

How Do Silver(I) Cations React with Hydrogen Cyanide? The Crystal Structure of $[\text{Ag}(\text{NCH})_2][\text{SbF}_6]$

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The reaction between Ag^+ and HCN in liquid sulphur dioxide leads to the linear silver(I) complex $[\text{Ag}(\text{NCH})_2]^+$, isolated as its $[\text{SbF}_6]^-$ salt.

The reaction between Ag^+ cations and cyanide is one of the best-known undergraduate experiments as a test for cyanide. The properties of the resulting AgCN are also well-known; the structure consists of linear chains with an $\text{Ag} \cdots \text{Ag}$ separation of 5.26 Å.¹ However, the reaction between AgSbF_6 and hydrogen cyanide in liquid sulphur dioxide leads to the unexpected formation of the co-ordination complex $[\text{Ag}(\text{NCH})_2][\text{SbF}_6]$.[†] The formation of the same cation in liquid hydrogen fluoride has been proposed,² but no product was isolated.

The X-ray structure analysis of $[\text{Ag}(\text{NCH})_2][\text{SbF}_6]$ shows an almost linear cation (Figure 1).[‡] The co-ordination geometry

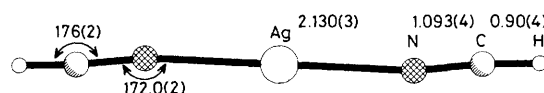


Figure 1. The $[\text{Ag}(\text{NCH})_2]^+$ cation in the crystal of its $[\text{SbF}_6]^-$ salt (radii arbitrary), showing independent bond lengths (Å) and angles (°).

at silver is exactly linear, with $\text{Ag}-\text{N}$ 2.130(3) Å; this agrees well with the 2.117(6) Å in the linearly co-ordinated polymeric $[\text{Ag}(\text{NCSSCN})]^+$ (ref. 3) and the 2.140(4) Å in the linear $[\text{Ag}(\text{NCCI})_2]^+$.⁴ The $\text{N}-\text{C}$ bond is rather short at 1.093(4) Å; it may be affected by libration. Four $\text{Ag} \cdots \text{F}$ contacts of 2.800 Å complete an irregular octahedral geometry at silver.

As far as we are aware, this is the first silver complex of the HCN ligand to be isolated and structurally characterized.

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Further details of the structure determination (atomic co-ordinates, complete bond lengths and angles, structure factors, and temperature factors) have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 52945. Atomic co-ordinates, bond lengths and angles, and thermal parameters have also been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

[†] 2.06 g AgSbF_6 were cooled to -186°C in a Schlenk vessel and HCN (0.65 g) and liquid SO_2 (30 ml) were condensed into the vessel. After slow warming to room temperature, the mixture was stirred for 20 h in the dark. Excess HCN and SO_2 were removed *in vacuo*. The crude product was recrystallized twice from SO_2 , giving crystals suitable for X-ray diffraction. The colourless crystals disintegrate when the last traces of SO_2 are removed, but they contain no solvent of crystallization. I.r. spectrum (KBr mull): 3200, 2140 cm^{-1} for $\nu(\text{C}-\text{H})$ and $\nu(\text{C}=\text{N})$, respectively [cf. 2178 cm^{-1} for $\nu(\text{C}\equiv\text{N})$ in AgCN]. Satisfactory elemental analyses were obtained. ^1H N.m.r.: δ 4.23 (s, $^1J_{\text{CH}}$ 280.9 Hz); ^{13}C n.m.r.: δ 111.03; ^{15}N n.m.r.: δ -157.8 p.p.m. (relative to ext. MeNO_2) ($^2J_{\text{NH}}$ 10.4 Hz).

[‡] Crystal data: $\text{C}_2\text{H}_2\text{AgF}_6\text{N}_2\text{Sb}$, $M = 397.7$, orthorhombic, space group $Pn\bar{m}$, $a = 5.226(1)$, $b = 12.278(2)$, $c = 6.927(1)$ Å, $U = 444.4$ Å³ (by refinement of 2 θ values of 50 reflections in the range 20–23°), $Z = 2$, $D_c = 2.97$ g cm^{-3} , $F(000) = 360$, crystal size 0.7 × 0.4 × 0.15 mm, $\mu(\text{Mo}-K_\alpha) = 5.3$ mm^{-1} . Data were collected using a Stoe-Siemens four-circle diffractometer, monochromated $\text{Mo}-K_\alpha$ radiation ($\lambda = 0.71069$ Å), 1806 profile-fitted intensities⁶ ($2\theta_{\text{max}}$ 55°), 551 unique reflections (R_{int} 0.012), 506 with $F > 4\sigma(F)$ used for all calculations (program system SHELX, locally modified by the author). Absorption correction based on ψ -scans; transmissions 0.43–0.99. Ag and Sb located from Patterson method; C, N, and F atoms from subsequent tangent recycling (intensity distribution strongly pseudo- B); H atom from plot of difference electron density after high-angle refinement. Non-H atoms refined anisotropically on F to $R = 0.022$, $R_w = 0.025$; weighting scheme $w^{-1} = \sigma^2(F) + 0.00015 F^2$. Extinction correction of the form $F_{\text{corr}} = F_c/[1 + xF_c^2/\sin 2\theta]^{0.25}$, where x refined to $4.0(4) \times 10^{-6}$. 40 Parameters, S 2.0, max. shift/e.s.d. 0.002, max. residual electron density 0.4 e Å⁻³. Special positions: Ag on 0.5, 0, 0.5 (symmetry 2/m), Sb on 0, 0, 0 (2/m), N, C, H in $x, y, 0.5$ (m), F1 in $x, y, 0$ (m). The anion (not shown) displays the usual octahedral geometry, with $\text{Sb}-\text{F}$ 1.859, 1.863 Å.