

Fig. 2. The coordination polyhedron of praseodymium in the structure of the β 1 phase. The undistorted square antiprism is represented by a dashed line. The angle is shown between the normals to the base planes of distorted and undistorted polyhedra.

$T_{[100]}^{\beta 1} = T_{[100]}^{\alpha}$ between the β 1 phase and the α phase of the neodymium derivative, indicating the close structural relationship of these phases.

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Structures of Zinc(II) and Copper(II) Chloride *N,N*-Dimethylformamide Solvates

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Abstract. (I) Dichlorobis(*N,N*-dimethylformamide)-zinc(II), $[\text{ZnCl}_2(\text{C}_3\text{H}_7\text{NO})_2]$, $M_r = 282.5$, monoclinic, $C2/c$, $a = 13.296(4)$, $b = 13.254(4)$, $c = 14.702(6)$ Å, $\beta = 113.76(3)^\circ$, $V = 2371(2)$ Å³, $Z = 8$, $D_x = 1.583$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 25.5$ cm⁻¹, $F(000) = 1152$, $T = 226$ K, $R = 0.035$ for 2825 independent reflections. The Zn atom has a tetrahedral environment of two O atoms from two *N,N*-dimethylformamide (DMF) molecules and two Cl atoms, with Zn—O distances of 2.003(2) and 1.993(2) Å and Zn—Cl distances of 2.203(1) and 2.214(1) Å. (II) Di- μ -chloro-bis[chlorobis(*N,N*-

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dimethylformamide)copper(II)], $[\text{CuCl}_2(\text{C}_3\text{H}_7\text{NO})_2]_2$, $M_r = 561.3$, monoclinic, $P2_1/n$, $a = 11.568(5)$, $b = 11.617(7)$, $c = 8.992(4)$ Å, $\beta = 111.87(5)^\circ$, $V = 1121(1)$ Å³, $Z = 2$, $D_x = 1.662$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 24.1$ cm⁻¹, $F(000) = 572$, $T = 265$ K, $R = 0.054$ for 2577 independent reflections. The structure consists of centrosymmetric chlorine-bridged dimers, the bridging Cu—Cl distance being 2.661(2) Å. The coordination around copper is distorted tetragonal pyramidal with two *cis* O atoms [Cu—O = 1.973(3) and 1.989(3) Å] and two Cl atoms [Cu—Cl = 2.247(2) and 2.284(1) Å] in the basal plane and the bridging Cl atom axial. The Cu...Cu separation in the dimer is 3.613(2) Å. In

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both complexes, the DMF ligands are essentially planar and coordinated to the metal ion in the lone-pair direction of the oxygen donor atom.

Introduction. *N,N*-Dimethylformamide (DMF) is a prominent member of aprotic solvents which act as oxygen-donor ligands, and a number of metal complexes containing DMF have been synthesized and their structures reported. Recently, studies on complexation equilibria between bivalent transition metal and chloride ions in DMF (Ishiguro, Jeliaskova & Ohtaki, 1985; Ishiguro, Ozutsumi & Ohtaki, 1987) have aroused our particular interest in the structure of metal chloride DMF solvates. Detailed structural information, such as coordination bond lengths, bond angles, and interactions between ligands, is valuable for elucidating the role of solvents in the thermodynamics of complexation reactions in DMF. Here we report structures of zinc(II) and copper(II) chloride DMF solvates.

Experimental. The complexes $[\text{ZnCl}_2\{(\text{CH}_3)_2\text{NCHO}\}_2]$ (I) and $[\text{CuCl}_2\{(\text{CH}_3)_2\text{NCHO}\}_2]$ (II) were crystallized from DMF solution of the corresponding anhydrous metal chloride. Complex (I) was stable at room temperature, but complex (II) was less stable and a gradual decomposition was observed, so that the latter crystal was stored at 273 K and used for measurement within two weeks after preparation. Prismatic crystals (approx. $0.4 \times 0.4 \times 0.5$ mm) used for X-ray measurement, Rigaku AFC-5 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation, lattice parameters from least-squares refinement of 2θ values of 25 reflections [$21 < 2\theta < 28^\circ$ for (I) and $20 < 2\theta < 25^\circ$ for (II)], ω - 2θ scan, scan speed 4° min^{-1} , scan width $(0.8 + 0.5 \tan \theta)^\circ$, background 8 s at each end of scan, $2\theta_{\text{max}} = 60^\circ$, hkl range -18 – 18 , 0 – 18 , 0 – 20 for (I) and -16 – 16 , 0 – 16 , 0 – 12 for (II); three standard reflections measured every 100 reflections showed no significant decay; 3690 reflections measured of which 2825 with $F_o > 3\sigma(F_o)$ for (I), 3645 reflections measured of which 2577 with $F_o > 3\sigma(F_o)$ for (II), no correction for absorption. Structures were solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least-squares analysis minimizing the function $\sum w(F_o - |F_c|)^2$ with *UNICS*III (Sakurai & Kobayashi, 1979); H atoms were located in difference Fourier maps and included in the refinement. Final $R = 0.035$, $wR = 0.043$ with $w = [\sigma^2(F_o) + (0.020F_o)^2]^{-1}$, $S = 1.49$, $(\Delta/\sigma)_{\text{max}} = 0.32$, $(\Delta\rho)_{\text{max}} = 0.80$ and $(\Delta\rho)_{\text{min}} = -0.63 \text{ e } \text{Å}^{-3}$ for (I); $R = 0.054$, $wR = 0.061$ with $w = [\sigma^2(F_o) + (0.025F_o)^2]^{-1}$, $S = 1.78$, $(\Delta/\sigma)_{\text{max}} = 0.31$, $(\Delta\rho)_{\text{max}} = 2.5$ and $(\Delta\rho)_{\text{min}} = -1.7 \text{ e } \text{Å}^{-3}$ (both near the Cu atom) for (II). Slight decomposition of crystal (II) is

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors of non-H atoms in $[\text{ZnCl}_2(\text{DMF})_2]$ (I) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
Zn	0.23616 (2)	0.10737 (2)	0.24940 (2)	2.5
Cl(1)	0.31067 (5)	-0.03142 (4)	0.33122 (5)	3.8
Cl(2)	0.06099 (5)	0.11361 (5)	0.14528 (5)	3.6
O(1)	0.25951 (12)	0.22421 (11)	0.34210 (11)	3.0
O(2)	0.32716 (14)	0.15140 (12)	0.17704 (13)	3.6
N(1)	0.18614 (14)	0.34992 (13)	0.39970 (13)	2.6
N(2)	0.4054 (2)	0.26900 (14)	0.11593 (13)	3.1
C(1)	0.1787 (2)	0.2682 (2)	0.3481 (2)	2.7
C(2)	0.2911 (2)	0.3989 (2)	0.4536 (2)	3.9
C(3)	0.0883 (2)	0.3994 (2)	0.3985 (2)	4.3
C(4)	0.3495 (2)	0.2405 (2)	0.1675 (2)	3.1
C(5)	0.4450 (2)	0.1960 (2)	0.0650 (2)	4.6
C(6)	0.4340 (3)	0.3746 (2)	0.1113 (3)	5.5

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors of non-H atoms in $[\text{CuCl}_2(\text{DMF})_2]_2$ (II) with e.s.d.'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq} (Å ²)
Cu	0.11141 (4)	0.11326 (3)	0.51788 (4)	2.2
Cl(1)	0.22641 (8)	0.06705 (8)	0.37286 (10)	3.1
Cl(2)	0.12879 (7)	-0.06419 (7)	0.63362 (9)	2.5
O(1)	0.0995 (2)	0.1899 (2)	0.7094 (3)	2.9
O(2)	0.0719 (3)	0.2646 (2)	0.4113 (3)	3.0
N(1)	0.0300 (3)	0.1965 (3)	0.9132 (3)	2.7
N(2)	0.0912 (3)	0.4571 (2)	0.4001 (3)	2.4
C(1)	0.0262 (3)	0.1588 (3)	0.7740 (4)	2.6
C(2)	0.1234 (4)	0.2795 (3)	1.0070 (4)	3.3
C(3)	-0.0627 (4)	0.1595 (4)	0.9785 (5)	4.1
C(4)	0.1264 (3)	0.3562 (3)	0.4692 (4)	2.3
C(5)	0.1615 (4)	0.5612 (3)	0.4645 (5)	3.5
C(6)	-0.0138 (4)	0.4674 (4)	0.2486 (4)	3.5

a possible reason for the residual deviations in the final differential Fourier map. Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Final atomic coordinates for non-H atoms are given in Tables 1 and 2.* Bond lengths, bond angles and relevant torsion angles are given in Tables 3 and 4. Figs. 1 and 2 are *ORTEP* drawings (Johnson, 1965) showing the atomic numbering scheme.

Discussion. In complex (I), the Zn atom is coordinated to two O atoms of DMF and two Cl atoms forming a tetrahedral environment (Fig. 1). Bond angles around Zn (100 – 122°) indicate a slight distor-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54065 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å), bond angles (°) and relevant torsion angles (°) in [ZnCl₂(DMF)₂] (I) with *e.s.d.*'s in parentheses

Zn—Cl(1)	2.2028 (8)	N(1)—C(1)	1.303 (3)
Zn—Cl(2)	2.2139 (11)	N(1)—C(2)	1.451 (3)
Zn—O(1)	2.0028 (16)	N(1)—C(3)	1.452 (4)
Zn—O(2)	1.993 (2)	N(2)—C(4)	1.314 (4)
O(1)—C(1)	1.257 (3)	N(2)—C(5)	1.447 (4)
O(2)—C(4)	1.239 (3)	N(2)—C(6)	1.460 (4)
Cl(1)—Zn—Cl(2)	121.68 (3)	C(1)—N(1)—C(2)	121.4 (2)
Cl(1)—Zn—O(1)	111.21 (5)	C(1)—N(1)—C(3)	120.74 (18)
Cl(1)—Zn—O(2)	107.44 (6)	C(2)—N(1)—C(3)	117.7 (2)
Cl(2)—Zn—O(1)	105.85 (5)	C(4)—N(2)—C(5)	121.1 (2)
Cl(2)—Zn—O(2)	108.41 (6)	C(4)—N(2)—C(6)	121.5 (3)
O(1)—Zn—O(2)	100.13 (7)	C(5)—N(2)—C(6)	117.4 (3)
Zn—O(1)—C(1)	120.27 (12)	O(1)—C(1)—N(1)	124.03 (18)
Zn—O(2)—C(4)	124.30 (19)	O(2)—C(4)—N(2)	123.8 (2)
Zn—O(1)—C(1)—N(1)	-173.70 (17)	C(2)—N(1)—C(1)—O(1)	1.6 (3)
Zn—O(2)—C(4)—N(2)	-176.81 (17)	C(3)—N(1)—C(1)—O(1)	176.6 (2)
O(2)—Zn—O(1)—C(1)	128.84 (16)	C(5)—N(2)—C(4)—O(2)	0.4 (4)
O(1)—Zn—O(2)—C(4)	-24.9 (2)	C(6)—N(2)—C(4)—O(2)	-176.9 (3)
Cl(2)—Zn—O(1)—C(1)	16.25 (17)		

Table 4. Bond lengths (Å), bond angles (°) and relevant torsion angles (°) in [CuCl₂(DMF)₂]₂ (II) with *e.s.d.*'s in parentheses

Cu—Cl(1)	2.2474 (15)	N(1)—C(1)	1.312 (5)
Cu—Cl(2)	2.2841 (14)	N(1)—C(2)	1.459 (5)
Cu—Cl(2')	2.6611 (17)	N(1)—C(3)	1.466 (7)
Cu—O(1)	1.989 (3)	N(2)—C(4)	1.319 (4)
Cu—O(2)	1.973 (3)	N(2)—C(5)	1.452 (5)
O(1)—C(1)	1.246 (5)	N(2)—C(6)	1.454 (4)
O(2)—C(4)	1.248 (4)		
Cl(1)—Cu—Cl(2)	94.48 (4)	Cu—O(1)—C(1)	123.5 (2)
Cl(1)—Cu—O(1)	148.92 (9)	Cu—O(2)—C(4)	124.6 (2)
Cl(1)—Cu—O(2)	90.65 (10)	C(1)—N(1)—C(2)	121.8 (4)
Cl(2)—Cu—O(1)	91.85 (8)	C(1)—N(1)—C(3)	121.0 (3)
Cl(2)—Cu—O(2)	172.20 (9)	C(2)—N(1)—C(3)	117.2 (3)
O(1)—Cu—O(2)	86.75 (11)	C(4)—N(2)—C(5)	121.6 (3)
Cl(1)—Cu—Cl(2')	112.50 (5)	C(4)—N(2)—C(6)	121.2 (3)
Cl(2)—Cu—Cl(2')	86.43 (4)	C(5)—N(2)—C(6)	117.0 (3)
O(1)—Cu—Cl(2')	98.23 (9)	O(1)—C(1)—N(1)	124.1 (3)
O(2)—Cu—Cl(2')	86.18 (9)	O(2)—C(4)—N(2)	122.8 (3)
Cu—Cl(2)—Cu'	93.57 (4)		
Cu—O(1)—C(1)—N(1)	169.2 (3)	Cl(1)—Cu—Cl(2)—Cu'	-112.32 (3)
Cu—O(2)—C(4)—N(2)	-174.7 (2)	O(1)—Cu—Cl(2)—Cu'	98.14 (8)
C(2)—N(1)—C(1)—O(1)	-0.5 (6)	O(2)—Cu—Cl(2)—Cu'	18.7 (6)
C(3)—N(1)—C(1)—O(1)	177.4 (4)	Cl(1)—Cu—Cl(2')—Cu'	93.38 (4)
C(5)—N(2)—C(4)—O(2)	-175.8 (3)	O(1)—Cu—Cl(2')—Cu'	-91.35 (8)
C(6)—N(2)—C(4)—O(2)	-0.9 (5)	O(2)—Cu—Cl(2')—Cu'	-177.51 (8)

Symmetry-equivalent position: (i) $-x, -y, 1-z$.

tion from a regular tetrahedron (Table 3). The Zn—Cl distances (2.203 and 2.214 Å) are in good agreement with those of 2.209 (4) and 2.220 (3) Å in an analogous tetrahedral complex [ZnCl₂(DMA)₂] (III) (DMA = *N,N*-dimethylacetamide) reported by Herceg & Fischer (1974), but shorter than those (average 2.27 Å) in a tetrahedral [ZnCl₄]²⁻ anion (Søtofte, Hazell & Rasmussen, 1976). The Zn—O distances (1.993 and 2.003 Å) are slightly longer than those of 1.964 (7) and 1.975 (8) Å in (III) (Herceg & Fischer, 1974).

A noticeable difference between the structures of (I) and (III) is found in the conformation around the metal—amide bonds: In (I), the O(2)—Zn—O(1)—C(1) and O(1)—Zn—O(2)—C(4) torsion angles (φ) are 129 and -25° , respectively, whereas the corresponding O—Zn—O—C torsion angles are 155 and -161° in (III) (Herceg & Fischer, 1974). Thus, the DMA molecules in (III) coordinate towards the 'trans' conformation ($\varphi = \pm 180^\circ$) relative to each other, possibly owing to the steric hindrance of the

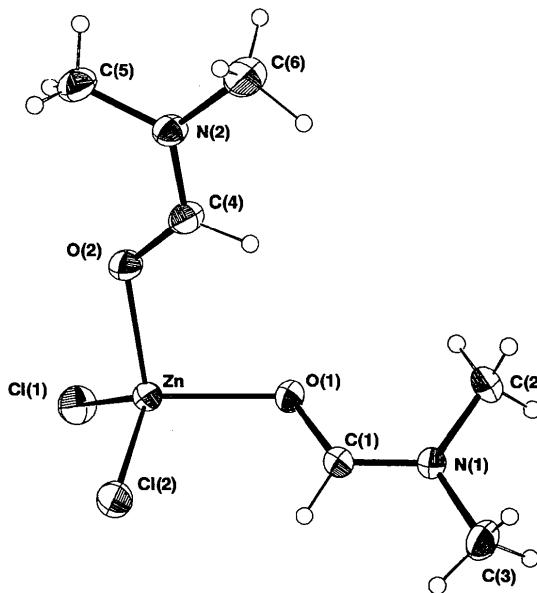


Fig. 1. Molecular structure and labeling scheme for [ZnCl₂(DMF)₂] (I) with 30% probability thermal ellipsoids for non-H atoms.

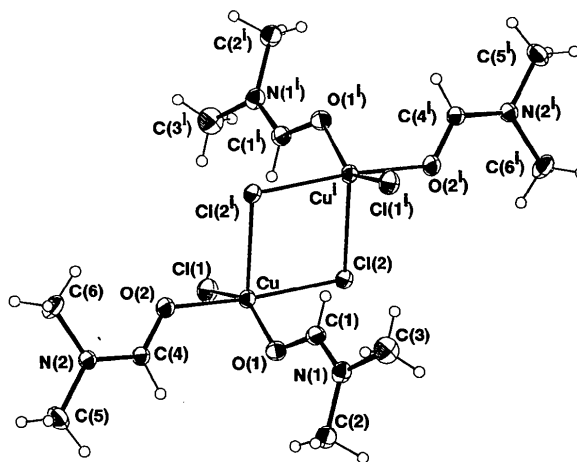


Fig. 2. Molecular structure and labeling scheme for [CuCl₂(DMF)₂]₂ (II) with 30% probability thermal ellipsoids for non-H atoms. The atoms Cu and Cu' etc. are related by a crystallographic center of symmetry.

methyl(acetyl) group of DMA. In contrast, DMF molecules in (I) seem to prefer the 'cis' ($\varphi = 0^\circ$) and 'eclipse' ($\varphi = \pm 120^\circ$) forms. Interactions between the formyl H atom of DMF and the adjacent ligands may play a significant role in determining the conformation. Indeed, the distance between Cl(2) and the C(1)-attached H atom [2.80 (3) Å] is shorter than the van der Waals sum of 2.95 Å (Bondi, 1964); the distance between O(1) and the C(4)-attached H atom, however, is 2.79 (3) Å, which is just comparable with the van der Waals sum (2.72 Å).

Complex (II) has a centrosymmetric dimer structure consisting of two crystallographically equivalent *cis*-[CuCl₂(DMF)₂] moieties (Fig. 2). Each moiety may be viewed as a distorted square plane, and the molecules in the dimeric unit are held together by two weaker Cu—Cl bonds which form the axes of the elongated tetragonal pyramidal arrangements around the Cu atoms. The two Cu—O and two short Cu—Cl distances (Table 4) are within the range expected for short copper—ligand bond lengths (Filipenko, Krasochka & Atovmyan, 1984; Filipenko, Ponomarev & Atovmyan, 1986; Hathaway, 1987; Ozutsumi, Ishiguro & Ohtaki, 1988*a,b*). The bridging Cu—Cl(2) distance of 2.284 Å is slightly longer than the terminal Cu—Cl(1) distance of 2.247 Å. The axial Cu—Cl(2ⁱ) bond is much longer (2.661 Å). It is, however, nearly the shortest among the long Cu—Cl distances (2.66–3.74 Å) in di- μ -chloro-bridged copper(II) dimers (Hathaway, 1987). The Cu...Cu separation in (II) is 3.613 (2) Å, which is intermediate in the range 3.45–4.08 Å for these dimers.

The angles Cl(2)—Cu—O(2) ($\theta = 172.2^\circ$) and Cl(1)—Cu—O(1) ($\varphi = 148.9^\circ$) indicate a marked distortion from an idealized tetragonal pyramid ($\theta = \varphi = 180^\circ$). The Cl(1)—Cu—Cl(2ⁱ) angle (112.5°) is close to 120° for the trigonal bipyramidal extreme ($\theta = 180^\circ$, $\varphi = 120^\circ$). These in-plane angular distortions may be evaluated by the trigonality index $\tau = [(\theta - \varphi)/60] \times 100$, which represents a percentage distortion of a tetragonal pyramidal stereochemistry towards a trigonal bipyramidal one (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984; Hathaway, 1987). The value $\tau = 39\%$ for complex (II) points to an intermediate structure between these extremes. Such a distortion is generally involved in five-coordinate copper(II) complexes, and may be rationalized in terms of the second-order Jahn–Teller effect (Hathaway, 1987).

A somewhat different structure was reported for (II) (Lavrentiev, Korableva, Lavrentieva, Nifontova, Khidekel, Gusakovskaya, Larkina, Arutyunian, Filipenko, Ponomarev & Atovmyan, 1979, 1980; Nifontova, Lavrentiev, Ponomarev, Filipenko, Krasochka, Atovmyan & Khidekel, 1982). Essentially the structure is the same as ours, the complex

being a centrosymmetric dimer with two bridging chlorines and the Cu atoms being five coordinated. Nonetheless, the Cu—Cl bond lengths, 2.266 (2), 2.464 (2) and 2.794 (2) Å, are markedly longer than our corresponding values. It was also observed that one of the coordinated DMF molecules has unusually long (by 0.02–0.19 Å) intramolecular bond lengths, which is not the case with our results. The structure was determined at 300 K, so such differences might arise from a phase transition below this temperature; the results are rather questionable, however, because the crystal was found to be very unstable under radiation at room temperature, and the number of the reflections used (965) was less than half that used by us (2577).

The intramolecular bond lengths and angles of the DMF molecules in (I) and (II) (Tables 3 and 4) are in good agreement with those found in other DMF solvates (Baumgartner, 1986; Day & Hoard, 1970; Florian & Corey, 1968; Pignedoli & Peyronel, 1979; Ziolo & Extine, 1981). The O—C distances of the coordinated DMF molecules (1.24–1.26 Å) are each slightly longer than that of gaseous DMF (1.20 Å; Vilkov, Akishin & Presnyakova, 1962), and that of non-coordinating DMF (1.22 Å) in the crystal structure of chlorobis(2-thiouracil)copper(I) (Hunt, Griffith & Amma, 1976). DMF is essentially planar, and none of its non-H atoms are removed from the least-squares plane by more than 0.032 Å. The M—O—C bond angles ($M = \text{Zn or Cu}$) are 120–125°, and the metal atom is nearly coplanar with DMF, with a slight displacement from the DMF mean plane of 0.07–0.29 Å; thus, the coordination occurs in the lone-pair direction of the O atom. In the [Mg(DMF)₆]²⁺ cation, the Mg—O—C angles are 122–139° and deviations of Mg from the DMF mean plane are 0.11–0.54 Å (Rao, Rao & Rao, 1984). The Fe—O—C angles are 118–134° in the [Fe(DMF)₆]²⁺ cation (Baumgartner, 1986; Young, Walters & Dewan, 1989).

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Single-Crystal Neutron Diffraction: Structure of Sodium Tris(acetato)-dioxouranate(1 –)

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Abstract. Na[$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$], $M_r = 467.09$, cubic, $P2_13$, $a = 10.691(8) \text{ \AA}$, $V = 1222(3) \text{ \AA}^3$, $Z = 4$, $D_x = 2.562 \text{ g cm}^{-3}$, $\lambda = 0.831(1) \text{ \AA}$, $\mu = 1.2 \text{ cm}^{-1}$ (evaluated), $F(000) = 258.9 \text{ fm}$ for cell content, room temperature, $R = 0.037$, $wR = 0.029$ for 452 observed reflections. The structure of the compound determined by neutron diffraction is essentially the same as that obtained by X-ray diffraction, excluding the hydrogen atoms. The uranyl ion lies on the threefold axis surrounded by three symmetrically related acetate groups. The coordination polyhedron of the sodium atom is intermediate between an octa-

hedron and a trigonal prism; six oxygen atoms from six different acetate ligands participate in this coordination. The hydrogen atoms of the methyl group are observed in two positions which do not coincide with those proposed from X-ray studies.

Introduction. The crystal structure of Na[$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$] was first determined by conventional X-ray methods by Fankuchen (1935), and more completely by Zachariasen & Plettinger (1959). A recent redetermination, including anomalous scattering, by Templeton, Zalkin, Ruben & Templeton (1985) led to more accurate parameters and to the absolute configuration of the structure; the coordinate system corresponds to a crystal with a negative sign for optical activity.

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