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A new type of multilayer system–silver(I) complexes of polycyclic aromatic compounds

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Contents

Abstract

A new type of silver(I) coordination complex derived from silver(I) perchlorate (or triflate) and polycyclic aromatic compounds is reviewed. Structural studies by single-crystal X-ray diffraction have shown that all compounds contain extended one- to three-dimensional structures in which several metal atoms are sandwiched between two fused polycyclic systems. Special attention is paid to the combination of the plasticity of the metal ion,

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coordinative versatility of the aromatic ligand, solvent effect and the nature of the counterions for designing metal complexes with a wide range of infinite frameworks.

Keywords: Silver(I) compounds; Polycyclic aromatics; Multilayer compounds; Cation-π interaction; Triple-layer compounds; Double-layer compounds

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1. Introduction

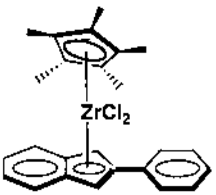
Transition metal multilayer complexes, that are based on either bifacial metal coordination to a single unsaturated ligand or coordination to two such ligands joined in a stack, continue to attract attention as a result of their structure diversity, their interesting and unusual properties and their application as special materials [1–5]. The conventional metal sandwich compounds comprised essentially of metal atoms and planar ligands such as cyclopentadiene, cyclophanes, and carboranes can in principle be synthesized by a variety of straightforward or stepwise reactions [1–7]. The latest developments in polycyclic aromatic chemistry initiated a renaissance in the use of aromatic units of any type and configuration to construct complex molecular architectures characterized inter alia by π-electron interactions [8–15]. This has led to a rapid growth of the interdisciplinary research area involving synthetic chemists [8,9], crystallographers [10,11], theoreticians [12,13], and materials scientists [14,15]. This article is concerned with the particular aspect of multilayer silver(I) complexes of polycyclic aromatic compounds with which we are involved. Although there has been some discussion regarding the cation–aromatic complexes, it is now clear that these cation-π interactions provide a powerful tool for the building of novel molecular architectures and allow the introduction of a wide variety of useful electric and electrochemical properties. The aim of this article is to review the application of X-ray spectroscopy to the study of processes occurring in the solid state. Therefore, this review is neither exhaustive nor comprehensive but illustrative. Section 1 is a general introduction, Section 2 is devoted to the highlights relevant to the present work including earlier studies on multilayer metal systems and silver(I) complexes of aromatic compounds, and Sections 3 and 4 describe in detail the work on construction of multilayer systems with polycyclic aromatic compounds.

2. Background

2.1. Earlier studies on multilayer metal complexes

Since the first report on the synthesis of [2,2]paracyclophane in which two benzene rings are held face-to-face by methylene bridges [16,17] and the accidental discovery of the epoch-making compound ferrocene [18,19], the metal sandwich systems have enjoyed unabated research interest in modern organometallic chemistry for half a century. These two prototypes together with arenes, carboranes, polycyclic aromatics, and even porphyrins have generated numerous organotransition metal sandwiches. Different double-, triple-, tetra-, penta-, hexa-, and multi-layered compounds have been made. The majority of the literature in this area has appeared in the last three decades and reports continue to appear apace. As much of the informative background work has been reviewed elsewhere, in this section we only tabulate some examples closely relevant to our work.

Metallocenes [1] and cyclophanes [6,7] are the most thoroughly investigated double-layer molecules in organometallic and organic chemistry and in particular, the chemistry of metallocene compounds $M(C_5H_5)_2$ has become a well-established field of broad proportions and the literature in this regard is very extensive. General accounts of ferrocene chemistry have appeared [20,21], and ferrocene-based polymers have been reviewed [22]. In addition, the structural, stereochemical and electronic features of arene–metal sandwich complexes have been covered [23]. A book describing the preparations, structures and reactions of sandwich metal compounds derived from $C_5H_5{}^-$, C_6H_6, $C_7H_7{}^+$, C_8H_8 species, and heterocycles containing boron, nitrogen, phosphorus and sulfur atoms, has been published [24].



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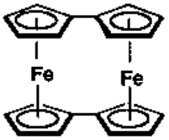

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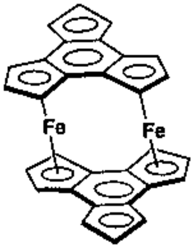

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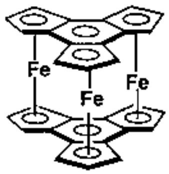
Apart from these, novel sandwich compounds have been reported in a number of metal π-complexes based on benzene or cyclopentadienyl groups and the ring-anellated derivatives of the cyclopentadienyl anions such as indenyl$^-$, fulvalenediyl^{2-} and azulene [25–27]. Ferrocene structure has been found in zirconium complex $[Cp^*Zr(2\text{-PhInd})]Cl_2]$ (**1**) where both Cp* and 2-phenylindenyl ligands are η^5 bonded to the metal center [26]. The crystal structure of bis-μ(fulvalene)diiron, $[Fe_2(C_{10}H_8)_2]$ (**2**), was reported which consists of two symmetry-related ferrocenylene units connected by the C–C bonds [27]. The reaction of the trindene dianion with ferrous chloride has given sandwich complexes $[Fe_2(C_{15}H_9)_2]$ (**3**) and $[Fe_3(C_{15}H_9)_2]$ (**4**), the structures of which, determined by ^1H NMR, MS and UV spectroscopy, have shown that the two planar aromatic hydrocarbons are united by two and three metal atoms, respectively [28]. Likewise, in bis-(*as*-indacenyliron), $[Fe_2(C_{12}H_8)_2]$ (**5**), the two metal atoms are sandwiched between a pair of aromatic rings in a *trans* form [29]. The use of azulene as an unusual η^6-ligand has been revealed in $[Mo(C_{10}H_8)(C_6H_6)]$ (**6**), which was prepared by the reaction of dibenzenemolybdenum and azulene in toluene [30].



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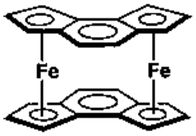

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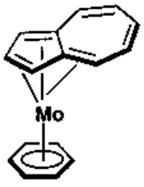

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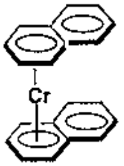
The crystallographic data show that the azulene molecule is coordinated, via the fulvene system formally contained in it, to the [(benzene)Mo] fragment. Using the ferrocene units as the connecting element, a new type of metallocenophanes with sandwich structures, such as $[Fe(C_{19}H_{17})_2]$ and $[CpFe(C_{19}H_{17})]$, has been obtained [31]. In both compounds the position of the iron atom is not directly above the center of the substituted cyclopentadienyl rings but is displaced away from the 6-membered rings.



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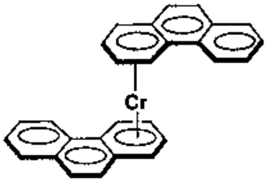

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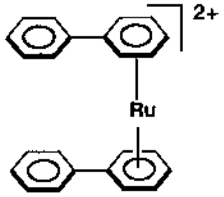

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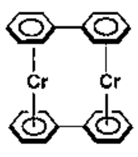
Neutral sandwich complexes of anellated arenes are also known. Bisnaphthalenechromium $[Cr(C_{10}H_8)_2]$ (**7**), which was prepared from the ligands and chromium atoms, is such an example [32]. In the case of higher anellated arenes like phenanthrene **8**, triphenylene and coronene, the metal atom preferentially coordinated to the ring with the highest index of local aromaticity [24]. The η^6-biphenyl sandwiched Ru(II) complex $[Ru(Ph\text{–}Ph)_2][BF_4]_2$ (**9**) exhibits an outstanding structural feature as the two biphenyl ligands are directly over each other in *syn* configuration and the nonbonded benzene rings are tilted away from coplanarity by an angle of 24.6° [33]. In contrast, in a structurally related chromium complex, $[Cr_2(Ph\text{–}Ph)_2]$ (**10**), the two biphenyl ligands sandwich two metal atoms between the two aromatic rings [34].

Triple-layer complexes form a significant class of sandwich compounds involving Lewis acid ligands in the bridging position to hold two metal complex fragments together [1–5]. The possible existence of such structure was first suggested in 1964 on the bases of mass spectroscopic studies for $M_2Cp_3{}^+$ type complexes ($M = Ni$ or Fe) [35a], whereas the first isolated triple-decker complex, $Cp_3Ni_2 + BF_4{}^-$ appeared in 1972 by Werner and Salzer [35b]. The electronic structures of these species together with cobalt counterparts were later analyzed by Hoffmann [36] and the triple-layer sandwich structure **11** was crystallographically proved by a number of cyclopentadiene complexes with the iron group elements [37–39].



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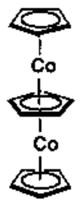

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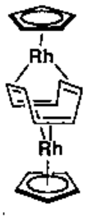

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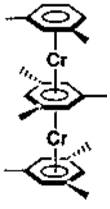

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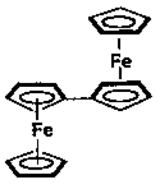
The first examples of arene-bridged, binuclear vanadium complexes $[(C_5H_5)_2V_2(\mathrm{arene})]$ with triple-decker sandwich structure were reported in which two (cyclopentadienyl)vanadium moieties are linked by benzene, toluene, *n*-propylbenzene, or mesitylene [40]. A series of analogous dimetallic complexes with cyclooctatetraene as a bridging ligand have been characterized independently by two different groups [41,42]. An X-ray analysis of one of them, $[(C_5H_5)Rh(C_8H_8)Rh(C_5H_5)]$ (**12**), shows a 1,2,5,6-η-3,4,7,8-η-coordination of tub-shaped C_8H_8 to the two rhodium centers [41]. A complex of this type for mesitylene was reported involving chromium group metals, $[Cr_2(C_6Me_3H_3)_3]$ (**13**) in which all three mesitylene rings are nearly perfectly eclipsed when viewed down the three-fold Cr–Cr axis which lies normal to the aromatic ring planes [43].

Parallel to the development of cyclopentadiene sandwiched triple-layer complexes, Grimes synthesized the first neutral triple-layer cobalt complexes with the carboranyl ring $C_2B_3H_5$ bridging the two CoCp moieties [44]. Since then, this group has characterized a series of triple-layer metallacarborane sandwiches containing transition metal atoms [4,5,45–48]. The structure, reactivity and electrochemistry of closely related diborolene complexes, which contain C_3B_2 rings, were studied by Siebert's group [49–52]. In addition, the formation of *cyclo*-E_5 and *cyclo*-E_6 rings ($E = P$, As) opens the new way to the rich triple-decker and double-decker sandwich chemistry [53].

The anellated cyclopentadienes and arenes are also known to act favorably as bridging ligands in the triple-layer systems. The synthesis of a new class of triple- and quadruple-decker complexes of iron and cobalt derived from pentalene has been attempted [54]. Intersandwich compounds with fulvalenediyl bridges have been extensively studied as model compounds in the context of intramolecular electron transfer and the mixed-valence phenomenon. In this respect the molecular structure of biferrocenium tri-iodide $[(C_5H_5)Fe(C_{10}H_8)Fe(C_5H_5)]I_3$ (**14**) has been determined and the intramolecular electron transfer process studied by ^{57}Fe Mössbauer spectroscopy [55].



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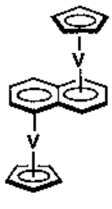

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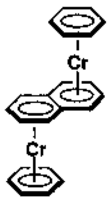

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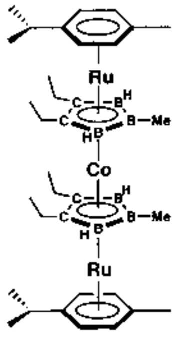

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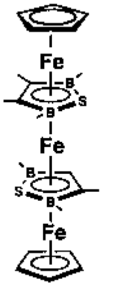

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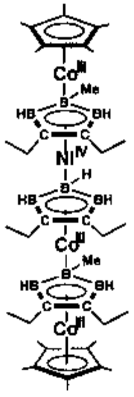

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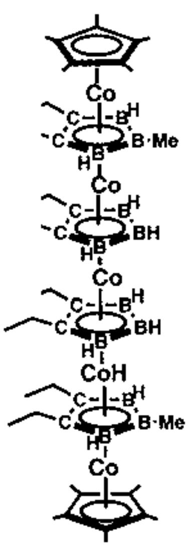
The crystallographic data show that the mixed-valence biferrocenium cation has a *trans*-conformation with the two iron ions in the cation sitting on opposite sides of the planar fulvenide ligand. The structure is best described as a slipped triple-decker, as opposed to the conventional triple-decker structure wherein the metal atoms are coaxial with the center of the cyclopentadienyl rings. The structurally relevant slipped triple-decker sandwich compound $[(C_5H_5)V(C_{10}H_8)V(C_5H_5)]$ (**15**) consists of two cyclopentadienyl–vanadium units bridged by a naphthalene [56]. Another slipped triple-layer complex with naphthalene bridging has been found in the neutral chromium complex $[(C_6H_6)_2Cr_2(C_{10}H_8)]$ (**16**) which was synthesized in the ligand exchange reaction of bis(η^6-naphthalene)dichromium with benzene in THF [57].

Triple-layer structures have also been observed in stacked porphyrins. Employment of a linear, stepwise sequence with the diaminoporphyrin in the two outer ring positions, a closely stacked triple-decker porphyrin compound was isolated [58]. The ^{1}H NMR, UV–vis and fluorescence spectroscopic evidence confirms the sandwich structure and shows strong interaction between the rings. A doubly cofacial porphyrin trimer was synthesized and characterized as a new model for the study of photoinduced intramolecular electron transfer [59]. The optical absorption and fluorescence properties of the molecule show that the structure is comprised of a Zn mesoporphyrin–Zn mesoporphyrin–mesoporphyrin stack.

Together tetra-deckers **17** and **18**, penta-decker **19**, hexa-decker **20**, and staircase oligomeric sandwich complexes **21** account for most metal sandwich complexes.



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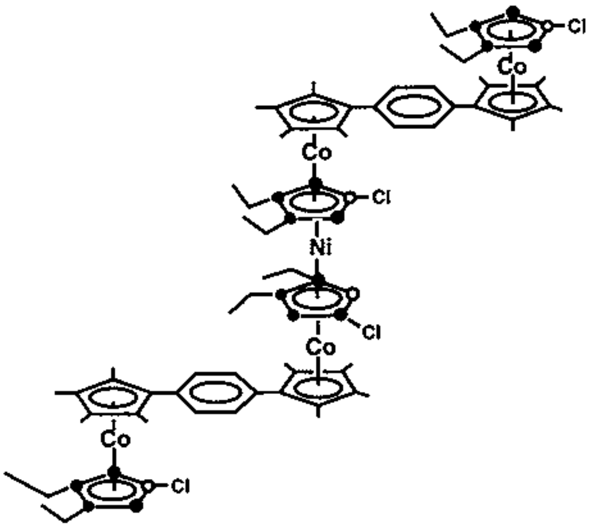

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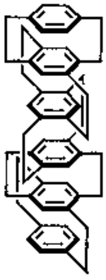
They only occur in carborane [60–65] or thiaborolene [66–69] ligands. There has been a great interest in the synthesis and properties of one-dimensional organometallic polymers based on sandwich compounds due to their potential applications as advanced materials. Multilayer compounds based on cyclophanes **22** have been extensively investigated [70,71].



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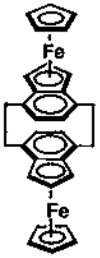

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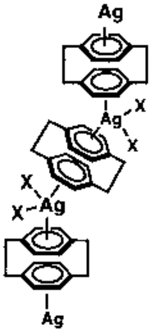

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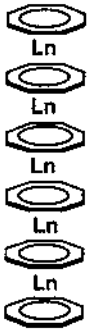

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Hopf suggested that paracyclophane and ferrocene might be linked with each other so as to form multilayer systems **23** having the general structure in which inorganic and organic structural elements alternate [72,73]. The coinage metal coordination polymers involving paracyclophane have been systematically studied [74,75]; among them the silver complex $[Ag(GaCl_4)\cdot\{(p\text{-}C_6H_4CH_2CH_2)_2\}]$ (**24**) forms a multilayer structure in which each ligand group is η^2/η^3 bonded to two metal centers.

Finally, multilayer lanthanide metal complexes have attracted recent research attention [76,77]. For example, organometallic lanthanide complexes of cyclooctatetraene $[Ln_n(C_8H_8)_m]$ (**25**) have been prepared by a combination of laser vaporization and molecular beam methods [77]. These magic-nembered complexes have been shown by mass spectrometry, photoionization spectroscopy and photoelectron spectroscopy to form multilayer sandwich structures in which Ln atoms and the C_8H_8 molecules are alternately piled up.

2.2. Earlier studies on silver(I) aromatic complexes

The investigation of silver(I) complexes with aromatic compounds was initiated almost 80 years ago [78], but prior to 1950 only sporadic reports appeared in the literature based on phase studies [79,80]. From 1950 investigations were intensified, following the theoretical models formulated by Mulliken and Dewar for the bonding in silver perchlorate and benzene [81,82]. The gross crystal structures of $C_6H_6{\cdot}AgClO_4$ was reported in 1950 [83], which was later accurately refined [84]. The complex consists of –benzene–Ag–benzene–Ag– chains and perchlorate ions. At the same time solution equilibrium studies on metal-π interactions were reviewed [85] and a molecular orbital theoretical treatment of the electronic requirements of silver–aromatic hydrocarbon complexes was published in 1961 [86].

Soon after the discovery of the pleated sheet structure of $C_6H_6{\cdot}CuAlCl_4$ [87,88], an important X-ray analysis was carried out on the corresponding silver complex $C_6H_6{\cdot}AgAlCl_4$ [89]. The structure is made up of infinite sheets composed of $AlCl_4^-$ tetrahedral connected by Ag–Cl bonds with Ag–aromatic π interactions perpendicular to the sheet. From this point on, Amma and his co-workers undertook a systematic investigation on silver(I)–aromatic complexes. Salient crystal data of some examples are summarized in Table 1. Thus, the formation of Ag(I)–aromatic complexes has now been well-established by crystallographic determination of the structures of a number of the complexes in a wide range of stoichiometries and stereochemistries, including benzene [83,84,89], toluene [90], *m*-xylene [91], *o*-xylene [92], mesitylene [93], 1,4-benzodioxan [94], indene [95], cyclohexylbenzene [96,97], acenaphthene [98], acenaphthylene [98], naphthalene [99,100], anthracene [99,101], paracyclophane [74], $[2_3](1,4)$cyclophane [102,103], deltaphane [102], 9,10-diphenylanthracene [104], rubrene [104], and stilbene [105]. In all of these structures the aromatics are always found to be η^2/η^1 coordinated to the silver ions. The Ag–C bond distances range from 2.16(3) Å observed in mesitylene [93] to 2.921(9) Å observed in paracyclophane [74]; thus, exactly where a significant individual metal-π interaction begins and ends is a matter of debate. On the other hand, most of the compounds studied contain perchlorate ions coordinated in a variety of ways to the metal ions.

The search for new types of organosilver compounds involving aromatic hydrocarbon ligands is still active and an impressive number of silver(I) complexes with polycyclic aromatic compounds have been prepared and investigated. The main emphasis of these investigation has been on cation-π interactions and only recently have we and others simultaneously initiated a study of polycyclic aromatic compounds as a building-block in multilayer organometallic systems.

Table 1
Crystallographic data on silver(I)–aromatic derived compounds

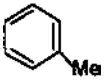
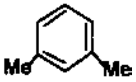
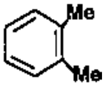
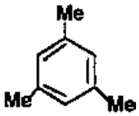
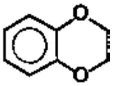
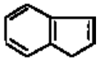
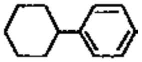
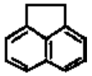
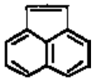
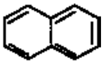
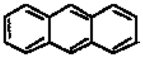
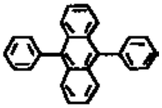
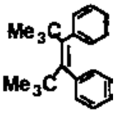
Aromatic	Formula	Ag–C bond distance (Å)	Comment	Ref.
	$(C_6H_6)AgClO_4$	2.496(6), 2.634(8)	Structure features an infinite –benzene–Ag–benzene–Ag– cationic chain	[83,84]
	$(C_6H_6)AgAlCl_4$	2.47(6), 2.57(6)	Ag-π interactions are perpendicular to the infinite sheets of AlCl$^-$	[89]
	$[AgOTeF_5$-$(C_6H_5Me)_2]_2$	2.443(5)–2.697(6)	Each teflate group bridges two Ag/(η^2-toluene)$_2$ moieties giving a dinuclear structure	[90]
	$(C_6H_4Me_2)_2$ $AgClO_4$	2.45(2)	Alternating arrangement of the Ag-*m*-xylene moieties and ClO_4^- ions gives a chain structure	[91]
	$(C_6H_4Me_2)_2$-$AgClO_4$	2.53(3), 2.57(3)	One oxygen atom bridging between two metal centers results in a dimeric structure	[92]
	$[Ag_4(C_6H_2Me_3)_4]$	2.16(3)–2.755(3)	Structure consists of center-symmetric tetrameric units	[93]
	$(C_8H_8O_2)_2$-$AgClO_4$	2.471(7), 2.572(7)	The $AgClO_4$ chain is sandwiched by two layers of benzodioxan molecules	[94]
	$(C_9H_8)AgClO_4$	2.36(2)–2.76(2)	The (indene–$AgClO_4$)$_2$ dimeric unit is in a half-open hinge arrangement	[95]
	$(C_6H_{11}C_6H_5)$-$AgClO_4$	2.48(1), 2.68(1)	Structure features alternating layers of $AgClO_4$ and the hydrocarbon	[96,97]

Table 1 (*Continued*)

Aromatic	Formula	Ag–C bond distance (Å)	Comment	Ref.
	$(C_{12}H_{10})AgClO_4$	2.44(1)–2.51(1)	The infinite chain of $AgClO_4$ is sandwiched by aromatic groups on either side	[98]
	$(C_{12}H_8)AgClO_4$		Structure features 1-D chains of alternating aromatic and perchlorate groups	[98]
	$(C_{10}H_8)(AgClO_4)_4\cdot 4H_2O$	2.61(1)	Each naphthalene is associated with four different hydrated silver ions in a sheet arrangement	[99,100]
	$(C_{14}H_{10})(AgClO_4)_4\cdot H_2O$	2.454(8)–2.560(8)	Alternate arrangement of the cross-hatched network of $AgClO_4/H_2O$ and anthracene	[99,101]
	$[Ag(GaCl_4)$ $(C_6H_4CH_2–CH_2)_2]$	2.434(7)–2.921(9)	$Ag(GaCl_4)$ group is sandwiched between two paracyclophane molecules	[74]
	$(C_{24}H_{24})AgX$, $X = CF_3SO_3^-$ or ClO_4^-	2.40(1)–2.69(1)	Sliver(I) ion is complexed exterior to the cyclophane moiety	[102,103]
	$(C_{30}H_{30})AgCF_3SO_3$	2.41–2.48	Ag(I) ion is symmetrically complexed exterior to the deltaphane moiety	[102]
	$(C_{26}H_{18})$-$AgClO_4(C_6H_6)_2$	2.49(1)–2.68(1)	Monomeric structure	[104]
	$(C_{42}H_{28})(AgClO_4)_4$-$(H_2O)_4$	2.40(1)–2.68(1)	Each aromatic ligand is π bonded to eight silver atoms	[104]
	$(C_{22}H_{28})AgCF_3SO_3$	2.510(5)–2.583(5)	Ag(I) ion is located between the cleft formed by the phenyl rings	[105]

3. A new approach to multilayer system–silver(I) aromatic complexes

As discussed above, much of the current interest in the extended polymeric metal sandwich compounds hinges on the design of new solids with structural diversity and desired physical and chemical properties. The recent report that electrochemical oxidation of a nine-ring polyaromatic hydrocarbon produced a new type of conductive ladder polymer with striking electrochromic properties presents an alternative route to layered organic polymers [10]. The possibility that polymers derived from transition metal complexes of polycyclic aromatic hydrocarbons might show interesting electrical and/or magnetic properties associated with electron delocalization and electronic cooperative interactions has motivated us to prepare various supramolecular silver(I) complexes with a diversity of topologies [104,106]. We have recently succeeded in constructing new types of air-stable metal sandwich organosilver(I) systems with polycyclic aromatic hydrocarbons, L^1–L^{20} (Fig. 1) based on cation-π interactions [107–109]. These aromatic ligands, unlike the aforementioned centrally π-bonded cyclophane or ferrocene multilayered systems where all the carbon atoms on the delocalized ligand plane participate in coordination, exhibit only η^2 coordination by peripheral carbon atoms; η^4 or η^6 coordination is never observed. Such ligands, combining good ligating properties and perfect planarity concurrently interacting with metal ions above and below rings, have great promise as an alternative approach to the effective self-assembly of high-nuclearity complexes in a multilayer fashion as shown in Fig. 2.

3.1. Double-layer structures

Treatment of a solution of $AgClO_4 \cdot H_2O$ in toluene with benzo[*ghi*]perylene (L^1) at room temperature (r.t.) gave a yellow solution. The solution was allowed to stand for 1 month from which the yellow plate single crystals of $[Ag(L^1)(ClO_4)]_4 \cdot C_6H_5Me$ (**26**) were isolated by diffusion into *n*-pentane [107]. The structure contains two types of cationic chains, Ag(1)/Ag(2) and Ag(3)/Ag(4). The basic unit of the well-defined portion of the structure is a dimeric double-layered $[Ag(L^1)(ClO_4)]_2$ species with the two silver atoms bridged by one perchlorate group. The metal–metal distance between Ag(1) and Ag(2) is 4.08 Å and that between Ag(3) and Ag(4) is 4.20 Å. Within each double-layer unit the two silver ions are sandwiched by two μ-di-η^2-benzo[*ghi*]perylene moieties with Ag–C distances ranging from 2.404(8) to 2.576(7) Å. Each double-layer unit is linked to its two nearby counterparts via the coordination of a second perchlorate group to each polyhedral metal ion. This gives a pair of independent infinite one-dimensional $AgClO_4$ chains sandwiched by the hydrocarbons (Fig. 3). These two chains are held together via extensive face-to-face interchain π–π interactions between the two adjacent aromatic planes [110,111]. The interplanar separations are within a 3.36–3.51 Å range, and the complexes are thus linked in a columnar fashion to generate a supramolecular architecture of an infinite two-dimensional sheet.

Reactions of $AgClO_4$ and 1-methylpyrene in toluene and benzene gave, respectively, a sandwich tetramer $[Ag(L^2)ClO_4]_4$ (**27**) and a double-layer polymer

$[Ag(L^2)ClO_4]_2 \cdot C_6H_6$ (**28**) [108]. In the former structure, the two crystallographically independent L^2 groups exhibit μ-η^2, η^2- and μ-η^2, η^1-coordination fashion, respectively, sandwiching two metal centers, notwithstanding the dihedral angle of 59° between the two aromatic planes (Fig. 4). Among four perchlorate ions in the formula, two interact terminally with Ag(2) and Ag(2′) atoms with short Ag(2)–O(8) distance of 2.345(7) Å, while the other two bridge two dinuclear core leading to a tetrameric structure. The molecular structure of **28** is a reminiscence of **26** in

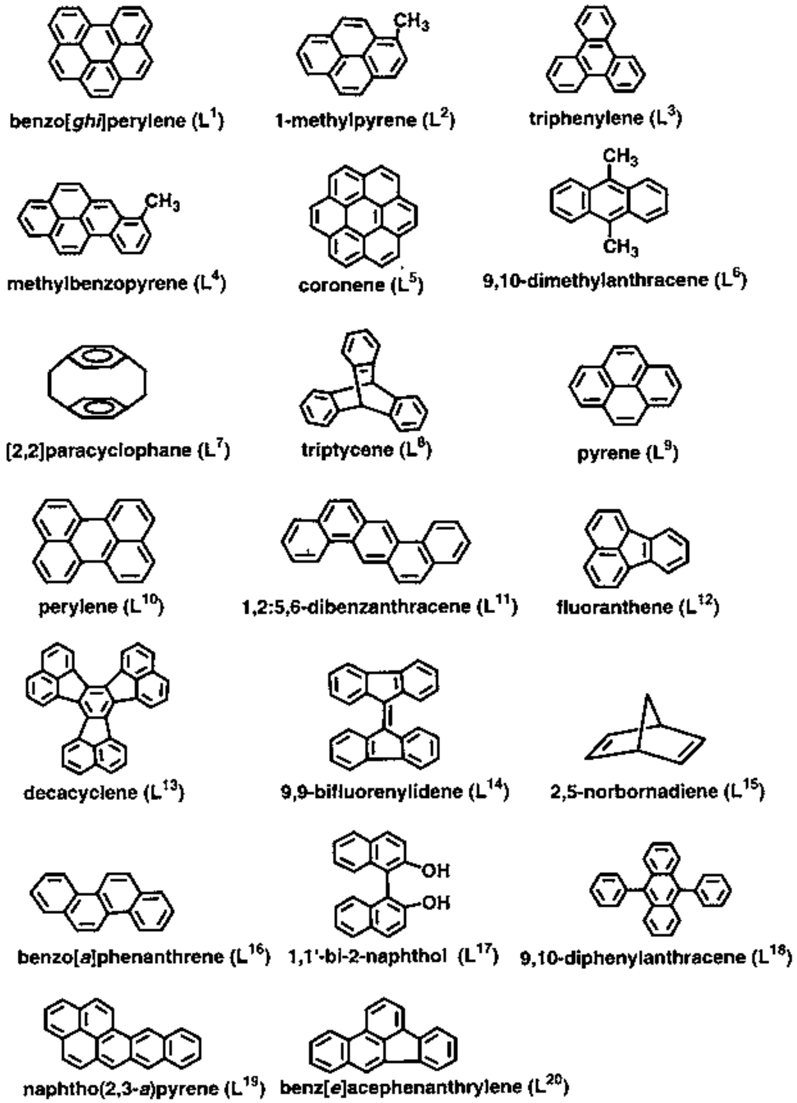


Fig. 1. List of polycyclic aromatic ligands studied in this work.

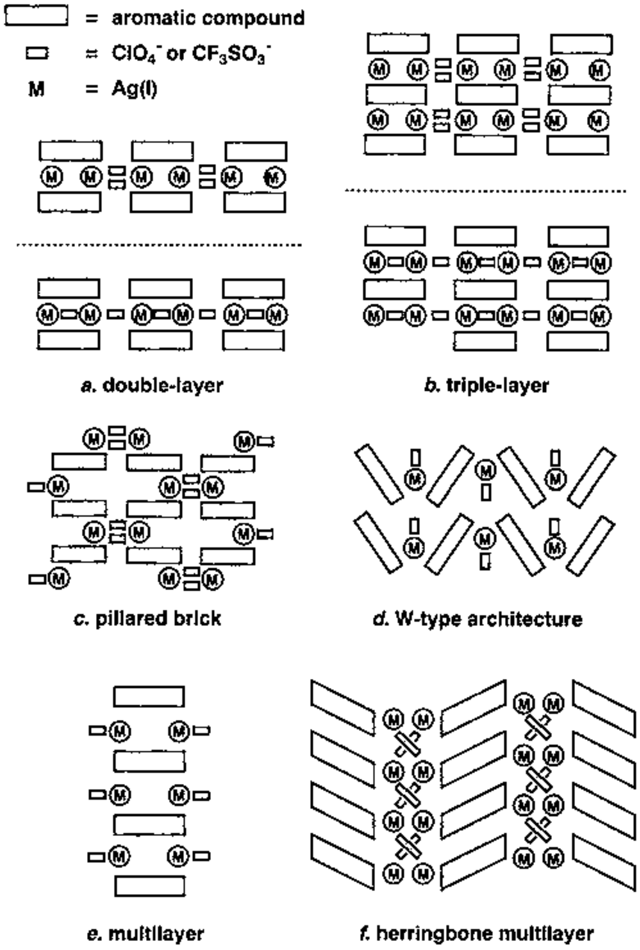


Fig. 2. Different frameworks observed in sandwiched silver(I) aromatic systems.

a sense that this structure also contains a dimeric double-layered unit with two silver atoms bridged by one perchlorate group (Fig. 5). The solvate benzene molecules occupy the void space between the chains and are not involved in intermolecular contacts. In contrast to the interchain π–π interactions observed in **26**, there is no such interaction found in **28** as the closest C···C contact between the adjacent chains is 8.22 Å.

Another 1:1 metal:ligand complex involving L^3 has been found in metallotriphenylenophane complex **29**, synthesized by the reaction of $AgClO_4$ with an equimolar amount of triphenylene in *p*-xylene [108]. The structure contains a dinuclear core double-bridged by two perchlorate ions with Ag···Ag separation of 4.06 Å. The tetrahedral coordination environment of the metal center is completed by interaction with two symmetry-related L^3 groups with comparatively short Ag–C

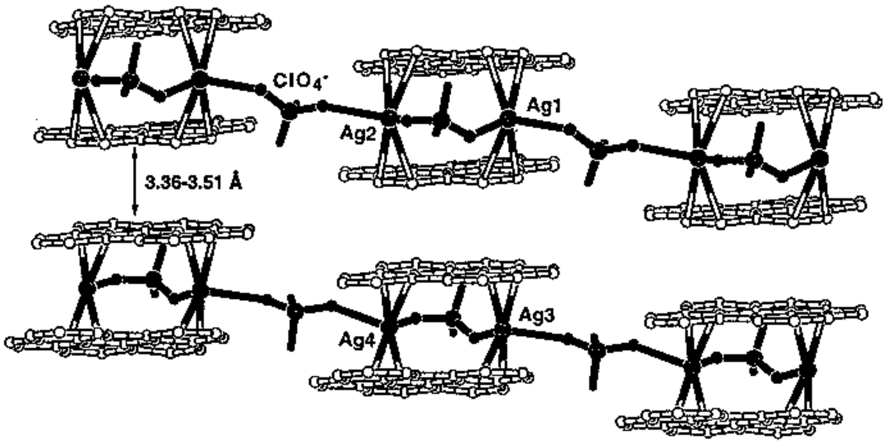


Fig. 3. Double-layer polymeric structure of $[Ag(L^1)(ClO_4)]_4 \cdot (C_6H_5Me)$ (**26**).

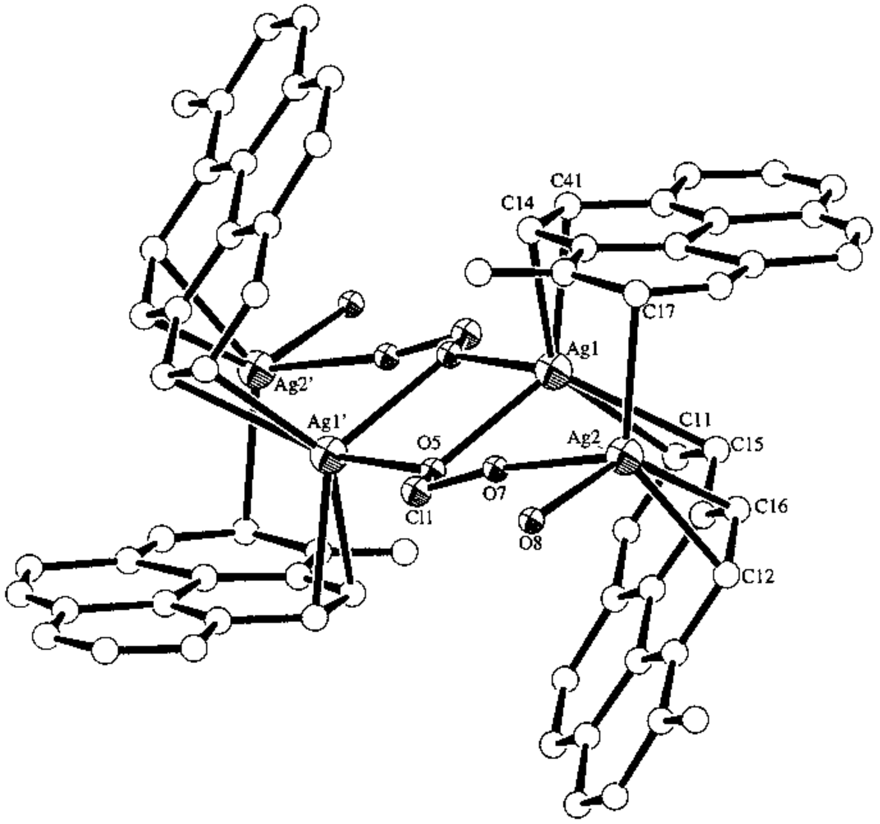


Fig. 4. Sandwich tetrameric structure of $[Ag(L^2)ClO_4]_4$ (**27**). The non-coordinating oxygen atoms of the perchlorate ions are omitted.

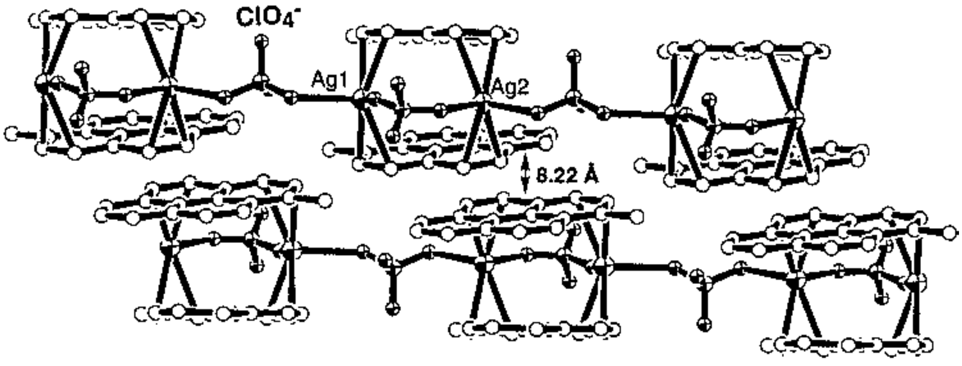


Fig. 5. Double-layer polymeric structure of $[Ag(L^2)ClO_4]_2 \cdot C_6H_6$ (**28**).

bond distances of 2.504(3) and 2.387(3) Å for C(1) and C(2), respectively. Each μ-di-η^2 aromatic ligand interacts with two metal ions generating a linear metallo-triphenylenophane polymeric chain as shown in Fig. 6. Between chains there exists aromatic interaction with interplane separation varying from 3.53 to 3.67 Å. Such interaction causes bent conformation of the aromatic plane outward by 0.36 Å defined by the average distance of the two coordinated carbon atoms to the central six-membered ring.

Slipped double-layered structure has been observed in silver(I) complex of the pyrene derivatized ligand methylbenzopyrene (L^4), $[Ag_2(L^4)(ClO_4)_2(C_6H_5Me)_{0.5}]$ (**30**), which was prepared by the direct reaction of $AgClO_4$ and L^4 in toluene [108]. Structure determination revealed that the aromatic molecule asymmetrically interacts in μ-tri-η^2 fashion with three metal centers forming an infinite slipped double-layer chain as shown in Fig. 7. The two nearby chains are connected together by symmetric π-interactions of the solvate toluene molecule between two Ag(1) atoms with Ag(1)–C(23) and Ag(1)–C(24) bond distances of 2.588(8) and

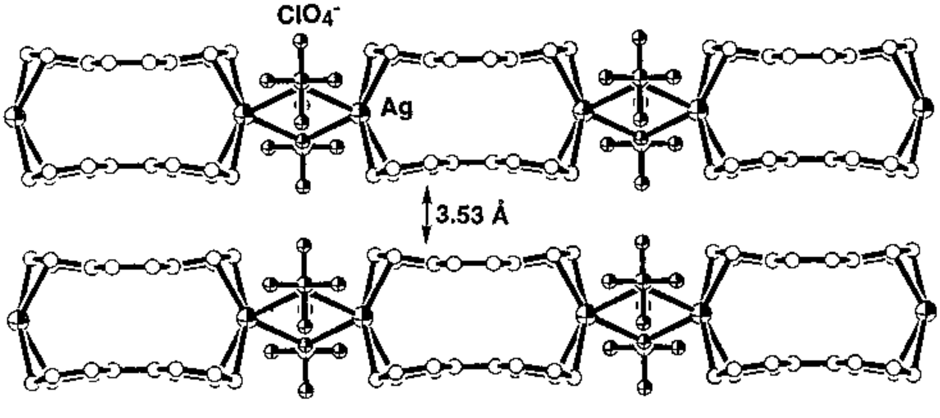


Fig. 6. Double-layer polymeric structure of $[Ag(L^3)ClO_4]$ (**29**).

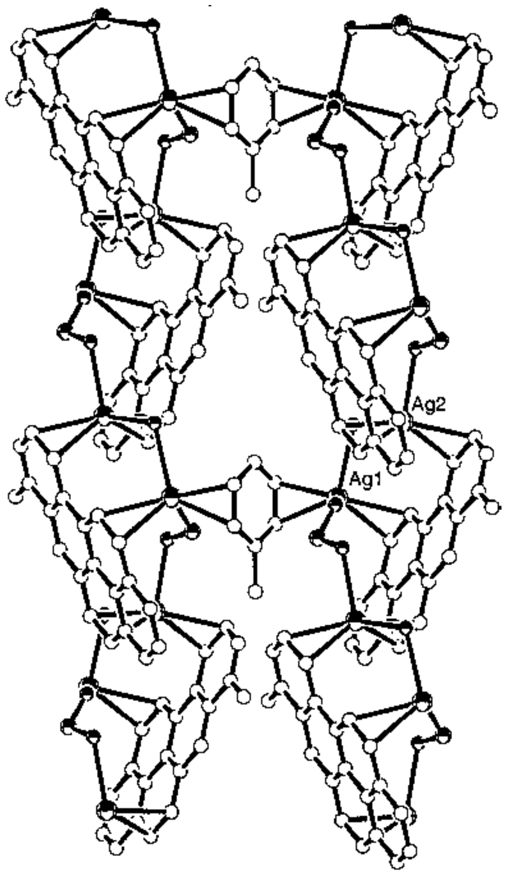


Fig. 7. Slipped double-layer polymeric structure in $[Ag_2(L^4)(ClO_4)_2(C_6H_5Me)_{0.5}]$ (**30**). The non-coordinating oxygen atoms of the perchlorate ions are omitted.

2.472(8) Å, respectively. The coordination of a toluene molecule to a silver(I) ion is reported in a dinuclear complex $[Ag(OTeF_5(C_6H_5Me)_2]_2$ where each η^2-C_6H_5Me group interacts with one metal ion [90]. The unique bridging function of the toluene molecule in **30** might be the major effect for the stability of the compound.

3.2. Triple-layer structures

These complexes are less common than double-layer complexes. One such example occurs in coronene complex, $[Ag_4(L^5)_3(ClO_4)_4]$ (**31**). This compound was prepared by diffusion of *n*-hexane into a mixed solution of coronene and $AgClO_4$ in benzene [104]. The structure exists in the solid state as an aromatic-linked polymer of dimers. Within the dimer, there are two independent Ag(I) ions coupled by one bridging perchlorate with Ag(1)···Ag(2) separation of 3.9798(5) Å. The two dimeric subunits are bridged by the second perchlorate ion with Ag–O bond

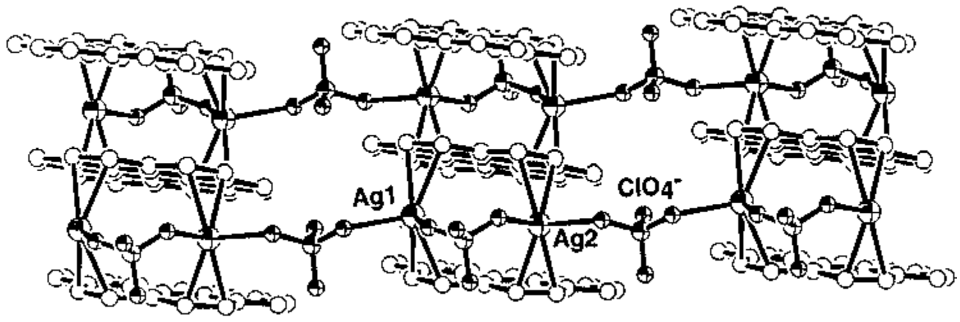


Fig. 8. Triple-layer polymeric structure of $[Ag_4(L^5)_3(ClO_4)_4]$ (**31**).

distances of 2.456(3) Å for Ag(1) and 2.483(3) Å for Ag(2). Each triple-layered unit consists of a centrosymmetric middle metallomacrocycle, an outer metallomacrocycle and its centrosymmetric pair. Each coronene moiety in the middle layer exhibits a tetra-η^2-coordination, bridging sequentially four metal centers and resulting in a unique triple-layered polymeric structure shown in Fig. 8. Packing diagram shows that the compound involves both intramolecular and intermolecular $\pi-\pi$ interactions, which constitutes a columnar aromatic stacks. The total result is that the strong intermolecular interactions cause the two outer coronene planes in the triple-layered unit severely bent outwards by 0.25 Å.

Reaction of $AgClO_4$ with an equimolar ratio of 9,10-dimethylanthracene (L^6) in *p*-xylene afforded yellow single crystals of $[Ag_2(L^6)(ClO_4)_2(p\text{-xylene})_2]$. The molecular structure of this compound in the crystalline state features an infinite chain arrangement of silver atoms linked alternately by the aromatics and perchlorate ions [108]. The silver atom interacts with both 9,10-dimethylanthracene and perchlorate groups, and in particular with the latter in a manner which leads to bridging about a crystallographic inversion center, so that a dinuclear core, Ag_2O_2, is formed with two perchlorate anions symmetrically bridging between the two metal centers at Ag–O(2) of 2.465(9) Å. Each L^6 group is acting as a bridge between the two dinuclear units interacting with two symmetry-related metal ions by a μ-di-η^2-coordination fashion. The pseudotetrahedral coordination sphere around the silver atom is completed by further coordination of one crystallized solvate *p*-xylene molecule. This results in a one-dimensional array of silver atoms sandwiched by 9,10-dimethylanthracene and *p*-xylene molecules propagating parallel to the *b* axis.

3.3. Pillared brick frameworks

Colorless brick single crystals of $[Ag(L^7)(ClO_4)]$ were isolated from the reaction of $AgClO_4$ and [2,2]paracyclophane in benzene [107]. The structure contains a dinuclear core, Ag_2O_2, in which each silver(I) ion is tetrahedrally coordinated to one oxygen atom of the two symmetry related perchlorate anions and sandwiched by two distinct paracyclophane ligands. Each paracyclophane group is acting as a linkage between the two dinuclear units in a μ-di-η^2-coordination fashion. The two paracyclophanes bonded to the same metal ion face up to each other, not stacked one above the other but slightly slipped, and are associated together by weak π–π interactions with an intermolecular separation ranging from 3.47 to 4.20 Å. A two-dimensional pillared brick arrangement of the aromatic sandwiched metal units results which spreads out along the diagonal axis of the *ac* plane. The structure differs significantly from that of [2,2]paracyclophane(tetrachlorogallato)silver, $[AgL^6(GaCl_4)]$, where the two-dimensional network is based on chains of metal ions cross linked by μ-η^2/η^3 hydrocarbons and μ-$GaCl_4^-$ anions [74].

The reaction of $AgClO_4$ with triptycene (L^8) in benzene followed by diffusion of the mixed solution into *n*-pentane has been found to give colorless brick crystals of $[Ag_3(L^8)_3(ClO_4)_3](C_6H_6)_2$ (**32**) [108]. The structure is comprised of alternate pillared brick arrangement of Ag atoms and L^8 groups as shown in Fig. 9 where the perchlorate ions act only as spacers, rather than as linkages or bridges between metal centers as usually observed, to fulfill the tetrahedral coordination environment of the Ag(I) ions.

3.4. W-type architectures

Among the silver(I) complexes of polycyclic aromatic compounds we have observed a unique type of structures with the aromatics sandwiching the metal centers in a zigzag manner that we named as W-type architectures [106]. The preparations and crystal structures of two new silver(I) complexes with pyrene (L^9) and perylene (L^{10}), $[Ag_2(L^9)(ClO_4)_2]$ (**33**) and $[Ag_2(L^{10})(ClO_4)_2]$ (**34**), have been reported [106]. Each pyrene molecule in the former complex exhibits tetra-η^2-coordination, bridging sequentially four metal centers and resulting in a one-dimensional polymeric W-type sandwich of alternating aromatic and silver(I) perchlorate groups running along the *b* axis as shown in Fig. 10. In contrast, the terminal bonding of the perchlorate ion does not occur in **34**, thus, the structure consists of a two-dimensional framework of the metal ions bridged by the bidentate counterions and the tetra-η^2-arene groups. The W-type sandwich sheets of alternating perylene and silver(I) perchlorate are strongly interacted by the superposed intersheet aromatic π–π stackings at an average distance of 3.31 Å (Fig. 11). The unique structural feature of these two compounds is an unusual tetra-η^2-coordination for the highly-symmetric polycyclic aromatic compounds. In addition, both complexes display typical radical cation ESR spectra upon light irradiation.

Addition of $AgClO_4$ to the toluene solution containing 1,2:5,6-dibenzanthracene (L^{11}) gave yellow plate single crystals of $[Ag_2(L^{11})(ClO_4)_2]$. This complex crystallized in the orthorhombic space group rather than in monoclinic space group as observed in **33** or **34**; however, it shares the same structural features [108]. As in **33**, there exists a dinuclear unit made up by two crystallographically independent silver(I) ions. Here again, as each aromatic ligand bridges sequentially four metal centers and the Ag(2) ion is bonded to a terminally coordinating perchlorate group, a one-dimensional polymeric W-type sandwich of alternating aromatic and silver(I) perchlorate groups is resulted. There also exist aromatic π–π stacking interactions

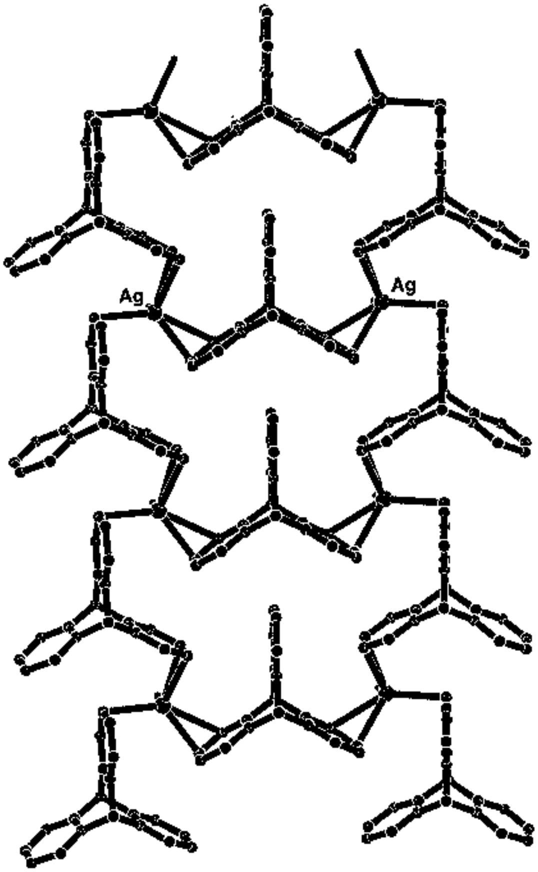


Fig. 9. Pillared polymeric structure of $[Ag_3(L^8)_3(ClO_4)_3](C_6H_6)_2$ (**32**) viewed down the *c* axis where perchlorate ions are omitted.

between the adjacent chains as observed in **34**, with the interplanar distances ranging from 3.57 to 4.0 Å.

Another example of a silver(I) complex with W-type architecture has been found in $[Ag_3(L^{12})_2(ClO_4)_3]$, which was synthesized by the reaction of $AgClO_4$ and fluoranthene (L^{12}) in toluene [107]. The crystallographic studies revealed that the complex exists in the solid state as a two-dimensional polymer of silver(I) sandwiched by the aromatic groups. The crystallographically independent Ag(1) and Ag(2) atoms lie in a mirror plane along with two oxygens of each perchlorate group. Each aromatic group asymmetrically interacts in a μ-tri-η^2 fashion with three metal ions below and above the ligand plane, linking two $-Ag-O_2ClO_2-Ag-$ chains. The overall result of this arrangement is that the $AgClO_4$ chains lie in sheets with aromatics on either side such that the packing consists of a sequence of sheets: ···aromatic···ionic···aromatic··· in a W-type fashion. The complex is unusual in a sense that all the fluoranthene molecules are arranged alternately in two different

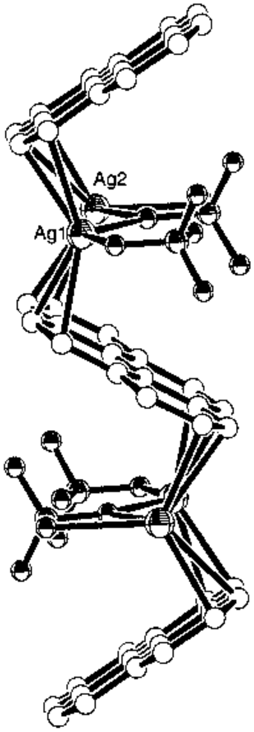


Fig. 10. W-type sandwich arrangement of pyrene and silver(I) perchlorate groups in $[Ag_2(L^9)(ClO_4)_2]$ (**33**).

orientations in order to give an overall equal number of π interactions (three) on both sides of the plane for every two neighboring aromatics in spite of asymmetric bonding of each individual group.

3.5. Multilayer structures

The first multilayer silver(I) complex of the polycyclic compound we have obtained involves decacyclene (L^{13}), $[Ag_2(L^{13})(ClO_4)_2(C_6H_6)]$ (**35**), which was synthesized from the reaction of $AgClO_4$ and L^{13} in a mixed solution of benzene and nitrobenzene [107]. Since decacyclene is sparingly soluble in benzene or toluene, hot nitrobenzene was employed in the preparation to assist dissolution of the aromatic. The complex exists in the solid state as an aromatic-linked polymeric multidecker lying approximately on the *ab* plane as shown in Fig. 12. The multilayer structure is formed by the cationic $[Ag_2(L^{13})]$ building blocks while the ClO_4^- anions and solvate benzene molecules reside on the side of the parallel layers. The decacyclene molecules are arranged alternately in two orientations and adopt staggered conformation within a pair. Each aromatic ligand exhibits a μ-tetra-η^2-coordination bound to four metal centers with two on each side of the ring. Remarkably, in

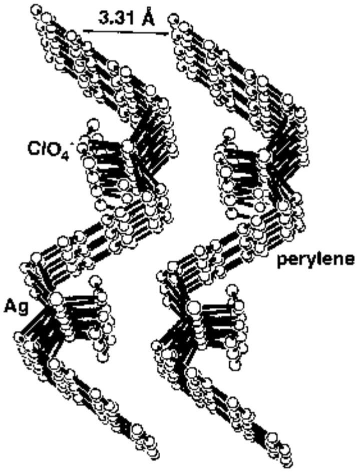


Fig. 11. W-type sandwich frameworks in $[Ag_2(L^{10})(ClO_4)_2]$ (**34**). The non-coordinating oxygen atoms of the perchlorate ions are omitted.

order to achieve such a structure, it is necessary for the highly symmetric decacyclene (D_{3h}) to be asymmetrically coordinated to four Ag(I) ions at irregular positions. In addition, the deviation from ideal planar geometry is most readily seen by inspecting the dihedral angles between the acenaphthene plane and the central benzene ring. Although each of the three acenaphthene moieties of the decacyclene group is essentially planar, it deviates from the mean plane of the central benzene ring by 7.25–13.73°.

A new type of stable polymeric chain compound involving polycyclic aromatic and involving a multilayer structure analogous to that observed in **35** has been prepared in high yield by the diffusion of *p*-xylene solution containing $AgClO_4$ and 9,9-bifluorenylidene (L^{14}) into *n*-pentane [108]. The colorless needle crystals with formula $[Ag(L^{14})(ClO_4)]\cdot(C_6H_4Me_2)_{0.5}$ (**36**) also contains a dinuclear core with Ag···Ag separation of 4.33 Å double-bridged by two perchlorate ions. Each μ-di-η^2 L^{14} group bridges between two dinuclear units leading to a two-dimensional network of metal ions linked as shown in Fig. 13.

Reaction of $AgClO_4$ with 2,5-norbornadiene (L^{15}) in THF has been found to give colorless brick crystals of $[Ag(L^{15})(ClO_4)]$ (**37**) [108]. Alternate arrangement of Ag atoms and the ligand groups by metal-π interactions results in an infinite chain structure. The counter anions act as linkages between chains. The rhombic Ag_2O_2 core thus formed, constitutes an unusual stair-like multilayer structure as illustrated in Fig. 14.

A slipped multilayer structure has been observed in $[Ag_3(L^{16})(ClO_4)_3(H_2O)_2]$ (**38**) which was prepared by the reaction of $AgClO_4$ and benzo[*a*]phenanthrene (L^{16}) in benzene [108]. The structure contains a trinuclear unit comprised of three crystallographically independent metal centers, in which each metal ion interacts with one aromatic group. In addition, the Ag(1) atom coordinates with two perchlorate ions

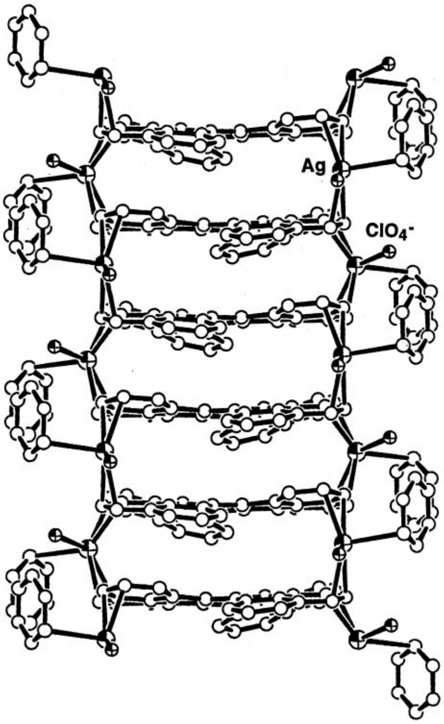


Fig. 12. Multilayer structure of $[Ag_2(L^{13})(ClO_4)_2(C_6H_6)]$ (**35**). The non-coordinating oxygen atoms of the perchlorate ions are omitted.

(one terminal and one bridging), the Ag(2) with terminal perchlorate group and one bridging water molecule, whereas the Ag(3) coordinates with one bridging perchlorate ion and one terminal water molecule. The aromatic ligand involves two different coordination modes, one displaying a μ-di-η^2 coordination fashion bridging two metal ions and the other exhibiting a μ-tetra-η^2 coordination fashion linking four metal centers. The overall result of such connection is a slipped multilayer structure as shown in Fig. 15. The IR spectrum of the compound confirms that bridging water ligands are retained. Although the presence of coordinating water molecules in silver(I) complexes is well-established [112], bridging water ligands are much less commonly encountered thus far. Owing to the presence of both terminal bonding and bridging water ligands the structure features presence of an extensive hydrogen bonding network.

A multilayer structure involving channel networks has been found in $[Ag_2(L^{17})(ClO_4)_2(C_6H_6)_2]$ (**39**), where L^{17} = 1,1′-bi-2-naphthol [108]. The reaction of $AgClO_4$ with L^{17} in benzene yielded colorless brick crystals at r.t. The tetrahedral coordination geometry about the metal center comprises one ligand group, one benzene molecule and two ClO_4^- ions. Each μ-di-η^2 L^{17} moiety is interacting with two metal atoms affording extending 2-D network containing microchannels in

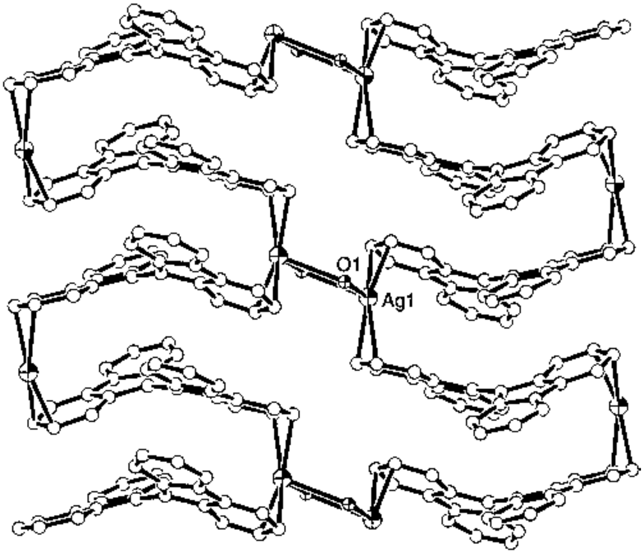


Fig. 13. Multilayer structure of $[Ag(L^{14})(ClO_4)]\cdot(C_6H_4Me_2)_{0.5}$ (**36**) viewed down the *a* axis. The non-coordinating oxygen atoms of the perchlorate ions are omitted.

which Ag atoms are rallied along the wall and each bridging perchlorate ion interacts with two Ag atoms belonging to two different layers (Fig. 16). The interplane distance between the two aromatic molecules is 8.76 Å. A similar reaction carried out between $AgCF_3SO_3$ and 9,10-diphenylanthracene (L^{18}) in benzene gave pale yellow brick single crystals of $[Ag_2(L^{18})_{0.5}(CF_3SO_3)_2(C_6H_6)_{0.5}]$, whose molecular structure also consists of microporous frameworks constructed on two-dimensional arrangement of metal ions bridged by both aromatic ligands and the triflate ions [108]. Again, each silver atom involves a tetrahedral coordination geometry comprising one C–C moiety from L^{18}, one oxygen atom of two distinct triflate ions. The fourth coordination site is occupied by the bridging benzene molecule between the 2-D networks.

A herringbone multilayer structure has been found in the silver(I) complex of naphtho(2,3-*a*)pyrene (L^{19}), $[Ag_2(L^{19})(CF_3SO_3)_2]$ (**40**), synthesized by the treatment of $AgCF_3SO_3$ solution in toluene and L^{19} in THF [109]. Although the preparation does not involve elaborate procedures, patience is required as growth of single crystals suitable for X-ray analysis takes about 6 months. Once isolated, however, the complex is thermally stable at ambient temperature. The structure consists of a disilver unit double-bridged by two triflate anions, and features unusual herringbone multilayer arrangement of aromatic planes constructed on terminal interactions with two dinuclear cores as shown in Fig. 17. The interplane distances between the aromatic molecules range from 3.42 to 3.56 Å suggesting that strong $\pi-\pi$ interactions are present. The multilayer arrangement of the aromatic hydrocarbons hinges upon the unusual tridentate structure of $CF_3SO_3^-$ ion in which each trifluoromethanesulfonate oxygen is bound to one metal center with reasonable

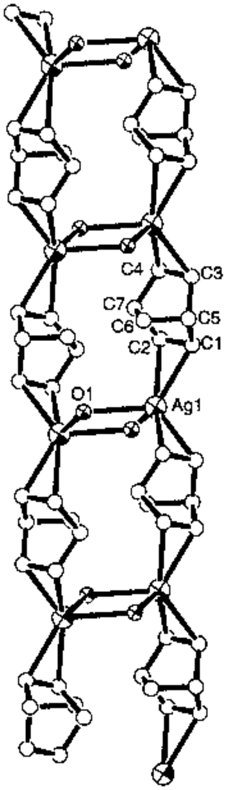


Fig. 14. Stair-like multilayer structure of $[Ag(L^{15})(ClO_4)]$ (**37**) viewed down the *b* axis. The non-coordinating oxygen atoms of the perchlorate ions are omitted.

Ag–O bond distances (2.39–2.44 Å). This is the first case for triflate anion bridging three silver(I) ions [113].

An alternate multilayer structure has been identified in benz[*e*]acephenanthrylene (L^{20}) coordinated complex $[Ag_7(L^{20})_5(ClO_4)_7]$ (**41**) which was prepared by the reaction of $AgClO_4$ and L^{20} in toluene [109]. The structure consists of two crystallographically different types of aromatic ligands that constitute two alternate infinite multilayers of aromatic hydrocarbons running along the *c* axis. One layer involves μ-di-η^2 hydrocarbons interacting with two metal ions above and below the aromatic plane while the other involves μ-tri-η^2 hydrocarbons interacting with three metal centers on same side of the aromatic plane. A dihedral angle of 48.8° has been found between these two layers, although the distortion of the aromatic ligand from planarity in either case is little. Close insight into the aromatic groups on the tridentate aromatic layer revealed two different orientations of the asymmetric ligand groups alternately appeared in spite of their symmetry related nature (Fig. 18).

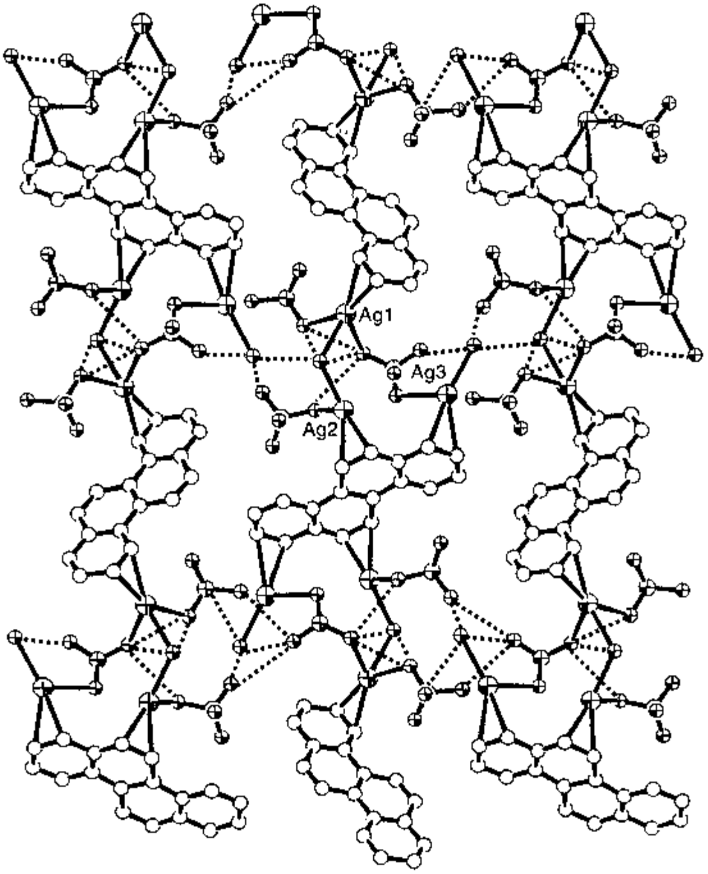


Fig. 15. Slipped multilayer structure of [$Ag_3(L^{16})(ClO_4)_3(H_2O)_2$] (**38**). Hydrogen bonds are shown in dotted lines.

4. Synthetic considerations and physicochemical properties

Characterization of the above silver(I) complexes of polycyclic aromatic compounds containing sandwich structures was mainly based on X-ray diffraction studies. Thus, in order to obtain diffraction-quality single crystals for X-ray analysis it is necessary to have versatile methods available for the facile, high-yield, multimilligram preparation of the complex. There are no general synthetic routes for preparing the solid materials of predictable features. All crystallization of the silver complexes were carried out in the dark at r.t. Apart from the conventional crystallization of the products by slow evaporation of the reaction solution in different ways, we have extensively employed the liquid diffusion method in our syntheses, which has been proved to be an exclusively effective method for the multimilligram preparations. Very often the desired product cannot be isolated in a few months time because of weak coordination interactions involved. To curb this

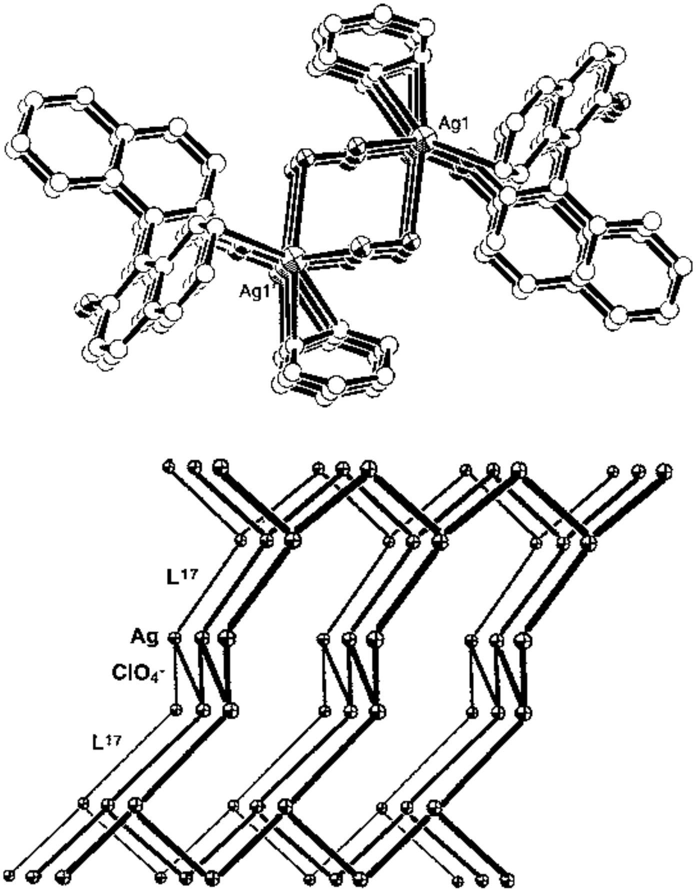


Fig. 16. Multilayer structure of $[Ag_2(L^{17})(ClO_4)_2(C_6H_6)_2]$ (**39**) generates micropores. The non-coordinating oxygen atoms of the perchlorate ions are omitted.

problem we have designed a special reaction vessel with a rubber stopper for slow absorption of the solvent and gas diffusion purposes.

The synthesis of these organometallic species can be thought of as a type of dynamic combinatorial chemistry, achieved by combining the appropriate metal salt and an aromatic ligand in a suitable solvent. The metal centers in these coordination polymers may be thought of as the keys to assembling and templating the aromatic groups. Although copper(I) is also a preferred ligand linker because of its coordination flexibility, our efforts to synthesize the corresponding copper(I) complexes containing polycyclic aromatic compounds have been unsuccessful due to the sensitivity of Cu(I) species towards moisture and air oxidation.

The results gathered thus far, indicate that both the relative concentrations of reactants and the nature of the counteranions present in solution can often be used to influence the structure of the product. Among the silver(I) salts in hand, both the

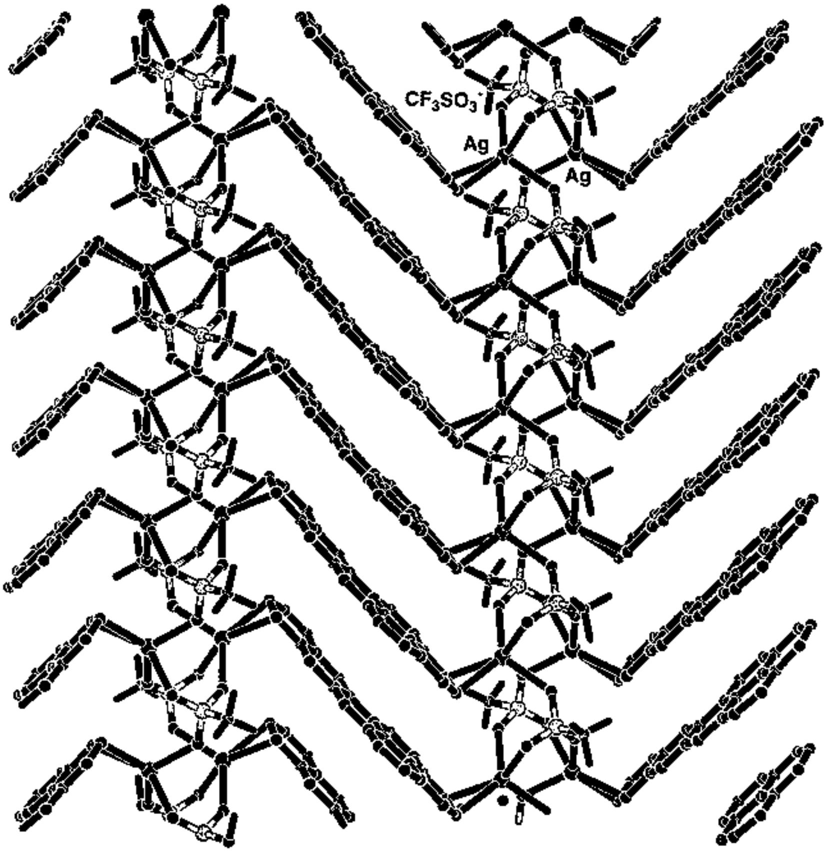


Fig. 17. Herringbone multilayer structure in $[Ag_2(L^{19})(CF_3SO_3)_2]$ (**40**).

nitrate and acetate have low solubility in organic solvents such as benzene, toluene, and xylene. All the compounds we have studied contain perchlorate or triflate ions coordinated in a variety of ways to the silver ions, such as terminal bonding to one metal, or bridging two metal centers by one or two oxygen atoms of the ion. The tridentate structure of $CF_3SO_3^-$ ion involving each trifluoromethanesulfonate oxygen bound to one metal center in the silver(I) complex of naphtho(2,3-*a*)pyrene, in particular, generates an overall herringbone multilayer structure of **40**. It seems that large size coordinating oxyanions such as ClO_4^- and $CF_3SO_3^-$ play a crucial role in stabilizing the silver(I) π complexes. Due to the large size of the polycyclic aromatics, the unique functions of the counteranions as spacers and linkages between aromatic π-sandwiched metal units seem to be even more profound in the stabilization of the complex and in construction of the extended multilayered systems.

Coordination of an aromatic ligand to metal ions can in principle be achieved via a stoichiometric reaction, but on several occasions excess of metal ions has to be

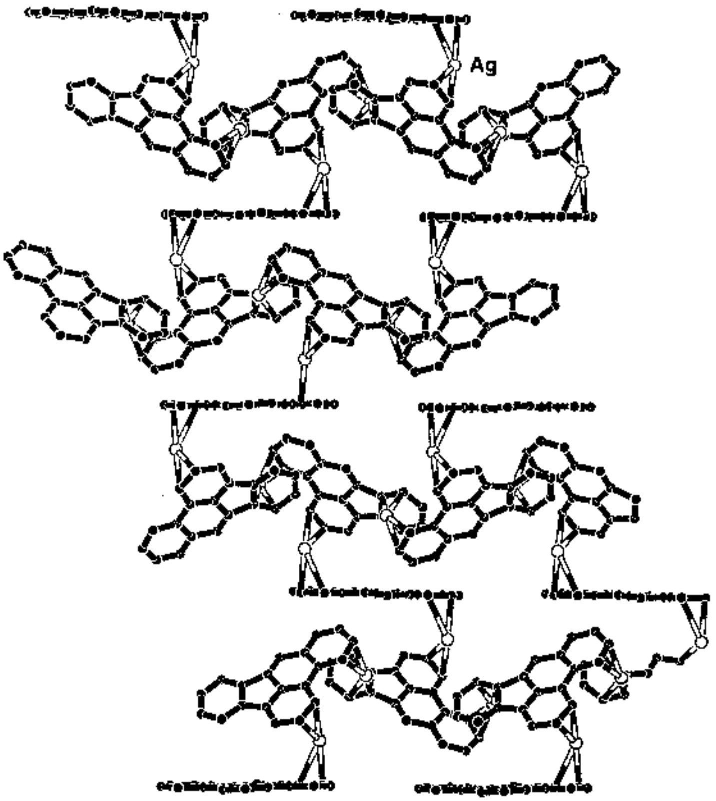


Fig. 18. Alternate multilayer structure in $[Ag_7(L^{20})_5(ClO_4)_7]$ (**41**) viewed down the *b* axis. The perchlorate ions are omitted.

implemented in order to obtain desired products. For example, during the preparation of multilayer complexes **35**, **40** and **41** a two- to three-fold excess of stoichiometric amounts of silver salts is employed. The reason attributable to this is two-fold: (i) as shown in Table 1, the solvents benzene and toluene form silver(I) complexes, which consume partial silver(I) ions; and (ii) when a complex formed in solution is 'incongruently saturating', its crystal cannot be obtained via a stoichiometric reaction.

Apart from metal ions, the relative concentrations of reactants and nature of the anion, the final structures and frameworks of these aromatic sandwich compounds may well depend on a variety of factors such as solvents. The reactivity of $AgClO_4$ with the aromatic hydrocarbons was systematically examined in solvents with different polarity. In general, we have found both benzene and toluene to be the most favorable solvents to isolate the compounds in solution in the majority of cases. Very often we have employed mixed solvent such as nitrobenzene to assist dissolution of the aromatic compounds and *n*-pentane or *n*-hexane as diffusion solvents. Similar reactions performed in other solvents such as methanol, acetone and diethyl ether lead to no evidence for formation of an isolable complex, although the variation of the ^{1}H NMR spectra line widths in these solvents suggests that some interaction may occur. For example, silver(I) perchlorate does react with decacyclene in tetrahydrofuran, but the crystals isolated turned out to be a discrete monomer containing coordinated THF molecules rather than a multilayer complex of **35**. These facts indicate that polymeric aromatic structures containing silver(I) ions are solvent dependent.

In addition to exploring the formation and structural characterization of a range of newly created silver(I) complexes of polycyclic aromatic compounds, work in this area also focused on their properties. Aromatic hydrocarbons in their transition metal complexes can form charge transfer species or even organic radicals depending on the degree of charge transfer in the ground state [2,114,115]. The electronic structures of radicals were studied by electron spin resonance spectroscopy. The aromatic hydrocarbon radicals have been reported in W-type sandwich silver(I) complexes with pyrene **33**, perylene **34**, and fluoranthene. Although no strong ESR signal was observed for each complex at r.t., their light irradiated samples turned black and showed a characteristic g value of 2.003 for hydrocarbon radicals.

Both the double-layer complex **26** and the multilayer complex **35** even exhibit a well-resolved intense resonance with $g = 2.003$ and 2.0047, respectively, without irradiation [107]. However, the formation of Ag(0) or Ag(II) species accompanied by the electron transfer was not observed because of the low sensitivity. The spin densities for the organic radicals, estimated from the comparison with the DPPH (diphenylpicrylhydrazyl) standard, were low, being 0.004% for **26** and 0.0072% for **35**. The UV–vis spectra of these two compounds in solution exhibit one major and one or more small bands, with the dominant band having maximum absorbance between 400 and 420 nm. This falls within the range of maxima in the spectra of donor–acceptor complexes of the highly conjugated aromatic molecules pyrene and perylene [116]. In addition, the high extinction coefficients are strongly suggestive of charge-transfer excitations.

The redox behavior of compounds **26**, **35**, and **40** was probed by solution electrochemistry [107–109]. Solutions of up to ca. 1 mM were prepared in THF and proved adequate for electrochemical measurements. Each voltammogram shows two distinct redox processes, related respectively, to one aromatic-based and one metal-based electrochemical reactions. In support of this, the CV of the free ligands were recorded in the same conditions which showed only one redox process in each case in the region of -1.35 to -0.24 V. Each of the reduction peaks and oxidation peaks was accompanied by a corresponding oxidation peak and reduction peak. The waves generally showed poor electrochemical reversibility with anodic to cathodic peak potential separated widely.

The electrical conductivity of double- and multilayer complexes was measured by a two-probe technique employing gold or silver paste coated probes. Generally these complexes are non-conducting or low-conducting at r.t. However, the compounds showed fluctuation of resistance in the trend of decrease with time at r.t. The complexes are thus noted as novel examples of current-induced conducting species.

5. Conclusions

An upsurge of interest, created by the elucidation of the ferrocene sandwich structure in the early 1950s, resulted in an intensive study during the following 4–5 decades in the synthesis and properties of multilayer organometallic compounds. A new dimension has been opened in the field of sandwich organometallic chemistry because of the successful syntheses of a variety of thermally stable metal sandwich complexes comprising aromatic hydrocarbons. The purpose of this review is to demonstrate that polycyclic aromatic compounds are a group of particularly useful ligands capable of holding two or more metal ions in close proximity with high relevance for multilayered organometallic systems. We have shown that the propensity of $AgClO_4 \cdot (AgCF_3SO_3)$ to form adducts with a variety of aromatic compounds appears to be unmatched by any other transition metal salt. As an important component in the sandwich system, each aromatic group in most cases interacts with two or four metal ions equally divided below and above the ring. For the highly symmetric aromatics such as pyrene, perylene, and coronene, the metal-π interaction always takes place at symmetric positions. The carbon–carbon atoms with the shortest and the second shortest C–C bonds are most vulnerable to the cation attacking. In contrast, the π interaction occurs at unsymmetric positions for less symmetric aromatics such as fluoranthene and benzo[*ghi*]perylene. The symmetry of the aromatic compounds not only affects the coordination positions, but also decides the final structure of the product. In particular, with the use of highly symmetric ligands with potential for aromatic stackings, intramolecular and intermolecular interactions seems to be especially advantageous since these lead to a corresponding complex with a well-organized multilayered structure. Furthermore, the nature of the counteranions, acting either as spacers or linkages between metal-π interacting networks, plays an important role in the aggregate. This process is exemplified by all the structures presented herein.

While a multitude of new structural types have been characterized and quite a lot of interesting and unhoped-for results attained, the process of formation and the information leading to future rational syntheses remain enigmatic. Moreover, the requirements for the desired physical and chemical properties are, as yet, hardly well-defined. The work has not only broadened our insight into the field but has also clearly pointed to the need for more penetrating physicochemical investigations on their formation and a much clearer understanding of the nature of bond(s) involved therein. We hope that this review in bringing the most important structural elements to light, will be of use in stimulating further research in this area.

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