Preparative and Structural Studies of Pentahalogeno-Oxometallate(V) Salts of the Transition Metals Cr, Mo, W, Tc, Re

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Pentahalogeno-oxometallate(V) complex salts $A_2[MOX_5]$, A = K, Rb, Cs, M = Cr, Mo, W, Tc, Re and X = Cl, Br were studied in order to extend the series of salts. The isolation of a product depends on the inter-relation of factors such as solubility, redox stability of the anion and disproportionation reactions. The Cs^+ salts are all cubic and the K^+ and Rb^+ salts orthorhombic. The single crystal analysis of $Cs_2[MoOBr_5]$ was completed. Statistical disorder prevented accurate bond lengths being obtained, but Mo–O = 164 pm and Mo–Br = 249.2(6) pm. The formation of low solubility $A_2[Tc(OH)X_5]$ salts is a common feature of technetium(IV) halogeno-chemistry.

Introduction

The transition metals Cr, Mo, W, Tc and Re all form pentahalogeno-oxo complex anions $[MOX_5]^{2-}$ (where M = transition metal and X = Cl, Br). Solid products are isolated with the use of an appropriate cation. The K^+, Rb^+ and Cs^+ salts reported are as follows:

Anion	K^+	Rb^+	Cs^+
$[CrOCl_5]^{2-}$			X
$[MoOCl_5]^{2-}$	X	X	X
$[MoOBr_5]^{2-}$		X	X
$[WOCl_5]^{2-}$		X	X
$[WOBr_5]^{2-}$		X	X
$[TcOCl_5]^{2-}$	X		X
$[TcOBr_5]^{2-}$			
$[ReOCl_5]^{2-}$	X	X	X
$[ReOBr_5]^{2-}$			X

An obvious feature of this table is the absence of some potassium salts. This is mainly a problem of solubility, as the potassium salts are the more soluble.

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We have now isolated $K_2[CrOCl_5]$, $Rb_2[CrOCl_5]$, $K_2[MoOBr_5]$ and $Cs_2[TcOBr_5]$. The potassium salts of $[WOX_5]^{2-}$ could not be isolated, and our work has raised doubts over the existence of pure rubidium salts of $[WOX_5]^{2-}$ and $K_2[ReOCl_5]$.

Preparations

In order to produce $[CrOCl_5]^{2-}$ salts uncontaminated with Cr(III) species the reaction solution of CrO_3 in acetic acid saturated with HCl gas must not be heated. From this solution the K^+, Rb^+ and Cs^+ [1, 2] salts can be isolated. The red salts appear to be photochemically decomposed and need to be kept in the dark. The corresponding bromides cannot be isolated as the HBr reduces Cr(VI) directly to Cr(III) [3].

The isolation of $K_2[MoOCl_5]$ [4] requires repeated removal (4 to 5 times) of KCl and replenishment of the filtrate from a stock solution of $[MoOCl_5]^{2-}$. This is necessary because KCl is less soluble in acid than $K_2[MoOCl_5]$. The problem does not arise for the Rb^+ and the Cs^+ [2, 5] salts. The potassium salt of $[MoOBr_5]^{2-}$ is made in a similar manner.

The potassium salts of $[WOX_5]^{2-}$ could not be isolated from solution. The salt $Rb_2[WOCl_5]$ [5] was obtained, but it decomposes very rapidly, and we were unable to obtain the reported $Rb_2[WOBr_5]$ [5]. Instead a brown powder, with a cubic structure (a_o = 1059.7(1) pm) formed, the infrared spectrum of which suggested it was a W(VI) dioxo-complex.

Numerous attempts to prepare pure $K_2[ReOCl_5]$ [4, 6, 7] were unsuccessful, by both reported and new methods. Instead a green product was obtained (especially when warmed) which was principally $K_2[ReCl_6]$. However, in some products a weak absorption at 955 cm^{-1} was observed in the infrared spectrum, suggesting the presence of $K_2[ReOCl_5]$. The same product also had an absorption at 172 cm^{-1}, distinctive of the δ(ClReCl) bending mode of $K_2[ReCl_6]$ and bands due to ReO_4^- [8]. Since a single crystal X-ray structure analysis of the oxo-salt has

been reported [6], though the details have not been published, we suggest that some crystals of K_2-[ReOCl$_5$] had been selected from the reaction product (mainly K_2[ReCl$_6$]). As yet K_2[ReOCl$_5$] can not be obtained free of K_2[ReCl$_6$]. A disproportionation reaction occurs when the solutions are warmed

$$3[ReOCl_5]^{2-} + H_2O \rightleftharpoons 2[ReCl_6]^{2-} + ReO_4^- +$$
$$+ 3Cl^- + 2H^+,$$
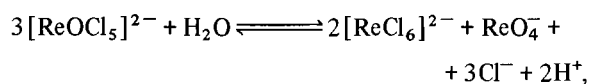
and would account for the observations. Only the caesium salt [9] of [ReOBr$_5$]$^{2-}$ was sufficiently insoluble to be isolated before reduction to [ReBr$_6$]$^{2-}$ occurred with HBr.

Only the caesium salts, Cs$_2$[TcOCl$_5$] [10] and Cs$_2$[TcOBr$_5$] could be isolated from the treatment of TcO$_4^-$ with HCl or HBr respectively. If hydroiodic acid was used as the reducing agent, as required in the rhenium preparations, insoluble salts of the Tc(IV) pentahalogeno hydroxo complex ions [Tc(OH)X$_5$]$^{2-}$ were isolated [11].

The isolation of solid pentavalent halogeno-oxo salts A$_2$[MOX$_5$] depend on three inter-relating factors; the solubility of the salts (Cs$^+$ < Rb$^+$ < K$^+$), the stability of the pentavalent oxidation state in the presence of reducing agents, including the halide ion (Cr < Mo, W, Tc < Re), and disproportionation reactions. The results of this study can be summarised as follows:

Anion	K$^+$	Rb$^+$	Cs$^+$
[CrOCl$_5$]$^{2-}$	√	√	X
[MoOCl$_5$]$^{2-}$	X^a	X	X
[MoOBr$_5$]$^{2-}$	√	X	X
[WOCl$_5$]$^{2-}$	np^b	v. unstable	X
[WOBr$_5$]$^{2-}$	np^b	X?^{c}	X
[TcOCl$_5$]$^{2-}$	X	na	X
[TcOBr$_5$]$^{2-}$	na	na	√
[ReOCl$_5$]$^{2-}$	v. impure, X	X	X
[ReOBr$_5$]$^{2-}$	np^d	np^d	X

X = reported previously, √ = new product, np = no product, na = preparation not attempted, ^{a}controlled conditions necessary to obtain a pure product, ^{b}too soluble, ^{c}dioxo complex formed?, ^{d}tetravalent oxidation state more stable.

Structures

The crystal unit cell parameters were obtained for all the salts isolated (Table I). All of the caesium salt crystals are cubic. The remaining (non-cubic) salts all had X-ray powder diffraction patterns which indicated isomorphism with K_2[MoOCl$_5$] and (NH$_4$)$_2$-[MoOBr$_5$], for which single crystal structure analyses confirmed the orthorhombic space group Pnma [4, 12]. Both cubic and orthorhombic structural types can be considered to be based on close packing of the anions [MOX$_5$]$^{2-}$ with cations in tetrahedral holes.

TABLE I. Crystal Data on A$_2$[MOX$_5$] Complexes.

Compound [Ref.]	Crystal system	Cell dimensions (pm)			Cell Volume pm^3 × 10^6	ν(M=O)^e A$_1$ (cm^{-1})
		a$_o$	b$_o$	c$_o$		
K$_2$[CrOCl$_5$]	orthorhombic^{a,b}	1318.2(6)	962.8(6)	690.0(3)	876	956
Rb$_2$[CrOCl$_5$]	orthorhombic^{a,b}	1365.5(1)	990.3(5)	693.4(2)	938	950
Cs$_2$[CrOCl$_5$] [1]	cubic^a	1014.6(1)			1044	933
K$_2$[MoOCl$_5$] [4]	orthorhombic^a	1353.1(2)	989.2(1)	692.1(1)	926	975
Rb$_2$[MoOCl$_5$]	orthorhombic^{a,b}	1379.0(4)	1003.5(2)	700.3(2)	969	970
Cs$_2$[MoOCl$_5$] [9]	cubic^a	1022.7(1)			1070	945
K$_2$[MoOBr$_5$]	orthorhombic^{a,b}	1411.7(2)	1037.4(1)	729.7(1)	1069	972
Rb$_2$[MoOBr$_5$]	orthorhombic^{a,b}	1434.3(7)	1050.2(4)	735.3(4)	1108	968
Cs$_2$[MoOBr$_5$] [9]	cubic^a	1065.0(6)			1208	
Cs$_2$[MoOBr$_5$] [9]	cubic^c	1065.4(1)			1209	
(NH$_4$)$_2$[MoOBr$_5$]	orthorhombic^a	1424.3(7)	1046.9(3)	730.0(4)	1089	
Cs$_2$[WOCl$_5$] [9]	cubic^a	1023.0(1)			1071	960
Cs$_2$[WOBr$_5$] [9]	cubic^a	1065.5(1)			1210	964
Rb$_2$[ReOCl$_5$]	orthorhombic^{a,b}	1370.1(7)	1011.1(2)	692.3(1)	959	980
Cs$_2$[ReOCl$_5$] [35]	cubic^a	1019.0(1)			1058	959
Cs$_2$[ReOBr$_5$] [9]	cubic^a	1062.0(1)			1198	956
Cs$_2$[TcOCl$_5$]	cubic^{b,d}	1019.9(1)			1061	955
Cs$_2$[TcOBr$_5$]	cubic^{b,d}	1067.2(3)			1215	950

^{a}Measured with X-ray powder diffractometer. ^{b}Measured for the first time. ^{c}Measured with single crystal X-ray diffractometer. ^{d}Measured with powder photography using film. ^{e}Rb$_2$WOCl$_5$ 967 cm^{-1}.

TABLE II. Final Parameters of X-ray Structural Analysis of $Cs_2[MoOBr_5]$.[a]

Atom	Fractional Coordinates			Thermal Parameters (pm^2)					
	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0	0	0	820(60)	0	0	0	0	0
Cs	0.25	0.25	0.25	230	230	230	39	39	39
Br	0.2339(6)[b]	0	0	40(6)	112(3)	67(7)	0	0	0
O	0.1539	0	0	507	0	0	0	0	0

[a]Scale Factor 1.06; Mo–O 164 pm; Mo–Br 249.2(6) pm; $R_1 = 0.06$, $R_2 = 0.073$.   [b](6) error is last figure.

The radii of the anions $[MOX_5]^{2-}$ for the caesium salts are 273 pm (X = Cl) and 292 pm (X = Br), while for orthorhombic $K_2[MoOCl_5]$ the radius of $[MoOCl_5]^{2-}$ is 5% greater, *i.e.* 287 pm (assuming $r_{Cs^+} = 169$ pm and $r_{K^+} = 133$ pm, the Pauling six-coordinate ionic radii). This corresponds to a 15% increase in volume of the anion. It could be argued that to improve the packing between the large anion and the large Cs^+ ion the structure assumes the cubic lattice where the cation-anion contact is compressed and where the radius ratio (0.62 for chloro-complex) is greater. This feature may contribute to the lower solubility of the Cs^+ salts by virtue of an increased lattice energy. The cell volume varies with the alkali metal cation, and transition metal atom size in the expected way.

A 1.0 to 1.5% contraction in unit cell volume occurs, for a number of the compounds, with drop in temperature from 296 K to 186 K, while over the range 296–148 K the volume contracts by 2% for $Cs_2[MoOBr_5]$. Over these temperatures the contraction is not sufficient to change the orthorhombic salts into cubic, and in all cases no structural changes were observed.

A single crystal X-ray structural analysis of $Cs_2[MoOBr_5]$ was completed. The cubic space group requires the ligands around the molybdenum to be statistically disordered. The parameters obtained for this structure are given in Table II. Final convergence was obtained by placing $\frac{1}{6}$ of an oxygen atom at x = 0.1539, and by (a) holding fixed the O atom coordinates, the Cs and O thermal parameters and the extinction coefficient, and (b) allowing for variation of the Mo and Br thermal parameters, and the Br x fractional coordinate. The large U_{11} parameter for Mo, may be accounted for by some displacement of the metal atom out of the plane of the *cis*-ligands towards the oxo-group. Reported displacements range from 7 to 34 pm [4, 13–19]. The statistical disorder for $Cs_2[MoOBr_5]$ prevents accurate determination of the displacement, but the U_{11} value—the mean square amplitude of vibrations of the Mo atom—suggests a value of around 28 pm ($=\sqrt{800}$). However, a displacement of this magnitude is not consistent with fixing the oxygen atom at x = 0.1539

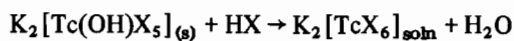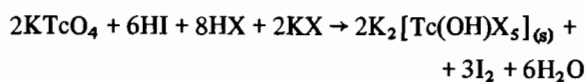(*i.e.* 164 pm from the metal). Attempts at refining the oxygen at x > 0.1539 led to higher R values.

This structural result, together with others reported for bromo-oxo complexes [15, 20] casts some doubt on the results reported for $(NH_4)_2[MoOBr_5]$ [12]. The Mo–Br bond lengths in this latter compound, 283 and 256 pm, are longer than reported by others and ourselves, *i.e.* within the range 229–252 pm.

Infrared Spectra

The infrared spectra of most of the complexes were recorded, and the new salts had spectra that compared well with reported data. The $\nu(M{=}O)$ stretching mode occurs in the region 933–980 cm^{-1} (see Table I) while the $\delta(M{-}O)$ bending mode (rocking) is halogen sensitive occurring at 215–240 cm^{-1} for the chloro-salts and 190–210 cm^{-1} for the bromo-salts. The $\nu(M{-}X)$ stretching modes are at 320–370 cm^{-1} (chloro-salts) and 220–260 cm^{-1} (bromo-salts), while the bending modes were observed at 160–200 cm^{-1} and 115–140 cm^{-1} respectively. Lattice modes were observed as absorptions below 100 cm^{-1}. The $\delta(M{-}O)$ bending mode is also sensitive to change in temperature, and splits into two well resolved bands (approximately 15 cm^{-1} apart) at 176 K. This is improved resolution as the structures of the compounds do not vary with temperature.

Technetium(IV) Salts

During the investigation of $[TcOX_5]^{2-}$ species, pentahalogenohydroxotechnetium(IV) salts $A_2[Tc(OH)Cl_5]$ (A = K, Rb, Cs) and $Cs_2[Tc(OH)Br_5]$ were obtained, when HI was used as the reducing agent. The structure of the salt $K_2[Tc(OH)Cl_5]$ has been reported [11], together with strong circumstantial evidence for the presence of the OH group. The salts form because of their insolubility in acid, but when treated with hot HX they slowly dissolve to give the hexahalogenotechnetium(IV) ion.

$$2KTcO_4 + 6HI + 8HX + 2KX \rightarrow 2K_2[Tc(OH)X_5]_{(s)} +$$
$$+ 3I_2 + 6H_2O$$

$$K_2[Tc(OH)X_5]_{(s)} + HX \rightarrow K_2[TcX_6]_{soln} + H_2O$$

The chloro-complexes are red and the bromo brown, while the hexahalogeno complexes are yellow and orange respectively. The colour difference is due to the enhanced intensity of absorption bands, in the solid state, at 540 and 600 nm for the $Cs_2[Tc(OH)Cl_5]$ and $Cs_2[Tc(OH)Br_5]$ salts respectively. In all other respects the visible solid state spectra are identical to those of $A_2[TcX_6]$. The band has been assigned to $^4A_2 \rightarrow {}^2T_2$, the $^2T_2$ split by a low symmetry component [11, 21].

The complexes are cubic (X-ray powder film data) with a_o (pm) values 985.1(2), 996.4(1), 1031.5(2) and 1071.5(3) for $A_2[Tc(OH)Cl_5]$ A = K, Rb and Cs and $Cs_2[Tc(OH)Br_5]$ respectively. The first value is in good agreement with the single crystal data (982.9 pm) [11].

As for $K_2[Tc(OH)Cl_5]$ [11, 21] the salt, $Cs_2[Tc(OH)Cl_5]$ is paramagnetic ($\mu = 3.5$ BM) confirming that the complexes are not diamagnetic oxo-bridged species as is the case for rhenium.

The infrared spectra of the materials do not possess an absorption attributable to $\nu(OH)$. The exchange of OH^- with Br^- of the KBr plates is a possible explanation. However, the slow conversion of the hydroxy complexes to the hexahalogeno salts in hot acid, and the absence of any sign (under magnification) of attack on the KBr plates suggests this is not happening. The absence of $\nu(OH)$ is puzzling, as it is often observed as a strong band around 3400 cm^{-1}. In the low frequency region, bands for $A_2[Tc(OH)Cl_5]$ occur at 320–360 cm^{-1} ($\nu(Tc-Cl)$ stretch) and 180–190 cm^{-1} ($\delta(ClTcCl)$ bend). The $\nu(Tc-Br)$ stretch in $Cs_2[Tc(OH)Br_5]$ occurs at 245–253 cm^{-1}. For the two caesium salts a weak band is observed at 286 cm^{-1} (Cl) and 226 cm^{-1} (Br). This may be assigned to a Tc—OH rocking mode, but only tentatively.

It is interesting to note that the $\nu(Tc-X)$ stretching mode occurs at the same wavelength for both $[Tc(V)OX_5]^{2-}$ and $[Tc(IV)(OH)X_5]^{2-}$, irrespective of the technetium oxidation state. This suggests that the significant σ and π donation from the oxo-ligand to the metal in $[TcOX_5]^{2-}$ leads to a charge density on Tc(V) similar to that of technetium(IV).

Experimental

Preparations

All samples (except the Tc compounds) were checked for homogeneity under a microscope. Hygroscopic materials were collected under a dry N_2 atmosphere and washed with 9:1 ether:thionyl-chloride solution [22], and then dry ether. Compounds were dried under high vacuum and stored in a dry box.

Oxopentachlorochromium(V) salts, $A_2[CrOCl_5]$

Acetic acid was saturated with HCl gas at as low a temperature as possible without freezing (0 to −10 °C) [23]. Chromium trioxide and the required AX were separately dissolved in a minimum of this solution, and mixed to give dark red precipitates. To prepare pure K^+ and Rb^+ salts the CrO_3 was dissolved in the acetic acid/HCl mixture without heating. *Anal.* $K_2[CrOCl_5]$: Cl found, 55.1%; calc., 54.8%. $Rb_2[CrOCl_5]$: Cl found, 42.5%; calc., 42.6%. $Cs_2[CrOCl_5]$: Cl found 34.7%, calc., 34.7%.

Oxopentahalogenomolybdenum(V) salts, $A_2[MoOX_5]$

An acid solution of oxo-pentachloromolybdenum(V) was obtained by dissolving molybdic acid in concentrated HCl and reducing with the stoichiometric amount of HI, freshly distilled from red phosphorus. The solution was warmed for two hours and I_2 removed by extracting into cold chloroform. The Rb^+ and Cs^+ salts were precipitated by adding RbCl or CsCl dissolved in water, respectively, and bubbling HCl gas through the solution at −5 °C. For the K^+ salt the initial precipitate was mainly KCl. This was removed and the filtrate treated with an equal volume of the $[MoOCl_5]^{2-}$ stock solution. The volume was reduced by half and HCl gas bubbled through at −5 °C. This process was repeated 4 to 5 times until a sample of $K_2[MoOCl_5]$ formed with very little contamination from KCl. The bromides were made in a similar manner to the chloro- Cs^+ and Rb^+ salts after $[MoOCl_5]^{2-}$ had been converted to $[MoOBr_5]^{2-}$ by repeated treatments with HBr and evaporation to near dryness. *Anal.* $K_2[MoOCl_5]$: Cl found, 48.2%; calc. 48.3%. $Rb_2[MoOCl_5]$: Cl found, 38.9%; calc. 38.5%. $Cs_2[MoOCl_5]$: Cl found, 32.3%; calc. 31.9%. $K_2[MoOBr_5]$: Br found, 68.3%, calc. 67.7%. $Rb_2[MoOBr_5]$: Br found, 59.3%; calc. 58.5%; $Cs_2[MoOBr_5]$: Br found, 51.3%, calc. 51.4%.

Oxopentahalogenotungsten(V) salts, $A_2[WOX_5]$

The salt $Na_3WO_2(C_2O_4)_2$ was prepared as reported [23], and dissolved in concentrated HCl to give a blue solution, which turned to green when saturated with HCl gas at −5 °C, *i.e.* forms $[WOCl_5]^{2-}$. The Cs and Rb salts were isolated by treating with aqueous solutions of CsCl and RbCl. The salts are unstable and turn blue, the rubidium salt quite rapidly. Potassium salts could not be isolated. The $Cs_2[WOBr_5]$ was prepared in a similar manner using HBr, HBr gas and CsBr in place of the chlorides above. For rubidium a brown powder was obtained which was cubic ($a_o = 1059.7(1)$ pm). Satisfactory analyses could not be obtained for the tungsten compounds.

Oxopentahalogenorhenium(V) salts, $A_2[ReOX_5]$

The Rb^+ and Cs^+ chloro salts were made according to a reported method [8]. A pure potassium salt [7] could not be isolated by this technique or when using more concentrated solutions, or when warming the solutions as reported in the literature [24–31]. In all cases the principal product was $K_2[ReCl_6]$. Precipitation with organic reagents was also unsuccessful. Using $ReCl_5$ (0.6 g in conc. HCl 5 ml) as the starting material also gave $K_2[ReCl_6]$, on the addition of KCl, and a very little $K_2[ReOCl_5]$ (from infrared evidence). The bromo-salt $Cs_2[ReOCl_5]$ was made as for the corresponding chloro-complex, while attempts to produce the Rb^+ salt only gave $Rb_2[ReBr_6]$. *Anal.* $Rb_2[ReOCl_5]$: Cl found, 31.7%, calc. 32.2%. $Cs_2[ReOCl_5]$: Cl found, 27.4%, calc. 27.5%. $Cs_2[ReOBr_5]$: Br found, 46.0%, calc. 46.1%.

Technetium Compounds

The salt $Cs_2[TcOCl_5]$ was obtained by adding CsCl to a warm solution of $NaTcO_4$ in conc. HCl. If HI was used (as in the rhenium preparations [8]) $Cs_2[Tc(OH)Cl_5]$ was produced. The potassium and rubidium salts of $[Tc(OH)Cl_5]^{2-}$ were formed similarly, as was $Cs_2[Tc(OH)Br_5]$. In all preparations the solutions were warmed for one hour (with an IR lamp) before concentrating.

Structures

Single Crystal Analysis of $Cs_2[MoOBr_5]$

Crystals were grown from the mother liquor by placing the solution in an evacuated desiccator over solid KOH. They were sealed in a 0.2 mm Linderman tube to avoid hydrolysis. The data was collected on a Hilger-Watts computer controlled four circle diffractometer, using Zr filtered $MoK\alpha$ radiation. The experimental and crystal data are listed in Table III. Atomic scattering factors were obtained from Tables [32] as well as anomalous dispersion corrections for Mo, Br, and Cs [33]. All calculations were carried out on a Burroughs B6718 computer using programs HILGOUT (derived from DRED, J. F. Blout), PICKOUT (R. J. Doedens), ABSORB (A. Zalkin), CUCLS, FOURIER (derived from ORFLS, W. R. Busing, K. O. Martin and H. A. Levy) and FORDAP (A. Zalkin).

Low temperature cell dimensions of $Cs_2[MoOBr_5]$ were obtained using a Cryo-tip system (Air Products and Chemicals Inc. N.Y., U.S.A.) and a precession camera. The temperature range used was +25° to –125 °C.

X-ray powder data were obtained on a film using a Debye-Scherrer camera with $CuK\alpha$ radiation (Ni filter). Low temperature photographs were also obtained as described previously [34]. X-ray powder diffractograms were recorded with a Phillips Powder Diffractometer fitted with a PW 1050/25 goniometer

TABLE III. Crystal and Experimental Data for Single Crystal X-ray Structural Determination of Cs_2MoOBr_5.

Formula	$Cs_2[MoOBr_5]$
F.W.	777 a.u.
crystal system	cubic
space group	Fm3m
a_0	1065.4(2) pm
volume	1209×10^6 pm^3
density found	$>CH_2I_2 = 3.238$ g/cm^3
density calculated	4.27 gm/cm^3
z	4
F(000)	1340
X-rays	$MoK\alpha$, $\lambda = 71.07$ pm
linear absorption coefficient, μ	245.43 cm^{-1}
crystal dimensions	0.1875 mm(max.) 0.06 mm(min.)
mosaicity	0.08–0.10°
θ scan range	0.48°
Scan time	48 secs
Total background time	24 secs
θ limit	24°
Total reflections	294
independent reflections	79
reflections used in refinement	47 for which $|F|^2 > \sigma|F^2|$
minimum absorption factor	7.653
maximum absorption factor	12.238
Ratio of observations to parameters in least-squares	6:1

using Ni filtered $CuK\alpha$ radiation. Cell parameters were calculated from 2θ data corrected using a KCl internal calibrant ($a_0 = 629.3$ pm) and using a least squares refinement programme POWDER.

Spectra

The infrared spectra were recorded on a Shimadzu 27G spectrophotometer (4000–400 cm^{-1}) and a RIIC Fourier Spectrophotometer (400–40 cm^{-1}). Nujol mulls were used on KBr plates or polythene discs. Low temperature IR spectra were obtained on the Fourier Spectrophotometer using a copper dewar as described previously [34].

Acknowledgements

References

1 E. Wendling, *Bull. Soc. Chim. France*, 5 (1967).
2 E. Wendling and R. Rohmer, *Bull. Soc. Chim. France*, 8 (1967).
3 F. Petillon, M. T. Youinou and J. E. Guerchais, *Compt. Rend.*, (C) *268*, 615 (1969).

4 V. V. Tkachev, O. N. Krasochka and L. O. Atovmyan, *J. Struc. Chem., 17*, 807 (1977).

5 A. Sabatini and I. Bertini, *Inorg. Chem., 5*, 204 (1966).

6 J. Hanuza, M. Baluka and B. Jezowska-Trzebiatowska, *Acta Physica Polon., A42*, 537 (1972).

7 B. Jezowska-Trzebiatowska and J. Hanuza, *J. Mol. Struct., 19*, 109 (1973).

8 J. E. Fergusson and J. L. Love, *Aust. J. Chem., 24*, 2689 (1971).

9 D. A. Edwards and R. T. Ward, *J. Mol. Struct., 6*, 421 (1970).

10 M. Baluka, J. Hanuza and B. Jezowska-Trzebiatowska, *Bull. Akad. Sci. Polon. Sci., 20*, 271 (1972).

11 M. Elder, J. E. Fergusson, G. J. Gainsford, J. H. Hickford and B. R. Penfold, *J. Chem. Soc. (A)*, 1423 (1967).

12 L. O. Atovmyan, O. A. Dyachenko and E. B. Lobkovskii, *J. Struct. Chem., 11*, 429 (1970).

13 F. A. Cotton and S. J. Lippard, *Inorg. Chem., 4*, 1621 (1965).

14 F. A. Cotton and S. J. Lippard, *Inorg. Chem., 5*, 416 (1966).

15 J. E. Scane, *Acta Cryst., 23*, 85 (1967).

16 D. Grandjean and R. Weiss, *Bull. Soc. Chim. France*, 3054 (1967).

17 D. Grandjean and R. Weiss, *Bull. Soc. Chim. France*, 3044 (1967).

18 Y. E. Gorbunova, V. I. Pakhomov, V. G. Kuzetsov and E. S. Kovaleva, *J. Struct. Chem., 13*, 154 (1972).

19 P. W. Frais and C. J. L. Lock, *Canad. J. Chem., 50*, 1181 (1972).

20 W. P. Griffith, *Coord. Chem. Revs., 14*, 115 (1974).

21 J. H. Hickford, Ph. D. Thesis, Univ. of Canterbury, New Zealand (1967).

22 D. Brown, *J. Chem. Soc.*, 1224 (1964).

23 G. W. A. Fowles, *Prep. Inorg. React.*, Editor Jolly W. M., Interscience/Wiley, 121 (1974).

24 L. I. Evteev, *Russ. J. Inorg. Chem., 10*, 1000 (1965).

25 D. E. Grove and G. Wilkinson, *J. Chem. Soc. (A)*, 1224 (1966).

26 B. Jezowska-Trzebiatowska, S. Wajda and M. Baluka, *J. Struct. Chem., 8*, 456 (1967).

27 B. N. Ivanov-Emin and D. K. Chakrabarti, *Russ. J. Inorg. Chem., 12*, 1281 (1967).

28 R. D. Swarnakar and D. K. Chakrabarti, *Chem. Abstr., 77*, 159637 (1972).

29 R. Colton, *Aust. J. Chem., 18*, 435 (1965).

30 B. N. Ivanov-Emin, D. K. Chakrabarti and A. I. Ezhov, *Russ. J. Inorg. Chem., 11*, 733 (1966).

31 M. Pavlova, *J. Inorg. Nucl. Chem., 36*, 1623 (1974).

32 D. T. Cromer and J. B. Mann, *Acta Cryst., 24A*, 321 (1968).

33 D. T. Cromer, *Acta Cryst., 18*, 17 (1965).

34 J. E. Fergusson and A. M. Greenaway, *Aust. J. Chem., 33*, 209 (1980).

35 B. D. Padalia, S. N. Gupta and V. Krishnan, *J. Chem. Phys., 58*, 2084 (1973).