

Tris[(*R,R*)-1,2-cyclohexanediamine]nickel(II) Bromide Trihydrate

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Abstract. $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_3]\text{Br}_2 \cdot 3\text{H}_2\text{O}$, $M_r = 614.7$, cubic, $P2_13$, $a = 13.829$ (13) Å, $V = 2645$ (3) Å³, $Z = 4$, $D_m = 1.54$, $D_x = 1.544$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 37.6$ cm⁻¹, $F(000) = 1280$, $T = 293$ K, $R = 0.059$ for 1135 unique observed reflections. The complex ion has pseudosymmetry D_3 . The central Ni atom is bonded nearly octahedrally to six N atoms of the (*R,R*)-1,2-cyclohexanediamine (1*R*,2*R*-chxn) molecules, which act as bidentate ligands completing a rigid λ *gauche* conformation of a five-membered chelate ring. The complex ion takes the *lel* form resulting in the absolute configuration Δ .

Introduction. We have extensively studied the synthesis and characterization of transition-metal complexes containing *N*-glycoside(s) derived from sugars and diamines. During our investigations, we used chiral 1,2-cyclohexanediamine (1*R*,2*R*- or 1*S*,2*S*-chxn) as a diamine unit to regulate the stereochemistry of the *N*-glycoside ligands, and we have found a stereo-selective complexation between some C-2 epimeric aldoses (Takahashi, Yano, Yoshikawa & Hidai, 1987). It is said that metal binding of *trans*-1,2-chxn gives a five-membered chelate of a rigid *gauche* conformation owing to the stable chair conformation of the cyclohexane ring. However, the detailed structure of the starting Ni^{II} complex has not been completely determined, unlike the analogous Co^{III} complexes (Marumo, Utsumi & Saito, 1970; Kobayashi, Marumo & Saito, 1972). Thus we have undertaken the X-ray crystal-structure analysis of the title compound in order to elucidate the structural details.

Experimental. The title compound was synthesized by the known method (Treptow, 1968). Violet crystal,

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Ni	3808 (3)	3808 (3)	3808 (3)	2.0
Br(1)	8746 (2)	8746 (2)	8746 (2)	3.2
Br(2)	2009 (2)	2009 (2)	2009 (2)	4.1
N(1)	3217 (5)	4868 (5)	4754 (5)	2.2
N(2)	2724 (5)	4351 (5)	2845 (5)	2.3
C(1)	2605 (6)	5536 (6)	4164 (6)	1.9
C(2)	1935 (7)	6147 (7)	4793 (6)	3.1
C(3)	1278 (8)	6794 (7)	4169 (7)	4.5
C(4)	703 (6)	6181 (8)	3415 (7)	4.3
C(5)	1401 (6)	5578 (7)	2799 (7)	2.9
C(6)	2045 (6)	4936 (6)	3428 (6)	2.0
O'(1)	4553 (5)	6265 (6)	5913 (5)	5.7

Table 2. Bond lengths (Å) and angles (°) for non-H atoms with e.s.d.'s in parentheses

Ni–N(1)	2.128 (7)	Ni–N(2)	2.141 (8)
N(1)–C(1)	1.495 (11)	N(2)–C(6)	1.479 (11)
C(1)–C(2)	1.526 (12)	C(1)–C(6)	1.525 (12)
C(2)–C(3)	1.539 (14)	C(3)–C(4)	1.561 (14)
C(4)–C(5)	1.535 (13)	C(5)–C(6)	1.529 (12)
N(1)–Ni–N(2)	82.6 (3)	Ni–N(1)–C(1)	108.0 (5)
Ni–N(2)–C(6)	107.3 (5)	N(1)–C(1)–C(2)	112.1 (7)
N(1)–C(1)–C(6)	108.4 (6)	N(2)–C(6)–C(1)	109.8 (7)
N(2)–C(6)–C(5)	112.2 (7)	C(1)–C(2)–C(3)	111.1 (7)
C(2)–C(1)–C(6)	111.9 (7)	C(2)–C(3)–C(4)	111.1 (8)
C(3)–C(4)–C(5)	110.2 (7)	C(4)–C(5)–C(6)	111.5 (8)
C(1)–C(6)–C(5)	111.1 (7)		

rectangular plate, recrystallized by slow evaporation from methanol with dimensions $0.7 \times 0.7 \times 0.4$ mm. Density measured by flotation in a mixture of 1,2-dichloroethane and 1,2-dibromoethane. Rigaku AFC-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$. Cell dimensions determined with 20 reflections ($20 < 2\theta < 30^\circ$) by least-squares method. Systematic

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absences $h00$, $0k0$, $00l$ for odd h , k , l . Intensity data $2 < 2\theta < 30^\circ$, ω scan, $30 < 2\theta < 60^\circ$, $\omega-2\theta$ scan, scan speed 4° min^{-1} . Three standard reflections (322, 280, 0,0,10) monitored every 100 reflections showed only random variations within 4%. 2942 reflections ($h = 0$ to 19, $k = 0$ to 19, $l = 0$ to 19) observed. Since the intensities show threefold symmetry (hkl , klh , lkh), the space group was determined to be cubic $P2_13$. 1135 unique reflections with $|F_o| > 3\sigma(|F_o|)$ used. Number of unobserved reflections 469. An absorption correction was applied (transmission factors 0.12–0.21). Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The coordinates of Ni and two Br

atoms were obtained from the initial *E* map and the remaining non-H atoms were located from subsequent Fourier syntheses. H atoms were placed at idealized positions. Least-squares refinement on F_o with anisotropic temperature factors for non-H atoms, isotropic for H. The absolute configuration was determined using the known asymmetric carbon atoms of the diamine as an internal reference for the asymmetric center. Atomic scattering factors and f' , f'' values from *International Tables for X-ray Crystallography* (1974). $R = 0.059$, $wR = 0.044$, $w = 1/[\sigma(F_o)]^2$, $S = 2.92$. $\Delta\rho(\text{max.}) = 1.68 \text{ e } \text{Å}^{-3}$ [around Br(2)]. $\Delta/\sigma < 0.033$. All computations were performed on a FACOM M-780 computer at the Institute of Physical and Chemical Research with *UNICSIII* (Sakurai & Kobayashi, 1979).

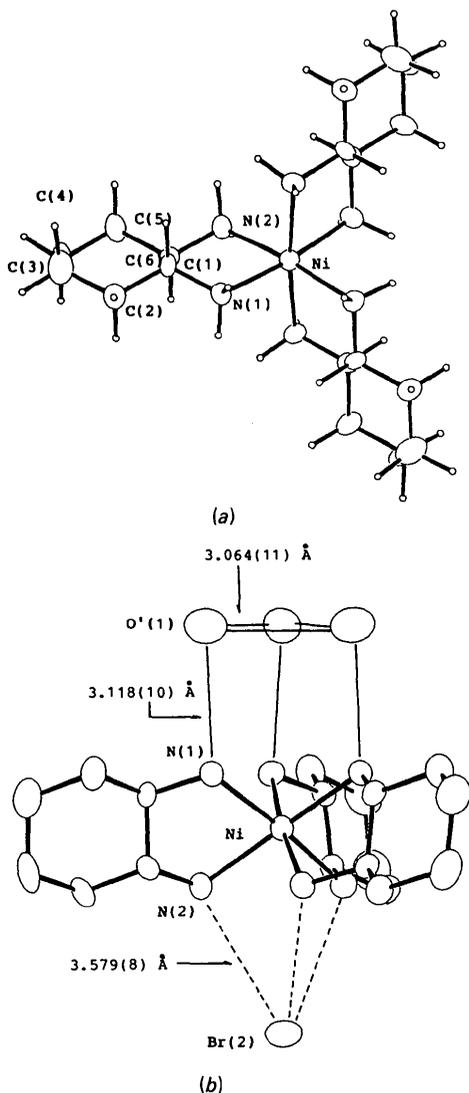


Fig. 1. (a) A perspective view of the complex cation projected along the threefold axis, with the numbering scheme. (b) A perspective view vertical to the threefold axis showing the hydrogen bonds. [Fine lines indicate probable hydrogen bonds, and dashed lines show weak interactions between the three N atoms and Br(2).]

Discussion. Final atomic parameters and bond lengths and angles are given in Tables 1 and 2.* An *ORTEP* (Johnson, 1965) drawing of the complex cation with the atom-numbering scheme is shown in Fig. 1(a). The central Ni atom is octahedrally coordinated to three 1*R*,2*R*-chxn molecules *via* N atoms of the amino groups. The complex cation has pseudosymmetry D_3 with a rigorous threefold rotation axis. The octahedron is shortened along the threefold rotation axis. The cyclohexane rings of the ligand molecules appear to have the ideal chair conformation from the calculations of their mean planes and deviations. All five-membered chelates (Ni–N–C–C–N) adopt the symmetrical λ *gauche* conformation, in which the C–C bonds are nearly parallel to the threefold rotation axis (*lel* form) resulting in the absolute configuration of the complex

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, selected torsion angles and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44351 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

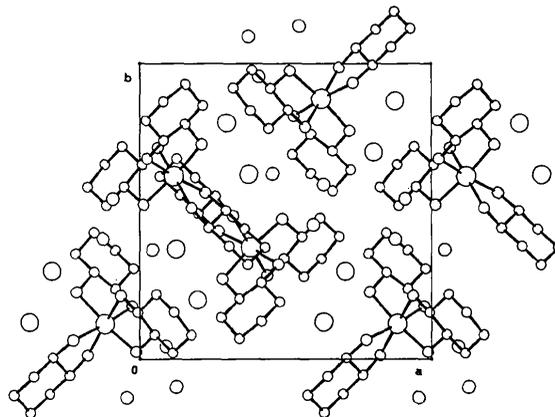


Fig. 2. Packing of the crystal structure in the unit cell (projection along the *c* axis).

ion being Δ . Thermal motions of the C atoms of five-membered rings are relatively small, indicating the rigidity of the 1*R*,2*R*-chxn chelate rings. The Ni–N distances and the N–Ni–N angles are common to those of Ni^{II} diamine complexes such as [Ni(en)₃]²⁺ (Swink & Atoji, 1960). All other bond lengths and angles are normal.

The packing of the crystal structure projected along the *c* axis is presented in Fig. 2. A unit cell contains four complex ions, eight Br counter anions, and 12 waters of crystallization. Weak hydrogen bonds are observed between the water molecules and the amino groups and also between the water molecules, which are shown in Fig. 1(b).

In the present crystal-structure determination, it is clear that the five-membered chelate ring of 1*R*,2*R*-chxn adopts a rigid λ *gauche* form even in the substitution-labile Ni^{II} complex. These structural features indicate the reason why the use of chiral 1,2-chxn is effective for the stereochemical regulation of the *N*-glycoside ligands in the Ni^{II} *N*-glycoside complexes (Takahashi *et al.*, 1987). In addition, the assumptions of the configurational and CD spectral assignments of [Ni(1*R*,2*R*-chxn)₃]²⁺ (Treptow, 1968; Harding, Mason & Peart, 1973) are confirmed.

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Structure of the Ordered and Disordered Forms of Aquachloro(2,6-diacetylpyridine disemicarbazone)copper(II) Chloride Dihydrate

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Abstract. The crystal structures of an ordered, (I), and a disordered form, (II), of the seven-coordinate copper complex aquachloro(2,6-diacetylpyridine disemicarbazone)copper(II) chloride dihydrate have been determined. (I) Pale yellow, [Cu(C₁₁H₁₅N₇O₂)Cl(H₂O)]·Cl·2H₂O, *M_r* = 465.82, triclinic, *P*1, *a* = 7.093 (4), *b* = 7.768 (3), *c* = 18.477 (12) Å, α = 86.37 (4), β = 84.90 (5), γ = 67.00 (4)°, *V* = 933.0 (9) Å³, *Z* = 2, *D_x* = 1.66 g cm⁻³, *Mo K α* , λ = 0.71093 Å, μ = 15.4 cm⁻¹, *F*(000) = 478, *T* = 300 K, *R* = 0.066 and *wR* = 0.051 for 2471 reflections and 235 parameters.

(II) Golden yellow, [Cu(C₁₁H₁₅N₇O₂)Cl_{*x*}(H₂O)_{2-*x*}]·Cl_{2-*x*}·(*x*+1)H₂O where *x* = 0.974 (6), *M_r* = 465.82, monoclinic, *I*2/*a*, *a* = 17.980 (5), *b* = 13.192 (2), *c* = 7.956 (4) Å, β = 99.95 (3)°, *V* = 1859 (1) Å³, *Z* = 4, *D_x* = 1.66 g cm⁻³, μ (*Mo K α*) = 15.2 cm⁻¹, *F*(000) = 956, *T* = 300 K, *R* = 0.064 and *wR* = 0.044 for 1637 reflections with 139 parameters. In both cases the cation is seven coordinate. The ligand 2,6-diacetylpyridine disemicarbazone forms a planar pentagon around the central Cu^{II} ion in both structures. In (I) the apical Cl and H₂O are ordered while in (II) the two groups are disordered and the complex cation has twofold symmetry.

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