The Crystal Structure of Ca$_3$WO$_5$Cl$_2$ and the Configuration of the WO$_5^{4-}$ Ion

By Z. Zikmund

*Institute of Solid State Physics, Czechoslovak Academy of Sciences, Cukrovarnická 10,
162 53 Prague 6, Czechoslovakia*

Ca$_3$WO$_5$Cl$_2$ is orthorhombic, space group *Pnam*, with $a=11\cdot820$ (2), $b=11\cdot132$ (1), $c=5\cdot587$ (1) Å, $Z=4$. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to $R=0\cdot088$ for 1563 independent counter reflexions. The W atom is surrounded by five O atoms in the form of a tetragonal pyramid. The WO$_5$ groups are highly regular and form isolated anions. The W–O distances are $1\cdot725$ (to the apex), $1\cdot888$ and $1\cdot911$ Å. The WO$_5$ groups are joined by Ca atoms in layers perpendicular to **a**. The Ca–O distances vary from $2\cdot287$ to $2\cdot440$ Å and the Ca–Cl from $2\cdot707$ to $2\cdot811$ Å. The Cl atoms are bound to Ca atoms only.

Introduction

The substance was prepared by a method described by Barta, Schultze, Wilke & Žemlička (1971). It belongs to a group of compounds of general formula M$_3$RO$_5$A$_2$ (M = Ca, Sr or Ba, R = Mo or W, A = Cl or Br) which possess luminescent properties (Barta, Dolejší & Bohun, 1970).

Ca$_3$WO$_5$Cl$_2$ forms small colourless or light red-brown transparent crystals with imperfect crystal faces. It is unstable in air and water.

Experimental

Weissenberg photographs (Cu *Kα* radiation) showed the absences: $k+l\neq2n$ for $0kl$ and $h\neq2n$ for $h0l$ reflexions, corresponding to the space groups *Pna2$_1$* or *Pnam* (*International Tables for X-ray Crystallography*, 1952). *Pnam* was chosen, the space group *Pna2$_1$* being excluded during the refinement.

Further measurements were performed on an automated four-circle Hilger & Watts diffractometer. A spherical crystal with diameter 0·35 mm was sealed in a Lindemann glass capillary. Determination of the crystallographic orientation was achieved by Laue photographs. Lattice parameters were found from θ of the $h00$, $0k0$ and $00l$ reflexions. Measurements were performed at room temperature for all good measurable peaks of Mo *Kα* (Zr filter) and of Mo *Kβ* reflexions up to (sin θ)/$\lambda=0\cdot81709$ Å^{-1}. The crystallographic data are given in Table 1.

Table 1. *Crystallographic data of* Ca$_3$WO$_5$Cl$_2$

Symmetry: orthorhombic, space group *Pnam*

Cell dimensions:	a	$=$	$11\cdot820$ (2) Å
	b	$=$	$11\cdot132$ (1)
	c	$=$	$5\cdot587$ (1)
	V	$=$	$735\cdot2$ Å^3
	Z	$=$	4
Density:	D_x	$=$	$4\cdot11$ g cm^{-3}
	D_m	$=$	$3\cdot96$*

* Tentative value.

Intensities were collected by the 'moving-crystal moving-counter' technique in ω intervals of 0·72° in 36 steps for 4 s per step. The background was measured at both ends of the scan for 36 s. Four octants corresponding to hkl, $h\bar{k}l$, $h\bar{k}\bar{l}$ and $hk\bar{l}$ were collected up to (sin θ)/$\lambda=0\cdot81709$ Å^{-1}. Mo *Kα* radiation (Zr-filtered) and a scintillation counter were used. A standard reflexion measured after every sixth recording showed a decrease up to 30% after subtracting background, probably owing to sample damage.

The background was approximated by linear interpolation between both experimental points. Intensities were placed on a common scale through the standard reflexion, and the mean integrated intensity of each set of symmetrically equivalent reflexions and its $\sigma(I)/I$ were evaluated. The sets with $\sigma(I)/I>0\cdot7$ were excluded. Lorentz–polarization and absorption corrections were applied. For the latter ($\mu=193$ cm^{-1}) the values for spherical samples given in *International Tables for X-ray Crystallography* (1959) were used. 1806 symmetrically independent reflexions were collected from which 243 reflexions were excluded in prior processing. The remaining 1563 were used for the structure determination.

The density was measured pycnometrically.

Determination and refinement of the crystal structure

The structure was solved by Patterson and Fourier methods. From electron density maps it was apparent that in *Pna2$_1$* the positions of all atoms differ from the corresponding *Pnam* positions by only small amounts.

Refinement was by full-matrix least-squares calculations in several ways: (*a*) in the symmetry assumed (*Pna2$_1$* or *Pnam*), (*b*) including or ignoring anomalous dispersion, (*c*) by the minimization process ($Y=|F|$ or $|F|^2$), and (*d*) in the atomic scattering factors, *i.e.* the assumed ionization states of the atoms. A local version of the Busing, Martin & Levy (1962) program with anomalous dispersion modification (Novák, 1973) and a Cruickshank weight $w=[2P+Y_o+(2/Q)Y_o^2]^{-1}$ were employed.

A secondary extinction correction was performed for strong reflexions with low θ and with $|F_c| \gg |F_o|$ by a modified version of Zachariasen's (1963) method. The extinction coefficient g was found by optimization of the linear dependence $y = gx$, where $y \equiv 1 - (|F_o|/|F_c|)^2$ and $x \equiv (1/A^*) \, (\partial A^*/\partial \mu) \, (p_2 L/p_1) \, (q_o/K^2) \, |F_c|^2$, by least-squares, and corrected values of $|F_o|$ were found from $|F_{cor}|^2 = |F_o|^2/(1-gx)$. In the expression for x, A^*, L, p_1, and K are the absorption, Lorentz, polarization and scale factors respectively; $p_2 = (1 + \cos^4 2\theta)/2$ and $q_o = N^2 e^4 \lambda^3/m^2 c^4$, where N is the number of cells in unit volume of the crystal. The approximate values of $\partial A^*/\partial \mu$ for given μ were found from *International Tables for X-ray Crystallography* (1959). $|F_c|$, $|F_o|$ and $|F_{cor}|$ are on the same scale, determined by the scale factor K. The mean value of $(|F_{cor}| - |F_o|)/|F_o|$ for corrected reflexions was 13·8%. However experimental points showed a significant variance around the optimized linear dependence, and the values of $||F_c| - |F_{cor}||$ were often large.

All possibilities based on $Pna2_1$ led to physically unacceptable values $B_i < 0$ for the isotropic temperature factors, or to anisotropic factors which were not positive definite. However refinement in $Pnam$ gave reasonable results. The probability that W, Ca, Cl and O(1) occupy special positions of $Pnam$ was also confirmed by large values of $\sigma(z)$ for these atoms in $Pna2_1$. Thus $Pnam$ was accepted. The values of the structure parameters were found by refinement on $|F|^2$, with anomalous dispersion included. Scattering factors corresponding to neutral W and Ca²⁺ and Cl⁻ ions were used; O(1) was considered as neutral and O atoms in general positions, O(2) and O(3), as O⁻. The ionization states were chosen to reflect the bond relations between atoms. Values of f, $\Delta f'$ and $\Delta f''$ were taken from *International Tables for X-ray Crystallography* (1962). The final value of $R = \Sigma \Delta F_o/\Sigma |F_o|$ is 0·088. Values of atomic position and anisotropic thermal parameters are given in Table 2. The largest Δ/σ was 0·08 for position and 0·24 for thermal parameters. The final weight analysis is given in Table 3. 54 reflexions with $1/3 \le |F_o|/|F_c| \le 3$ are excluded. 35 reflexions with $|F_o| < |F_c|$ and with large values of ΔF_o cause large values of $w(\Delta F_o^2)^2$ for values of $|F_o|$ from 115·3 to 466·8 and for values of $(\sin \theta)/\lambda$ from 0 to 0·40118. Values of $|F_o|$ and $|F_c|$ of all 1563 reflexions are compared in Table 4.

Description of the structure

Positions of symmetry-related atoms are described (Table 5 and Figs 2–4) by symmetry operations in parentheses, except that O(4) and O(5) are related to O(2) and O(3) by the mirror plane at $z = \frac{1}{4}$. The choice of origin is such that the n glide lies at $x = \frac{1}{4}$, the a glide at $y = \frac{1}{4}$, and the 2_1 axis at $x = y = 0$.
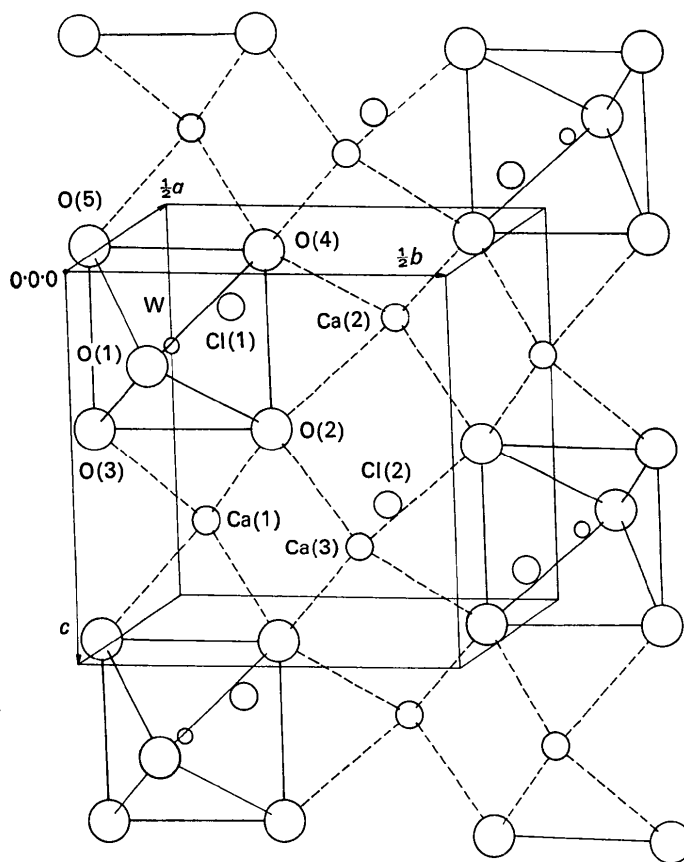

Fig. 1. The crystal structure of Ca₃WO₅Cl₂; part of the infinite layer. The lines joining atoms – full lines between O atoms in the WO₅ pyramid, dashed between Ca atoms and the nearest O atoms in the same layer – are drawn to emphasize the geometry; lines joining Ca and O atoms also represent bonds.

Table 2. *Final atomic position and thermal parameters of* Ca₃WO₅Cl₂

Numbers in parentheses are e.s.d.'s in the last significant digits. Anisotropic thermal parameters refer to the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Values of β_{ij} are times 10^{-5}.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0·19152 (6)	0·08470 (6)	0·25	77 (4)	63 (4)	424 (18)	1 (3)	0	0
Ca(1)	0·3415 (3)	0·0810 (4)	0·75	150 (19)	149 (21)	740 (93)	6 (18)	0	0
Ca(2)	0·3611 (3)	0·3352 (3)	0·25	119 (19)	129 (22)	955 (104)	−18 (17)	0	0
Ca(3)	0·1661 (3)	0·3301 (4)	0·75	148 (20)	126 (22)	912 (103)	−3 (17)	0	0
Cl(1)	0·4795 (6)	0·0853 (7)	0·25	354 (40)	471 (47)	2092 (206)	231 (39)	0	0
Cl(2)	0·4657 (4)	0·2876 (5)	0·75	125 (24)	198 (28)	1531 (152)	22 (22)	0	0
O(1)	0·0458 (12)	0·0919 (14)	0·25	138 (79)	132 (88)	1067 (414)	−45 (69)	0	0
O(2)	0·2405 (9)	0·1988 (9)	0·4774 (20)	197 (59)	149 (58)	563 (254)	30 (46)	−98 (106)	−59 (103)
O(3)	0·2361 (9)	−0·0322 (9)	0·4821 (20)	197 (58)	123 (57)	583 (256)	−26 (46)	40 (109)	−134 (105)

Table 3. *Final weight analysis*

Final values of weight constants are $P = 50$ and $Q = 2 \times 10^5$, N_o is the number of symmetrically independent reflexions, $|F_o|$ and $w(\Delta F_o^2)^2$, where $\Delta F_o^2 = |F_o|^2 - |F_c|^2$, are given on an absolute scale.

$|F_o|$	N_o	$w(\Delta F_o^2)^2$	$(\sin \theta)/\lambda$	N_o	$w(\Delta F_o^2)^2$
0·0– 31·1	215	51·7	0 −0·40118	216	167·4
31·1– 42·7	217	58·6	0·40118–0·51469	215	52·9
42·7– 55·2	214	39·0	0·51469–0·59516	216	53·2
55·2– 71·2	217	29·2	0·59516–0·66078	216	44·1
71·2– 88·2	213	30·6	0·66078–0·72182	215	38·0
88·2–115·3	215	31·5	0·72182–0·77165	216	31·9
115·3–466·8	218	180·8	0·77165–0·81709	215	35·4

The more important interatomic distances and bond angles are listed in Table 5 and were not corrected for thermal vibrations.

Only five O atoms are in the coordination sphere of the W atom. These atoms form a slightly deformed tetragonal pyramid (Fig. 1). O(2) to O(5), forming the base, are coplanar by symmetry, and W is 0·553 Å above this plane. These WO_5 pyramids are bound to one another by Ca atoms. Each Ca(1) atom joins two pyramids the apices of which point in the same direction, approximately parallel to **a**. Thereby an infinite

Table 4. *Observed and calculated structure amplitudes*

chain along c is formed (Figs. 1 and 2). Ca(2) and Ca(3) join chains lying in the same plane perpendicular to a. Each of these Ca atoms joins only one O atom from two different WO_5 pyramids of the same chain with two O atoms of a third pyramid from a neighbouring chain. The role of two neighbouring Ca(2) and Ca(3) atoms is complementary: Ca(2) joins one pyramid of one chain with two pyramids of the other, while Ca(3) joins two pyramids of the former chain with one of the latter. Ca(2) and Ca(3) atoms with their nearest O atoms also form an infinite chain joining two neighbouring chains of WO_5 pyramids and Ca(1) atoms (Figs. 1 and 3). In this way infinite layers of WO_5 pyramids joined by Ca atoms are formed. These layers are perpendicular to a with a repeat distance of $a/2$. The bonding of the chains is shown in Figs. 1 and 4. Cl atoms fill empty spaces between layers. Cl(1) completes the WO_5 pyramid to form a very distorted octahedron but the distance (3·403 Å) excludes participation in a tungstate complex. Cl(2) is situated in holes between Ca atoms and their nearest O atoms. Cl(2) is bound to Ca(1) and Ca(3) of two different layers; the joining of the layers is made also by bonds from O(1) to both W and Ca(2). O(1) simultaneously completes the arrangement of O atoms around Ca(2) to form a tetragonal pyramid similar to, but more deformed than, the WO_5 pyramid. For the other Ca atoms the fifth O atom is replaced by Cl. For Ca(3) only one Cl is involved and the surroundings of Ca(3) are similar to those of Ca(2). Cl(1) atoms are always bound to a single Ca(1) atom and do not join layers.

The structure may be described from another point of view. Atoms belonging to any given layer lie near to the plane n in symmetry-related positions. It is pos-

Table 5. *Interatomic distances and bond angles*

Interatomic distances are given in Å, bond angles in deg. Data are not corrected for thermal vibrations.

W–O(1)	1·725				
W–O(2) ⎱ W–O(4) ⎰	1·888	O(1)–W–O(2) ⎱ O(1)–W–O(4) ⎰	106·0	O(1)–O(2) ⎱ O(1)–O(4) ⎰	2·886
W–O(3) ⎱ W–O(5) ⎰	1·911	O(1)–W–O(3) ⎱ O(1)–W–O(5) ⎰	107·9	O(1)–O(3) ⎱ O(1)–O(5) ⎰	2·942
		O(2)–W–O(4)	84·6	O(2)–O(4)	2·541
		O(3)–W–O(5)	85·4	O(3)–O(5)	2·594
		O(2)–W–O(3) ⎱ O(4)–W–O(5) ⎰	85·2	O(2)–O(3) ⎱ O(4)–O(5) ⎰	2·572
		O(2)–W–O(5) ⎱ O(3)–W–O(4) ⎰	146·1	O(2)–O(5) ⎱ O(3)–O(4) ⎰	3·634
Ca(1)–O(2) ⎱ Ca(1)–O(4) (c) ⎰	2·338	O(2)————Ca(1)——O(4) (c)	81·3	O(2)–O(4) (c)	3·046
Ca(1)–O(3) ⎱ Ca(1)–O(5) (c) ⎰	2·320	O(3)————Ca(1)——O(5) (c)	80·4	O(3)–O(5) (c)	2·993
		O(2)————Ca(1)——O(3) ⎱ O(4) (c)————Ca(1)——O(5) (c) ⎰	67·1		
		O(2)————Ca(1)——O(5) (c) ⎱ O(3)————Ca(1)——O(4) (c) ⎰	116·8		
Ca(2)–O(2) ⎱ Ca(2)–O(4) ⎰	2·440	O(2)————Ca(2)——O(4)	62·8		
Ca(2)–O(3) (n, −c) ⎱ Ca(2)–O(5) (n) ⎰	2·396	O(3) (n, −c)–Ca(2)——O(5) (n)	77·3	O(2)————O(5) (n) ⎱ O(3) (n, −c)–O(4) ⎰	3·015
		O(2)————Ca(2)——O(5) (n) ⎱ O(3) (n, −c)–Ca(2)——O(4) ⎰	77·2		
		O(2)————Ca(2)——O(3) (n, −c) ⎱ O(4)————Ca(2)——O(5) (n) ⎰	115·4		
Ca(3)–O(2) ⎱ Ca(3)–O(4) (c) ⎰	2·287	O(2)————Ca(3)——O(4) (c)	83·5		
Ca(3)–O(3) (n) ⎱ Ca(3)–O(5) (n) ⎰	2·317	O(3) (n)————Ca(3)——O(5) (n)	68·1		
		O(2)————Ca(3)——O(5) (n) ⎱ O(3) (n)————Ca(3)——O(4) (c) ⎰	81·9		
		O(2)————Ca(3)——O(3) (n) ⎱ O(4) (c)————Ca(3)——O(5) (n) ⎰	127·1		
Ca(2)–O(1) (a)	2·328	Ca(2)–O(1) (a)–W(a)	162·3		
		O(1) (a)–Ca(2)–O(2) ⎱ O(1) (a)–Ca(2)–O(4) ⎰	139·9		
		O(1) (a)–Ca(2)–O(3) (n, −c) ⎱ O(1) (a)–Ca(2)–O(5) (n) ⎰	103·6		
Ca(1)–Cl(1) (2₁,a)	2·811				
Ca(1)–Cl(2)	2·729	Cl(1) (2₁,a)–Ca(1)–Cl(2)	98·6		
Ca(3)–Cl(2) (a, −a)	2·707	Ca(1)–Cl(2)–Ca(3) (a)	93·6		
Cl(1)–O(2) ⎱ Cl(1)–O(4) ⎰	3·345	Cl(2)–O(2) ⎱ Cl(2)–O(4) (c) ⎰	3·222	Cl(1)–Cl(1) (2₁,a) ⎱ Cl(1)–Cl(1) (2₁,a−c) ⎰	3·412
Cl(1)–O(3) ⎱ Cl(1)–O(5) ⎰	3·416	Cl(2)–O(3) (n) ⎱ Cl(2)–O(5) (n) ⎰	3·376	Cl(1)–Cl(2) ⎱ Cl(1)–Cl(2) (−c) ⎰	3·592
Cl(1)–W	3·403	Cl(2)–O(1) (n)	3·391		
		Cl(2)–O(1) (a) ⎱ Cl(2)–O(1) (a,c) ⎰	3·240		

sible to divide each layer into sublayers. O(2) to O(5) lie close to the plane, with displacements 0·112 Å for O(2) or O(4) and 0·164 Å for O(3) or O(5). The arrangement in this oxygen layer is almost a plane trapezoidal net. The W and Ca atoms are shifted from this plane by 0·691 Å for W, 1·082 Å for Ca(1), 1·314 Å for Ca(2), and 0·992 Å for Ca(3); the signs of the displacements alternate along **b** or **c**. The W and Ca atoms thereby form layers on both sides of each oxygen layer. The alternation of the displacements means that each atom of the oxygen layer is surrounded by four atoms, W and Ca(1) to Ca(3), forming a very deformed tetrahedron. The oxygen layers and the adjacent layers of heavy atoms form sheets. The remaining O(1) and Cl atoms lie between two of these sheets.

Discussion

Fivefold coordination of W or Mo has been found in $Eu_2(WO_4)_3$ (Templeton & Zalkin, 1963), $KY(MoO_4)_2$ (Klevtsova & Borisov, 1967), Nd_2WO_6 (Polyanskaya, Borisov & Belov, 1970), $NdWO_4OH$ (Klevtsova & Borisov, 1969) or $K_2Mo_3O_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968). In the first four structures it is
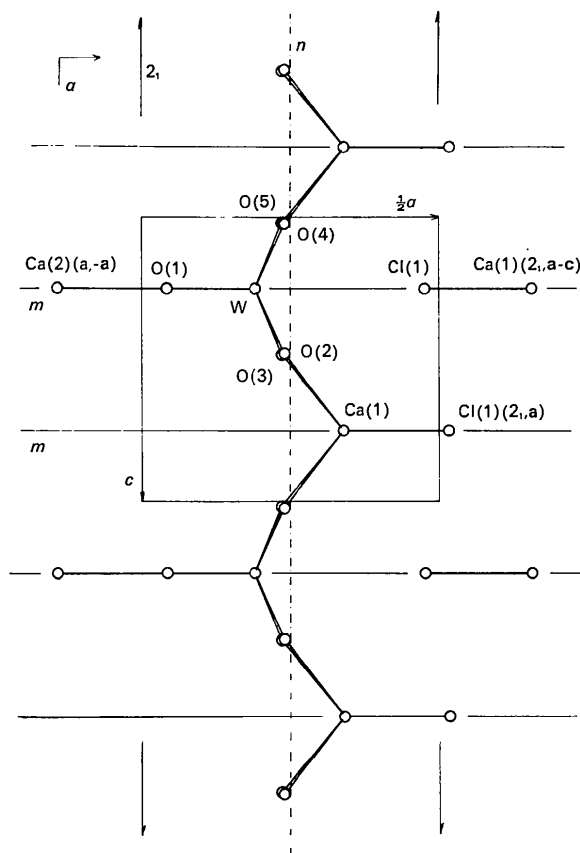

Fig. 2. Part of the infinite chain of WO₅ pyramids joined by Ca(1) atoms and the arrangement of atoms in its immediate surroundings viewed along **b**. Lines joining atoms denote bonds.
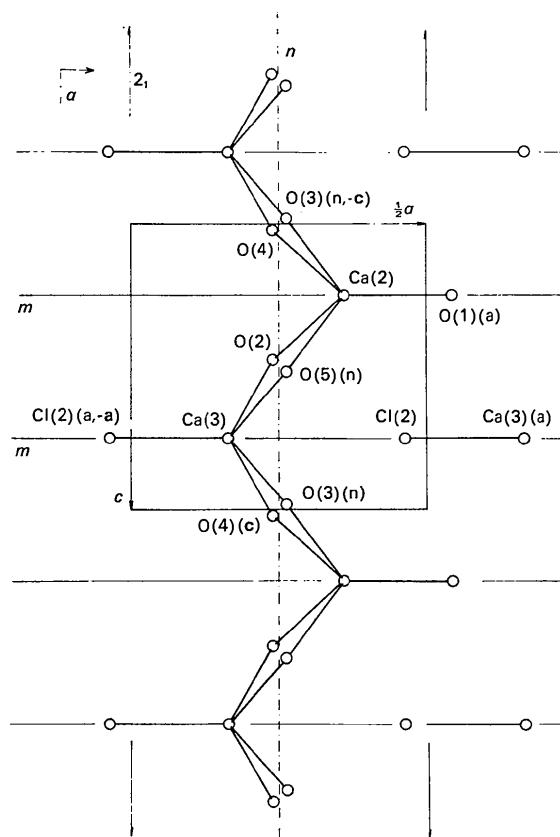

Fig. 3. Part of the infinite row of Ca(2) and Ca(3) atoms joining neighbouring chains of WO₅ pyramids and the arrangement of atoms in its immediate surroundings viewed along **b**. Lines joining atoms denote bonds.

possible to regard the coordination as tetrahedral with the addition of a weakly bonded fifth O atom; its distance from the central atom is about the same as that found in octahedral complexes. Alternatively the coordination sphere may be regarded as a very deformed trigonal bipyramid. $K_2Mo_3O_{10}$ may be regarded as either a distorted tetragonal pyramid or a distorted trigonal bipyramid. Except for Nd_2WO_6 and $NdWO_4OH$ there are neighbouring coordination polyhedra joined by two shared O atoms; in $K_2Mo_3O_{10}$ these polyhedra form with octahedra the $(Mo_3O_{10})_\infty$ chain.

In the WO₅ pyramid found in $Ca_3WO_5Cl_2$ one W–O distance is shorter than the others, which are almost equal. No other atom is bound to the W atom. Thus independent WO_5^{4-} ions are present. The configuration is close to a regular tetragonal pyramid.

The W–O distances observed in WO_5^{4-} are similar to values found elsewhere: the lengths W–O(2) to W–O(5) correspond to values for WO₆ octahedra, e.g. FeWO₄, 1·776 to 2·124 Å (Ülkü, 1967); Cu₃WO₆, 1·791 and 2·085 Å (Gebert & Kihlborg, 1969) and are close to the mean value of octahedral W–O bond lengths (1·95 Å). The W–O(1) bond is much shorter and corresponds to

short octahedral bonds or to bonds found in WO_4 tetrahedra, *e.g.* 1·785 or 1·788 Å in $CaWO_4$ [Burbank (1965), from data of Kay, Frazer & Almodovar (1964), or from data of Zalkin & Templeton (1964)]; 1·695 to 1·829 Å in $Sc_2(WO_4)_3$ (Abrahams & Bernstein, 1966). Known lengths of W^{vi}–Cl^i bonds are considerably shorter than the W–Cl distance; *e.g.* 2·28₆ Å in $WOCl_4$ (Hess & Hartung, 1966); 2·311 Å in WO_2Cl_2 (Jarchow, Schröder & Schulz, 1968).

The coordination of Ca by O atoms is fourfold with the exception of Ca(2) which is fivefold. However Ca(3) and Ca(1) are also bound to one and two Cl atoms respectively. The lengths of the Ca–O bonds agree with lengths found in other substances. In *International Tables for X-ray Crystallography* (1962) a range of 2·30 to 2·55 Å (mean 2·40 Å) is given for sixfold coordination. The lengths in $CaWO_4$ (eightfold coordination) are 2·438 and 2·478 Å or 2·436 and 2·475 Å [Burbank (1965), from data of Kay, Frazer & Almodovar (1964), or from data of Zalkin & Templeton (1964)]; in $CaCl_2.4H_2O$, where Cl and O atoms surround the Ca, Ca–O lengths range from 2·352 to 2·468 Å (Thewalt & Bugg, 1973). The lengths of the Ca–Cl bonds agree well with the 2·70 to 2·76 Å observed in $CaCl_2$ (Wyckoff, 1948), while the unique Ca(1)–Cl(1) bond is somewhat longer but again shorter than bonds in $CaCl_2.4H_2O$ (2·842 and 2·853 Å).

Thermal vibrations

The values of r.m.s. deviations and the angles with crystallographic axes are given in Table 6. It is evident from this table that except for Ca(1) and W the thermal vibrations of all other atoms, especially O(3) and Cl(1), are significantly anisotropic. For symmetry reasons the thermal ellipsoids of all atoms which lie in special positions are oriented so that one axis of the ellipsoid is parallel to **c**. Except for Cl(1) it is always the longest axis of the ellipsoid. For W and Ca(3) the other axes of the ellipsoids are almost parallel to the crystallographic axes. In spite of the fact that $\beta_{ij} \lesssim \sigma(\beta_{ij})$, $i \neq j$, for all atoms except Cl(1), the directions and magnitudes of the thermal vibrations agree well with the proposed bonding in the structure. For example O(3) and O(5) and also O(2) and O(4) have their greatest amplitudes transversely and their smallest longitudinally to the planes of the oxygen layers. Excellent agree-

ment is observed for Cl(1) which is bound by a unique bond to Ca(1). The plane of both longer axes (considerably greater than the shortest axis) of the ellipsoid is almost perpendicular to the direction of this bond: the angle between the shortest axis and the direction of the bond is only 0·4°. Even if such perfect coincidence is fortuitous, it may be regarded as confirmation of the presence of the Ca(1)–Cl(1) bond.
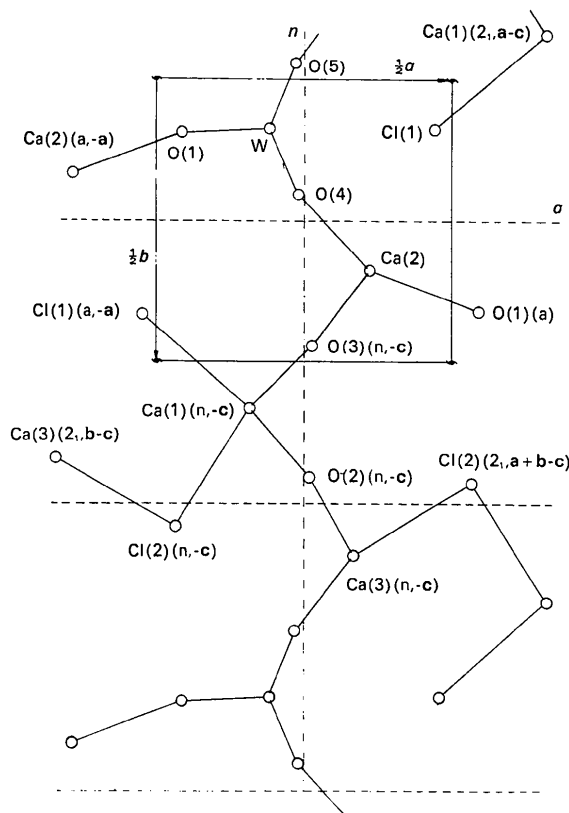
Fig. 4. Part of an infinite layer limited by planes with $z = 0$ and $z = \frac{1}{2}$ and its immediate surroundings viewed along **c**. Lines joining atoms denote bonds.

Table 6. *Thermal vibrations*

The r.m.s. deviations (Å) arranged in increasing magnitude and the angles (°) of the corresponding directions of the principal axes of thermal ellipsoids with *a*, *b* and *c* respectively. Special values 90·0 and 0·0 follow from symmetry.

W	0·063	87·5	177·5		0·074	2·5	87·5		0·082			
Ca(1)	0·096	73·7	163·7		0·104	16·3	73·7		0·108			
Ca(2)	0·084	48·8	41·2		0·098	138·8	48·8	90·0	0·123	90·0	90·0	0·0
Ca(3)	0·089	85·6	4·4	90·0	0·102	175·6	85·6		0·120			
Cl(1)	0·108	139·2	49·2		0·182	90·0	90·0	0·0	0·207	49·2	40·8	90·0
Cl(2)	0·091	19·6	109·6		0·114	70·4	19·6	90·0	0·156	90·0	90·0	0·0
O(1)	0·077	51·9	38·1		0·110	141·9	51·9		0·130			
O(2)	0·084	73·7	64·8	30·7	0·094	61·0	146·7	75·2	0·128	34·1	69·8	116·2
O(3)	0·065	87·1	39·4	50·8	0·106	53·0	61·2	129·6	0·125	142·8	65·6	116·2

References

ABRAHAMS, S. C. & BERNSTEIN, J. L. (1966). *J. Chem. Phys.* **45**, 2745–2752.

BARTA, Č., DOLEJŠÍ, J. & BOHUN, A. (1970). *Krist. Tech.* **5**, 433–443.

BARTA, Č., SCHULTZE, D., WILKE, K.-T. & ŽEMLIČKA, J. (1971). *Z. anorg. allgem. Chem.* **380**, 41–44.

BURBANK, R. D. (1965). *Acta Cryst.* **18**, 88–97.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.

GATEHOUSE, B. M. & LEVERETT, P. (1968). *J. Chem. Soc.* (*A*), pp. 1398–1405.

GEBERT, E. & KIHLBORG, L. (1969). *Acta Chem. Scand.* **23**, 221–231.

HESS, H. & HARTUNG, H. (1966). *Z. anorg. allgem. Chem.* **344**, 157–166.

International Tables for X-ray Crystallography (1952). Vol I. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JARCHOW, O., SCHRÖDER, F. & SCHULZ, H. (1968). *Z. anorg. allgem. Chem.* **363**, 58–72.

KAY, M. I., FRAZER, B. C. & ALMODOVAR, I. (1964). *J. Chem. Phys.* **40**, 504–506.

KLEVTSOVA, R. F. & BORISOV, S. V. (1967). *Dokl. Akad. Nauk SSSR*, **177**, 1333–1336.

KLEVTSOVA, R. F. & BORISOV, S. V. (1969). *Kristallografiya*, **14**, 904–907.

NOVÁK, C. (1973). *Czech. J. Phys.* A **23**, 402–403.

POLYANSKAYA, T. M., BORISOV, S. V. & BELOV, N. V. (1970). *Dokl. Akad. Nauk SSSR*, **193**, 83–86.

SELEBORG, M. (1966). *Acta Chem. Scand.* **20**, 2195–2201.

TEMPLETON, D. H. & ZALKIN, A. (1963). *Acta Cryst.* **16**, 762–766.

THEWALT, U. & BUGG, C. E. (1973). *Acta Cryst.* B **29**, 615–617.

ÜLKÜ, D. (1967). *Z. Kristallogr.* **124**, 192–219.

WYCKOFF, R. W. G. (1948). *Crystal Structures.* Section I. New York: Interscience.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

ZALKIN, A. & TEMPLETON, D. H. (1964). *J. Chem. Phys.* **40**, 501–504.

The Crystal and Molecular Structure of the Bis-(5-ethyl-5-isoamylbarbiturato)bis(imidazole) Complex of Nickel(II)

BY LUIGI NASSIMBENI AND ALLEN RODGERS

Department of Physical Chemistry, University of Cape Town, Republic of South Africa

The structure of the title compound has been determined from single-crystal X-ray diffraction data collected on a four-circle diffractometer. The analysis was carried out with 3741 independent reflexions and refined by full-matrix least-squares computations to a final R of 0·056. The crystals are triclinic, space group $P\bar{1}$, with $a = 10·615$ (5), $b = 10·544$ (5), $c = 7·457$ (5) Å, $\alpha = 111·156$ (2), $\beta = 97·360$ (2), $\gamma = 82·675$ (2)°, $Z = 1$. The nickel atom is involved in distorted octahedral coordination; the donor atoms are the deprotonated nitrogen atoms of the barbiturate anions [Ni–N: 2·078 (2) Å], the nitrogen atoms of the imidazole moieties [Ni–N: 2·055 (3) Å] and two centrosymmetrically related barbiturato oxygen atoms [Ni–O: 2·226 (2) Å]. The molecules are linked by N–H⋯O hydrogen bonds arising from the barbiturato and imidazole N–H groups.

Introduction

The structure of the title compound is another in our series of X-ray determinations on compounds of the general formula M(II)(barb)$_2$L$_2$ where M is a transition metal, barb is the anion of a substituted barbituric acid and L is an organic base. We have reported in earlier publications the crystal structures of the bis-(5,5′-diethylbarbiturato)bispyridine complex of copper(II) (Caira, Fazakerley, Linder & Nassimbeni, 1973) the bis-(5,5′-diethylbarbiturato)bispicoline dihydrate complex of copper(II) (Fazakerley, Linder, Nassimbeni & Rodgers, 1973, 1974 *a*), the bis-[5-allyl-5-(2-bromoallyl)-barbiturato]bispyridine dihydrate complex of copper-(II) (Fazakerley, Linder, Nassimbeni & Rodgers, 1974 *b*) and the bis-(5,5′-diethylbarbiturato)bispicoline complex of zinc(II) (Nassimbeni & Rodgers, 1974). The title compound is thus the first involving nickel and an X-ray analysis was undertaken (i) to determine the molecular structure and hence the coordination type, (ii) to verify that the coordination site on the barbiturate anion is a deprotonated nitrogen atom as has been found in our earlier structures and (iii) to investigate the nature of hydrogen bonding which has been found to be a prominent feature of other structures in this series.