

différence entre les deux structures réside dans la localisation des atomes d'hydrogène des groupements hydroxyles.

Pour  $\text{KTeO}_3(\text{OH})$  il y a une seule possibilité car une seule distance  $\text{O}-\text{O} = 2,48 \text{ \AA}$  convient à l'existence d'une liaison  $\text{OH}-\text{O}$ , forte. Par contre, cette localisation est plus difficile dans le cas de  $\text{NH}_4\text{TeO}_3(\text{OH})$  car il existe deux distances  $\text{O}-\text{O}$  voisines  $\text{O}(1)-\text{O}(1) = 2,535 \text{ \AA}$  et  $\text{O}(4)-\text{O}(4) = 2,506 \text{ \AA}$  mettant en jeu des atomes d'oxygène d'octaèdres différents.

Ces couples d'atomes d'oxygène étant constitués d'atomes équivalents, la seule localisation possible des atomes d'hydrogène est en position particulière sur les centres d'inversion ( $\frac{1}{2}, \frac{1}{2}, 0$  et  $\frac{1}{2}, 0, \frac{1}{2}$ ) faisant correspondre respectivement les deux atomes  $\text{O}(1)$  et  $\text{O}(4)$ . Dans ces conditions, il y aurait formation de ponts d'hydrogène  $\text{O} \cdots \text{H} \cdots \text{O}$  (Fig. 1) symétriques avec consolidation de la cohésion entre chaîne  $(\text{TeO}_4)_n$ .

Pour vérifier cette hypothèse nous avons entrepris une étude complémentaire par spectrométrie infrarouge. Le spectre obtenu ne présente pas de bandes d'absorption caractéristiques de  $\text{Te}-\text{OH}$  comme dans  $\text{H}_2\text{Te}_2\text{O}_3\text{F}_4$  (Jumas, Maurin & Philippot, 1976) avec  $\delta(\text{Te}-\text{O}-\text{H}) = 1120 \text{ cm}^{-1}$  et deux  $\delta(\text{Te}-\text{O}-\text{H}) = 2238 \text{ cm}^{-1}$ . Par contre, on note entre 1900 et  $800 \text{ cm}^{-1}$  une absorption attribuable à la

vibration de valence de la liaison hydrogène courte  $\nu_{\text{as}}(\text{O}-\text{H}-\text{O})$  avec un centre de gravité vers  $1250 \text{ cm}^{-1}$ . Cette particularité caractérise (Rozière, 1973) une liaison hydrogène courte et symétrique et confirme la localisation proposée des atomes d'hydrogène.

#### Références

- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.  
 DANIEL, F., MAURIN, M., MORET, J. & PHILIPPOT, E. (1977). *J. Solid State Chem.* **22**, 385–399.  
 DANIEL, F., MORET, J., PHILIPPOT, E. & MAURIN, M. (1977). *J. Solid State Chem.* **22**, 113–119.  
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–399.  
 JUMAS, J. C., MAURIN, M. & PHILIPPOT, E. (1976). *J. Fluorine Chem.* **8**, 329–340.  
 LINDQVIST, O. (1972). *Acta Chem. Scand.* **26**, 4107–4120.  
 MEYER, J. & HOLOWATYJ, M. (1948). *Chem. Ber.* **81**, 119–123.  
 MORET, J., MAURIN, M. & PHILIPPOT, E. (1979). *Rev. Chim. Minér.* **16**, 39–47.  
 ROZIERE, J. (1973). Thèse de Spécialité, Montpellier.  
 SUSA, K. & STEINFINK, H. (1971). *J. Solid State Chem.* **3**, 75–82.  
 SWARTZ, W. E., WYNNE, K. J. & HERCULES, D. M. (1971). *Anal. Chem.* **43**, 1884–1887.

*Acta Cryst.* (1980). **B36**, 141–142

## Hexakis(thionitrosyl fluoride)cobalt(II) Hexafluoroarsenate

BY BRUNO BUSS, PETER G. JONES,\* RÜDIGER MEWS, MATHIAS NOLTEMAYER AND GEORGE M. SHELDRIK

*Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany*

(Received 29 August 1979; accepted 4 October 1979)

**Abstract.**  $[\text{Co}(\text{NSF})_6](\text{AsF}_6)_2$ ,  $M_r = 827.17$ , monoclinic,  $P2_1/n$ ,  $a = 13.105(9)$ ,  $b = 9.201(7)$ ,  $c = 9.366(6) \text{ \AA}$ ,  $\beta = 90.43(4)^\circ$ ,  $U = 1129 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 2.432 \text{ Mg m}^{-3}$ ,  $\mu = 4.3 \text{ mm}^{-1}$  (Mo  $K\alpha$ ).  $R = 0.104$  for 1296 unique observed reflexions. The Co atom lies at the origin and is octahedrally coordinated. The S–N and S–F distances are much shorter than in free NSF, but the N–S–F angle is not greatly altered.

**Introduction.** The unstable thionitrosyl fluoride, NSF, can be stabilized by its incorporation as a ligand in transition-metal complexes. We report here the structure of the  $\text{Co}^{\text{II}}$  derivative. A preliminary note has

appeared (Buss, Jones, Mews, Noltemeyer & Sheldrick, 1979).

Black crystals were obtained from liquid  $\text{SO}_2$  and sealed in glass capillaries. A crystal  $0.5 \times 0.5 \times 0.5 \text{ mm}$  was used to collect data on a Syntex  $P2_1$  diffractometer with monochromated Mo  $K\alpha$  radiation. 3314 reflexions were collected in the range  $3 < 2\theta < 55^\circ$ ; after application of Lp and empirical absorption corrections, averaging equivalent reflexions gave 1296 reflexions with  $F > 3\sigma(F)$ .

All attempts to solve the structure in space group  $P2_1/n$  were unsuccessful. Application of direct methods in  $P2_1$ , with the program XCS D and renormalized  $E$  values to allow for weak parity groups, gave three peaks interpreted as Co and two As atoms. The

\* To whom correspondence should be addressed.

Table 1. Atom coordinates ( $\times 10^4$ ) and effective isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
As(1)	2456 (1)	-502 (2)	5041 (2)	58
F(11)	2635 (17)	867 (14)	3989 (13)	204
F(12)	3689 (9)	-734 (20)	5192 (17)	207
F(13)	2343 (16)	-1946 (17)	6046 (14)	198
F(14)	1229 (8)	-308 (20)	4902 (17)	202
F(15)	2449 (12)	-1603 (12)	3606 (11)	128
F(16)	2465 (8)	597 (13)	6480 (11)	123
Co(1)	0	0	0	38
S(1)	364 (3)	2046 (5)	-3079 (4)	62
S(2)	364 (4)	-3124 (5)	-2032 (5)	69
S(3)	2604 (3)	44 (6)	753 (5)	77
N(1)	276 (9)	1144 (14)	-1883 (12)	58
N(2)	298 (9)	-1936 (14)	-1104 (12)	61
N(3)	1538 (8)	126 (16)	569 (12)	66
F(1)	-277 (8)	3508 (10)	-3034 (12)	105
F(2)	-332 (10)	-3007 (13)	-3406 (10)	120
F(3)	3207 (8)	-509 (17)	-559 (11)	154

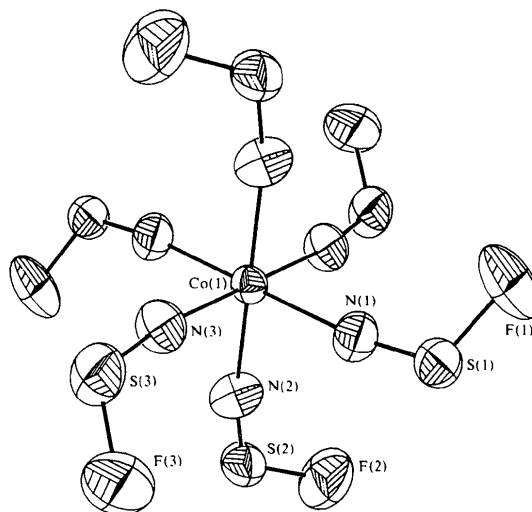
Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

As(1)-F(11)	1.617 (12)	As(1)-F(14)	1.622 (10)
As(1)-F(12)	1.635 (11)	As(1)-F(15)	1.683 (10)
As(1)-F(13)	1.636 (14)	As(1)-F(16)	1.685 (10)
Co(1)-N(1)	2.088 (11)	Co(1)-N(2)	2.098 (12)
Co(1)-N(3)	2.084 (10)	N(1)-S(1)	1.400 (11)
N(2)-S(2)	1.400 (11)	N(3)-S(3)	1.408 (11)
S(1)-F(1)	1.587 (10)	S(2)-F(2)	1.575 (10)
S(3)-F(3)	1.552 (11)		
F(11)-As(1)-F(12)	90.4 (10)	F(11)-As(1)-F(13)	175.8 (10)
F(11)-As(1)-F(14)	90.8 (10)	F(11)-As(1)-F(15)	89.0 (6)
F(11)-As(1)-F(16)	91.1 (6)	F(12)-As(1)-F(13)	86.4 (10)
F(12)-As(1)-F(14)	178.8 (10)	F(12)-As(1)-F(15)	89.4 (7)
F(12)-As(1)-F(16)	90.5 (6)	F(13)-As(1)-F(14)	92.4 (10)
F(13)-As(1)-F(15)	88.3 (7)	F(13)-As(1)-F(16)	91.6 (6)
F(14)-As(1)-F(15)	90.2 (7)	F(14)-As(1)-F(16)	90.0 (6)
F(15)-As(1)-F(16)	180.0 (2)		
N(1)-Co(1)-N(2)	88.7 (5)	N(1)-Co(1)-N(3)	90.8 (5)
N(1)-Co(1)-N(3)	180.0	N(2)-Co(1)-N(3)	91.3 (5)
N(1)-Co(1)-N(3)	89.2 (5)	N(2)-Co(1)-N(3)	89.4 (5)
N(2)-Co(1)-N(2)	180.0	N(2)-Co(1)-N(3)	90.6 (5)
N(3)-Co(1)-N(3)	180.0	N(1)-S(1)-F(1)	115.8 (7)
N(2)-S(2)-F(2)	114.6 (8)	N(3)-S(3)-F(3)	115.5 (7)
Co(1)-N(1)-S(1)	172.3 (9)	Co(1)-N(2)-S(2)	169.1 (9)
Co(1)-N(3)-S(3)	170.0 (9)		

Symmetry transformation: (i)  $-x, -y, -z$ .

complete structure was generated from these atoms by successive difference maps in  $P2_1$ , after which it was transformed back to  $P2_1/n$  for the final refinement. The final  $R = 0.104$  (all atoms anisotropic), with  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.073$ . The weighting scheme was  $w = 1/\sigma^2(F)$ , which gave mean  $w\Delta^2$  independent of  $|F_o|$  or  $\sin \theta$ . [The earlier reported  $R$  of 0.083 (Buss *et al.*, 1979) was for reflexions with  $F > 4\sigma(F)$ ; the inclusion of weaker reflexions gave marginally improved e.s.d.'s for positional parameters.] Final atomic parameters are given in Table 1,\* bond lengths

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34831 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. Thermal-ellipsoid plot of the  $[\text{Co}(\text{NSF})_6]^{2+}$  cation.

and angles in Table 2. A diagram of the structure is given in Fig. 1.

**Discussion.** The determination confirms the cation as  $[\text{Co}(\text{NSF})_6]^{2+}$ . The Co atom lies at the origin and the cation is thus centrosymmetric; the bond angles at Co approximate closely to octahedral values. The most notable feature of the structure is the shortening of the N-S and N-F bonds from 1.446, 1.646  $\text{\AA}$  respectively in the free ligand [determined by microwave spectroscopy; Kirchhoff & Wilson (1963)] to average values of 1.403 (11), 1.571 (11)  $\text{\AA}$  in the complex. These S-N bonds are the shortest yet reported. The N-S-F angle [116.5° in the free ligand, average 115.3 (7)° in the complex] does not alter appreciably on complex formation. A possible explanation is that the Co atom withdraws  $\pi$ -electron density, reducing interelectronic repulsions and hence shortening the S-N bond relative to the free ligand. The angles at N are approximately linear [average 170.5 (8)°].

As may be seen from Fig. 1, the S and N atoms show almost isotropic thermal motion, whereas the F atoms are appreciably anisotropic. This indicated that a considerable librational shortening would only be expected for the S-F bonds. Reliable librational corrections are difficult (in this case), because the low deformation frequencies of the ligands invalidate the usual rigid-body assumptions.

We thank the Niedersächsisches Zahlenlotto for their support and the University of Cambridge for use of a diffractometer.

#### References

- BUSS, B., JONES, P. G., MEWS, R., NOLTEMAYER, M. & SHELDRIK, G. M. (1979). *Angew. Chem.* **91**, 253.  
KIRCHHOFF, W. H. & WILSON, E. B. JR (1963). *J. Am. Chem. Soc.* **85**, 1726-1729.