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The Crystal and Molecular Structure of a New Type of Paramagnetic Binuclear Rhenium(IV) Compound, $Cs_3Re_2OCl_{10}$

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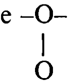
The crystal and molecular structure of $Cs_3Re_2OCl_{10}$ has been determined by single-crystal diffractometry. All atoms conform to the space group $I4/mmm$ with $a=7{\cdot}393$ (3), $c=17{\cdot}51$ (2) Å; $Z=2$. The intensities of 558 reflexions were collected on a $P2_1$ Syntex four-circle diffractometer with a graphite monochromator using Mo $K\alpha$ radiation and the 2θ–ω scan technique. The structure was solved by the heavy-atom method and refined by block-diagonal least squares. The final $R=0{\cdot}035$, $R_w=0{\cdot}033$ for 371 non-zero reflexions. The molecular anion has a linear arrangement of the Cl–Re–O–Re–Cl group, Re–O = 1·832 (3) Å. The bridging O atom is formally occupied by one unpaired electron and that is the reason for the paramagnetism of the compound.

Introduction

The binuclear rhenium(IV) complex of the $K_4Re_2OCl_{10}$ type was prepared for the first time by Jeżowska-Trzebiatowska (1939). Morrow (1962) suggested that this compound crystallizes as a salt like $K_4Re_2OCl_{10}.H_2O$ Our crystallographic studies (Lis, Głowiak and Jeżowska-Trzebiatowska, 1975) have shown that this compound forms non-hydrated crystals. This complex forms a blood-red compound in a dilute hydrochloric acid solution when oxidizing agents are added. The effect of the addition of oxidizers to μ-oxochlororhenate was discovered by Jeżowska-Trzebiatowska (1951), Jeżowska-Trzebiatowska & Przywarska (1955, 1958*a*, *b*, 1961) and Jeżowska-Trzebiatowska, Mroziński & Wojciechowski (1969). On the basis of more experimental results it was suggested that the blood-red compound has the formula $Cs_3Re_2O_2HCl_{10}$, and that the  $-\underset{\underset{\textstyle O}{|}}{O}-$ or –O–O– group forms a bridge between two rhenium(IV) atoms. Hence the determination of the detailed crystal structure of this compound was of considerable interest. We obtained crystals of the blood-red compound for the caesium, potassium and quinoline salts. In this paper are given the results of investigations on the crystal structure of the caesium salt.

Experimental

The investigated compound was prepared by applying a modification of the method given by Jeżowska-Trzebiatowska, Mroziński & Wojciechowski (1969). Hydrogen peroxide was added to the μ-oxochlororhenate in $3M$ hydrochloric acid solution until the solution turned blood-red. The blood-red solution was treated with saturated caesium chloride in hydrochloric acid. The caesium chloride solution was kept in capillaries of about 0·5 mm diameter. In a few hours dark brown-red crystals were obtained, which were tetragonal bipyramids or rectangular parallelepipeds. They are stable in air, but when stood in HCl solution give a little of the $Cs_4Re_2OCl_{10}$ by-product.

Crystal data

Systematic absences were observed for *hkl* when $h+k+l=2n+1$. Since the Laue symmetry is $4/mmm$ the space group is $I\bar{4}2m$, $I4mm$, $I422$, $I\bar{4}m2$ or $I4/mmm$. A crystal of approximate size 0·1 × 0·1 × 0·1 mm was selected for data collection. A Syntex $P2_1$ diffractometer with a graphite monochromator and Mo $K\alpha$ radiation were used for lattice-parameter and intensity measurements. The crystal data are: $Cs_3Re_2OCl_{10}$, M.W. 1141·7, tetragonal, space group $I4/mmm$, $a=7{\cdot}393$ (3), $c=17{\cdot}51$ (2) Å, $Z=2$, $D_m=3{\cdot}9$, $D_x=3{\cdot}96$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda=0{\cdot}71069$) = 104·3 cm^{-1}.

The intensities of $0kl$–$5kl$ reflexions were measured by the 2θ–ω scan technique. Of 558 accessible reflexions 371 with the $I > 1{\cdot}96\sigma(I)$ were used for the structure determination. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The 220 reflexion suffered from strong extinction and was omitted from the calculations. The calculations were performed on the NOVA minicomputer with programs supplied by Syntex.

Structure determination and refinement

The heavy-atom method was employed for the crystal structure determination. The Re–Re vectors were easily identified in a three-dimensional Patterson function with the $I4/mmm$ space group assumed. All the strong peaks on the Patterson map may be explained if the Re atoms lie on the fourfold axis and the Cs^+ cations occupy 2(*b*) and 4(*d*) positions in this space group. A three-dimensional electron density map, calculated with signs based on the Re and Cs^+ positions, showed the positions of the Cl and O atoms, suggesting the formula $Cs_3Re_2OCl_{10}$ and not the one previously expected. At this stage *R* was 0·08. The structure was then refined by block-diagonal least squares, with anisotropic temperature factors for Re, Cs^+, Cl^- and O^-. The scattering curves were those of Cromer &

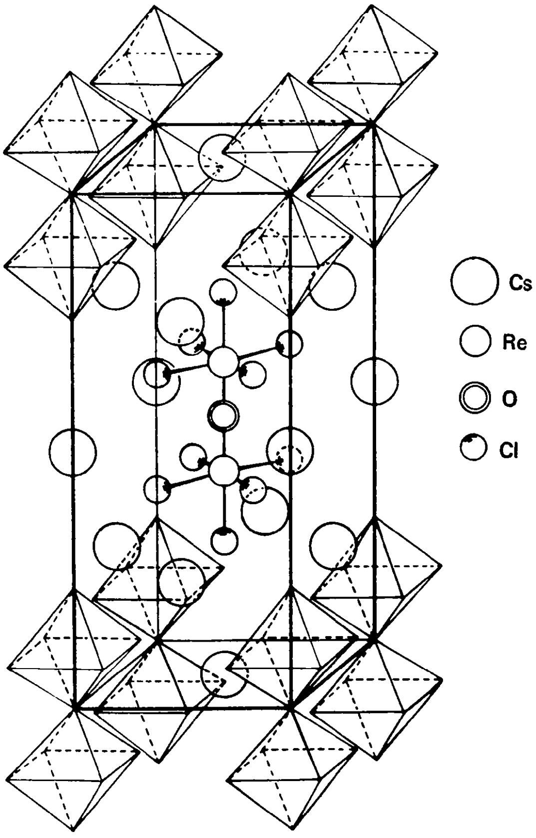


Fig. 1. The crystal structure of $Cs_3Re_2OCl_{10}$.

Table 1. *The final atom parameters with standard deviations in parentheses*

Anisotropic temperature factors are expressed as $\exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	Position	$x=y$	z	$B_{11}=B_{22}$	B_{33}	B_{12}	$B_{13}=B_{23}$
Re	4(*e*)	0	0·10460 (6)	1·45 (2)	1·21 (3)	0	0
Cs(1)	4(*d*)		$\frac{1}{4}$	2·41 (4)	2·40 (6)	0	0
Cs(2)	2(*b*)	0	$\frac{1}{2}$	2·16 (6)	2·59 (9)	0	0
O	2(*a*)	0	0	2·1 (7)	1·8 (10)	0	0
Cl(1)	4(*e*)	0	0·24049 (31)	2·32 (16)	1·21 (21)	0	0
Cl(2)	16(*m*)	0·22449 (27)	0·11047 (16)	2·49 (8)	2·63 (11)	−1·00 (11)	0·12 (8)

Table 2. *Comparison of bond distances* (Å) *in the* $Me_2OX_{10}^{n-}$ *anions*

Compound	Me–O	Me–X_{trans}	Me–X_{cis}	Reference
$Cs_3Re_2OCl_{10}$	1·832 (3)	2·379 (7)	2·349 (4)	This paper
$K_4Re_2OCl_{10}$	1·865 (2)	2·397 (11)	2·385 (3)	Lis, Głowiak & Jeżowska-Trzebiatowska (1975)
$K_4W_2OCl_{10}$	1·871 (1)	2·406 (5)	2·410 (2)	Głowiak, Sabat & Jeżowska-Trzebiatowska (1975)
$K_4Ru_2OCl_{10}$	1·80	2·34	2·34	Mathieson, Mellor & Stephenson (1952)
$Cs_4Os_2OCl_{10}$	1·778	2·433 (7)	2·367–2·376	Tebbe & Schnering (1973)
$Cr_2O(NH_3)_{10}Cl_4.H_2O$	1·821	2·127	2·098–2·136	Yevitz & Stanko (1971)

Waber, as given in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for all atoms. The final agreement indices were $R=0{\cdot}035$ and $R_w=0{\cdot}033$. A difference synthesis computed towards the end of the refinement contained no peaks.*

Results and discussion

The final atomic coordinates, temperature factors and their estimated standard deviations are listed in Table 1. Crystals of $Cs_3Re_2OCl_{10}$ are composed of complex anions $Re_2OCl_{10}^{3-}$ and Cs^+ cations. The crystal structure is shown in Fig. 1. The complex anion consists of two octahedra with a common corner; the common corner is occupied by an O atom, while the remaining corners are filled by Cl atoms. The complex anions have D_{4h} symmetry. The Re atoms are not located in the Cl plane perpendicular to the fourfold axis of the anion but on the axis 0·103 Å distant from the Cl plane on the side toward the O atom. Thus O–Re–Cl_{cis} bond angle is 92·7 (1)°. The Re–Cl distances are: Re–Cl_{cis} 2·349 (4), Re–Cl_{trans} 2·379 (7) Å.

Our X-ray studies forced the assumption that in the $Re_2OCl_{10}^{3-}$ ion both rhenium atoms are in the +4 oxidation state, and that one unpaired electron is most probably located on the O atom, and therefore oxygen should be in the −1 oxidation state. This type of oxy-compound, *i.e.* with the bridge O atom containing one unpaired electron, has not been previously reported in the literature. The formation of the compound investigated can be written as

$$2Re_2OCl_{10}^{4-}+2H^+ +H_2O_2 \rightarrow 2Re_2OCl_{10}^{3-}+2H_2O\,.$$

In this reaction either H_2O_2 or some other oxidizing agent takes up one electron from the O bridge atom in the $Re_2OCl_{10}^{4-}$ ion. Both the above scheme and the reaction mechanism can be compared with the data collected in Table 2. As may be seen, the Me–O bonding length in the $Re_2OCl_{10}^{4-}$ ion exceeds by 0·03 Å that in the $Re_2OCl_{10}^{3-}$ ion and its value is the largest in all the μ-oxo complexes (apart from $K_4W_2OCl_{10}$) examined with X-rays. Moreover, all Re–Cl bondings are shorter in $Cs_3Re_2OCl_{10}$ than in $K_4Re_2OCl_{10}$. The confirmation can be given in terms of the molecular orbital scheme calculated theoretically for $K_4Re_2OCl_{10}$ (Jeżowska-Trzebiatowska, Kozłowski & Natkaniec, 1971). In the $Re_2OCl_{10}^{4-}$ ion all antibonding orbitals are filled and that is why the Re–O distance is 'long'. The $Re_2OCl_{10}^{3-}$ anion contains one electron less in the antibonding orbital and hence the Re–O bonding length is shorter than in the $Re_2OCl_{10}^{4-}$ anion.

The difference in the Re–O bond length in these two compounds is reflected in their infrared spectra. Since the Re–O bond length in $K_4Re_2OCl_{10}$ is larger than in $Cs_3Re_2OCl_{10}$, the ν_{as} Re–O–Re absorption band for $K_4Re_2OCl_{10}$ should appear at a lower frequency than that for $Cs_3Re_2OCl_{10}$. Jeżowska-Trzebiatowska, Mroziński & Wojciechowski (1969) on the basis of the infrared spectra for the $K_4Re_2OCl_{10}$ complex assigned 860 cm^{-1} as ν_{as} Re–O–Re, and 875 cm^{-1} as ν_{as} O–O for the blood-red complex. The results reported here indicate that the band at 875 cm^{-1} also corresponds to ν_{as} Re–O–Re and the frequency shift is due to the change of the Re–O bond length.

The magnetic moment of the complex investigated is 3·57 BM per molecule (Jeżowska-Trzebiatowska, Mroziński & Wojciechowski, 1969). This value of the magnetic moment, measured for the powder of the precipitated substance, exceeds one electron per molecule. This is most probably because it was impossible to synthesize a larger amount of the pure compound.

As reported earlier, the compound investigated, unlike other rhenium(IV) compounds, does not hydrolyse immediately to ReO_2 in an alkali solution, but is transformed into a yellow complex; its crystal structure will be investigated.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31312 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.