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Acta Cryst. (1985). C41, 844–846

Structure of {Diaqua[*N,N'*-bis(β -carbamoylethyl)-2-hydroxy-trimethylenediamine]}nickel(II) Dichloride,* [Ni(C₉H₂₀N₄O₃)(H₂O)₂]Cl₂

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(Received 12 October 1984; accepted 2 January 1985)

Abstract. $M_r = 397.89$, monoclinic, $P2_1/m$, $a = 7.002$ (6), $b = 17.483$ (11), $c = 7.369$ (7) Å, $\beta = 117.73$ (5)°, $U = 827.74$ (1) Å³, $Z = 2$, $D_x = 1.596$, $D_m = 1.60$ (5) Mg m⁻³ (by flotation in CCl₄/hexane mixture), $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.515$ mm⁻¹, $F(000) = 416$, $T = 296$ (4) K, $R(F) = 0.047$ for 3153 observed reflections [$I > 3\sigma(I)$]. The coordination geometry about Ni^{II} is a pseudo-octahedron comprising two O atoms of amide groups [Ni–O 2.056 (2) Å] and two N atoms of amine groups [Ni–N 2.085 (2) Å] at the four corners of the equatorial plane and two O atoms of water molecules at the two apices [Ni–O 2.100 (3), 2.159 (2) Å]. The two H atoms of the amine groups are in *cis* configuration with respect to the equatorial plane and the two chiral amine N centers have the *RS* configuration. Besides the ionic interaction, the Cl⁻ ions form intra- and intermolecular hydrogen bonds with the coordinated water molecules.

Introduction. In a previous work we have reported the crystal structure of [Cu(bchtn)](ClO₄)₂ (Lee, Hong, Liu, Chung & Lee, 1984) [bchtn is *N,N'*-bis(β -carbamoylethyl)-2-hydroxytrimethylenediamine]. In this work the crystal structure of [Ni(bchtn)(H₂O)₂]Cl₂ is reported.

Experimental. [Ni(bchtn)(H₂O)₂]Cl₂ crystals were obtained similarly to those of [Cu(bchtn)](ClO₄)₂, except that NiCl₂ was used in place of Cu(ClO₄)₂. The crystals thus obtained were light blue and 0.3 ~ 0.5 mm in size.

Experimental data and structure-solution parameters together with the standard refinement procedures are listed in Table 1. The H atoms of the amine, amide and OH groups were located in the difference Fourier maps. Other H-atom parameters were treated as in our previous work (Lee *et al.*, 1984).

Discussion. The atomic coordinates and temperature factors are listed in Table 2.‡ A perspective view of the molecule and the numbering scheme and deviations of atoms from the least-squares plane through O(1)–N(2)–N(2')–O(1') are shown in Fig. 1 (*a*).

The Ni^{II} ion in the title complex is surrounded pseudo-octahedrally. Two N atoms and two O atoms of bchtn are coordinated to the Ni^{II} ion in a plane. The two axial coordination sites are occupied by two O atoms of water molecules at distances of 2.159 (2) and 2.100 (3) Å, respectively. The bond distances and bite angles about the metal ion are given in Table 3 along

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and details of the least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42005 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* [Diaqua(6-hydroxy-4,8-diazaundecanediamide)]nickel(II) dichloride.

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with the reported values of $[\text{Cu}(\text{bchtn})](\text{ClO}_4)_2$ for comparison. These results reveal that the geometry around the Ni^{II} atom is a slightly tilted octahedron. In contrast to $[\text{Cu}(\text{bchtn})](\text{ClO}_4)_2$, there is no significant Jahn–Teller effect in the coordination sphere. The slight difference in the two axial coordination bonds could be attributed to the effect of hydrogen bonds. This is revealed by the fact that the axis $\text{OW}(1)\text{—Ni—OW}(2)$ is bent toward the open mouth of the coordinated *bchtn*, *i.e.* toward the resultant-force direction of the hydrogen bonds, with bond angle $178.8(1)^\circ$. The hydrogen-bond lengths (Table 4) agree with those of $[\text{Ni}(\text{meso-Me}_6-$

$[\text{14}]\text{aneN}_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (Ito & Toriumi, 1981).* The complex has the *RS* configuration for the chiral amine N centers, which is the same as that of $[\text{Cu}(\text{bchtn})](\text{ClO}_4)_2$. The two amine H atoms are on the same side of the 'bchtn' plane. The C, N and the two H atoms of each amide group are coplanar as usual (Lee *et al.*, 1984; Diaddario, Robinson & Margerum, 1983).

* *meso-Me*₆[14]aneN₄ is [7*R*(*S*), 14*S*(*R*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

Table 1. Experimental data and structure-refinement parameters

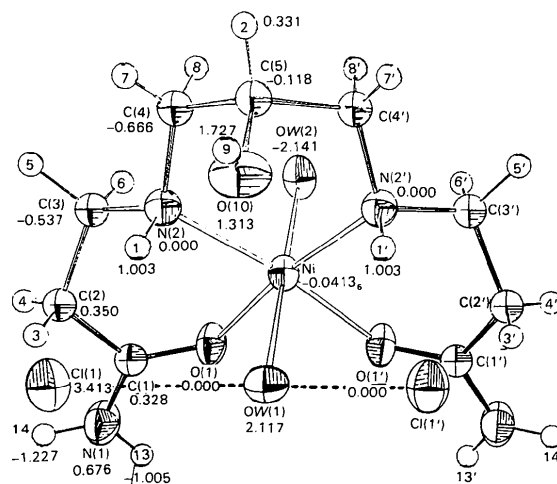
Crystal size	Sphere, diameter 0.35 mm
Diffractometer and data-collection technique	ω -2 θ scan, four-circle diffractometer (Syntex P1), graphite monochromator
Scan width ($^\circ$)	$2.0 + 0.7 \tan \theta$; starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$
Number and θ range used for measuring lattice parameters	15 reflections with $12^\circ < 2\theta < 25^\circ$
Absorption correction applied (North, Phillips & Mathews, 1968)	Experimental absorption correction based on ψ scan
Transmission factor	0.588
No. of standard reflections (variation)	3 (< 3%)
Number of reflections measured	6091
Method used to solve the structure	Patterson and Fourier methods
Parameters refined, all atoms (coordinates and anisotropic temperature factors of nonhydrogen atoms)	131
Quantity minimized	$\sum w(\Delta F)^2$; $w = 1/\sigma_F^2$
Atomic scattering factors f' and f''	International Tables for X-ray Crystallography (1974)
Maximum value of $(\sin \theta)/\lambda$ reached in intensity measurements (\AA^{-1})	0.6691
R (wR)	0.047 (0.060)
R_{int}	0.033
S	1.265
Secondary-extinction correction	None
Final residual electron densities (e \AA^{-3}) for max. peak	0.27
Average, max. Δ/σ	0.2, 0.6
Programs used	Tsing Hua crystal package* and ORTEPII (Johnson, 1976)

* The user's guide and source program of this crystal program package can be obtained from Professor T. Y. Lee, Computer Center, National Tsing Hua University, Hsinchu, Taiwan.

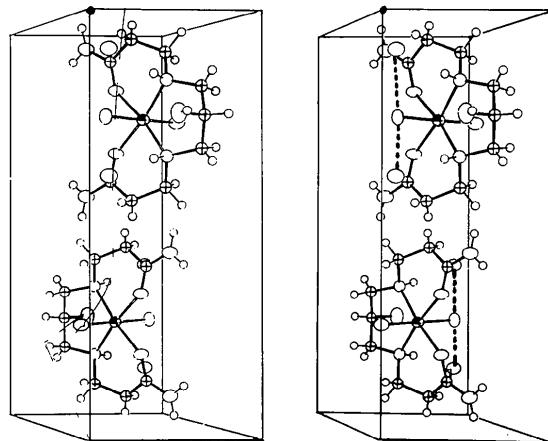
Table 2. Atomic positional parameters and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j b_{ij}$, where the a_i 's are the cell-length vectors in direct space. OW(1) and OW(2) are O atoms of water molecules.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Ni	0.4278 (1)	0.2500	0.2117 (1)	1.9
Cl(1)	-0.0466 (1)	0.1088 (1)	-0.2922 (1)	3.0
O(1)	0.3559 (3)	0.1735 (1)	0.3772 (3)	2.7
O(10)	0.3528 (5)	0.2500	-0.2734 (4)	3.6
OW(1)	0.0912 (4)	0.2500	0.0010 (4)	2.8
OW(2)	0.7534 (5)	0.2500	0.4215 (4)	2.8
N(1)	0.2040 (5)	0.0698 (1)	0.4317 (4)	3.7
N(2)	0.4793 (4)	0.1606 (1)	0.0576 (3)	2.2
C(1)	0.3050 (5)	0.1049 (1)	0.3445 (4)	2.4
C(2)	0.3547 (5)	0.0578 (1)	0.2049 (4)	2.8
C(3)	0.5388 (5)	0.0890 (2)	0.1729 (4)	2.6
C(4)	0.6368 (5)	0.1774 (2)	-0.0162 (4)	2.9
C(5)	0.5785 (7)	0.2500	-0.1400 (6)	2.8



(a)



(b)

Fig. 1. (a) Perspective view showing the atom-numbering scheme and displacements (\AA) of atoms from the least-squares plane of O(1), N(2), O(1') and N(2'). *E.s.d.*'s are estimated to be 0.003–0.005 \AA . Thermal ellipsoids are depicted at the 50% probability level. (b) Stereoview of the packing of the molecules in a unit cell. Origin: top left (indicated by a dot), *a* axis to right, *b* axis down, *c* axis into page. Compared to (a), the top molecule is turned 90° clockwise about the *z* axis so that the atoms in the molecule can be easily identified. Hydrogen bonds are indicated by broken lines and H atoms of water molecules are not shown. H atoms are plotted as circles by arbitrarily setting $B = 1.0 \text{\AA}^2$.

Table 3. Bond distances (Å), bond angles (°) and deviations (Å) of atoms from the least-squares-fit plane in the coordination sphere

	[Ni(bchtn)(H ₂ O) ₂ Cl ₂] (M = Ni)	[Cu(bchtn)(ClO ₄) ₂] (M = Cu)
M—O(1)	2.056 (2)	1.966 (7)
M—N(2)	2.085 (2)	1.998 (10)
M—O(long axis)	2.159 (2)	2.641 (11)
M—O(short axis)	2.100 (3)	2.448 (11)
O—M—O	178.8 (1)	163.5 (3)
Bite angles around the metal ion		
O(1)—M—N(2)	90.8 (1)	93.1 (3)
N(2)—M—N(2')	97.1 (1)	93.1 (4)
N(2')—M—O(1')	90.8 (1)	93.4 (3)
O(1)—M—O(1')	81.2 (1)	81.2 (3)

* N(2') = N(3) and O(1') = O(2) in the Cu complex (Lee *et al.*, 1984).

The Ni^{II} ion, the two O atoms of the water molecules and the OH group are all on a mirror plane, $y = 0.25$. All other atoms in the complex are mirror-related. Fig. 1(a) indicates that C(2) and C(2') are 0.350 (4) Å above the equatorial plane and the whole molecule has a boat shape as shown in Fig. 1(b); C(5) on the middle chelate ring is 0.118 (3) Å below this plane. The chelate ring, Ni—N(2)—C(4)—C(5)—C(4')—N(2'), is in a stable chair form.

The authors wish to thank the National Science Council of Taiwan for the financial support for this study.

Acta Cryst. (1985), **C41**, 846–850

Studies of Tetramethylammonium Tetrabromometallates. II. Structure of Tetramethylammonium Tetrabromozincate, [N(CH₃)₄]₂[ZnBr₄], in its Low-Temperature Phase

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(Received 10 February 1984; accepted 14 January 1985)

Abstract. $M_r = 533.0$, monoclinic, $P2_1/a$, $a = 12.534$ (2), $b = 9.142$ (3), $c = 15.772$ (4) Å, $\gamma = 89.69$ (2)°, $V = 1807$ (2) Å³, $Z = 4$, $D_x = 1.898$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 108$ cm⁻¹, $F(000) = 1024$, $T = 193$ K, final $R = 0.101$ for 2408 observed reflections. No superlattice reflection appears in the low-temperature phase. Domains were exhibited in the crystal and a program has been written to solve this structure. Compared with the high-temperature phase, a large decrease of the temperature factors is observed. Bond lengths and angles of the [ZnBr₄]²⁻ tetrahedron are almost identical with those of the high-temperature phase.

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Table 4. Bond distances (Å) and bond angles (°)

(a) Covalent bond lengths			
C(1)—O(1)	1.243 (3)	C(3)—N(2)	1.476 (4)
C(1)—N(1)(amide)	1.324 (5)	C(4)—N(2)	1.480 (4)
C(1)—C(2)	1.509 (5)	C(4)—C(5)	1.522 (4)
C(2)—C(3)	1.519 (5)	C(5)—O(10)	1.434 (5)
(b) Bond angles around the chelate rings			
Ni—O(1)—C(1)	129.2 (3)	C(3)—N(2)—Ni	111.9 (2)
O(1)—C(1)—C(2)	122.0 (3)	N(2)—C(4)—C(5)	111.6 (3)
C(1)—C(2)—C(3)	113.9 (2)	C(4)—C(5)—C(4')	113.0 (3)
C(2)—C(3)—N(2)	111.9 (2)	O(10)—C(5)—Ni	85.3 (3)
(c) Parameters for the hydrogen bonds			
O—H...Cl	O...Cl	H...Cl	∠O—H...Cl
OW(1)—H(10)...Cl(1)	3.171 (2) Å	2.390 (1) Å	139.8 (2)°
OW(2)—H(11')...Cl(1')	3.166 (2)	2.270 (1)	159.4 (2)

Symmetry code: (') $x, -y, z$.

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Introduction. It is well known that many crystals of the A_2XY_4 family have a sequence of successive phase transitions [$A = \text{K, Rb, NH}_4, \text{N}(\text{CH}_3)_4$; $X = \text{Zn, Cu, Co}$; $Y = \text{Cl, Br}$]. Most of the members of this family present an incommensurate phase transition. As regards the structural aspects, they have an orthorhombic high-temperature phase with space group $Pnma$ and generally very large temperature factors (Wiesner, Srivastava, Kennard, Di Vaira & Lingafelter, 1967; Clay, Murray-Rust & Murray-Rust, 1975; Kamenar & Nagl, 1976; Kallel, Bats & Daoud, 1981). For the structures of the other phases, few studies have been made. To our knowledge, only the $(\text{NH}_4)_2[\text{ZnCl}_4]$

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