

## The First Complexes of Cyanogen Halides with Silver(I): Crystal Structure of $[\text{Ag}(\text{NCCl})_2][\text{SbF}_6]^-$ \*

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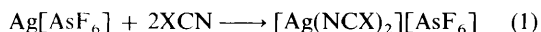
The reactions of  $\text{Ag}[\text{AsF}_6]$  or  $\text{Ag}[\text{SbF}_6]$  with  $\text{ClCN}$ ,  $\text{BrCN}$ , and  $\text{ICN}$  yield the complexes  $[\text{Ag}(\text{NCCl})_2][\text{AsF}_6]$ ,  $[\text{Ag}(\text{NCCl})_2][\text{SbF}_6]$ ,  $[\text{Ag}(\text{NCBr})_2][\text{AsF}_6]$ ,  $[\text{Ag}(\text{NCBr})_2][\text{SbF}_6]$ , and  $[\text{Ag}(\text{NCl})_2][\text{AsF}_6]$ . The salt  $[\text{Ag}(\text{NCCl})_2][\text{SbF}_6]$  was characterized by an X-ray single-crystal structure investigation. The cation is monomeric. The cyanogen halide is bonded to the silver through nitrogen, with  $\text{Ag}-\text{N}$  2.140(4) Å. The co-ordination geometry at silver is exactly linear.

The chemistry of cyanogen halides is extensive and varied. Several reactions of cyanogen chloride with silver halides have been reported. Treatment of  $\text{ClCN}$  with  $\text{AgF}^1$  or  $\text{AgF}_2^2$  results in the formation of fluorine-containing compounds such as  $\text{CF}_3\text{N}=\text{NCF}_3$ . The reaction of  $\text{Ag}_2\text{O}$  with  $\text{ClCN}$  yields  $\text{AgCl}$  and  $\text{AgNCO}^3$  while  $\text{ClCN}$  and  $\text{AgNCO}$  give polymeric  $(\text{NCNCO})_x^4$ .

Woolf<sup>5</sup> reported that, by mixing  $\text{AgClO}_4$  and  $\text{ICN}$  in benzene, a solid is formed immediately that contains  $\text{AgCN}$ ,  $\text{AgClO}_4$ , and  $\text{ICN}$ . To our knowledge, however, no adducts of  $\text{Ag}^+$  and cyanogen halides are known. We now report for the first time the preparation, properties, and structures of silver complexes containing cyanogen halides as ligands.

### Results and Discussion

In previous experiments we showed that ligands such as  $\text{NC}-\text{CN}^6$  or  $\text{NCS}-\text{SCN}^7$  are able to co-ordinate silver(I) through nitrogen; the products were polymeric cations, isolated as  $\text{AsF}_6^-$  salts. The experiments were conducted in liquid  $\text{SO}_2$  and we did not observe the formation of  $\text{AgCN}$  or  $\text{AgSCN}$  under these conditions. This prompted us to investigate the reactions between silver(I) and  $\text{ClCN}$ ,  $\text{BrCN}$ , or  $\text{ICN}$ . The three cyanogen halides react with  $\text{Ag}^+$  to form 1:2 complexes;  $\text{Ag}[\text{AsF}_6]$  and  $\text{Ag}[\text{SbF}_6]$  were used as starting materials [equation (1) ( $X = \text{Cl}, \text{Br}, \text{or I}$ )]. The formation of silver halides



was not observed. All the isolated silver complexes are colourless, crystalline solids that are stable at room temperature. They are formed in nearly quantitative yields.

The crystal structure determination of  $[\text{Ag}(\text{NCCl})_2][\text{SbF}_6]$  shows that the monomeric cation has crystallographically imposed inversion symmetry and is thus exactly linear at silver (Figure 1). The  $\text{Ag}-\text{N}$  bond length, 2.140(4) Å, is similar to that of 2.117(6) Å in the linearly co-ordinated polymeric  $[\text{Ag}(\text{NCS})_2]^+$ . The  $\text{Ag}-\text{N}-\text{C}$  bond angle of 164.3(4)° is

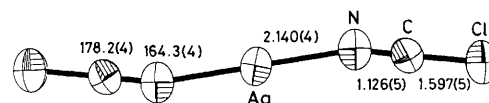


Figure 1. Thermal ellipsoid plot (50% level) of the  $[\text{Ag}(\text{NCCl})_2]^+$  cation, showing the atom labelling scheme and the bond lengths (Å) and angles (°).

somewhat larger than those of 152–159° in most related derivatives (see ref. 7 and refs. therein). The bond lengths are probably somewhat affected by libration; rigid-body corrections of +0.004, 0.013, and 0.016 Å for  $\text{Ag}-\text{N}$ ,  $\text{N}-\text{C}$ , and  $\text{C}-\text{Cl}$  were calculated, although the approximations involved may not be strictly applicable ( $R_{\text{lib}} 0.09$ ). Short  $\text{Ag} \cdots \text{F}$  contacts to  $\text{F}(1)$  and  $\text{F}(3)$  atoms (two of 2.770 and two of 2.774 Å) complete an irregular octahedral co-ordination at silver (Figure 2).

### Experimental

All reactions were performed under a dry nitrogen atmosphere or *in vacuo* using modified Schlenk-line techniques.<sup>8</sup> Sulphur dioxide was distilled immediately prior to use from  $\text{P}_4\text{O}_{10}$ . Infrared spectra were recorded using a Perkin-Elmer 180 spectrophotometer. The elemental microanalyses were carried out by Beller Laboratory, Göttingen. The salt  $\text{Ag}[\text{AsF}_6]$  was prepared by the literature method.<sup>8</sup>

**Preparations.**— $[\text{Ag}(\text{NCCl})_2][\text{AsF}_6]$  (1). Because the products are sensitive to daylight, the reaction was carried out in a flask wrapped in aluminium foil. A mixture of freshly prepared  $\text{Ag}[\text{AsF}_6]$  (2.36 g, 7.95 mmol) and  $\text{ClCN}$  (0.98 g, 15.94 mmol) was allowed to react in sulphur dioxide (30  $\text{cm}^3$ ); the  $\text{ClCN}$  and  $\text{SO}_2$  were condensed into a Schlenk apparatus *in vacuo* at liquid-air temperature. After warming to room temperature the solution was stirred for 2 h, filtered, and the  $\text{SO}_2$  removed *in vacuo*. The product was isolated in a glove-box. Yield: 3.24 g (97%) of a colourless solid. Single crystals were obtained when  $\text{SO}_2$  was removed under normal pressure (Found:  $\text{Ag}$ , 23.7.  $\text{C}_2\text{AgAsCl}_2\text{F}_6\text{N}_2$  requires  $\text{Ag}$ , 25.7%). I.r. in Nujol:  $\nu(\text{C}\equiv\text{N})$  2 250  $\text{cm}^{-1}$ .

$[\text{Ag}(\text{NCCl})_2][\text{SbF}_6]$  (2). The salt  $\text{Ag}[\text{SbF}_6]$  (2.99 g, 8.70 mmol) and  $\text{ClCN}$  (1.07 g, 17.4 mmol) were stirred in  $\text{SO}_2$  (30  $\text{cm}^3$ ) at room temperature for 12 h. During the reaction light was excluded. The resulting solution was colourless. After filtration the  $\text{SO}_2$  was removed *in vacuo* and a white solid of

\* Bis(cyanogen chloride-*N*)silver(I) hexafluoroantimonate(V).

Supplementary data available: complete bond lengths and angles, structure factors, and thermal parameters have been deposited with the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany. Any request for this material should quote the reference number CSD 52904 and a full literature citation.

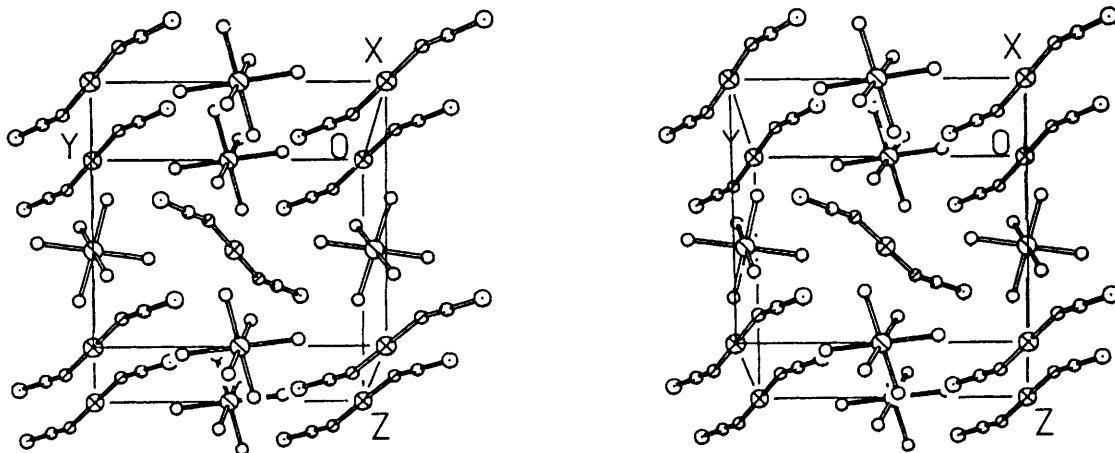


Figure 2. Stereo packing plot of  $[\text{Ag}(\text{NCCL})_2][\text{SbF}_6]$ . Radii arbitrary

composition (2) resulted (4.0 g, 98%). Suitable crystals for X-ray investigation were obtained when (2) was redissolved in  $\text{SO}_2$  and the solvent slowly removed under normal pressure (Found: C, 5.1; Cl, 14.7; N, 5.8.  $\text{C}_2\text{AgCl}_2\text{F}_6\text{N}_2\text{Sb}$  requires C, 5.15; Cl, 15.2; N, 6.0%). I.r. in Nujol:  $\nu(\text{C}\equiv\text{N})$  2 248  $\text{cm}^{-1}$ .

$[\text{Ag}(\text{NCBr})_2][\text{AsF}_6]$  (3). The salt  $\text{Ag}[\text{AsF}_6]$  (2.0 g, 6.74 mmol) and  $\text{BrCN}$  (1.42 g, 13.41 mmol) were stirred at room temperature in liquid  $\text{SO}_2$  (30  $\text{cm}^3$ ) for 2 h; the reaction mixture was filtered and the  $\text{SO}_2$  removed *in vacuo*. The resulting solid was recrystallized from liquid  $\text{SO}_2$  to yield colourless crystals (3.4 g, 98%) (Found: C, 4.9; Ag, 20.9; Br, 31.3; N, 5.2.  $\text{C}_2\text{AgAsBr}_2\text{F}_6\text{N}_2$  requires C, 4.7; Ag, 21.2; Br, 31.4; N, 5.5%). I.r. in Nujol:  $\nu(\text{C}\equiv\text{N})$  2 240  $\text{cm}^{-1}$ .

$[\text{Ag}(\text{NCBr})_2][\text{SbF}_6]$  (4). The same procedure as described for (3) was employed. The salt  $\text{Ag}[\text{SbF}_6]$  (2.00 g, 5.82 mmol) reacted with  $\text{BrCN}$  (1.23 g, 11.61 mmol) to yield (4) (3.18 g, 98.5%) (Found: C, 4.3; N, 4.9.  $\text{C}_2\text{AgBr}_2\text{F}_6\text{N}_2\text{Sb}_2$  requires C, 4.3; N, 5.05%). I.r. in Nujol:  $\nu(\text{C}\equiv\text{N})$  2 235  $\text{cm}^{-1}$ .

$[\text{Ag}(\text{NCI})_2][\text{AsF}_6]$  (5). The salt  $\text{Ag}[\text{AsF}_6]$  (2 g, 6.74 mmol) reacted with  $\text{ICN}$  (2.16 g, 14.12 mmol) in liquid  $\text{SO}_2$  (30  $\text{cm}^3$ ) to yield 3.95 g (97.3%) of colourless crystals after two recrystallizations from  $\text{SO}_2$  (Found: C, 4.3; Ag, 18.5; N, 4.8.  $\text{C}_2\text{AgAsF}_6\text{I}_2\text{N}_2$  requires C, 4.0; Ag, 17.9; N, 4.65%). I.r. in Nujol:  $\nu(\text{C}\equiv\text{N})$  2 215  $\text{cm}^{-1}$ .

**X-Ray Structure Determination of  $[\text{Ag}(\text{NCCL})_2][\text{SbF}_6]$ .**—*Crystal data.*  $\text{C}_2\text{AgCl}_2\text{F}_6\text{N}_2\text{Sb}$ ,  $M = 466.6$ , monoclinic, space group  $P2_1/n$ ,  $a = 7.779(3)$ ,  $b = 8.877(4)$ ,  $c = 8.240(4)$  Å,  $\beta = 113.34(3)^\circ$ ,  $U = 522.4$  Å<sup>3</sup> (by refinement of 2θ values of 30 reflections in the range 20–25°),  $Z = 2$ ,  $D_c = 2.97$  g  $\text{cm}^{-3}$ ,  $F(000) = 424$ , crystal size 0.5 × 0.4 × 0.3 mm,  $\mu(\text{Mo-K}\alpha) = 5.0$   $\text{mm}^{-1}$ .

*Data collection and processing.* Stoe-Siemens four-circle diffractometer, monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71069$  Å), 1 821 profile-fitted intensities<sup>9</sup> ( $2\theta_{\text{max}}$  50°), 911 unique ( $R_{\text{int}}$  0.024), 801 with  $F > 4\sigma(F)$  used for all calculations (program system SHELX 76, locally modified). Absorption correction based on  $\psi$  scans.

*Structure analysis and refinement.* Silver and Sb located from Patterson function, other atoms by tangent recycling. Anisotropic refinement of 68 parameters on  $F$  to  $R$  0.037,  $R'$  0.046; weighting scheme  $w^{-1} = \sigma^2(F) + 0.0005 F^2$ . Extinction

Table. Atomic co-ordinates ( $\times 10^4$ )

Atom	x	y	z
Ag	0	0	0
N	2 228(6)	−971(4)	−553(6)
C	3 419(7)	−1 696(5)	−545(7)
Cl	5 148(2)	−2 677(2)	−522(3)
Sb	0	5 000	0
F(1)	2 392(5)	5 475(5)	1 589(5)
F(2)	741(5)	5 516(4)	−1 802(4)
F(3)	−789(6)	6 962(3)	104(7)

correction of the form  $F_{\text{corr}} = F_c/[1 + xF_c^2/\sin^2\theta]^{0.25}$ , where  $x$  refined to  $4.0(7) \times 10^{-6}$ . Final atomic co-ordinates are given in the Table, bond lengths and angles of the cation in Figure 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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### References

- W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, 1962, **84**, 2337.
- J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *Inorg. Chem.*, 1967, **6**, 417.
- E. V. Zappi, *An. Asoc. Quim. Argent.*, 1933, **21**, 37.
- E. Mayer, *Monatsh. Chem.*, 1970, **101**, 834.
- A. A. Woolf, *J. Chem. Soc.*, 1954, 252.
- H. W. Roesky, H. Hofmann, J. Schimkowiak, P. G. Jones, K. Meyer-Bäse, and G. M. Sheldrick, *Angew. Chem.*, 1985, **97**, 403; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 417.
- H. W. Roesky, J. Schimkowiak, K. Meyer-Bäse, and P. G. Jones, *Angew. Chem.*, 1986, **98**, 998; *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1005.
- H. W. Roesky and M. Witt, *Inorg. Synth.*, 1986, **24**, 72.
- W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

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