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The Crystal and Molecular Structure of Tetrapotassium μμ′-Dioxo-tetraoxalatodirhenium(IV) Trihydrate

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The crystal and molecular structure of the compound $K_4[Re_2O_2(C_2O_4)_4].3H_2O$ has been determined by single-crystal diffractometry. The space group is $P\bar{1}$ and the dimensions of the reduced cell are: $a=8{\cdot}806$ (3), $b=10{\cdot}836$ (7), $c=15{\cdot}837$ (9) Å, $\alpha=112{\cdot}57$ (5), $\beta=100{\cdot}73$ (5) and $\gamma=120{\cdot}39$ (5)°. Data to $2\theta\simeq 55°$ (Mo $K\alpha$ radiation) for 3391 reflexions were measured on a $P2_1$ Syntex four-circle diffractometer. The structure was solved by the heavy-atom technique and refined by the block-diagonal least-squares method. The final $R=0{\cdot}032$, $R_w=0{\cdot}029$ for 2396 non-zero reflexions. The complex ion consists of two octahedrally coordinated rhenium atoms with the octahedra joined on a common edge; the bridging atoms on this common edge are two oxo oxygen atoms. The quadrilateral formed by the two bridging atoms and the two rhenium atoms is practically planar, with a Re–Re distance of 2·362 (1) Å.

Introduction

It is known (Sen & Ray, 1953), that solutions of freshly prepared ReO_2 in oxalic acid form dark brown diamagnetic rhenium(IV) oxalato complexes. The complexes were considered by the authors to be binuclear and their diamagnetism was explained by assuming metallic bonds between rhenium atoms:

$$K_4[C_2O_4(OH)_4Re \vdots\vdots Re(OH)_4C_2O_4]\,.$$

Disagreeing with these authors, Jeżowska-Trzebiatowska & Wajda (1958), on the basis of larger experimental material, suggested that during the dissolution of ReO_2 in oxalic acid binuclear single-oxygen-bridged complexes are formed. These authors obtained two rhenium complexes in the form of potassium salts:

(I) $K_4Re_2(OH)_6(C_2O_4)_2O$ (dark-brown crystalline powder),
(II) $K_4Re_2(OH)_2(C_2O_4)_4O$ (green crystals).

Recently, similar complexes have been obtained by Bashidova & Shodiev (1973). The determination of the detailed structure of the diamagnetic rhenium(IV) oxalate complexes and the nature of the rhenium–rhenium interactions are therefore of considerable interest.

Experimental

To obtain diamagnetic oxalatooxo complexes of rhenium(IV), rhenium dioxide was heated under reflux with oxalic acid and potassium oxalate in the molar ratio $Re:H_2C_2O_4:K_2C_2O_4=1:3:1$. After cooling, ethyl alcohol was added to the dark red-brown solution. The separate brown precipitate was filtered off. Ethyl alcohol was added to the filtrate until an olive-green precipitate was produced. This precipitate was then dissolved in water and recrystallized. In contrast to Jeżowska-Trzebiatowska & Wajda (1958), three kinds of crystals were obtained by slow evaporation of that solution:

(1) dark-red; space group $Pnn2$ ($a=14{\cdot}27$, $b=27{,}21$, $c=17{\cdot}52$ Å);
(2) red; space group $Pbca$ ($a=16{\cdot}1$, $b=14{\cdot}7$, $c=34{\cdot}8$ Å);
(3) green-red.

In the present paper the results of investigations of the crystal structure of the green-red compound are given.

An irregularly shaped crystal of approximate size $0{\cdot}10\times0{\cdot}08\times0{\cdot}08$ mm was selected for the data collection. A Syntex $P2_1$ diffractometer and Mo $K\alpha$ radiation with graphite monochromator were used for lattice-parameter and intensity measurements. The crystal data are: $K_4[Re_2O_2(C_2O_4)_4].3H_2O$, M.W. 967, triclinic, space group $P\bar{1}$, $a=8{\cdot}806$ (3), $b=10{\cdot}836$ (7), $c=15{\cdot}837$ (9) Å, $\alpha=112{\cdot}57$ (5), $\beta=100{\cdot}73$ (5), $\gamma=120{\cdot}39$ (5)°, $Z=2$, $D_m=3{\cdot}01$ (3), $D_x=3{\cdot}036$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda=0{\cdot}71069)=129{\cdot}8$ cm^{-1}.

The intensities of reflexions were measured by the 2θ–ω-scan technique. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. Of 3391 accessible reflexions below $2\theta=55°$, 2396 with $|F_c|\geq1{\cdot}96\sigma$ were used for the structure determination. The calculations were performed on the NOVA minicomputer with programs supplied by Syntex.

Determination of the structure

The heavy-atom method was employed for the phase determination. The Re–Re vectors were identified in a three-dimensional Patterson function. A three-dimensional electron density map calculated with signs based on the Re structure showed the positions of the potassium cations. Refinement, using block-diagonal least-squares methods, lowered the residual R to 0·203. A difference Fourier map at this point revealed the positions of 29 peaks of similar density. All these peaks were used for determination of the light-atom positions in the $K_4Re_2O_2(C_2O_4)_4.3H_2O$ formula, and R then dropped to 0·066. The observed density, measured by flotation in a mixture of $CHBr_3$ and CBr_4, is 3·01 (3) g cm^{-3}, which agrees well with the calculated density of 3·036 g cm^{-3} assuming two molecules in the unit cell. The structure was than refined by block-diagonal least-squares methods. The final agreement indices were $R=0·032$ and $R_w=0·029$. A difference synthesis computed towards the end of the refinement contained the highest two peaks about $\frac{1}{4}$ the peak density for carbon atoms on earlier difference Fourier maps, but water hydrogen atoms were not resolvable.

Results and discussion

The final atomic coordinates, temperature factors and their estimated standard deviations are listed in Table 1. Crystals of potassium $\mu\mu'$-dioxo-tetraoxalatodirhenium(IV) trihydrate are composed of complex anions $Re_2O_2(C_2O_4)_4^{4-}$, potassium cations and water molecules. The arrangement of the molecules in projection on the (100) plane is shown in Fig. 1.

Fig. 2 shows the overall structure and numbering scheme of the $Re_2O_2(C_2O_4)_4^{4-}$ ions. The bond lengths and angles in the complex anion are given in Table 2. The rhenium atoms are bridged by two oxo oxygen atoms O(9) and O(10). These oxo oxygen atoms occupy two corners, common to the two octahedra, while the remaining corners are filled by oxalate oxygen atoms. The molecular structure as a whole possesses neither crystallographic nor virtual symmetry higher than C_1. However, the inner coordination sphere (Fig. 2) has effective D_2 symmetry. The investigated crystal itself is optically inactive: it is built up of two optically active isomers of opposite signs of rotation.

The Re–Re distance (2·362 Å) in $K_4Re_2O_2(C_2O_4)_4.3H_2O$ is only a little larger than in binuclear rhenium(III) compounds: 2·22 Å in

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

Positional parameters are given as fractions of cell edges × 10^4 (× 10^5 for rhenium). Anisotropic temperature factors are expressed as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	1227 (12)	1326 (10)	9411 (6)	2·8 (4)	2·3 (4)	1·4 (3)	2·0 (3)	1·3 (3)	1·2 (3)
O(2)	2046 (12)	2939 (10)	8482 (6)	2·2 (4)	1·9 (4)	2·2 (4)	1·4 (3)	1·1 (3)	1·0 (3)
O(3)	383 (12)	136 (10)	3564 (6)	2·4 (4)	2·5 (4)	1·7 (3)	2·0 (3)	1·0 (3)	1·1 (3)
O(4)	8012 (11)	307 (10)	7647 (6)	2·3 (4)	2·4 (4)	2·2 (4)	1·8 (3)	1·8 (3)	1·8 (3)
O(5)	7866 (11)	923 (10)	882 (6)	2·2 (4)	2·3 (4)	1·2 (3)	1·4 (3)	0·3 (3)	0·8 (3)
O(6)	299 (11)	4027 (10)	2564 (5)	2·1 (4)	1·4 (4)	1·3 (4)	0·7 (4)	0·2 (3)	0·5 (3)
O(7)	9780 (11)	2707 (10)	3931 (6)	1·8 (4)	1·8 (4)	1·7 (3)	1·1 (3)	0·6 (3)	0·8 (3)
O(8)	6786 (11)	1902 (10)	2528 (6)	2·3 (4)	2·7 (4)	1·2 (3)	1·7 (4)	0·7 (3)	1·0 (3)
O(9)	2894 (11)	703 (10)	8007 (6)	1·5 (4)	2·2 (4)	1·7 (3)	0·9 (3)	0·6 (3)	0·9 (3)
O(10)	1400 (11)	2066 (10)	2520 (6)	2·5 (4)	2·2 (4)	2·2 (4)	1·7 (3)	1·5 (3)	1·6 (3)
O(11)	2992 (13)	3768 (11)	958 (6)	3·4 (5)	3·7 (5)	1·5 (4)	2·4 (4)	0·4 (4)	0·5 (4)
O(12)	6573 (14)	4565 (11)	68 (7)	3·6 (5)	1·9 (4)	4·3 (5)	1·9 (4)	1·5 (4)	0·8 (4)
O(13)	2147 (13)	9969 (11)	4638 (6)	3·1 (5)	4·1 (5)	2·2 (4)	2·3 (4)	1·0 (4)	2·3 (4)
O(14)	5996 (12)	302 (11)	6577 (7)	2·9 (4)	3·6 (5)	3·8 (5)	2·5 (4)	1·7 (4)	2·7 (4)
O(15)	8199 (13)	1874 (12)	9872 (6)	3·9 (5)	4·6 (5)	2·1 (4)	2·8 (4)	1·5 (4)	2·4 (4)
O(16)	9302 (13)	4724 (11)	8296 (7)	3·5 (5)	2·8 (4)	4·3 (5)	2·0 (4)	2·0 (4)	2·8 (4)
O(17)	8868 (12)	3390 (10)	5123 (6)	3·0 (4)	2·7 (4)	1·4 (3)	1·9 (4)	1·3 (3)	1·1 (3)
O(18)	6238 (12)	3317 (11)	3718 (6)	2·6 (4)	2·9 (4)	2·3 (4)	2·1 (4)	1·0 (3)	1·2 (3)
C(1)	2289 (18)	2989 (16)	21 (9)	2·0 (6)	2·6 (6)	1·7 (5)	1·5 (5)	0·8 (5)	0·8 (5)
C(2)	2671 (18)	3932 (15)	9469 (9)	2·0 (6)	2·3 (6)	2·8 (6)	1·8 (5)	0·9 (5)	1·1 (5)
C(3)	8323 (17)	24 (14)	6130 (8)	2·0 (6)	1·5 (5)	1·0 (5)	1·0 (5)	0·0 (4)	0·6 (4)
C(4)	7315 (19)	220 (14)	6833 (9)	3·4 (7)	1·3 (5)	2·6 (6)	1·4 (5)	1·7 (5)	1·6 (5)
C(5)	8630 (17)	2169 (16)	730 (9)	1·5 (6)	3·5 (6)	2·8 (6)	1·9 (5)	1·1 (5)	2·4 (5)
C(6)	26 (18)	4004 (17)	1737 (9)	2·1 (6)	3·2 (6)	3·6 (6)	2·1 (6)	1·9 (5)	2·3 (6)
C(7)	8675 (17)	2972 (14)	4274 (9)	1·7 (6)	1·0 (5)	2·8 (6)	0·5 (5)	1·1 (5)	0·8 (5)
C(8)	7062 (16)	2735 (14)	3461 (8)	1·4 (5)	1·1 (5)	1·2 (5)	0·5 (4)	0·2 (4)	0·4 (4)
K(1)	6389 (4)	2420 (4)	5950 (2)	2·4 (1)	2·3 (1)	2·2 (1)	1·5 (1)	1·0 (1)	1·4 (1)
K(2)	6790 (4)	2462 (4)	8620 (2)	2·3 (1)	2·5 (1)	2·4 (1)	1·5 (1)	1·2 (1)	1·6 (1)
K(3)	3468 (5)	1667 (4)	1439 (2)	3·0 (2)	3·5 (2)	3·3 (1)	2·3 (1)	1·7 (1)	2·2 (1)
K(4)	1880 (5)	2894 (4)	5648 (2)	3·3 (2)	4·1 (2)	2·1 (1)	2·8 (1)	1·2 (1)	1·4 (1)
$H_2O(1)$	5499 (13)	4328 (11)	5562 (7)	2·6 (5)	2·9 (4)	4·3 (5)	1·6 (4)	0·9 (4)	2·3 (4)
$H_2O(2)$	4476 (13)	2892 (11)	7147 (7)	3·3 (5)	3·5 (6)	3·5 (4)	2·5 (4)	2·0 (4)	2·5 (4)
$H_2O(3)$	2605 (16)	4950 (14)	7596 (8)	6·3 (6)	6·6 (5)	4·9 (6)	5·4 (6)	3·7 (5)	3·8 (5)
Re(1)	4645 (7)	3243 (6)	78845 (4)	1·64 (2)	1·42 (2)	1·25 (2)	0·99 (2)	0·63 (2)	0·68 (2)
Re(2)	89241 (7)	16457 (6)	23855 (3)	1·59 (2)	1·45 (2)	1·27 (2)	0·96 (2)	0·58 (2)	0·71 (2)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30907 (60 pp., 2 microfiches). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$(pyH)_2(Re_2Cl_8)$ (Kuznetsov & Koz'min, 1963) and 2·241 Å in $K_2Re_2Cl_8.2H_2O$ (Cotton & Harris, 1965), in which one observes strong rhenium–rhenium interactions. In the $Re_2Cl_8^{2-}$ anion there are only direct rhenium–rhenium bonds and the authors assumed that the Re–Re bonds are quadruple.

The Re–O_b and Re–Re lengths in
(1) $K_4Re_2O_2(C_2O_4)_4.3H_2O$,
(2) $Re_2OCl_5(C_2H_5CO_2)[P(C_6H_5)_3]_2$ (Cotton & Foxman, 1968) and (3) $Re_2OCl_3(C_2H_5CO_2)_2[P(C_6H_5)_3]_2$ (Cotton, Eiss & Foxman, 1969), are given in Table 3. In (2) and (3), where the bridging atoms are O and Cl, the authors assumed a double bond between rhenium atoms according to the criterion of distance. In all three studied oxo compounds the Re–O_b bonds are chemically identical. Differences between the Re–Re distances probably show the influence of the different ligands (O and Cl).

Thus according to the criterion of distance one may assume that in $Re_2O_2(C_2O_4)_4^{4-}$ ions a covalent Re–Re bond occurs. A short Re–Re distance with a very strong rhenium–rhenium interaction results in the diamagnetism of the investigated compound.

A strong metal–metal interaction was also observed in μμ'-dioxo-bridged dimeric oxomolybdates(V), by

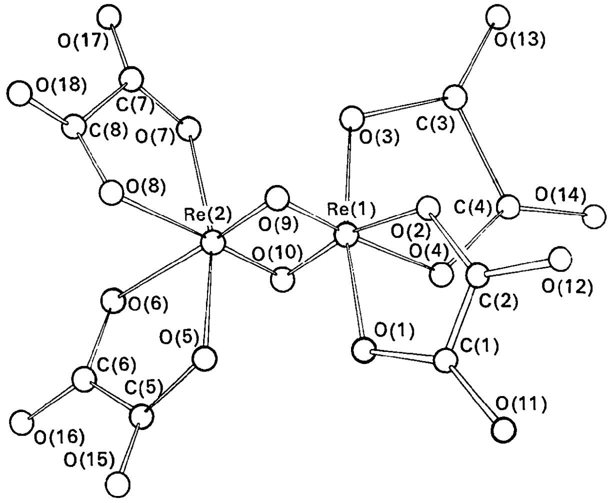

Fig. 2. The overall structure and numbering scheme of the $Re_2O_2(C_2O_4)_4^{4-}$ ions.

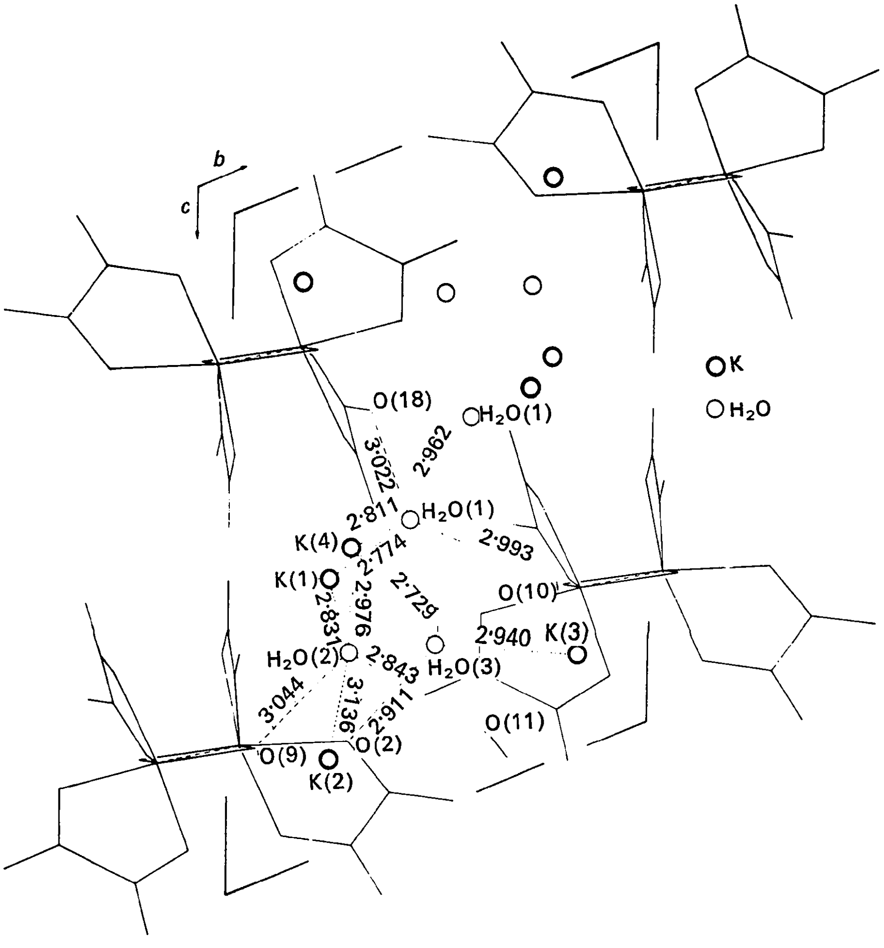

Fig. 1. The crystal structure of $K_4Re_2O_2(C_2O_4)_4.3H_2O$: projection on the (100) plane.

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* $[Re_2O_2(C_2O_4)_4]^{4-}$ *anion*

See Fig. 2 for numbering.

Re(1)–O(1)	2·029 (7)	O(1)—Re(1)–O(2)	79·0 (4)
Re(1)–O(2)	2·079 (10)	Re(1)–O(1)—C(1)	116·6 (9)
O(1)—C(1)	1·296 (17)	Re(1)–O(2)—C(2)	115·3 (9)
O(2)—C(2)	1·301 (15)	O(1)—C(1)—C(2)	114·8 (13)
O(11)–C(1)	1·209 (14)	O(2)—C(2)—C(1)	113·9 (13)
O(12)–C(2)	1·200 (19)	O(11)–C(1)—C(2)	121·8 (14)
C(1)—C(2)	1·540 (22)	O(12)–C(2)—C(1)	120·8 (14)
Re(1)–O(3)	2·044 (8)	O(3)—Re(1)–O(4)	78·4 (4)
Re(1)–O(4)	2·111 (11)	Re(1)–O(3)—C(3)	116·5 (9)
O(3)—C(3)	1·273 (20)	Re(1)–O(4)—C(4)	114·8 (9)
O(4)—C(4)	1·264 (16)	O(3)—C(3)—C(4)	114·6 (12)
O(13)–C(3)	1·214 (15)	O(4)—C(4)—C(3)	114·7 (13)
O(14)–C(4)	1·217 (22)	O(13)–C(3)—C(4)	120·3 (13)
C(3)—C(4)	1·565 (22)	O(14)–C(4)—C(3)	119·3 (14)
Re(2)–O(5)	2·038 (7)	O(5)—Re(2)–O(6)	77·7 (4)
Re(2)–O(6)	2·087 (10)	Re(2)–O(5)—C(5)	116·9 (9)
O(5)—C(5)	1·313 (20)	Re(2)–O(6)—C(6)	117·1 (9)
O(6)—C(6)	1·275 (17)	O(5)—C(5)—C(6)	114·1 (13)
O(15)–C(5)	1·202 (16)	O(6)—C(6)—C(5)	113·7 (14)
O(16)–C(6)	1·222 (21)	O(15)–C(5)—C(6)	123·8 (14)
C(5)—C(6)	1·540 (20)	O(16)–C(6)—C(5)	120·9 (15)
Re(2)–O(7)	2·039 (7)	O(7)—Re(2)–O(8)	77·6 (4)
Re(2)–O(8)	2·076 (12)	Re(2)–O(7)—C(7)	117·9 (9)
O(7)—C(7)	1·298 (20)	Re(2)–O(8)—C(8)	117·1 (9)
O(8)—C(8)	1·295 (14)	O(7)—C(7)—C(8)	113·1 (12)
O(17)–C(7)	1·189 (15)	O(8)—C(8)—C(7)	112·1 (12)
O(18)–C(8)	1·211 (20)	O(17)–C(7)—C(8)	122·3 (13)
C(7)—C(8)	1·561 (20)	O(18)–C(8)—C(7)	121·6 (13)
Re(1)–O(9)	1·918 (11)	O(9)—Re(1)–O(10)	104·6 (4)
Re(1)–O(10)	1·962 (10)	O(9)—Re(2)–O(10)	105·1 (4)
Re(2)–O(9)	1·928 (10)	Re(1)–O(9)—Re(2)	75·8 (4)
Re(2)–O(10)	1·938 (11)	Re(1)–O(10)–Re(2)	74·6 (4)

Table 3. *Comparison of bond distances* (Å) *in the* $\mathrm{Re}{<}^{\mathrm{lig}}_{\mathrm{O}}{>}\mathrm{Re}$ *ring*

	Re–Re	Re–O
$Re_2OCl_5(C_2H_5CO_2)\,[P(C_6H_5)_3]_2$	2·522 (1)	1·889 (8)
$Re_2OCl_3(C_2H_5CO_2)_2\,[P(C_6H_5)_3]_2$	2·514 (1)	1·916 (6)
$K_4Re_2O_2(C_2O_4)_4.3H_2O$	2·362 (1)	1·936 (25)

Jeżowska-Trzebiatowska, Rudolf, Natkaniec & Sabat (1974). The presence of strong metal-metal bonds in dimeric oxygen-bridged oxomolybdates(V) was confirmed by SCCC MO calculations.

In all three oxo compounds (Table 3), the $\mathrm{Re}{<}^{\mathrm{lig}}_{\mathrm{O}}{>}\mathrm{Re}$ groups are planar. The least-squares plane of the Re_2O_2 grouping is described in Table 4. It is interesting to note that the distance Re–O *trans* to the oxo oxygen atoms are little longer (2·075–2·111 Å) than the remaining Re–O distances (2·026–2·045 Å).

Table 4. *Analysis of the planarity of the* $\mathrm{Re}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Re}$ *ring*

The equation of the least-squares plane is:

$$0{\cdot}2829X+0{\cdot}9108Y-0{\cdot}3008Z=1{\cdot}0957$$

Atomic deviations (Å)

Re(1)	0·0087	O(9)	−0·0087
Re(2)	−0·0086	O(10)	0·0086

The bond distances and angles within the chelate rings (Table 2) are in a good agreement with values found in other complexes $K_2[MoO_2(C_2O_4)\,(H_2O)]_2O$ (Cotton, Morehouse & Wood, 1964), and $BaMo_2O_4(C_2O_4)_2.5H_2O$ (Cotton & Morehouse, 1965); however, in the rhenium complex the oxalato ions are not quite planar.

The different types of contacts between water molecules and other atoms (the shortest are shown on Fig. 1) suggest that the water molecules stabilize the structure. The K–H_2O distances range between 2·73 and 3·14 Å, and the H_2O–O distances are longer than 2·84 Å, indicating that the hydrogen bonds are comparatively weak.

The potassium ions are surrounded by various numbers of oxygen atoms (from water and oxalate ions) forming an irregularly shape.

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