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Structure of Hexakis(acetonitrile)nickel(II) Hexafluoroantimonate(V)

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Abstract. $[Ni(NCCH_3)_6][SbF_6]_2$, $M_r = 776.5$, rhombohedral, $R\bar{3}$, $a = 8.764(2)$Å, $\alpha = 80.92(2)°$, $V = 650.3$ Å^3, $Z = 1$, $D_x = 1.983$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 30.8$ cm^{-1}, $F(000) = 370$, $T = 293(1)$ K, final $R = 0.031$, $wR = 0.039$ for 783 observed reflections $[I > 3\sigma(I)]$. The structure consists of discrete $[Ni(NCCH_3)_6]^{2+}$ cations and $[SbF_6]^-$ anions. The Ni (on $\bar{3}$ position) is octahedrally coordinated by the six nitrogens of the acetonitrile ligands [Ni—N distance 2.075(3) Å], whilst Sb (on threefold axis) has six fluorines at distances 1.825(4) and 1.827(4) Å respectively.

Introduction. Metal(II) hexafluoroantimonates of the type $MF_2.2SbF_5$ where M is Sn (Birchall, Dean & Gillespie, 1971), Mn, Fe, Ni (Dean, 1975) and Mg, Cr, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb (Gantar, Leban, Holloway & Frlec, 1987) have been prepared and characterized. A single-crystal X-ray study of AgF$_2$.-2SbF$_5$ has shown that it contains Ag^{2+} ions in planar coordination with two Ag—F distances at 2.09 and 2.13 Å and two further atoms at 2.43 Å completing a distorted octahedron. The F atoms are associated with distorted [SbF$_6$]$^-$ octahedra in the structure (Gantar, Leban, Holloway & Frlec, 1987).

Recently, we have shown that dissolution of some metal(II) hexafluoroantimonates (metal = M = Cr, Fe, Co, Ni, Cu, Cd, Hg) in acetonitrile gives rise to ternary adducts of formula $MF_2.2SbF_5.xCH_3CN$ which can be isolated from the solutions. Vibrational spectroscopic data have shown that the acetonitrile in these adducts is coordinated *via* the N (Gantar, Leban, Frlec, Russell & Holloway, in preparation).

Although a variety of fluoro compounds containing coordinated acetonitrile have been reported (*e.g.* Berry, Prescott, Sharp & Winfield, 1977; Halstead, Eller & Eastman, 1979; Hathaway, Holah & Underhill, 1962; Holloway, Laycock & Bougon, 1984) little is known about their crystal structures. Only one simple fluoride structure, WSF$_4$.CH$_3$CN (Holloway, Kaučič & Russell, 1983), appears to have been studied, while others such as [Re(CH$_3$CN)$_3$(CO)$_3$][BF$_4$] (Chan, Isaacs & Graham, 1977), [Rh(CH$_3$CN)(PPh$_3$)$_3$][BF$_4$] (Pimblett, Garner & Clegg, 1985) and Co(CH$_3$CN)$_2$(PO$_2$F$_2$)$_2$ (Begley, Dove, Hibbert, Logan, Nunn & Sowerby, 1985) are more complex.

Details of the synthesis and spectroscopy of [Ni-(NCCH$_3$)$_6$][SbF$_6$]$_2$ and its relatives, together with X-ray single-crystal data for some of the compounds, will be published separately (Gantar, Leban, Frlec, Russell & Holloway, in preparation).

Experimental. Solid NiF$_2$.2SbF$_5$, prepared as described previously (Gantar, Leban, Holloway & Frlec, 1987), was loaded into a pre-dried and fluorinated Pyrex tube and dried acetonitrile was introduced by distillation.

Pale violet single crystals were grown from the violet-coloured solution by slow evaporation of the solvent. Suitable crystals were transferred into pre-fluorinated Pyrex capillaries and sealed under vacuum for the structure determination.

Preliminary Weissenberg photographs suggested the space group $R3$ or $R\bar{3}$, and the latter was borne out by a successful structure analysis. Cell dimensions were obtained by a least-squares fit from angular settings of 50 reflections ($7 < \theta < 11°$) centred on a diffractometer (Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å). A prismatic pale violet crystal ($0.22 \times 0.28 \times 0.32$ mm) was used for data collection on an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation, graphite monochromator). Reflections were scanned in the ω–2θ mode with a variable scan rate {2θ scan width, $(0.8 + 0.2\tan\theta)°$; scan rate ($°\text{min}^{-1}$), min. $= 5.6$, max. $= 16.7$; background, $\frac{1}{4}$ of the scan time at each of the scan limits; $[(\sin\theta)/\lambda]_{max} = 0.70\,\text{Å}^{-1}$; max. scan time (s) $= 60$; aperture (mm), $2.5 + 0.9\tan\theta$; six reference reflections for orientation and intensity checks}. Out of 5848 measured reflections ($\pm h$, $\pm k$, $-l$) 1842 were unique (mean discrepancy on $I = 0.03$); 783 reflections were classified as observed $[I > 3\sigma(I)]$ with $h-8/9$, $k-7/9$, l $1/13$. The data were corrected for variation in reference reflections (intensity decrease, 0.8%), Lorentz and polarization effects. An exact absorption correction based on the equations of the six crystal faces was also applied (max. and min. transmission, 0.25, 0.17%). A Patterson function suggested the placing of Ni at a $\bar{3}$ position and Sb at a threefold axis (0.333, 0.333, 0.333), and the positions of F, N and C atoms were found in the subsequent electron density map. Atom parameters were then refined by full-matrix least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$, where the weighting w was chosen to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin\theta)/\lambda$ and $|F_o|$. A difference synthesis revealed the 3 H atoms of the methyl group as discrete peaks close to the expected positions. The positions of hydrogens with a common isotropic temperature factor were included in a further refinement with bond-length constraints for bonds C–H and H–H. Non-hydrogen atoms were refined anisotropically. An empirical isotropic extinction parameter X was refined to 0.0143 (4) (Sheldrick, 1976) with the final $R = 0.031$ and $wR = 0.039$; the final weighting scheme was $w = [\sigma^2(F_o) + 0.001F_o^2]^{-1}$. Maximum and minimum values of electron density in a final difference map were between 0.59 and $-0.43\,\text{e\,Å}^{-3}$. The average shift/e.s.d. in the last cycle was 0.11 with a maximum of 0.94 for y of H(1). Scattering factors for neutral Sb, Ni, F, N, C and H were those included in SHELX76 (Sheldrick, 1976).

Calculations were performed on a DEC 10 computer at RCU, Ljubljana, and on a VAX-CLUSTER, University Computer Centre, Leicester. The DATCOR program of XRAY80 (Stewart, 1980) was used for data

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å²)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}$; $U_{iso} = 0.118$ (7) Å² (for H).

	x	y	z	U_{eq}
Ni	0	0	0	0.0363 (3)
Sb	0.32906 (3)	$= x$	$= x$	0.0491 (2)
F(1)	0.2512 (7)	0.5207 (5)	0.3860 (6)	0.162 (4)
F(2)	0.1380 (5)	0.2686 (7)	0.4042 (7)	0.158 (4)
C(1)	0.4864 (6)	−0.2069 (8)	0.1439 (6)	0.065 (3)
C(2)	0.3334 (5)	−0.1382 (5)	0.1014 (4)	0.046 (2)
N	0.2164 (4)	−0.0852 (4)	0.0699 (4)	0.048 (2)
H(1)	0.481 (6)	−0.267 (6)	0.234 (5)	
H(2)	0.563 (6)	−0.258 (5)	0.073 (5)	
H(3)	0.552 (5)	−0.135 (6)	0.177 (6)	

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ni(NCCH$_3$)$_6^{2+}$ octahedron

Ni–N, N^i, N^{ii}, N^{iii}, N^{iv}, N^v	2.075 (3)	N–Ni–N^{ii}	91.5 (1)
C(2)–N	1.114 (5)	N–Ni–N^{iv}	88.5 (1)
C(1)–C(2)	1.460 (6)	C(1)–C(2)–N	179.5 (4)
C(1)–H(1)	0.88 (4)	Ni–N–C(2)	175.5 (3)
C(1)–H(2)	0.95 (5)	C(2)–C(1)–H(1)	113 (3)
C(1)–H(3)	1.01 (6)	C(2)–C(1)–H(2)	122 (3)
		C(2)–C(1)–H(3)	117 (3)
		H(1)–C(1)–H(2)	108 (4)
		H(1)–C(1)–H(3)	94 (4)
		H(2)–C(1)–H(3)	99 (4)

SbF$_6^-$ octahedron

Sb–F(1), F(1^{ii}), F(1^{iv})	1.825 (4)	F(1)–Sb–F(2)	87.9 (3)
Sb–F(2)–F(2^{ii}), F(2^{iv})	1.827 (4)	F(1)–Sb F(1^{ii})	93.3 (3)
		F(1)–Sb–F(2^{ii})	87.1 (3)
		F(1)–Sb–F(2^{iv})	178.7 (3)
		F(2)–Sb–F(2^{ii})	91.7 (3)

Symmetry code: (i) $-x$, $-y$, $-z$; (ii) y, z, x; (iii) $-y$, $-z$, $-x$; (iv) z, x, y; (v) $-z$, $-x$, $-y$.

reduction. The structure was also used as a test example for SHELXS86 automatic Patterson interpretation (Sheldrick, 1986).

Discussion. The final atomic coordinates are listed in Table 1* and relevant distances and angles are given in Table 2. Fig. 1 shows a view of the [Ni(NCCH$_3$)$_6$]$^{2+}$ octahedron, and Fig. 2 a stereoview of the unit-cell contents. The crystal structure is built up from discrete [Ni(NCCH$_3$)$_6$]$^{2+}$ cations and [SbF$_6$]$^-$ anions.

Space-group constraints require the [Ni-(NCCH$_3$)$_6$]$^{2+}$ to occupy the positions 1(a) (symmetry $\bar{3}$), thus forcing a nearly ideal octahedral arrangement of six nitrogens around the nickel atom. The Ni–N distance [2.075 (3) Å] is slightly longer than the 2.054 (5) Å found in the similar compound [Ni-(NSF)$_6$][AsF$_6$]$_2$ (Hartmann, Jones, Mews & Sheldrick, 1980).

The distances C(2)–N [1.114 (5) Å] and C(1)–C(2) [1.460 (6) Å] within the acetonitrile ligand are typical for bonds of the type $-\text{C}{\equiv}\text{N}$: and C($sp^3$)–C($sp$),
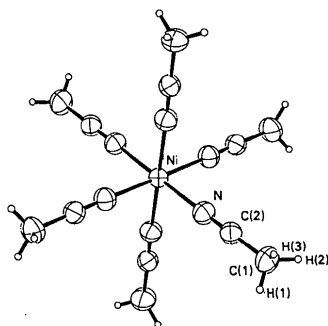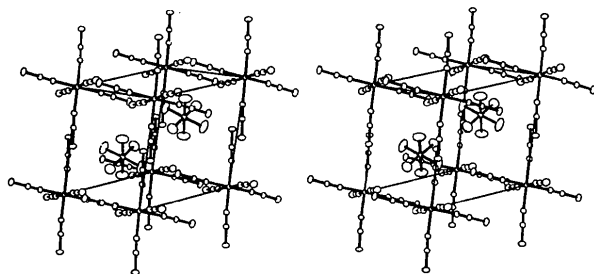
Fig. 1. A view of the $[Ni(NCCH_3)_6]^{2+}$ entity.

Fig. 2. A stereoview (Johnson, 1965) showing the crystal packing. H atoms were omitted for clarity.

respectively. The angles Ni—N—C(2) [175·5 (3)°] and N—C(2)—C(1) [179·5 (4)°] are also very close to the ideal value of 180°.

The $[SbF_6]^-$ octahedra exhibit C_3 symmetry with three equivalent Sb—F(1) and Sb—F(2) distances of 1·825 (4) and 1·827 (4) Å respectively. The angles F—Sb—F vary from 93·3 (3) to 87·9 (3)°. This distortion is probably due to ionic interactions between the structural units.

No significant intermolecular contacts were observed.

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Coordination of Thioether to the Hard Metals Ti^{IV} and Pb^{II}

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Abstract. Trichloro(1,5-dithiacyclooctan-3-olato-*O,S,S'*)titanium(IV), (1), [Ti(C$_6$H$_{11}$OS$_2$)Cl$_3$], $M_r =$ 317·53, $Pn2_1a$, $a = 12·852$ (4), $b = 12·177$ (5), $c =$ 7·584 (3) Å, $V = 1187$ (1) Å^3, $Z = 4$, $D_m(298 K) =$ 1·73, $D_x(130 K) = 1·78$ g cm^{-3}, Mo $K\alpha$, $\lambda =$ 0·71069 Å, $\mu = 17·0$ cm^{-1}, $F(000) = 640$, $T = 130$ K, $R = 0·028$, 1094 unique reflections. Bis(1,5-dithia-cyclooctan-3-ol-*O,S,S'*)dinitratolead(II), (2), [Pb(C$_6$-H$_{12}$OS$_2$)$_2$(NO$_3$)$_2$], $M_r = 659·78$, $P2_1/a$, $a = 13·550$ (2), $b = 10·732$ (1), $c = 14·073$ (1) Å, $\beta = 96·49$ (1)°, V

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