1355

Fluoride Ion Donor Properties of UF₂O₂; Preparation and Characterization of the Adducts UF₂O₂ $\cdot nSbF_5$ (n = 2 or 3) and Crystal Structure of UF₂O₂ 3SbF₅

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The adducts $UF_2O_2 \cdot nSbF_5$ (n = 2 or 3) have been obtained as pale green and pale yellow-green solids respectively from the reaction of UF_2O_2 with SbF_5 in HF solvent. The solid adducts have been characterized by observation of reaction stoicheiometries, chemical analyses, and vibrational spectra. An X-ray diffraction study has shown that crystals of $UF_2O_2 \cdot 3SbF_5$ are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 11.040(7), b =12.438(12), c = 12.147(8) Å, $\beta = 111.16(20)^\circ$, and Z = 4. The structure has been refined by three-dimensional least-squares methods to R = 0.0773 for 1 613 reflections. The structure is best regarded as a fluorine-bridged network of UF_2O_2 and SbF_5 molecules in which the antimony is surrounded by a distorted octahedron of fluorine atoms and the uranium by a pentagonal-bipyramidal array of five fluorines and two oxygens. Two of the uraniumfluorine distances are long and this means that the structure can also be described in terms of zigzag chains of UO_2 groups fluorine-bridged to SbF_6 units with Sb_2F_{11} side-chains attached to the uraniums.

ALTHOUGH acid properties of uranyl fluoride, UF_2O_2 , have been demonstrated by its reaction with alkali metal^{1,2} and ammonium^{1,3,4} fluorides no evidence for basic character in this compound has been reported. Following our recent studies of the reaction of UF_4O with SbF_{5} ,^{5,6} which yielded the new adducts $UF_4O \cdot nSbF_5$ (n = 1-3), it seemed likely that similar adducts might also be formed with UF₂O₂. Investigation of the reaction of anhydrous UF₂O₂ with SbF₅ has resulted in the isolation and characterization of two new adducts, UF2O2. 2SbF₅ and UF₂O₂·3SbF₅, the first examples of compounds resulting from the reaction of uranyl fluoride with a Lewis acid. The structure of UF₂O₂·3SbF₅ has been determined and can be described as a three-dimensional network of UF₂O₂ and SbF₅ molecules linked by fluorine bridges.

RESULTS AND DISCUSSION

The adduct $UF_2O_2 \cdot 3SbF_5$ was prepared by reaction of UF_2O_2 with an excess of SbF_5 at 30—40 °C in anhydrous HF as solvent, followed by the removal of excess of SbF_5 and solvent under dynamic vacuum at room temperature until no further weight loss occurred. The $UF_2O_2 \cdot 2SbF_5$ adduct was prepared by heating the 1 : 3 adduct under dynamic vacuum at 120—130 °C. The 1 : 2 adduct is stable at temperatures up to 240 °C whereupon decomposition to UF_2O_2 and SbF_5 occurs.

The thermal degradation of the 1:3 adduct was confirmed by microcalorimetric measurement. Two endothermic peaks were observed at temperatures of approximately 125 and 245 °C, the weight changes corresponding to the conversion of UF_2O_2 . $3SbF_5$ to UF_2O_2 . $2SbF_5$ and of UF_2O_2 . $2SbF_5$ to UF_2O_2 respectively (see Scheme). There was no evidence for the formation of a 1:1 adduct.

$$UF_{2}O_{3} \cdot 3SbF_{5} \xrightarrow{(i)} UF_{2}O_{2} \cdot 2SbF_{5} \xrightarrow{(ii)} UF_{2}O_{2} \dagger$$

Scheme
(i) 125 °C; $\Delta H = 107.4 \text{ kJ mol}^{-1}$

(*ii*) 245 °C;
$$\Delta H = 231.6$$
 kJ mol⁻¹

 \dagger Identified by vibrational spectroscopy and X-ray powder diffraction.

The vibrational spectra obtained for the two new adducts (Figures 1 and 2) were found to be distinctly different from those of UF_2O_2 and SbF_5 (see Table 1). For UF_2O_2 · $3SbF_5$ the asymmetric stretch associated with the UO_2 group appears at 1 012 cm⁻¹ in the i.r. spectrum which is 22 cm⁻¹ higher than that (at 990 cm⁻¹) in UF_2O_2 itself. A similar shift to higher frequency is observed for the U=O stretching vibration when UF_4O is converted to UF_4O · SbF_5 , UF_4O · $2SbF_5$, or UF_4O · $3SbF_5$. This can be interpreted in terms of withdrawal of electron density from the uranium oxide fluorides to the highly



FIGURE 1 I.r. spectrum of UF₂O₂·3SbF₅

F ₂ O ₂ ^{a,b}	SbF₅ ⁰	UF2O2·3SbF5	UF2O2·2SbF5	UF₄O•2SbF₅ ^d	Assignment
990		1 012	1 004		UO ₂ asymmetric stretch
				912	U=Ö stretch
		747)	
	742	735	730	732	
		725			
		718	714	722	
	705	709	708	710 L	Sb-F(terminal) stretching
		696		ĺ	
		678			
	669	664	667	657	
		656	652		
		597	590	596∫	
		570)	
		554	566	546	U···F(bridging) and
		524	536	526	$Sh \cdots F(bridging)$
				518	stretching
				502	
	~ 450	466	433	457J	
		392			
		382			
	~310	310			
000		295			
280		270			

TABLE 1

acidic SbF_5 groups, and implies that the UF₄O and UF₂O₂ have some fluoride ion donor character.

Bands in the 750—590 cm⁻¹ region of the i.r. spectrum can be attributed to Sb-F stretching modes.⁷⁻¹² However, there are far more bands in this region in the spectrum of UF₂O₂·3SbF₅ than in the spectra of the UF₄O-SbF₅ adducts. This, coupled with the fact that there is an increased number of high frequency bands in UF₂O₂·3SbF₅, suggests the presence of polymeric groups such as $[Sb_2F_{11}]^-$ rather than, or in addition to, $[SbF_6]^$ ions.¹² The presence of polymeric species is also implied



FIGURE 2 I.r. spectrum of UF₂O₂·2SbF₅

by the bands at 554 and 466 cm⁻¹ which can be assigned to fluorine bridging modes, the latter of which is almost certainly due to ν [Sb · · · F(bridging)].^{8-10,12-14} This suggestion has been vindicated by a single-crystal X-ray structure determination on the 1:3 adduct.

The i.r. spectrum of $UF_2O_2 \cdot 2SbF_5$ is related to that of $UF_2O_2 \cdot 3SbF_5$ but has fewer high frequency Sb-F stretching bands. The shift of the UO_2 asymmetric stretch to higher frequency increases in the series $UF_2O_2 \cdot nSbF_5$ (n = 3 > n = 2) as was found in the corresponding series $UF_4O \cdot nSbF_5$ (n = 3 > n = 2 > n = 1) (Table 2), and is consistent with an increasingly positive charge

TABLE 2

Observed trend in i.r. uranium-oxygen stretching frequencies (cm⁻¹) for uranium oxide fluoride-antimony pentafluoride adducts

on the uranium atom as the number of attached ${\rm SbF}_5$ groups is increased. In general the spectra obtained are too complex definitively to be assigned. Both the ${\rm UF}_2{\rm O}_2\cdot 2{\rm SbF}_5$ and ${\rm UF}_2{\rm O}_2\cdot 3{\rm SbF}_5$ adducts exhibit the characteristic Raman fluorescence spectrum of the uranyl ion.

A single-crystal X-ray study on the 1:3 adduct has been carried out. The uranium and three antimony atoms are linked into a fluorine-bridged network shown in Figures 3—5. The uranium atom is surrounded by a pentagonal-bipyramidal array of light atoms (see angles,



FIGURE 3 A view of the asymmetric unit of UF_2O_2 ·3SbF₅ showing the atomic numbering; thermal ellipsoids are at the 50% probability level

Table 3), the two non-bridging atoms in the axial positions being readily identified as oxygen atoms from their short bonding distance (Table 3) and the vibrational spectroscopic evidence for the presence of a UO_2 group. The five equatorial fluorine atoms all form bridging bonds

to antimony atoms. This co-ordination arrangement is different to that found in UF_2O_2 , where the UO_2 groups are at right angles to a slightly puckered close-packed array of six fluorine atoms.¹⁵

The fluorine-bridged network consists of a polymeric system of six- and eight-membered rings. Two uranium atoms and two of the antimony atoms [Sb(1) and Sb(3)] alternate in a fluorine-bridged eight-membered ring of the type commonly found in metal pentafluoride and tetrafluoride oxide structures, e.g. SbF₅,¹⁶ RhF₅,¹⁷ OsF₅,¹⁸ WF₄O,¹⁹ ReF₄O·SbF₅,²⁰ and UF₄O·2SbF₅.⁶ The rings are linked through their uranium corners into polymeric chains. One edge of each ring [U · · · F(3) · · · · Sb(1)] also forms part of a fused six-membered ring incorporating the third antimony atom [Sb(2)]. Six-membered rings have been found in hexagonal TcF₄O, metastable forms of MoF₄O and ReF₄O,²¹ and 2XeF₆·AuF₅,²² but not previously in the same structure with eight-membered rings.

The average U=O bond length [1.68(3) Å] is marginally



FIGURE 4 A view of the fluorine-bridged network in UF₂O₂·3SbF₅



FIGURE 5 Stereoscopic view of the unit-cell contents of UF2O2.3SbF5 approximately along a

shorter than that found in UF₂O₂ [1.74(2) Å],¹⁵ consistent with the trend in ν (U=O). The U · · · F(bridging) distances are in the range 2.35—2.45 Å, the mean value of 2.39 Å has a larger σ (= 0.05 Å) than expected, suggesting that the two values involving Sb(1), both 2.45 Å, are different to the three which involve Sb(2) and Sb(3),

TABLE 3

Bond lengths (Å) and angles (°) in UF₂O₂·3SbF₅ with estimated standard deviations in parentheses

1.69(3)	Sb(2) - F(2)	1.93(2)
1.66(3)	Sb(2)-F(5)	2.11(2)
2.35(2)	Sb(2) - F(9)	1.83(2)
2.38(2)	Sb(2) - F(10)	1.83(2)
2.45(2)	Sb(2) - F(11)	1.76(3)
2.45(2)	Sb(2) - F(12)	1.84(3)
2.33(2)	Sb(3)-F(1)	1.98(3)
1.895(19)	Sb(3) - F(13)	1.84(2)
1.842(19)	Sb(3)-F(14)	1.85(3)
1.97(2)	Sb(3) - F(15)	1.99(2)
1.84(2)	Sb(3)-F(16)	1.87(2)
1.85(3)	Sb(3) - F(17)	1.83(2)
1.907(18)		
179 3(1 3)	F(11) - Sb(2) - F(2)	88 1(1.5)
170.0(1.0)	F(11) - Sb(2) - F(5)	82 2(1 3)
92 2(1 1)	F(11) - Sb(2) - F(9)	93.7(1.6)
87.4(1.2)	F(11) - Sb(2) - F(10)	98.2(1.4)
91.3(1.0)	F(12) - Sb(2) - F(2)	83.4(1.4)
92.0(1.3)	F(12) - Sb(2) - F(5)	83.4(1.3)
86.5(1.4)	F(12) - Sb(2) - F(9)	91.5(1.4)
88.4(1.2)	F(12) - Sb(2) - F(10)	95.6(1.5)
92.3(1.1)	- () - () Moom	90 5(5 7)
89.1(1.2)	Mean	89.5(0.7)
88.0(1.2)	F(19) - F(1)	99 9/1 9
92.9(1.2)	F(13) = Sb(3) = F(14)	08.2(1.2)
90 0(2 2)	F(13) - Sb(3) - F(15)	83 5(0.9)
30.0(2.2)	F(13) - Sb(3) - F(17)	95 3(1 1)
70 4/0 7)	F(16) - Sb(3) - F(1)	85 2(1.3)
68.5(0.7)	F(16) - Sb(3) - F(14)	94.4(1.3)
73.4(1.2)	F(16) - Sb(3) - F(15)	85.9(1.1)
76.3(1.0)	F(16) - Sb(3) - F(17)	94.1(1.2)
71.5(1.1)	Mean	80 7 (5 4)
72 0(2 7)	141CdII	05.7(0.4)
•===(==•;	U - F(1) - Sb(3)	142.8(1.3)
88.2(1.1)	U-F(2)-Sb(2)	166.5(1.3)
93.5(1.2)	U - F(3) - Sb(1)	161.4(1.0)
87.7(1.1)	U - F(8) - Sb(1)	178.8(1.2)
93.1(1.0)	U-F(15)-Sb(3)	141.1(1.2)
84.9(1.2)	Sb(1) - F(5) - Sb(2)	153.2(1.3)
93.2(1.2)		• •
88.1(1.2)		
90.3(1.1)		
89.9(3.0)		
	$\begin{array}{c} 1.69(3)\\ 1.66(3)\\ 2.35(2)\\ 2.35(2)\\ 2.35(2)\\ 2.35(2)\\ 2.45(2)\\ 2.33(2)\\ 1.895(19)\\ 1.842(19)\\ 1.97(2)\\ 1.84(2)\\ 1.85(3)\\ 1.907(18)\\ \hline \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

(average 2.35, $\sigma = 0.02$ Å). It can be seen from Figure 4 that Sb(1) is bonded to three bridging and three terminal fluorine atoms, whereas Sb(2) and Sb(3) only have two of their six fluorine atoms bridging other metal atoms. The U $\cdot \cdot \cdot$ F(bridging) distances are long in comparison to U-F(terminal), typically 1.92—1.98 Å,^{23,24} and an alternative, ionic description of the structure is suggested. Using this approach, the structure consists of $[UO_2]^{2+}$ ions surrounded by symmetry related pairs of $[SbF_6]^-$ [Sb(3)] and $[Sb_2F_{11}]^-$ ions [Sb(1) and Sb(2)].

The rather large range of Sb-F(bridging) distances, 1.895—2.11 Å, can be rationalised in terms of the ionic description. The Sb \cdots F distances involved in the

 $[UO_2]^{2+} \cdots [Sb_2F_{11}]^-$ interactions form one set of similar values, $Sb(1) \cdots F(3)$, $Sb(1) \cdots F(8)$, and $Sb(2) \cdots F(2)$, mean 1.911(14) Å; the two longer distances, $Sb(3) \cdots F(1)$ and $Sb(3) \cdots F(15)$, average 1.985 Å, are involved in the $[UO_2]^{2+} \cdots [SbF_6]^-$ interaction, and the Sb(1) \cdots F(5) and Sb(2) \cdots F(5) distances within the $[Sb_2F_{11}]^-$ unit average to 2.04 Å. The latter pair are significantly different but there is no obvious reason for the discrepancy. This pattern of Sb \cdots F(bridging) distances suggests that the structure contains essentially covalent fluorine-bridged chains of $[\cdots UO_2 \cdots F \cdots SbF_5 \cdots]^+$ units with $[Sb_2F_{11}]^-$ units linked through weaker fluorine bridges to the uranium atoms. This conclusion can be conveniently illustrated in terms of the previously defined ionicity value I (ref. 20) based on Sb \cdots F(bridging) bond lengths, where \mathcal{I} varies from 1.0 in ionic K[SbF₆] to 0.0 in covalently bridged (SbF₅)₄. In UF₂O₂·3SbF₅ the UO₂-SbF₆ interaction has $\mathscr{I} = 0.20$ whereas for UO_2 -Sb₂F₁₁, $\mathscr{I} = 0.62$. It is also interesting that, in agreement with this model, the two shortest $U \cdots F(bridging)$ distances are in the UO₂-SbF_e system.

The $UF_2O_2 \cdot 2SbF_5$ adduct may well have a structure related to that of the 1:3 adduct. On the basis of the vibrational spectroscopic data it seems likely that the Sb_2F_{11} unit is replaced by SbF_6 .

EXPERIMENTAL

Starting Materials.—Anhydrous UF_2O_2 was prepared by heating $UF_2O_2 \cdot 2H_2O$ under vacuum at 200 °C until the weight remained constant. The dihydrate was prepared by reaction of UF_6 with aqueous HF. Antimony pentafluoride was prepared by direct fluorination of the metal in a flow system and was purified by repeated distillation under vacuum. The anhydrous HF was treated with gaseous fluorine, to remove traces of water, before being distilled. Vibrational spectroscopy and X-ray powder diffraction attested to the purity of anhydrous UF_2O_2 and vibrational spectroscopy confirmed the purity of SbF_5 .

Apparatus.—All reactions were carried out in Kel-F or FEP reaction tubes, fitted with Kel-F or Teflon (Production Techniques, Fleet, Hants.) valves. The reaction vessels were leak checked, warmed, treated with gaseous fluorine or chlorine trifluoride, and pumped to high vacuum before use. The volatile materials were manipulated in a Monel Autoclave Engineers vacuum line, and the non-volatile materials were handled in an inert atmosphere glove box (Vacuum Atmospheres Co.).

Characterizations.—Reaction stoicheiometries were monitored by weighing the reaction tubes and their contents on a modified Stanton analytical balance (maximum weight 300 g, sensitivity 0.1 mg). Infrared spectra were recorded with a Perkin-Elmer 580 spectrophotometer, with the powdered solids pressed between KBr or polyethene discs. The Raman spectra of the solid compounds were recorded in Pyrex Lindemann capillaries using a Coderg model T800 spectrophotometer. Samples for X-ray powder diffraction measurement were mounted in Pyrex capillaries and their diffraction patterns recorded photographically on a Philips camera (diameter 11.46 cm) with Cu- K_{α} filtered radiation.

Preparation of UF2O2.3SbF5.-In a typical experiment anhydrous UF₂O₂ (0.54 mmol) was placed into a pre-seasoned FEP reaction tube in an inert atmosphere glove box. A large excess of antimony pentafluoride (7.22 mmol) was distilled onto the solid, followed by a small quantity of anhydrous HF solvent. The mixture was warmed gently (30-40 °C) to aid solution and a yellow-green solution was obtained. The HF and unreacted SbF_5 were then slowly removed by pumping at room temperature and the loss of SbF_5 was monitored by weighing. The rate of loss of volatile material progressively decreased until no further weight loss was observed. A pale yellow-green crystalline solid remained, the weight of which corresponded to that calculated for UF_2O_2 ·3SbF₅.

Preparation of $UF_2O_2 \cdot 2SbF_5$.—The 1:2 adduct was prepared by pumping on the 1:3 adduct, in a glass reaction vessel, at ca. 125 °C until no further weight loss occurred. The weight of the pale green solid residue corresponded to that for UF₂O₂·2SbF₅.

Microcalorimetric Studies .- Measurements were made on an ARION type MCB microcalorimeter at the Centre D'Études Nucléaires de Saclay, France.

Single-crystal Examination.—Crystals of the 1:3 adduct were transferred in an inert atmosphere glove box into short lengths of Pyrex capillary for crystallographic examination. The identity of the crystals as UF_2O_2 ·3SbF₅ was confirmed by comparison of the d spacings measured from an X-ray powder diffraction pattern of a bulk sample of the 1:3 adduct with calculated values from the single-crystal unit cell.

Crystal data. $F_{17}O_2Sb_3U$, M = 958.25, monoclinic (green crystals), a = 11.040(7), b = 12.438(12), c = 12.147-(8) Å, $\beta = 111.16(20)^{\circ}$, U = 1.555.5 Å³, Z = 4, $D_{c} = 4.092$ $g \text{ cm}^{-3}$, $\mu(\text{Mo-}K_{\alpha}) = 165 \text{ cm}^{-1}$, F(000) = 2.039.8, space group $P2_1/n$.

The cell dimensions were determined from an oscillation photograph about the b axis of an irregular block-shaped crystal and from its optimized counter angles for zero and upper layer reflections on a Weissenberg diffractometer. The intensities of reflections with $0.08 < (\sin\theta/\lambda) < 0.7$ Å⁻¹ were collected at 22-25 °C on a Stoe Weissenberg diffractometer with Mo- K_{α} radiation ($\lambda = 0.7107$ Å) and an ω scan technique. The 1 613 reflections having $I \ge 3σ(I)$ were corrected for Lorentz and polarization effects. All subsequent computations were carried out using the computer program SHELX.²⁵ Scattering factors for neutral atoms were taken from ref. 26 with full correction for anomalous scattering and the structure solved by conventional Patterson and difference Fourier techniques. Fullmatrix least-squares refinement of positional and isotropic thermal parameters for all atoms reduced R to 0.18. An absorption correction was applied to the data (absorption factor range from 0.5383 to 0.1374). Further cycles of refinement using anisotropic thermal parameters for all atoms reduced R to 0.081. Final cycles employed a weighting parameter g (0.000 916) { $w \propto [1/\sigma^2(E) + gF^2]$ } and an isotropic extinction parameter x (0.000 05) { $F_{\rm c} = F[1 - (xF^2/$ $\sin\theta$)]}. The final residual indices were $R = \Sigma w(|F_0| -$ $|F_{\rm c}|^2$ 0.0773 and $R' \{ = [\Sigma w (|F_{\rm o}| - |F_{\rm c}|)^2 / \Sigma w |F_{\rm o}|^2]^{\frac{1}{2}} \}$ 0.0711. A final difference Fourier was featureless other than residual 5 e peaks at ≤ 1.0 Å from the uranium atom. An analysis of the weighting scheme over $|F_0|$ and $(\sin \theta)/\lambda$ was satisfactory.

Observed and calculated structure factors and atomic

* For details see Notices to Authors No. 7, J. Chem. Soc., Dalton Trans., 1981, Index issue.

1359

thermal parameters have been deposited as Supplementary Publication No. SUP 23286 (7 pp.).* Final positional coordinates and their estimated standard deviations are listed in Table 4.

TABLE 4

Atomic positional parameters for UF₂O₂·3SbF₅, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
U	$0.241\ 03(15)$	$0.095\ 23(11)$	0.175 35(12)
Sb(1)	0.203 7(3)	0.404 1(2)	0.009 6(2)
Sb(2)	0.1607(3)	0.146 9(2)	-0.1933(2)
Sb(3)	0.175 2(3)	0.296 6(2)	0.415 6(2)
O(1)	$0.077 \ 9(26)$	0.094 5(19)	0.138 8(23)
O(2)	0.401 3(30)	0.094 8(24)	$0.210 \ 4(20)$
F(1)	0.270 5(26)	0.212 5(18)	$0.334\ 7(21)$
F(2)	0.202 8(30)	$0.104 \ 6(19)$	-0.030 6(17)
F(3)	$0.235 \ 9(23)$	0.281 6(16)	$0.108 \ 9(16)$
F(4)	0.166 1(26)	0.519 8(16)	-0.0919(19)
F(5)	$0.182 \ 0(27)$	0.302 3(19)	-0.120 0(18)
F(6)	$0.378\ 6(21)$	0.407 0(18)	$0.033 \ 9(21)$
F(7)	0.030 8(25)	0.381 1(23)	-0.011 6(23)
F(8)	0.225 7(22)	0.487 5(14)	0.147 2(16)
F(9)	0.114 0(31)	$0.218 \ 6(22)$	0.334 4(19)
F(10)	0.143 9(31)	0.007 5(20)	-0.244 5(22)
F(11)	0.328 6(29)	$0.162\ 0(26)$	-0.1624(28)
F(12)	-0.0045(24)	0.158 5(25)	-0.1921(29)
F(13)	$0.069 \ 5(25)$	$0.329\ 0(20)$	0.263 1(19)
F(14)	0.098 9(30)	0.391 6(21)	$0.488\ 0(23)$
F(15)	$0.280\ 6(23)$	0.418 7(15)	0.393 3(19)
F(16)	$0.317 \ 4(29)$	$0.267 \ 3(20)$	$0.553\ 0(24)$
F(17)	$0.086 \ 5(26)$	0.175 1(19)	0.426 5(23)

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REFERENCES

- ¹ A. E. Baker and H. M. Haendler, Inorg. Chem., 1962, 1, 127; L. L. Zaitseva, L. V. Lipis, V. V. Fomin, and N. T. Chebo-tarev, Russ. J. Inorg. Chem. (Engl. Transl.), 1962, 7, 795.
 ² I. P. Sokolov and V. P. Seleznev, Russ. J. Inorg. Chem.
- (Engl. Transl.), 1977, 22, 1854.
- N. P. Galkin, U. D. Veryatin, and V. I. Karpov, Russ. 1. Inorg. Chem. (Engl. Transl.), 1962, 7, 1043.
- ⁴ A. A. Tsvetkov, V. P. Seleznev, B. N. Sudarikov, and B. V. Gromov, *Russ. J. Phys. Chem. (Engl. Transl.)*, 1971, 45, 563.
 ⁶ R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *C.R. Acad. Sci., Ser. C*, 1978, 287, 423.
 ⁶ R. Bougon, J. Fawcett, J. H. Holloway, and D. R. Russell, *C.L. Computer Science*, 2017, 100 (2017).
- J. Chem. Soc., Dalton Trans., 1979, 1881.
- ⁷ I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, J. Chem. Soc. A, 1969, 958. ⁸ B. B. Chaivanov, Russ. J. Phys. Chem. (Engl. Transl.), 1972,
- 46, 13. ⁹ R. D. Peacock and I. L. Wilson, J. Chem. Soc. A, 1969,
- 2030.
 - ¹⁰ J. K. Ruff, Inorg. Chem., 1967, 5, 1791.
- ¹¹ G. M. Begun and A. C. Rutenberg, Inorg. Chem., 1967, 6, 2212.
- 18 B. Frlec and J. H. Holloway, J. Chem. Soc., Dalton Trans., 1975, 535.
- ¹³ J. Weidlein and K. Dehnicke, Z. Anorg. Allg. Chem., 1966, **348**, 278.
- R. J. Gillespie and G. P. Pez, Inorg. Chem., 1969, 8, 1229.
 M. Atoji and M. T. McDermott, Acta Crystallogr., Sect. B.
- 1970, **26**, 1540. A. J. Edwards and P. Taylor, Chem. Commun., 1971, 1376.
- ¹⁷ B. K. Morrell, A. Zalkin, A. Tressaud, and N. Bartlett, Inorg. Chem., 1973, 12, 2640.
- 18 S. J. Mitchell and J. H. Holloway, J. Chem. Soc. A, 1971, 2789.

¹⁹ A. J. Edwards and G. R. Jones, J. Chem. Soc. A, 1968, ¹⁹ A. J. Edwards and G. R. Jones, J.
^{2074.}
²⁰ J. Fawcett, J. H. Holloway, and D. R. Russell, J. Chem. Soc., Dalton Trans., 1981, 1212.
²¹ A. J. Edwards, G. R. Jones, and R. J. C. Sills, J. Chem. Soc. A, 1970, 2521.
²² K. Leary, A. Zalkin, and N. Bartlett, J. Chem. Soc., Chem. Commun., 1973, 131.

- ²³ K. W. Bagnall, D. Brown, and J. F. Easy, J. Chem. Soc. A, 1968, 2223.
 ²⁴ W. Sawodny, K. Rediess, and U. Thewalt, Z. Anorg. Allg. Chem., 1980, 469, 81.
 ²⁵ G. M. Sheldrick, SHELX-76 Program for Crystal Structure Determination, University of Cambridge, 1976.
 ²⁶ ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99-100, 149-150.