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The Crystal and Molecular Structure of Bis(salicylato)-(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)

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The crystal and molecular structure of monomeric bis(salicylato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-copper(II), $Cu(C_7H_5O_3)_2(C_6H_{16}N_2)$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the space group $P2_1/n$, with $Z = 4$ ($D_x = 1{\cdot}40$, $D_m = 1{\cdot}39$ g cm^{-3}) and the cell dimensions: $a = 7{\cdot}389\,(4)$, $b = 13{\cdot}807\,(6)$, $c = 21{\cdot}188\,(11)$ Å, $\beta = 90{\cdot}50\,(5)°$. The structure was solved by the heavy-atom method. The refinement was carried out with a combination of block-diagonal and full-matrix least-squares techniques applied to 1292 observed reflexions and converged at a conventional R value of 0·060. The coordination polyhedron around the metal atom is a very distorted octahedron. The Cu atom lies in the least-squares plane of two diamine N atoms [Cu—N(1) = 2·040 (10), Cu—N(2) = 2·020 (9) Å] and of two carboxyl O atoms [Cu—O(1) = 1·975 (8), Cu—O(5) = 2·001 (8) Å] from different salicylate ligands. The remaining two carboxyl O atoms are involved in weaker interactions with the metal atom [Cu—O(2) = 2·596 (9), Cu—O(4) = 2·520 (8) Å]. The more distant axial-site O atoms have moved nearly symmetrically away from the plane and the diamine ligand and the lines from these atoms to Cu make angles of 61·2 and 63·8° with the least-squares plane.

Introduction

The crystal and molecular structure of monomeric bis(salicylato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-copper(II) has been determined in connection with investigations in this department into complexes formed by Cu^{II} salts with diamines. Our primary interest is in the behaviour of salicylate as a ligand, since studies of its corresponding aqua complexes have shown that the salicylate ligand offers several possibilities for coordination to transition metals through its O atoms (Hanic & Michalov, 1960; Ablov, Kiosse, Dimitrova, Malinowski & Popovich, 1974; Jagner, Hazell & Larsen, 1976; Venkatasūbramanian, Chiesi Villa, Gaetani Manfredotti & Guastini, 1972).

Experimental

Crystal preparation and analyses

Copper(II) salicylate was prepared in finely powdered form by the method described by Orama, Huttner, Lorenz, Marsili & Frank (1976) for the preparation of copper *m*-bromobenzoate and was dissolved, without prior analysis, in a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in methanol (molar ratio 1:1). Separation of the crude product from the concentrated solution by filtration, followed by recrystallization from methanol, yielded blue well-developed crystals of the title compound.

Copper was analysed electrolytically. Analysis calculated for $Cu(C_7H_5O_3)_2(C_6H_{16}N_2)$: Cu 14·00%; found: Cu 14·06%.

Space group and unit cell

Oscillation and equi-inclination Weissenberg photographs were taken around all three axes and revealed that the crystals were monoclinic. The cell parameters measured from Weissenberg photographs were refined by the least-squares method, using data obtained from a powder photograph taken with a camera of Guinier–Hägg type. Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) was employed and calcium fluoride ($a = 5{\cdot}4630$ Å) was the internal standard. The systematic extinctions of reflections $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group $P2_1/n$ (general equivalent positions x,y,z; $-x,-y,-z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$), a non-standard setting of the space group $P2_1/c$. Unit-cell parameters obtained were $a = 7{\cdot}389\,(4)$, $b = 13{\cdot}807\,(6)$, $c = 21{\cdot}188\,(11)$ Å, $\beta = 90{\cdot}50\,(5)°$ and $V = 2161$ Å^3. The calculated density of 1·39 g cm^{-3} for four molecules per unit cell agrees with the experimental density of 1·40 g cm^{-3} measured by the flotation method in a mixture of *n*-propanol and carbon tetrachloride.

Intensity data

A crystal of dimensions 0·27 × 0·15 × 0·10 mm was mounted along the *a* axis. Intensity data from levels $0kl$–$6kl$ were collected with a two-circle Stoe–

Güttinger diffractometer equipped with a scintillation counter and a pulse-height analyser and using Ni-filtered Cu radiation [λ(Cu $K\alpha$) = 1·5418 Å]. The ω-scan, background–peak–background, technique was applied. The scan range was 3·0° and the scan speed 1° min^{-1}. The scanning times were 30, 180 and 30 s. Of the 3179 reflections recorded [$(\sin\theta)/\lambda < 0{\cdot}584$ Å^{-1}], 1292 with $I > 3\sigma(I)$ were used for the structure analysis. $\sigma(I) = (N_{\text{tot}})^{1/2}$ where N_{tot} is the total number of counts in an intensity measurement. The data were corrected for Lorentz and polarization factors but not for absorption [μ(Cu $K\alpha$) = 17·7 cm^{-1}].

Structure determination and refinement

The position of the Cu atom was found from a three-dimensional Patterson vector map. A Fourier synthesis based on the Cu atom position was then calculated, and from this six donor atoms were gradually located upon comparison of observed and calculated structure factors. A new Fourier synthesis based on these seven atom positions gave the approximate positions of all the remaining non-hydrogen atoms. An initial refinement of the structure carried out by the block-diagonal least-squares technique with isotropic thermal parameters and individual scale factors for all levels led to the values R = 0·117 and R_w = 0·171. The agreement factors were defined in the usual way as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The refinement was then continued by the full-matrix least-squares technique with anisotropic thermal parameters and subsequently fixing the scale factors, when the R values reduced to R = 0·071 and R_w = 0·089. At this stage a difference electron density map was calculated and from this the probable positions of all but two H atoms were determined. With their atomic coordinates and isotropic thermal factors included as parameters the final values of R = 0·060 and R_w = 0·077 were obtained. In the last cycle the average parameter shifts expressed as fractions of the e.s.d.'s were 0·47. Because two H atoms could not be located unambiguously in the regions of the O atoms, H atom parameters are not published. The weighting scheme was $w = 1/(a + |F_o| + b|F_o|^2)$ with a = 70·0 and b = 0·009, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The scattering curves used for Cu^{II}, O, N and C were those proposed by Cromer & Mann (1968) and those used for H atoms were from Stewart, Davidson & Simpson (1965).

Calculations were carried out on a Univac 1108

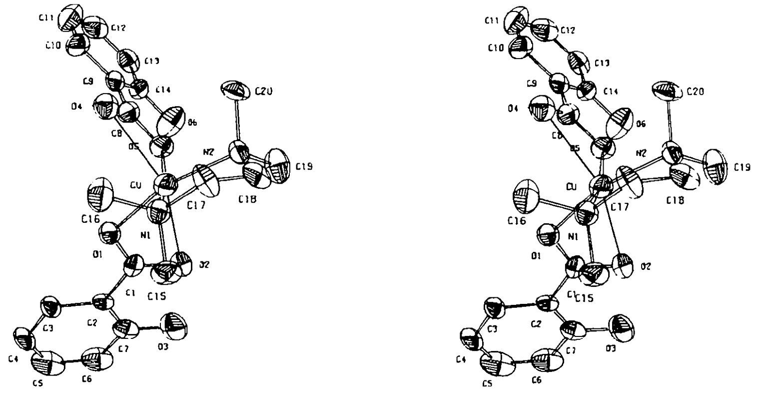

Fig. 1. A stereoscopic view of the coordination around Cu^{II}. Thermal ellipsoids are scaled to enclose 50% probability.

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses, for nonhydrogen atoms*

	x	y	z		x	y	z
Cu	331 (2)	3639 (1)	2301 (1)	C(7)	−1381 (18)	1485 (9)	4141 (5)
O(1)	−1624 (11)	3252 (6)	2879 (4)	C(8)	−1175 (16)	2712 (10)	1369 (5)
O(2)	754 (12)	2504 (7)	3268 (4)	C(9)	−1834 (15)	1951 (10)	915 (5)
O(3)	345 (13)	1205 (8)	4114 (5)	C(10)	−3161 (18)	2237 (12)	470 (6)
O(4)	−1753 (11)	3566 (7)	1355 (4)	C(11)	−3677 (20)	1527 (14)	33 (8)
O(5)	−18 (11)	2438 (6)	1785 (4)	C(12)	−2981 (23)	612 (13)	64 (7)
O(6)	41 (15)	737 (8)	1374 (6)	C(13)	−1732 (21)	297 (12)	496 (7)
N(1)	339 (12)	5025 (8)	2634 (5)	C(14)	−1150 (16)	1002 (9)	946 (6)
N(2)	2772 (12)	3936 (7)	1925 (4)	C(15)	624 (18)	5074 (10)	3319 (6)
C(1)	−892 (17)	2674 (9)	3286 (6)	C(16)	−1403 (20)	5474 (11)	2459 (8)
C(2)	−2061 (15)	2213 (8)	3759 (5)	C(17)	1848 (17)	5535 (9)	2307 (6)
C(3)	−3882 (16)	2497 (9)	3824 (6)	C(18)	3381 (18)	4843 (10)	2225 (6)
C(4)	−4973 (18)	2051 (15)	4255 (7)	C(19)	4039 (19)	3104 (11)	2056 (8)
C(5)	−4336 (29)	1309 (14)	4623 (7)	C(20)	2635 (19)	4079 (11)	1215 (5)
C(6)	−2550 (27)	1025 (12)	4574 (7)				

computer using programs of the XRAY systems (Stewart, Kruger, Ammon, Dickinson & Hall, 1972; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The structure of $Cu(C_7H_5O_3)_2(C_6H_{16}N_2)$ is shown in Fig. 1, and the final positional parameters, with their standard deviations, for non-hydrogen atoms are given in Table 1.*

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

The labelling of atoms is in accordance with Fig 1.

The copper environment			
Cu–O(1)	1·975 (8)	Cu–O(5)	2·001 (8)
Cu–O(2)	2·596 (9)	Cu–N(1)	2·040 (10)
Cu–O(4)	2·520 (8)	Cu–N(2)	2·020 (9)
O(1)–Cu–O(2)	55·3 (3)	O(2)–Cu–N(2)	109·4 (3)
O(1)–Cu–O(4)	92·1 (3)	O(4)–Cu–O(5)	57·1 (3)
O(1)–Cu–O(5)	91·3 (3)	O(4)–Cu–N(1)	108·2 (3)
O(1)–Cu–N(1)	92·2 (4)	O(4)–Cu–N(2)	103·6 (3)
O(1)–Cu–N(2)	163·7 (4)	O(5)–Cu–N(1)	165·1 (4)
O(2)–Cu–O(4)	132·2 (3)	O(5)–Cu–N(2)	93·7 (4)
O(2)–Cu–O(5)	86·8 (3)	N(1)–Cu–N(2)	86·9 (4)
O(2)–Cu–N(1)	107·1 (3)		
The amine ligand			
N(1)–C(15)	1·466 (15)	N(2)–C(19)	1·507 (18)
N(1)–C(16)	1·474 (18)	N(2)–C(20)	1·519 (14)
N(1)–C(17)	1·494 (16)	C(17)–C(18)	1·493 (19)
N(2)–C(18)	1·472 (17)		
C(17)–N(1)–Cu	106·3 (7)	C(18)–N(2)–C(19)	112·4 (10)
C(17)–N(1)–C(15)	109·7 (9)	C(18)–N(2)–C(20)	109·5 (10)
C(17)–N(1)–C(16)	109·8 (10)	C(19)–N(2)–Cu	109·1 (8)
C(15)–N(1)–Cu	112·7 (8)	C(19)–N(2)–C(20)	108·5 (10)
C(15)–N(1)–C(16)	110·4 (10)	C(20)–N(2)–Cu	111·4 (7)
C(16)–N(1)–Cu	107·9 (8)	N(1)–C(17)–C(18)	108·8 (10)
C(18)–N(2)–Cu	105·8 (7)	C(17)–C(18)–N(2)	111·4 (10)
First salicylate ligand			
C(1)–O(1)	1·291 (15)	C(5)–C(4)	1·368 (26)
C(1)–O(2)	1·240 (15)	C(5)–C(6)	1·382 (29)
C(1)–C(2)	1·473 (17)	C(7)–C(6)	1·416 (21)
C(3)–C(2)	1·409 (16)	C(7)–C(2)	1·383 (16)
C(3)–C(4)	1·370 (20)	C(7)–O(3)	1·334 (16)
O(1)–C(1)–O(2)	120·1 (11)	C(3)–C(4)–C(5)	121·0 (14)
O(1)–C(1)–C(2)	118·5 (11)	C(4)–C(5)–C(6)	119·6 (16)
O(2)–C(1)–C(2)	121·4 (11)	C(5)–C(6)–C(7)	120·6 (14)
C(1)–C(2)–C(3)	120·8 (10)	C(6)–C(7)–C(2)	119·0 (13)
C(1)–C(2)–C(7)	120·0 (11)	C(6)–C(7)–O(3)	119·1 (12)
C(3)–C(2)–C(7)	119·2 (11)	C(2)–C(7)–O(3)	121·9 (11)
C(2)–C(3)–C(4)	120·5 (12)		
Second salicylate ligand			
C(8)–O(4)	1·255 (16)	C(12)–C(11)	1·365 (25)
C(8)–O(5)	1·280 (14)	C(12)–C(13)	1·365 (22)
C(8)–C(9)	1·503 (18)	C(14)–C(13)	1·427 (20)
C(10)–C(9)	1·412 (18)	C(14)–C(9)	1·405 (18)
C(10)–C(11)	1·399 (23)	C(14)–O(6)	1·311 (17)
O(4)–C(8)–O(5)	121·3 (11)	C(10)–C(11)–C(12)	121·1 (14)
O(4)–C(8)–C(9)	122·2 (10)	C(11)–C(12)–C(13)	125·4 (15)
O(5)–C(8)–C(9)	116·5 (11)	C(12)–C(13)–C(14)	115·4 (14)
C(8)–C(9)–C(10)	116·8 (12)	C(13)–C(14)–C(9)	119·9 (11)
C(8)–C(9)–C(14)	120·5 (10)	C(13)–C(14)–O(6)	118·0 (12)
C(10)–C(9)–C(14)	122·7 (12)	C(9)–C(14)–O(6)	122·1 (11)
C(9)–C(10)–C(11)	115·4 (14)		

Results and discussion

The coordination around Cu^{II}

In the molecule $Cu(C_7H_5O_3)_2(C_6H_{16}N_2)$, the two salicylate ligands coordinate bidentately through their carboxyl O atoms to the same metal atom. Because the diamine ligand also coordinates in the normal way bidentately through its two N atoms, the coordination polyhedron around Cu^{II} is a very distorted octahedron. As can be seen in Fig. 1 and Tables 2 and 3 the Cu atom lies in the least-squares plane of two N atoms [Cu–N(1) = 2·040 (10), Cu–N(2) = 2·020 (9) Å] and of two O atoms from different salicylate ligands [Cu–O(1) = 1·975 (8), Cu–O(5) = 2·001 (8) Å]. Of the plane-determining atoms one N and one O atom are 0·27 Å above and the other two atoms 0·27 Å below the plane. The lines from the axial-site O atoms to Cu [Cu–O(2) = 2·596 (9), Cu–O(4) = 2·520 (8) Å] deviate noticeably from 90°, making angles of 61·2 and 63·8° with the least-squares plane respectively. Moreover these O atoms have moved nearly symmetrically away from the plane and the diamine molecule. This kind of deviation in axial sites shows the rigidity of the carboxyl group. A similar situation is found in the copper complexes of substituted phenols (Hobson, Ladd & Povey, 1973; Bullock, Hobson & Povey, 1974; Ladd & Povey, 1976), but the deviations there are

Table 3. *Equations of the least-squares planes and, in square brackets, distances of atoms from these planes* (Å)

X,Y,Z are orthogonalized coordinates derived through the transformations $X = xa + zc \cos \beta$, $Y = yb$ and $Z = zc \sin\beta$.

Plane I: N(1), N(2), O(1), O(5)

$$0{\cdot}56334X - 0{\cdot}40451Y + 0{\cdot}72043Z = 1{\cdot}60284$$

[N(1) –0·274, N(2) 0·271, O(1) 0·269, O(5) –0·265, Cu –0·009, O(2) 2·267, O(4) –2·271]

Plane II: C(2)–C(7)

$$0{\cdot}25973X + 0{\cdot}66869Y + 0{\cdot}69670Z = 7{\cdot}18790$$

[C(2) –0·010, C(3) –0·001, C(4) 0·011, C(5) –0·010, C(6) –0·001, C(7) 0·011, C(1) –0·056, Cu –0·379, O(1) –0·261, O(2) 0·076, O(3) 0·043, N(2) –0·190]

Plane III: C(9)–C(14)

$$-0{\cdot}74052X - 0{\cdot}27369Y + 0{\cdot}61378Z = 1{\cdot}48534$$

[C(9) –0·016, C(10) 0·016, C(11) –0·007, C(12) –0·002, C(13) 0·002, C(14) 0·008, C(8) –0·068, Cu –0·018, O(4) –0·094, O(5) –0·050, O(6) 0·019, N(1) –0·108]

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33331 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

about 10° smaller than the deviations with the salicylate ligand. This may be understood because the corresponding Cu and O, C atom rings are five- and four-membered respectively.

The two axial-site O atoms have different environments with respect to the phenol O atoms. O(2) is at a distance of 2·56 Å from O(3), whereas O(4) has no O atom [except O(5)] near it. The O(2)···O(3) distance (2·56 Å) and the O(5)···O(6) distance (2·51 Å) are of the magnitude found in strong hydrogen bonds. Contacts of approximately the same magnitude have been found in copper and cadmium salicylate aqua complexes (Hanic & Michalov, 1960; Jagner, Hazell & Larsen, 1976; Venkatasubramanian, Chiesi Villa, Gaetani Manfredotti & Guastini, 1972). It is noteworthy that the two C—O distances in each carboxyl group seem not to be equal; the shorter involves the O atom forming the longer coordinative bond with Cu. On the other hand, this fact, which is frequently observed in copper carboxylate complexes and, in the present case, could be explained by the resonance effect, is not definitely proved in this complex, the differences in all carboxylate C—O bonds being statistically insignificant ($\Delta/\sigma < 2{\cdot}5$).

The salicylate ligands

The dihedral angles between the two ring planes, between the first benzene ring plane and its carboxyl group, and between the second benzene ring plane and its carboxyl group are 87·0, 9·3 and 1·2° respectively. In salicylic acid the plane of the carboxyl group is inclined 1·1° to the benzene plane (Sundaralingam & Jensen, 1965). The shortest contact between these ligands [O(1)···O(5)] is 2·84 Å, about twice the van der Waals radius of O reported by Pauling (1960) (2·80 Å) but less than that of Bondi (1964) (3·04 Å). The average ring bond lengths and angles are 1·39, 1·40 Å and 120, 120° for the first and second ligand respectively. Although the angle averages are the same, the variations for the second ligand are larger. The average length of 1·32 Å for the uncoordinated phenol C—O bond does not deviate significantly ($>3\sigma$) from the corresponding length of 1·36 Å found for salicylic acid (Sundaralingam & Jensen, 1965).

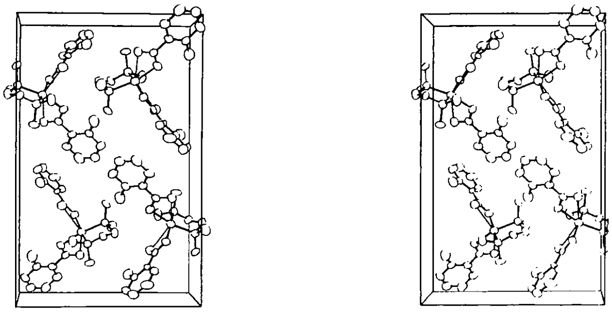

Fig. 2. Stereoscopic view of the unit cell. The *b* axis is horizontal (left to right), the *c* axis is vertical (pointing up along the paper), and the view direction is along +**a**.

Table 4. *Intramolecular contacts* (<3·1 Å) *involving* O *and* N *atoms*

O(1)···O(5)	2·844 (11)	N(1)···O(1)	2·894 (13)
O(2)···O(3)	2·556 (13)	N(2)···O(5)	2·933 (12)
O(5)···O(6)	2·505 (14)	N(1)···N(2)	2·792 (13)

The diamine ligand

As a whole the geometry of the diamine ligand in this compound is almost the same as in numerous other compounds. The ring has the unsymmetrical *gauche* conformation, so that the ring C atoms C(17) and C(18) deviate −0·308 and 0·343 Å from the N(1)—Cu—N(2) plane respectively. The vectors N(1)—C(15) and N(2)—C(20) make angles of 61 and 64° with this plane and thus possess axial character; the corresponding angles for vectors N(1)—C(16) and N(2)—C(19) are 47 and 42° and they have neither axial nor equatorial character. The average N—C bond lengths of these two methyl substituent classes are 1·493 and 1·491 Å. The dihedral angle between the planes N(1)—C(17)—C(18) and C(17)—C(18)—N(2), describing the puckering, is 51·9°.

Molecular packing

The molecular packing is shown in Fig. 2. The shortest distance between the non-hydrogen atoms of the separate molecules C(20)···O(3) ($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) is 3·37 Å. Short intramolecular contacts involving O and N atoms are given in Table 4.

We wish to thank Professor A. Pajunen for proposing this problem.

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The Crystal Structure of Diammonium Uranyl Tetraformate: $(NH_4)_2UO_2(HCOO)_4$

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The crystal structure of diammonium uranyl tetraformate has been established by X-ray diffraction on a single crystal at 18 °C. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 9{\cdot}0850$ (9), $b = 17{\cdot}231$ (2), $c = 7{\cdot}711$ (2) Å, $\beta = 93{\cdot}13$ (1)°, $Z = 4$. The structure has been determined by the heavy-atom method from 2416 Mo $K\alpha$ intensities measured on a four-circle diffractometer, and refined by full-matrix least-squares computations. The final weighted R was 0·091 (conventional $R = 0{\cdot}110$). The U atom is at the centre of a pentagonal bipyramid. The apical O atoms are those of the uranyl group, which is nearly linear [O–U–O = 178 (1)°]. Two O atoms of the equatorial plane of the bipyramid belong to the same formato group. The ammonium groups form layers nearly perpendicular to the [100] axis. These layers are interconnected to the U polyhedra through the remaining three formato groups.

Introduction

In order to elucidate the mechanism of the photolytic decompositions of complex uranyl formates, we have undertaken, at the Laboratoire de Cinétique et Génie Chimiques, the preparation and structural studies of several of these complexes. The structures of $UO_2(HCOO)_2.H_2O$ (Mentzen, Puaux & Loiseleur, 1977) and $NaUO_2(HCOO)_3.H_2O$ (Mentzen, 1977) have recently been published, and, like both these solids, $(NH_4)_2UO_2(HCOO)_4$ is sensitive to visible, UV and X radiations. Claudel, Mentzen, Puaux & Sautereau (1977) reported the preparation and preliminary IR and X-ray investigations of diammonium uranyl tetraformate. The interpretation of the IR spectrum led to the following conclusions: (1) There are at least two types of formato groups. (2) There are two different types of ammonium groups in the solid.

Experimental results

Diammonium uranyl tetraformate has been prepared according to a method described elsewhere (Claudel, Mentzen, Puaux & Sautereau, 1977). The crystals are very soft, and owing to their high solubility in H_2O–HCOOH solutions their shape is not well defined. Nevertheless, we picked out of the mother liquor a nearly cubic crystal of 0·25 mm edge ($\mu r = 2{\cdot}27$). This crystal was mounted on the four-circle Enraf–Nonius CAD-4 automatic diffractometer of the Centre de Diffraction Automatique, Lyon. 4907 intensities corresponding to the hkl, $hk\bar{l}$, $\bar{h}k\bar{l}$ and $\bar{h}\bar{k}\bar{l}$ triplets (half reflexion sphere) were collected with the ω–2θ scan for $1 < \theta < 40°$ and $I > 2\sigma(I)$. After data reduction 2416 reflexions, of which 1412 are unique, were obtained and their intensities corrected for Lorentz and polarization factors as well as for absorption. Furthermore, the