grids are formed which further associate into double layers through argentophilic contacts. In magnetic measurements it has been demonstrated that a spin transition (from high spin (HS) to low-spin (LS)) occurs at 235 K. This is accompanied by a phase transition (from *C*2/*c* to *Cc*), but the structures are very similar. However, there is nevertheless a shortening of the Ag–Ag contact from 3.224 (293 K) to 3.073 Å (at 80 K). Notably, this shrinkage is very considerably more pronounced than common thermal contraction (see Section 2.3).[249] The crystal structure of the compound [Fe(3cp)$_2${Ag(CN)$_2$}$_2$(H$_2$O)$_{2/3}$] with 3cp = 3-cyanopyridine, has also been determined both at 240 and 145 K. In this range there is no phase transition, but a HS→LS cross-over. In the crystal structure the components form 3D grids of the NbO type. The Ag–Ag contacts between the interpenetrating grids shrink from 3.256(2) to 3.1593(6) Å, again a substantial deviation from data for normal thermal expansion/contraction.[250] In earlier work, pyrazine and pyrimidine ligands had given similar structural results.[251]

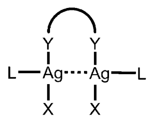


73

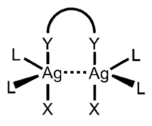
Manganese(II) is the coordination center in a compound [Mn(dipy)$_2${Ag(CN)$_2$}$_2$H$_2$O] with dipy = 2,2′-dipyridyl. In the crystals of the complex, only one [Ag(CN)$_2$] unit is a monodentate ligand to the hexacoordinated manganese atom which also bears two bipy ligands and a water molecule. The second [Ag(CN)$_2$] unit is a free anion and its only interaction is an argentophilic contact to the coordinated Ag center (Ag–Ag 3.253 Å).[252] With 2-aminopyrazine (ampyz) and benzimidazole (benzim) as ligands to manganese(II), the complexes [Mn(ampyz){Ag$_3$(CN)$_5$}(H$_2$O)(ampyz)] and [Mn-(benzim)$_2${Ag(CN)$_2$}$_2$(benzim)] have been crystallized, respectively. In the ampyz complex, the manganese atoms are connected by [NCAgCN] and [NCAgNCAgCN] spacers to form a corrugated grid of rectangles with wave-like edges of 10.5 and 15.6 Å length (Mn to Mn). Adjacent layers establish Ag–Ag contacts of 3.0530(3), 3.0320(3), and 3.3420(4) Å. The benzim complex also forms undulating sheets, but with rhombic units having wave-like edges of uniform length (Mn to Mn 10.7 Å). Argentophilic contacts between the layers have a distance of 3.2551(3) Å. Intercalated between the sheets are [(benzim)AgCN] molecules which entertain an Ag–Ag contact of 3.1225(5) Å with silver atoms of the sheets.[253]

3.6. Mono-Bridged (Semi-Bridged) Ag–Ag Contacts

There is a large variety of silver(I) complexes with semi-bridged intramolecular Ag–Ag contacts. In general, a neutral or anionic ligand with two donor functions separated by one, two, or more atoms has a silver cation attached at either end. If the ligand is flexible, or if it has a fixed hair-pin geometry, then the two silver atoms can approach each other to the common Ag–Ag equilibrium distance of approximately 3.0 Å. The coordination sphere of the silver atoms may be strictly two-coordinate (**2a**, **2b**) or contain additional ligands or counterions (**74a**, **74b**). With only one ligand per silver cation, the complex cations $[(L)Ag]^+$ can form macrocyclic aggregates $[\{(L)Ag\}_n]^{n+}$ or chains $[\{(L)Ag\}_\infty]^{\infty+}$ (**35c**).[186] Examples of these modes of organization have been observed with many different types of ligands. In the following, only selected cases are presented including some more recent work.



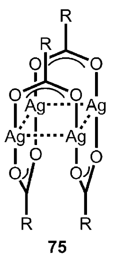
74a



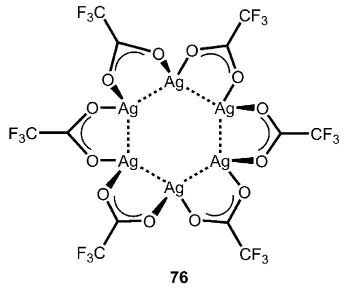
74b

3.6.1. Carboxylate O,O-Mono-Bridging

The most common mono-bridging ligands are carboxylates $RCOO^-$. A classical example is the structure of disilver succinate. Four silver atoms form a square with Ag–Ag contacts of 2.938(1) Å. Each edge is bridged by a carboxylate group alternatingly above or below the plane of the silver atoms (**75**, $R = CH_2CH_2COO$). These units are further connected in the same way through the terminal carboxylate groups at the substituents R to give a three-dimensional diamantoid network.[167,254] Another illustrative case is the hexanuclear complex $[\{Ag(CF_3COO)\}_6]\cdot 6\,Ph_3PS$. The CF_3COO groups are positioned alternately above and below the ring of silver atoms, and the average length of the six Ag–Ag contacts is 3.20 Å. Three consecutive silver atoms are always capped by the triphenylphosphine sulfide ligands through Ag–S coordination (not shown in **76**).[186] With the involvement of N-donor functions at the carboxylic acid, as for example, in silver pyrazine carboxylate,[255] the distance between multi-N/O-coordinated silver atoms is 3.0686(7) Å.

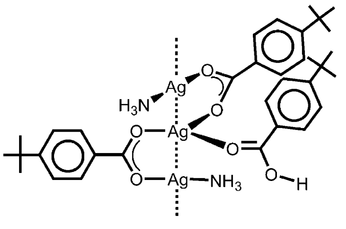


75



76

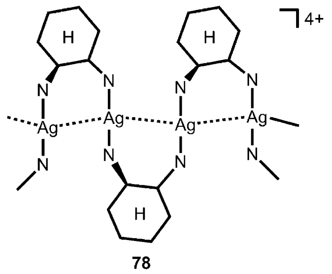
In trinuclear subunits of the stoichiometry $[Ag_3(tbb)_3(NH_3)_2]$, two 4-^{t}butylbenzoate groups (tbb) are bridging the three silver atoms while two NH_3 molecules and the third tbbH group are terminal ligands (**77**). These subunits are grouped into chains by further Ag–Ag contacts (3.028(1)–3.091(1) Å). The crystals are strongly luminescent ($\lambda_{ex} = 300$ nm, $\lambda_{em} = 430$ nm).[117]



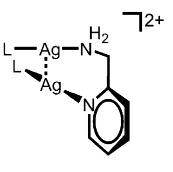
77

3.6.2. Mono-Bridging with N,N-Donor Ligands

Mono-bridging by N,N donor ligands along chains is most readily illustrated by the phenomena observed with *trans*-1,2-diaminocyclohexane (**78**). The folding induced by the chiral ligands (C_2 symmetry) brings all the atoms along the chain into contacts with slightly alternating distances of 3.126(1) and 3.274(1) Å. Alternatively, the Ag–Ag contacts may be established between the chains with distances of 3.111(1) Å.[256] In the nitrate salt, there are no intra-chain Ag–Ag contacts, but the chains are linked by inter-chain interactions (3.2327(6) Å; type **33a**).[257] 2-Aminomethyl pyridine (L) has also been found to establish single bridges between silver atoms (2.9137(3) Å) in the product with 3:2 stoichiometry (with triflate counterions; **79**). For the 2:1 stoichiometry, only unsupported contacts (av. 3.02 Å) between the complex cations have been observed.[258] Similar contacts (2.9749(5) Å) are present in the complex generated using a macrocyclic hexaaza ligand with four pendent 2-pyridylmethyl groups and silver nitrate, but the structure is otherwise exceedingly complicated.[259]

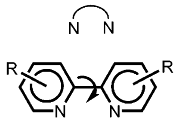


78

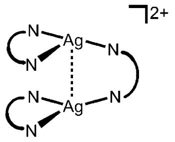


79

Mono-supported Ag–Ag contacts are frequently observed with 2,2′-bipyridines (**80a**). As an example, complexation of silver cations by 5-(thien-2-yl)-2,2′bipyridine with silver hexafluorophosphate leads to dinuclear units with an Ag–Ag distance of 3.087(1) Å (**80b**).[260] Disubstituted 2,2′-bipyridines (**80a**, R = H, Me, C(O)OEt, or $C(O)OC_{16}H_{33}$ in the 5,5′ positions) react with silver salts to give products with structures strongly depending on the nature of the substituents and of the counterions. Owing to the promesogenic nature of the bipyridine groups arising from a twist of the C–C bond connecting the two pyridyl rings (**80a**) and the influence of long hydrocarbon chains in the ester functions, complex helical arrangements are formed which are co-directed by the close Ag–Ag contacts.[261]



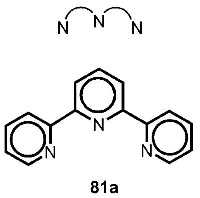
80a



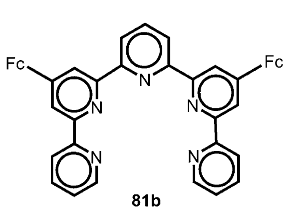
80b

As perhaps expected, similar structures arise with terpyridyls (**81a**) or a quinquepyridine (**81b**).[262–264] A particularly intimate aggregation by semi-supported Ag–Ag contacts has been found in the 1:1 complex of $AgPF_6$ with the terpyridine **81a** phenylated in the 4-position. Pairs of silver atoms are tied up by two tpy ligands to have one silver atom two-coordinated and the other four-coordinated by the six nitrogen donors (**81c**). In these dinuclear dications with a two-bladed propeller configuration, the Ag–Ag distances are as short as 2.8441(7) and 2.8955(6) Å (two crystallographically independent dications). These units are stacked in an alternating sequence and linked by external Ag–Ag contacts of 2.879(7) and 3.2148(7) Å. The Ag-Ag-Ag angles are strictly linear by symmetry keeping all silver atoms of a given chain on the same line. The compound is luminescent at room temperature ($\lambda_{ex} = 335$ nm, $\lambda_{em} = 420$–500 nm).[265] Ag–Ag contacts between chains formed by bridging silver cations with the ligand 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl are 3.1332(5) and 3.2745(6) Å long, depending on the mole ratio of the components (with azide as the counterion).[262]

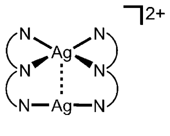
Pincer-type ligands H_2L such as 2,6-bis(5-methyl-1-H-pyrazol-3-yl)pyridine (**81d**) are bridging units for silver atoms either in chains $[\{Ag_2(H_2L)\}(NO_3)_2H_2O\}_n]$ or in hexanuclear aggregates $[\{Ag_6(HL)_4\}(NO_3)_2]$ where one or two pyrazol rings are protonated (R′ = H). The Ag–Ag contacts are short at 2.889(1) and 2.893(1) Å in the chain and 2.874(1), 2.905(1) and 2.908(1) Å between and within two triatomic units.[266]



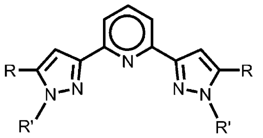
81a



81b



81c

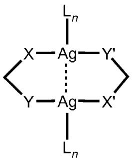


81d

3.7. Double-Bridged Ag–Ag Contacts

The installation of two ligand bridges at a pair of linearly two-, T-shaped three-, or pseudo-tetrahedrally four-coordinate silver atoms is one of the most common structural variants in which argentophilic contacts are established (**2c**, **2d**, **2e**). Many examples are known in the literature, some of them dating back to times when metallophilicity phenomena were not yet the focus of structural studies.[267,268] In this Section, the results of a series of recent investigations is presented which, however, cannot be taken as comprehensive owing to the sheer number of examples.

The general formula **82** shows a prototype of complexes where two bridging ligands form an eight-membered dimetallacycle which allows for a transannular Ag–Ag contact. In most cases it is not easy to decide if the Ag–Ag interaction has a major influence on the conformation and geometry of the molecules, which may be largely imposed by the ligand matrix. Note that there are all kinds of distributions of X and Y, making the Ag atoms either homo- or heteroleptically coordinated with X = Y or X ≠ Y. There appears to be no case where more than two different donor atoms are present (no need to add atoms Z etc.). The compounds may be without an auxiliary ligand L ($n = 0$), but examples for $n = 1$, 2 are much more common with silver than with gold.

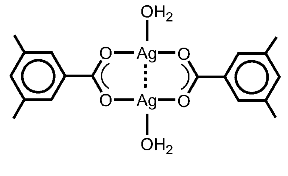


82

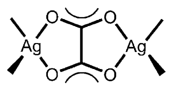
3.7.1. Double Support by Carboxylate O,O-Bridging

In a recent representative publication reporting the crystal structure of silver(I) 3,5-dimethylbenzoate (**83**, type **2d**), the result—an Ag–Ag contact of only 2.7719(5) Å—was discussed in the context of existing data in the CSD base, which shows an average of 2.962 Å for about a hundred published examples.[269] The shortest distance known to date is 2.746(1) Å in the silver benzoate dimer embedded in a complex network with hexamethylenetetramine as a tetrafunctional co-ligand, which can also be prepared with acetate (Ag–Ag (2.9144(8) Å) and maleate anions (2.8115(1) Å). Interestingly, with oxalate the chelation of the silver atoms (**84**) is preferred over the metal bridging.[270] In $[\{Ag(CF_3COO)\}_2]\cdot C_6H_6$ the contact is also short at 2.853/2.893 Å for two independent molecules.[268] In a 1:2 adduct of trimethylenediamine with silver 4-fluorobenzoate, the contact between the two N,O,O three-coordinate silver atoms is 2.798(2) Å.[126] Silver(I) 4-methylbenzoate and silver 4-nitrobenzoate were crystallized with di(2-pyridyl)amine. The distance between the two N-coordinated silver atoms of the silver 4-nitrobenzoate species is 2.855(3) Å, complemented by Ag–Ag contacts between the dimers (3.158(2) Å).[271]

The eight-membered ring of $[Ag_2(RCOO)_2]$ dimers (shown in **83** as an example) can be completely planar, slightly folded approaching a chair conformation, or subject to some torsional twist (skew–skew) depending on the substitution pattern of the carboxylate group or the auxiliary ligands. The dimers can be linked into chains if an R–R connectivity exists as in malic, succinic, suberic, or tereph-

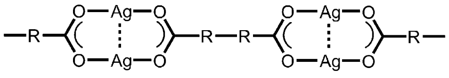


83



84

thalic acid (-R-R- CH_2CH_2, $(CH_2)_6$, 1,4-C_6H_4, **85**)[272–274] or in naphthalene-1,4-dicarboxylic acid.[275] Dicarboxylic acids with a more constrained structure (phthalic and 3-nitro-phthalic acid, 1,1′-biphenyl-2,2′-dicarboxylic,[276,277] and naphthalene-2,3-dicarboxylic acid[278] etc.) afford more complex connectivities, but the eight-membered ring motif still prevails.[55] 1,3,5-Benzene tricarboxylic acid in combination with pyrazine affords a hexagonal three-dimensional framework with rods of silver atoms aggregated through multiple Ag–Ag contacts and connected by the tricarboxylate anions. The temperature dependence of its emission was shown in Figure 3.[113]

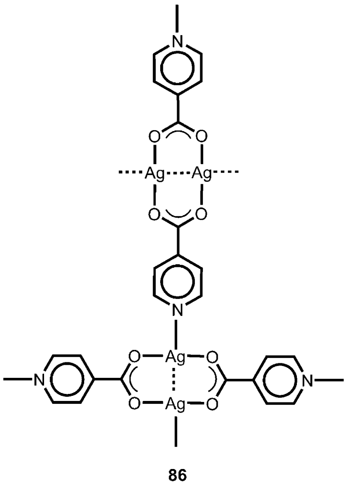


85

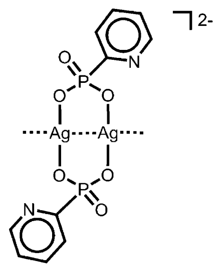
The silver salts of benzene-1,2,3,4-tetracarboxylic (H_4btca) and -1,2,3,4,5-pentacarboxylic acids (H_5bpca) form fascinating honeycomb layers and tubular motifs templated by the geometry of the multifunctional carboxylate ligands and stabilized by an extensive network of argentophilic interactions. The former has the composition $[Ag(NH_3)_2Ag_3(btca)\cdot CH_3OH\cdot H_2O]_n$ with Ag–Ag distances in the broad range of 2.988–3.384 Å, very similar to those in $[\{Ag_5(bpca)(H_2O)_2\}_n]$ with a range of 2.904–3.184 Å. For details see Ref. [279]. As expected, the structures obtained with 1,1′-biphenyl-2,2′,4,4′-tetracarboxylic acid and 1,1′-biphenyl-2,2′-dicarboxylic acid are also three-dimensional networks with multi-connectivity including Ag–Ag contacts depending on the counterions and on the solvation (in several hydrates).[280,281] Extremely complex structures have been found for silver(I) salts of all-*cis* 1,2,3,4,5,6-cyclohexane hexacarboxylic acid. Ag–Ag distances in the multidimensional frameworks are in the range 2.904(1)—3.329(2) Å with variations depending on the deprotonation step of the polycarboxylic acid by base (ammonia).[282]

Distortions, but no fundamental changes of the eight-membered rings of silver carboxylate dimers also arise upon the introduction of donor or hydrogen-bonding functions at the group R of the carboxylic acid, as recently demonstrated for indol-3-butyric acid.[283] Silver(I) pyrazine-2,3-dicarboxylate in combinations with difunctional amines forms porous three-dimensional frameworks in which Ag–Ag contacts (3.10–3.3 Å) appear to make significant contributions to the overall stability. The products may have applications in gas storage.[284] The use of 2-sulfobenzoate leads to multidimensional aggregates through silver coordination at both the thiolate and the carboxylate functions with various supporting Ag-Ag contacts.[285] A similar structural pattern arises in the double-chains generated in crystals of silver 4-[(1-H-imidazol-4-yl)methylamino]benzoic acid (LH). The $[L_2Ag_2]$ molecules are formed by a common eight-membered disilver dicarboxylate ring (Ag–Ag 2.98 Å). Double-chains arise through a head-to-tail coordination of imidazole N atoms to silver atoms of neighboring rings. The compound is luminescent ($\lambda_{ex} = 347$, $\lambda_{em} = 381$ nm).[286] With 4-(2-pyrimidylthiomethyl)-benzoic acid, the eight-membered ring of type **83** has a trans-annular Ag–Ag distance of 2.914(1) Å. The silver atoms are coordinated by a terminal pyrimidyl nitrogen atom of neighboring molecules generating undulated layers.[287]

Isonicotinic acid (IsoH) has also been used to generate extended chains with alternating N-Ag-N, C(O)O-Ag-N, and C(O)O-Ag-O(O)C units. In a hemi-hydrate $Ag_2(Iso)_2(H_2O)$the Ag–Ag contacts in the C(O)O-Ag-O(O)C units are 2.8808(8) Å.[288] The arrangement may be different depending on the mode of preparation and the solvent mixture employed. One of the connectivity patterns is shown in **86**.[289] In the complexes with the homologous 4-pyridylacetic acid, the corresponding unit has the Ag–Ag distance at 2.983(3) Å.[290] Eight-membered dimetallacycles have also been detected in silver 2-pyridylphosphonates. In the O-P-O double-bridged arrangements the Ag–Ag distance is 3.0543(6) Å (**87**). These units are connected with external silver atoms (3.3627(5) Å) generating a zigzag chain supported by single- and double-bridging phosphonate ligands.[291] There is also a resemblance to the structure of silver pyridine-3-sulfonate.[292]



86

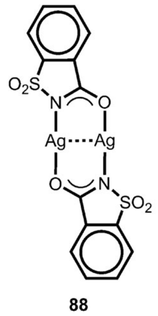


87

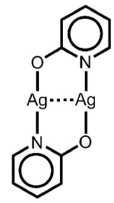
3.7.2. *Double Support by N,O- and N,S-Coordinating Ligands*

Eight-membered rings with N,O instead of O,O donor functions in 1,3-position of the ligand have been found in silver saccharinates (**88**) with the Ag–Ag distances near 2.85 Å depending on the nature of the auxiliary ligands (acetonitrile, ethylenediamine, N-methyl- and *N*,*N*′-dimethylethylenediamine, 2-pyridinylethanol, 2-methylpyrazine, pyrazine-2-carboxamide).[293–297] Further examples for N,O coordination have been studied in 2,2′-biypridin-6-one and phenanthroline-2-one complexes. The intramolecular Ag–Ag contacts across the eight-membered rings are short at 2.7903(4) and 2.7886(5)/2.7963(5) Å (two independent molecules), and complemented by longer intermolecular Ag–Ag contacts (ca. 3.15 Å), which lead to an association into dimeric or trimeric units. The Ag–Ag interactions have been studied by DFT calculations which have resulted in bond-energy values of as much as approximately 25 kcal mol^{-1}.[298] N,O bridging has also been found in tetracarboxydiimides based on a bicyclo[2.2.2]oct-7-ene linker (L). Interestingly, the two silver atoms have a homoleptic coordination (O,O and N,N) with an Ag–Ag contact of 2.993 Å. The argentophilic bonding was analyzed in a model system with maleinimide ligands (**5**). NBO calculations have indicated the presence of weak interactions, as based on the Wiberg bond indices (bond order 0.16). In the crystals of the compound with the composition $[Ag_4(L)_2(4,4'\text{-bipy})(H_2O)_8]$ the dinuclear units are linked through unsupported Ag–Ag contacts of the remaining three silver atoms (3.087 and 3.114 Å) which are coordinated by two imino nitrogen atoms or two water oxygen atoms. The bond order of the contacts in stacks of alternating model $[(H_2O)Ag(H_2O)]^+$ cations and $[(\text{maleinimide})_2Ag]^-$ anions is smaller at 0.12. The parent compound is strongly luminescent ($\lambda_{ex} = 246$ nm, $\lambda_{em} = 390$ nm at room temperature).[54]

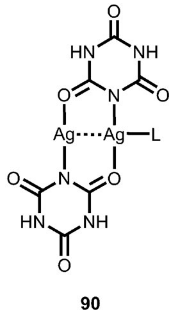
The silver salt of 2-hydroxypyridine has a highly condensed columnar structure consisting of dimetallacycles with transannular Ag–Ag contacts of 2.775(2) Å (**89**). These units are stacked to establish intermolecular contacts of 3.045(2) and 3.064(2) Å. The compound shows a blue emission ($\lambda_{ex} =$ 439.0 nm, $\lambda_{em} = 459.5$ nm for crystals at room temperature).[299] Silver isocyanurate crystallizes with 4,4′bipyridine (L) to give two eight-membered rings with N-Ag-O coordination connected on one side by the bipy ligand (Ag–Ag 3.004(2) Å, **90**). These units are connected into layers through hydrogen bonding to give honeycomb arrays, which are further associated into bilayers through short interlayer Ag–Ag contacts of 3.069(3) Å. The crystals are strongly luminescent ($\lambda_{ex} = 350$, $\lambda_{em} = 450$ nm).[300]



88

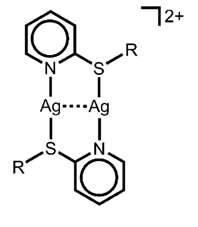


89

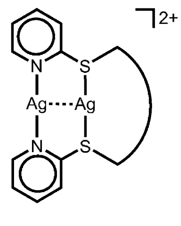


90

Rings built with the corresponding N,S donor functions are found in pyridine-2-thiolates (**89**, S for O) with larger Ag–Ag distances near 2.95 Å for several examples. The corresponding alkylsulfides form dicationic rings with heteroleptic coordination (**91a**), but with the substituents tied together the homoleptic alternative is enforced (**91b**).[301] For the same reason, 1,2-bis[(imidazol-2-yl)thiomethyl]benzene also forms silver complexes with homoleptic N,N/S,S coordination.[302] Eight-membered rings with two N,S ligands are also present in the structures of silver thiosaccharinates (**88**, S for bridging O). The N-Ag-S coordinated silver atoms are 2.9194(4) Å apart. With pyridine or phenanthroline as secondary ligands, these units are bridged, but structurally largely unchanged (Ag–Ag 2.9681(8) Å). The results of DFT calculations of model systems have provided evidence for significant argentophilic bonding.[303,304]



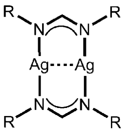
91a



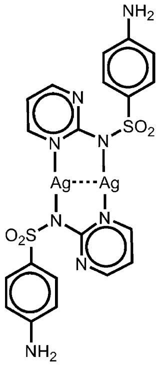
91b

3.7.3. *Double-Bridging by N,N, N,P, and P,P Coordinating Ligands*

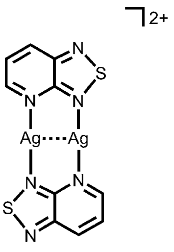
Ligands with two 1,3-positioned N donor sites that can give eight-membered dimetallacycles have long been used in the coordination chemistry of the coinage metals. Classical examples are the dinuclear formamidinato complexes $[\{[RN(CH)NR]Ag\}_2]$ and related compounds. The molecule with R = *p*-tolyl has a very short transannular contact of 2.705 Å length which is typical for this type of ligand (**92**).[41] In very early work the crystal structure of silver sulfadiazine (a pharmaceutical for burn treatment) has been determined. Surprisingly, its eight-membered ring is also formed exclusively by the N-atoms, excluding any O–Ag coordination (Ag–Ag 2.916(1) Å, **93a**).[305,306] A related structural pattern is obtained with 1,2,5-sulfa- or -selenadiazolopyridine with transannular distances near 2.931 Å. The Ag–Ag interaction has been probed by the atoms-in-molecules approach. Single-point calculations gave a bond critical point between the silver atoms substantiating weak metal–metal bonding (**93b**).[307]



92



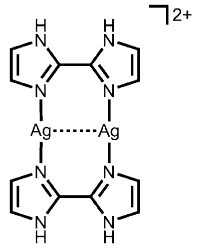
93a



93b

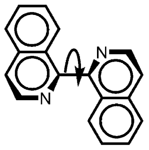
Interesting macrocyclic variants have been discovered with N-methyl-2,2′-dipicolylamine. In the perchlorate salt the centrosymmetrical cations show a short transannular Ag–Ag distance of 2.9152(3) Å with N-Ag-N angles bent inwards to 161.78(5)°, which in the absence of other constraints show significant metal–metal attraction.[308]

Ten-membered dimetallacycles (**94**) are formed with bi-imidazole, and in the dications the Ag–Ag distances across the ring are as short as 2.818(1) and 2.844(1) Å (in the sulfate and oxalate salt). The corresponding perchlorate salt has a chain structure in with the silver atoms are semi-bridged by the ligands (type **35c**). The crystals are luminescent ($\lambda_{ex} = 360$, $\lambda_{em} = 439$ for the sulfate).[309]

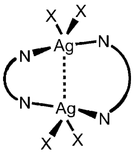


94

Even with the rotationally highly constrained ligand 1,1′-bis(isoquinoline) (L, **95a**, compare **80a**) the resulting macrocycle in $[(L)_2Ag_2]OSO_2CF_3$ has only a slightly longer contact (3.0737(6) Å) across the ten-membered ring achieved through a twist of the ligands to reach an almost perpendicular arrangement of the two isoquinoline rings (**95b**), $X = CF_3SO_3$).[310] Ten-membered rings are also formed in the silver complexes with tris(pyrazolyl)methane ligands. In crystals of the tetrafluoroborate THF solvate, one of the three N donor sites is less tightly bound and a short Ag–Ag contact of 2.8664(4) Å is observed.[311] Even in the ten-membered rings formed upon 1:1 complexation of $AgBF_4$ or $AgOSO_2CF_3$ with an “N-confused” bis-porphyrin (having one “extrovert” N atom in each carbaporphyrinoid) the perpendicular arrangement of the bis-porphyrins leads to an Ag–Ag contact of only 3.107(2) Å.[312]



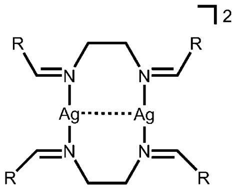
95a



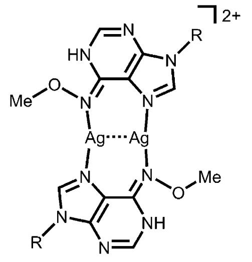
95b

Ten-membered rings with short transannular contacts (average 3.0 Å) were also found in the silver complexes of Schiff bases derived from ethylenediamine owing to the folding of the metallocycle (**96**).[313] Dimetallacycles with the same ring size were again discovered with the oxime tautomer of N^6-methoxyadenine (**97a**). The short Ag–Ag contacts across the ring (2.803(1) and 2.919(1) Å for ClO_4 or NO_3 counterions, respectively) arise from a significant inward bending of the two N-Ag-N axes (165–170°).[314] Ligands of the type **28a** give dinuclear complexes with $AgClO_4$ or $AgPF_6$ in which the Ag–Ag contact (2.9082(9) Å) is double-bridged by the central N atoms of the triazine rings and by the N atoms of the terminal pyrazole rings.[169]

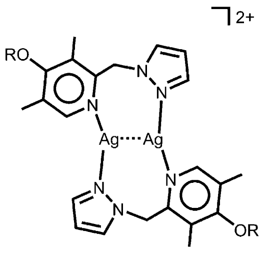
Twelve-membered rings with short transannular Ag–Ag distances of 2.945(1) Å have been observed with pyrazolylmethylpyridines (**97b**). The relevance of the argentophilic interaction has been supported by an atoms-in-molecules analysis of the electron density. The compound can be used as a precursor for the deposition of silver thin films on steel.[315]



96

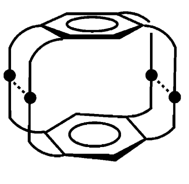


97a



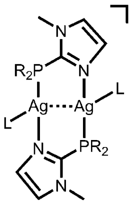
97b

The tetrafunctional ligand 1,2,4,5-tetrakis(benzimidazol-1-ylmethyl)benzene forms tetranuclear complexes with $AgNO_3$ with pairs of silver atoms in 22-membered rings with transannular Ag-Ag distances of 3.3231(6) and 3.306(1) Å (in two different solvates, **98**, benzimidazoles shown as arcs).[316] 24-Membered rings have been obtained in crystals of the complexes of silver perchlorate or triflate with a double Schiff base of type **96** with di(4-aminophenyl)methane as the parent amine.[313]



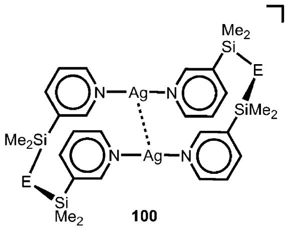
98

Ligands with N and P in 1,3-position, as in 2-pyridylphosphines, also form dinuclear dications with Ag–Ag contacts of 3.094(1) Å across the eight-membered ring. The silver atoms may be two- or three-coordinate depending on the number of pyridyl substituents at the phosphorus atom (already shown for the Cl-bridged units in **61**).[201,317] The structural situation is similar in the complex of AgSCN with the ligand 2-(diphenylphosphino)-1-methylimidazole. The eight-membered ring of the dication (with two Ag-coordinated acetonitrile co-ligands) has a transannular Ag–Ag contact of 2.993(1) Å, which is significantly longer than in the corresponding gold(I) complex (2.826(1) Å) in which the acetone solvate molecules are not Au coordinated. Interestingly, the P-Ag-N axes are strongly bent (157.5(1)°) while the P-Au-N axes are close to linear (178.0(4)°) (**99**).[318] (Diphenylphosphinomethyl)(2-pyridyl)alkylamines also form dimetallacyclic dications in which all three donor functions (N,N,P) are attached to each silver atom. The transannular distance between the three-coordinate silver atoms in the strongly puckered rings is 2.890(2) Å.[319]

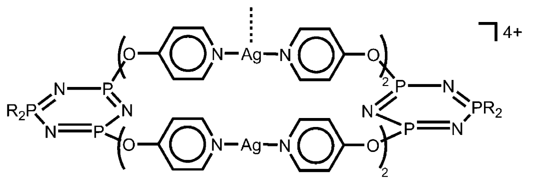


99

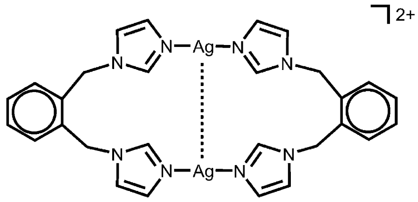
Recent work has provided impressive examples for transannular Ag–Ag contacts in macrocyclic systems with flexible disiloxane- and 1,2-disilylethane linkers having terminal N-donor centers. The 24- and 26-membered rings (**100**, E = O or CH_2CH_2) have Ag–Ag distances of 3.231(4), 3.283(1), and 3.321(1) Å in the 24-membered rings (depending on the nature of the anion NO_3^-, ClO_4^-, $CF_3SO_3^-$) and 3.243(1) and 3.346(1) Å (two independent dimers of the perchlorate) in the 26-membered rings. It is important to note that in all these cases the metal atoms are significantly closer to each other than the π–π stacked pyridine rings.[320–322] In the large dimetallamacrocycles produced by the coordination of $AgOSO_2CF_3$ or $AgPF_6$ to a cyclotetraphosphazene bearing pyridinoxy substituents, the folding of the ring depends on the position of the pyridine nitrogen atoms: With 3-pyridinoxy groups, Ag–Ag contacts of 3.199(2) are established across two 20-membered rings, while with 4-pyridinoxy groups the two silver atoms are kept further apart owing to the ligand constraints. Therefore, only an intermolecular contact of 3.408 Å is established (**101**).[323,324] 24-membered dimetallamacrocycles are also present in the complexes with 1,2-bi(1-imidazolylmethyl)benzene ligands. A conformation is established which allows Ag–Ag contacts of 3.27–3.35 Å depending on the anion. The silver atoms are brought close together through a twist of the macrocycles (skew–skew) to reach a crossing of the two N-Ag-N axes (not drawn in formula **102**)[325,326]



100



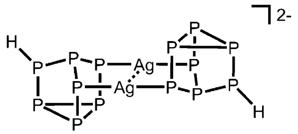
101



102

As already mentioned in Section 2.2, it has long been known that 1,3-diphosphorus functionality as in bis(diphenylphosphino)methane (dppm) can be employed to generate eight-membered rings with the coinage metals, for example, $[Ag_2(dppm)_2][NO_3]_2$ (**19**). The Ag atoms in this example are 3.085(1) Å apart,[327] and similar values have been found for diphosphines with several substituents other than phenyl and with other innocent anions.[65,328] With strongly coordinating anions, such as diisopropyl dithiophosphate $[(i\mathrm{PrO})_2PS_2]^-$, the silver atoms are in a quasi-trigonal planar $SAgP_2$ environment owing to an additional SPS bridge (from **19** as type **2c**, to a variant of type **2g**). The Ag–Ag distance is still in the usual range (2.918(1) Å).[329] As summarized in a recent Review, the silver atoms in eight-membered rings of the type **2c** (= **19**) can also be further bridged (type **2g**) by a series of thiometalate anions with only minor alterations in the Ag–Ag distances in the resulting tricyclic dinuclear complexes.[330]

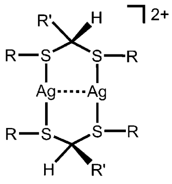
The reaction of K_3P_7 with AgCl in an ethylenediamine solution of a cryptand for the potassium cations leads to a dinuclear complex $[Ag_2(P_7H)_2]^{2-}$ (**103**). The dianion has the two silver atoms in eight- and ten-membered rings with a short Ag–Ag contact of 2.947(1) Å. The molecular structure has been reproduced by DFT calculations.[331]



103

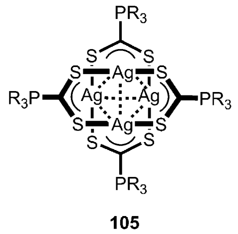
3.7.4. Double-Bridging with S,S-coordinating Ligands

Eight-membered dimetallacycles are also readily obtained with difunctional S,S donors. Dicationic eight-membered rings formed with S,S donors have been obtained with dithioethers $RS(CH_2)SR$. For R = benzyl and perchlorate as the counterion, the transannular Ag–Ag distance in the dication is 3.0361(1) Å (**104**, R = Bz,R' = H).[332] More recent examples have shown that dicationic dithioether complexes can also be obtained with electroneutral bis(methylthio)methylsilanes (**104**, R = Me, R' = $SiMe_3$). In crystals of the triflate salt, the dication shows a transannular Ag–Ag distance of 3.1133(7) Å which reflects the larger atomic radius of sulfur as compared to oxygen (Section 3.7.2).[333] With a higher ligand-to-metal ratio, tricyclic complexes are also formed which have a three-blade paddlewheel structure (type **2e**). Remarkably short transannular Ag–Ag contacts are established (2.866(3) Å).[334]



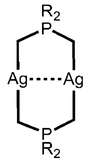
104

A remarkable structure with two eight-membered rings has been discovered in the product of the reaction of the CS_2-adduct of the carbodiphosphorane $(Ph_3P)_2C$. The principle of the arrangement is shown schematically in **105**. The two metallacycles have their best planes parallel, but are in a staggered conformation (rotated by 90°). The transannular Ag–Ag distances are 2.9425(4) and 2.9872(4) Å, but there are additional Ag–Ag contacts of similar length (2.9958(4)–3.0702(4) Å) between the rings which represent the remaining four edges of the central Ag_4 tetrahedron.[335] Similar arrangements have been found in fluoren-9-ylidene-methanedithiolates (**105**, fluoren-9-ylidene for PR_3).[336] This family of compounds was later studied by DFT calculations.[337]



105

Compounds of type **82** with X and Y representing carbon atoms are extremely rare, and no crystal structures have been determined. However, analytical and spectroscopic data have confirmed the existence of the silver dialkylphosphonium bis(methylides) **106** for which there are also fully characterized gold(I) and copper(I) analogues.[338,339]



106

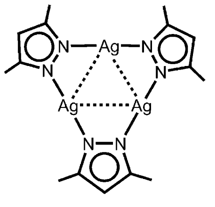
3.8. Complexes with Triangular Ag_3 and Square Ag_4 core units

For a long time, significant Ag–Ag interactions have been suggested for compounds with a triangular Ag_3 core where the silver atoms have remarkably short Ag–Ag distances. The edges of the triangle may be bridged by only one atom each or by a difunctional donor with a larger span. An example for single-atom bridges was found with NHC ligands bearing extra donor substituents as already shown in formula **21** (Ag–Ag 2.7725(1)–2.772(1) Å).[75] The bonding situation in suitable models of carbene-stabilized units $[Ag_3(NHC)_3]^{3+}$ in their ground and excited states has recently also been analyzed by DFT calculations. The $[Ag_3]^{3+}$ core appears to be stabilized by a MO largely composed of 5s and 5p atomic orbitals, complemented by contributions from a weakly bonding $4d^{10}$ core.[340]

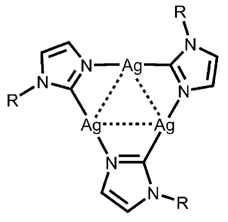
Two-atom bridging as observed with pyrazolates (**107a**) has been studied most extensively owing to the intriguing photophysical properties of these systems with rigid nine-membered triargentacycles. An early Review is available, which accordingly is not duplicated herein.[341] The N–N bridges between each pair of silver atoms lead to larger intra-trimer Ag–Ag distances in the range 2.95–3.35 Å. More often than not, the triangle of silver atoms is not equilateral, but irregular with significantly different Ag–Ag distances. In the silver 3,5-diphenylpyrazolate trimer, the Ag–Ag contacts are 3.36, 3.49, and 3.52 Å and all are longer than the intermolecular contacts between stacked molecules (2.97 Å).[342] The various stacking modes of these compounds may lead to only a single intermolecular Ag–Ag contact,[342] but two or three contacts are also common.[343–345] With very bulky substituents, the organization of the crystals is determined by other contacts where available, mainly between halogen atoms.[346] The arrangements are influenced not only by the substituent pattern of the individual components, but also by the presence of solvate molecules,[347] predominantly aromatic hydrocarbons.[348] The aromatic hydrocarbons become inserted between the stacked metallacycles leading to modified UV/Vis absorption and emission properties, observed, for example, in the vapochromic behavior of the luminescent crystals of these compounds.[96,342–347,349–351] The different results obtained from crystals and solutions of the compounds have suggested that the inter-trimer contacts are the origin of the photochromic effects in most cases. The majority of pertinent studies focused on gold compounds of this type, with the silver analogues being complementary.

Similar structural characteristics and properties are found in the carbeniates examples of which are shown in **107b** and **107c**.[350] As in coinage-metal pyrazolate chemistry, there is ample precedent for these types of trinuclear carbeniate complexes mainly in gold chemistry pioneered by the groups of Balch, Bonati, Burini, and Fackler and widely quoted in the literature.[351–353] In very recent work a P analogue of type **107d** has been prepared, but with Au instead of Ag. The silver compound is still missing.[354]

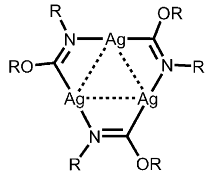
A square-planar arrangement of four silver atoms is found in the tetranuclear complex with pyrazole ligands bearing two carbene functions in the 3,5-position (**108a**). Two opposing pairs of silver atoms are bridged by a pyrazole unit, and each silver atom is further engaged in bonding with a carbene substituent of the pyrazole bridge of the opposite pair (**108b**). The Ag–Ag distances are 3.295(2) (pyrazole bridged) and 3.208(2) Å. The analogous gold complex is isostructural with almost identical Au–Au distances of 3.292(1) (pyrazole bridged) and 3.276(1) Å. The two complexes are thus another pair of compounds which show that silver and gold atoms have very similar covalent radii, and probably comparable metallophilic bonding capacities.[355] The bonding has therefore recently been analyzed in more detail by DFT calculations. It has been shown that compared to systems with closer M–M distances, the Ag–Ag and Au–Au interactions in this case (**108b**) are on the weak side owing to the longer distances (close to 3.3 Å) imposed by the ligand span of the pyrazole ligand.[356]



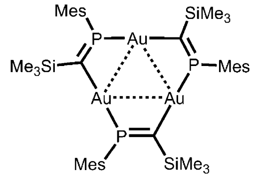
107a



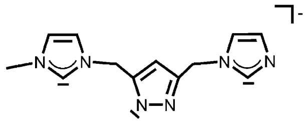
107b



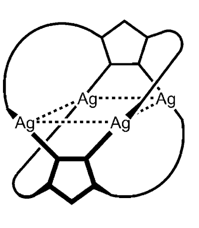
107c



107d



108a



108b

Rhomboide arrays of silver atoms in which the argentophilic interactions are multi-supported not only by NHCs, but also by halogen atoms which are capping edges or parts of the faces (above and below), have been observed in compounds of the type $[Ag_4(\mu_3\text{-I})_2(\mu_2\text{-I})_2(\mu_2\text{-S},C_{NHC})_2]$. The S-functionalized carbene ligands (S,C_{NHC}) are of the *N*-mesityl-*N'*-[(2-ethylthio)ethyl]imidazol-2-ylidene type.[357] This is another example of the many possible combinations of ligand support for argentophilic bonding. As mentioned in the Introduction, the scope is widened further by including other metals to generate mixed-metal clusters.

4. Summary and Conclusions

Based on growing experimental evidence and on the corroborative results of extensive theoretical calculations, the concept of argentophilic interactions between silver(I) centers in and between molecules has found wide acceptance in inorganic and organometallic chemistry. The delay of this recognition was due no doubt to the simple fact that this attractive interaction is clearly counterintuitive as it occurs against Coulomb repulsion between atoms which were assigned a "closed shell" of electrons. However, it is now clear from a plethora of molecular and supramolecular structures that—in the absence of any major steric hindrance—silver(I) centers are drawn together to sub-van der Waals distances near 3.00 Å. This average distance is about midway between the sum of two standard van der Waals radii (3.44 Å) and the distance of a Ag–Ag single bond (e.g. 2.53 Å in Ag_2), and close to the distance between silver atoms in cubic close-packed crystals of metallic silver (2.89 Å). The high affinity responsible for the Ag–Ag contacts is most clear from the ubiquitously observed phenomenon that independent molecules become aligned—or associated otherwise—in an organizational pattern in which the silver atoms are placed next to each other even in the absence of any discernible constraints.

From IR, Raman, and UV/Vis spectral data for unsupported aggregation, as well as from the thermodynamic data for association equilibria in solution, the associated Ag–Ag binding energy can be estimated to be in the range 5–15 $\mathrm{kcal\,mol^{-1}}$ depending on the nature of the ligands and counterions. These estimations have been confirmed by the results of the quantum chemical calculations on various level of theory. With these data, argentophilic interactions can be rated as "weak forces". They are closest in energy to hydrogen bonding, with which they share the multiple affinity and the lack of a clear directionality: Silver atoms may be associated with several other silver atoms in various geometries to produce oligomers, rings, chains, and layers.

These structural and dynamic features of silver(I) compounds associated with argentophilicity are in many respects qualitatively similar to those well established for aurophilic interactions in gold(I) chemistry. A major difference arises from the more pronounced tendency of silver(I) to adopt coordination numbers higher than two, which causes an abundance of argentophilically bonded silver centers each carrying three, four, or even more ligands. In contrast, for gold(I) there is a clear dominance of coordination number two which is ascribed to stronger relativistic effects for gold. Building on relativity considerations, it has also been assumed that aurophilic bonding should be stronger than argentophilic bonding, but even after quite a number of dedicated experimental and theoretical investigations this point has remained the subject of debate. The unsupported Ag–Ag and Au–Au distances in pairs of analogous compounds are generally found in the same range (2.9–3.1 Å) owing to very similar atomic radii of the two elements, which also arise from the strong relativistic contraction of the gold orbitals. This is borne out not only by the similar lattice constants of silver and gold metal, but also by the structural data throughout the chemistry of gold and silver. The Ag–Ag distance has been found slightly smaller or larger than the Au–Au distance in a given pair of compounds with metallophilic contacts, while in their copper analogue the Cu–Cu distance is always much shorter (ca. 2.6 Å). From the distance criterion it can therefore be concluded that metallophilic bonding of Ag and Au is very similar.

The paucity of data from criteria other than the Ag–Ag distance means that there is little basis on which to draw conclusions regarding Ag−Ag and Au−Au bond energies. Notwithstanding, various specific thermal and spectroscopic properties of silver(I) compounds are relevant and should be given special consideration: Argentophilic interactions in the Kagomé nets of silver atoms built in crystals of various metal(III) dicyanoargentates lead to surprising macroscopic properties, such as negative thermal expansion or compressibility owing to an unusually modified thermal motion of the silver atoms. Photochemical activation of silver atoms with argentophilic contacts leads to the formation of excited states in which the Ag−Ag bonding is stronger than in the ground state, a situation that has remarkable consequences for the emission properties. Both observations have attracted considerable attention in recent years and are currently the focus of many investigations which follow up previous studies in gold chemistry. The emissive behavior can be strongly altered by establishing Ag–Ag contacts, and the emission can also be quenched by the insertion of other molecules thus providing sensor capabilities for various uses. For all that, silver chemistry offers more opportunities than gold chemistry owing to the greater versatility in coordination numbers and geometries, and also because of the economic advantages even if the performance of analogous systems is not fully comparable.

Another important development under way for quite some time already is the clustering of silver cations around atoms and pairs of atoms as nucleation centers. It is apparent that after the highly successful endeavors with halide or chalcogenide anions $[X]^{n-}$, and even more so with various even-number (of carbon atoms) carbide anions $[(C\equiv C)_n]^{2-}$ and alkynylide anions $[R\text{-}(C\equiv C)_n]^{-}$, there should be still enormous potential and scope for further discoveries with other elements as core units for silver clustering. This could follow suit—or go beyond—some of the already well-documented examples in gold chemistry.

Received: June 13, 2014

---

[1] M. Jansen, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1098; *Angew. Chem.* **1987**, *99*, 1136.

[2] P. Meyer, A. Rimsky, R. Chevalier, *Acta Crystallogr. Sect. B* **1978**, *34*, 1457.

[3] G. A. P. Dalgaard, A. C. Hazell, R. G. Hazell, *Acta Crystallogr. Sect. B* **1974**, *30*, 2721.
[4] P. K. Mehrotra, R. Hoffmann, *Inorg. Chem.* **1978**, *17*, 2187.
[5] A. Dedieu, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 2074.
[6] Y. Jiang, S. Alvarez, R. Hoffmann, *Inorg. Chem.* **1985**, *24*, 749.
[7] J. K. Burdett, *Prog. Solid State Chem.* **1984**, *15*, 173.
[8] B. Armer, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 101; *Angew. Chem.* **1970**, *82*, 120.
[9] L.-S. Wang, *Phys. Chem. Chem. Phys.* **2010**, *12*, 8694.
[10] P. Schwerdtfeger, P. D. W. Boyd, A. K. Burrell, W. T. Robinson, *Inorg. Chem.* **1990**, *29*, 3593.
[11] M. C. Gimeno, A. Laguna, *Chem. Rev.* **1997**, *97*, 511.
[12] P. G. Jones, *Gold Bull.* **1986**, *19*, 46, and references therein.
[13] F. Scherbaum, A. Grohmann, B. Huber, C. Krüger, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1544; *Angew. Chem.* **1988**, *100*, 1602.
[14] F. Scherbaum, A. Grohmann, G. Müller, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 463; *Angew. Chem.* **1989**, *101*, 464.
[15] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, *24*, 391.
[16] H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3.
[17] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931.
[18] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370.
[19] J. Vicente, M.-T. Chicote, M.-C. Lagunas, *Inorg. Chem.* **1993**, *32*, 3748.
[20] P. Pyykkö, J. Li, N. Runeberg, *Chem. Phys. Lett.* **1994**, *218*, 133.
[21] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.
[22] P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1451.
[23] N. Runeberg, M. Schütz, H.-J. Werner, *J. Chem. Phys.* **1999**, *110*, 7210.
[24] H. L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* **2001**, *7*, 5333.
[25] P. Pyykkö, *Angew. Chem. Int. Ed.* **2002**, *41*, 3573; *Angew. Chem.* **2002**, *114*, 3723.
[26] P. Schwerdtfeger, H. L. Hermann, H. Schmidbaur, *Inorg. Chem.* **2003**, *42*, 1334.
[27] E. O'Grady, N. Kaltsoyannis, *Phys. Chem. Chem. Phys.* **2004**, *6*, 680.
[28] G. Hacker, J. Gu, *Gold and Silver Staining*, *Techniques in Molecular Morphology*, CRC, Boca Raton, **2010**.
[29] A. de Lucca, W. A. Hadler, *Acta Histochem.* **1988**, *84*, 15.
[30] A. Hirano, N. R. Ghatak, A. B. Johnson, M. J. Partnow, A. J. Gomori, *Arch. Neurol.* **1972**, *26*, 530.
[31] A. Hirano, R. Tuazon, H. M. Zimmerman, *Acta Neuropathol.* **1968**, *11*, 257.
[32] R. B. Short, M. L. Catrett, *J. Parasitol.* **1973**, *59*, 1041.
[33] H. Ditrich, *Tissue Cell* **1986**, *18*, 645.
[34] R. C. Currau, J. Crocker, *Atlas der Histopathologie*, 5th ed., Springer, Berlin, **2003**.
[35] L. Martinez-Pomares, M. Kosko-Vilbois, E. Darley, P. Tree, S. Herren, J. Y. Bonnefoy, S. Gordon, *J. Exp. Med.* **1996**, *184*, 1927.
[36] G. Harms, C. D. Dijkstra, M. J. Hardonk, *Cell Tissue Res.* **1990**, *262*, 35.
[37] S. Sculfort, P. Braunstein, *Chem. Soc. Rev.* **2011**, *40*, 2741.
[38] A. F. Wells in *Structural Inorganic Chemistry*, 5. Aufl., Clarendon, Oxford, **1984**, S. 1098.
[39] P. W. R. Corfield, H. M. M. Shearer, *Acta Crystallogr.* **1966**, *20*, 502.
[40] T. Tsuda, S. Ohba, M. Takahashi, M. Ito, *Acta Crystallogr. Sect. C.* **1989**, *45*, 887.
[41] F. A. Cotton, X. Feng, M. Matusz, R. Poli, *J. Am. Chem. Soc.* **1988**, *110*, 7077.
[42] L. Magnko, M. Schweizer, G. Rauhut, M. Schuetz, H. Stoll, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006.
[43] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[44] B. Simard, P. A. Hackett, A. M. James, P. R. R. Langridge-Smith, *Chem. Phys. Lett.* **1991**, *186*, 415.
[45] A. Bayler, A. Schier, G. A. Bowmaker, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 7006.
[46] P. Nockemann, G. Meyer, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1636.
[47] P. Woidy, F. Kraus, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2643.
[48] R. B. Corey, K. Z. Pestrecov, *Kristallografiya* **1934**, *89*, 528.
[49] T. Yamaguchi, O. Lindquist, *Acta Chem. Scand. A* **1983**, *37*, 685.
[50] U. Zachwieja, H. Jacobs, *Z. Kristallogr.* **1992**, *201*, 207.
[51] I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270.
[52] A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095.
[53] S.-L. Zheng, C. L. Nygren, M. Messerschmidt, P. Coppens, *Chem. Commun.* **2006**, 3711.
[54] X.-Z. Song, C. Qin, W. Guan, S.-Y. Song, H.-J. Zhang, *New J. Chem.* **2012**, *36*, 877.
[55] D. Sun, F.-J. Liu, R.-B. Huang, L.-S. Zheng, *CrystEngComm* **2013**, *15*, 1185.
[56] W. Meng, F. Kraus, *Eur. J. Inorg. Chem.* **2008**, 3068.
[57] T. Pretsch, H. Hartl, *Inorg. Chim. Acta* **2005**, *358*, 1179.
[58] J. Xu, S. Gao, S. W. Ng, E. R. T. Tiekink, *Acta Crystallogr. Sect. E* **2012**, *68*, m639.
[59] C. Y. Chen, J. Y. Zeng, H. M. Lee, *Inorg. Chim. Acta* **2007**, *360*, 21.
[60] M. P. Carranza, B. R. Manzano, F. A. Jalon, A. M. Rodriguez, L. Santos, M. Moreno, *New J. Chem.* **2013**, *37*, 3183.
[61] P. D. Harvey, *Coord. Chem. Rev.* **1996**, *153*, 175.
[62] J. Muñiz, C. Wang, P. Pyykkö, *Chem. Eur. J.* **2011**, *17*, 368.
[63] E. Kargiannis, C. A. Tsipis, *Organometallics* **2010**, *29*, 847.
[64] B. Assadollahzadeh, P. Schwerdtfeger, *Chem. Phys. Lett.* **2008**, *462*, 222.
[65] C.-M. Che, M.-C. Tse, M. C. W. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *J. Am. Chem. Soc.* **2000**, *122*, 2464.
[66] I. J. B. Lin, C. S. Vasam, *Comments Inorg. Chem.* **2004**, *25*, 75.
[67] I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642.
[68] J. C. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978.
[69] L. Ray, M. M. Shaikh, P. Ghosh, *Inorg. Chem.* **2008**, *47*, 230.
[70] P. De Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301.
[71] C. Topf, C. Hirtenlehner, M. Zabel, M. List, M. Fleck, U. Monkowius, *Organometallics* **2011**, *30*, 2755.
[72] X.-Y. Lu, F. Chen, W.-F. Xu, X.-T. Chen, *Inorg. Chim. Acta* **2009**, *362*, 5113.
[73] B. Pinter, L. Broeckaert, J. Turek, A. Ruzicka, F. De Proft, *Chem. Eur. J.* **2014**, *20*, 734.
[74] J. Muñiz, C. Wang, P. Pyykkö, *Chem. Eur. J.* **2011**, *17*, 368.
[75] V. J. Catalano, M. A. Malwitz, *Inorg. Chem.* **2003**, *42*, 5483.
[76] P. Ai, A. A. Danopoulos, P. Braunstein, K. Y. Monakhov, *Chem. Commun.* **2014**, *50*, 103.
[77] B. K. Najafabadi, J. F. Corrigan, *Dalton Trans.* **2014**, *43*, 2104.
[78] A. Ilie, C. I. Rat, S. Scheutzow, C. Kiske, K. Lux, T. M. Klapötke, C. Silvestru, K. Karaghiosoff, *Inorg. Chem.* **2011**, *50*, 2675.
[79] X. Zhang, S. Gu, Q. Xia, W. Chen, *J. Organomet. Chem.* **2009**, *694*, 2359.
[80] M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle, H. H. Patterson, *Inorg. Chem.* **1998**, *37*, 1380.
[81] S. Dawn, S. S. Salpage, M. D. Smith, S. K. Sharma, L. S. Shimizu, *Inorg. Chem. Commun.* **2012**, *15*, 88.
[82] D. Perreault, M. Drouin, A. Michel, V. M. Viskowski, W. P. Schaefer, P. D. Harvey, *Inorg. Chem.* **1992**, *31*, 695.
[83] K. H. Leung, D. L. Phillips, M.-C. Tse, C.-M. Che, V. M. Miskowski, *J. Am. Chem. Soc.* **1999**, *121*, 4799.

[84] A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. Tucker, *Science* **2008**, *319*, 794.
[85] A. L. Goodwin, D. A. Keen, M. G. Tucker, M. T. Dove, L. Peters, J. S. O. Evans, *J. Am. Chem. Soc.* **2008**, *130*, 9660.
[86] M. J. Conterio, A. L. Goodwin, M. G. Tucker, D. A. Keen, M. T. Cove, L. Peters, J. S. O. Evans, *J. Phys. Condens. Matter* **2008**, *20*, 255225.
[87] A. L. Goodwin, D. A. Keen, M. G. Tucker, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18708.
[88] Z. Assefa, B. Noren, A. Oskarson, *Inorg. Chem.* **1994**, *33*, 2187.
[89] Z. Assefa, R. J. Staples, J.-P. Fackler Jr., H. H. Patterson, G. Shankle, *Acta Crystallogr. Sect. C* **1995**, *51*, 2527.
[90] K. Kalachnikova, Z. Assefa, R. E. Sykora, *Acta Crystallogr. Sect. E* **2007**, *63*, i162.
[91] J. C. F. Colis, R. Staples, C. Tripp, D. Labrecque, H. H. Patterson, *J. Phys. Chem. B* **2005**, *109*, 102.
[92] M. A. Rawashdesh-Omary, C. L. Larochelle, H. H. Patterson, *Inorg. Chem.* **2000**, *39*, 4527.
[93] P. A. Tanner, X. Zhou, W.-T. Wong, C. Kratzer, H. Yersin, *J. Phys. Chem. B* **2005**, *109*, 13083.
[94] L.-R. Guo, J.-W. Tong, X. Liang, J. Köhler, J. Nuss, Y.-Z. Li, L.-M. Zheng, *Dalton Trans.* **2011**, *40*, 6392.
[95] C. Yang, X. Wang, M. A. Omary, *Angew. Chem. Int. Ed.* **2009**, *48*, 2500; *Angew. Chem.* **2009**, *121*, 2538.
[96] C. Yang, O. Elbjeirami, C. S. P. Gamage, H. V. R. Dias, M. A. Omary, *Chem. Commun.* **2011**, *47*, 7434.
[97] G. Bowmaker in *Gold*, *Progress in Chemistry*, *Biochemistry and Technology* (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**, p. 841.
[98] G. W. Eastland, M. A. Mazid, D. R. Russell, M. C. R. Symons, *J. Chem. Soc. Dalton Trans.* **1980**, 1682.
[99] G. Blaise, P. Meyer, C. Legras, *J. Phys. Lett.* **1977**, *38*, 183.
[100] M. A. Rawashdeh-Omary, M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **2000**, *122*, 10371.
[101] W. R. Mason, *J. Am. Chem. Soc.* **1973**, *95*, 3573.
[102] W. R. Mason, *J. Am. Chem. Soc.* **1976**, *98*, 5182.
[103] K. M. Merz, R. Hoffmann, *Inorg. Chem.* **1988**, *27*, 2120.
[104] K. W. Klinkhammer, P. Pyykkö, *Inorg. Chem.* **1995**, *34*, 2120.
[105] Y. Yoshida, K. Muroi, A. Otsuka, G. Saito, M. Takahashi, T. Yoko, *Inorg. Chem.* **2004**, *43*, 1458.
[106] M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **1998**, *120*, 7696.
[107] V. W.-W. Yam, K. K. W. Lo, *Chem. Soc. Rev.* **1999**, *28*, 323.
[108] A. Vogler, H. Kunkely, *Chem. Phys. Lett.* **1989**, *158*, 74.
[109] P. C. Ford, A. Vogler, *Acc. Chem. Res.* **1993**, *26*, 220.
[110] G. J. S. Venter, A. Roodt, R. Meijboom, *Inorg. Chim. Acta* **2009**, *362*, 2475.
[111] M. Henary, J. I. Zink, *Inorg. Chem.* **1991**, *30*, 3111.
[112] X. Liu, G.-C. Guo, M.-L. Fu, W.-T. Chen, Z.-J. Zhang, J.-S. Huang, *Dalton Trans.* **2006**, 884.
[113] R.-W. Huang, Y. Zhu, S.-Q. Zang, M.-L. Zhang, *Inorg. Chem. Commun.* **2013**, *33*, 38.
[114] A. Barbieri, G. Accorsi, N. Armaroli, *Chem. Commun.* **2008**, 2185.
[115] M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houka, *Chem. Soc. Rev.* **2009**, *38*, 1330.
[116] J. Jin, W.-Y. Wang, Y.-H. Liu, H.-W. Hou, Y.-T. Fan, *Chem. Commun.* **2011**, *47*, 7461.
[117] F.-J. Liu, D. Sun, H.-J. Hao, R. B. Huang, L.-Z. Zheng, *Inorg. Chem. Commun.* **2012**, *15*, 136.
[118] D. Sun, L. Zhang, H. Lu, S. Feng, D. Sun, *Dalton Trans.* **2013**, *42*, 3528.
[119] I. Tsyba, B. B. K. Mui, R. Bau, P. Noguchi, K. Nomiya, *Inorg. Chem.* **2003**, *42*, 8028.
[120] K. Nomiya, S. Takahashi, R. Noguchi, *J. Chem. Soc. Dalton Trans.* **2000**, 2091.
[121] Q. Chu, D. C. Swenson, L. R. MacGillivray, *Angew. Chem. Int. Ed.* **2005**, *44*, 3569; *Angew. Chem.* **2005**, *117*, 3635.
[122] I. G. Georgiev, D.-K. Bucar, L. R. MacGillivray, *Chem. Commun.* **2010**, *46*, 4956.
[123] R. Santra, K. Biradha, *Cryst. Growth Des. CrystGrowth&Design* **2010**, *10*, 3315.
[124] G. K. Kole, G. K. Tan, J. J. Vittal, *Cryst. Growth Des.* **2012**, *12*, 326.
[125] J.-X. Dai, H.-L. Zhu, A. Rothenberger, Q.-F. Zhang, *Z. Naturforsch. B* **2007**, *62*, 1112.
[126] Y.-G. Li, Q.-B. Jiang, K. Cheng, H. Yan, H.-L. Zhu, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2572.
[127] C.-C. Wang, H.-Y. Li, G.-L. Guo, *Transition Met. Chem.* **2013**, *38*, 275.
[128] L. Pan, E. B. Woodlock, X. Wang, K.-C. Lam, A. L. Rheingold, *Chem. Commun.* **2001**, 1762.
[129] Y.-F. Li, Z.-H. Pan, T.-J. Lou, *Acta Crystallogr. Sect. C* **2007**, *63*, m516.
[130] C.-M. Jin, Z.-F. Chen, H.-F. Mei, X.-K. Shi, *J. Mol. Struct.* **2009**, *921*, 58.
[131] D. Sun, R. Cao, Y. Sun, W. Bi, X. Li, Y. Wang, Q. Shi, X. Li, *Inorg. Chem.* **2003**, *42*, 7512.
[132] G. Ou, J. Gu, T. Lu, R. D. Luck, *J. Mol. Struct.* **2005**, *740*, 143.
[133] Y.-Q. Gong, J.-T. Chen, D.-Q. Yuan, M.-Y. Wu, Y.-G. Huang, F.-L. Jiang, M.-C. Hong, *Inorg. Chim. Acta* **2007**, *360*, 2207.
[134] Z.-X. Lian, J. Cai, C.-H. Chen, H.-B. Luo, *CrystEngComm* **2007**, *9*, 319.
[135] G. A. Broker, E. R. T. Tiekink, *Acta Crystallogr. Sect. E* **2007**, *63*, m2467.
[136] G. A. Broker, E. R. T. Tiekink, *Acta Crystallogr. Sect. E* **2007**, *63*, m2485.
[137] N. S. Yue, M. C. Jennings, R. J. Puddephatt, *Dalton Trans.* **2006**, 3886.
[138] C. Desmarets, I. Azcarate, G. Gontard, H. Amouri, *Eur. J. Inorg. Chem.* **2011**, 4558.
[139] Y.-N. Chi, K.-L. Huang, F.-Y. Cui, Y.-Q. Xu, C.-W. Hu, *Inorg. Chem.* **2006**, *45*, 10605.
[140] M. Quirós, *Acta Crystallogr. Sect. C* **1994**, *50*, 1236.
[141] R. P. Feazell, C. E. Carson, K. K. Klausmeyer, *Inorg. Chem.* **2006**, *45*, 2635.
[142] X.-D. Chen, M. Du, T. C. W. Mak, *Chem. Commun.* **2005**, 4417.
[143] X.-D. Chen, T. C. W. Mak, *J. Mol. Struct.* **2005**, *743*, 1.
[144] X.-D. Chen, c.-Q. Wan, H. H.-Y. Sung, I. D. Williams, T. C. W. Mak, *Chem. Eur. J.* **2009**, *15*, 6518.
[145] W.-W. Dong, J. Zhao, L. Xu, *J. Solid State Chem.* **2008**, *181*, 1149.
[146] Y. Zhou, W. Chen, D. Wang, *Dalton Trans.* **2008**, 1444.
[147] A. Stephenson, M. D. Ward, *Chem. Commun.* **2012**, *48*, 3605.
[148] G. Yuan, C. Zhu, Y. Liu, W. Xuan, Y. Cui, *J. Am. Chem. Soc.* **2009**, *131*, 10452.
[149] Y.-H. Li, D. Sun, G.-G. Luo, F.-J. Liu, H.-J. Hao, Y.-M. Wen, Y. Zhao, R.-B. Huang, L.-S. Zheng, *J. Mol. Struct.* **2011**, *1000*, 85.
[150] G. A. Senchyk, V. O. Bukhan′ko, A. R. Lysenko, H. Krautscheid, E. B. Rusanov,, A. N. Chernega, M. Karbowiak,, K. V. Domasevitch, *Inorg. Chem.* **2012**, *51*, 8025.
[151] B. Schneider, S. Demeshko, S. Dechert, F. Meyer, *Inorg. Chem.* **2012**, *51*, 4912.
[152] D. Pogozhev, S. A. Baudron, M. W. Hosseini, *Dalton Trans.* **2011**, *40*, 437.
[153] L. Koskinen, S. Jääskelainen, L. Oresma, M. Haukka, *CrystEngComm* **2012**, *14*, 3509.
[154] N. L. S. Yue, M. C. Jennings, R. J. Puddephatt, *Dalton Trans.* **2010**, *39*, 1273.
[155] C.-Q. Wan, S. A. Al-Thabaiti, X.-D. Chen, T. C. W. Mak, *Eur. J. Inorg. Chem.* **2013**, 5265.
[156] C.-Q. Wan, T. C. W. Mak, *Cryst. Growth Des.* **2011**, *11*, 832.

[157] O.-S. Jung, Y.-A. Lee, Y. J. Kim, J. Hong, *Cryst. Growth Des.* **2002**, *2*, 497.
[158] L. Dobrzańska, H. G. Raubenheimer, L. J. Barbour, *Chem. Commun.* **2005**, 5050.
[159] S. Lee, K. H. Oark, J. Ahn, Y.-A. Lee, O.-S. Jung, *J. Mol. Struct.* **2011**, *996*, 115.
[160] J. J. Henkelis, S. A. Barnett, L. P. Harding, M. J. Hardie, *Inorg. Chem.* **2012**, *51*, 10657.
[161] H. Abbas, A. L. Pickering, D.-L. Long, P. Kögerler, L. Cronin, *Chem. Eur. J.* **2005**, *11*, 1071.
[162] S.-M. Chen, C.-Z. Lu, Y.-Q. Yu, Q.-Z. Zhang, Y. He, *Inorg. Chem. Commun.* **2004**, *7*, 1041.
[163] R. Villanneau, A. Proust, F. Robert, P. Gouzerh, *Chem. Commun.* **1998**, 1491.
[164] C. Streb, C. Ritchie, D.-L. Long, P. Kögerler, L. Cronin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7579; *Angew. Chem.* **2007**, *119*, 7723.
[165] Z.-Y. Shi, J. Peng, Y.-G. Li, Z.-Y. Zhang, X. Yu, K. Alimaje, X. Wang, *CrystEngComm* **2013**, *15*, 7583.
[166] L. Dai, W. You, E. Wang, S, Wu, Z. Su, Q. Du, Y. Zhao, Y. Fang, *Cryst. Growth Des.* **2009**, *9*, 2110.
[167] E.-M. Zerbe, P. G. Jones, O. Moers, A. Blaschette, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2623.
[168] N. Gerasimchuk, A. N. Esaulenko, K. N. Dalley, C. Moore, *Dalton Trans.* **2010**, *39*, 749.
[169] M. P. Carranza, B. R. Manzano, F. A. Jalón, A. M. Rodríguez, L. Santos, M. Moreno, *Inorg. Chem.* **2010**, *49*, 3828.
[170] M.-D. Su, *Inorg. Chem.* **2005**, *44*, 4829.
[171] J. Moussa, K. Boubekeur, H. Amouri, *Eur. J. Inorg. Chem.* **2005**, 3808.
[172] S. Riedel, P. Pyykkö, R. A. Mata, H.-J. Werner, *Chem. Phys. Lett.* **2005**, *405*, 148.
[173] M. M. Alam, E. Fromager, *Chem. Phys. Lett.* **2012**, *554*, 37.
[174] C. W. Liu, I.-J. Shang, J.-C. Wang, T.-C. Keng, *Chem. Commun.* **1999**, 995.
[175] C. Latouche, S. Kahlal, E. Furet, P.-K. Liao, Y.-R. Lin, C.-S. Fang, J. Cuny, C. W. Liu, J.-Y. Saillard, *Inorg. Chem.* **2013**, *52*, 7752.
[176] C.-W. Liu, C.-S. Feng, R.-J. Fu, H.-W. Jang, J.-Y. Saillard, S. Kahlal, J.-C. Wang, I.-J. Chang, *Inorg. Chem.* **2010**, *49*, 4934.
[177] C.-W. Liu, I.-J. Shang, R.-J. Fu, B.-J. Liaw, J.-C. Wang, I.-J. Chang, *Inorg. Chem.* **2006**, *45*, 2335.
[178] I. G. Dance, *Inorg. Chem.* **1977**, *25*, L17.
[179] G. Dance, L. J. Fitzpatrick, A. D. Rae, M. L Scudder, *Inorg. Chem.* **1983**, *22*, 3785.
[180] S. Akerström, *Acta Chem. Scand.* **1964**, *18*, 1308.
[181] I. G. Dance, *Inorg. Chem.* **1981**, *20*, 1487.
[182] L. S. Ahmed, J. R. Dilworth, J. R. Miller, N. Wheatley, *Inorg. Chim. Acta* **1998**, *278*, 229.
[183] E. Barreiro, J. S. Casas, M. D. Couce, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, A. Sanchez, J. Sordo, E. M. V. López, *Dalton Trans.* **2013**, *42*, 5916.
[184] H. U. Rehmann, S. Ahmad, H. Ajaz, M. Hanif, M. Altaf, H. Stoeckli-Evans, *J. Struct. Chem.* **2011**, *52*, 160.
[185] See Ref. [118].
[186] B. Djorjevic, O. Schuster, H. Schmidbaur, *Inorg. Chem.* **2005**, *44*, 673.
[187] M. Rubio, M. A. Siegler, A. L. Spek, J. N. H. Reek, *Dalton Trans.* **2010**, *39*, 5432.
[188] B. K. Teo, J. C. Calabrese, *J. Chem. Soc. Chem. Commun.* **1976**, 185.
[189] F. A. Cotton, D. M. L. Goodgame, *J. Chem. Soc.* **1960**, 5267.
[190] A. M. Aly, D. Neugebauer, O. Orama, U. Schubert, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 125; *Angew. Chem.* **1978**, *90*, 125.
[191] H. Schmidbaur, A. A. M. Ali, U. Schubert, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 846; *Angew. Chem.* **1978**, *90*, 905.
[192] A. Serpe, F. Artizzu, L. Marchiò, M. L. Mercuri, L. Pilia, P. Deplano, *Cryst. Growth Des.* **2011**, *11*, 1278.
[193] G.-C. Guo, T. C. W. Mak, *Angew. Chem. Int. Ed.* **1998**, *37*, 3183; *Angew. Chem.* **1998**, *110*, 3296.
[194] Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 7608.
[195] Q.-M. Wang, T. C. W. Mak, *Chem. Commun.* **2000**, 1435.
[196] C. W. Liu, H.-W. Chang, C.-S. Fang, B. Sarkar, J.-C. Wang, *Chem. Commun.* **2010**, *46*, 4571.
[197] J.-H. Liao, C. Latouche, B. Li, S. Kahlal, J.-Y. Saillard, C. W. Liu, *Inorg. Chem.* **2014**, *53*, 2260.
[198] C. W. Liu, H.-C. Hala, C.-M. Hung, B. K. Santra, B.-J. Liaw, *Inorg. Chem.* **2004**, *43*, 4464.
[199] Y.-J. Li, C. Latouche, S. Kahlal, J.-H. Liao, R. S. Dhayal, J.-Y. Saillard, C. W. Liu, *Inorg. Chem.* **2012**, *51*, 7439.
[200] D. Rais, D. M. P. Mingos, R. Vilar, A. J. P. White, D. J. Williams, *J. Organomet. Chem.* **2002**, *652*, 87.
[201] T. Zhang, C. Ji, K. Wang, D. Fortin, P. D. Harvey, *Inorg. Chem.* **2010**, *49*, 11069.
[202] T. C. W. Mak, X.-L. Zhao, Q.-M. Wang, G.-C. Guo, *Coord. Chem. Rev.* **2007**, *251*, 2311.
[203] J. A. Shaw, E. Fisher, *J. Am. Chem. Soc.* **1946**, *68*, 2745.
[204] G. C. Guo, G.-D. Zhou, T. C. W. Mak, *J. Am. Chem. Soc.* **1999**, *121*, 3136.
[205] G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T. C. W. Mak, *Angew. Chem. Int. Ed.* **1998**, *37*, 630; *Angew. Chem.* **1998**, *110*, 652.
[206] Q.-G. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2000**, *122*, 7608.
[207] T. Hu, T. C. W. Mak, *Inorg. Chem.* **2013**, *52*, 9066.
[208] Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 7594.
[209] T. C. W. Mak, L. Zhao, *Chem. Asian J.* **2007**, *2*, 456.
[210] S. C. K. Hau, T. C. W. Mak, *J. Am. Chem. Soc.* **2014**, *136*, 902.
[211] B. Li, S.-Q. Zang, R. Liang, Y.-J. Wu, T. C. W. Mak, *Organometallics* **2011**, *30*, 1710.
[212] B. Li, S.-Q. Zang, H.-Y. Li, Y.-J. Wu, T. C. W. Mak, *J. Organomet. Chem.* **2012**, *708*, 112.
[213] S.-Q. Zang, T. C. W. Mak, *Inorg. Chem.* **2008**, *47*, 7094.
[214] S. C. K. Hau, T. C. W. Mak, *Chem. Eur. J.* **2013**, *19*, 5387.
[215] P.-S. Cheng, S. Marivel, S.-Q. Zang, G.-G. Gao, T. C. W. Mak, *Cryst. Growth Des.* **2012**, *12*, 4519.
[216] B. Li, R.-W. Huang, S.-Q. Zang, T. C. W. Mak, *CrystEngComm* **2013**, *15*, 4087.
[217] L. Zhao, W.-Y. Wong, T. C. W. Mak, *Chem. Eur. J.* **2006**, *12*, 4865.
[218] T. Zhang, Y. Hu, J. Kong, X. Meng, X. Dai, H. Song, *CrystEngComm* **2010**, *12*, 3027.
[219] T. Zhang, J. Kong, Y. Hu, X. Meng, H. Yin, D. Hu, C. Ji, *Inorg. Chem.* **2008**, *47*, 3144.
[220] Y. Zhao, P. Zhang, B. Li, X. Meng, T. Zhang, *Inorg. Chem.* **2011**, *50*, 9097.
[221] Z.-G. Jiang, K. Shi, Y.-M. Lin, Q.-M. Wang, *Chem. Commun.* **2014**, *50*, 2353.
[222] Y.-P. Xie, T. C. W. Mak, *J. Am. Chem. Soc.* **2011**, *133*, 3760.
[223] Y.-P. Xie, T. C. W. Mak, *Chem. Commun.* **2012**, *48*, 1123.
[224] J. Qiao, K. Shi, Q.-M. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 1765; *Angew. Chem.* **2010**, *122*, 1809.
[225] Y.-Y. Li, F. Gao, J. E. Beves, Y.-Z. Li, J.-L. Zuo, *Chem. Commun.* **2013**, *49*, 3658.
[226] G.-G. Gao, P.-S. Cheng, T. C. W. Mak, *J. Am. Chem. Soc.* **2009**, *131*, 18257.
[227] X.-L. Zhao, T. C. W. Mak, *Inorg. Chem.* **2010**, *49*, 3676.
[228] Q.-M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 1501.
[229] M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.* **2008**, *37*, 1884.
[230] K.-J. Range, M. Zabel, H. Meyer, H. Fischer, *Z. Naturforsch. B* **1985**, *40*, 1618.
[231] M. A. Omary, H. H. Patterson, *Inorg. Chem.* **1998**, *37*, 1060.
[232] X. Liu, M.-L. Fu, X.-H. Liu, M.-S. Wang, J.-S. Huang, *Inorg. Chem.* **2006**, *45*, 3679.

[233] X. Liu, L. Li, Y.-Z. Yang, K.-L. Huang, *Dalton Trans.* **2014**, *43*, 4086.

[234] D. M. Pham, D. Rios, M. M. Olmstead, A. L. Balch, *Inorg. Chim. Acta* **2005**, *358*, 4261.

[235] C. Kappenstein, A. Ouali, M. Guerin, J. Černák, J. Chomič, *Inorg. Chim. Acta* **1988**, *147*, 189.

[236] L. Triščíková, J. Chomič, K. A. Abboud, J.-H. Park, M. W. Meisel, J. Černák, *Inorg. Chim. Acta* **2004**, *357*, 2763.

[237] J. Černák, J. Chomič, W. Massa, *Acta Crystallogr. Sect. C* **2002**, *58*, m490.

[238] C. J. Shorrock, B.-Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick, D. B. Leznoff, *Inorg. Chem.* **2002**, *41*, 6743.

[239] L. Triščíková, I. Potočňák, C. Wagner, *Acta Crystallogr.*, *Sect. C* **2002**, *58*, m246.

[240] L. Triščíková, I. Potočňák, J. Chomič, *Trans. Met. Chem.* **2003**, *28*, 808.

[241] A. M. Madalan, N. Avarvari, M. Andruh, *Cryst. Growth Des.* **2006**, *6*, 1671.

[242] C. Paraschiv, M. Andruh, S. Ferlay, M. W. Hosseini, N. Kyritsakas, J.-M. Planeix, N. Stanica, *Dalton Trans.* **2005**, 1195.

[243] J.-P. Costes, C. Duhayon, L. Vendier, E. Colacio, A. A. J. Mota, V. J. Suarez, *Inorg. Chem.* **2012**, *51*, 1011.

[244] H. Zhang, Y. Zhang, C. Wang, L. Cai, Y. Xie, G. Xue, *Inorg. Chem. Commun.* **2006**, *9*, 555.

[245] M. Monim-ul-Mehbob, M. Ramzan, T. Rüffer, H. Lang, S. Naddem, M. Akhtar, S. Ahmad, *Z. Naturforsch. B.* **2013**, *68*, 161.

[246] H.-X. Zhang, Z.-N. Chen, C.-Y. Su, C. Ren, B.-S. Kang, *J. Chem. Crystallogr.* **1999**, *29*, 1239.

[247] X.-D. Zheng, L. Jiang, X.-L. Feng, T. B. Lu, *Inorg. Chem.* **2008**, *47*, 10858.

[248] M. C. Muñoz, A. B. Gaspar, A. Galet, J. A. Real, *Inorg. Chem.* **2007**, *46*, 8182.

[249] T. Kosone, Y. Suzuki, S. Ono, C. Kanadani, T. Saito, T. Kitazawa, *Dalton Trans.* **2010**, *39*, 1786.

[250] A. Galet, V. Niel, M. C. Muñoz, J. A. Real, *J. Am. Chem. Soc.* **2003**, *125*, 14224.

[251] V. Niel, A. L. Thompson, A. E. Goeta, C. Enachescu, A. Hauser, A. Galet, M. C. Munoz, J. A. Real, *Chem. Eur. J.* **2005**, *11*, 2047.

[252] Y. Guo, Y. Ma, N. Zhou, Z.-Q. Liu, Q.-L. Wang, S. P. Yan, D.-Z. Liao, *Z. Anorg. Allg. Chem.* **2010**, *636*, 865.

[253] N. Wannarit, V. Hahnvajanawong, C. Pakawatchai, S. Youngme, *Trans. Met. Chem.* **2012**, *37*, 79.

[254] A. Michaelides, V. Kiritsis, S. Skoulika, A. Aubry, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1495; *Angew. Chem.* **1993**, *105*, 1525.

[255] K. L. Seward, J. M. Ellsworth, Z. M. Khaliq, M. D. Smith, H.-C. zur Loye, *Acta Crystallogr. Sect. E* **2007**, *63*, m2333.

[256] I. Kalf, M. Braun, Y. Wang, U. Englert, *CrystEngComm* **2006**, *8*, 916.

[257] H.-L. Zhu, X.-M. Zhang, G.-F. Liu, D.-Q. Wang, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1059.

[258] R. P. Feazell, C. E. Carson, K. K. Klausmeyer, *Eur. J. Inorg. Chem.* **2005**, 3287.

[259] L. Valencia, R. Bastida, A. Macías, M. Vicente, P. Pérez-Lourido, *New J. Chem.* **2005**, *29*, 424.

[260] E. C. Constable, C. E. Housecroft, P. Kopecky, M. Neuburger, J. A. Zampese, *Inorg. Chem. Commun.* **2013**, *27*, 159.

[261] A. Bellusci, M. Ghedini, L. Giorgini, F. Gozzo, E. I. Szerb, A. Crispini, D. Pucci, *Dalton Trans.* **2009**, 7381.

[262] T. Ni, Y. Zhao, M. Shao, S. Zhu, F. Xing, M. Li, *Z. Anorg. Allg. Chem.* **2011**, *637*, 689.

[263] S. B. Silong, J. D. Kildea, W. C. Patalinghug, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1994**, *47*, 1545.

[264] J. E. Aguado, M. J. Calhorda, P. J. Costa, O. Crespo, V. Félix, M. C. Gimeno, P. G. Jones, A. Laguna, *Eur. J. Inorg. Chem.* **2004**, 3038.

[265] L. Hou, D. Li, *Inorg. Chem. Commun.* **2005**, *8*, 128.

[266] See Ref. [146].

[267] C. B. Acland, H. C. Freeman, *Chem. Commun.* **1971**, 1016.

[268] G. W. Hunt, T. C. Lee, E. L. Amma, *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 909.

[269] Y. Wang, U. Englert, *Inorg. Chim. Acta* **2010**, *363*, 2539.

[270] M.-L. Tong, S.-L. Zheng, X.-M. Chen, *Chem. Eur. J.* **2000**, *6*, 3729.

[271] M. Odoko, T. Ise, N. Okabe, *Acta Crystllogr. Sect. C* **2007**, *63*, m22.

[272] H.-J. Hao, D. Sun, Y.-H. Li, F.-J. Liu, R.-B. Huang, L.-S. Zheng, *Cryst. Growth Des.* **2011**, *11*, 3564.

[273] G.-G. Luo, D.-L. Wu, L. Liu, S.-H. Wu, D.-X. Li, Z.-J. Xiao, J.-C. Dai, *J. Mol. Struct.* **2012**, *1014*, 92.

[274] D. Sun, Q.-J. Xu, C.-Y. Ma, N. Zhang, R.-B. Huang, L.-S. Zheng, *CrystEngComm* **2010**, *12*, 4161.

[275] F.-J. Liu, D. Sun, H.-J. Hao, R.-B. Huang, L.-S. Zheng, *J. Mol. Struct.* **2012**, *1014*, 70.

[276] P.-X. Yin, Jj. Zhang, Z.-J. Li, Y.-Y. Qin, J.-K. Jeng, L. Zhang, Q.-P. Lin, Y.-G. Yao, *Cryst. Growth Des.* **2009**, *9*, 4884.

[277] X. Zhang, Y.-Y. Huang, Z.-S. Liu, Y.-G. Yao, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1042.

[278] S.-M. Fang, M. Hu, Q. Zhang, M. Du, C.-S. Liu, *Dalton Trans.* **2011**, *40*, 4527.

[279] B. Li, C. Ji, S.-Q. Zang, H.-W. Hou, T. C. W. Mak, *Dalton Trans.* **2012**, *41*, 9151.

[280] B. Li, S.-Q. Zang, C. Ji, H.-W. Hou, T. C. W. Mak, *Cryst. Growth Des.* **2012**, *12*, 1443.

[281] See Ref. [276].

[282] J. Wang, S. Hu, M.-L. Tong, *Eur. J. Inorg. Chem.* **2006**, 2069.

[283] Y. Zorlu, H. Can, *J. Mol. Struct.* **2013**, *1037*, 109.

[284] O. Z. Yesilel, G. Günay, C. Dracan, M. S. Soylu, S. Keskin, S. W. Ng, *CrystEngComm* **2012**, *14*, 2812.

[285] X.-F. Zheng, L. G. Zhu, *Cryst. Growth Des.* **2009**, *9*, 4407.

[286] J. Xu, Q. Yuan, Z.-S. Bai, Z. Su, W.-Y. Sun, *Inorg. Chem. Commun.* **2009**, *12*, 58.

[287] L. Han, D. Yuan, B. Wu, C. Liu, M. Hong, *Inorg. Chim. Acta* **2006**, *359*, 2232.

[288] B. Liu, Q. Yuan, *Inorg. Chem. Commun.* **2005**, *8*, 1022.

[289] Z. Liu, P. Liu, Y. Chen, J. Wang, M. Huang, *New J. Chem.* **2005**, *29*, 474.

[290] M. Du, C.-P. Li, X.-J. Zhao, *Cryst. Growth Des.* **2006**, *6*, 335.

[291] J. A. Fry, C. R. Samanamu, J. L. Montchamp, A. F. Richards, *Eur. J. Inorg. Chem.* **2008**, 463.

[292] Y.-B. Lu, F.-M. Jian, *Acta Crystallogr. Sect. E* **2012**, *68*, m101.

[293] V. T. Yilmaz, S. Hamamci, W. T. A. Harrison, C. Thöne, *Polyhedron* **2005**, *24*, 693.

[294] I. Ilker, O. Z. Yesilel, G. Günay, O. Büyükgüngör, *J. Organomet. Chem.* **2009**, *694*, 4178.

[295] V. T. Yilmaz, E. Senel, E. Guney, C. Kazak, *Inorg. Chem. Commun.* **2008**, *11*, 1330.

[296] V. T. Yilmaz, S. Hamamci, C. Kazak, *J. Organomet. Chem.* **2008**, *693*, 3885.

[297] V. T. Yilmaz, S. Hamamci, C. Kazak, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1961.

[298] J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin, X.-M. Chen, *Chem. Eur. J.* **2005**, *11*, 552.

[299] Z.-L. You, L. Zhang, D.-H. Shi, L.-L. Ni, *Inorg. Chem. Commun.* **2009**, *12*, 1231.

[300] J. Zhang, Y.-C. Shen, Y.-Y. Qin, Z.-J. Li, Y.-G. Yao, *CrystEngComm* **2007**, *9*, 636.

[301] Y. An, X. Li, H. Chen, W. Liu, S. Ng, Y. Zhang, J. Wang, *Inorg. Chim. Acta* **2011**, *376*, 230.

[302] L. Dobrzańska, *Eur. J. Inorg. Chem.* **2012**, 945.

[303] M. Dennehy, O. V. Quinzani, R. A. Burrow, *Acta Crystallogr. Sect. C* **2007**, *63*, m395.

[304] M. Dennehy, R. M. Ferullo, O. V. Quinzani, S. D. Mandolesi, N. Castellani, M. Jennings, *Polyhedron* **2008**, *27*, 2243.

[305] N. C. Baenziger, A. W. Straus, *Inorg. Chem.* **1976**, *15*, 1807.

[306] D. S. Cook, M. F. Turner, *J. Chem. Soc. Perkin Trans.* **1975**, 1021.

[307] G. Mukherjee, P. Singh, C. Ganguri, S. Sharma, H. B. Singh, N. Goel, U. P. Singh, R. J. Butcher, *Inorg. Chem.* **2012**, *51*, 8128.

[308] K. Seubert, D. Böhme, J. Kösters, W.-Z. Shen, E. Freisinger, J. Müller, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1761.

[309] R.-L. Sang, L. Xu, *Eur. J. Inorg. Chem.* **2006**, 1260.

[310] M. Bardají, A. B. Miguel-Coello, P. Espinet, *Inorg. Chim. Acta* **2012**, *386*, 93.

[311] D. L. Reger, R. F. Sumeniuc, M. D. Smith, *Dalton Trans.* **2008**, 2253.

[312] P. J. Chmielewski, *Angew. Chem. Int. Ed.* **2005**, *44*, 6417; *Angew. Chem.* **2005**, *117*, 6575.

[313] R. H. Laye, *Inorg. Chim. Acta* **2007**, *360*, 439.

[314] S. Khanna, S. Verma, *Cryst. Growth Des.* **2012**, *12*, 3025.

[315] I. Bassanetti, C. P. Twist, M.-G. Kim, A. M. Seyam, H. S. Bazzi, Q. J. Wang, Y.-W. Chung, L. Marchio, M. Delferro, T. J. Marks, *Inorg. Chem.* **2014**, *53*, 4629.

[316] J.-Y. Wu, Y.-F. Lin, C.-H. Chuang, T.-W. Tseng, Y.-S. Wen, K.-L. Lu, *Inorg. Chem.* **2008**, *47*, 10349.

[317] Y. Inoguchi, B. Milewski-Mahrla, D. Neugebauer, G. P. Jones, H. Schmidbaur, *Chem. Ber.* **1983**, *116*, 1487.

[318] See Ref. [307].

[319] V. J. Catalano, S. J. Horner, *Inorg. Chem.* **2003**, *42*, 8430.

[320] J. Ahn, C. W. Kim, T. H. Noh, O.-S. Jung, *Transition Met. Chem.* **2011**, *36*, 145.

[321] C. W. Kim, T. H. Noh, O.-S. Jung, *Inorg. Chim. Acta* **2011**, *365*, 496.

[322] O.-S. Jung, Y. J. Kim, Y.-A. Lee, S. W. Kang, S. N. Choi, *Cryst. Growth Des.* **2004**, *4*, 23.

[323] V. Chandrasekhar, R. S. Narayanan, *Dalton Trans.* **2013**, *42*, 6619.

[324] E. W. Ainscough, A. M. Brodie, R. J. Davidson, G. B. Jameson, C. A. Otter, *CrystEngComm* **2013**, *15*, 4379.

[325] H.-Y. Tan, H.-X. Zhang, H.-D. Ou, B.-S. Kang, *Inorg. Chim. Acta* **2004**, *357*, 869.

[326] C.-L. Chen, H.-Y. Tan, J.-H. Yao, Y.-Q. Wan, C.-Y. Su, *Inorg. Chem.* **2005**, *44*, 8510.

[327] D. M. Ho, R. Bau, *Inorg. Chem.* **1983**, *22*, 4073.

[328] H. H. Karsch, U. Schubert, *Z. Naturforsch. B* **1982**, *37*, 186.

[329] C. W. Liu, B. Sarkar, B. J. Liaw, Y.-W. Lin, T. S. Lobana, J.-C. Wang, *J. Organomet. Chem.* **2009**, *694*, 2134.

[330] Z.-N. Chen, N. Zhao, Y. Fan, J. Ni, *Coord. Chem. Rev.* **2009**, *253*, 1.

[331] C. M. Knapp, C. S. Jackson, J. S. Large, A. L. Thompson, J. M. Goicoechea, *Inorg. Chem.* **2011**, *50*, 4021.

[332] J.-R. Li, X.-H. Bu, J. Jiao, W.-P. Du, X.-H. Xu, R.-H. Zhang, *Dalton Trans.* **2005**, 464.

[333] C. Rim, H. Zhang, D. Y. Son, *Inorg. Chem.* **2008**, *47*, 11993.

[334] J. L. Hess, M. D. Young, C. A. Murillo, M. Y. Darensbourg, *J. Mol. Struct.* **2008**, *890*, 70.

[335] W. Petz, B. Neumüller, I. Krossing, *Z. Anorg. Allg. Chem.* **2006**, *632*, 859.

[336] J. Vicente, P. Gonzáles-Herrero, Y. García-Sánchez, P. G. Jones, *Inorg. Chem.* **2009**, *48*, 2060.

[337] J. Tan, S. Yu, Q. Zeng, M. Yang, *Comput. Theor. Chem.* **2011**, *965*, 206.

[338] H. Schmidbaur, J. Adlkofer, W. Buchner, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 415; *Angew. Chem.* **1973**, *85*, 448.

[339] H. Schmidbaur, R. Franke, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 416; *Angew. Chem.* **1973**, *85*, 449.

[340] A. Muñoz-Castro, *J. Phys. Chem. A* **2012**, *116*, 520.

[341] G. La Monica, G. A. Ardizzoia, *Prog. Inorg. Chem.* **1997**, *46*, 151.

[342] A. A. Mohamed, L. M. Perez, J. P. Fackler Jr., *Inorg. Chim. Acta* **2005**, *358*, 1657.

[343] G. Yang, P. Baran, A. R. Martinez, R. G. Raptis, *Cryst. Growth Des.* **2013**, *13*, 264.

[344] K. Singh, J. R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* **1997**, *119*, 2942.

[345] A. C. Jahnke, K. Pröpper, C. Bronner, J. Teichgräber, S. Dechert, M. John, O. S. Wenger, F. Meyer, *J. Am. Chem. Soc.* **2012**, *134*, 2938.

[346] C. V. Hettiarachchi, M. A. Rawashdeh-Omary, D. Korir, J. Kohistani, M. Yousufuddin, H. V. Rasika-Dias, *Inorg. Chem.* **2013**, *52*, 13576.

[347] R. Galassi, S. Ricci, A. Burini, A. Macchioni, L. Rocchigiani, F. Marmottini, S. M. Tekarli, V. N. Nesterov, M. A. Omary, *Inorg. Chem.* **2013**, *52*, 14124.

[348] H. V. Rasika-Dias, C. S. P. Gamage, J. Keltner, H. V. K. Diyabalanage, I. Omari, Y. Eyobo, N. R. Dias, N. Roehr, L. McKinney, T. Poth, *Inorg. Chem.* **2007**, *46*, 2979 and references therin.

[349] T. Grimes, M. A. Omary, H. V. Rasika-Dias, T. R. Cundari, *J. Phys. Chem. A* **2006**, *110*, 5823.

[350] A. A. Mohamed, R. Galassi, F. Papa, A. Burini, J. P. Fackler, Jr., *Inorg. Chem.* **2006**, *45*, 7770.

[351] A. Burini, A. Mohamed, J. P. Fackler, Jr., *Comments Inorg. Chem.* **2003**, *24*, 253.

[352] M. A. Omary, A. A. Mohamed, M. A. Rawashdeh-Omary, J. P. Fackler, Jr., *Coord. Chem. Rev.* **2005**, *249*, 1372.

[353] J. C. Vickery, M. M. Olmstead, E. Y. Fung, A. L. Balch, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1179; *Angew. Chem.* **1997**, *109*, 1227.

[354] T.-G. Kocsor, G. Nemes, N. Saffon, S. Mallet-Ladeira, D. Madec, A. Castel, J. Escudié, *Dalton Trans.* **2014**, *43*, 2718.

[355] Y. Zhou, W. Chen, *Organometallics* **2007**, *26*, 2742.

[356] R. G. Maturana, M. P. Vargas, A. Muñoz-Castro, *J. Phys. Chem. A* **2012**, *116*, 8737.

[357] C. Fliedel, P. Braunstein, *Organometallics* **2010**, *29*, 5614.