Acta Chemica Scandinavica A 39 (1985) 79–83

The Crystal Structure of Potassium Oxalatooxodiperoxotungstate(2−), $K_2[WO(O_2)_2(C_2O_4)]$

ROLF STOMBERG and SOLVEIG OLSON

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

The crystal structure of $K_2[WO(O_2)_2(C_2O_4)]$ has been determined and refined from single-crystal X-ray diffractometer data to a final R_F-value of 0.033 for 1372 observed independent reflexions. The compound crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a=13.650(5), b=8.881(3), c=6.911(3) Å, β=93.06(3)° and Z=4, and has been shown to be isomorphous with its molybdenum analogue. Tungsten is thus coordinated in the pentagonal-bipyramidal way, the two peroxo groups and one oxalato oxygen atom forming the equatorial plane and the double-bonded oxygen atom and another oxalato oxygen atom being apically situated.

Bond distances: $W{=}O_{apical}$ 1.716(7) Å, $W{-}O_{apical}$ 2.245(6) Å, $W{-}O_{equatorial}$ 2.033(6) Å, *trans* $W{-}O_{peroxo}$ 1.965(8) and 1.968(7) Å, *cis* $W{-}O_{peroxo}$ 1.928(6) and 1.941(6) Å, and $(O{-}O)_{peroxo}$ 1.510(10) and 1.496(10) Å.

The crystal structures of only two peroxotungstates seem to have been determined hitherto, *i.e.* $K_2[O\{WO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$,[1] and $(C_9H_8NO)_2[WF_4O(O_2)]\cdot 3H_2O$.[16]

We have, therefore, extended our synthetic and structural work on peroxometallates to those containing tungsten. Stomberg reported the structure of $K_2[MoO(O_2)_2(C_2O_4)]$ in 1969.[2] Shortly afterwards, Šljukić *et al.* published crystal data for this compound and for the corresponding tungsten analogue.[3] The compounds crystallize in the same space group, $P2_1/n$, and have similar cell dimensions. Judging from this they were claimed to be isomorphous or closely related. Stomberg showed, however, that $K_2[O\{MoO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$ is not isomorphous with $K_2[O\{WO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$, even though they both crystallize in space group $P\bar{1}$ and have almost equal cell dimensions.[4] Since the situation might be similar for the oxalato compounds, structural investigation of $K_2[WO(O_2)_2(C_2O_4)]$ has been undertaken.

EXPERIMENTAL

Preparation. Solutions of 0.8 g K_2WO_4 in 10 ml H_2O and 1 g $H_2C_2O_4$ in 10 ml H_2O were mixed and 5 ml 30 % H_2O_2 were added. Within a couple of hours at 5 °C colourless prismatic crystals had separated.

X-Ray method. Intensity data were collected with a SYNTEX $P2_1$ X-ray diffractometer (graphite-monochromatized Mo$K\alpha$ radiation, θ–2θ scan method, scan speed 3.5–29.3 °/min, two test reflexions). Integrated intensity values were obtained with the Lehmann-

0302-4377/85 $2.50

Larsen profile analysis method.[5] Several crystals were used and data collection was performed both at 18 and −100 °C. In all cases the crystals showed decomposition. For the data set finally adopted, a crystal with the dimensions 0.10×0.18×0.20 mm was used and the intensities were collected at 18 °C for $3.5° \leqq 2\theta \leqq 50°$ and then for $50° \leqq 2\theta \leqq 60°$. Due to the decomposition, data above $2\theta = 50°$ had to be discarded. Of the 1596 independent reflexions collected up to $2\theta = 50°$, 1372 having $I \geqq 3\sigma(I)$ were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz, polarization and absorption effects. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

CRYSTAL DATA

$K_2[WO(O_2)_2(C_2O_4)]$ F.W.=430.06

Space group $P2_1/n$ (No. 14; non-standard setting) $a=13.650(5)$ Å, $b=8.881(3)$ Å, $c=6.911(3)$ Å, $\beta=93.06(3)°$, $V=836.6(5)$ Å^3, $Z=4$, $D_x=3.415$ g cm^{-3}, $\mu(\text{Mo}K\alpha)=15.6$ mm^{-1}.

STRUCTURE DETERMINATION

Patterson and electron density calculations indicated isomorphism with $K_2[MoO(O_2)_2(C_2O_4)]$,[2] whose atomic coordinates therefore were used as starting parameters in the least-squares refinement of the structure. Refinement of positional and isotropic thermal parameters gave an R-value of 0.070 ($R=\sum||F_o|-|F_c||/\sum|F_o|$)before applying the absorption correction and 0.043 after, using an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart.[6] The introduction of anisotropic thermal parameters led to a further reduction of the R-value to 0.033 (0.044 before absorption correction). The atomic scattering factors for K, W, O and C were taken from Ref. 7. Weights were applied according to $w=(50+|F_o|+0.006|F_o|^2+0.0002|F_o|^3)^{-1}$.[8] The highest peak in the final electron density difference map was 1.2 e/Å^3. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Ref. 9. Lists of structure factors and anisotropic thermal parameters are available from R.S. on request.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for $K_2[WO(O_2)_2(C_2O_4)]$. $B_{eq}=\frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Atom	x	y	z	B_{eq}/Å^2
W	0.16910(2)	0.20437(4)	0.26368(4)	1.54(1)
K1	0.4781(2)	0.3532(2)	0.2669(3)	2.78(5)
K2	0.2299(1)	0.4320(2)	0.7357(3)	2.27(4)
O1	0.1455(6)	0.2224(8)	−0.0183(11)	3.4(2)
O2	0.1678(5)	0.0637(8)	0.0486(9)	2.7(2)
O3	0.1384(6)	0.1746(9)	0.5360(10)	3.0(2)
O4	0.1654(5)	0.0330(7)	0.4344(9)	2.7(2)
O5	0.2883(5)	0.2654(9)	0.2926(12)	3.2(2)
O6	0.1111(5)	0.4141(7)	0.2857(11)	2.8(2)
O7	−0.0209(5)	0.5581(8)	0.2699(11)	3.1(2)
O8	0.0060(5)	0.1702(7)	0.2370(11)	2.5(2)
O9	−0.1336(6)	0.2963(7)	0.2586(16)	3.9(2)
C1	0.0171(7)	0.4353(11)	0.2730(14)	2.5(2)
C2	−0.0448(7)	0.2906(9)	0.2523(14)	2.1(2)

Table 2. Bond distances (Å) and angles (°) in $K_2[WO(O_2)_2(C_2O_4)]$.

Distance	Angle	Angle	Angle
W–O1 1.965(8)	O1–W–O2 45.5(3)	O3–W–O4 45.2(3)	W–O2–O1 68.1(4)
W–O2 1.941(6)	O1–W–O3 158.1(3)	O3–W–O5 100.4(4)	W–O3–O4 66.0(4)
W–O3 1.968(7)	O1–W–O4 131.5(3)	O3–W–O6 87.0(3)	W–O4–O3 68.8(4)
W–O4 1.928(6)	O1–W–O5 101.2(4)	O3–W–O8 78.4(3)	W–O6–C1 121.1(6)
W–O5 1.716(7)	O1–W–O6 87.5(3)	O4–W–O5 103.5(3)	W–O8–C2 114.8(6)
W–O6 2.033(6)	O1–W–O8 80.6(3)	O4–W–O6 130.9(3)	O6–C1–O7 123.8(9)
W–O8 2.245(6)	O2–W–O3 130.7(3)	O4–W–O8 83.4(3)	O6–C1–C2 114.9(8)
O1–O2 1.510(10)	O2–W–O4 87.8(3)	O5–W–O6 94.2(3)	O7–C1–C2 121.3(8)
O3–O4 1.496(10)	O2–W–O5 105.2(3)	O5–W–O8 169.1(3)	O8–C2–O9 125.6(8)
C1–C2 1.540(13)	O2–W–O6 131.3(3)	O6–W–O8 75.0(2)	O8–C2–C1 114.1(8)
C1–O6 1.295(11)	O2–W–O8 83.2(3)	W–O1–O2 66.4(4)	O9–C2–C1 120.3(8)
C1–O7 1.207(12)			
C2–O8 1.281(11)			
C2–O9 1.217(13)			

Table 3. Cation environment in $K_2[WO(O_2)_2(C_2O_4)]$.[a]

Distance/Å		Distance/Å		Distance/Å	
K1···O7^{i}	2.700(7)	K1···O4^{iv}	2.833(7)	K2···O4^{vi}	2.774(7)
K1···O5	2.720(8)	K1···O2^{iv}	3.059(7)	K2···O1^{vii}	2.808(8)
K1···O1^{ii}	2.742(9)	K2···O2^{iv}	2.733(7)	K2···O7^{v}	2.852(7)
K1···O3^{iii}	2.787(8)	K2···O9^{v}	2.749(7)	K2···O3	2.917(8)
K1···O8^{iv}	2.824(7)	K2···O9^{ii}	2.752(8)		

[a]Symmetry codes: ^{i} $(\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z)$. ^{ii} $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$. ^{iii} $(\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$. ^{iv} $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. ^{v} $-x, 1-y, 1-z)$. ^{vi} $(\frac{1}{2}-x, \frac{1}{2}+y, 1\frac{1}{2}-z)$. ^{vii} $(x, y, 1+z)$.

RESULTS AND DISCUSSION

Positional and thermal parameters are given in Table 1, bond distances in Table 2 and coordination distances to the potassium ions in Table 3. A stereoscopic drawing of the unit cell is shown in Fig. 1 and the anion in Fig. 2.

The structure analysis has shown that $K_2[WO(O_2)_2(C_2O_4)]$ is isomorphous with the corresponding molybdenum compound, which means that tungsten has pentagonal-bipyramidal coordination geometry. The discussion of $K_2[MoO(O_2)_2(C_2O_4)]$ is equally applicable to $K_2[WO(O_2)_2(C_2O_4)]$, but due to improved accuracy some additional remarks can be made.

The O–O distances, 1.510(10) and 1.496(10) Å, compare well with the mean peroxo bond length 1.50(3) Å observed for $K_2[O\{WO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$,[1] but may be longer than those observed in peroxovanadates, the weighted mean in these being 1.464(6) Å (see Refs. 7–17 in Ref. 10).

In most tungstates studied hitherto the coordination polyhedra are linked together and show a wide range of W–O distances (1.5–2.5 Å). In the recently studied monomeric hexaphenoxotungstate(V) ion[11] the W–O distances, 1.906(6)–1.956(4) Å, are comparable to those obtained in the present investigation, *i.e.* 1.928(6)–1.968(7) Å. In

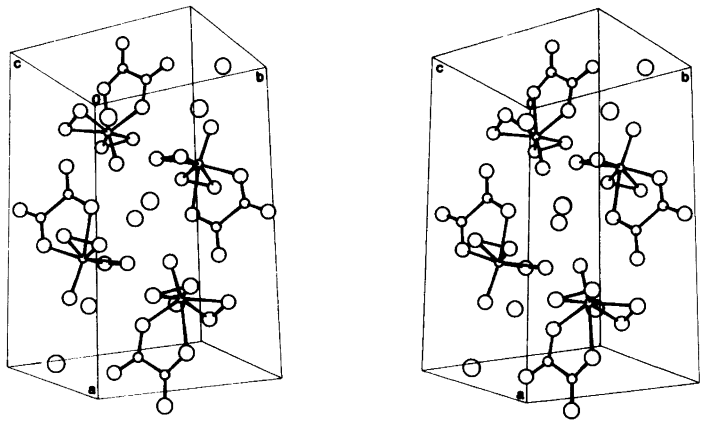

Fig. 1. Stereoscopic drawing of the unit cell of $K_2[WO(O_2)_2(C_2O_4)]$.

$K_2[O\{WO(O_2)_2(H_2O)\}_2]\cdot 2H_2O$,[1] the mean W–O and W=O bond lengths were found to be 1.93(2) and 1.68(3) Å, respectively, the latter value being insignificantly different from the value 1.716(7) Å observed in $K_2[WO(O_2)_2(C_2O_4)]$. The $W-O_{cis}$ bond lengths, 1.965(8) and 1.968(7) Å, seem to be significantly longer than the $W-O_{trans}$ bond lengths, 1.941(6) and 1.928(6) Å. A similar asymmetry has been observed in a number of peroxovanadates, *e.g.* $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$,[12] $(NH_4)_3[VF_2O(O_2)_2]$,[13] and $(NH_4)_2[VFO(O_2)_2]$.[14] The reasons for this asymmetry have been discussed in Ref. 12 (note the different notation as to *cis* and *trans* in Ref. 12).

As in $K_2[MoO(O_2)_2(C_2O_4)]$ the oxalato group is not planar; in this case the two "CO_2" groups form an angle of 6.9° with each other (5.1° in the molybdenum analogue and 2.8° in $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O$). In $K_2[WO(O_2)_2(C_2O_4)]$ C1–O6 and C2–O8, 1.295(11) and 1.281(11) Å, are significantly longer than C1–O7 and C2–O9, 1.207(12) and 1.217(13) Å, respectively, where O6 and O8 are coordinated to tungsten, while O7 and O9 are terminal oxygen atoms. The same situation was observed in $K_2[MoO(O_2)_2(C_2O_4)]$ as well as in

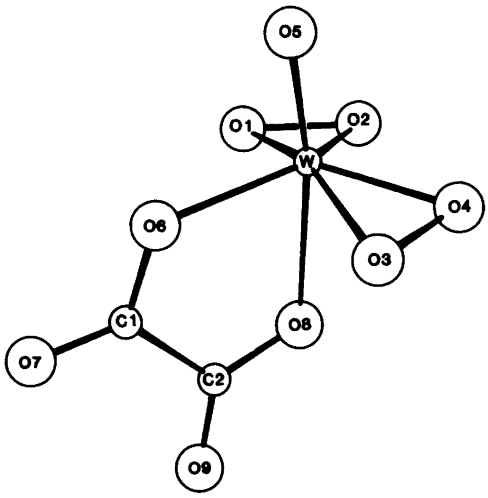

Fig. 2. The anion $[WO(O_2)_2(C_2O_4)]^{2-}$.

$K_3[VO(O_2)_2(C_2O_4)] \cdot H_2O$. In Refs. 2 and 12 and references therein an explanation of this is given as well as of the fact that the difference in bond length between C1–O6 and C1–O7 is larger than that between C2–O8 and C2–O9.

The largest and r.m.s. deviations of the atoms from the equatorial pentagonal plane are 0.024 and 0.016 Å, respectively. Tungsten is displaced 0.358 Å from this plane in the direction of the double-bonded oxygen atom; in the molybdenum analogue this displacement is 0.35 Å, a value also reported for $K_2[O\{WO(O_2)_2(H_2O)\}_2] \cdot 2H_2O$.[1] For further comparison, see the compilation of observed displacements of the metal from the equatorial plane in peroxometallates given in Table V in Ref. 15.

Acknowledgement. We wish to thank Dr. Susan Jagner for her kind help in revising the English text.

REFERENCES

1. Einstein, F.W.B. and Penfold, B.R. *Acta Crystallogr. 17* (1964) 1127.
2. Stomberg, R. *Acta Chem. Scand. 24* (1970) 2024.
3. Šljukić, M., Vuletić, N., Matković, B. and Kojić-Prodić, B. *Croat. Chem. Acta 42* (1970) 499.
4. Stomberg, R. *Acta Chem. Scand. 22* (1968) 1076.
5. Lehmann, M.S. and Larsen, F.K. *Acta Crystallogr. A 30* (1974) 580.
6. Walker, N. and Stuart, D. *Acta Crystallogr. A 39* (1983) 158.
7. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4.
8. Cruickshank, D.W.J. *Crystallographic Computing,* Munksgaard, Copenhagen 1970, p. 195.
9. Lindgren, O. *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates,* Diss., Chalmers University of Technology and University of Göteborg, Göteborg 1977.
10. Stomberg, R., Olson, S. and Svensson, I.-B. *Acta Chem. Scand. A 38* (1984) 653.
11. Davies, J.I., Gibson, J.F., Skapski, A.C., Wilkinson, G. and Wong, W.-K. *Polyhedron 1* (1982) 641.
12. Begin, D., Einstein, F.W.B. and Field, J. *Inorg. Chem. 14* (1975) 1785.
13. Stomberg, R. *Acta Chem. Scand. A 38* (1984) 541.
14. Stomberg, R. and Olson, S. *Acta Chem. Scand. A 38* (1984) 801.
15. Szentivanyi, H. *Structural Studies on Some Heteroligand Oxoperoxovanadium(V) Compounds,* Diss., Chalmers University of Technology and University of Göteborg, Göteborg 1983.
16. Ružić-Toroš, Z., Kojić-Prodić, B., Gabela, F. and Šljukić, M. *Acta Crystallogr. B 33* (1977) 692.

Received June 18, 1984.