

Fig. 2. Edge view of the molecule projected along [100].

with the uranium atom lying 0.94 Å out of the plane. (This is much further than would have been predicted from any salen complexes.) The other nine atoms, N(2), O(3), and C(3) to (9), show a mean deviation of 0.05 Å from their least-squares plane, but this figure contains rather large contributions from N(2) and O(3), which are twisted from this plane by being shared with the pentagonal coordination plane of the uranium.

The large dihedral angle (31.0°) between the salicylideneimine plane and the coordination plane is possibly another sign of strain in this molecule, as the values for salen complexes rarely exceed 15°, except in highly strained systems such as Cosalen benzoylacetonate (Bailey *et al.*, 1972). The two salicylideneimine planes of the molecule meet at a dihedral angle of 59.1° and each is at 60.5° to the mirror plane. So these three planes intersect one another (at almost exactly 60°) in a common line, which is nearly parallel to the direction of the U–N(1) bond, as can be seen from the edge-on view of the molecule in Fig. 2.

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References

- AKHTAR, M. N., MCKENZIE, E. D., PAINE, R. E. & SMITH, A. J. (1969). *Inorg. Nucl. Chem. Lett.* **5**, 673–677.
 AUGUSTIN, M., KERRINNES, H. J. & LANGENBECK, W. (1964). *J. Prakt. Chem.* **26**, 130–136.
 BAILEY, N. A., HIGSON, B. M. & MCKENZIE, E. D. (1972). *J. Chem. Soc. Dalton*, pp. 503–508.
 BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.
 CALLIGARIS, M., NARDIN, G. & RANDACCIO, L. (1972). *Coord. Chem. Rev.* **7**, 385–403, and references therein.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 MCKENZIE, E. D. & PAINE, R. E. (1969). Personal communication.
 NGUYEN QUY DAO (1972). *Acta Cryst.* **B28**, 2011–2015.
 ROOF, R. B. JR (1959). *Phys. Rev.* **113**, 820–825.
 ROOF, R. B. JR (1961). *Acta Cryst.* **14**, 934–940.

Acta Cryst. (1973). **B29**, 279

An X-ray and Infrared Study of Bis(isocyanurato)diamminecopper(II)

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A three-dimensional structural analysis and an infrared study of an ammine isocyanuric acid copper complex are reported. The complex, which has the formula $[\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$, crystallizes in space group $P\bar{1}$, with unit-cell dimensions $a = 7.03$, $b = 9.05$, $c = 6.91$ Å, $\alpha = 42.19^\circ$, $\beta = 90.39^\circ$, $\gamma = 95.56^\circ$. Least-squares refinement led to a final agreement index of 10% on 837 reflexions. The complex consists of ammine groups and isocyanuric acid rings, bonded through nitrogen to copper atoms, forming square-planar arrangements cross-linked by hydrogen bonds. Some infrared bands are assigned by comparison of the spectra of $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$ with the following: $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{H}_2\text{O})_2]$, the deuterated analogues, cyanuric acid and diammine isocyanurato complexes of other metals.

Introduction

Work in this laboratory (Taylor, 1972) has shown that some metal oxides and salts react directly with heated

urea to form cyanurato complexes which have received little attention from chemists during the last 50 years, and have not yet been structurally defined.

Cyanurato complexes of copper were originally re-

ported by Wöhler (1847) and by Wiedermann (1848). Further work on the copper complex was carried out by Claus & Putensen (1888) who also prepared related compounds of Ni, Zn, Co, Mn and Mg.

The crystal structure of bis(isocyanurato)diammine-copper(II) was investigated as part of work in this laboratory concerned with metal cyanurates and their agricultural use, e.g. as sources of slowly available trace elements in soils.

Experimental

The crystals for X-ray analysis were supplied by Mr R. M. Taylor of these laboratories. For the remainder of the work described, crystals of identical structure

and composition were prepared as follows: an aqueous solution of boiling cyanuric acid, in slight excess of that required by the formula, was allowed to react with cupric chloride. The copper complex was precipitated with ammonia then recrystallized from a hot, dilute ammonia solution by standing. The crystals of $[Cu(C_3N_3O_3H_2)_2(NH_3)_2]$ are lavender-pink and typically triclinic pinacoidal.

To assist infrared assignments the equivalent diaquo complex, $(Cu(C_3N_3O_3H_2)_2(H_2O)_2)$, was prepared as above except that instead of ammonia, the stoichiometric quantity of sodium hydroxide was used. Deep blue crystals separated on cooling. Deuterated analogues of the diammine and diaquo complexes were prepared using D_2O throughout those preparations.

Table 1. Comparison of observed and calculated structure factors

h	k	l	Fe	Fe	h	k	l	Fe	Fe	h	k	l	Fe	Fe	h	k	l	Fe	Fe	h	k	l	Fe	Fe
0	0	0	48.1	39.2	0	0	0	37.1	36.1	0	0	0	44.8	47.9	0	0	0	44.8	47.9	0	0	0	44.8	47.9
0	0	1	48.9	39.7	0	0	1	37.1	36.6	0	0	1	44.8	47.9	0	0	1	44.8	47.9	0	0	1	44.8	47.9
0	0	2	49.7	40.2	0	0	2	37.1	36.6	0	0	2	44.8	47.9	0	0	2	44.8	47.9	0	0	2	44.8	47.9
0	0	3	50.5	40.7	0	0	3	37.1	36.6	0	0	3	44.8	47.9	0	0	3	44.8	47.9	0	0	3	44.8	47.9
0	0	4	51.3	41.2	0	0	4	37.1	36.6	0	0	4	44.8	47.9	0	0	4	44.8	47.9	0	0	4	44.8	47.9
0	0	5	52.1	41.7	0	0	5	37.1	36.6	0	0	5	44.8	47.9	0	0	5	44.8	47.9	0	0	5	44.8	47.9
0	0	6	52.9	42.2	0	0	6	37.1	36.6	0	0	6	44.8	47.9	0	0	6	44.8	47.9	0	0	6	44.8	47.9
0	0	7	53.7	42.7	0	0	7	37.1	36.6	0	0	7	44.8	47.9	0	0	7	44.8	47.9	0	0	7	44.8	47.9
0	0	8	54.5	43.2	0	0	8	37.1	36.6	0	0	8	44.8	47.9	0	0	8	44.8	47.9	0	0	8	44.8	47.9
0	0	9	55.3	43.7	0	0	9	37.1	36.6	0	0	9	44.8	47.9	0	0	9	44.8	47.9	0	0	9	44.8	47.9
0	0	10	56.1	44.2	0	0	10	37.1	36.6	0	0	10	44.8	47.9	0	0	10	44.8	47.9	0	0	10	44.8	47.9
0	0	11	56.9	44.7	0	0	11	37.1	36.6	0	0	11	44.8	47.9	0	0	11	44.8	47.9	0	0	11	44.8	47.9
0	0	12	57.7	45.2	0	0	12	37.1	36.6	0	0	12	44.8	47.9	0	0	12	44.8	47.9	0	0	12	44.8	47.9
0	0	13	58.5	45.7	0	0	13	37.1	36.6	0	0	13	44.8	47.9	0	0	13	44.8	47.9	0	0	13	44.8	47.9
0	0	14	59.3	46.2	0	0	14	37.1	36.6	0	0	14	44.8	47.9	0	0	14	44.8	47.9	0	0	14	44.8	47.9
0	0	15	60.1	46.7	0	0	15	37.1	36.6	0	0	15	44.8	47.9	0	0	15	44.8	47.9	0	0	15	44.8	47.9
0	0	16	60.9	47.2	0	0	16	37.1	36.6	0	0	16	44.8	47.9	0	0	16	44.8	47.9	0	0	16	44.8	47.9
0	0	17	61.7	47.7	0	0	17	37.1	36.6	0	0	17	44.8	47.9	0	0	17	44.8	47.9	0	0	17	44.8	47.9
0	0	18	62.5	48.2	0	0	18	37.1	36.6	0	0	18	44.8	47.9	0	0	18	44.8	47.9	0	0	18	44.8	47.9
0	0	19	63.3	48.7	0	0	19	37.1	36.6	0	0	19	44.8	47.9	0	0	19	44.8	47.9	0	0	19	44.8	47.9
0	0	20	64.1	49.2	0	0	20	37.1	36.6	0	0	20	44.8	47.9	0	0	20	44.8	47.9	0	0	20	44.8	47.9
0	0	21	64.9	49.7	0	0	21	37.1	36.6	0	0	21	44.8	47.9	0	0	21	44.8	47.9	0	0	21	44.8	47.9
0	0	22	65.7	50.2	0	0	22	37.1	36.6	0	0	22	44.8	47.9	0	0	22	44.8	47.9	0	0	22	44.8	47.9
0	0	23	66.5	50.7	0	0	23	37.1	36.6	0	0	23	44.8	47.9	0	0	23	44.8	47.9	0	0	23	44.8	47.9
0	0	24	67.3	51.2	0	0	24	37.1	36.6	0	0	24	44.8	47.9	0	0	24	44.8	47.9	0	0	24	44.8	47.9
0	0	25	68.1	51.7	0	0	25	37.1	36.6	0	0	25	44.8	47.9	0	0	25	44.8	47.9	0	0	25	44.8	47.9
0	0	26	68.9	52.2	0	0	26	37.1	36.6	0	0	26	44.8	47.9	0	0	26	44.8	47.9	0	0	26	44.8	47.9
0	0	27	69.7	52.7	0	0	27	37.1	36.6	0	0	27	44.8	47.9	0	0	27	44.8	47.9	0	0	27	44.8	47.9
0	0	28	70.5	53.2	0	0	28	37.1	36.6	0	0	28	44.8	47.9	0	0	28	44.8	47.9	0	0	28	44.8	47.9
0	0	29	71.3	53.7	0	0	29	37.1	36.6	0	0	29	44.8	47.9	0	0	29	44.8	47.9	0	0	29	44.8	47.9
0	0	30	72.1	54.2	0	0	30	37.1	36.6	0	0	30	44.8	47.9	0	0	30	44.8	47.9	0	0	30	44.8	47.9
0	0	31	72.9	54.7	0	0	31	37.1	36.6	0	0	31	44.8	47.9	0	0	31	44.8	47.9	0	0	31	44.8	47.9
0	0	32	73.7	55.2	0	0	32	37.1	36.6	0	0	32	44.8	47.9	0	0	32	44.8	47.9	0	0	32	44.8	47.9
0	0	33	74.5	55.7	0	0	33	37.1	36.6	0	0	33	44.8	47.9	0	0	33	44.8	47.9	0	0	33	44.8	47.9
0	0	34	75.3	56.2	0	0	34	37.1	36.6	0	0	34	44.8	47.9	0	0	34	44.8	47.9	0	0	34	44.8	47.9
0	0	35	76.1	56.7	0	0	35	37.1	36.6	0	0	35	44.8	47.9	0	0	35	44.8	47.9	0	0	35	44.8	47.9
0	0	36	76.9	57.2	0	0	36	37.1	36.6	0	0	36	44.8	47.9	0	0	36	44.8	47.9	0	0	36	44.8	47.9
0	0	37	77.7	57.7	0	0	37	37.1	36.6	0	0	37	44.8	47.9	0	0	37	44.8	47.9	0	0	37	44.8	47.9
0	0	38	78.5	58.2	0	0	38	37.1	36.6	0	0	38	44.8	47.9	0	0	38	44.8	47.9	0	0	38	44.8	47.9
0	0	39	79.3	58.7	0	0	39	37.1	36.6	0	0	39	44.8	47.9	0	0	39	44.8	47.9	0	0	39	44.8	47.9
0	0	40	80.1	59.2	0	0	40	37.1	36.6	0	0	40	44.8	47.9	0	0	40	44.8	47.9	0	0	40	44.8	47.9
0	0	41	80.9	59.7	0	0	41	37.1	36.6	0	0	41	44.8	47.9	0	0	41	44.8	47.9	0	0	41	44.8	47.9
0	0	42	81.7	60.2	0	0	42	37.1	36.6	0	0	42	44.8	47.9	0	0	42	44.8	47.9	0	0	42	44.8	47.9
0	0	43	82.5	60.7	0	0	43	37.1	36.6	0	0	43	44.8	47.9	0	0	43	44.8	47.9	0	0	43	44.8	47.9
0	0	44	83.3	61.2	0	0	44	37.1	36.6	0	0	44	44.8	47.9	0	0	44	44.8	47.9	0	0	44	44.8	47.9
0	0	45	84.1	61.7	0	0	45	37.1	36.6	0	0	45	44.8	47.9	0	0	45	44.8	47.9	0	0	45	44.8	47.9
0	0	46	84.9	62.2	0	0	46	37.1	36.6	0	0	46	44.8	47.9	0	0	46	44.8	47.9	0	0	46	44.8	47.9
0	0	47	85.7	62.7	0	0	47	37.1	36.6	0	0	47	44.8	47.9	0	0	47	44.8	47.9	0	0	47	44.8	47.9
0	0	48	86.5	63.2	0	0	48	37.1	36.6	0	0	48	44.8	47.9	0	0	48	44.8	47.9	0	0	48	44.8	47.9
0	0	49	87.3	63.7	0	0	49	37.1	36.6	0	0	49	44.8	47.9	0	0	49	44.8	47.9	0	0	49	44.8	47.9
0	0	50	88.1	64.2	0	0	50	37.1	36.6	0	0	50	44.8	47.9	0	0	50	44.8	47.9	0	0	50	44.8	47.9
0	0	51	88.9	64.7	0	0	51	37.1	36.6	0	0	51	44.8	47.9	0	0	51	44.8	47.9	0	0	51	44.8	47.9
0	0	52	89.7	65.2	0	0	52	37.1	36.6	0	0	52	44.8	47.9	0	0	52	44.8	47.9	0	0	52	44.8	47.9
0	0	53	90.5	65.7	0	0	53	37.1	36.6	0	0	53	44.8	47.9	0	0	53	44.8	47.9	0	0	53	44.8	47.9
0	0	54	91.3	66.2	0	0	54	37.1	36.6	0	0	54	44.8	47.9	0	0	54	44.8	47.9	0	0	54	44.8	47.9
0	0	55	92.1	66.7	0	0	55	37.1	36.6	0	0	55	44.8	47.9	0	0	55	44.8	47.9	0	0	55	44.8	47.9
0	0	56	92.9	67.2	0	0	56	37.1	36.6	0	0	56	44.8	47.9	0	0	56	44.8	47.9	0	0	56	44.8	47.9
0	0	57	93.7	67.7	0	0	57	37.1	36.6	0	0	57	44.8	47.9	0	0	57	44.8	47.9	0	0	57	44.8	47.9
0	0	58	94.5	68.2	0	0	58	37.1	36.6	0	0	58	44.8	47.9	0	0	58	44.8	47.9	0	0	58	44.8	47.9
0	0	59	95.3	68.7	0	0	59	37.1	36.6	0	0	59	44.8	47.9	0	0	59	44.8	47.9	0	0	59	44.8	47.9
0	0	60	96.1	69.2	0	0	60	37.1	36.6	0	0	60	44.8	47.9	0	0	60	44.8	47.9	0	0			

Crystal data

Bis(isocyanurato)diamminecopper(II)
 $\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2$, M.W. 353.74
 Crystal class: triclinic

$a = 9.051 \pm 0.015$, $b = 13.006 \pm 0.019$, $c = 5.018 \pm 0.008$ Å
 $\alpha = 91.36 \pm 0.18$, $\beta = 82.69 \pm 0.19$, $\gamma = 93.23 \pm 0.18^\circ$
 Unit-cell volume $U = 584.9 \pm 1.6$ Å³, $Z = 2$, $D_m = 1.97$
 (determined by the flotation method),
 $D_c = 1.95$ g cm⁻³, $F(000) = 334$
 (excluding hydrogens).
 $\mu = 50.43$ cm⁻¹ (Co $K\alpha$).

The systematic absences are: hkl absent when $k+l$ is odd, which indicates that the cell described above is centred upon the (100) face. The space group is therefore $A1$ or $A\bar{1}$.

Although the cell described above was used for convenience in the present study, the following parameters describe a primitive cell derived from it.

$a = 7.026 \pm 0.014$, $b = 9.051 \pm 0.015$, $c = 6.914 \pm 0.010$ Å
 $\alpha = 42.19 \pm 0.17$, $\beta = 90.39 \pm 0.18$, $\gamma = 95.56 \pm 0.17^\circ$

The three-dimensional intensity data were recorded with iron-filtered Co $K\alpha$ radiation ($\lambda = 1.7889$ Å), by means of Weissenberg photographs, with the multiple exposure technique and integration processes. Two crystals were used; on the first, four layers with [001] as rotation axis ($l = 0$ to 3) were taken, while on the second, three layers with [100] as rotation axis ($h = 0$ to 2) were measured. 933 reflexions were measured with a Zeiss microdensitometer and processed with a program written by one of us (E.W.R.). Corrections were made for Lorentz and polarization factors. No absorption corrections were applied in view of the small sizes of specimens used for the analysis.

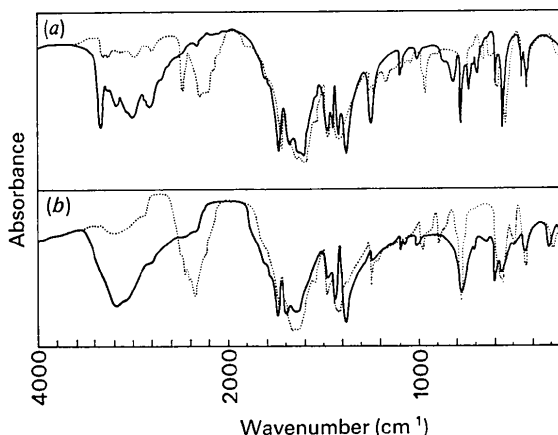


Fig. 1. Infrared absorption spectra of (a) $[\text{Cu}_3(\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$, shown as — and its deuterated equivalent as ····· and (b) $[\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{H}_2\text{O})_2]$, shown as — and its deuterated equivalent as ·····.

Infrared spectra

Spectra were recorded on a Perkin-Elmer 521 spectrophotometer using potassium bromide pellets, Nujol mulls and attenuated total reflectance. For studies with polarization, using a gold wire grid analyser in the common beam, thin sections of the largest single crystals were cut to give maximum area (0.45×0.3 by 0.05 mm thickness) and were positioned in a multi-reflectance beam condenser with the light beam along the b axis. Measurements at 15° intervals through 180° gave absorption maxima for each band. The molecular orientation in the sections was established by X-ray diffraction.

Bands were assigned by comparison of the spectrum of $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$ with the spectra of the following: $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{H}_2\text{O})_2]$, the deuterated analogues, cyanuric acid, and the isocyanuratediammine complexes of other metals. Angles of polarization for absorption maxima of the copper complex were also used (with due caution, since resultant dipole moment vibrations may not necessarily coincide with bond directions).

Determination of the structure

The structure was determined by the heavy-atom method. The chemical formula suggested that the basic structural units were cyanuric acid groups arranged with two per copper atom. With $Z = 2$, and in the centred triclinic cell chosen, phases were assigned to the observed structure factors for a three-dimensional Fourier synthesis by placing the copper atoms at $0, 0, 0$, and $0, \frac{1}{2}, \frac{1}{2}$. A three-dimensional Fourier synthesis was then calculated. Images of all the atoms of the structure were clearly resolved and no additional peaks were found. Although the Fourier map phased upon the copper atoms had to be centrosymmetrical, deviations from true centrosymmetry on the part of the molecule could have produced distorted peaks if the deviations were small. No such deviations were noticed. After two cycles of least-square refinement of scale factors and positional parameters respectively, an R value for all reflexions of 0.20 resulted.

Refinement

The least-squares cycles mentioned above were based upon space group $A\bar{1}$. A third cycle of refinement of positional parameters in $A1$ returned values somewhat different to those previously calculated. However, an attempt to vary individual temperature and positional parameters in $A1$ produced shifts which were quite meaningless. This result accords with a conclusion reached by Parthasarthy, Sime & Speakman (1969) in which they comment that when in doubt about a space group it is not necessarily safe to use that of lower symmetry for refinement.

The space group $A\bar{1}$ seems to have been confirmed by a fourth refinement cycle, in that space group, of all temperature factors and positional parameters. This cycle produced a further convergence of R to 0.15 and

returned reasonable values for the temperature factors. The reliability index was further reduced initially by applying Cruickshank's weighting scheme, followed by rejection facilities introduced into the *ORFLS* program of Busing, Martin & Levy (1962). The first of these rejection features deleted observations with $[(|F_o| - |F_c|)/\sigma|F_o|]$ greater than 0.25 and the second rejected reflexions whose $(\sin \theta/\lambda)^2$ was greater than 0.28. The 10% of reflexions rejected by these schemes were reviewed one by one, and their deletion found to be justified by poor measurements, extinction and high backgrounds due to white radiation. The final *R* value obtained was 0.10 on 837 reflexions. Anisotropic temperature factors were not applied.

The scattering factors for C (valence), N, O and Cu^{2+} were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 1, which does not list those reflexions rejected by the weighting scheme and rejection options. Table 2 gives the final positional and temperature parameters with their standard deviations. The interatomic distances and bond angles were calculated by the *ORFFE* program of Busing, Martin & Levy (1964). Intramolecular distances and bond angles are reported in Tables 3 and 4 respectively. The closest

Table 2. Atomic coordinates and temperature factors, with standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Cu^{2+}	0.0	0.5	0.5	2.4 (0)
N(1')	0.4495 (14)	0.4193 (7)	0.7357 (24)	2.0 (2)
N(2')	0.1990 (15)	0.4364 (7)	0.5451 (25)	2.2 (2)
N(3')	0.3513 (15)	0.3220 (7)	0.3578 (25)	2.3 (2)
N(4')	0.0834 (14)	0.6227 (7)	0.3290 (24)	2.3 (2)
C(1')	0.2118 (18)	0.3648 (9)	0.3434 (34)	2.3 (3)
C(2')	0.4644 (18)	0.3472 (9)	0.5334 (31)	2.0 (3)
C(3')	0.3085 (17)	0.4624 (9)	0.7217 (31)	1.9 (3)
O(1')	0.1126 (14)	0.3386 (7)	0.1718 (23)	3.3 (2)
O(2')	0.5904 (13)	0.3113 (7)	0.5462 (21)	2.6 (2)
O(3')	0.3037 (12)	0.5273 (6)	0.9106 (21)	2.7 (2)

intermolecular distances are reported in Table 5. All atoms designated by singly primed symbols are related by a centre of symmetry to their doubly primed equivalents.

Table 3. Bond distances, with their standard deviations

$\text{Cu}^{2+}-\text{N}(1')$	2.06 (1) Å
$\text{Cu}^{2+}-\text{N}(4')$	1.90 (1)
$\text{N}(2')-\text{C}(1')$	1.36 (2)
$\text{C}(1')-\text{N}(3')$	1.42 (2)
$\text{N}(3')-\text{C}(2')$	1.45 (2)
$\text{C}(2')-\text{N}(1')$	1.36 (2)
$\text{N}(1')-\text{C}(3')$	1.43 (2)
$\text{C}(3')-\text{N}(2')$	1.43 (2)
$\text{C}(1')-\text{O}(1')$	1.35 (2)
$\text{C}(2')-\text{O}(2')$	1.27 (2)
$\text{C}(3')-\text{O}(3')$	1.25 (2)
$\text{N}(4')-\text{O}(3')$	4.21 (3)
$\text{N}(4')-\text{O}(1')$	2.93 (3)
$\text{N}(4')-\text{O}(1')$	3.78 (3)
$\text{N}(4')-\text{O}(3')$	4.00

Table 4. Bond angles, with standard deviations

$\text{N}(4')-\text{Cu}^{2+}-\text{N}(2')$	97° 3' (1° 10')
$\text{C}(1')-\text{N}(2')-\text{C}(3')$	125.41 (1.15)
$\text{C}(3')-\text{N}(1')-\text{C}(2')$	105.30 (1.15)
$\text{C}(2')-\text{N}(3')-\text{C}(1')$	130.44 (1.10)
$\text{N}(3')-\text{C}(1')-\text{N}(2')$	104.40 (1.29)
$\text{N}(2')-\text{C}(1')-\text{O}(1')$	127.41 (1.15)
$\text{O}(1')-\text{C}(1')-\text{N}(3')$	127.38 (1.15)
$\text{N}(3')-\text{C}(2')-\text{N}(1')$	123.45 (1.13)
$\text{N}(3')-\text{C}(2')-\text{O}(2')$	131.41 (1.15)
$\text{N}(1')-\text{C}(2')-\text{O}(2')$	104.34 (1.25)
$\text{N}(2')-\text{C}(3')-\text{N}(1')$	129.36 (1.6)
$\text{N}(1')-\text{C}(3')-\text{O}(3')$	101.29 (1.10)
$\text{O}(3')-\text{C}(3')-\text{N}(2')$	128.50 (1.13)

Table 5. Shortest intermolecular distances

See also Fig. 3.	
$\text{N}(4'') \cdots \text{O}(1'')$	3.27 Å
$\text{N}(4'') \cdots \text{O}(3'')$	3.00
$\text{N}(4'') \cdots \text{O}(2'')$	3.16
$\text{N}(3'') \cdots \text{O}(2'')$	2.66

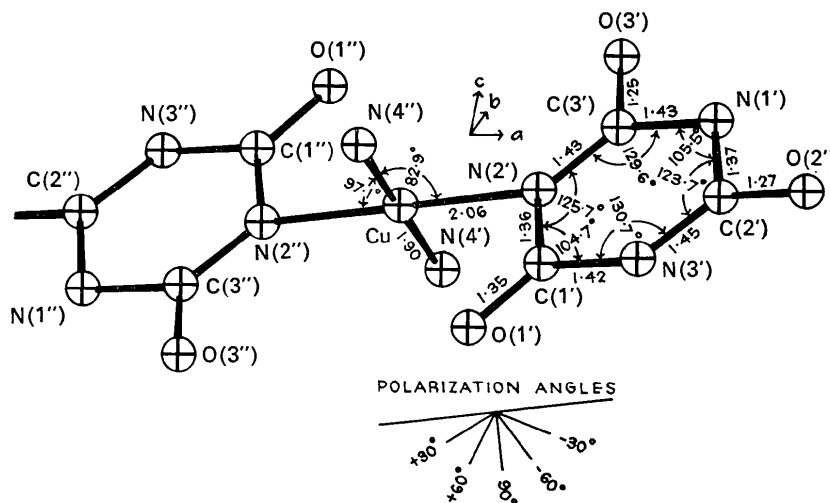


Fig. 2. The molecular structure of $[\text{Cu}(\text{C}_3\text{N}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$.

Infrared results

Although not identical in every respect, the cyanurato complexes with Cr, Ni, Fe, Cd, Cu, Co, Mn and Ni have common bands in the ranges shown in Table 6, which also gives the results for cyanuric acid.

Table 6. *Infrared absorption spectra**

Cyanuric acid

3415*m*, 3200*s*, 3046*s*, 2875*w*, 2824*w*,
1775*sh*, 1751*sh*, 1716*vs*, 1693*vs*, 1455*m*,
1414*m*, 1397*s*, 1059*m*, 1049*m*, 842*m*,
792*m*, 761*w*, 741*w*, 690*m*, 546*sh*, 532*s*,
447*m*, 412*m*

Metal complexes

2840–2800, 1730–1700, 1480–1447,
1427–1407, 1385–1350, 1160–1120,
1090–1050, 1000–970, 870–820,
785–760, 708–680, 615–583,
557–530, 437–420.

* All bands in cm^{-1} . *s*=strong, *m*=medium, *w*=weak, *sh*=shoulder.

Infrared absorption bands for $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$ and its deuterated analogue are given in Table 7 along with the angles at which maximum adsorption occurred on polarization. These angles are given for an incident beam in the $+b$ direction and with 0° close to the a direction as shown in Fig. 2. The spectra of the compounds in Table 7 are

compared with those for the aquo complex and its analogue in Fig. 1.

Discussion

The basic structural units consist of two isocyanuric acid rings and two ammonia groups bound each through nitrogen atoms to a central copper atom to form an approximately square-planar arrangement. The ammonia groups lie approximately 13.5° away from the normals to the rings. The configuration is illustrated in Fig. 2. Cross-linking between these molecular units is very likely achieved by hydrogen bonds discussed below and indicated in Fig. 3.

Hydrogen bonding

Although no attempt was made to directly determine hydrogen positions from the Fourier maps, the presence of at least four $\text{N}-\text{H}\cdots\text{O}$ bonds can be inferred from a consideration of the infrared $\text{N}-\text{H}$ stretching frequency region and interatomic distances.

In this region five major bands are found for $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$: doublets at 3346, 3003, and 2820 cm^{-1} and single bands at 3265 and 3176 cm^{-1} . All bands show deuteration shifts. For $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{H}_2\text{O})_2]$ bands occurred at 3180, 3100 and 3040 cm^{-1} and all shifted on deuteration.

These bands have been assigned to the following NH groups. To N(1)-H is assigned 3176 cm^{-1} since it is present in both complexes; this is in agreement with the assignment of 3180 to the 'free imide', $-\text{NH}-$

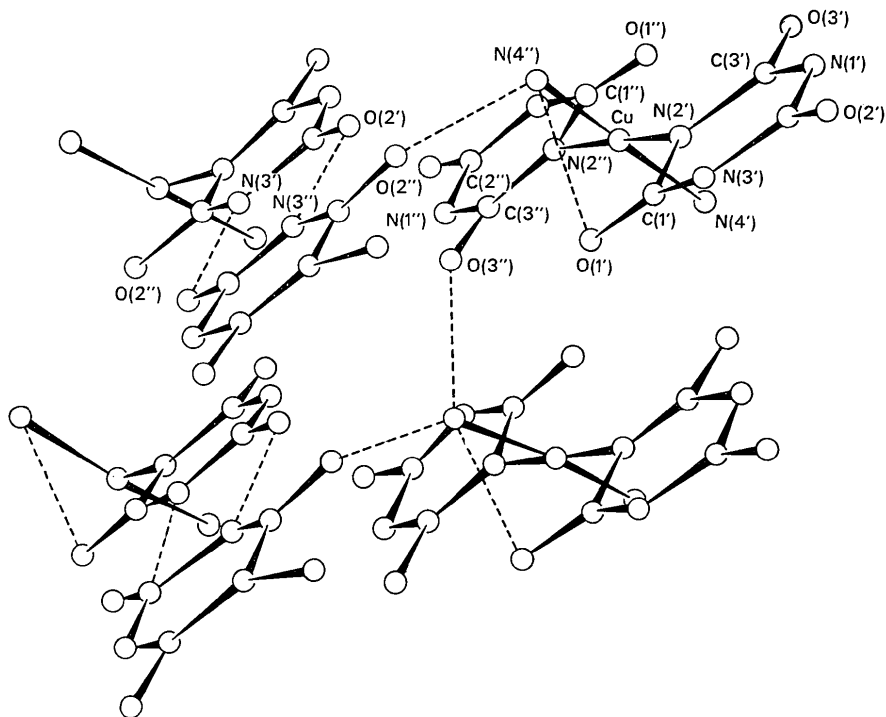


Fig. 3. View near $[010]$ showing the arrangement of molecular units and the network of hydrogen bonds that link them.

of the nitrogen bonded biuret complexes of Cu (II) by McLellan & Melson (1967) and also of 3220 and 3210 cm^{-1} by Aida, Musya & Kinumaki (1963) and Kedzia, Armendarez & Nakamoto (1968) respectively. To N(3)-H is assigned the doublet at 2820 cm^{-1} . To N(4)-H is assigned the doublet at 3346 and also the single band at 3265 cm^{-1} because both are absent in the aquo complex. This agrees with the frequencies given for the amide groups coordinated with copper in the above mentioned biuret complexes and 3270 cm^{-1} given by Nakamoto (1963) for the NH_3 groups of the Cu(II) tetra-ammine chloro complex.

A form of the Lennard-Jones potential function:

$$\Delta\nu_s (\text{cm}^{-1}) = 50 \left[\left(\frac{3.4}{D} \right)^{12} - \left(\frac{3.4}{D} \right)^6 \right]$$

has been successfully used by Bellamy & Owen (1969) to correlate N-H...O bond lengths (D in Å) with shifts in the N-H stretching frequency ($\Delta\nu_s$), assuming a 'free' NH stretching frequency of 3450 cm^{-1} .

This equation predicts the bond lengths shown in Table 8. Bellamy & Owen's equation has known deficiencies (Nakamoto, Margoshes & Rundle, 1955). In spite of these, the agreement between the bond lengths which it predicts and those determined by X-rays is good; the bond at 3.02 Å shows the greatest deviation but this is within the limits of scatter of experimental points about Bellamy & Owen's curve (see also Nakamoto, Margoshes & Rundle, 1955).

Table 8. Bond lengths predicted from infrared measurement and found by X-rays

Bond	Frequency	Length	
		Predicted	Found
N(4'')H...O(2')*	3346 cm^{-1}	3.02 Å	3.16 Å
N(4'')H...O(3'')	3330	3.00	3.00
N(4'')H...O(1')†	3265	2.92	2.93
N(3')H...O(2'')	2810	2.68	2.66

* Intermolecular bond.

† Intramolecular bond.

Table 7. Infrared absorption bands of bis(isocyanurato)diamminecopper(II) and its deuterated analogue, angles of polarization with respect to zero as in Fig. 2 and main assignments

Copper complex $\text{cm}^{-1}\dagger$	Polarization angle	Deuterated analogue cm^{-1}	Assignment†
3346	10	2496s	$\nu\text{N}(4'')\text{-H}\cdots\text{O}(2')$ (intermolecular)
3330vs	80	2482s	$\nu\text{N}(4'')\cdots\text{O}(3'')$
3265w	90	2414w	$\nu\text{N}(4'')\cdots\text{O}(1')$ (intramolecular)
3176s	80	2305s	$\nu\text{N}(1)\text{-H}$ (imide)
3003vs	-60	2260w } 2228m }	$\nu\text{N}(3')\text{-H}\cdots\text{O}(2'')$ unsymmetrical (intermolecular)
2847sh	60	2160sh }	
2810s	-45	2120w }	$\nu\text{N}(3')\text{-H}\cdots\text{O}(2'')$ symmetrical (intermolecular)
1734vs	0*	1724s	$\nu\text{C}(3)\text{-O}(3)$ (of cyanuric acid)
1678vs		1176m	$\nu_{\text{as}}\text{C}(2)\text{-O}(2) + \delta\text{N}(3)\text{-H}$ (hydrogen bonded)
1631vs		1650vs	$\nu_{\text{a}}\text{C}(2)\text{-O}(2)$
1608vs		1605vs	$\nu\text{C}(2)\text{-O}(2)$ due to partial enolization
1482s	50	1482vs	$\nu\text{C}(1)\text{-O}(1)$
1453s	0	1046w	$\delta\text{N}(4)\text{-H}$ (hydrogen bonded)
1425s	70	1429vs	$\nu\text{C-N}$ broadens on deuteration (shorter ring bonds)
1382vs	0	981w } 966s }	$\delta\text{N}(1)\text{-H}$
1256sh	-85	1257m }	
1252s		1241s }	$\nu\text{C-N}$
1096m } 1086w }	50	911w	ν ring in aquo complex, absent on deuteration
1006w	-60	981w	$\pi\text{N}(3)\text{-H}$ (hydrogen bonded)
865w	90	668m } 625m }	$\nu_{\text{a}}\text{N}(4)\text{H}_3$ absent in aquo complex
823m	90	778s	$\delta\text{C}(2)\text{-O}(2)$ in plane of ring (raised by hydrogen bond)
780s	80	756m	$\delta\text{C-O}$ in plane of ring
754w	-50 }		$\pi\text{N}(1)\text{-H}$
738m		546vs	
711w	-50 }	679w	$\delta\text{N-C-O}$
692m } 688m }	50		
590s	-10	585s	$\pi\text{C}(3)\text{-O}(3)$
554s	60	546vs	$\pi\text{C}(2)\text{-O}(2)$
454m	60	452	$\nu\text{Cu-N}$ (ammine) } ? with ring deformation
431m	20	425m	$\nu\text{Cu-N}$ (ring)
291w	55	289w	$\delta\text{N-Cu-N}$

* Region of intense absorption; common angle appears to be at 0°.

† Abbreviations: ν , very; s , strong; m , medium; w , weak; sh , shoulder; ν , stretch; δ , deformation; ν_{a} , rock; π , out of plane bend; a , asymmetric; s , symmetric.

The strong band at 3003 cm^{-1} has been assigned to an unsymmetric N(3)H stretch associated with ring linkages.

The shortest hydrogen bonds, of length 2.66 \AA , which link $\text{N}(3')\text{H}\cdots\text{O}(2'')$ and $\text{N}(3'')\text{H}\cdots\text{O}(2')$ are instrumental in bonding the molecular units together to form chains. These extend across unit cells, through the copper atoms at origins and points of face centring. The remaining two intermolecular $\text{NH}\cdots\text{O}$ bonds crosslink these chains to form a three-dimensional network.

The effect of the intramolecular $\text{N}(4')\cdots\text{O}(1')$ bond will be discussed later.

The ligand molecules

Cyanuric acid has recently been carefully studied by Verschoor & Keulen (1971) and by Coppens & Vos (1971). In the present structure, coordination to copper has had a considerable effect on the dimensions of the cyanuric acid molecule. However, the coordinated rings in $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{NH}_3)_2]$ remain planar, as shown by a calculation of the dihedral angle between planes defined by three carbon atoms and three nitrogen atoms within such a ring; the dihedral angle did not significantly differ from zero.

The various bonds of the structure are now discussed and their infrared assignments suggested.

The relatively short C(3)–O(3) bond of length 1.25 \AA (1734 cm^{-1}) is comparable with similar bonds in cyanuric acid. By contrast, the long C(1)–O(1) bond of length 1.35 \AA (1482 cm^{-1}) appears, from the comprehensive empirical correlations of Stals (1970), to have a 30% partial double-bond character.

The C(2)–O(2) bonds, associated with those hydrogen bonds forming ring linkages have a length of 1.27 \AA and give rise to a number of frequencies as found for example in the β -diketones (Colthup, Daly & Wiberley, 1964). Thus to C(2)–O(2) are assigned 1678 cm^{-1} (symmetrical stretch) and 1631 cm^{-1} (asymmetrical stretch). These combine to form a single band at 1650 cm^{-1} on deuteration.

Of the six C–N bonds in each ring, four have lengths between 1.42 and 1.45 \AA ; these are normal lengths for C–N single bonds, but are longer than those in cyanuric acid and the analogous compounds listed by Verschoor & Keulen (1971). The other two, C(1)–N(2) and C(2)–N(1), have lengths (1.36 – 1.37 \AA) similar to those in cyanuric acid, and possess an appreciable double bond character.

As discussed for example by Cutmore & Hallam (1969) and Hallam (1969), the grouping of $\text{O}=\text{C}-\text{N}-\text{H}$ may suffer a delocalization thus $\text{O}\cdots\text{C}\cdots\text{N}-\text{H}$,
 $\begin{array}{c} | \quad | \\ \delta^+ \quad \delta^- \\ \text{O}\cdots\text{C}\cdots\text{N}-\text{H} \\ | \quad | \\ \delta^- \quad \delta^+ \end{array}$
 the interacting dipole $>\text{C}=\text{O}$ being of opposite polarity to $>\text{N}-\text{H}$. The latter group may have another atom R instead of hydrogen to give $>\text{N}-\text{R}$. It is suggested that such a delocalization is the cause for the two

short C–N bonds. Partial enolization of the group containing C(2)–O(2) is suggested by the absorption band at 1608 cm^{-1} , see Table 7. Delocalization is supported by the known electron-withdrawing power of the copper and the long C(1)–O(1) bond already discussed.

Environment of copper atom

The copper atom is bonded to four nitrogen atoms, two lying at 1.90 \AA and two at 2.06 \AA . It is clear from the results of Sacconi, Sabatini & Gans (1964) on metal ammine complexes that the infrared absorption band at 431 cm^{-1} is associated with a Cu–N(ring) stretch. Because the band at 454 cm^{-1} is absent in $[\text{Cu}(\text{N}_3\text{C}_3\text{O}_3\text{H}_2)_2(\text{H}_2\text{O})_2]$ it is assigned to Cu–N(ammine) stretch. Two less intense bands occur at about these frequencies in cyanuric acid so that these two bands may be coupled with ring bending modes. A band frequently observed at 291 cm^{-1} is assigned to a N–Cu–N deformation.

The N(2')–Cu–N(4'') angle is $82^\circ 57'$ in the present structure. This compares with $82^\circ 18'$ in $(\text{C}_5\text{H}_5\text{N}_2)_2\text{Cu}(\text{II})$ (Tewari & Srivastava, 1971); 83° in $\text{K}_2[\text{Cu}(\text{NH}_2\text{CH}_2\text{CONCH}_2\text{COO})_2] \cdot 6\text{H}_2\text{O}$ (Sugihara, Ashida, Sadada & Kakudo, 1968) and 90° in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}$ (Mazzi, 1953). A calculation of the angle between the normals to the planes defined by N(4'), Cu, N(2') and C(1'), C(2'), C(3') returned a value of $76^\circ 42' \pm 36'$, so that the ammonia groups lie approximately $13^\circ 30'$ away from the normals to the rings.

The room temperature magnetic moment of the complex was 1.87 B.M. This is a typical value for Cu^{2+} with a d^9 electronic configuration and accords well with the result of 1.88 B.M. found by McLellan & Melson (1967) for Cu^{2+} surrounded by four nitrogen atoms from two biuret ligands.

In summary the structure of bis(isocyanurato)diamminecopper(II) consists of two iso-cyanuric acid rings and two ammonia groups each bound through nitrogen atoms to a central copper atom. Cross linking between molecular units is achieved by hydrogen bonds.

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References

- AIDA, K., MUSYA, Y. & KINUMAKI, S. (1963). *J. Inorg. Chem.* **2**, 1268–1269.
 BELLAMY, L. J. & OWEN, A. J. (1969). *Spectrochim. Acta*, **25A**, 329–333.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.
 CLAUS, A. & PUTENSEN, P. (1888). *J. Prakt. Chem.* **38**, 208–229.

- COLTHUP, N. B., DALY, L. H. & WIBERLEY, S. E. (1964). *Introduction to Infrared and Raman Spectroscopy*. New York and London: Academic Press.
- COPPENS, P. & VOS, A. (1971). *Acta Cryst.* B27, 146–158.
- CUTMORE, E. A. & HALLAM, H. E. (1969). *Spectrochim. Acta*, 25A, 1767–1785.
- HALLAM, H. E. (1969). *Spectrochim. Acta*, 25A, 1785–1789.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KEDZIA, B. B., ARMENDAREZ, P. X. & NAKAMOTO, K. (1968). *J. Inorg. Nucl. Chem.* 30, 849–860.
- MAZZI, F. (1953). *R. C. Soc. Mineral. Ital.* 9, 148–172.
- MCLELLAN, A. W. & MELSON, G. A. (1967). *J. Chem. Soc. (A)*, pp. 137–142.
- NAKAMOTO, K., MARGOSHES, M. & RUNDLE, R. E. (1955). *J. Amer. Chem. Soc.* 77, 6480–6486.
- NAKAMOTO, K. (1963). *Infrared Spectra of Inorganic and Coordination Compounds*. London: Wiley.
- PARTHASARATHY, R., SIME, J. G. & SPEAKMAN, J. C. (1969). *Acta Cryst.* B25, 1201–1202.
- SACCONI, L., SABATINI, A. & GANS, P. (1964). *J. Inorg. Chem.* 3, 1772–1774.
- STALS, J. (1970). *Rev. Pure Appl. Chem.* 20, 1–22.
- SUGIHARA, A., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1968). *Acta Cryst.* B24, 203–211.
- TAYLOR, R. M. (1972). *Z. anorg. allgem. Chem.* 390, 85–96.
- TEWARI, R. & STRIVASTAVA, R. C. (1971). *Acta Cryst.* B27, 1644–1649.
- VERSCHOOR, G. C. & KEULEN, E. (1971). *Acta Cryst.* B27, 134–145.
- WEIDERMANN, G. (1848). *Liebigs Ann.* 68, 324–326.
- WÖHLER, F. (1847). *Liebigs Ann.* 62, 241–253.

Acta Cryst. (1973). B29, 286

Hydrogen Bonding in the Crystalline State. Crystal Structure of $\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$, Roesslerite*

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Roesslerite, magnesium hydrogen arsenate heptahydrate ($\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$), crystallizes in the monoclinic system, space group $C2/c$. Unit-cell parameters are: $a_0 = 6.6918$ (5), $b_0 = 25.744$ (2), $c_0 = 11.538$ (1) Å, $\beta = 95.15$ (1)°; $Z = 8$. The crystal structure was refined anisotropically to $R = 0.030$, using 2157 non-zero reflexions measured on an automatic three-circle diffractometer (Cu $K\alpha$ radiation). Corrections for absorption, secondary extinction (including an increase of the mosaicity during the measurements) and anomalous scattering were applied. The hydrogen atoms were located from difference maps and the acidic hydrogen atom appears to be involved in two symmetrical hydrogen bonds. The two crystallographically independent magnesium atoms are coordinated by six water molecules; the seventh water molecule is linked by hydrogen bonds only. No oxygen atoms are shared by coordination polyhedra and the crystal structure can be described in terms of layers parallel to (010) or to (001).

Introduction

Roesslerite, magnesium hydrogen arsenate heptahydrate ($\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$), is a secondary mineral usually associated with other arsenates (Palache, Berman & Frondel, 1963) and, according to its known properties, is isostructural with $\text{MgHPO}_4 \cdot 7\text{H}_2\text{O}$, phosphoroesslerite.

An X-ray crystal-structure determination of roesslerite has been carried out as a part of a programme of structural research on hydrogen bonding and on the role of the water molecule in the crystalline state [cf. Ferraris & Franchini-Angela (1972), Chiari & Ferraris (1971) and references therein]; in particular, acidic arsenates (or phosphates) are often likely to have symmetrical hydrogen bonds [cf. Ferraris, Jones & Yerkess (1972) and references therein].

Preparation and crystal data

Transparent, colourless crystals of $\text{MgHAsO}_4 \cdot 7\text{H}_2\text{O}$, suitable for X-ray study, were grown by the method of Mattrat & Guérin (1960). Cu $K\alpha$ X-ray diffraction analyses (Weissenberg and single-crystal diffractometry) confirmed the monoclinic symmetry (Palache *et al.*, 1963) and, to a first approximation, the unit-cell parameters reported by Fischer (1964); the crystals are tabular {010} and elongated along [100]. The space group $C2/c$ (C_{2h}^6 , No. 15) has been chosen on the basis of systematic absences (Cc or $C2/c$), the absence of a piezoelectric effect,* and the examination of the Harter sections; the successful refinement of the structure confirmed the validity of this choice.

The reciprocal unit-cell parameters were refined by a least-squares procedure using 36 θ values greater than 65°, which were measured at room temperature on a single-crystal diffractometer ($\lambda\alpha_1 = 1.54050$, $\lambda\alpha_2 =$

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