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Anhydrite: a Refinement

BY H. MORIKAWA, I. MINATO, T. TOMITA AND S. IWAI

Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, *Japan*

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Abstract. $CaSO_4$ (Berchtesgaden, Germany): orthorhombic, *Bmmb*, $a=6{\cdot}992$ (1), $b=6{\cdot}999$ (1), $c=6{\cdot}240$ (1) Å, $Z=4$, $D_x=2{\cdot}96$ g cm^{-3}. Refinement with diffractometer data yielded a final R value of 0·021. The two independent S–O bond lengths are 1·474 (2) and 1·475 (2) Å.

Introduction. Intensities were collected from a cube-shaped crystal (edge length about 0·12 mm) with a Rigaku automated four-circle diffractometer and Mo $K\alpha$ radiation monochromatized by a graphite plate. The ω–2θ scan technique was employed with a scan speed of 2° min^{-1} in ω. In all, 266 independent reflexion data were obtained within the range $2\theta \leq 70°$. Intensities were corrected for Lorentz and polarization effects. The systematic absences were hkl for $h+l$ odd and $hk0$ for k odd. Starting with the atomic parameters given by Cheng & Zussman (1963), the structure refinement was carried out with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). Unit weights were allotted to all reflexions. The atomic scattering factors for neutral atoms with corrections for the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). On applying anisotropic temperature factors and a correction for secondary extinction (isotropic), a final R value of 0·021 was obtained.* The final atomic parameters are given in Table 1. The interatomic distances and bond angles calculated by *UNICS* (Sakurai, 1967) are given in Table 2.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Symmetry code

None	x	y	z
i	$-x$	y	z
ii	x	$\frac{3}{2}-y$	z
iii	x	$-\frac{1}{2}+y$	$1-z$
iv	x	$1-y$	$-z$
v	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}-z$

Sulphate ion		Ca–O distances	
S——O(1)	1·475 (2)	Ca–O(1^{iv})	2·561 (2)
S——O(2)	1·474 (2)	Ca–O(1^{v})	2·459 (2)
O(1)–O(1^{i})	2·377 (3)	Ca–O(2)	2·341 (2)
O(1)–O(2)	2·427 (3)	Ca–O(2^{iii})	2·510 (2)
O(2)–O(2^{ii})	2·360 (3)		
O(1)–S–O(1^{i})	107·4 (1)		
O(1)–S–O(2)	110·8 (1)		
O(2)–S–O(2^{ii})	106·4 (1)		

Discussion. The crystal structure of anhydrite was first investigated by Wasastjerna (1925) and refined by Höhne (1962) and Cheng & Zussman (1963) with projections. Swanson, Fuyat & Ugrinic (1955) reported cell dimensions $a=6{\cdot}991$, $b=6{\cdot}996$ and $c=6{\cdot}238$ Å (in good agreement with the present study) by the powder method with metallic silicon as the standard. Höhne (1962) and Cheng & Zussman (1963) assigned the space group *Amma*, labelling the axes in the order $b>a>c$. They did not redetermine the cell dimensions and adopted the values of Swanson *et al.* (1955). The present study has revealed that the labelling of a and b should be interchanged if the space group *Amma* is assumed. Conversely, if we label the axes as $b>a>c$, then the space group becomes *Bmmb*. The refinement was carried out on the basis of the latter choice.

Höhne (1962) refined the structure of anhydrite from three projections, while Cheng & Zussman (1963) obtained the three-dimensional parameters from the (010) projection assuming equal S–O distances in the SO_4 tetrahedron. Agreement between the two sets of coordinates is very good except for the O(1) atom ($x=0{\cdot}171$, $z=0{\cdot}015$ in Cheng & Zussman and $x=0{\cdot}173$, $z=0{\cdot}020$ in Höhne). The present values are very close to those of Cheng & Zussman.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30990 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final atomic parameters* ($\times 10^4$) *in anhydrite*

Positional parameters are given in fractions of cell edges. Standard deviations are given in parentheses. Anisotropic temperature factors are expressed in the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	0*	2500*	3478 (1)	45 (1)	33 (1)	41 (2)	0*	0*	0*
S	0*	7500*	1556 (2)	36 (2)	35 (2)	35 (2)	0*	0*	0*
O(1)	1700 (3)	7500*	157 (4)	36 (3)	84 (4)	54 (4)	0*	11 (4)	0*
O(2)	0*	5814 (3)	2972 (3)	79 (4)	32 (3)	58 (5)	0*	0*	10 (3)

* Parameter fixed by symmetry.

In the structure of anhydrite there are two crystallographically distinct sulphate oxygen atoms. The sulphur–oxygen distances are practically identical, with a mean value of 1·475 Å. This should be compared with the mean S–O distance 1·473 Å in sulphate structures reported by Baur (1970) and also with 1·473 Å for an isolated sulphate anion (McGinnety, 1972) derived from the S–O bond lengths in K_2SO_4. In gypsum, $CaSO_4.2H_2O$ (Cole & Lancucki, 1974), the S–O distances, 1·457 and 1·461 Å, are a little shorter than the present values. Ferraris & Catti (1973) have recently deduced an empirical relationship between predictive length (L) and bond strength (p) of the form:

$$(L-L_m)/L_m=k(p-2)$$

where L_m is the mean bond length. For the S–O bonds in anhydrite, $k=0{\cdot}082$, $L_m=1{\cdot}473$ Å and $p=2$ v.u. The predictive value is equal to the mean value of 1·473 Å.

The point symmetry of the sulphate ion in anhydrite is very close to sphenoidal $\bar{4}2m$ although the exact point symmetry belongs to $mm2$. The sulphate ion in anhydrite is more regular than that in gypsum. The lowering of the symmetry of the sulphate ion in gypsum is explained by the formation of hydrogen bonds (Cole & Lancucki, 1974).

The Ca atom in anhydrite is surrounded by eight oxygen atoms with an average distance of 2·468 Å, which can be compared with an average distance of 2·458 Å in gypsum. Four symmetry-related O(1) atoms make a planar trapezoid around the Ca atom and the O(2) atoms also make a planar trapezoid normal to that of the O(1) atoms.

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Bis-(*N*-methylsalicylideneiminato)dioxomolybdenum(VI)

BY KOJI TSUKUMA,* TAKEMI KAWAGUCHI† AND TOKUNOSUKÉ WATANABÉ‡

Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Japan

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Abstract. $C_{16}H_{16}MoN_2O_4$, orthorhombic, $P2_12_12_1$, $a=12{\cdot}840(1)$, $b=19{\cdot}496(1)$, $c=6{\cdot}6346(5)$ Å, $V=1661{\cdot}02$ Å^3, $Z=4$, D_m(flotation)$=1{\cdot}602$, $D_x=1{\cdot}585$ g cm^{-3}. The molybdenum atom is coordinated by two nitrogen and two oxygen atoms in chelate rings and two oxo (terminal) oxygen atoms, forming a distorted octahedron. The two terminal oxygen atoms are *cis* to each other.

Introduction. Crystals made available to us by Professor S. Yamada (Yamanouchi & Yamada, 1974) are thin yellow parallelepipeds. The cell dimensions were determined by least-squares refinement of 20 and 30 2θ values respectively obtained from the $h0l$ and $0kl$ Weissenberg photographs. The crystal used has the dimensions $0{\cdot}12\times0{\cdot}08\times0{\cdot}60$ mm. 1824 independent non-zero reflexions ($0kl\sim7kl$, $hk0\sim hk4$) were collected on equi-inclination Weissenberg photographs taken

* Present address: Scientific and Industrial Research Institute, Osaka University, Suita, Osaka, Japan.
† Present address: Research division, Nippon Crucible Co. Ltd, 925 Inada, Higashi-Osaka 577, Japan.
‡ Present address: Kanazawa Medical University, Uchinada, Ishikawa-ken, Japan.