Spectroscopic Studies of *trans*-Bis(hexafluoroarsenato)tetrakis(thiazyl trifluoride)metal(II) Complexes (M = Mn, Fe, Co, Ni, or Cu); Crystal Structure of the Manganese(II) Complex: † an Example of Exceptionally Short N–S Bonds and of AsF_6^- as a Unidentate Ligand

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The i.r. spectra of the series $[M(NSF_3)_4(AsF_6)_2]$ (M = Mn, Fe, Co, Ni, or Cu) indicate that the compounds are isostructural, with *trans*-AsF_6 groups co-ordinated to the metal atom, and N–S bonds appreciably stronger than in free NSF_3. This is confirmed by the crystal structure of *trans*-$[Mn(NSF_3)_4(AsF_6)_2]$. It crystallises in the monoclinic space group $P2_1/n$, with a = 7.496(4), b = 10.378(5), c = 13.979(6) Å, β = 94.33(3)°, and Z = 2. The structure was refined to R = 0.048 for 1 226 diffractometer data. The metal ion is octahedrally co-ordinated, with Mn–$N_{av.}$ 2.187, Mn–F 2.193(4), and N–$S_{av.}$ 1.365 Å.

WE have reported the preparation of metal thiazyl trifluoride complexes $[M(NSF_3)_4(AsF_6)_2]$ from $M[AsF_6]_2$ and NSF_3 in liquid sulphur dioxide.[1] We present here a structural investigation of the series (M = Mn, Fe, Co, Ni, or Cu) by means of i.r. spectroscopy, and the crystal structure of the manganese(II) complex. Unusual features of these complexes are the co-ordination of the AsF_6 groups to the metal atom, and the shortening of the NS triple bond on co-ordination, which results in the shortest known NS bond and possibly the shortest bond involving a second-row element.

EXPERIMENTAL

The complexes $[M(NSF_3)_4(AsF_6)_2]$ (M = Mn, Fe, Co, Ni, or Cu) were prepared by reaction of the corresponding $[M(SO_2)_2(AsF_6)_2]$ complexes with NSF_3; the SO_2 complexes were prepared [2] by the action of AsF_5 on the powdered metal in liquid SO_2, followed by removal of AsF_3 and excess of SO_2 under vacuum at −20 °C.

Preparation of $[M(NSF_3)_4(AsF_6)_2]$.—Solvent SO_2 (*ca.* 5 cm^3) and NSF_3 (30 mmol) were condensed at −196 °C onto the appropriate SO_2 complex (3—4 mmol) in an evacuated vessel. After being allowed to warm up slowly, the mixture was stirred for 5 h at room temperature, and the excess of SO_2 and NSF_3 then pumped off. A quantitative yield of the analytically pure complex remained in the flask. The complexes may be recrystallised out of SO_2 or an SO_2ClF–SO_2 mixture. Analytical data are summarised in Table 1.

TABLE 1

Analytical data and melting/decomposition temperatures for $[M(NSF_3)_4(AsF_6)_2]$

M	M.p. (θ_c/°C)	Analysis (%) * As	F	N	S
Mn	226	17.8 (17.7)	53.4 (54.0)	6.55 (6.65)	15.4 (15.2)
Fe	172	17.8 (17.7)	53.5 (53.9)	6.50 (6.60)	15.3 (15.2)
Co	173	17.3 (17.6)	53.2 (53.7)	6.65 (6.60)	15.4 (15.1)
Ni	*ca.* 150	(17.6)	(53.7)	6.70 (6.60)	15.4 (15.1)
Cu	187	17.7 (17.5)	53.6 (53.4)	6.45 (6.55)	15.5 (15.0)

* Calculated values are given in parentheses.

X-*Ray Structural Analysis*.—The preparation of $[Mn(NSF_3)_4(AsF_6)_2]$ afforded colourless crystals suitable for data collection. Intensities were measured on a Stoe four-circle diffractometer with monochromated Mo-K_α radiation and a crystal 0.55 × 0.7 × 0.25 mm (sealed in a Lindemann-glass capillary because of extreme sensitivity to oxygen and moisture). A total of 1 538 intensities were measured in the range $3 < 2\theta < 45°$; after application of Lorentz, polarization, and empirical absorption corrections, averaging equivalent reflections gave 1 414 unique data, 1 228 of which with $F > 4\sigma(F)$ were used for all calculations.

TABLE 2

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mn	0	0	0
As	−3 085(1)	2 573(1)	−1 148(1)
F(1)	−1 989(5)	1 126(4)	−876(3)
F(2)	−4 957(6)	1 927(5)	−783(5)
F(3)	−4 183(7)	3 984(4)	−1 393(5)
F(4)	−1 155(7)	3 166(6)	−1 460(6)
F(5)	−2 510(8)	3 057(6)	−18(4)
F(6)	−3 658(9)	2 016(7)	−2 236(4)
F(13)	−4 743(5)	767(5)	1 550(4)
F(21)	3 691(5)	3 355(4)	1 096(3)
F(12)	−3 001(7)	−43(5)	2 779(3)
F(22)	2 324(6)	3 828(4)	−330(3)
F(11)	−2 613(6)	1 969(4)	2 287(4)
F(23)	844(5)	4 012(4)	978(3)
N(1)	−1 588(7)	187(5)	1 248(4)
N(2)	1 466(6)	1 743(5)	440(4)
S(1)	−2 772(2)	646(2)	1 852(1)
S(2)	1 979(2)	3 010(1)	527(1)

Crystal data. $As_2F_{24}MnN_4S_4$, Monoclinic, $P2_1/n$, a = 7.496(4), b = 10.378(5), c = 13.979(6) Å, β = 94.33(3)°, U = 1 084.4 $Å^3$, Z = 2, D_c = 2.589 g cm^{-3}, $F(000)$ = 798, Mo-K_α radiation, λ = 0.710 69 Å, μ = 41.8 cm^{-1}.

The structure was solved by automatic direct methods; the best E map showed peaks corresponding to Mn, As, and S atoms. Other atoms were obtained from subsequent difference syntheses. Refinement, with all atoms anisotropic, and complex, neutral-atom scattering factors, proceeded to $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$ = 0.052, R = 0.048. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.001F^2$. Results are given in Tables 2—4. Thermal parameters and observed

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† *trans*-Bis(hexafluoroarsenato)tetrakis(sulphur trifluoride nitride-*N*)manganese(II).

and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22921 (11 pp.).*

Spectroscopic Data.—Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer.

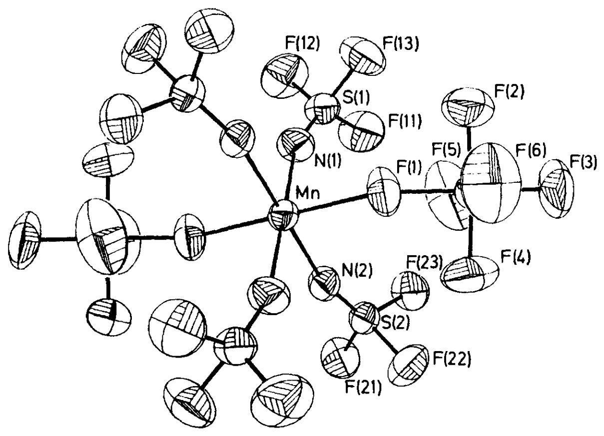
TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

Mn–F(1)	2.193(4)	Mn–N(1)	2.193(6)
Mn–N(2)	2.181(5)		
As–F(1)	1.740(4)	As–F(2)	1.669(5)
As–F(3)	1.701(5)	As–F(4)	1.660(6)
As–F(5)	1.683(6)	As–F(6)	1.654(6)
S(1)–N(1)	1.357(6)	S(2)–N(2)	1.373(5)
S(1)–F(11)	1.503(5)	S(2)–F(21)	1.501(4)
S(1)–F(12)	1.501(5)	S(2)–F(22)	1.507(5)
S(1)–F(13)	1.511(4)	S(2)–F(23)	1.511(4)

RESULTS AND DISCUSSION

The crystal structure shows that the metal ion is co-ordinated octahedrally by four NSF_3 and two *trans* AsF_6^- ligands. The metal lies on the special position (0,0,0). As far as we are aware, this is the first instance of AsF_6^- functioning as a ligand. The bond lengths and angles of the AsF_6 group correspond closely to those of the unco-ordinated AsF_6^- ion,[3,4] except for As–F (1) 1.740(4) (bridging), *cf.* average non-bridging As–F 1.673 Å. The Mn–F distance is 2.193(4) Å; this may be compared with 2.14 Å in MnF_2.[5] The average Mn–N bond length is 2.187 Å, thus completing an approximately octahedral geometry at the metal atom (the maximum deviation from 90° angles at Mn is 1.3°). The Mn–N–S and Mn–F–As angles deviate surprisingly far from linearity.



The complex $[Mn(NSF_3)_4(AsF_6)_2]$ showing 50% probability thermal ellipsoids

The N–S and S–F bonds are considerably shorter than in the free ligand, although the N–S–F angles are not greatly affected (see below). The N–S bond appears to be the shortest yet reported, and should not be significantly affected by libration, because the thermal motion of the N and S atoms approximates to isotropic.

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

F(1)–Mn–N(1)	90.6(2)	F(1)–Mn–N(2)	91.3(2)
N(1)–Mn–N(2)	89.7(2)		
F(1)–As–F(2)	88.9(2)	F(1)–As–F(3)	178.8(3)
F(2)–As–F(3)	90.1(2)	F(1)–As–F(4)	88.3(2)
F(2)–As–F(4)	176.6(3)	F(3)–As–F(4)	92.6(3)
F(1)–As–F(5)	88.2(3)	F(2)–As–F(5)	89.7(3)
F(3)–As–F(5)	91.1(3)	F(4)–As–F(5)	88.3(3)
F(1)–As–F(6)	89.2(3)	F(2)–As–F(6)	88.5(3)
F(3)–As–F(6)	91.6(3)	F(4)–As–F(6)	93.4(4)
F(5)–As–F(6)	176.8(3)		
Mn–F(1)–As	150.6(2)		
Mn–N(1)–S(1)	161.1(4)	Mn–N(2)–S(2)	162.0(3)
N(1)–S(1)–F(11)	122.5(3)	N(2)–S(2)–F(21)	119.8(3)
N(1)–S(1)–F(12)	119.5(3)	N(2)–S(2)–F(22)	122.2(3)
N(1)–S(1)–F(13)	121.9(3)	N(2)–S(2)–F(23)	122.2(3)
F(12)–S(1)–F(11)	95.5(3)	F(21)–S(2)–F(22)	95.5(3)
F(13)–S(1)–F(11)	94.7(3)	F(21)–S(2)–F(23)	95.8(2)
F(12)–S(1)–F(13)	96.1(3)	F(22)–S(2)–F(23)	94.6(2)

The spectroscopic data for the series (Table 5) are consistent with the crystallographic results; thus the N–S and S–F stretching frequencies are higher than in the free ligand, in agreement with the shorter bond lengths in the manganese complex. The F_{1u} i.r.-active As–F stretch of undistorted AsF_6^- is split into three components in all the complexes, and a further As–F stretch is observed at 590w cm^{-1}, which would be i.r. inactive for a regular octahedron. A splitting of the *E* symmetry FSF deformation also indicates a deviation from local C_{3v} symmetry of the NSF_3 ligands, consistent with the deviation of Mn–N–S from linearity. The ν(NS) values for the series of analogous derivatives $[M(NSF_3)_4(AsF_6)_2]$ increase with atomic number (Mn→Cu). This is consistent with increasing Lewis-acid properties of the central metal ion with decreasing size, if it is assumed that the observed strengthening of N–S and S–F bonds (compared with free NSF_3) is due to withdrawal by the

TABLE 5

Infrared frequencies (cm^{-1}) for $[M(NSF_3)_4(AsF_6)_2]$*

				ν(AsF_6^-)							
M	ν(NS)	$\nu_e(SF_3)$	$\nu_s(SF_3)$					δ_s(NSF)	δ_e(FSF)	δ(AsF_6^-)	δ_e(NSF)
Mn	1 578	886 (875)	835	721	702	674	590	548/540	456/448	397	352
Fe	1 590	883 (872)	837.5	723	702	673	588	548/536	450/442	393	352
Co	1 597	884 (875)	839	721	702	675	590	551/545	453/446	398	353
Ni	1 610	884 (875)	840	722	702	673	590	553/544	451/422	396	351
Cu	1 618	904 (888)	850	713	700	678	590	568/557	450/445	397	*ca.* 360
	s	vs(sh)	s	vs	m	m	w	m	m	s	w—m

* s = Strong, m = medium, w = weak, v = very, sh = shoulder. Infrared frequencies (H. Richert and O. Glemser, *Z. anorg. Chem.*, 1961, **307**, 328) and dimensions (W. H. Kirchhoff and E. B. Wilson, *J. Amer. Chem. Soc.*, 1962, **84**, 334) for free NSF_3 are ν(NS) 1 515; ν(SF) 775, 811; $\delta(SF_3)$ 521, 492, 342 cm^{-1}; *r*(NS) 1.416(3), *r*(SF) 1 552(3) Å; FSF 94.0 (0.3)°.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

metal of π-electron density from the ligand, with consequent reduction of interelectronic repulsions.

The copper(II) compound may not be strictly comparable with those of the other metals; for the d^9 system an appreciable Jahn–Teller distortion would be expected, leading to longer Cu–F distances. This may be reflected in its smaller ν(AsF_6) splitting.

We thank the Verband der Chemischen Industrie for financial support and Dr. F.-M. Schnepel for discussion of the i.r. spectra. Calculations were performed using an Eclipse S-250 mini-computer (which also controlled the diffractometer) using programs written by W. C. and G. M. S.

[0/1035 *Received, 3rd July*, 1980]

REFERENCES

[1] R. Mews, *J.C.S. Chem. Comm.*, 1979, 278; F. M. Schnepel, R. Mews, and O. Glemser, *J. Mol. Structure*, 1980, **60**, 89.

[2] P. A. W. Dean, *J. Fluorine Chem.*, 1975, **5**, 499; C. D. Desjardins and J. Passmore, *ibid.*, 1975, **6**, 379.

[3] B. Buss, P. G. Jones, R. Mews, M. Noltemeyer, and G. M. Sheldrick, *Acta Cryst.*, 1980, **B36**, 141.

[4] C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, 1971, **10**, 2781.

[5] J. W. Stout and S. A. Reed, *J. Amer. Chem. Soc.*, 1954, **76**, 5279.