

N(1)—C(1)	1.355 (6)	C(3)—C(4)	1.379 (8)
N(1)—C(5)	1.343 (6)	C(4)—C(5)	1.391 (7)
N(2)—C(6)	1.481 (6)	C(5)—C(6)	1.499 (7)
N(2)—C(7)	1.492 (6)	C(7)—C(8)	1.546 (7)
C(1)—C(2)	1.381 (7)	C(8)—C(9)	1.477 (9)
C(2)—C(3)	1.376 (9)		
Cl(1)—Cu—Cl(1')	96.83 (5)	Cl(2)—Cu—N(1)	95.70 (12)
Cl(1)—Cu—Cl(2)	94.29 (5)	Cl(2)—Cu—N(2)	176.91 (11)
Cl(1)—Cu—N(1)	165.60 (11)	N(1)—Cu—N(2)	81.24 (15)
Cl(1)—Cu—N(2)	88.80 (11)	Cu—Cl(1)—Cu'	83.17 (4)
Cl(1')—Cu—Cl(2)	93.49 (5)	Cu—N(1)—C(1)	127.0 (3)
Cl(1')—Cu—N(1)	92.89 (12)	Cu—N(1)—C(5)	114.0 (3)
Cl(1')—Cu—N(2)	86.29 (12)		

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

The structure was solved by direct methods and refined by full-matrix least-squares methods, with all non-H atoms anisotropic. H atoms were included in calculated positions. All computing was performed using the NRCVAX system (Gabe *et al.*, 1989).

Data collection: *TEXSAN* (Molecular Structure Corporation, 1992). Cell refinement: *TEXSAN*.

The authors wish to thank the Natural Sciences and Engineering Council of Canada and the US Army Research Office for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1213). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[di(2-aminoethyl)amine-*N,N',N''*]-nickel(II) Chloride Monohydrate, a Redetermination

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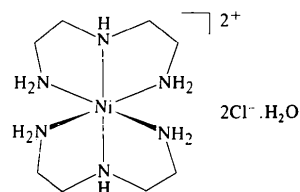
(Received 1 March 1996; accepted 7 May 1996)

Abstract

A redetermination of the structure of the title compound, $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$, from diffractometer data leads to considerably more accurate geometric parameters than those obtained in a previous determination using film data. The coordination geometry around the Ni^{II} atom in the $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2]^{2+}$ cation is a distorted octahedron, with the Ni—N distances in the range 2.083 (4)–2.166 (4) Å and the *trans*-N—Ni—N angles in the range 161.9 (2)–177.5 (2)°.

Comment

We have been interested in the coordination chemistry of transition metal complexes with alkoxy ligands (Bradford, Hynes, Payne, & Willis, 1990; Hynes, Willis & Payne, 1990, 1992; Willis, 1988). In the course of our investigation on the coordination chemistry of the $\text{HOC}(\text{CF}_3)_2\text{OH}$ ligand, $[\text{Ni}(\text{dien})_2][\text{HOC}(\text{CF}_3)_2\text{O}]_2$ [dien is di(2-aminoethyl)amine] was prepared (Hynes, 1989). On recrystallization from a mixture of CH_2Cl_2 and CH_3OH , purple hexagonal plates of $[\text{Ni}(\text{dien})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$, (I), were obtained as the main product. The structure of this compound is reported here.



(I)

The structure of (I) was previously determined from multiple-layer Weissenberg photographs; the intensity data were measured photometrically and refined to $R_{\text{obs}} = 0.092$ (Paoletti, Biagini & Cannas, 1969; Biagini & Cannas, 1970); no absorption correction was applied. This redetermination, using modern diffraction appa-

tus and computational methods, corroborates the previous results and improves the precision significantly. The structure is isomorphous with [M(dien)₂]Br₂·H₂O [M = Cu (Stephens, 1969) and Zn (Hodgson & Penfold, 1974)]. The structure consists of [Ni(dien)₂]²⁺ cations, Cl⁻ ions and water molecules in the crystal lattice; a view of the asymmetric unit is shown in Fig. 1. In the cation, the two chelating tridentate dien ligands are bonded to the Ni^{II} atom to give a distorted octahedral coordination geometry. The terminal amino groups within the dien ligands are *trans* with respect to one another and similarly the secondary amines are *trans* to define the cation as a meridional isomer. Selected dimensions are given in Table 2. The Ni—N bond distances [range 2.083 (4)–2.166 (4) Å] are normal and comparable to the values reported by Biagini & Cannas (1970) [2.050 (15)–2.190 (15) Å].

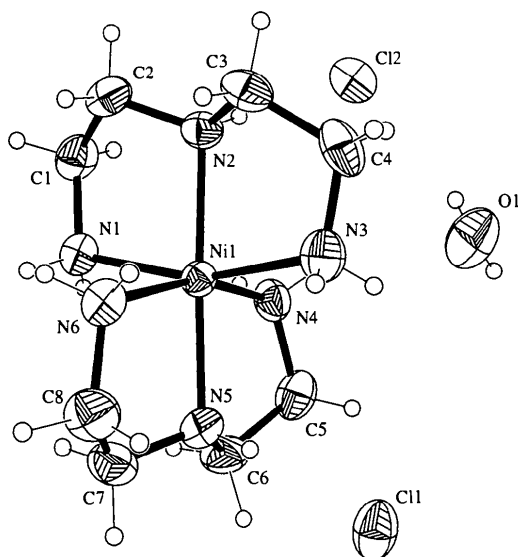


Fig. 1. A view of the asymmetric unit of (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

The cations, anions and water molecules are linked by a hydrogen-bonding network which utilizes all N—H (except the N3 H atoms) and O—H moieties; details are in Table 3. The Cl1 anion takes part in four such interactions and the Cl2 anion in five.

Experimental

To an NiCl₂·6H₂O (1 mmol) solution in ethanol (10 ml), a fivefold excess of dien, HOC(CF₃)₂OH (2 mmol) and KOH (2 mmol) in ethanol (15 ml) were added. After stirring for about 30 min, the solvent and precipitated KCl were removed. The powder was recrystallized from a methanol/ethanol/2-propanol mixture to give [Ni(dien)₂][HOC(CF₃)₂O]₂ in

quantitative yield (m.p. 433 K). Analysis calculated for C₁₄H₂₈F₁₂N₆NiO₄: C 26.64, H 4.47, N 13.31%; found: C 26.81, H 4.40, N 13.68%. The crystals obtained by this method, however, were not suitable for single-crystal X-ray diffraction analysis. On recrystallization from CH₂Cl₂/MeOH by the diffusion method, the alkoxy anions was replaced by chloride anions from the solvent to give single crystals of [Ni(dien)₂]Cl₂·H₂O. All the chemicals were of reagent grade and were used as received. C, H and N analyses were performed by Guelph Chemical Laboratories Ltd. The synthesis was carried out in air.

Crystal data

[Ni(C₄H₁₃N₃)₂]Cl₂·H₂O

M_r = 353.97

Monoclinic

*P*2₁/*c*

a = 13.5109 (13) Å

b = 8.7204 (11) Å

c = 13.9723 (16) Å

β = 102.177 (9)°

V = 1609.2 (3) Å³

Z = 4

D_x = 1.461 Mg m⁻³

D_m = 1.48 (5) Mg m⁻³

D_m measured by flotation

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 44 reflections

θ = 12.51–15.24°

μ = 1.538 mm⁻¹

T = 293 (2) K

Irregular hexagonal plate

0.25 × 0.20 × 0.10 mm

Purple

Data collection

Siemens *P4* diffractometer

θ–2θ scans

Absorption correction:

Gaussian (*SHELXTL/PC*;
Sheldrick, 1990b)

T_{min} = 0.8109, *T_{max}* =
0.8764

2955 measured reflections

2236 independent reflections

1834 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0205

θ_{max} = 23°

h = –1 → 14

k = –1 → 9

l = –15 → 15

3 standard reflections
monitored every 297

reflections

intensity decay: 0.08%

Refinement

Refinement on *F*²

R(*F*) = 0.0350

wR(*F*²) = 0.0833

S = 1.034

2236 reflections

170 parameters

Only coordinates of hydroxy

H atoms refined, others

riding (*SHELXL93*

defaults; C—H 0.97,

N—H 0.90 and 0.91 Å)

w = 1/[σ²(*F_o*²) + (0.0302*P*)²
+ 0.4511*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.256 e Å⁻³

Δρ_{min} = –0.226 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ni1	0.26115 (5)	0.11221 (7)	0.06218 (4)	0.0275 (2)
N1	0.2036 (3)	0.0877 (5)	–0.0939 (3)	0.0332 (10)
N2	0.2465 (3)	–0.1264 (5)	0.0561 (3)	0.0328 (10)

N3	0.3252 (4)	0.0603 (6)	0.2127 (3)	0.0501 (13)
N4	0.1134 (3)	0.1615 (5)	0.0836 (3)	0.0376 (11)
N5	0.2750 (3)	0.3496 (5)	0.0746 (3)	0.0374 (11)
N6	0.4110 (3)	0.1356 (5)	0.0321 (3)	0.0353 (11)
C1	0.1727 (4)	-0.0728 (7)	-0.1133 (4)	0.0434 (14)
C2	0.2446 (4)	-0.1761 (7)	-0.0448 (4)	0.0428 (14)
C3	0.3263 (4)	-0.1895 (6)	0.1336 (4)	0.0431 (14)
C4	0.3244 (4)	-0.1054 (7)	0.2280 (4)	0.048 (2)
C5	0.1089 (4)	0.3244 (7)	0.1111 (4)	0.048 (2)
C6	0.1742 (4)	0.4166 (6)	0.0591 (4)	0.0458 (15)
C7	0.3433 (4)	0.3967 (7)	0.0129 (4)	0.049 (2)
C8	0.4366 (4)	0.3005 (7)	0.0348 (5)	0.053 (2)
C11	0.40654 (10)	0.4498 (2)	0.29790 (9)	0.0463 (4)
C12	0.03964 (10)	-0.2220 (2)	0.14121 (10)	0.0474 (4)
O1	0.1160 (4)	0.0396 (7)	0.2998 (4)	0.072 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ni1—N1	2.166 (4)	Ni1—N4	2.125 (4)
Ni1—N2	2.090 (4)	Ni1—N5	2.083 (4)
Ni1—N3	2.146 (4)	Ni1—N6	2.162 (4)
N1—Ni1—N3	161.9 (2)	N4—Ni1—N6	162.7 (2)
N2—Ni1—N5	177.5 (2)		
N1—C1—C2—N2	55.4 (6)	N4—C5—C6—N5	-51.8 (6)
N2—C3—C4—N3	-50.7 (6)	N5—C7—C8—N6	50.8 (7)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1O...C12	0.76 (6)	2.50 (6)	3.195 (6)	153 (7)
O1—H2O...C12 ⁱ	0.87 (6)	2.33 (6)	3.187 (6)	171 (6)
N1—H1...C12 ⁱⁱ	0.90	2.59	3.419 (4)	154
N1—H1'...C11 ⁱⁱⁱ	0.90	2.59	3.415 (4)	153
N2—H2...C12	0.91	2.47	3.365 (4)	169
N4—H4...C12 ⁱⁱ	0.90	2.59	3.418 (4)	153
N4—H4'...O1	0.90	2.38	3.195 (7)	151
N5—H5...C11	0.91	2.46	3.364 (4)	172
N6—H6...C11 ^{iv}	0.90	2.55	3.446 (4)	176
N6—H6'...C11 ⁱⁱⁱ	0.90	2.46	3.344 (4)	167

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, -y, -z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTLPC (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{4-Methyl-2-[(2-oxidobenzylidene)amino]-phenolato(2-)-N,O,O'}(piperidine-N)-nickel(II)

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Abstract

In the title compound, $[\text{Ni}(\text{C}_{14}\text{H}_{11}\text{NO}_2)(\text{C}_5\text{H}_{11}\text{N})]$, the coordination geometry at the Ni atom was found to be a slightly distorted square-planar polygon formed by the O, N and O' donor atoms of the tridentate ligand and the N donor atom of the monodentate ligand [O—Ni—N 86.6 (2)–95.9 (3)°, Ni—O 1.810 (5) and 1.833 (4), Ni—N 1.862 (6) and 1.933 (7) Å]. The diamagnetic properties of the complex, determined by the Gouy method, are in agreement with the planar coordination.

Comment

Schiff bases and their biologically active complexes have been extensively studied over the last two decades. Several complexes of salicylaldehyde (Stewart & Lin-