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Structure of the *cis*-Facial Isomer of Bis[2,2′-iminodi(acetamide oxime)-*N*,*N*′,*N*″]nickel(II) Dichloride, $[Ni(C_4H_{11}N_5O_2)_2]Cl_2$

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Abstract. $M_r = 451\cdot95$, monoclinic, $C2/c$, $a = 10\cdot427\,(3)$, $b = 14\cdot738\,(4)$, $c = 11\cdot438\,(3)$ Å, $\beta = 91\cdot62\,(2)°$, $V = 1757\cdot0\,(8)$ Å^3, $Z = 4$, $D_m = 1\cdot70$, $D_x = 1\cdot708$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 14\cdot52$ cm^{-1}, $F(000) = 936$, $T = 297$ K, final $R = 0\cdot024$ for 1483 observed reflections. The complex cation, $[Ni\{HN(CH_2C(=NOH)NH_2)_2\}_2]^{2+}$, has a twofold axis through the nickel ion, which bisects the N(3)—Ni—N(3′) and the N(5)—Ni—N(5′) angles. The two terdentate ligands are attached to opposite faces of the distorted nickel(II) octahedron through the amino nitrogen and the two oxime nitrogens; the amino nitrogens of the two ligands are *cis* to each other.

Introduction. The ligand 2,2′-iminodi(acetamide oxime), ibo, forms only two isomers with nickel(II) chloride. The structure of the *cis*-facial (*fac*) isomer is reported here, and the structure of the *trans*-facial (*fac*) isomer was reported earlier (Cullen, Lingafelter & Eddy, 1970). In aqueous solution the *cis*-facial isomer isomerizes to the less-soluble *trans*-facial isomer; we suggest the isomerization mechanism is the Bailar twist. After this isomerization became known to us, slow evaporation of an aqueous solution of the *cis*-facial isomer was avoided, and crystals for the present study were obtained quickly from solution to avoid isomerization.

Experimental. Concentrated aqueous solutions of ligand and nickel(II) chloride were mixed at room temperature; the violet *trans*-facial crystals that immediately formed were filtered off; the purple solution was passed through a Sephadex G-10 column, and elution with water washed out first the violet isomer then the desired purple *cis*-facial isomer. Saturated aqueous potassium chloride solution was added to the purple eluate to speed crystallization; purple crystals of suitable size were formed overnight. D_m measured using pycnometer with toluene as covering liquid (Berman, 1939). Purple crystal $0\cdot20 \times 0\cdot22 \times 0\cdot25$ mm with well-defined faces and edges, glass-fiber mount, extinguished plane-polarized light. Syntex $P2_1$ automated four-circle diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters by least-squares fit of 15 2θ values ($20\cdot2 < 2\theta < 23\cdot1°$). hkl and $\bar{h}kl$ reflections with 2θ from 3 to 55° measured; range of hkl: h −13 to +12, k 0 to 19, l 0 to 14. Intensity data collected by $2\theta/\theta$ scan technique, variable scan rate 2·0 to 29·3° min^{-1}, range from 0·8° 2θ below calc. $K\alpha_1$ peak to 1·0° above calc. $K\alpha_2$ peak positions. Corrections for Lorentz and polarization effects and absorption (Busing & Levy, 1957), max. and min. absorption corrections to intensities 0·780 and 0·738. 2290 reflections collected, which include standards and non-unique data; 2039 unique; 1483 with $I > 3\sigma_I$ used in structure refinement; 248 unobserved reflections with $I < 3\sigma_I$. Internal consistency index $R_{\text{int}} = 0\cdot021$.

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Direct methods for structure solution. Calculations performed on DEC VAX 11/780 computer using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Correct positions for Ni and Cl atoms deduced from *E* map. Weighted difference Fourier synthesis with only Ni atom contributing to calculated structure factors revealed positions for all but three remaining non-H atoms (highest peak in map confirmed Cl position). Subsequent least-squares and difference Fourier calculations gave positions for rest of atoms in asymmetric unit, including hydrogens. In final cycle of full-matrix least-squares refinement all non-hydrogen atomic positions were varied with anisotropic thermal parameters and all hydrogen-atom coordinates refined with isotropic thermal parameters; $\sum w\{||F_o| - |F_c||\}^2$ minimized, where $w = 1{\cdot}11/[\sigma_{F_o}^2 + (pF_o)^2]$, $p = 0{\cdot}017$, the ignorance factor (Corfield, Doedens & Ibers, 1967). Successful convergence of least squares indicated by max. Δ/σ of 0·005 for final cycle. Final *R* and *wR* 0·024 and 0·030 respectively for 1483 reflections used in refinement. Max. and min. peak heights in final difference Fourier synthesis +0·32 and −0·22 e Å^{-3}. Source of atomic scattering factors: Ibers & Hamilton (1974, pp. 99–101). Anomalous-dispersion effects applied (Ibers & Hamilton, 1974, pp. 149–150). Space group *C*2/*c* confirmed by probability distribution of intensities, and successful refinement of proposed model in centrosymmetric space group *C*2/*c*, rather than *Cc*.*

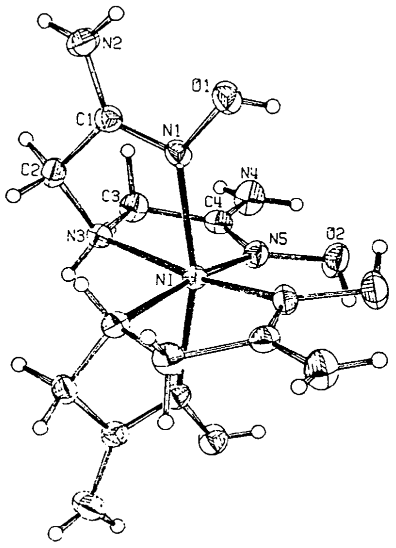

Fig. 1. An *ORTEP* (Johnson, 1971) drawing of the title ion with the non-hydrogen atoms of one asymmetric unit labeled. The thermal ellipsoids are drawn at the 50% probability level.

Table 1. *Positional parameters* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^4) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	*y*	*z*	U_{eq}
Ni	0	7613·6 (2)	7500·0	183 (2)
Cl	−2396·5 (6)	9719·0 (4)	1710·8 (5)	347 (3)
O(1)	2999 (2)	7332 (1)	7037 (2)	293 (8)
O(2)	−0851 (2)	5811 (1)	6162 (2)	363 (10)
N(1)	1818 (2)	7801 (1)	6807 (2)	216 (9)
N(2)	3145 (2)	8820 (2)	5845 (2)	334 (11)
N(3)	−0327 (2)	8582 (1)	6101 (2)	216 (9)
N(4)	−1161 (2)	6631 (2)	4177 (2)	333 (12)
N(5)	−0679 (2)	6769 (1)	6184 (2)	242 (9)
C(1)	2016 (2)	8532 (1)	6219 (2)	216 (10)
C(2)	0852 (2)	9124 (1)	6000 (2)	241 (10)
C(3)	−0657 (2)	8108 (2)	4995 (2)	267 (11)
C(4)	−0858 (2)	7106 (1)	5152 (2)	231 (10)

Discussion. The structure of one bis(ibo)nickel(II) cation is shown in Fig. 1; the atoms in one asymmetric unit are numbered. Nickel(II) displays a slightly distorted octahedral coordination. Each of the two terdentate ibo molecules is bound to the nickel through the two oxime nitrogens, N(1) and N(5), and the central amine nitrogen, N(3); each ligand occupies an octahedral face, and the amine nitrogens of the two ligands are adjacent to give a *cis*-facial arrangement. The oxime groups are all on one side of the ion, making it polar. Positional and thermal parameters are given in Table 1. Bond lengths and angles are given in Table 2. The view in Fig. 2 shows four cations and eight chloride ions in the unit cell. The two chloride ions closest to a given nickel ion are at a distance of 4·488 Å, so they are not involved in coordination. Extensive hydrogen bonding helps hold the ions together in the crystal; this bonding is shown as narrow lines in Fig. 2 and the bonds are listed in Table 3. Five hydrogen bonds involving each chloride ion are postulated: they involve the hydrogens on the amine N, both amide N's and both oxime O's. Three intraionic hydrogen bonds between the amide N's and the oxime O's are also indicated. In each ligand one Ni—N(oxime) is longer than the other: Ni—N(1) = 2·094 (2) and Ni—N(5) = 2·063 (2) Å. These distances are longer than metal–oxime nitrogen distances in azidobis(dimethylglyoximato)(triphenylphosphine)cobalt(III) (Nelson, Takach, Bresciani-Pahor, Randaccio & Zangrando, 1984), for example. The Ni—N(amine) bond length of 2·164 (2) Å is longer than in some other octahedral nickel(II) complexes (Sacconi, 1968). The planarity of the chelate rings was tested by calculating the least-squares planes, and it was found that neither ring was planar. The Ni—N(5)—C(4)—C(3)—N(3) ring was less puckered than the Ni—N(1)—C(1)—C(2)—N(3) ring; neither was Ni—N(5)—O(2) coplanar with Ni—N(5′)—O(2′).

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* Lists of structure factors, thermal parameters, hydrogen-atom coordinates and non-essential bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42116 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Ni—N(1)	2·094 (2)	C(1)—N(2)	1·334 (3)
Ni—N(3)	2·164 (2)	C(4)—N(4)	1·347 (3)
Ni—N(5)	2·063 (2)	C(2)—N(3)	1·473 (3)
C(1)—C(2)	1·510 (3)	C(3)—N(3)	1·478 (3)
C(3)—C(4)	1·502 (3)	N(1)—O(1)	1·430 (2)
C(1)—N(1)	1·290 (3)	N(5)—O(2)	1·424 (2)
C(4)—N(5)	1·290 (3)		
N(oxime)—Ni—N(amine)		C(2)—C(1)—N(2)	118·4 (2)
Intrachelate		C(1)—C(2)—N(3)	110·0 (2)
N(5)—Ni—N(3)	79·33 (7)	C(4)—C(3)—N(3)	113·1 (2)
N(1)—Ni—N(3)	76·00 (6)	C(3)—C(4)—N(4)	116·3 (2)
Interchelate		C(3)—C(4)—N(5)	118·1 (2)
N(5)—Ni—N(3^{i})	168·83 (7)	N(4)—C(4)—N(5)	125·6 (2)
N(1^{i})—Ni—N(3)	93·89 (6)	Ni—N(5)—C(4)	118·2 (1)
N(oxime)—Ni—N(oxime)		Ni—N(3)—C(2)	107·6 (1)
Intrachelate		Ni—N(3)—C(3)	110·5 (1)
N(1)—Ni—N(5)	95·68 (7)	C(2)—N(3)—C(3)	111·4 (2)
Interchelate		Ni—N(1)—C(1)	117·9 (1)
N(5^{i})—Ni—N(5)	105·76 (7)	Ni—N(1)—O(2)	130·5 (1)
N(1^{i})—Ni—N(1)	164·83 (6)	Ni—N(5)—O(2)	130·7 (1)
N(1^{i})—Ni—N(5)	93·46 (7)	C(4)—N(5)—O(2)	110·6 (2)
N(3)—Ni—N(3^{i})	95·48 (7)	C(1)—N(1)—O(1)	110·5 (2)
C(2)—C(1)—N(1)	115·4 (2)	N(1)—C(1)—N(2)	126·1 (2)

Symmetry code: (i) $-x, y, \frac{3}{2}-z$.

Table 3. *Hydrogen bonds in cis-facial* [Ni(*ibo*)$_2$]Cl$_2$

Type *A*—H···*B*	*A*	H	*B*	Distance (Å) *A*—*B*	*A*—H	H—*B*	Angle (°) *A*—H—*B*
N—H···Cl	N(3)amine	H(6)	Cl	3·391 (2)	0·88 (2)	2·53 (2)	168 (2)
	N(2)amide	H(2)	Cl	3·283 (3)	0·84 (3)	2·55 (3)	146 (3)
	N(4)amide	H(9)	Cl	3·338 (2)	0·88 (2)	2·61 (3)	142 (3)
O—H···Cl	O(2)oxime	H(11)	Cl	3·181 (2)	0·78 (3)	2·41 (3)	167 (3)
	O(1)oxime	H(1)	Cl	3·072 (2)	0·78 (3)	2·30 (3)	169 (3)
N—H···O	N(4)amide	H(9)	O(2)	2·584 (3)	0·79 (3)	2·27 (3)	101 (2)
	N(2)amide	H(3)	O(1)	2·590 (3)	0·86 (3)	2·23 (3)	106 (2)
	N(4)amide	H(10)	O(1)	2·996 (3)	0·79 (3)	2·20 (3)	175 (3)

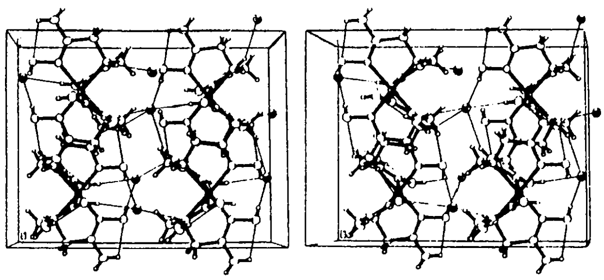

Fig. 2. Packing diagram (50% probability ellipsoids). A stereoview down the *b* axis of the *ac* plane with the origin at left back corner and the *c* axis vertical, shaded ellipsoids for the Ni and Cl atoms; the narrow lines depict the rather extensive hydrogen bonding.

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Acta Cryst. (1985). C**41**, 1031–1033

Structure of a Fully Conjugated Macrocyclic Complex: (1,4,8,11-Tetraazacyclotetradeca-2,4,6,9,11,13-hexaene-2,3,9,10-tetracarbonitrilato)nickel(II), [Ni($C_{14}H_6N_8$)]

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(*Received* 18 *December* 1984; *accepted* 4 *March* 1985)

Abstract. $M_r = 344·95$, monoclinic, $C2/m$, $a = 13·674$ (3), $b = 14·469$ (4), $c = 3·7696$ (8) Å, $\beta = 96·55$ (2)°, $V = 740·95$ Å^3, $Z = 2$, $D_m = 1·57$, $D_x = 1·55$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 1·324$ mm^{-1}, $F(000) = 348$, $T = 298$ K, final $R = 0·042$ for 879 observed reflections. The complex molecule is nearly planar and has crystallographic $2/m$ symmetry. The molecules are packed in a parallel fashion along the c axis with a close interplanar distance of 3·357 (3) Å. The bond pattern of the macrocyclic ligand in the complex consists of a delocalized six-membered ring and a five-membered ring with a localized C=C double bond linked by two single C—N bonds.

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