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Coordination chemistry in and of sulfur dioxide☆

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☆ Dedicated to Professor R.J. Gillespie on the occasion of his 75th birthday.

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Abstract

The review describes the syntheses of metal salts with weakly interacting anions ($AlCl_4^-$, AsF_6^-, SbF_6^-) in the poorly coordinating solvent SO_2. The metal centers in the resulting complexes might be considered as almost 'naked', their unusual coordination chemistry is discussed.

Keywords: Weakly coordinating anions; Sulfur dioxide complexes; 'Naked' metal cations; Coordination chemistry

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1. Introduction

One topical field of research in fluorine chemistry is the synthesis of large, weakly interacting anions. In combination with poorly coordinating solvents, routes to almost 'naked', highly reactive cations are made possible by this approach.

An ideal combination of poorly interacting anions, weakly coordinating solvents and ready preparative availability is the system AF_6^-–SO_2–M^{n+} (A = As, Sb), introduced into synthetic chemistry by Gillespie and his group [1,2]. The versatility of the oxidizing properties of the combinations AsF_5/SO_2 and SbF_5/SO_2 was demonstrated in the reaction with mercury. Alchemists' dreams seemed to have been realized with the most exciting result, $[Hg_{2.86}(AsF_6)]_n$ (Fig. 1) [3,4], where liquid 'quick silver' was transformed into gold, and thrilled not only the scientific community, as reports in newspapers and journals documented. Depending on the

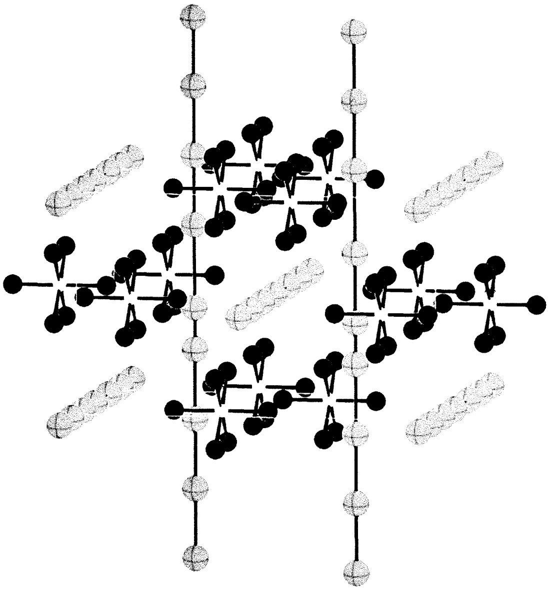


Fig. 1. Crystal structure of $Hg_{2.86}(AsF_6)$ [4].

stoichiometry, a series of polyatomic mercury cations was isolated [5]. Although first reports on the oxidation of chalcogens and other non-metal systems by AsF_5/SO_2 and SbF_5/SO_2 date back 30 years and extensive review articles have been published by Gillespie and Passmore [6–8], many areas of this field are still unexploited.

Metal chemistry is not restricted to mercury, Gillespie's school extended it to Groups 11, 12, 14 and transition metals [9,10]. The possibilities of 'naked' metal centers in coordination chemistry have been demonstrated by Dean [11], our group [12] and by Roesky [13,14].

Weakly coordinating fluoroanions (AsF_6^-, SbF_6^-, $[(SbF_5)_nF]^-$, etc.) are readily available and, in combination with other suitable solvents, e.g. HF and FSO_3H, will lead to the formation and stabilization of unique metal-, non-metal and organometallic cations. 'Naked' metal cations, generated in the superacidic systems AF_5/HF or AF_5/HSO_3F will coordinate even weak σ-donors, e.g. CO to give unprecedented highly-charged carbonyl cations even of the noble metals [15,16]. However, due to the aggressive nature of the solvent-system no broad application in coordination chemistry is possible.

General considerations for the construction of ideal anions for this purpose have been recently discussed in detail: large size; low charge, uniformly distributed over the surface of the anion; strong element-fluorine bonds in the anion to prevent F^- transfer [17,18]. The newest development in this direction seems to be multiteflate anions e.g. $[Sb(OTeF_5)_6]^-$ [19] and the older $[B(OTeF_5)_4]^-$ [20] or $[Nb(OTeF_5)_6]^-$ and $[Ta(OTeF_5)_6]^-$ [21]. The ultimate and almost unexploited development in this direction is the very recent generation of the $[C_2B_{10}(CF_3)_{12}]^-$ anion [22].

This paper is restricted to the coordination chemistry of 'naked' metal cations M^{n+} in and of SO_2. Earlier general discussions of the solvent properties of SO_2 are available [23–25]. Reports on the ligand properties of SO_2 in organometallic chemistry, the chemistry of organometallic SO_2 complexes [26,27] and the behavior of organometallic complexes towards SO_2 [28] can be found in the literature.

2. Syntheses of metal hexafluoroantimonates, hexafluoroarsenates and tetrachloroaluminates in liquid SO_2

The most simple and straightforward method for the preparation of metal salts with weakly interacting anions should be the reactions of metal fluorides and chlorides with strong fluoro and chloro Lewis acids:

$$\textbf{A}:\quad MF_n + nAF_5 \xrightarrow{SO_2} [M(SO_2)_x](AF_6)_n \qquad A = As,\ Sb \tag{1}$$

$$MCl_n + nAlCl_3 \xrightarrow{SO_2} [M(SO_2)_x][AlCl_4]_n \tag{2}$$

The success of this method is dependent upon the donor properties of the metal halides, and on the halide acceptor strength of the halo Lewis acid. According to the acid strength scale recently reported by Christe et al. [29], the most suitable halo Lewis acid candidates are $SbF_5 > AlF_3 > AlCl_3 > AsF_5$, while PF_5 and BF_3 are much poorer acceptors. Halide donor properties decrease with decreasing size and increasing charge, with increasing Lewis acidity of the metal centers, which is, on the other hand, paralleled by the stability of the metal ligand bond in the resulting SO_2 complexes. Unfavorable donor/acceptor relations of MX_n/AX_m will lead to long reaction times and even no reaction might be observed for systems which could be prepared by other routes.

In many cases the method introduced by Gillespie for mercury, the direct oxidation of metals by AsF_5 or SbF_5 in liquid SO_2, is the easiest way to hexafluoroarsenates and antimonates:

$$\mathbf{B}:\quad M + 3AsF_5 \xrightarrow{SO_2} [M(SO_2)_x](AsF_6)_2 + AsF_3 \tag{3}$$

$$M + 3SbF_5 \xrightarrow{SO_2} [M(SO_2)_x](SbF_6)_2 + SbF_3 \tag{4}$$

With excess AsF_5, metals are oxidized to give the corresponding sulfur dioxide hexafluoroarsenates mostly in quantitative yield, the volatile by-product AsF_3 is readily removed. For metal hexafluoroantimonates an excess of metal will prevent impurities (SbF_5OSO, $Sb_2F_{11}^-$ etc.) in the final product, insoluble SbF_3 is readily separated. According to Dean [9] the transition metals Mn, Fe, Co and Ni react vigorously with AsF_5 and SbF_5. Care must be taken in reactions with alkaline earth or lanthanide metals. On direct contact with AsF_5 they catch fire. The best procedure to follow is to condense sufficient SO_2 at −196°C, via a vacuum-line, onto the metals to cover them completely with the solvent, AsF_5 is then added and the reaction mixture is allowed to warm slowly from −80°C to the corresponding reaction temperature.

A further approach is the 'silver salt method', the reaction of metal chlorides, bromides and iodides with $AgAsF_6$ or $AgSbF_6$ according to:

$$\mathbf{C}:\quad MX_n + n\,AgAF_6 \xrightarrow{SO_2} [M(SO_2)_x](AF_6)_2 + n\,AgX \tag{5}$$
$$X = Cl,\ Br,\ I;\ A = As,\ Sb$$

Even $AgBF_4$ or other silver salts with weakly interacting anions are suitable. Method C is quite reasonable if A and B cannot be employed, but side-reactions and separation problems may cause difficulties.

Exchange reactions are almost uninvestigated, although stronger fluoro Lewis acids should remove F^- from the weaker ones, e.g.

$$\mathbf{D}:\quad [M(SO_2)_x](AsF_6)_n + n\,SbF_5OSO \xrightarrow{SO_2} [M(SO_2)_x](SbF_6)_n + n\,AsF_5 \tag{6}$$

This would be a clean and simple method for hexafluoro-antimonates, -niobates or -tantalates, but reactions of this type might be extremely slow.

Since the intention of the investigations of metal hexafluoroantimonates, arsenates, etc. in liquid SO_2 was mainly the isolation of 'solvate-free' salts, most authors were not interested in the nature of the SO_2 ligand in $[M(SO_2)_x](AF_6)_n$. Solvate-free hexafluoroarsenates [30–33] and antimonates [34] of the main group metals and transition metals are readily prepared in anhydrous HF from the appropriate fluorides and AsF_5 or SbF_5, respectively. Single crystals of the solvate-free manganese salt [33] were obtained from this solvent and it is likely that other salts can be obtained in this way. More recently, via this method, fluorobasic lanthanide hexafluoroarsenates and antimonates have been obtained [35–37]. However, a pure hexafluoroarsenate, $Ln(AsF_6)_3$, has only been isolated for lanthanum [37]. Furthermore, the thermal lability and their high reactivity towards nucleophiles made X-ray structural investigations extremely difficult. It has only recently been possible to investigate the structures of these complexes due to the development of new experimental techniques in X-ray crystallography.

Although, e.g. $AgAsF_6$ could only be isolated solvate-free, the Ag^+ will be solvated in solution. With less interacting anions, e.g. $[Sb(OTeF_5)_6]^-$ [17–19] or $[B_{10}C_2(CF_3)_{12}]^-$ [22] even the isolation of silver sulfur dioxide complexes might be possible.

2.1. Main group metal SO_2 complexes

2.1.1. SO_2 complexes of alkali and alkaline earth metals

Alkali metal chlorides react with $AlCl_3$ in liquid SO_2 with solvate formation according to

$$\begin{aligned} &MCl + AlCl_3 \xrightarrow{SO_2} M^+[AlCl_4]^- \cdot nSO_2 \\ &\qquad\qquad\qquad M = Li,\ Na,\ K,\ NH_4 \end{aligned} \tag{7}$$

The stability of these solvates decreases with increasing cation size and with decreasing Lewis acidity of the metal center. In the ternary system $MCl/AlCl_3/SO_2$ distinct chloro-aluminate SO_2 adducts of the type $M[AlCl_4]\cdot 3SO_2$ and $M[AlCl_4]\cdot 1.5SO_2$ exist [38]. Because of their low melting points ($Li[AlCl_4]\cdot 3SO_2$, m.p. 24.7°C, $Na[AlCl_4]\cdot 1.5SO_2$, m.p. −8°C) crystallization and characterization by X-ray crystallography is rather difficult and requires special techniques [39,40].

In $\{[Li(OSO)_{6/2}][AlCl_4]\}_n$ (Fig. 2) the Li centers are octahedrally coordinated by

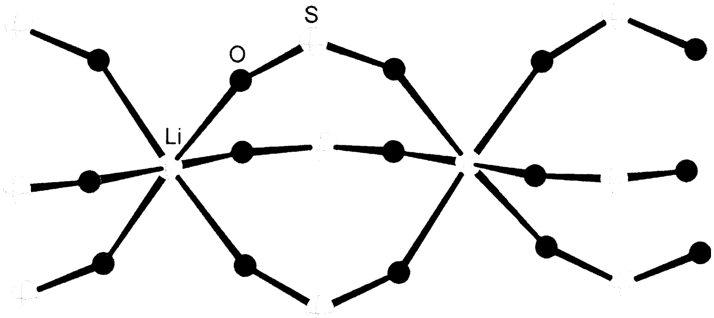


Fig. 2. Crystal structure of $[Li(OSO)_{6/2}]_n$ in $[Li(SO_2)_3][AlCl_4]$ [39].

O,O′-bridging SO_2 ligands to form $[Li(OSO)_{6/2}]_n^{n+}$ chains. The spaces between the chains are occupied by nearly ideal tetrahedral $AlCl_4^-$ ions [39].

In $\{Na[AlCl_4]\cdot 1.5SO_2\}_n$ (Fig. 3) terminal O- and bridging OO′-SO_2 ligands as well as bridging $AlCl_4^-$-tetrahedra complete the octahedral coordination sphere of the sodium centers [40].

The alkaline earth metals are readily oxidized by AsF_5 according to

$$\begin{array}{l} M + 3AsF_5 \xrightarrow{SO_2} [M(SO_2)_x](AsF_6)_2 + AsF_3 \\ \qquad\qquad M = Mg\ [41],\ Ca,\ Sr,\ Ba\ [42] \end{array} \tag{8}$$

The reaction takes place on slow warming from −40°C to room temperature (r.t.), and yields range from 60 to 85%. It is not known whether Be reacts in the same way.

The stability of the SO_2 complexes decreases with increasing atomic number as observed for the alkali metals. The only structure determination reported in the literature is for the Mg complex [41]. Since the Ca, Sr, Ba complexes readily lose the SO_2 ligand, single crystals are difficult to obtain. Despite their instability, these complexes are extremely useful starting materials for further coordination chemistry (Section 4.1.1).

The crystal structure analysis of $[Mg(OSO)_2(F_2AsF_4)_{4/2}]_n$ (Fig. 4) [41] shows that the Mg centers are bridged by edges of the AsF_6^- octahedra to form eight-membered $(–AsFMgF–)_2$ rings. These rings are connected by the Mg centers to chains. The four F^- of the bridging AsF_6^- are arranged in a square plane around the Mg and the two remaining coordination sites are occupied by SO_2 ligands. Preliminary results for $[Ca(SO_2)_{1.5}(AsF_6)_{6/3}]_n$ show that the SO_2 ligand is bound both terminally

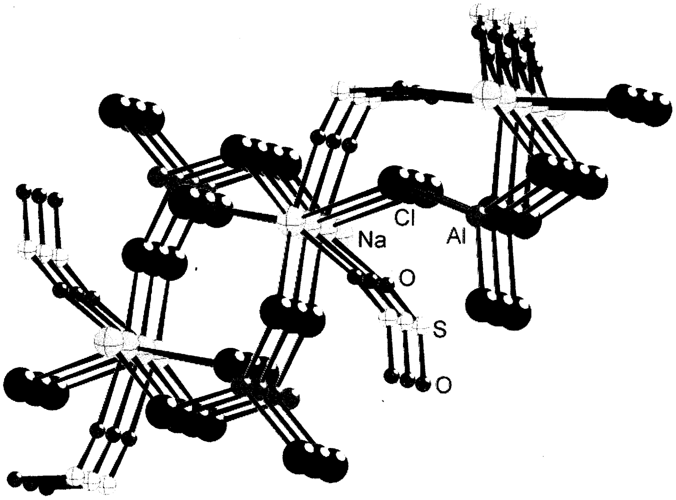


Fig. 3. Crystal structure of $[Na(SO_2)_{1.5}AlCl_4]_n$ [40].

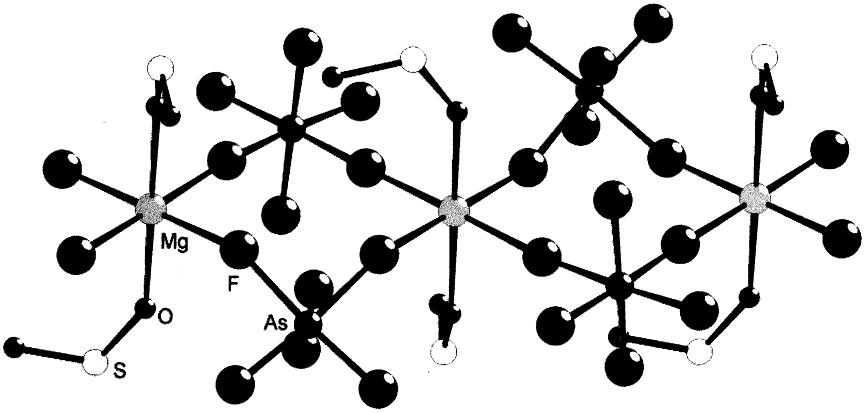


Fig. 4. Crystal structure of $[Mg(SO_2)_2(F_2AsF_4)_{4/2}]_n$ [41].

and via OO′-bridges. The coordination number 9 at the calcium centres is completed by coordinated hexafluoroarsenates [43].

2.1.2. SO_2 complexes of Group 13 metals

Since AlF_3, GaF_3 and InF_3 are even stronger Lewis acids than AsF_5 [29], the preparation of cationic species by fluoride ion abstraction is highly unlikely. The reaction of $AlCl_3$ with $AgAsF_6$ in liquid SO_2, for example, produced $AsCl_4^+AsF_6^-$ by Cl/F exchange as well as an insoluble residue. The IR spectra of this residue showed the presence of SO_2 and AsF–, as well as AlF-species, but no further characterisation was possible [42].

From the increasing stability of the $+1$ oxidation state with increasing atomic number, the hexafluorometallates are accessible, and $Tl^+SbF_6^-$ is reported [44]. Since $Ga[AlCl_4]$ [45], $In[AlCl_4]$ and similar species have been prepared, coordination chemistry of these 'naked' M^+ cations should also be possible in SO_2.

2.1.3. SO_2 complexes of Group 14 metals

SnF_2 reacts with strong fluoro Lewis acids according to method A to form 1:1 adducts. On the basis of vibrational and Mössbauer spectra these are formulated as salts of the fluorine-bridged $(SnF)_n^{n+}$ cation [46] with the anions AsF_6^-, SbF_6^- and BF_4^-, this was later confirmed by X-ray crystallography (Fig. 5) [47]. Reaction of SnF_2 with MF_5 in the molar ratio 2:1 or of $[SnF](MF_6)$ and SnF_2 in liquid SO_2 results in the salt $[Sn_2F_3](AF_6)$ (A = As, Sb) [48].

$$SnF_2 + AF_5 \rightarrow 1/n[(SnF)(AF_6)]_n \quad A = As, Sb \tag{9}$$

$$SnF_2 + BF_3 \rightarrow 1/n[(SnF)(BF_4)]_n \tag{10}$$

$$MF_2 + AsF_5(\text{excess}) \xrightarrow{SO_2} [M(SO_2)_x](AsF_6)_2 \quad M = Sn, Pb \tag{11}$$

$$MF_2 + 2SbF_5 \rightarrow M(SbF_6)_2 \tag{12}$$

$$PbO + PF_5 + 2AsF_5 \xrightarrow{SO_2} [Pb(SO_2)_x](AsF_6)_2 + OPF_3 \quad (13)$$

SnF_2 and PbF_2 form the corresponding SO_2 soluble hexafluoroarsenates with excess AsF_5. Whereas the rather unstable $[Sn(SO_2)_x](AsF_6)_2$ readily decomposes with loss of SO_2 and AsF_5, $[Pb(SO_2)_x](AsF_6)_2$ ($x = 1$) seems to be stable at r.t. and even the SO_2 is difficult to remove [49].

An interesting alternative route to $[Pb(SO_2)_x](AsF_6)_2$ starts from PbO, which is transformed by PF_5 to PbF_2 which further reacts with AsF_5 to give the desired product [50].

Spectroscopic results show appreciable covalent anion–cation interaction in $M(SbF_6)_2$ (M = Sn, Pb), both compounds are insoluble in liquid SO_2. Edwards and Khallow obtained single crystals of $Sn(SbF_6)_2$ from AsF_3. The structure determination of $[Sn(AsF_3)_3(SbF_6)_{6/3}]_n$ showed that the tin atom is nine-coordinate with six fluorine atoms from the SbF_6^- ions at the corners of a trigonal prism and three AsF_3 fluorines capping the rectangular faces [51].

2.1.4. SO_2 complexes of Group 15 metals

Sb and Bi metals are oxidized by excess AsF_5 and SbF_5 to the +3 oxidation state, in the case of Bi polyatomic species, e.g. Bi_8^{2+} and Bi_5^{3+} are also observed [52,53].

$$2Sb + 8SbF_5 \xrightarrow{SO_2} 5SbF_3{\cdot}SbF_5 \quad (14)$$

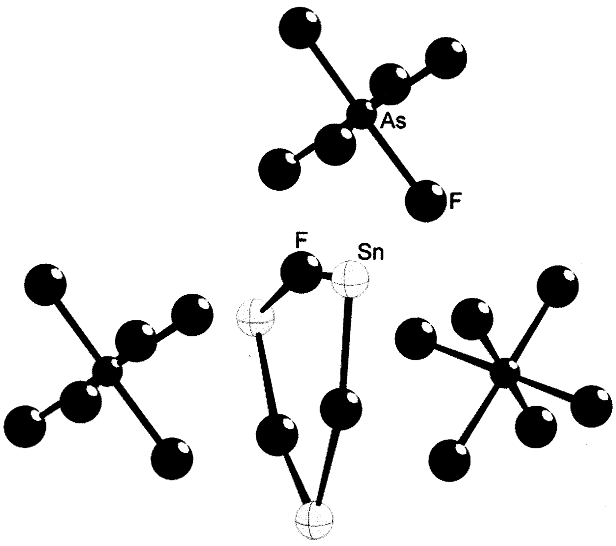


Fig. 5. Crystal structure of $[SnF^+]_3(AsF_6^-)_3$ [47].

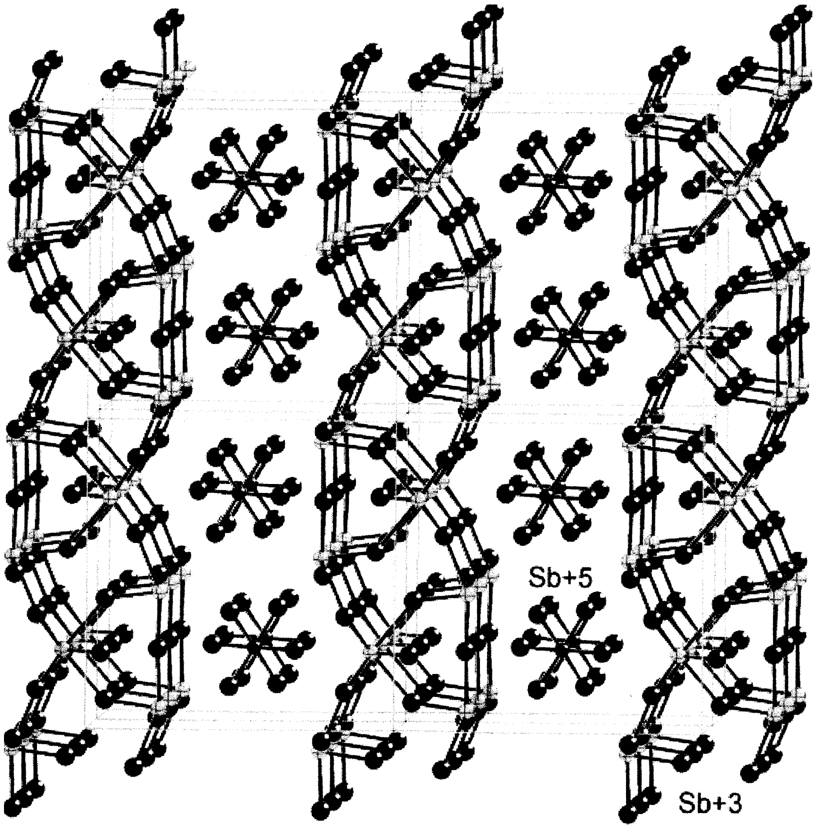
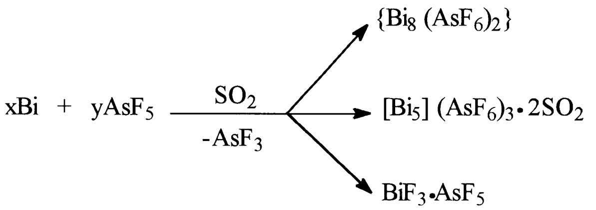


Fig. 6. Crystal structure of $SbF_3 \cdot SbF_5$ [55].



(15,15a,15b)

Starting from the trifluorides, no reaction with the weaker Lewis acid BF_3 was observed. While SbF_3 and BiF_3 form only 1:1 adducts even with excess AsF_5, the reaction of BiF_3 with excess SbF_5 leads to $BiF_3 \cdot 3SbF_5$. This can be formulated as $Bi(SbF_6)_3$, but Raman spectra indicate extensive anion–cation interaction. On the observation that the '$SbF_3 \cdot SbF_5$' from the metal oxidation differed from the '$SbF_3 \cdot SbF_5$' from the direct reaction of the components, and that the two forms were not interconvertable [54], several structure determinations followed. These showed the extraordinary diversity of the SbF_3/SbF_5 system. To date $SbF_3 \cdot SbF_5$ (Fig. 6) [55], $2SbF_3 \cdot SbF_5$ [56], $3SbF_3 \cdot SbF_5$ [57], $3SbF_3 \cdot 4SbF_5$ [58], two different forms of $5SbF_3 \cdot 3SbF_5$ [59,60] and $6SbF_3 \cdot 5SbF_5$ [56,61] have all been characterized.

2.2. SO_2 complexes of Group 11 (Cu^I, Ag^I) and Group 12 (Zn, Cd, Hg) metals

Cu [10] and Ag [62] are readily oxidized by AsF_5 in liquid SO_2 as follows:

$$2M + 3AsF_5 \rightarrow 2M^+(AsF_6)^- + AsF_3 \quad M = Cu, Ag \tag{16}$$

$$Cu(AsF_6)_2 + Cu \xrightarrow{SO_2} 2Cu(AsF_6) \tag{17}$$

The conproportionation of $Cu(AsF_6)_2$ with Cu also gives the expected product in quantitative yield. The solvate-free salts were isolated after removal of the volatiles by vacuum, but continued pumping on the Cu salt resulted in a gradual loss of AsF_5 and a constant weight was not achieved [10].

Several methods are reported for the preparation of salts of Zn^{2+} and Cd^{2+}: oxidation of the metals with excess AsF_5 according to method B [41], reaction of the fluorides with AF_5 (A = As, Sb) [63] according to A, and the reaction of the corresponding oxides with a mixture of PF_5/AsF_5 [64].

The most convenient method is the direct oxidation of the metals:

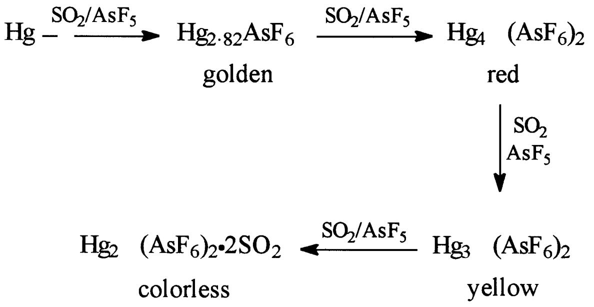
$$Zn + 3AsF_5 \xrightarrow{SO_2} Zn(AsF_6)_2\cdot 2SO_2 + AsF_3 \tag{18}$$

$$Cd + 3AsF_5 \xrightarrow{SO_2} Cd(AsF_6)_2\cdot xSO_2 + AsF_3 \tag{19}$$

$$2Hg + 3AsF_5 \xrightarrow{SO_2} Hg_2(AsF_6)_2\cdot 2SO_2 + AsF_3 \tag{20}$$

According to elemental analyses the Zn complex contains two ligands, for Cd no SO_2 content is reported. The structures of these complexes are not known.

The exciting oxidation and conproportionation reactions of mercury have been investigated in detail by Gillespie. With AsF_5 the first step is the formation of alchemist's gold, $Hg_{2.82}(AsF_6)$, followed by red Hg_4^{2+} (Fig. 7), yellow Hg_3^{2+} (Fig. 8) and colorless Hg_2^{2+} [3,4,65–68].



(21)

Equilibria between the different oxidation states make this system even more complicated.

$$Hg_4(AsF_6)_2 \rightleftharpoons Hg_{2.82}(AsF_6) + Hg_3(AsF_6)_2 \tag{22}$$

A similar reaction sequence is found with SbF_5, golden $Hg_{2.90}(SbF_6)$ is formed, followed by Hg_4^{2+}, etc. [5,67,68]. For pentafluorides not capable of oxidizing mercury, e.g. TaF_5 and NbF_5, the polymercury cations Hg^{3+} and Hg^{4+} as well as the metallic products with infinite mercury chains, $Hg_{3-\delta}[NbF_6]$ and $Hg_{3-\delta}[TaF_6]$, are obtained by conproportionation [5,69–71].

All structures of $Hg_{3-\delta}(AF_6)$ are of the same type, containing two orthogonal and non-intersecting linear chains of mercury, as shown in Fig. 1. The repeating distance between the mercury centers ($d = 264$ pm) in this low-dimensional metal is not consistent with the lattice dimensions ($a = b = 754$ pm). The non-stoichiometric empirical formula for these compounds was derived from the relationship a/b:d. From a neutron diffraction investigation it was concluded that the stoichiometry is Hg_3AF_6. The incommensurate structure is stabilized by anion vacancies, such that the formula, e.g. $Hg_{2.86}(AsF_6)_{0.953}$, results [72]. The compounds $Hg_{3-\delta}(AsF_6)$ and $Hg_{3-\delta}(SbF_6)$ disproportionate on contact with SO_2 below −20°C with formation of metallic Hg and a solution of Hg_4^{2+}. The Hg_4^{2+} itself is not completely stable in solution disproportionating to the solid metallic compound and Hg_3^{2+}, as also observed by ^{199}Hg-NMR spectroscopy [73].

If the golden crystals $Hg_{2.88}[TaF_6]$ and $Hg_{2.88}[NbF_6]$ are not removed from the mixture containing Hg_3^{2+}, Hg_4^{2+} and unreacted mercury they transform within a few hours to form flexible silvery plates which resemble aluminum foil [5,69]. The structure determination shows layers of close-packed NbF_6^- octahedra separated by a hexagonal net of mercury atoms (Fig. 9). On heating to 120°C the silver crystals are transformed back into the golden metallic form.

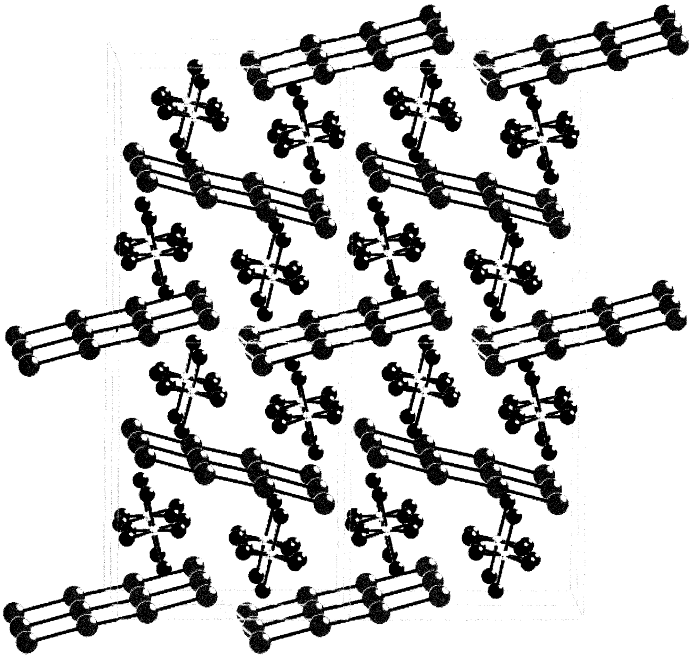


Fig. 7. Crystal structure of $Hg_4(AsF_6)_2$ [66]

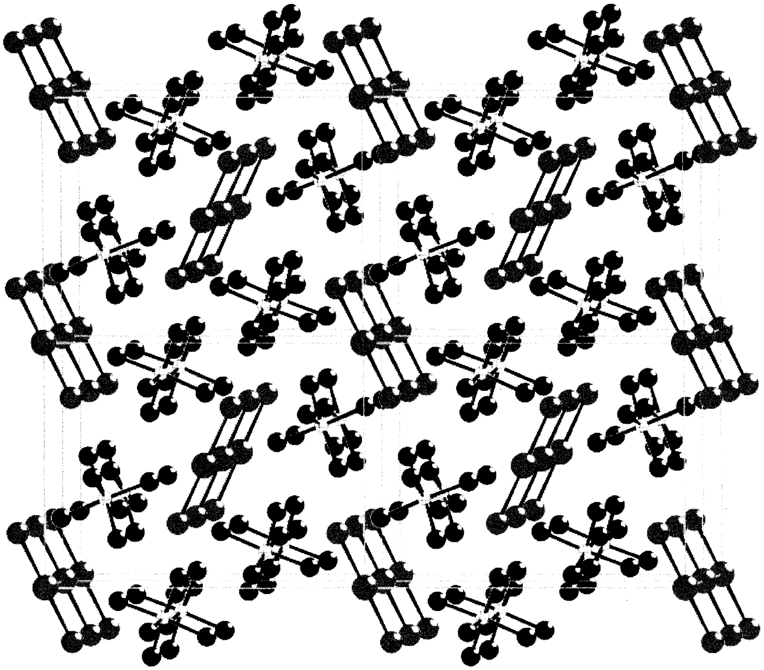


Fig. 8. Crystal structure of $Hg_3(AsF_6)_2$ [67].

Hg_3AsF_6 and Hg_3SbF_6 are readily prepared by electrochemical oxidation of Hg in liquid SO_2 [74]. Hg_3^{2+}, as the $AlCl_4^-$ salt, was obtained by the oxidation of metallic mercury or by conproportionation with Hg_2^{2+} in acidic chloroaluminate

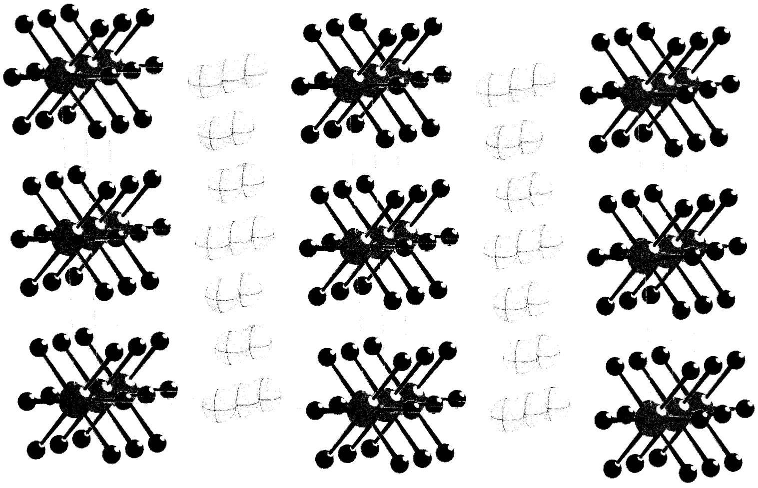


Fig. 9. Crystal structure of 'silvery' $Hg_3[NbF_6]$ [69].

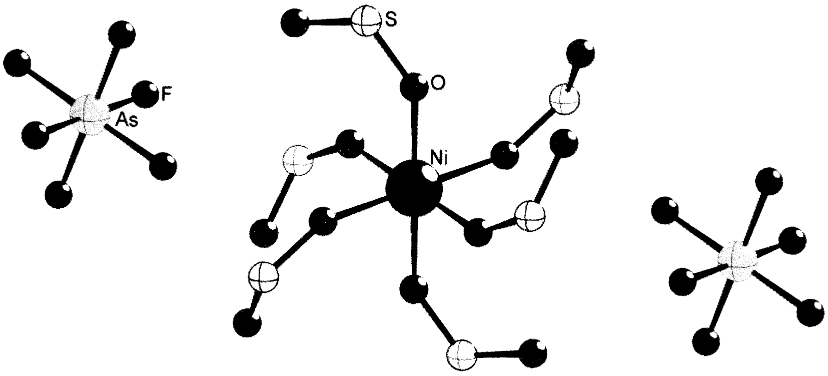


Fig. 10. Crystal structure of $[Ni(OSO)_6(FAsF_5)_2$ [78].

melts [75]. The structure of the Hg_3^{2+} cation in $Hg_3(AlCl_4)_2$ [76] is identical to that in $Hg_3(AsF_6)_2$ [67]

2.3. SO_2 complexes of the transition metals M^{2+} (M = Mn, Fe, Co, Ni, Cu)

These complexes might be prepared by methods A–C (Section 2), but the most convenient route is the direct oxidation of the metals by AsF_5 or SbF_5. With excess AsF_5, colorless (Mn), orange–yellow (Fe), purple (Co) [9], yellow (Ni) [9,10] and light-green (Cu) [10] solutions are readily formed in an exothermic reaction.

$$\begin{gathered} M + 3AsF_5 \xrightarrow{SO_2} [M(SO_2)_x](AsF_6)_2 + AsF_3 \\ M = Mn,\ x = 2\ [77], \\ M = Fe,\ Co,\ Cu,\ x = 4\ [77,78], \\ M = Ni,\ x = 6\ [78] \end{gathered} \tag{23}$$

Similar results are obtained with SbF_5. The hexafluoroarsenate salts are isolated in a pure state after removal of the by-product AsF_3 in dynamic vacuum at −20°C and recrystallization of the resulting products from SO_2 in the presence of some additional AsF_5. In the preparation of hexafluoroantimonates the SO_2 insoluble SbF_3 is readily removed. In order to avoid separation problems from $SbF_5{\cdot}OSO$ [79] or possibly formed $Sb_2F_{11}^-$ salts, an excess of metal should be used.

$$\begin{gathered} M + 3SbF_5 \xrightarrow{SO_2} [M(SO_2)_x](SbF_6)_2 + SbF_3 \\ M = Mn,\ Fe,\ Co,\ Ni\ [9] \end{gathered} \tag{24}$$

In SO_2 solution homoleptic $[M(OSO)_6]^{2+}$ ions are probably present, from these solutions single crystals were isolated at −10°C. The crystal structures of these complexes are shown in Figs. 10–13, a homoleptic complex was only isolated for Ni (Fig. 10). In the other complexes the AsF_6^- counter ions displace some of the SO_2 ligands during crystallisation. In contrast to $[Mg(OSO)_2](AsF_6)_2$ [41], in octahedrally coordinated $[Mn(OSO)_2](AsF_6)_2$ the SO_2 ligands are arranged in *cis*-positions, and each of the coordinated AsF_6^- bridges to a different Mn-center resulting in formation of a polymeric network (Fig. 11). While in $[Fe(OSO)_4(FAsF_5)_2]$ (Fig. 12) [78] and $[Co(OSO)_4(FAsF_5)_2]$ [77] the fluorine-bridged AsF_6^- ligands are arranged in *cis*-positions, in $[Cu(OSO)_4(FAsF_5)_2]$ (Fig. 13) [77] the loosely bonded AsF_6^- are *trans* to each other due to the Jahn–Teller effect.

The solid state structures of $[M(SO_2)_x](SbF_6)_2$ are not known, but it is not unlikely that homoleptic complexes of Fe and Co might be isolated due to the weaker nucleophilicity of the SbF_6^- ion.

Attempts to prepare solvate-free hexafluoroarsenates from the corresponding SO_2 complexes by removal of the volatiles at 50°C under vacuum were successful only for $Mn(AsF_6)_2$. For Fe, Co and Ni the simultaneous loss of SO_2 and AsF_5 gave fluorobasic salts $MF(AsF_6)$ [9]. $[Ni(OSO)_6](AsF_6)_2$ readily loses $4SO_2$ before further decomposition occurs [10]. Almost pure $Cu(AsF_6)_2$ was obtained by pumping on the solid overnight, but continued pumping resulted in a further decrease of weight [10]. The hexafluoroantimonates are more stable, and $Fe(SbF_6)_2$ and $Ni(SbF_6)_2$ were obtained in addition to $Mn(SbF_6)_2$. For Co a mixture of $CoF(SbF_6)$ and CoF_2 is reported [9].

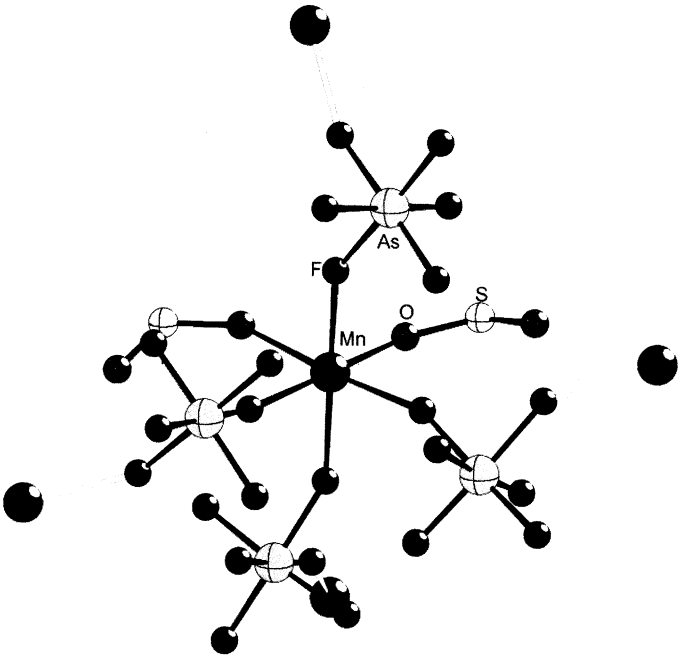


Fig. 11. Crystal structure of $[Mn(OSO)_2(F_2AsF_4)_{4/2}]_n$ [77].

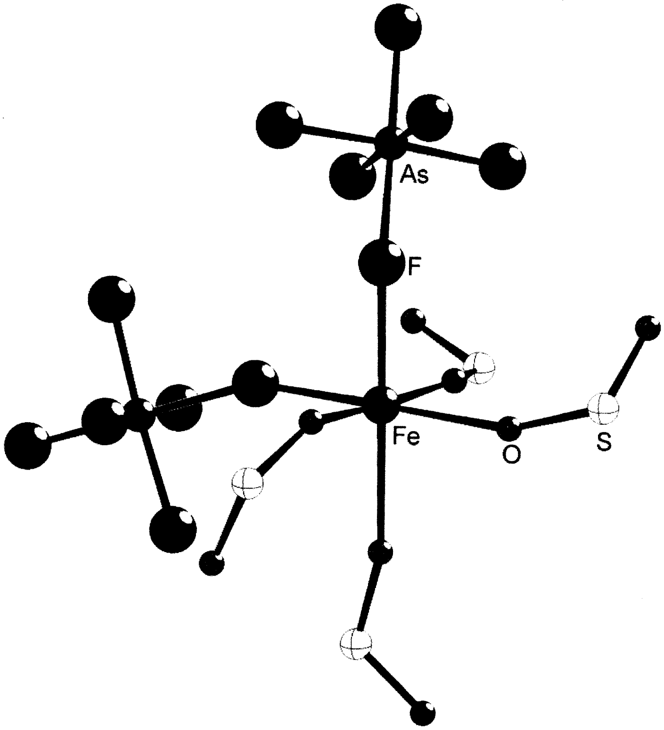


Fig. 12. Crystal structure of $[Fe(OSO)_4(FAsF_5)_2]$ [78].

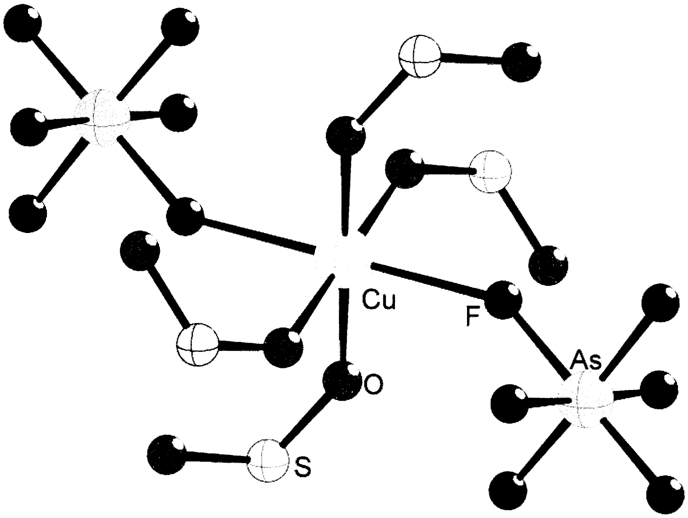


Fig. 13. Crystal structure of $[Cu(OSO)_4(FAsF_5)_2]$ [77].

2.4. Lanthanide SO_2 complexes

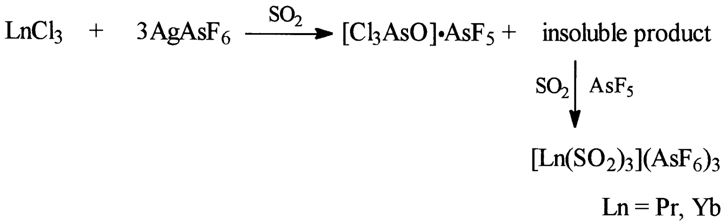
Although a first report on a lanthanide hexafluoroantimonate, $Nd(SbF_6)_3$ [35], dates back more than 40 years, no further attempts to investigate this class of compound have been reported. Žemva and co-workers recently isolated $LnF_3 \cdot 2AsF_5$, $2LnF_3 \cdot 3AsF_5$, $LnF_3 \cdot 2BF_3$ and $2LnF_3 \cdot 3BF_3$ from LnF_3 and AsF_5 or BF_3 from anhydrous HF [36,37]. A tris(hexafluoroarsenate) could only be obtained from LaF_3, the best fluoride base in this system [36]. In liquid SO_2 the formation of lanthanide hexafluoroarsenates from the fluorides according to method A is very slow, reaction time increases and yields decrease with decreasing size of the M^{3+} cation. The best results were obtained with LaF_3, within 4 weeks at r.t. 50–60% yields on a 3–5 mmol scale are obtainable [80].

$$\mathrm{LnF_3 + 3AsF_5 \xrightarrow[rt]{SO_2} [Ln(SO_2)_3](AsF_6)_3} \qquad (25)$$

$$\mathrm{Ln = La,\ Sm,\ Eu}$$

$$\mathrm{2Ln + 9AsF_5 \xrightarrow[-20°C]{SO_2} 2[Ln(SO_2)_3](AsF_6)_3 + 3AsF_3} \qquad (26)$$

$$\mathrm{Ln = Y,\ La,\ Ce,\ Pr,\ Nd,\ Sm,\ Gd,\ Dy,\ Er,\ Yb}$$



$$\begin{array}{ll} \mathrm{LnCl_3 + 3AgAsF_6 \xrightarrow{SO_2} [Cl_3AsO]\cdot AsF_5 +} & \text{insoluble product} \\ & \big\downarrow \mathrm{SO_2,\ AsF_5} \\ & \mathrm{[Ln(SO_2)_3](AsF_6)_3} \\ & \mathrm{Ln = Pr,\ Yb} \end{array} \qquad (27)$$

Although the highly reactive lanthanide metals are reported to undergo redox reactions with SO_2, these reactions are slow at low temperatures. By direct oxidation of the metals at −25°C the complete series of lanthanide sulfur dioxide hexafluoroarsenates can be prepared. At higher temperatures no hexafluoroarsenates are formed, probably as a result of passivation of the metal surface. $[Ln(SO_2)_x](AsF_6)_3$ might be prepared by the silver salt method C, but separation of the products from by-products is difficult [81].

The lanthanide sulfur dioxide hexafluoroarsenates are stable at low temperatures. At r.t. they can be stored in an atmosphere of SO_2. In vacuum, rapid loss of SO_2 and much more slowly, of AsF_5 occurs. The reaction is reversible.

Fascinating in lanthanide chemistry are the high coordination numbers of the metal centers. In $\{[Gd(OSO)_3(\mu\text{-}F_2AsF_4)_{6/2}]\cdot 0.25SO_2\}_m$ (Fig. 14) [80] the Gd^{III} ions are nine-coordinate, as in the corresponding Ca complex [43]. These two salts are, however not isostructural. In the Gd complex the fluorines of the AsF_6^- ions occupy the faces of the surrounding trigonal prism, the rectangular sides of the prism are capped by three OSO ligands. Stacks are formed by connection of the

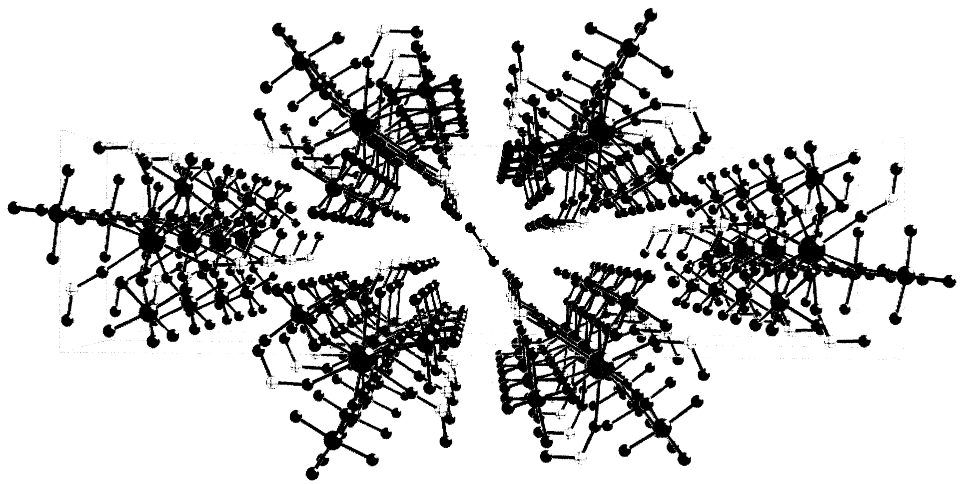


Fig. 14. Crystal structure of $[Gd(OSO)_3(\mu\text{-}F_2AsF_4)_{6/2}\cdot 0.25SO_2]_n$ [80].

Gd^{III} ions to the edges of the AsF_6^- octahedra and these are interconnected by weak fluoride-bridges between the AsF_6^- octahedra and the sulfur centers of the coordinated SO_2 ligands. As a result of this interaction $(\text{–GdFAsFSO–})_n$ rings ($n = 2$, 3, 4) are formed from which channels are created. In the largest of the channels additional SO_2 is inserted.

3. Properties of the SO_2 ligand

The bonding situation and the properties of the SO_2 ligand in organometallic compounds have been discussed in detail [26,82,83]. η^1-S or η^2-SO coordination is exclusively observed by interaction of the soft metal centers with the $4a_1$-HOMO and/or $2b_1$-LUMO of the SO_2 ligand. For a long time the only examples for O-coordination of the SO_2 ligand were $SbF_5\cdot OSO$ [79] and CH_3OSO^+ [84,85], but the present paper shows that hard and borderline metal centers can also act in the same way. The formation of d- , f-block and main group metal complexes suggests that the O-bonded SO_2 ligand acts only as a weak σ-donor. The stability of the complexes roughly parallels the Lewis acidity, i.e. the hardness of the metal centers. For Ag^+ no products with coordinated SO_2 have been isolated, structures of the rather unstable Hg^{2+} and $Hg_2^{2+}SO_2$ complexes are unknown, IR spectra do not fully exclude the possibility of S-coordination in these compounds. The IR-frequencies $\nu_{as}(SO_2)$ and $\nu_{sym}(SO_2)$ are characteristic for each bonding mode. For the structurally characterised main group, transition and lanthanide metals ν_{as} is in the range 1320–1340 cm^{-1}, ν_{sym} 1140–1170 cm^{-1}, in $[Zn(SO_2)_2](AsF_6)_2$ 1320 and 1150 cm^{-1}, respectively. For the latter compound O-coordination is also expected. For $[Hg_2(SO_2)_2](AsF_6)_2$ (1312, 1126 cm^{-1}) and $[Hg(SO_2)](AsF_6)_2$ (1316, 1102 cm^{-1}) [86] S-coordination cannot be fully excluded because these data are similar to those given by Kubas for η^1-planar S-coordination of SO_2 (ν_{as} 1303–1250 cm^{-1}, ν_{sym} 1130–1087 cm^{-1}) [82].

In comparison to the free ligand, the SO bond distance to the bridging oxygen increases on coordination, while the distance to the terminal oxygen decreases and the OSO angle closes slightly. The most reliable results were found for $[Ni(OSO)_6](AsF_6)_2$ [78] with bridging SO_b 144.7 pm, terminal SO_t 141.3 pm and OSO 116.9°. Recently, a low temperature (115 K) crystal structure determination gave $SO = 142.97(4)$ pm and $OSO = 117.5(1)°$ for the free ligand [87].

Premiliary investigations of the UV–Vis spectra of SO_2 solutions of the Fe^{II}, Co^{II} and Ni^{II} hexafluoroarsenates suggest the presence of octahedrally coordinated homoleptic complexes. The data show that SO_2 is a weaker ligand than H_2O in the spectrochemical series [41].

4. Coordination chemistry in liquid SO_2

According to the present results, the coordination chemistry of metal hexafluoroarsenates, and of hexafluoroantimonates, is almost unrestricted, even such weak σ-donors as CO and PF_3 could be introduced as ligands [88]. Since the metal centers are practically 'naked' almost no activation barriers have to be overcome; reactions proceed rapidly indeed at low temperatures. Thus, even extremely poor donors, thermally labile species and reactive intermediates might be introduced as ligands and stabilized at metal centers.

Only one literature report deals with the chemistry of main group metals [49]. The chemistry of Group 11 and 12 metals is dominated by interactions with soft ligands although O- and N-donors have also been introduced. This route has been used to introduce some rather unusual ligands into transition metal chemistry; first results on lanthanide complexes give an idea of the possibilities available for this system.

The SO_2 complexes are not only useful starting materials for coordination chemistry in liquid SO_2. Solvolysis reactions in inorganic or organic solvents e.g. $OPCl_3$, CH_3CN, THF etc. will afford the corresponding solvates, valuable starting materials for further inorganic and organometallic chemistry.

4.1. Coordination chemistry of main group metal tetrachloroaluminates, hexafluoroarsenates and hexafluoroantimonates in liquid SO_2

No attempts to exchange the SO_2 ligands in alkali metal tetrachloroaluminates have been reported. In alkaline earth metal sulfur dioxide complexes the SO_2 ligands are readily exchanged by weak N- and O-donors. The interactions of $Sn(SbF_6)_2$ and $Pb(SbF_6)_2$ with various mono- and multidentate phosphines and phosphine oxides are reported.

4.1.1. Alkaline earth metals

The unusual properties of metal sulfur dioxide hexafluoroarsenates are convincingly demonstrated by the surprising preparation of OPF_3 complexes:

$$[M(SO_2)_x](AsF_6)_2 + OPF_3\ (excess) \rightarrow [M(OPF_3)_4(FAsF_5)_2] + xSO_2 \qquad M = Mg,\ Ca \tag{28}$$

The crystal structure determination of the Ca complex (Fig. 15) shows that the metal center is surrounded by four OPF_3 ligands and two fluorine-bridged hexafluoroarsenates *trans* to each other [43].

NSF_3 [89], isoelectronic with OPF_3, reacts in the same way and extension of this reaction to derivatives of NSF_3 gives similar results [86,90]:

$$[M(SO_2)_x](AsF_6)_2 + NSF_3\ (excess) \rightarrow [M(NSF_3)_4(FAsF_5)_2] + xSO_2 \qquad M = Mg,\ Ca \tag{29}$$

$$[Mg(SO_2)_x](AsF_6)_2 + NSF_2R\ (excess) \rightarrow [Mg(NSF_2R)_4(FAsF_5)_2] + xSO_2 \qquad R = NMe_2,\ CF(CF_3)_2 \tag{30}$$

Addition of CH_3CN to solutions of the hexafluoroarsenates in liquid SO_2 or solvolysis of the SO_2 complexes in CH_3CN will lead to complete exchange of the SO_2 ligands [42,43]:

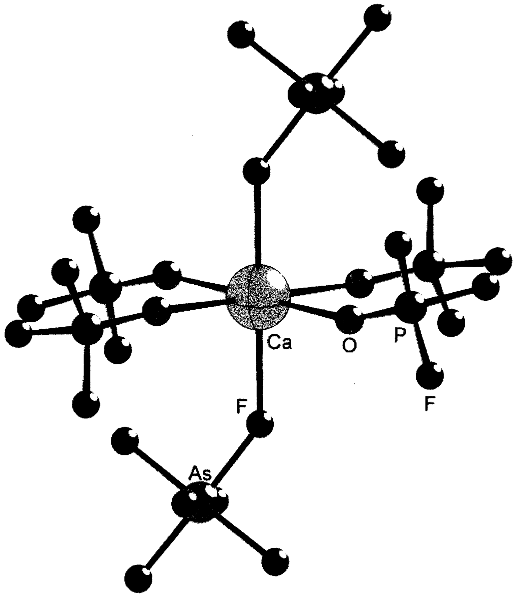


Fig. 15. Crystal structure of $[Ca(OPF_3)_4(FAsF_5)]_2$ [43].

$$[Ca(SO_2)_x](AsF_6)_2 + 6CH_3CN \rightarrow [Ca(NCCH_3)_6(FAsF_5)](AsF_6) + xSO_2 \quad (31)$$

$$[Ba(SO_2)_x](AsF_6)_2 + 9CH_3CN \rightarrow [Ba(NCCH_3)_9](AsF_6)_2 + xSO_2 \quad (32)$$

In the seven-coordinate Ca complex the ligands form an octahedron distorted by capping by an AsF_6^- ion where the Ca–N distances lie in the range 245.4(8)–249.8(8) pm.

In the nine-coordinate Ba complex the ligands form a slightly distorted tri-capped trigonal prism with Ba–N distances in the range 285.3(9)–292.4(6) pm [43].

4.1.2. The coordination chemistry of Group 4 metals

Only the interactions of phosphines and phosphine oxides with the hexafluoroantimonates of tin and lead have been reported in the literature [49]. For these reactions the SO_2-insoluble hexafluoroantimonates were used because solvate removal from the SO_2-soluble hexafluoroarsenates in vacuo led to products of variable composition. Since solvate removal is not necessary for reactions in liquid SO_2, the hexafluoroarsenates should also be useful starting materials in the coordination chemistry of Sn^{2+} and Pb^{2+}.

Reactions of $M(SbF_6)_2$ ($M = Sn$, Pb) with different phosphines in nitromethane solution were investigated by ^{31}P-NMR spectroscopy [49]. Both compounds dissolve exothermically in this solvent and with various di-, tri- and tetrahapto-phosphines, 1:1 complexes are formed:

$$\begin{aligned} M(SbF_6)_2 + L &\xrightarrow{\text{nitromethane}} [ML]^{2+} + 2SbF_6^- \\ &M = Sn,\ Pb; \\ L = Ph_2P(CH_2)_2PPh_2,\ &PhP[(CH_2)_2PPh_2]_2, \\ CH_3C[(CH_2)_2PPh_2]_3,\ &P[(CH_2)_2PPh_2]_3, \\ &[Ph_2P(CH_2)_2P(Ph)CH_2]_2 \end{aligned} \quad (33)$$

Interpretation of the ^{31}P-NMR spectra shows the formation of 1:1 complexes with no higher than tridentate ligands in the presence of $M(SbF_6)_2$. For the tetradentate ligands protonation is observed. The origin of the proton is unclear.

$$\begin{aligned} M(SbF_6)_2 + L &\xrightarrow{H^+} [MLH]^{3+} + 2SbF_6^- \\ &M = Sn,\ Pb; \\ L = &P[(CH_2)_2PPh_2]_2[(CH_2)_2PHPh_2]^+, \\ &Ph_2P[(CH_2)_2PPh]_2(CH_2)_2PHPh_2^+ \end{aligned} \quad (34)$$

Addition of the appropriate amount of chelating phosphine oxides to slurries of $M(SbF_6)_2$ ($M = Sn$, Pb) leads to the formation of solutions. After removal of the solvent the following 1:1 compounds were isolated:

$$\mathrm{M(SbF_6)_2 + L \xrightarrow{SO_2} [ML](SbF_6)_2{\cdot}}x\mathrm{SO_2} \qquad (35)$$

$$\mathrm{L = Ph_2P(O)(CH_2)_2P(O)Ph_2;\ M = Sn,\ Pb;}\ x = 0$$

$$\mathrm{L = OP[(CH_2)_2P(O)Ph_2]_3;\ M = Sn,}\ x = 3.5;\ \mathrm{M = Pb,}\ x = 0$$

$$\mathrm{L = PhP(O)[(CH_2)_2P(O)Ph_2]_2;\ M = Sn,}\ x = 2;\ \mathrm{M = Pb,}\ x = 1$$

Addition of around 1.5 mol $OPPh_3$ per mole of metal causes the $M(SbF_6)_2$ to dissolve in SO_2 and ^{31}P- and ^{19}F-NMR spectroscopy for $OP(p\text{-}C_6H_4F)_3$, shows evidence for $[ML_3]^{2+}$ and $[ML_2]^{2+}$ complexes.

For Pb^{2+}, these investigations show that a coordination number higher than three may be achieved but characterisation is not possible. For Sn^{2+} a maximum of three phosphoryl groups, probably in pseudo-tetrahedral coordination, can be accommodated around the central metal. Crystal structures of these compounds have not been determined to date.

4.2. The coordination chemistry of Group 11 (Cu^I, Ag^I) and Group 12 (Zn, Cd, Hg) metals

Dean and co-workers introduced metal hexafluoroarsenates into coordination chemistry. Their first reaction of Hg_2^{2+} with trifluorophosphine [11] was followed by investigations with a variety of phosphines, phosphine chalcogenides and different arenes. They extended this chemistry to Hg^{2+}, Zn^{2+}, Cd^{2+} and Ag^+, and as shown previously, to Sn^{2+} and Pb^{2+}. Roesky's group was mainly interested in the coordination chemistry of silver [14], nitrogen and oxygen as well as phosphorus, sulfur and selenium ligands were successfully introduced, some Zn^{2+} and Cd^{2+} complexes were also reported.

$CuAsF_6$ reacts with excess CO in liquid SO_2 at r.t. After pumping to dryness an analytically pure 1:1 adduct is obtained, which slowly decomposes at r.t. The extremely high CO stretching frequency (2180 cm^{-1}), the highest observed at that time, indicates that CO is mainly acting as a σ-donor [88].

$$\mathrm{Cu(AsF_6) + CO \xrightarrow[rt]{SO_2} [Cu(CO)](AsF_6)} \qquad (36)$$

$$\begin{tikzcd}
\mathrm{Cu(AsF_6)\ +\ PF_3} \arrow[r, "\mathrm{SO_2}", "\mathrm{rt}"'] & \mathrm{[Cu(PF_3)](AsF_6)} \arrow[d, shift right, "+\mathrm{PF_3}"'] \\
\mathrm{Cu(AsF_6)\ +\ xs.\ PF_3} \arrow[r, "\mathrm{SO_2}", "-78\,^{\circ}\mathrm{C}"'] & \mathrm{[Cu(PF_3)_2](AsF_6)} \arrow[u, shift right, "-\mathrm{PF_3}"']
\end{tikzcd} \qquad (37)$$

$$\mathrm{Ag(AsF_6) + PF_3 \rightarrow [Ag(PF_3)](AsF_6)} \qquad (38)$$

With excess PF_3 at -78°C $[Cu(PF_3)_2](AsF_6)$ is probably formed. On warming, PF_3 is lost and the 1:1 adduct is isolated in quantitative yield as a white, stable product.

The structures of the Cu salts are not known.

A similar 1:1 silver complex was isolated from a SO_2 solution with $PF_3:Ag^+ > 1$ and characterized by IR and NMR spectroscopies. It was not possible to obtain a pure product [91].

The extraordinary possibilities of the system $AgAsF_6/SO_2$ for an unusual coordination chemistry was demonstrated with a wide variety of N, P, O, S and Se ligands. Hydrogen cyanide [92] and even halocyanides [93] were added to give the corresponding bis(cyanide) complexes in almost quantitative yield:

$$AgAF_6 + 2RCN \rightarrow [Ag(NCR)_2](AF_6) \tag{39}$$

$$A = As,\ R = Cl,\ Br,\ I\ [93],\ NSF_2\ [94]$$

$$A = Sb,\ R = H\ [92],\ Cl,\ Br\ [93]$$

Structure determinations are reported for $[Ag(NCH)_2](SbF_6)$ (Fig. 16) [92] and $[Ag(NCCl)_2](SbF_6)$ [93]. The nitrile ligands coordinate exactly linearly to the central Ag^+. Four fluorines from bridging SbF_6^- complete the coordination sphere of the silver. As a result of these interactions layers are formed in the hydrogen cyanide salt with strong hydrogen-bonding between the layers. In the chlorocyanide complex, SbF_6-bridging leads to the formation of double chains.

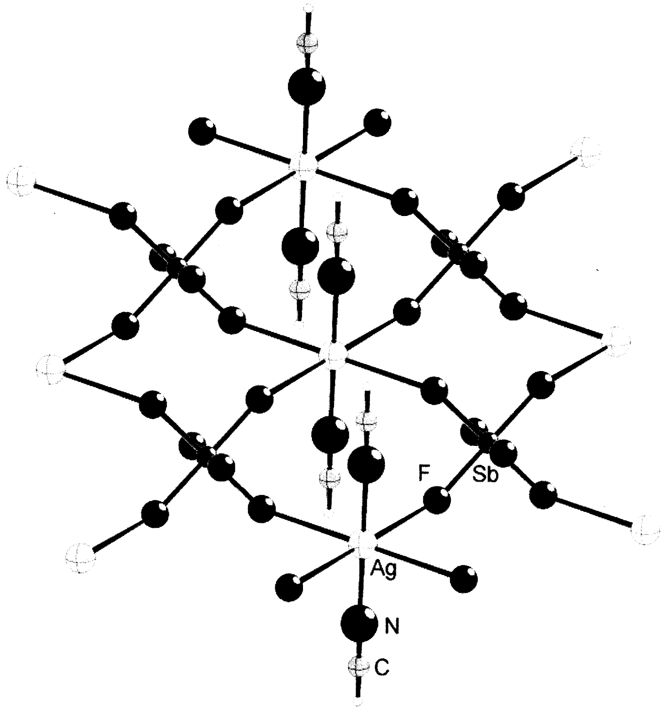


Fig. 16. Crystal structure of $\{[Ag(NCH)_2](SbF_6)_{4/4}\}_n$ [92].

Even more interesting is the coordination chemistry with bifunctional nitriles. Cyanogen reacts in the molar ratio 1:2 to give a polymeric network with square-planar coordinated silver centers (Fig. 17) [95].

$$\mathrm{AgAsF_6 + 2(CN)_2 \rightarrow 1/}n\mathrm{[Ag\{(CN)_2\}_2]}_n\mathrm{(AsF_6)}_n \tag{40}$$

$$\mathrm{AgAsF_6 + (NCS_2CN) \rightarrow 1/}n\mathrm{[Ag(SCN)_2]}_n\mathrm{(AsF_6)}_n \tag{41}$$

$$\mathrm{AgAsF_6 + 2(NCS}_m\mathrm{CN) \rightarrow 1/}n\mathrm{[Ag\{S}_m\mathrm{(CN)_2\}_2]}_n\mathrm{(AsF_6)}_n \quad m = 3,\ 4 \tag{42}$$

In the complex [NCS$_m$CN] ($m = 2$) with a 1:1 molar ratio the ligand bridges two cations with formation of a chain polymer [96], with $m = 3$ (Fig. 18) and $m = 4$ four nitrogens surround the central Ag$^+$ to form either a chain ($m = 3$) or layer polymer ($m = 4$) (Fig. 19) [97].

Acyclic and cyclic sulfur–oxygen ligands often give surprising results. From the reaction of bis(sulfinylimido)sulfur, S(NSO)$_2$, with AgAsF$_6$ the complex [Ag$_4$L$_9$](AsF$_6$)$_4$·SO$_2$ with two differently coordinated silver centers were isolated [98]. Ag(1) is surrounded by six nitrogen atoms from three bidentate S(NSO)$_2$ molecules, these units coordinate Ag(2) octahedrally by terminal oxygens (Fig. 20).

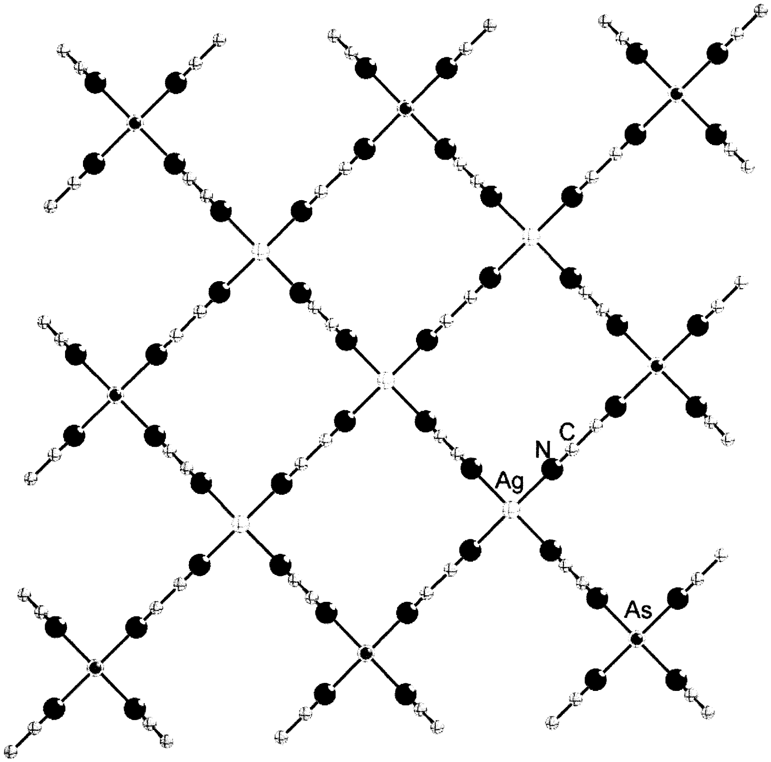


Fig. 17. Crystal structure of {[Ag(CN)$_{4/2}$}$_n$(AsF$_6$)$_n$ [95].

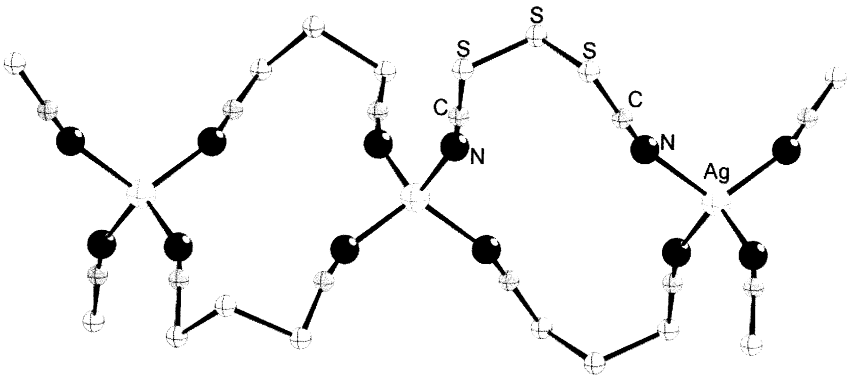


Fig. 18. Crystal structure of $[\mathrm{Ag(NCS_3CN)_{4/2}}]_n(\mathrm{AsF_6})_n$ [97].

$$4\mathrm{AgAsF_6} + 9\mathrm{S(NSO)_2} \xrightarrow{\mathrm{SO_2}} [\mathrm{Ag_4\{S(NSO)_2\}_9(AsF_6)_4{\cdot}SO_2}] \tag{43}$$

(44)

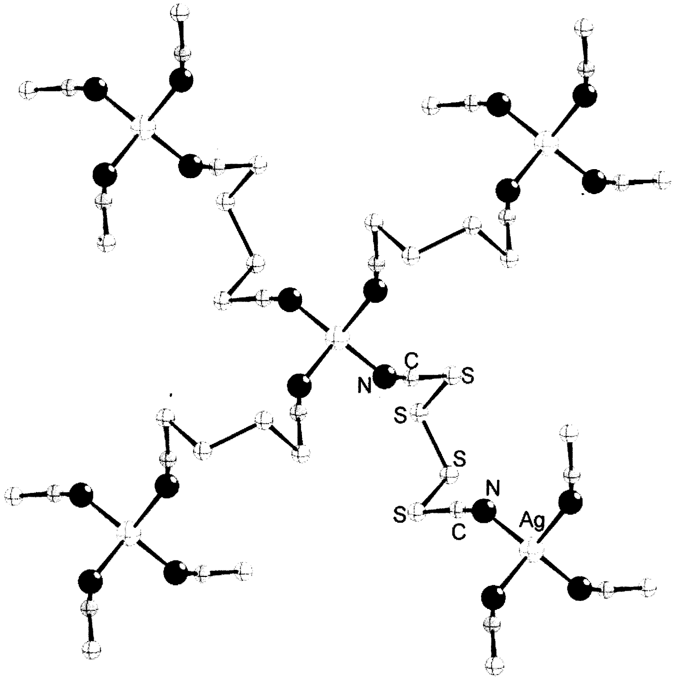


Fig. 19. Crystal structure of $[\mathrm{Ag(NCS_4CN)_{4/2}}]_n(\mathrm{AsF_6})_n$ [97].

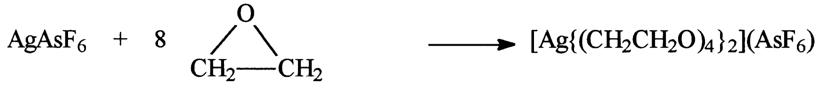
$$AgAsF_6 + 4S_4N_4O_2 \rightarrow [Ag(S_4N_4O_2)_4](AsF_6) \qquad (45)$$

Two five-membered rings (Scheme 44) are linked to the silver by the nitrogen adjacent to the SO-group (Fig. 21), the coordination sphere is completed by a weaker interaction with two oxygens from adjacent molecules and two fluorines from the AsF_6^- counterion [13]. In the 1,3,5,7-tetrathio-2,4,6,8-tetraaza-1,1-dioxide silver cation (Scheme 45) the central silver is surrounded by four of the nitrogens adjacent to the SO_2 groups [99].

Also interesting is the coordination chemistry with oxygen, sulfur and selenium heterocycles. With 1,3 dioxane a polymeric chain of $[AgL_3(FAsF_5)]_n$ is formed. Four of the octahedral positions around the silver centers are occupied by oxygens from bridging dioxane molecules. The remaining coordination sites are occupied by a terminal dioxane and one fluorine of the AsF_6^- counterion, both *trans* to each other [100]:

$$AgAsF_6 + 3\ 1{,}3\text{-}C_4H_8O_2 \rightarrow 1/n[Ag(1{,}3\text{-}C_4H_8O_2)_3(FAsF_5)]_n \qquad (46)$$

$$2AgAsF_6 + 2\ 1{,}3{,}5\text{-}C_3H_6O_3 \rightarrow [Ag_2(CH_2O)_6](AsF_6)_2 \qquad (47)$$



$$AgAsF_6 + 8\ \overset{O}{CH_2{-}CH_2} \longrightarrow [Ag\{(CH_2CH_2O)_4\}_2](AsF_6) \qquad (48)$$

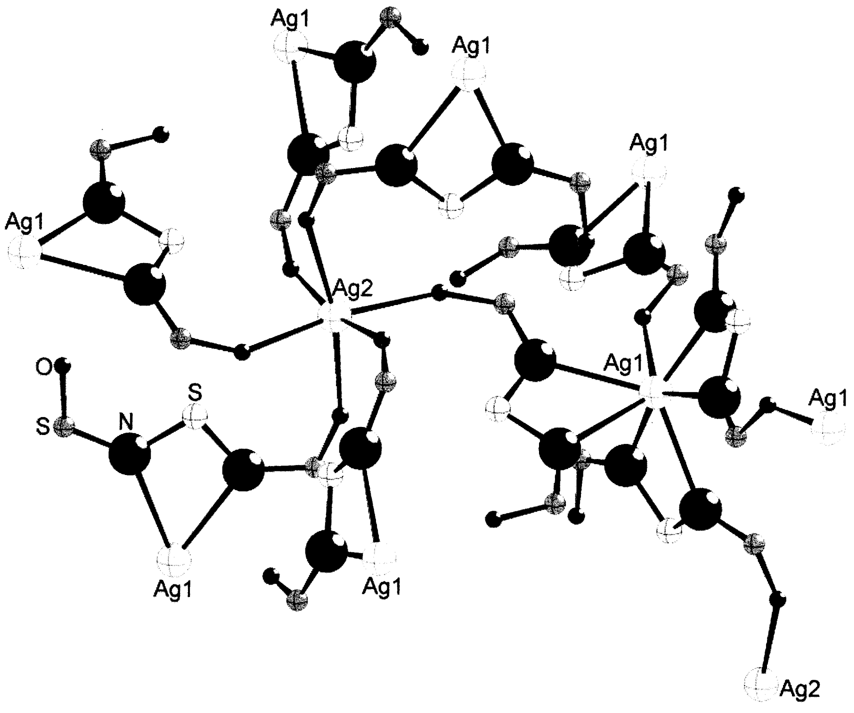


Fig. 20. Crystal structure of $[Ag_4(S(NSO)_2)_9](AsF_6)_4SO_2$ [98].

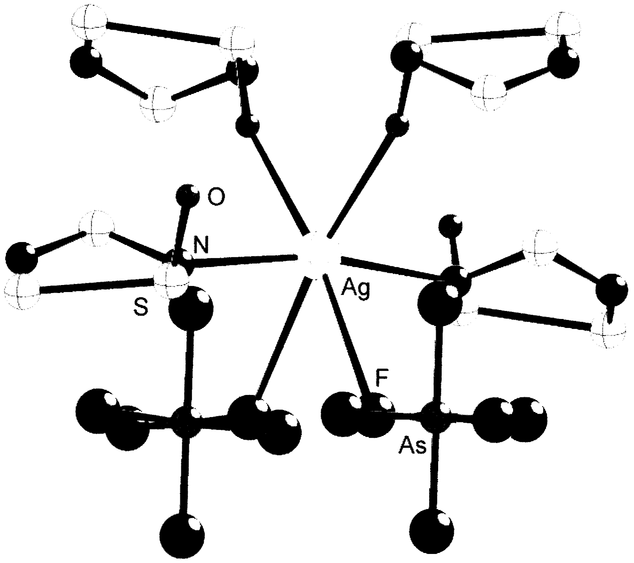


Fig. 21. Crystal structure of $[Ag(S_3N_2O)_2](AsF_6)$ [13].

The reaction with trioxane gave a rather surprising result. Catalysed by the silver centers, two six-membered rings were transformed into a twelve-membered heterocycle. The hexadentate ligand adopts a S (double-tub) conformation, with alternating oxygens coordinating to the two silver centers, the remaining three positions in the octahedral coordination sphere are occupied by fluorine ligands from bridging hexafluoroarsenates (Fig. 22) [101]. In the reaction with ethylene oxide Ag^+ acts as a template with 12-crown-4 being formed (Scheme 48) [102], two of the ligands coordinate to the metal center to form a sandwich-type complex (Fig. 23).

$$AgAsF_6 + 2\text{-}4(CH_2S)_3 \xrightarrow{SO_2} [Ag_2\{(CH_2S)_3\}_5](AsF_2)_2{\cdot}SO_2 + [Ag\{(CH_2S)_3\}_2](AsF_6) \quad (49)$$

$$AgAsF_6 + 2(CH_2Se)_3 \rightarrow [Ag\{(CH_2Se)_3\}_2](AsF_6) \quad (50)$$

$$2AgAsF_6 + 4Ph_2E_2 \rightarrow [Ag_2(Ph_2E_2)_4(F_2AsF_4)_2] \quad (E = S, Se) \quad (51)$$

$$AgAsF_6 + 2S_8 \rightarrow [Ag(S_8)_2](AsF_6) \quad (52)$$

The major product of the reaction with trimeric thioformaldehyde is the complex $[Ag_2L_5]^{2+}$ [103] with minor amounts of $[AgL_2]^+$ [104]. Structure determinations show the diverse possibilities of the ligand and the variability of the coordination sphere of the silver centers. In $[Ag_2L_5]^+$ one of the central ions is coordinated by five sulfur ligands from one tridentate, one monodentate and one sulfur from a bridging-ligand. As well as one sulfur from the bridging ligand the other center, with four occupied coordination sites, is surrounded by one mono- and one

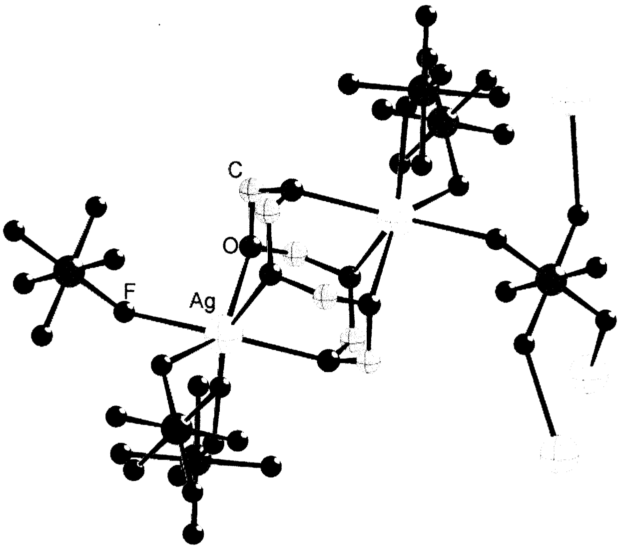


Fig. 22. Crystal structure of $[Ag_2(CH_2O)_6](AsF_6)_2$ [101].

bidentate ligand [103]. In $[AgL_2]$ ($L = (CH_2S)_3$) two monodentate ligands coordinate to the silver center, the SAgS angle (153°) deviates from linearity because of a weak interaction with a third sulfur from a neighboring complex [104]. In $[Ag(CH_2Se)_3]^+$ with two tridentate ligands a sandwich-type complex results [104].

In $[Ag_2(Ph_2E_2)_4(F_2AsF_4)_2]$ a six-membered Ag_2E_4-heterocycle is formed [105] with two bridging ligands, the remaining three coordination sites at the pentacoordinate Ag^+ centers are occupied by a monodentate Ph_2E_2 and a bidentate AsF_6^- ligand.

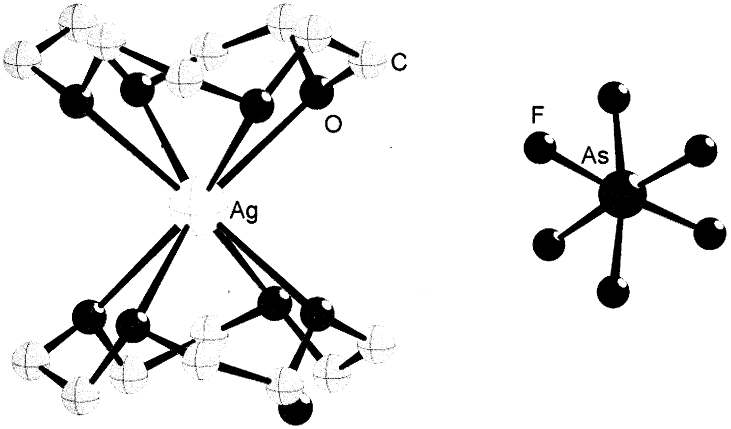


Fig. 23. Crystal structure of $[Ag\{(CH_2CH_2O)_4\}_2](AsF_6)$ [102].

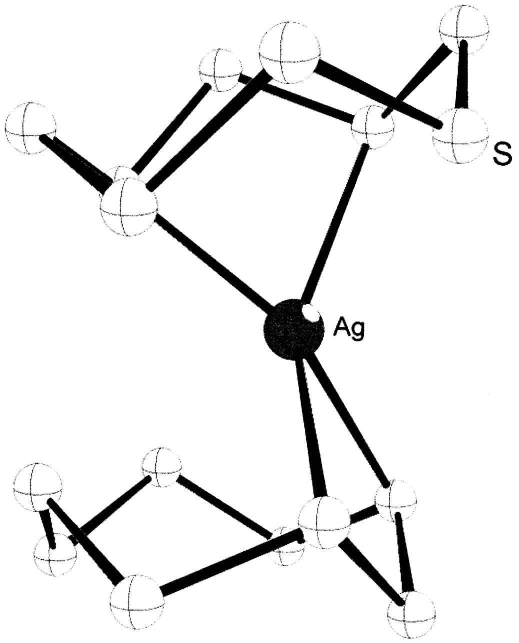


Fig. 24. Crystal structure of $[Ag(S_8)_2](AsF_6)$ [106].

The most exciting result was obtained with elemental sulfur, the S_8-ring can be coordinated without ring cleavage [106,107]. The structure determination shows some kind of slipped sandwich with four coordinating sulfurs [106] (Fig. 24).

4.3. Group 12 metals (Zn, Cd, Hg)

Dean and Damude demonstrated just how useful the combination of the weak donor solvent SO_2 and the poorly coordinating anions AsF_6^- and SbF_6^- is for coordination chemistry with the preparation of the first π-arene complexes of zinc, cadmium and mercury. From the reaction of $Zn(SbF_6)_2$, $Cd(AsF_6)_2$ and $Cd(SbF_6)_2$ 1:1 complexes were isolated as analytically pure salts [63,108]; naphthalene and biphenyl were decomposed rapidly by contact with $Zn(SbF_6)_2$ in SO_2 solution [63].

$$Zn(SbF_6)_2 + \text{arene} \xrightarrow{SO_2} Zn(SbF_6)_2 \cdot \text{arene} \quad (53)$$

$\text{arene} = Me_6C_6,\ Me_5C_6H$

$$Cd(AsF_6)_2 + \text{arene} \xrightarrow{SO_2} Cd(AsF_6)_2 \cdot \text{arene} \quad (54)$$

$\text{arene} = Et_6C_6,\ Me_6C_6,\ 1,2,4,5\text{-}Me_4C_6H_2,\ 1,4\text{-}Me_2C_6H_4,\ C_6H_6$

$$Cd(SbF_6)_2 + \text{arene} \xrightarrow{SO_2} Cd(SbF_6)_2 \cdot \text{arene} \quad (55)$$

$\text{arene} = Me_6C_6,\ MeC_6H_5,\ C_6H_6$

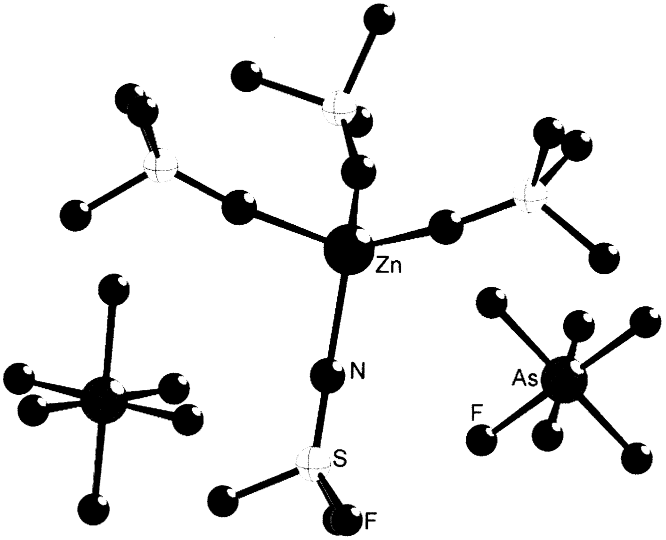


Fig. 25. Crystal structure of $[Zn(NSF_3)_4](AsF_6)_2$ [90].

The complexes were characterized by IR, ^{13}C- and ^{113}Cd-NMR spectroscopies. From the ^{13}C-NMR spectral complexation shifts it was concluded that Zn and Cd bind to the arene in a localized η^1-manner.

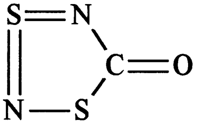
Surprisingly, almost no reactions of $Zn(AF_6)_2$ and $Cd(AF_6)_2$ (A = As, Sb) with nitrogen donors have been reported since even NSF_3 forms stable complexes although the donor properties of the thiazyl nitrogen are strongly reduced by the fluorine substituents at the sulfur. $[Zn(NSF_3)_4](AsF_6)_2$, the only homoleptic thiazyltrifluoride complex known, is obtained in quantitative yield. The structure of the complex is shown in Fig. 25 [90].

$$[Zn(SO_2)_x](AsF_6)_2 + 4NSF_3 \rightarrow [Zn(NSF_3)_4](AsF_6)_2 + xSO_2 \qquad (56)$$

$$[Cd(SO_2)_x](AsF_6)_2 + (CN)_2 \rightarrow 1/n[Cd\{(CN)_2\}_{4/2}(OSO)(\mu\text{-}F_2AsF_4)_2]_n + (x-1)SO_2 \qquad (57)$$

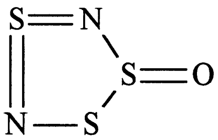
In the Cd–cyanogen complex the bridging $(CN)_2$ ligands connect the Cd centers to a corrugated square network. Two bidentate fluorine-bridged AsF_6^- counterions and one O-bonded SO_2 ligand complete the coordination [109].

The acyclic $S(NSO)_2$ ligand and the heterocycle,



(S_2N_2CO), have been introduced into Zn chemistry [110,111].

Zn and Cd complexes have been prepared from,



(S_3N_2O), [112].

In contrast to silver chemistry exclusively O-coordination is observed here as confirmed by crystal structure determinations.

$$[Zn(SO_2)_x](AsF_6)_2 + 2S(NSO)_2 \rightarrow 1/n[Zn\{S(NSO)_2\}_{4/2}(FAsF_5)_2 \cdot 2SO_2] + (x-2)SO_2 \quad (58)$$

$$[M(SO_2)_x](AsF_6)_2 + 6N_2S_3O \rightarrow [M(OS_3N_2)_6](AsF_6)_2 + xSO_2 \quad (59)$$

$$[Zn(SO_2)_x](AsF_6)_2 + 6N_2S_2CO \rightarrow [Zn(OCS_2N_2)_6](AsF_6)_2 + xSO_2 \quad (60)$$

In these complexes the Zn center is octahedrally coordinated, in the polymeric $[Zn\{S(NSO)_2\}_{4/2}(FAsF_5)_2 \cdot 2SO_2]_n$ besides four oxygens two fluorine-bridged AsF_6^- groups complete the coordination sphere [110].

Zn and Cd act as acceptors towards a variety of phosphine oxides, sulfides and selenides forming complexes which have been characterized in solution by ^{31}P- and ^{113}Cd-NMR spectroscopies [64,113–115].

$$[Zn(SO_2)_x](SbF_6)_2 + nL \rightarrow [ZnL_n]^{2+}(SbF_6^-)_2 + xSO_2 \quad (61)$$

$n = 6$, $L_2 = Ph_2P(O)CH_2P(O)Ph_2$, $L_3 = [Ph_2P(O)(CH_2)_2]P(O)Ph$;
$n = 4$, $L = (C_6H_{11})_3PE$ ($E = O$, S, Se), R_3PE ($R = Ph$, o-MeC_6H_4, $E = S$, Se),
$L_2 = Ph_2P(E)CH_2P(E)Ph_2$ ($E = O$, S, Se),
$L =$ bidentate $[Ph_2P(E)CH_2]_3CMe$ ($E = S$, Se);
$n = 3$, $L_3 = [Ph_2P(E)(CH_2)_2]_2P(E)Ph$ ($E = S$, Se), $L = R_3PE$
($R = C_6H_{11}$, Ph, o-MeC_6H_4 ($E = S$, Se)

By variation of the ratio Zn/ligand different degrees of coordination were detected, complexes with $n = 2$, 1 are also described as well as complexes with mixed ligands, e.g. $[Zn\{SeP(C_6H_{11})_3\}_x\{SP(C_6H_{11})_3\}_{n-x}]$ ($n = 3$, 4) [113].

Similar ^{31}P- and ^{113}Cd-NMR investigations of $Cd(AF_6)_2$ ($A = As$, Sb) with a wide variety of mono-, di- and tridentate phosphine oxides, sulfides and selenides (R_3PE: $R = Ph$, o-MeC_6H_4, p-MeC_6H_4 ($E = S$, Se), C_6H_{11} ($E = O$, S, Se), ^{t}Bu ($E = Se$), $R_3 = (o\text{-}MeC_6H_4)_2Ph$ ($E = S$, Se); $Ph_2P(E)(CH_2)_nP(E)Ph_2$ ($n = 1$, 2, $E = O$, S, Se); $(Ph_2P(E)CH_2)_3CMe$ ($E = S$, Se); $Ph_2P(E)(CH_2)_2P(E)Ph(CH_2)_2P(E)Ph_2$ ($E = O$, S, Se)) have been performed [64,114,115].

The maximum coordination number of 6 was achieved with phosphine oxides [114]. By variation of the metal/ligand ratio between two and four donor atoms could be attached to the Cd center. Complexes with mixed ligands were also characterized [115]. The synthesis of SO_2 insoluble $[Cd\{OP(C_6H_{11})_3\}_3](SbF_6)_2$ was reported [64].

A wide range of arene complexes has been prepared from $Hg_2(AsF_6)_2$ and the appropriate arene. Raman spectroscopy confirmed the integrity of the Hg_2^{2+} cation in these complexes, the existence of Hg_2^{2+} arene complexes was confirmed by ^{13}C-NMR spectroscopy [62].

$$[Hg_2(SO_2)_x](AsF_6)_2 + n\ \text{arene} \rightarrow [Hg_2(\text{arene})_n](AsF_6)_2 \tag{62}$$

In many cases the complex precipitated immediately on mixing and most of the materials isolated had a 1:1 stoichiometry (arene = benzene, biphenyl, naphthalene, 2-methyl- and 2,6-dimethylnaphthalene, acenaphthene, fluoranthene, fluorene, phenanthrene, anthracene, 9,10-dimethylanthracene, *m*-dinitrobenzene). In some cases (arene = benzene, biphenyl, fluoranthene, fluorene and napthalene and its derivatives) more soluble $n > 1$ complexes seemed to form with excess arene. Similarly to Zn and Ag complexes, it was concluded from ^{13}C-NMR spectroscopy that the Hg_2^{2+} is involved in a localized interaction with the arene and that there are preferred bonding sites [62].

Several methods for the preparation of Hg^{2+}–arene complexes have been reported

$$Hg(SbF_6)_2 + n\ \text{arene} \rightarrow [Hg(\text{arene})_n](SbF_6)_2 \tag{63}$$

$$2HgF(AsF_6) + 2\ \text{arene} \rightarrow [Hg(\text{arene})_2](AsF_6)_2 + HgF_2 \tag{64}$$

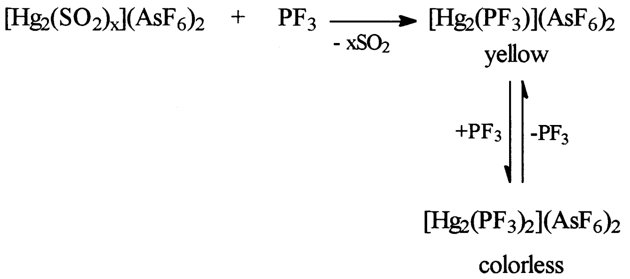
$$HgCl_2 + 2\ \text{arene} + 2AgAF_6 \rightarrow [Hg(\text{arene})_2](AF_6)_2 + 2AgCl \tag{65}$$

$$HgF(BF_4) + 2\ \text{arene} + BF_3 \rightarrow [Hg(\text{arene})_2](BF_4)_2 \tag{66}$$

Bis(arene) complexes were isolated with C_6H_6, MeC_6H_5, 1,3-$Me_2C_6H_4$, 1,3,5-$Me_3C_6H_3$; 1,2,4,5-$Me_4C_6H_2$, 1,2,3,4-$Me_4C_6H_2$, Me_5C_6H, Me_6C_6, naphthalene and biphenyl. With naphthalene and phenanthrene monoarene complexes were also obtained [116,117]. These and further 1:1 complexes with alkyl-substituted arenes were investigated by ^{13}C-NMR spectroscopy in SO_2 solution [116,117], and with selected solid examples by magic-angle spinning ^{13}C-NMR spectroscopy. These investigations confirm the formation of η^1-bonding of the arene at the mercury, with unsubstituted aryl carbon atoms being the strongly preferred site of mercury attachment [117].

$Hg_2(AsF_6)_2$, as well as $Hg(AsF_6)_2$, form complexes with NSF_3 of approximate composition $[Hg_2(NSF_3)_3](AsF_6)_2$ and $[Hg(NSF_3)_{3-4}](AsF_6)_2$ [86], but so far an unequivocal characterization by crystal structure determinations was not possible.

With PF_3 Hg_2^{2+} forms a yellow, SO_2-soluble 1:1 complex. On further ligand addition at low temperatures a colorless precipitate forms, probably $[Hg_2(PF_3)_2](AsF_6)_2$. When the volatiles are removed, the yellow solution is reformed and from this yellow crystals of $[Hg_2(PF_3)](AsF_6)_2$ are isolated [11].



(67)

The interaction of a variety of phosphines ($P(CF_3)_3$, PCl_3, $P(CF_3)Ph_2$, PPh_2Cl, PPh_3 and $P(OPh)_3$) with $Hg_2(AsF_6)_2$ was investigated by ^{31}P-NMR spectroscopy [91]. With $P(CF_3)_3$ no reaction was observed. $P(CF_3)Ph_2$ was added to Hg_2^{2+}, disproportionation occurs if the ratio $P(CF_3)Ph_2{:}Hg_2^{2+} > 1$:

$$\begin{tikzcd}
{[Hg_2(SO_2)_x](AsF_6)_2 + P(CF_3)Ph_2} \arrow[r, "-xSO_2"'] & {[Hg_2\{P(CF_3)Ph_2\}](AsF_6)_2} \arrow[d, "+P(CF_3)Ph_2"] \\
{[Hg\{P(CF_3)Ph_2\}_2](AsF_6)_2 + Hg} & {\{[Hg_2\{P(CF_3)Ph_2\}_2](AsF_6)_2\}} \arrow[l]
\end{tikzcd} \qquad (68)$$

With PPh_3 and $P(OPh)_3$ disproportionation occurs under all conditions.

With triphenylarsine, triphenylstibine, phosphine sulfides and phosphine selenides insoluble 1:1 complexes are formed, which were characterized by elemental analysis and vibrational spectroscopy. Excess of ligands also causes disproportionation [91].

$$[Hg_2(SO_2)_x](AsF_6)_2 + L \rightarrow [Hg_2L](AsF_6)_2 + x SO_2 \qquad (69)$$

$L = AsPh_3$, $SbPh_3$, $SPPh_3$, $SP(p\text{-}C_6H_4F)_3$, $SePPh_3$

Similarly to Cd^{2+}, the Hg^{2+} ion readily forms phosphine oxide complexes:

$$HgI_2 + 2AgAsF_6 + 3CH_2[PPh_2(O)]_2 \rightarrow [Hg\{(OPPh_2)_2CH_2\}_3](AsF_6)_2 + 2AgI \qquad (70)$$

The six-coordinate complex has been observed in solution [114].

4.4. Transition metals (Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II})

Although it was recognised many years ago that transition metal sulfur dioxide complexes, $[M(SO_2)_x](AsF_6)_2$, might open a route to an unprecedented coordination chemistry, even with extremely poor donor ligands [12], very little work has been done in this field. Due to their high reactivity even thermally unstable ligands can be added at low temperatures to the metal centers. Ligands with highly reactive dipolar multiple bonds will be stabilized. Thiazyl compounds $R\text{–}S{\equiv}N$ ($R = F$ [118,89], $(CF_3)_2NO$ [119,120]) are known to oligomerize and decompose quickly at r.t. In a dry atmosphere the hexathiazyl salts $[M(NSR)_6]^{2+}(AsF_6)_2$ can be stored indefinitely at r.t.

$$[M(SO_2)_x](AsF_6)_2 + 6RSN \rightarrow [M(NSR)_6(AsF_6)_2 + x SO_2 \qquad (71)$$

$M = Ni$, $R = F$ [121], $(CF_3)_2NO$ [122]; $M = Co$, $R = F$ [123,124]

$$[Ni(NSF)_6(AsF_6)_2 + x SO_2 \rightarrow [Ni(NSF)_{6-x}(OSO)_x](AsF_6)_2 + x NSF \qquad (72)$$

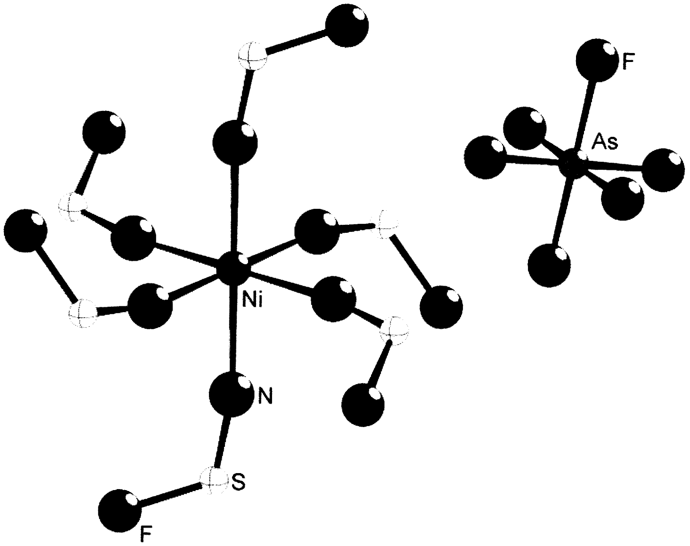


Fig. 26. Crystal structure of $[Ni(NSF)_6](AsF_6)_2$ [121].

$$[Ni(SO_2)_6](AsF_6)_2 + 4HNSO \rightarrow [Ni(HNSO)_4](AsF_6)_2 + 6SO_2 \tag{73}$$

Thiazyl fluoride is isoelectronic with SO_2, the structures of the two homoleptic octahedral nickel complexes $[Ni(NSF)_6](AsF_6)_2$ (Fig. 26) [121] and

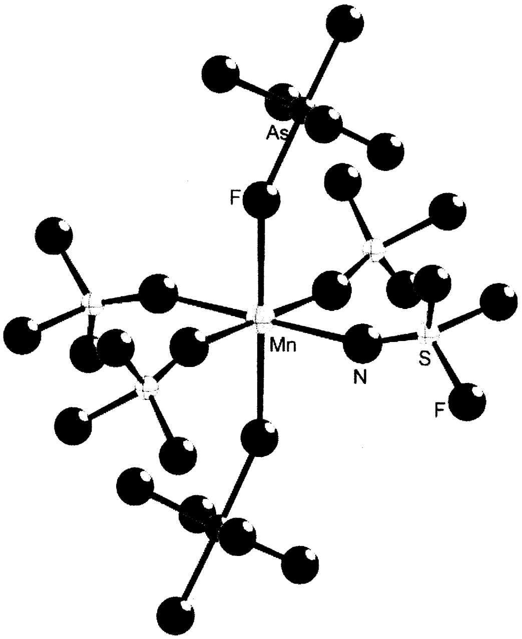


Fig. 27. Crystal structure of $[Mn(NSF_3)_4(FAsF_5)_2]$ [127].

$[Ni(OSO)_6](AsF_6)_2$ (Fig. 10) [78] are very similar. The stability of these complexes is in contrast to the stability of the free ligands; as discussed previously, the SO_2 complex will readily lose sulfur dioxide at r.t., however the NSF complexes are stable. In SO_2 solution at r.t. NSF is slowly partially exchanged and under these conditions the free ligand decomposes. Complexes with $x = 0–2$ were isolated (Scheme 72) with both isoelectronic ligands connected to one metal center. Due to random distribution the ligands cannot be distinguished by X-ray crystallography [125].

The very thermally-unstable aza-analogue of SO_2, thionylimide HNSO, is also stabilized at metal centers [126], but the structure of the complex is not known. The vibrational spectra show no distortion of the AsF_6^- ion from O_h symmetry.

Even with a large excess of thiazyl trifluoride, NSF_3, only four ligands add to the metal centers.

$$[M(SO_2)_x](AsF_6)_2 + NSF_3\ (\text{excess}) \rightarrow [M(NSF_3)_4(FAsF_5)_2] + xSO_2 \tag{74}$$

$$M = \text{Mn, Fe, Co, Ni, Cu [127]}$$

$$[Ni(SO_2)_6](AsF_6)_2 + L\ (\text{excess}) \rightarrow [NiL_6](AsF_6)_2 + 6SO_2 \tag{75}$$

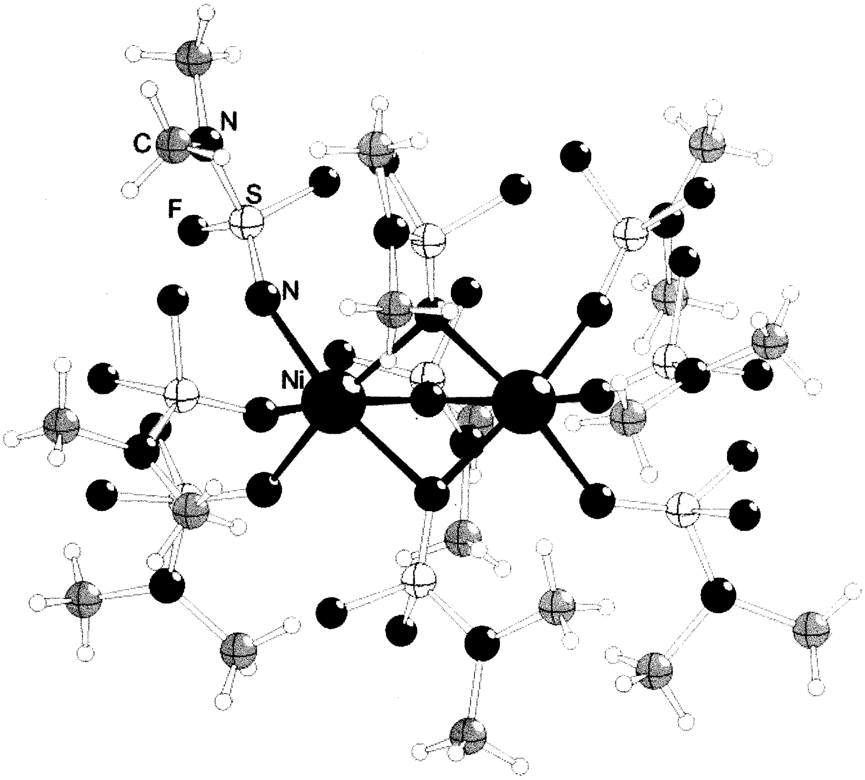


Fig. 28. Crystal structure of $[Ni_2(NSF_2NMe_2)_9](AsF_6)_4$ [128].

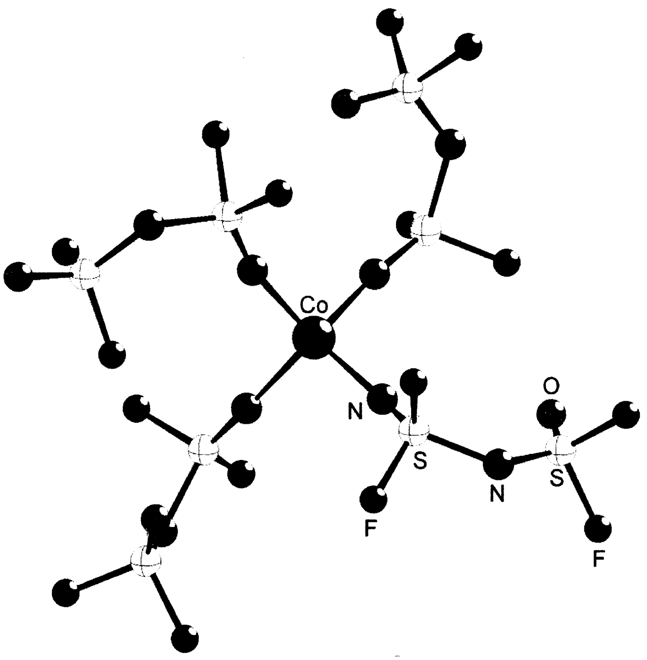


Fig. 29. Crystal structure of $[Co(NSF_2NS(O)F_2)_4](AsF_6)_2$ [129].

$$2[Ni(SO_2)_6](AsF_6)_2 + 9L \rightarrow [L_3Ni(\mu\text{-}L)_3NiL_3](AsF_6)_2 + 12SO_2 \quad L = NSF_2NMe_2\ [128] \tag{75a}$$

$$[Co(SO_2)_x](AsF_6)_2 + NSF_2NS(O)F_2\ (\text{excess}) \rightarrow [Co(NSF_2NS(O)F_2)_4](AsF_6)_2 \cdot SO_2 + (x-1)SO_2 \tag{76}$$

In the transition metal tetra(thiazyl trifluoride) complexes the metal centers are octahedrally coordinated by four thiazyl nitrogens and two fluorines from *trans*-coordinated hexafluoroarsenates [127]. An example of a typical structure, $[Mn(NSF_3)_4(FAsF_5)_2]$, is shown in Fig. 27.

Exchange of one of the sulfur-bonded fluorines in NSF_3 by a Me_2N group markedly enhances the donor properties of the thiazyl nitrogen. Furthermore, with Ni a homoleptic $[NiL_6]^{2+}$ complex is isolated when the ligand to metal ratio is 6 or higher [128]. From a 9:2 stoichiometry a dinuclear $[Ni_2L_9]^{4+}$ complex is isolated [128], in which two octahedra join a common face (Fig. 28). This is the first example where the nitrogen of a sulfur(VI)–nitrogen triple bond is in a bridging position [128]. In the homoleptic tetrahedral cobalt complex $[Co(N{\equiv}SF_2{-}N{=}S(O)F_2)_4]^{2+}$ the crystal structure determination (Fig. 29) shows the presence of a sulfur–nitrogen triple (138.9 pm), double (149.9 pm) and single bond (158.8 pm) in one ligand [129].

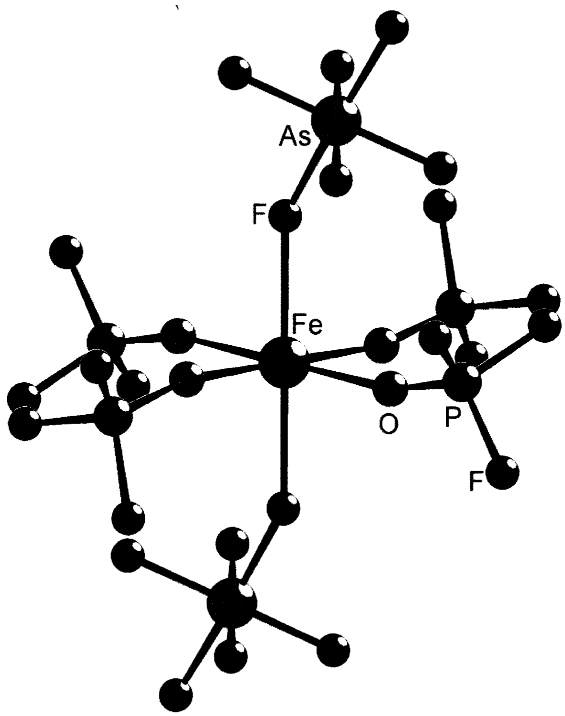


Fig. 30. Crystal structure of $[Fe(OPF_3)_4(FAsF_5)_2]$ [43].

As discussed in the previous sections various phosphine oxides and other phosphine chalcogenides react with metal hexafluoroarsenates and antimonates to give the corresponding complexes. OPF_3, isoelectronic with NSF_3, is only known to form stable adducts with SbF_5 [130,131], the strongest fluoro Lewis acid. The 'naked' transition metal centers add four ligands with formation of stable octahedrally coordinated complexes.

$$[M(SO_2)_x](AsF_6)_2 + OPF_3\ (\text{excess}) \rightarrow [M(OPF_3)_4(FAsF_5)_2] + xSO_2 \quad (77)$$

M = Mn, Ni [12,43], Fe, Co [43]

$$[M(SO_2)_x](AsF_6)_2 + OPF_2NMe_2\ (\text{excess}) \rightarrow [M((O)PF_2NMe_2)_4(FAsF_5)_2] + xSO_2$$

M = Co, Ni [43] (78)

$$[M(SO_2)_6](AsF_6)_2 + 2OP(NCO)_3 \rightarrow [M(OP(NCO)_3)_2](AsF_6)_2 + xSO_2 \quad (79)$$

M = Ni [12]

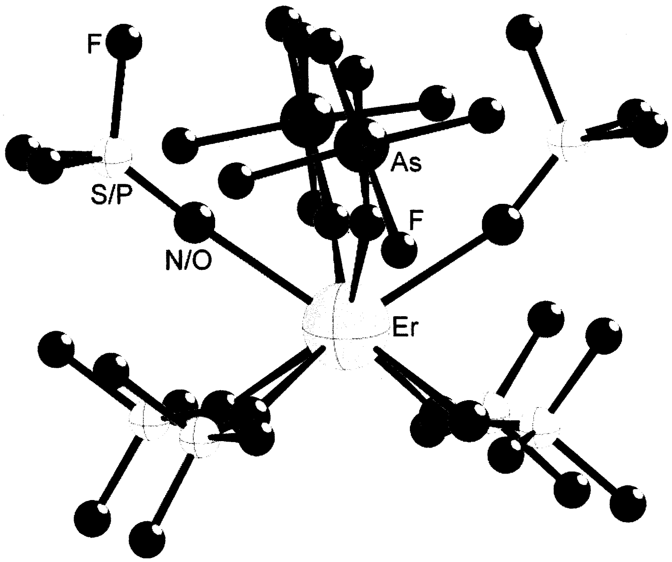


Fig. 31. Crystal structure of $[Er(ABF_3)_6(FAsF_5)_2](AsF_6)(ABF_3 = NSF_3, OPF_3)$ [42].

Crystal structure determinations of the OPF_3 complexes show the close relationship to the isoelectronic thiazyltrifluoride complexes (e.g. Fig. 30 [43]). Investigations of the coordination of $N \equiv SF_3 \leftrightarrow \overset{-2}{N} - \overset{+2}{S}F_3$ and $\overset{+1}{O} \equiv \overset{-1}{P}F_3 \leftrightarrow \overset{-1}{O} - \overset{+1}{P}F_3$ will help in the understand of the nature of the NS and OP multiple bonds in these systems.

4.5. Lanthanide metals

The few results obtained to date for exchange reactions with lanthanide sulfur dioxide complexes are promising for a fascinating chemistry. In a similar fashion to the reactions described for transition metals, weak, highly-fluorinated donor ligands can be readily introduced:

$$[Ln(SO_2)_x](AsF_6)_3 + NSF_3\ (\text{excess}) \rightarrow [Ln(NSF_3)_6(FAsF_5)_2](AsF_6) + xSO_2 \quad (80)$$

Ln = Sm, Er [42]

$$[Ln(SO_2)_x](AsF_6)_3 + OPF_3\ (\text{excess}) \rightarrow [Ln(OPF_3)_6(FAsF_5)_2](AsF_6) + xSO_2 \quad (81)$$

Ln = La, Er [42]

$$[La(SO_2)_x](AsF_6)_3 + OPCl_3\ (\text{excess}) \rightarrow [La(OPCl_3)_8(FAsF_5)](AsF_6)_2 + xSO_2 \quad (82)$$

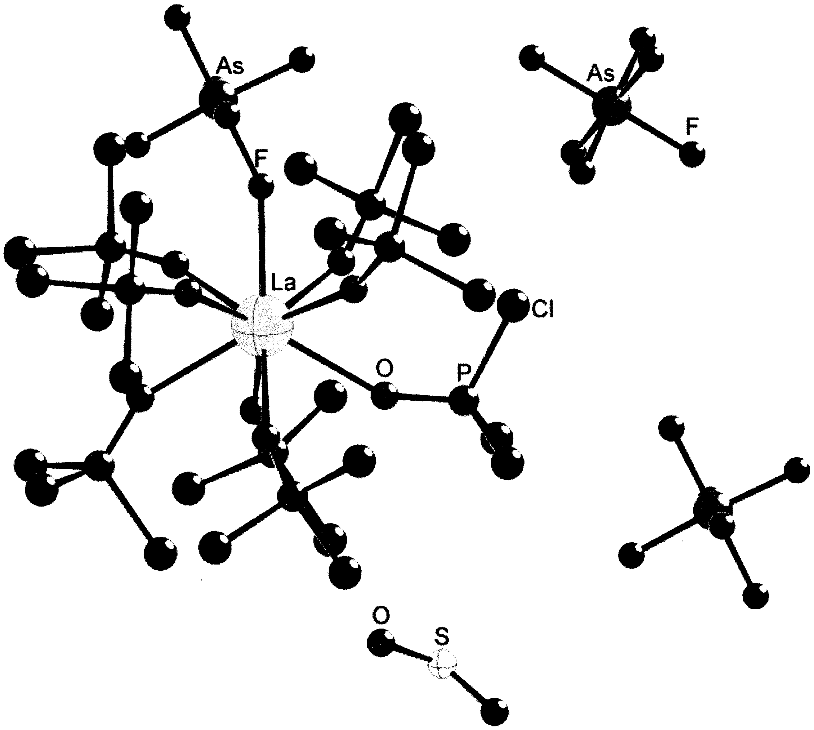


Fig. 32. Crystal structure of $[La(OPCl_3)_8(FAsF_5)](AsF_6)_2$ [77].

$$[Ln(SO_2)_x](AsF_6)_3 + CH_3CN\ (excess) \rightarrow [Ln(CH_3CN)_{8-9}](AsF_6)_3 \cdot nCH_3CN + xSO_2 \quad (83)$$

$Ln = La$, Sm [42,132]

A maximum of six NSF_3 and OPF_3 ligands were introduced [42]. At the eight-coordinate metal centers (Fig. 31) the ligands form a square antiprism, four NSF_3 (OPF_3) molecules occupy one face, while the other is formed by two additional ABF_3 ligands and two fluorine-bridged hexafluoroarsenates [77]. In $[La(OPCl_3)_8(FAsF_5)](AsF_6)_2$ (Fig. 32) the coordination number of the metal center is nine. In the tricapped trigonal prism the fluoride bridged $(FAsF_5)^-$ is in a capping position [77].

Lanthanide sulfur dioxide hexafluoroarsenates are converted to homoleptic acetonitrile complexes either by addition of an excess CH_3CN to SO_2 solutions of the appropriate complexes or by direct solvolysis of the SO_2 complexes in acetonitrile. Depending on the size of the metal centers coordination numbers eight or nine were observed [132].

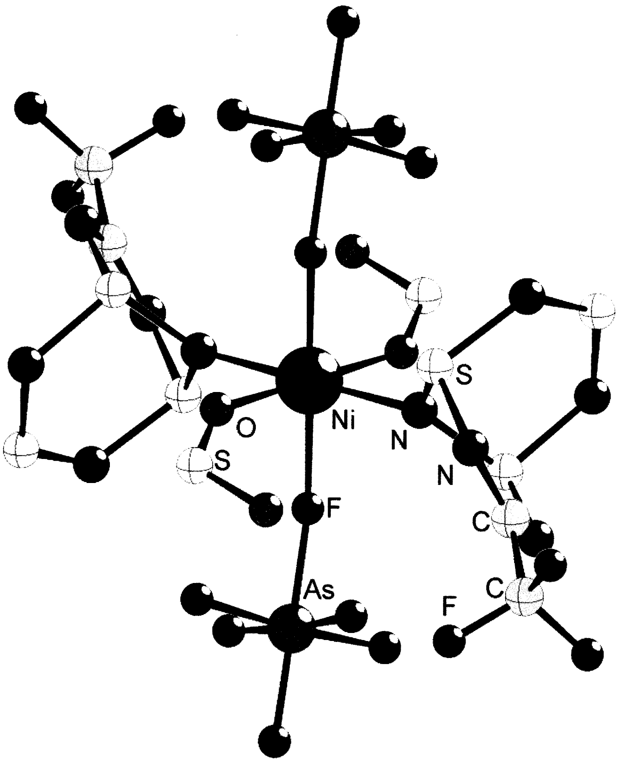


Fig. 33. Crystal structure of $[Ni(CF_3CN_4S_3)_2(OSO)_2(FAsF_5)_2]$ [133].

5. Summary and outlook

Since Gillespie's first report on the oxidation of mercury by AsF_5 in liquid SO_2 [2], coordination chemistry in this solvent has developed into an independent research area.

Metal ions in the $M^{n+}/SO_2/AF_6^-$ (A = As, Sb) system are almost 'naked' and this review article shows that even extremely weak donor ligands, thermally unstable ligands, multidentate heterocycles etc. may be added to the metal centers. Although several recent reports on 'better' anions for the generation of 'naked' cations have appeared in the literature, e.g. $[Sb(OTeF_5)_6]^-$ [17–19] and $[C_2B_{10}(CF_3)_{12}]^-$ [22], for most purposes the anions of choice are AsF_6^- and SbF_6^-, due to their ease of handling and preparation. Since there are so few research groups working in this area it is still very much in its infancy. As we previously discussed, there are no reports on the chemistry of the heavier Group 13 elements (Ga, In, Tl) in SO_2 and the coordination chemistry of the other main group element hexafluoroarsenates and antimonates have hardly been investigated. Reactions of Group 12 and Group 14 metal complexes with a variety of aromatic compounds [62,63,108,116,117], phosphines [49] and phosphine chalcogenides [49,64,113–115]

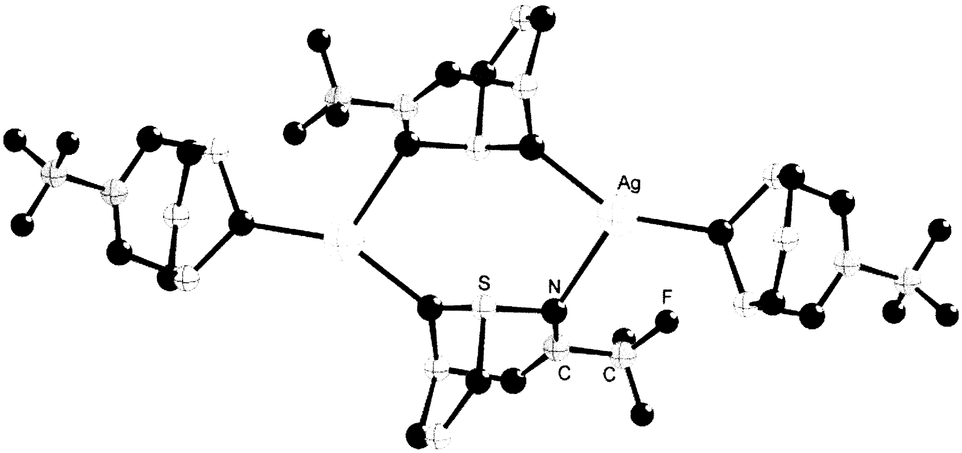
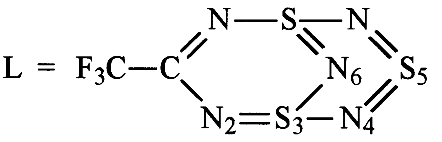


Fig. 34. Crystal structure of [$(CF_3CN_4S_3)Ag(\mu\text{-}CF_3CN_4S_3)_2Ag(CF_3CN_4S_3)](AsF_6)_2$ [133].

have been studied by multinuclear NMR spectroscopy. According to the Cambridge Crystal Structure Database no crystal structures of these compounds have been reported in the literature to date.

Reports on the chemistry of the d-block metals are restricted to Mn, Fe, Co, Ni and Cu but extension to other metals must be possible. The corresponding lanthanide complexes are very difficult to prepare [80] and the synthesis of this class of compounds needs to be improved.

The wide spectrum of ligands used gives a good impression of the further possibilities in this field of research. Reactions with multidentate polyelement heterocycles are particularly interesting. Simple MO-calculations of the electron density distributions show the various possible sites of metal attack at ligands, and the experimental results show that different metals make use of the different possibilities. The bicyclic compound L reacts with, for example $[Ni(SO_2)_6](AsF_6)_2$ to form $[NiL_2(OSO)_2(FAsF_5)_2]$ (Fig. 33). The metal attack at N_6, the site of the highest electron density, is as expected from theory. A binuclear complex, $[LAg(\mu\text{-}L)_2AgL](AsF_6)_2$ (Fig. 34) is formed with $AgAsF_6$. An eight-membered heterocycle is formed through bridging of N_2 and N_4 and the terminal ligands are bound at N_6 as in the nickel complex [133]. With $Hg(AsF_6)_2$ the primary attack also seems to be at N_6, however elimination of this nitrogen-bridge follows and the monocyclic $CF_3CN_4S_3^+$ is formed [134].



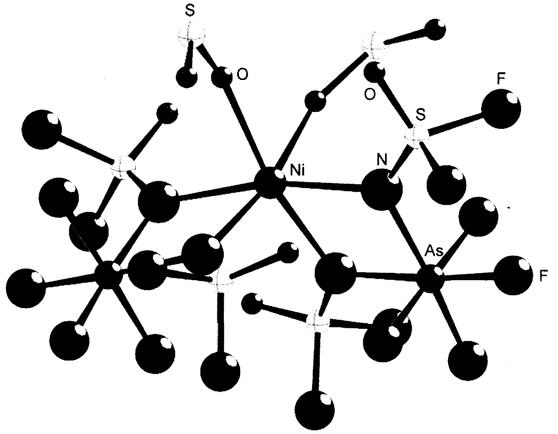


Fig. 35. Crystal structure of $[Ni\{AsF_4(NS(O)F_2)_2\}_2(OSO)_2]$ [134].

Catalysis is a further aspect of this chemistry; interaction of the ligands with the 'naked' metal centers leads to bond activation. It was previously discussed that the formation of $(CH_2O)_6$ from $(CH_2O)_3$ was catalysed by $AgAsF_6$ [101] and with Ag^+ as template, 4-crown-12 is produced from ethylene oxide [102]. The Si–N bond in $Me_3Si–NS(O)F_2$ is so highly activated by the metal centres that even a reaction with AsF_6^- occurs. The spiro complex $[Ni((NS(O)F_2)_2AsF_4)_2(OSO)_2]$ (Fig. 35) [135] was isolated from the reaction with $[Ni(SO_2)_6](AsF_6)_2$.

The chemistry of the hexafluoroarsenates and antimonates formed in SO_2 is not limited to this solvent. Further reactions can be carried out in inorganic solvents, e.g. $OPCl_3$ [43], or AsF_3 [51] or organic solvents, e.g. $MeNO_2$ [136,137] and CH_2Cl_2 [138]. Homoleptic solvates are formed in donor solvents such as MeCN or THF ($[M(CH_3CN)_x]^{m+}$; M = lanthanide [132], transition metal [43] or alkaline earth metal [43]; $[Ni(THF)_6](AsF_6)_2$ [43]) which can then be used as starting materials in organometallic chemistry.

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