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Structure of Bis(5,7-dichloro-8-quinolinolato-N,O)bis(pyridine)nickel(II)

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Abstract. [Ni($C_9H_4Cl_2NO$)$_2$(C_5H_5N)$_2$], $M_r = 643\cdot00$, monoclinic, space group $P2_1/c$, $a = 12\cdot6796$ (16), $b = 16\cdot0408$ (16), $c = 14\cdot5342$ (21) Å, $\beta = 113\cdot28$ (1)°, $V = 2715\cdot4$ (6) Å^3, $Z = 4$, $D_m = 1\cdot57$ (1), $D_x = 1\cdot57$ Mg m^{-3}, λ(Cu $K\alpha$) = $1\cdot54184$ Å, $\mu = 5\cdot022$ mm^{-1}, $F(000) = 1304$, $T = 290$ K, final $R = 0\cdot058$, $wR = 0\cdot060$ for 2177 observed reflections. The central Ni atom is pseudo-octahedrally coordinated by two 5,7-dichloro-8-quinolinol ligands and two pyridine ligands in *cis* positions. Distances and angles are normal [average Ni–N(quinoline) 2·080 (7), Ni–N(pyridine) 2·094 (8); Ni–O 2·045 (6) Å].

Introduction. The present paper describes the crystal structure of a new Ni[II] compound with 5,7-dichloro-8-quinolinol. In previous work, we have reported several structures of Ni coordination compounds having C-substituted ethylenediamines or 5-chloro-8-quinolinol as ligands (García-Granda & Gómez-Beltrán, 1986). This investigation has been undertaken in order to obtain enough data to understand the

chemical and physicochemical behaviour of these transition-metal compounds.

Experimental. A dark yellow crystal of approximately $0\cdot18 \times 0\cdot10 \times 0\cdot10$ mm was used during the measurements. Density measured by flotation in carbon tetrachloride/heptane. Throughout the experiment Cu $K\alpha$ radiation was used with a graphite crystal monochromator on a Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections. The intensity data of 10 734 reflections (one half sphere up to $\theta = 70°$), hkl range from (−15,−19,0) to (15,19,17), were measured, using the ω–2θ scan technique, with a scan angle of 1·50° and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min. The final drift correction factors were between 1·00 and 1·05. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0·91 to 1·00). Symmetry-equivalent reflections were averaged, $R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I = 0\cdot054$, resulting in 5146 unique reflections of which 2177 were observed with $I > 3\sigma(I)$.

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$$[Ni(C_9H_4Cl_2NO)_2(C_5H_5N)_2]$$

The structure was solved automatically, using *PATSYS* (Behm & Beurskens, 1985): the position of the Ni atom was located from the Patterson map, and input to *DIRDIF* (Beurskens *et al.*, 1982), and the positions of all non-hydrogen atoms were obtained. Isotropic least-squares refinement using *SHELX76* (Sheldrick, 1976) converged to $R = 0.120$. At this stage the empirical absorption correction was applied (Walker & Stuart, 1983), resulting in a further decrease of R to 0.112. All H atoms were located by difference Fourier synthesis. During the final stages of the refinement the positional parameters of all atoms and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The hydrogen atoms had fixed isotropic temperature factors of 0.06 Å^2. The final $R = 0.058$ and $wR = 0.060$ for the 2177 'observed' reflections and 406 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0.00040F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-to-e.s.d. ratio in the last full-matrix least-squares cycle was less than 0.06. The final difference Fourier map showed residual electron density within -0.4 and $+0.3 \text{ e Å}^{-3}$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Fig. 1 is drawn with *PLUTO* (Motherwell, 1976). Geometrical parameters are calculated with *PARST* (Nardelli, 1983). Final positional and thermal parameters are given in Table 1.*

Discussion. Bond lengths and selected angles are listed in Table 2. A view of the complex showing the geometry and the crystallographic numbering scheme is given in Fig. 1. The central Ni atom is coordinated by two 7,5-dichloro-8-quinolinol and two pyridine ligands in a *cis* pseudo-octahedral arrangement. The average Ni—N distance for the pyridine ligands is 2.094 (8) Å; this distance is shorter than the corresponding distance [2.145 (7) Å] found by García-Granda & Gómez-Beltrán (1986) in the analogous *trans*-5-chloro compound. The average Ni—N distance for the 5,7-dichloro-8-quinolinol ligand is 2.080 (7) Å, Ni—O is 2.045 (6) Å, and the average N—Ni—O quinolinol bite angle is 80.2 (3)°. The geometry of this ligand is very close to the geometry found in the *trans*-5-chloro compound. No unusual geometric features are present in the molecule.

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Table 1. *Fractional positional and equivalent isotropic thermal parameters* $(\text{Å}^2 \times 100)$ *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni(1)	0.23376 (11)	0.24766 (9)	0.37112 (11)	6.40 (6)
Cl(15)	0.77668 (24)	0.08047 (19)	0.54325 (26)	9.57 (16)
Cl(17)	0.42726 (23)	0.05627 (15)	0.66399 (19)	6.46 (12)
Cl(25)	0.32681 (28)	0.67320 (16)	0.41642 (24)	9.07 (16)
Cl(27)	0.09405 (24)	0.47176 (16)	0.10888 (19)	6.58 (11)
O(18)	0.3080 (5)	0.1700 (4)	0.4907 (4)	4.51 (26)
O(28)	0.1779 (5)	0.3355 (3)	0.2598 (4)	4.27 (24)
N(11)	0.3909 (6)	0.2277 (4)	0.3620 (5)	4.0 (3)
N(21)	0.3022 (6)	0.3547 (4)	0.4553 (5)	4.4 (3)
N(31)	0.0811 (6)	0.2538 (4)	0.3944 (5)	4.1 (3)
N(41)	0.1635 (6)	0.1491 (4)	0.2712 (6)	4.4 (3)
C(12)	0.4289 (9)	0.2567 (7)	0.2965 (8)	5.7 (5)
C(13)	0.5355 (10)	0.2365 (7)	0.2980 (9)	6.3 (5)
C(14)	0.6042 (9)	0.1845 (7)	0.3694 (10)	6.4 (5)
C(15)	0.6360 (8)	0.1040 (5)	0.5255 (8)	5.6 (5)
C(16)	0.5926 (9)	0.0756 (6)	0.5909 (8)	5.3 (5)
C(17)	0.4803 (8)	0.0973 (5)	0.5803 (6)	4.4 (4)
C(18)	0.4100 (8)	0.1470 (5)	0.5025 (7)	4.1 (4)
C(19)	0.4587 (8)	0.1764 (5)	0.4349 (7)	4.0 (4)
C(22)	0.3659 (10)	0.3622 (7)	0.5509 (9)	6.3 (5)
C(23)	0.4098 (12)	0.4377 (10)	0.5961 (8)	7.9 (6)
C(24)	0.3828 (10)	0.5082 (7)	0.5413 (9)	6.8 (5)
C(25)	0.2841 (8)	0.5714 (6)	0.3723 (8)	5.6 (5)
C(26)	0.2185 (10)	0.5607 (6)	0.2741 (8)	5.8 (5)
C(27)	0.1817 (7)	0.4813 (5)	0.2343 (7)	4.3 (4)
C(28)	0.2088 (7)	0.4092 (5)	0.2927 (7)	4.1 (4)
C(29)	0.2776 (7)	0.4244 (5)	0.3977 (7)	4.4 (4)
C(31)	−0.0123 (10)	0.2893 (7)	0.3288 (8)	5.6 (5)
C(32)	−0.1105 (11)	0.2973 (8)	0.3472 (12)	8.2 (7)
C(33)	−0.1139 (11)	0.2681 (8)	0.4321 (13)	8.1 (7)
C(34)	−0.0206 (13)	0.2302 (8)	0.4986 (11)	8.5 (7)
C(35)	0.0747 (10)	0.2246 (7)	0.4762 (10)	6.6 (6)
C(41)	0.1138 (12)	0.0841 (8)	0.2918 (9)	7.0 (6)
C(42)	0.0723 (11)	0.0191 (7)	0.2279 (11)	7.8 (6)
C(43)	0.0773 (12)	0.0195 (7)	0.1376 (10)	7.9 (6)
C(44)	0.1282 (14)	0.0862 (10)	0.1144 (9)	9.9 (8)
C(45)	0.1687 (11)	0.1481 (7)	0.1836 (11)	7.3 (6)
C(110)	0.5692 (8)	0.1533 (5)	0.4438 (7)	4.6 (4)
C(210)	0.3166 (8)	0.5044 (5)	0.4382 (7)	4.9 (4)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

|			
Ni(1)—O(18)	2.041 (6)	C(15)—C(16)	1.352 (14)
Ni(1)—O(28)	2.049 (6)	C(15)—C(110)	1.398 (13)
Ni(1)—N(11)	2.072 (8)	C(16)—C(17)	1.414 (13)
Ni(1)—N(21)	2.087 (7)	C(17)—C(18)	1.382 (12)
Ni(1)—N(31)	2.095 (7)	C(18)—C(19)	1.432 (13)
Ni(1)—N(41)	2.092 (8)	C(19)—C(110)	1.404 (12)
Cl(15)—C(15)	1.741 (10)	C(22)—C(23)	1.386 (18)
Cl(17)—C(17)	1.735 (10)	C(23)—C(24)	1.347 (17)
Cl(25)—C(25)	1.759 (10)	C(24)—C(210)	1.399 (14)
Cl(27)—C(27)	1.726 (9)	C(25)—C(26)	1.349 (14)
O(18)—C(18)	1.289 (10)	C(25)—C(210)	1.390 (13)
O(28)—C(28)	1.278 (10)	C(26)—C(27)	1.400 (13)
N(11)—C(12)	1.311 (14)	C(27)—C(28)	1.395 (11)
N(11)—C(19)	1.349 (10)	C(28)—C(29)	1.449 (12)
N(21)—C(22)	1.309 (13)	C(29)—C(210)	1.417 (11)
N(21)—C(29)	1.357 (11)	C(31)—C(32)	1.378 (17)
N(31)—C(31)	1.320 (13)	C(32)—C(33)	1.337 (19)
N(31)—C(35)	1.310 (14)	C(33)—C(34)	1.342 (19)
N(41)—C(41)	1.313 (14)	C(34)—C(35)	1.374 (16)
N(41)—C(45)	1.301 (16)	C(41)—C(42)	1.356 (16)
C(12)—C(13)	1.382 (16)	C(42)—C(43)	1.339 (18)
C(13)—C(14)	1.349 (16)	C(43)—C(44)	1.359 (19)
C(14)—C(110)	1.413 (15)	C(44)—C(45)	1.361 (19)
O(18)—Ni(1)—O(28)	172.4 (2)	N(11)—Ni(1)—N(31)	172.0 (3)
O(18)—Ni(1)—N(11)	80.1 (3)	N(21)—Ni(1)—N(31)	93.6 (3)
O(28)—Ni(1)—N(11)	95.5 (3)	O(18)—Ni(1)—N(41)	93.2 (3)
O(18)—Ni(1)—N(21)	93.3 (3)	O(28)—Ni(1)—N(41)	92.9 (3)
O(28)—Ni(1)—N(21)	80.3 (3)	N(11)—Ni(1)—N(41)	89.7 (3)
N(11)—Ni(1)—N(21)	88.7 (3)	N(21)—Ni(1)—N(41)	172.9 (3)
O(18)—Ni(1)—N(31)	92.1 (3)	N(31)—Ni(1)—N(41)	88.9 (3)
O(28)—Ni(1)—N(31)	92.4 (3)		
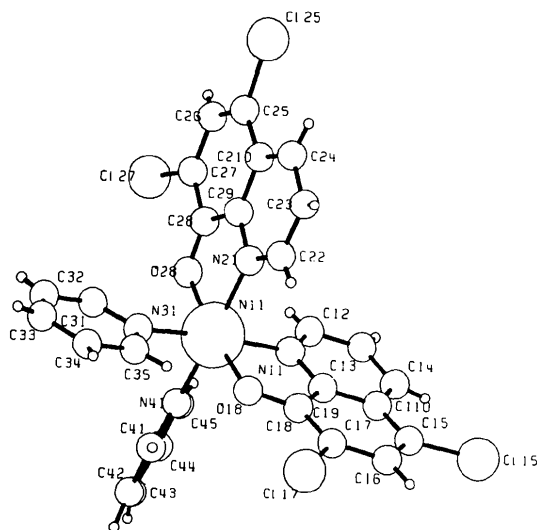
Fig. 1. View of the complex showing the nickel coordination and the atomic numbering.

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Structure of Sodium 1,1-Dicyanoethylene-2,2-dithiolate Trihydrate

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Abstract. $Na_2C_4N_2S_2.3H_2O$, $M_r = 240 \cdot 21$, monoclinic, $I2/m$, $a = 8 \cdot 750$ (1), $b = 7 \cdot 588$ (1), $c = 14 \cdot 479$ (2) Å, $\beta = 91 \cdot 00$ (2)°, $V = 961 \cdot 2$ Å³, $Z = 4$, $D_m = 1 \cdot 70$, $D_x = 1 \cdot 66$ Mg m⁻³, $\lambda(Ag\ K\alpha) = 0 \cdot 5591$ Å, $\mu = 0 \cdot 26$ mm⁻¹, $F(000) = 488$, room temperature, $R = 0 \cdot 045$ for 650 observed reflections up to $(\sin\theta)/\lambda = 0 \cdot 5527$ Å⁻¹. The 1,1-dicyanoethylene-2,2-dithiolate ligand (dedt) is planar with symmetry C_s. The structure contains two crystallographically different Na^+ ions at the centres of distorted octahedra, $NaO_2N_2S_2$ and NaO_4NS. The water molecules are involved in two approximately linear O—H⋯S hydrogen bonds (H⋯S = 2·25 and 2·50 Å) and one O—H⋯N hydrogen bond (H⋯N = 1·94 Å).

Introduction. This study was stimulated by the fact that the polydentate ligand dedt is thought to be a planar delocalized system while the geometry in the solid state is affected by various intermolecular and packing effects. In the series $M(\text{dedt}).n\text{H}_2\text{O}$ (M = Ca, Sr, n = 5; M = Ba, n = 3) dedt shows considerable deviations from planarity (Hummel & Wolf, 1985) while in $K_2(\text{dedt}).H_2O$ the ligand has approximate C_{2v} symmetry (Hummel, 1985). It might be expected that deviations from planarity of the $(S_2C_4N_2)^{2-}$ anion should increase with decreasing size of the counterion although this trend is not observed in the series of compounds with alkaline-earth cations.

Experimental. Single crystals of $Na_2(\text{dedt}).3H_2O$ from ethanol (Söderbäck, 1963). Crystal 0·08 × 0·08 × 0·08 mm. D_m determined pycnometrically. Precession photographs. Monoclinic, Laue class $2/m$, systematic extinctions hkl, $h + k + l = 2n + 1$, space group $I2/m$. PW 1100 four-circle diffractometer, graphite-monochromatized Ag $K\alpha$ radiation, ω scan, scan width $(1 \cdot 00 + 0 \cdot 20 \tan\theta)°$. Cell dimensions based on 25 high-indexed diffractometer-measured intensities ($7 \le \theta \le 12°$). 2833 symmetry-dependent reflections $(-16 \le h \le 16, -8 \le k \le 8, -9 \le l \le 9; 2 \le \theta \le 18°)$ averaged to give 722 symmetry-independent reflections, $R_{int} = 0 \cdot 030$. Three standard reflections, no significant