molécules d'eau, tous les atomes d'oxygène du groupement méthanesulfonato sont capables de liaisons avec le métal, et que dans ce cas le groupement joue le rôle de coordinat tridentate, alors qu'il se comporte comme monodentate dans le complexe cuivrique. Ainsi ces premiers résultats laissent entrevoir une grande variété de structures pour les méthanesulfonates métalliques.

Tableau 4. *Principales distances de liaisons* (Å)

Ca–O(1)	2,339 (4)	Ca–O(4)	2,285 (4)
S(1)–O(1)	1,449 (4)	S(2)–O(4)	1,446 (4)
S(1)–O(2)	1,456 (4)	S(2)–O(5)	1,441 (4)
S(1)–O(3)	1,429 (5)	S(2)–O(6)	1,442 (4)
S(1)–C(1)	1,760 (8)	S(2)–C(2)	1,748 (6)
C(1)–H(1)	0,93 (14)	C(2)–H(4)	1,25 (14)
C(1)–H(2)	0,99 (15)	C(2)–H(5)	1,13 (14)
C(1)–H(3)	1,03 (14)	C(2)–H(6)	0,99 (14)

Les calculs ont été éffectués sur ordinateur IBM 370-168 à Orsay (CIRCE) par l'intermédiare du terminal de l'Institut de Recherches sur la Catalyse de Lyon et à l'aide d'une bibliothèque de programmes organisée au Laboratoire de Chimie Analytique-II.

Tableau 5. *Principaux angles de liaisons* (°)

O(1)–S(1)–O(2)	111,9 (2)	O(4)–S(2)–O(5)	110,2 (3)
O(1)–S(1)–O(3)	113,5 (3)	O(4)–S(2)–O(6)	112,3 (3)
O(1)–S(1)–C(1)	107,0 (3)	O(4)–S(2)–C(2)	106,6 (3)
O(2)–S(1)–O(3)	112,0 (3)	O(5)–S(2)–O(6)	111,1 (3)
O(2)–S(1)–C(1)	106,0 (3)	O(5)–S(2)–C(2)	109,2 (4)
O(3)–S(1)–C(1)	105,9 (5)	O(6)–S(2)–C(2)	107,2 (4)
Ca–O(1)–S(1)	146,2 (3)	Ca–O(2^{i})–S(1^{i})	137,3 (2)
Ca–O(4)–S(2)	159,3 (3)	Ca–O(6^{iv})–S(2^{iv})	158,6 (3)
Ca–O(5^{ii})–S(2^{ii})	166,6 (4)	Ca–O(3^{iii})–S(1^{iii})	168,1 (4)

Références

CHARBONNIER, F., FAURE, R. & LOISELEUR, H. (1975*a*). *Acta Cryst.* B**31**, 2693–2694.

CHARBONNIER, F., FAURE, R. & LOISELEUR, H. (1975*b*). *J. Appl. Cryst.* **8**, 694–695.

GERMAIN, G. & WOOLFSON, M. M. (1968). *Acta Cryst.* B**24**, 91–96.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Acta Cryst. (1977). B**33**, 1481–1485

The Crystal Structure of Hydroxyl-chondrodite

BY KATSUHIRO YAMAMOTO

Water Research Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, *Japan*

(*Received* 2 *September* 1976; *accepted* 25 *October* 1976)

$Mg(OH)_2.2Mg_2SiO_4$, $P2_1/b$, a = 4·752 (1), b = 10·350 (2), c = 7·914 (2) Å, α = 108·71 (5)°, Z = 2. Most of the interatomic distances are longer than those in F-rich natural chondrodite. However, there are no significant differences in bonding angles or in the steric details of the Si tetrahedron. The radius of the coplanar-bonded three-coordinated OH is $1·35_8$ Å. A statistical distribution is suggested for the OH orientation.

Introduction

Chondrodite belongs to the humite group, $x[TiO_2].(1-x)[M(OH,F)_2].nM_2SiO_4$, where $0 \leq x \leq 1$, n = 1, 2, 3, 4 and M represents Mg, Fe, Mn, Ca or Zn in decreasing order of abundance (Jones, Ribbe & Gibbs, 1969). Gibbs, Ribbe & Anderson (1970) refined the structure of F-rich natural chondrodite (hereafter GRA-chondrodite). OH-chondrodite (equivalent to phase *D* in the system $MgO-SiO_2-H_2O$) was discovered by Yamamoto & Akimoto (1974, 1977). The present experiments were carried out to examine the effect of the replacement of F by OH on the structure of chondrodite.

Experimental procedure and results

The OH-chondrodite crystal used was synthesized from a $13Mg(OH)_2 + 4SiO_2$ mixture at 77 kbar and 1125 °C. The synthesis and stability field of OH-chondrodite were described previously (Yamamoto & Akimoto, 1974, 1977).

The diffraction intensities of 714 non-equivalent reflexions were collected with an automatic four-circle diffractometer and Cu $K\alpha$ radiation, and were corrected for Lorentz, polarization and absorption effects. The structure refinement was carried out with the full-matrix least-squares program *RSFLS*-4 (Sakurai, Nakatsu & Iwasaki, 1967), and the three-dimensional difference-synthesis program *RSSFR*-5 (Sakurai, 1967), of the *UNICS* system (Fujitsu, 1972). The scattering factors (f) for O^{2-} were taken from Tokonami (1965) and for Si^{4+} and Mg^{2+} from *International Tables for X-ray Crystallography* (1962). The dispersions ($\Delta f'$ and $\Delta f''$) were also from *International Tables* (1962). The positional parameters of Taylor & West (1928) were used as starting parameters.

A difference map calculated after refinement with an overall scale factor and positional and isotropic temperature parameters showed two peaks, H(1) and H(2), approximately 1 Å from O(5); this was the OH group. The peaks were considered to be a result of statistically distributed H. Further refinements with the positional parameters of all atoms except $M(1)$, the anisotropic temperature parameters of all atoms except H(1) and H(2), and the occupancies of H(1) and H(2) reduced R to 0·042. The f for O^- taken from *International Tables* (1962) was used for O(5), and the f for H from Stewart, Davidson & Simpson (1965) was used for H(1) and H(2). The temperature parameters of H(1) and H(2) were kept fixed at the isotropic value of

Table 1. *Atomic parameters for* OH-*chondrodite*

Space group $P2_1/b$ (α obtuse) is used, because it is consistent with that determined by Taylor & West (1928) and Gibbs *et al.* (1970) and is preferred to the other setting in the humite group. Thermal parameters are multiplied by 10^4.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$M(1)$	0·5	0	0·5	16 (7)	12 (2)	17 (3)	0	0	−1 (2)
$M(2)$	0·0073 (3)	0·1755 (1)	0·3089 (2)	47 (5)	10 (1)	20 (2)	−1 (2)	−2 (3)	3 (1)
$M(3)$	0·4875 (3)	0·8838 (1)	0·0771 (2)	38 (5)	15 (1)	22 (2)	0 (2)	−1 (3)	6 (1)
Si	0·0777 (2)	0·1408 (1)	0·7020 (1)	8 (4)	8 (1)	13 (1)	3 (1)	3 (2)	0 (1)
O(1)	0·7761 (6)	0·0027 (2)	0·2966 (3)	44 (12)	8 (2)	12 (4)	7 (4)	5 (5)	1 (2)
O(2)	0·7266 (6)	0·2446 (2)	0·1292 (3)	27 (12)	10 (2)	14 (4)	−3 (4)	3 (5)	3 (3)
O(3)	0·2249 (6)	0·1676 (2)	0·5291 (3)	22 (12)	10 (2)	14 (4)	−2 (4)	0 (5)	3 (2)
O(4)	0·2631 (6)	0·8566 (2)	0·2973 (3)	32 (11)	13 (2)	16 (4)	−4 (4)	2 (6)	0 (3)
O(5)	0·2650 (9)	0·0600 (3)	0·1064 (4)	135 (14)	18 (3)	59 (5)	20 (5)	55 (7)	16 (3)
H(1)*	0·15 (2)	0·03 (1)	0·06 (1)						
H(2)*	0·42 (2)	0·10 (1)	0·20 (1)						

* The occupancies of H(1) and H(2) are 0·59 (9) and 0·56 (9).

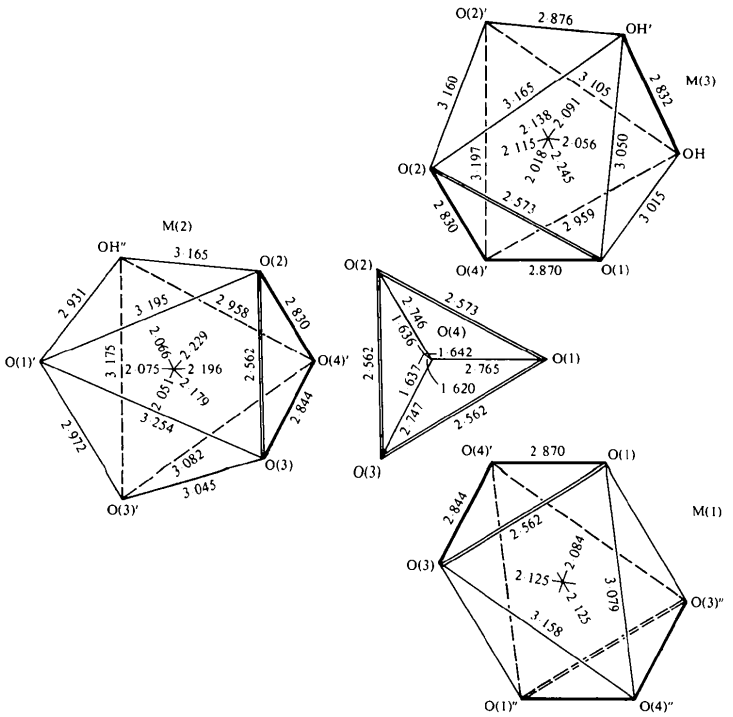

Fig. 1. Exploded diagram showing the steric details of cation coordination polyhedra in OH-chondrodite. The heavier lines are edges shared between two octahedra. Double lines are edges shared between a tetrahedron and an octahedron.

O(5). The validity of each structure modification was checked by Hamilton's (1965) R-factor ratio test at the 0·005 significance level. The final parameters are listed in Table 1.* The exploded diagram showing the steric details of the cation coordination polyhedra is shown in Fig. 1. A comparison of the volumes of all polyhedra in both chondrodites is in Fig. 2.

Discussion

The crystal structure of OH-chondrodite is almost identical with that of GRA-chondrodite.

Anion coordination and anion array

All intercation distances, except $M(3)$–$M(3)'$ around O(2) and $M(2)$–$M(2)'$ around O(3), in OH-chondrodite are 0·002 ~ 0·093 Å longer than those in GRA-chondrodite. The shorter $M(3)$–$M(3)'$ and $M(2)$–$M(2)'$ distances of OH-chondrodite are because of the large increments in (OH,F)–$M(2)$ and (OH,F)–$M(3)$ resulting from the replacement of F by OH. Although inter-cation distances for both chondrodites differ over rather a wide range (from −0·011 to 0·093 Å), the bond-angle differences are small compared with the bond-angle strains described by Gibbs *et al.* (1970). The mean anion–anion distances for each OH-chondrodite anion are 0·01 ~ 0·063 Å larger than those of GRA-chondrodite. The replacement of F by OH causes an expansion of the whole anion array.

Cation coordination

The volume and the mean Si–O and O–O distances of Si tetrahedra in both chondrodites are equal, and the steric details are similar. The Si tetrahedron is hardly affected by the replacement of F by OH. The volume and the mean $M(1)$–O and O–O distances of the $M(1)$ octahedron of OH-chondrodite are slightly larger than those of GRA-chondrodite. These differences are not explained by the fact that the $M(1)$ site of GRA-chondrodite contains 0·05Fe (Gibbs *et al.*, 1970; Ribbe & Gibbs, 1971), because the ionic radius of Fe (0·77 Å) is larger than that of Mg (0·72 Å) [Shannon & Prewitt's (1969) ionic radii are used throughout this paper]. The $M(1)$ octahedron is slightly affected by the replacement of F by OH, although the octahedron has no (OH,F) ligand. The volume and the mean $M(2)$–(O,OH) and O–(O,OH) distances of the $M(2)$ octahedron of OH-chondrodite are 0·28 Å^3, 0·017 Å and 0·024 Å larger than those of GRA-chondrodite. The volume and the mean $M(3)$–(O,OH) and (O,OH)–(O,OH) distances of the $M(3)$ octahedron of OH-chondrodite are 0·49 Å^3, 0·033 Å and 0·042 Å larger than those of GRA-chondrodite. The largest differences in the interatomic distances between both chondrodites are $M(3)$–O(1) (0·063 Å) and O(2)′–OH (0·108 Å).

The differences in the structures of both chondrodites indicate that the Si tetrahedron rotates approximately 1° about an axis approximately parallel to **a**, relative to the triangle $M(1)M(2)M(3)$, by the replacement of F by OH, where the tetrahedron shares three edges with the $M(1)$, $M(2)$ and $M(3)$ octahedra. This rotation makes the $M(1)$–O(1), $M(2)$–O(3) and $M(3)$–O(2) lengths of OH-chondrodite slightly short, compared with those of GRA-chondrodite, although the other Mg–(O,OH) bond length of OH-chondrodite is longer.

Effect of the composition of the (OH,F) *site on mean interatomic distances*

A comparison of some mean bond lengths for norbergite (Gibbs & Ribbe, 1969), OH-chondrodite (present work), GRA-chondrodite (Gibbs *et al.*, 1970), humite (Ribbe & Gibbs, 1971) and clinohumite (Robinson, Gibbs & Ribbe, 1973) is shown in Fig. 3 as a function of F content. The mean OH–Mg [one $M(2)$ and two $M(3)$] bond length in OH-chondrodite is 2·071 Å, whereas the mean $(OH_{0\cdot367}F_{0\cdot633})$–Mg bond length in GRA-chondrodite is 2·034 Å [according to Gibbs *et al.* (1970) and Ribbe & Gibbs (1971), $M(2)$ and $M(3)$ sites in GRA-chondrodite are substantially Fe-free]. Therefore, the effective radius of OH in chondrodite is determined to be 0·05$_8$ Å larger than that of F (1·300 Å). With these radii and the radius of Mg^{2+} (0·720 Å), the Mg–OH and Mg–F bond lengths are calculated to be 2·07$_8$ Å and 2·020 Å. These lengths are 0·007 Å shor-

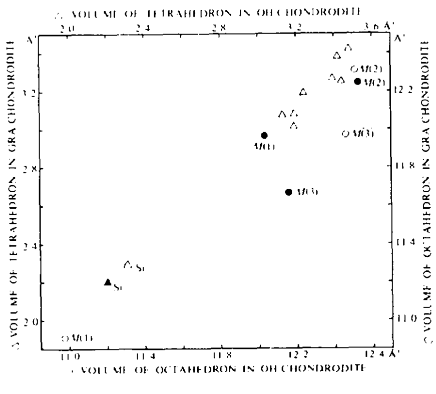

Fig. 2. Plots of the volumes of polyhedra in both chondrodites. Open and solid circles represent vacant and cation-occupied octahedra respectively. Open and solid triangles represent vacant and Si-occupied tetrahedra respectively. $\overline{\mathrm{Si}}$, $\overline{M(1)}$, $\overline{M(2)}$ and $\overline{M(3)}$ express the tetrahedron and the octahedra which share the planes [approximately parallel to (110)] with a Si tetrahedron and $M(1)$, $M(2)$ and $M(3)$ octahedra.

---

* A list of structure factors and tables of interatomic distances, bond angles and principal axes of thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32251 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ter than the mean OH—Mg bond length in OH-chondrodite and the F—Mg length expected from Fig. 3 respectively.

Ribbe & Gibbs (1971) determined the effective radius of the three-coordinated OH to be 1·34 Å using essentially the same lines as the dashed lines in Fig. 3. But it appears that the dashed lines give a radius approximately 0·08 Å larger than that of F.

Comparing the mean F—Mg bond length in F-tremolite with the OH—Mg bond length in OH-tremolite, Cameron & Gibbs (1973) also determined the effective radius of the three-coordinated OH to be 1·336 Å. The three-coordinated OH radius difference between chondrodite and tremolite is a result of the difference in the Mg arrays around OH. In chondrodite, (OH,F) is nearly coplanar with the three Mg ions to which it is bonded, whereas the array in tremolite is far from coplanar.

The *M*(3) octahedron has four O and two (OH,F) ligands and $M(2)_5$ has five O and one (OH,F). The dependences of the mean *M*(3)—(O,OH,F) and $M(2)_5$—(O,OH,F) distances upon F content (Fig. 3) are approximately three times larger than those expected from simple ionic-radius considerations.

Proton position

Since the O(5)—H(1) and O(5)—H(2) distances (0·7 and 1·0 Å) differ from the ordinary O—H bond length (~0·9 Å) observed in crystals such as brucite (Elleman & Williams, 1956), tremolite (Papike, Ross & Clark, 1969) and ice (Shimaoka, 1960), it is reasonable to assume that the large electron density of O(5) makes it difficult to obtain exact proton positions. However, the H(1) and H(2) positions and the shape of the temperature ellipsoid of O(5) suggest a statistical distribution (presumably hindered rotation) of the orientation of OH among the equilibrium positions shown in Fig. 4. The configuration in Fig. 4(*a*) is observed in brucite, where the O—O distance is 3·19 Å, longer than the unshared O(5)—O(5) distance of OH-chondrodite (3·06 Å). The configurations in Fig. 4(*b*) and (*c*) [in order to satisfy the symmetry condition of the space group $P2_1/b$, (*b*) and (*c*) must be realized in equal probability] are observed in ice, where the O—O distance is 2·76 Å, shorter than the unshared O(5)—O(5) distance of OH-chondrodite. The statistical distribution of the OH orientation among the configurations in which the O—O distances are different also explains why the temperature ellipsoid of O(5) is large and extends along the unshared O(5)—O(5) direction.

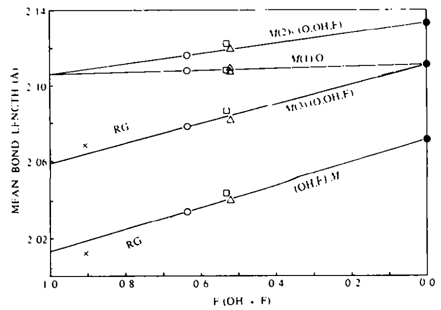

Fig. 3. Plots of the mean bond length in OH-chondrodite (solid circles), GRA-chondrodite (open circles), norbergite (crosses), humite (squares) and clinohumite (triangles) as a function of F content in the monovalent anion site. The subscript 5 of $M(2)_5$ indicates the *M*(2) octahedron which has one (OH,F) and five O ligands. Dashed lines (RG) are essentially the same lines as the dash-dot lines in Fig. 7 of Ribbe & Gibbs (1971).

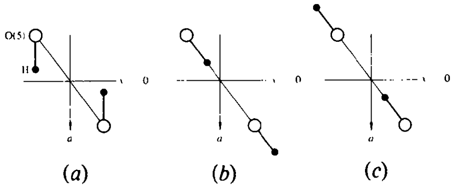

Fig. 4. Postulated configurations of OH orientation between unshared OH—OH.

The author is heartily grateful to Professor S. Akimoto of the Institute for Solid State Physics, University of Tokyo, for his comments and permission to use the equipment for the synthesis of the OH-chondrodite crystal. The X-ray diffraction intensity data were collected with the help of Professor J. Tanaka and Dr C. Katayama of Nagoya University. Their kind permission to use the automatic four-circle diffractometer is gratefully acknowledged. This work is partly supported by a grant from the Ministry of Education for scientific research.

References

Cameron, M. & Gibbs, G. V. (1973). *Amer. Min.* **58**, 879–888.

Elleman, D. D. & Williams, D. (1956). *J. Chem. Phys.* **25**, 742–744.

Fujitsu (1972). *FACŌM* 230-60 *UNICS*. No. 60505013-1, Fujitsu, Tokyo.

Gibbs, G. V. & Ribbe, P. H. (1969). *Amer. Min.* **54**, 376–390.

Gibbs, G. V., Ribbe, P. H. & Anderson, C. P. (1970). *Amer. Min.* **55**, 1182–1194.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

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

Jones, N. W., Ribbe, P. H. & Gibbs, G. V. (1969). *Amer. Min.* **54**, 391–411.

Papike, J. J., Ross, M. & Clark, J. R. (1969). *Miner. Soc. Amer. Spec. Pap.* **2**, 117–136.

Ribbe, P. H. & Gibbs, G. V. (1971). *Amer. Min.* **56**, 1155–1173.

Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1973). *Amer. Min.* **58**, 43–49.

SAKURAI, T. (1967). *Universal Crystallographic Computation Program System (UNICS)* I, pp. 45–52. The Crystallographic Society of Japan, Tokyo.
SAKURAI, T., NAKATSU, K. & IWASAKI, J. (1967). *Universal Crystallographic Computation Program System (UNICS)* I, pp. 61–65. The Crystallographic Society of Japan, Tokyo.
SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
SHIMAOKA, K. (1960). *J. Phys. Soc. Japan*, **15**, 106–119.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TAYLOR, W. H. & WEST, J. (1928). *Proc. Roy. Soc.* **A117**, 517–532.
TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
YAMAMOTO, K. & AKIMOTO, S. (1974). *J. Solid State Chem.* **9**, 187–195.
YAMAMOTO, K. & AKIMOTO, S. (1977). *Amer. J. Sci.* In the press.

Acta Cryst. (1977). **B33**, 1485–1489

The Crystal Structure of Bis[(*R*)-2-methyl-1,4,7-triazacyclononane]cobalt(III) Iodide Pentahydrate

BY M. MIKAMI, R. KURODA,[*] M. KONNO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, *Japan*

(*Received* 15 *October* 1976; *accepted* 27 *October* 1976)

Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ are trigonal, $R32$, with $a = 8{\cdot}799\,(1)$, $c = 32{\cdot}180\,(4)$ Å and $Z = 3$. The structure was refined by full-matrix least-squares methods to an R value of 0·039 for the 902 observed reflexions collected by diffractometry. The complex ion exhibits orientational disorder on a site of symmetry D_3 around the triad axis. Three of the nine I^- ions and the O atoms of water molecules show positional disorder. Two cyclic ligand molecules are spanned on opposite faces of an octahedron, being coordinated to the central Co atom with six N atoms. The Co—N distance is 1·974 Å. The conformation of each five-membered chelate ring is λ. The substituted methyl group is attached in an equatorial position with respect to the average plane of the chelate ring. The $[CoN_6]$ chromophore is elongated along the threefold axis, the Co—N bond being inclined at an angle of 51·3° with respect to the threefold axis. The chromophore is twisted around the threefold axis in the same way as in $\Delta\text{-}[Co(en)_3]^{3+}$.

Introduction

Mason & Peacock (1976) synthesized the cyclic tridentate (*R*)-(−)-2-methyl-1,4,7-triazacyclononane and its Co^{III} complex, $\{Co[(R)\text{-}MeTACN]_2\}^{3+}$. They found that the complex exhibits the largest ring-conformation *d*-electron optical activity for the (CoN_6) chromophore yet recorded (Mason & Peacock, 1976). Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ were subjected to X-ray crystal-structure analysis in order to provide structural data for the analysis of the observed optical activity for this complex ion (Mason & Seal, 1976).

Experimental

Crystals of $\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$ were kindly supplied by Professor S. F. Mason. They were recrystallized from water. The crystals are yellow transparent hexagonal prisms. The diffraction symmetry on Weissenberg photographs is $\bar{3}m$. The observed systematic absences, hkl for $-h + k + l = 3n$, indicated that the possible space group is $R\bar{3}m$, $R32$ or $R3c$. Since the crystal is optically active, the space group was uniquely determined to be $R32$.

Crystal data

$(-)_{589}$-$\{Co[(R)\text{-}MeTACN]_2\}I_3.5H_2O$, $C_{14}H_{44}N_6O_5\text{-}CoI_3$, $M_r = 816{\cdot}19$, trigonal, $a = 8{\cdot}799\,(1)$, $c = 32{\cdot}180\,(4)$ Å, $U = 2157{\cdot}6$ Å^3, $Z = 3$, $D_x = 1{\cdot}88$ g cm^{-3}, μ for Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) $= 35{\cdot}3$ cm^{-1}, space group $R32$ (No. 155).

A crystal with dimensions 0·26 × 0·23 × 0·33 mm was used for intensity measurement. Intensity data were collected on a Rigaku four-circle diffractometer by ω scans at 4° min^{-1}, with graphite-monochromated Mo $K\alpha$ radiation. The scan range was calculated according to $1{\cdot}1° + 0{\cdot}5° \tan\theta$. Of the 2404 reflexions

---

[*] Present address: Department of Chemistry, King's College, Strand, London WC2R 2LS, England.