

23 and 600°C result from the increased metal-metal distances. In order to maintain approximately constant metal-oxygen distances, the oxygens of the unshared octahedral face move farther apart while those of the shared face move together. At the same time the distance between the parallel shared and unshared faces decreases. This distortion of the filled octahedra allows both the M(1)-M(2) and M(1)-M(3) distances to increase while keeping the metal-oxygen distances essentially constant. This is consistent with the band structure proposed by Goodenough (1971) for V₂O₃. The metal-oxygen bands in this scheme lie some 4 eV below the Fermi level while metal-metal bands lie at or near this level. Temperature-induced changes in bonding in such a system would primarily effect the metal-metal interactions and, consequently, the metal-metal distances and would have little effect on the metal-oxygen interactions.

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The Crystal and Molecular Structure of Potassium Monoaquamono(nitritotriacetato)cobaltate(II) Dihydrate, K[Co(C₆H₆NO₆)(OH₂)]·2H₂O

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Crystals of potassium monoaquamono(nitritotriacetato)cobaltate(II) dihydrate, K[Co(C₆H₆NO₆)(OH₂)]·2H₂O, are monoclinic, space group *P*2₁/*n* with *a* = 16.36 (1), *b* = 9.99 (1), *c* = 7.13 (1) Å, β = 91.6 (1)° and *Z* = 4. The X-ray analysis was carried out by three-dimensional Patterson, Fourier and least-squares methods (final *R* = 3.4%). Coordination around Co^{II} is octahedral and involves the nitrogen and three carboxylic oxygens from the same nitritotriacetate ion, one water molecule and one carboxylic oxygen from an adjacent anion. The packing is determined by the K⁺···O interactions and by the water-water and water-carboxylic oxygen hydrogen bonds.

Introduction

Nitritotriacetic acid is a tetradentate ligand which can form 1:1 metal complexes. In the present paper the

results of the crystal structure analysis of potassium monoaquamono(nitritotriacetato)cobaltate(II) dihydrate are given. This study was carried out as part of a research programme on metal-aminoacid interactions.

Experimental

The title compound, prepared following Mori, Shibata, Kyuno & Kanaya (1961), occurs as prismatic pink crystals giving no pleochroic effects.

Crystal data, determined from rotation and Weissenberg photographs and from single-crystal diffractometer measurements (Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$), are as follows:

$\text{K}[\text{Co}^{\text{II}}(\text{C}_6\text{H}_6\text{NO}_6)(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$, $M = 340.2$, $a = 16.36(1)$, $b = 9.99(1)$, $c = 7.13(1) \text{ \AA}$; $\beta = 91.6(1)^\circ$, $V = 1165 \text{ \AA}^3$, $Z = 4$, $D_m = 1.93$, $D_c = 1.94 \text{ g cm}^{-3}$, $F(000) = 692$, $\mu = 19.2 \text{ cm}^{-1}$. Space group: $P2_1/n$ (from systematic absences).

The intensity data were collected on a Siemens 'on line' single-crystal diffractometer, using the $\omega/2\theta$ scan technique and Mo $K\alpha$ radiation. The sample was aligned with its [100] axis coincident with the φ axis of the diffractometer and all reflexions having $2\theta < 58^\circ$ were

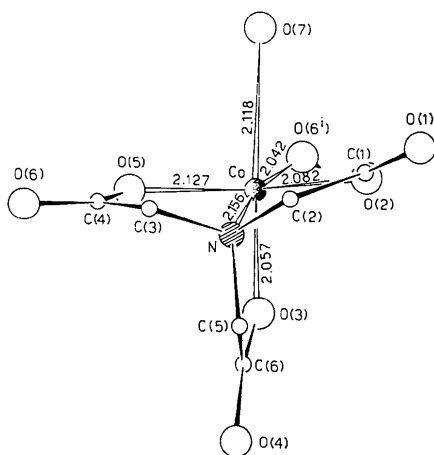


Fig. 1. Clinographic projection of the anion.

Table 1. Final atomic fractional coordinates ($\times 10^4$), thermal parameters ($\times 10 \text{ \AA}^2$) and *e.s.d.*'s for the non-hydrogen atoms

The anisotropic temperature factors are expressed in the form: $\exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* \cos \gamma^* + 2B_{13}hla^*c^* \cos \beta^* + 2B_{23}klb^*c^* \cos \alpha^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2086 (1)	-1527 (1)	1290 (1)	182 (1)	86 (1)	132 (1)	1 (1)	-22 (1)	10 (1)
K	1069 (1)	4643 (1)	1360 (1)	208 (2)	149 (2)	221 (2)	-22 (2)	1 (2)	-8 (2)
O(1)	245 (1)	-2972 (2)	-2028 (4)	295 (10)	235 (9)	358 (11)	-104 (8)	-73 (8)	8 (8)
O(2)	1372 (1)	-2904 (2)	-211 (4)	324 (10)	119 (7)	225 (8)	-21 (7)	-62 (7)	20 (6)
O(3)	3157 (1)	-1686 (2)	-138 (3)	257 (9)	264 (10)	256 (9)	79 (8)	31 (7)	102 (8)
O(4)	3810 (1)	-955 (2)	-2623 (3)	253 (9)	292 (10)	263 (9)	1 (8)	47 (8)	12 (8)
O(5)	2463 (1)	415 (2)	2180 (3)	275 (8)	120 (7)	184 (8)	-4 (6)	-86 (6)	2 (6)
O(6)	2347 (1)	2579 (2)	1450 (3)	371 (10)	103 (7)	218 (8)	-7 (7)	-78 (7)	-7 (6)
O(7)	989 (2)	-1178 (2)	2721 (4)	370 (11)	198 (9)	364 (11)	-29 (8)	144 (9)	-36 (8)
O(8)	755 (2)	1241 (2)	4302 (4)	326 (11)	198 (10)	502 (13)	-25 (8)	-29 (10)	82 (9)
O(9)	350 (1)	-3626 (2)	3898 (3)	281 (9)	263 (10)	319 (10)	-26 (8)	60 (8)	-29 (8)
N	1738 (1)	-355 (2)	-1144 (3)	186 (9)	101 (7)	134 (8)	-12 (7)	-30 (6)	-9 (7)
C(1)	855 (2)	-2388 (3)	-1329 (4)	247 (12)	137 (10)	178 (10)	-37 (9)	-5 (9)	-12 (8)
C(2)	960 (2)	-925 (3)	-1872 (4)	239 (12)	161 (11)	272 (12)	-46 (9)	-92 (10)	32 (9)
C(3)	1634 (2)	1028 (3)	-489 (4)	407 (15)	118 (10)	238 (12)	41 (10)	-160 (11)	-30 (9)
C(4)	2201 (2)	1354 (3)	1163 (4)	224 (11)	96 (9)	162 (9)	-2 (8)	-22 (8)	-13 (8)
C(5)	2396 (2)	-467 (4)	-2475 (4)	238 (13)	384 (16)	189 (11)	59 (11)	15 (9)	83 (11)
C(6)	3188 (2)	-1062 (3)	-1680 (4)	237 (11)	141 (10)	174 (10)	3 (9)	-10 (9)	-12 (8)

collected. The intensities of 3098 independent reflexions were measured: 2229 of them, with $I > 2\sigma(I)$, were used in the analysis.

After the usual data reduction, the intensities were put on an absolute scale first by Wilson's (1942) method, then by comparison between observed and calculated structure factors. No correction for absorption was applied, as the sample used to collect data was small enough to make this unnecessary (size of the crystal: 0.095, 0.190, 0.333 mm).

Determination of the structure and refinement

The structure was solved by the heavy-atom technique, starting from the three-dimensional Patterson distribution. Two successive Fourier syntheses gave the coordinates of all non-hydrogen atoms, which were refined by means of block-diagonal least-squares calculations to a value of 4.2% for the conventional R index. All the hydrogen atoms were then directly located on a final ΔF map and the complete least-squares refinement, isotropic for the hydrogen atoms, aniso-

Table 2. Fractional coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10 \text{ \AA}^2$) with *e.s.d.*'s for hydrogen atoms

	x/a	y/b	z/c	B
H(1)	49 (2)	-51 (4)	-120 (5)	43 (9)
H(2)	94 (2)	-80 (3)	-325 (4)	22 (7)
H(3)	107 (2)	109 (4)	25 (5)	38 (9)
H(4)	167 (2)	170 (4)	-155 (5)	33 (8)
H(5)	253 (2)	23 (4)	-322 (6)	50 (10)
H(6)	223 (2)	-104 (4)	-332 (6)	52 (11)
H(7)	77 (3)	-191 (4)	312 (6)	55 (10)
H(8)	88 (2)	-44 (4)	331 (6)	48 (10)
H(9)	115 (3)	185 (4)	470 (6)	56 (11)
H(10)	46 (2)	166 (5)	345 (6)	53 (10)
H(11)	38 (2)	-365 (4)	515 (5)	36 (8)
H(12)	18 (2)	-368 (4)	350 (5)	30 (8)

Table 3. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Symmetry code: $i \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

(a) In the coordination polyhedron

Co—N	2.156 (3)	Co—O(5)	2.127 (3)
Co—O(2)	2.082 (3)	Co—O(7)	2.118 (3)
Co—O(3)	2.057 (3)	Co—O(6 ⁱ)	2.042 (2)
N—Co—O(2)	79.2 (2)	O(2)—Co—O(7)	83.4 (2)
N—Co—O(3)	81.6 (2)	O(3)—Co—O(5)	88.5 (2)
N—Co—O(5)	79.2 (2)	O(3)—Co—O(6 ⁱ)	89.0 (2)
N—Co—O(6 ⁱ)	167.5 (1.4)	O(3)—Co—O(7)	174.9 (3.0)
N—Co—O(7)	95.1 (2)	O(5)—Co—O(2)	155.5 (7)
O(2)—Co—O(3)	99.7 (2)	O(5)—Co—O(6 ⁱ)	92.4 (2)
O(2)—Co—O(6 ⁱ)	110.7 (3)	O(5)—Co—O(7)	87.1 (2)
		O(6 ⁱ)—Co—O(7)	153.0 (9)

(b) In the amino-acid molecule

N—C(2)	1.476 (4)	C(4)—O(5)	1.254 (3)
N—C(3)	1.470 (4)	C(4)—O(6)	1.263 (4)
N—C(5)	1.459 (4)	C(4)—C(3)	1.514 (5)
C(1)—O(1)	1.248 (4)	C(6)—O(3)	1.266 (4)
C(1)—O(2)	1.257 (4)	C(6)—O(4)	1.240 (4)
C(1)—C(2)	1.523 (4)	C(6)—C(5)	1.521 (5)
C(2)—N—C(3)	111.6 (5)	N—C(3)—C(4)	112.0 (4)
C(2)—N—C(5)	112.8 (5)	N—C(5)—C(6)	115.1 (5)
C(3)—N—C(5)	111.9 (5)	C(3)—C(4)—O(5)	118.8 (6)
O(1)—C(1)—C(2)	116.2 (5)	C(3)—C(4)—O(6)	116.3 (5)
O(1)—C(1)—O(2)	125.3 (6)	O(5)—C(4)—O(6)	124.9 (6)
O(2)—C(1)—C(2)	118.4 (5)	C(5)—C(6)—O(3)	117.5 (6)
N—C(2)—C(1)	112.5 (4)	C(5)—C(6)—O(4)	117.9 (5)
		O(3)—C(6)—O(4)	124.5 (6)

(c) Involving hydrogen

C(2)—H(1)	1.01 (4)	O(7)—H(7)	0.87 (4)
C(2)—H(2)	0.99 (3)	O(7)—H(8)	0.87 (4)
C(3)—H(3)	1.08 (4)	O(8)—H(9)	0.92 (4)
C(3)—H(4)	1.01 (4)	O(8)—H(10)	0.87 (4)
C(5)—H(5)	0.91 (4)	O(9)—H(11)	0.90 (4)
C(5)—H(6)	0.87 (4)	O(9)—H(12)	0.91 (4)

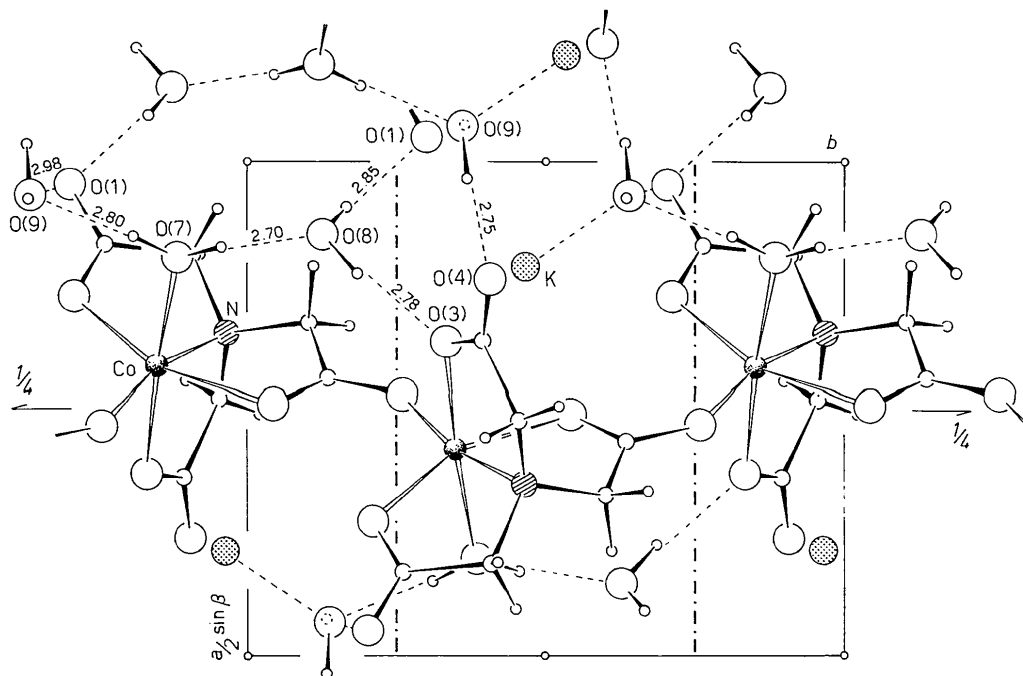


Fig. 2. Projection of the structure along [001].

tropic for the other atoms, improved the R index to 3.4%.

Final positional and thermal parameters with their e.s.d.'s are given in Tables 1 and 2.* The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for Co, K, O, N and C and those of Stewart, Davidson & Simpson (1965) for H.

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), using programs by Immirzi (1967).

Description of the structure and discussion

Coordination around cobalt is distorted octahedral (Fig. 1) involving the nitrogen atom and three carboxylic oxygens from the same nitrilotriacetate ion,

* The observed and calculated structure factors are available from the authors on request, and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30795 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

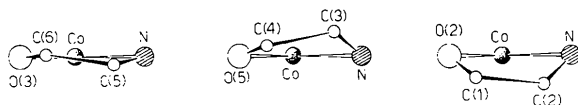


Fig. 3. Conformations of the chelation rings.

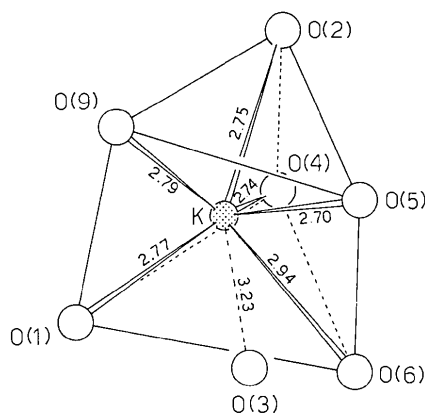


Fig. 4. Potassium environment.

one water molecule, and one carboxylic oxygen from an adjacent anion. The amino-acid anion is therefore behaving as a tetradentate chelating ligand and as a bridging agent (Fig. 2). The conformations of the three five-membered chelation rings are illustrated in Fig. 3. Bond distances and angles in the coordination polyhedron, which are given in Table 3, agree well with those found in other octahedral Co^{II} complexes containing nitrogen and oxygen as ligand atoms.

Bond distances and angles in the nitrilotriacetate ion (Table 3) and planarity of the carboxylic groups are all as expected. Two water molecules, which are not involved in coordination to cobalt, are present in the structure. They interact with K^+ and with the oxygen atoms of other water molecules and of the carboxylic groups.

Coordination around potassium involves seven oxygen atoms at the corners of a distorted trigonal prism with an extra position on a lateral face (Fig. 4, Table 4), these oxygen atoms belong to carboxylic groups and a water molecule. Packing is determined by the $\text{K}^+ \cdots \text{O}$ interactions and by the water-water and water-carboxylic oxygen hydrogen bonds. Fig. 2 and Table 5 show the hydrogen-bond system in the structure. The whole structure is built up of ribbons of complex anions running along $[010]$ and held together by interactions which the K^+ cations and the water molecules exert on each other and on the carboxylic oxygens. The other contacts less than 3.5 Å are shown in Table 6.

Bond distances and angles involving hydrogen atoms are in the normal ranges.

Table 4. Distances (Å) and angles ($^\circ$) in the potassium environment

Symmetry code: ii $\bar{x}, \bar{y}, \bar{z}$; iii $x, y+1, z$; iv $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; v $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$.

K-O(1 ⁱⁱ)	2.773 (3)	K-O(5 ^{iv})	2.703 (4)
K-O(2 ⁱⁱⁱ)	2.745 (4)	K-O(6)	2.936 (5)
K-O(3 ^{iv})	3.230 (6)	K-O(9 ⁱⁱⁱ)	2.787 (5)
K-O(4 ^v)	2.743 (6)		
O(1 ⁱⁱ)-K-O(2 ⁱⁱⁱ)	139.1 (5)	O(3 ^{iv})-K-O(4 ^v)	133.1 (6)
O(1 ⁱⁱ)-K-O(3 ^{iv})	84.1 (2)	O(3 ^{iv})-K-O(5 ^{iv})	58.2 (2)
O(1 ⁱⁱ)-K-O(4 ^v)	96.5 (3)	O(3 ^{iv})-K-O(6)	55.3 (2)
O(1 ⁱⁱ)-K-O(5 ^{iv})	142.2 (5)	O(3 ^{iv})-K-O(9 ⁱⁱⁱ)	82.9 (2)
O(1 ⁱⁱ)-K-O(6)	97.4 (2)	O(4 ^v)-K-O(5 ^{iv})	110.4 (4)
O(1 ⁱⁱ)-K-O(9 ⁱⁱⁱ)	85.3 (2)	O(4 ^v)-K-O(6)	78.3 (2)
O(2 ⁱⁱⁱ)-K-O(3 ^{iv})	129.5 (4)	O(4 ^v)-K-O(9 ⁱⁱⁱ)	144.0 (7)
O(2 ⁱⁱⁱ)-K-O(4 ^v)	77.2 (2)	O(5 ^{iv})-K-O(6)	64.4 (2)
O(2 ⁱⁱⁱ)-K-O(5 ^{iv})	74.6 (2)	O(5 ^{iv})-K-O(9 ⁱⁱⁱ)	87.3 (2)
O(2 ⁱⁱⁱ)-K-O(6)	120.0 (4)	O(6)-K-O(9 ⁱⁱⁱ)	137.3 (5)
O(2 ⁱⁱⁱ)-K-O(9 ⁱⁱⁱ)	78.3 (2)		

Table 5. Hydrogen-bond lengths (Å) and angles ($^\circ$)

Symmetry code: ii $\bar{x}, \bar{y}, \bar{z}$; iv $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; vi $x-\frac{1}{2}, \bar{y}-\frac{1}{2}, \frac{1}{2}+z$; vii $x, y, z+1$.

O(7) \cdots O(8)	2.698 (4)	O(7)-H(8) \cdots O(8)	171.3 (4)
O(7) \cdots O(9)	2.797 (4)	O(7)-H(7) \cdots O(9)	174.7 (4)
O(8) \cdots O(1 ⁱⁱ)	2.855 (4)	O(8)-H(10) \cdots O(1 ⁱⁱ)	165.2 (4)
O(8) \cdots O(3 ^{iv})	2.785 (4)	O(8)-H(9) \cdots O(3 ^{iv})	168.3 (4)
O(9) \cdots O(1 ⁱⁱⁱ)	2.986 (5)	O(9)-H(11) \cdots O(1 ⁱⁱⁱ)	155.0 (4)
O(9) \cdots O(4 ^{vi})	2.748 (4)	O(9)-H(12) \cdots O(4 ^{vi})	167.0 (4)

Table 6. *Contacts* (Å) less than 3.50 Å

Symmetry code			
i	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$	viii	$\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$
iv	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	ix	$\bar{x}, \bar{y}, 1-z$
vi	$x-\frac{1}{2}, \bar{y}-\frac{1}{2}, \frac{1}{2}+z$	x	$\bar{x}, \bar{y}-1, 1-z$
O(1)-O(4 ^{viii})	3.370 (4)	O(6)-O(2 ^{iv})	3.392 (5)
O(2)-O(5 ⁱ)	3.301 (4)	O(6)-O(3 ^{iv})	2.872 (5)
O(2)-O(4 ^{viii})	3.426 (4)	O(6)-O(5 ^{iv})	3.010 (4)
O(2)-O(7)	2.795 (3)	O(6)-O(7 ^{iv})	3.036 (4)
O(2)-O(9)	3.489 (4)	O(7)-N(1)	3.156 (3)
O(5)-O(7)	2.924 (2)	O(9)-O(4 ^{vi})	2.747 (2)
O(5)-O(8)	3.319 (2)	O(9)-O(8 ^{ix})	3.274 (4)
		O(9)-O(9 ^x)	3.379 (4)

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The Crystal and Molecular Structure of Bis-(2,4-pentanedionato)beryllium*

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The crystal structure of bis-(2,4-pentanedionato)beryllium, $\text{Be}(\text{CH}_3\text{COCHCOCH}_3)_2$, has been solved by direct methods. This compound crystallizes in space group $P2_1$ with cell dimensions $a_0 = 13.537$ (2), $b_0 = 11.378$ (2), $c_0 = 7.762$ (1) Å and $\beta = 100.76$ (1)° with two molecules in the asymmetric unit ($Z = 4$). Least-squares refinement of parameters using 2076 Mo $K\alpha$, counter-collected intensities yielded an R value of 0.066. The average interatomic separation for Be-O is 1.62 (2) Å and the average O-Be-O chelate ring angle is 107 (1)°. In one molecule the Be atom is located on each of the least-squares planes through the ring atoms of the two different chelate ligands while in the other molecule the Be atom is 0.20 Å removed from either of the two least-squares planes.

Introduction

Several years ago, discrepancies between the listed bond lengths and angles and those calculated using the published atomic parameters were noted in the crystal structure of bis-(2,4-pentanedionato)beryllium (or beryllium acetylacetonate), hereinafter $\text{Be}(\text{Acac})_2$, reported by Amirthalangam, Padmanabhan & Shankar (1960), hereinafter APS. Initial attempts to refine a set of peak-height intensity data using the published parameters were unsuccessful leading us to question the validity of the published structure. Various attempts (Stewart & Morosin, 1972) over several years to obtain the correct phases of a sufficient number of structure factors to lead to the correct structure were unsuccessful until the early coding of program *TANGEN* (X-RAY system: Stewart, Kruger, Ammon, Dickerson & Hall, 1972) was completed. With its use, the structure was then solved and refined.

Experimental details and results

The crystal specimens were grown from slowly evaporating methanol solutions. Weissenberg and precession photography verified previously assigned space groups as $P2_1$ or $P2_1/m$ (Bullen, 1957); the statistical distribution of the normalized structure factors corroborated APS's choice, based on the $N(z)$ test (Howells, Phillips & Rogers, 1950) of the noncentrosymmetric space group and the final solution of the structure confirmed it. Lattice constants were determined as $a_0 = 13.537$ (2), $b_0 = 11.378$ (2), $c_0 = 7.762$ (1) Å and $\beta = 100.76$ (1)° by measurements made on a Picker diffractometer (Cu $K\alpha$). There are two independent molecules in the asymmetric unit ($Z = 4$).

Over the period in which this material was studied, various data sets were collected from different specimens because of both instrumental changes as well as radiation degradation of the crystals. The successful solution of the structure employed a Mo $K\alpha$ intensity data set, I_b , obtained by taking averages on fixed-count, balanced-filter, hand-set (Morosin, 1965) data sets which individually had been approximately corrected

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