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Structure of {1-[(2-Hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O',N}-piperidinenickel(II)

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Abstract. [Ni(C₅H₁₁N)(C₁₇H₁₁NO₂)], $M_r = 405.12$, monoclinic, $P2_1/n$, $a = 10.471$ (1), $b = 15.524$ (2), $c = 12.554$ (1) Å, $\beta = 113.07$ (1)°, $V = 1877.5$ Å³, $Z = 4$, $F(000) = 848$, $D_m = 1.43$ Mg m⁻³ (pycnometrically), $D_x = 1.433$ Mg m⁻³, $\text{Mo } K\alpha = 0.7107$ Å, $\mu = 1.043$ mm⁻¹, $T = 293$ K, $R = 0.138$, $wR = 0.042$ for 3241 unique diffractometer data [$I > 1\sigma(I)$]. Nickel is in a slightly distorted square-planar environment of two oxygens [1.804(4) and 1.830(4) Å] and two nitrogens [1.848(4) and 1.947(4) Å] with O—Ni—N angles between 87.6(2) and 95.1(2)°. Ni is 0.033 Å out of the plane of its ligands.

Introduction. Copper(II) and nickel(II) ions react with tridentate anionic Schiff bases, giving dimerized complexes with square planar configurations (Maggio, Pizzino & Romano, 1974). The same authors report that *N*-(2-hydroxyphenyl)salicylaldimine reacts with the nickel(II) ion giving a pseudo-octahedral complex by polymerization. The purpose of our study is to understand what happens when the nickel(II) ion reacts with both the monodentate ligand piperidine and the tridentate ligand *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine. As an example we took the complex formed by the ligands *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine and piperidine with the nickel(II) ion.

Experimental. Suitable crystals were obtained directly from the synthesis of the compound. A solution of 0.01 mol *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine in 200 ml pure methanol was prepared and 0.6 ml piperidine was slowly added

to the solution, 0.01 mol Ni(CH₃COO)₂·4H₂O was dropwise dissolved in 20 ml hot methanol. The mixture of the two solutions was then refluxed for three hours. Red crystals were formed during the reflux operation.

A crystal of dimensions 0.15 × 0.15 × 0.08 mm was sealed in a Lindemann-glass capillary, 25 reflections with $2\theta > 18^\circ$ were used for the determination of the cell parameters, one standard reflection ($2\bar{3}\bar{1}$), no decomposition by X-rays, 4569 measured reflections ($-14 \leq h \leq 1$; $0 \leq k \leq 20$; $-16 \leq l \leq 16$; $R_{\text{int}} = 0.016$) resulted in 3241 unique reflections (of 4823 theoretically possible ones) with intensities $I > \sigma(I)$ which were used for the structure analysis; Nicolet R3 computer-controlled diffractometer, $2\theta/\theta$ scan, $2\theta_{\text{max}} = 56^\circ$; 4° min^{-1} ; no correction for extinction; empirical absorption correction according to the ψ method (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968); $T_{\text{min}}, T_{\text{max}} = 0.77, 0.87$. The phase problem was solved by direct methods (Sheldrick, 1983); all the non-H atoms were located in the first electron density synthesis (*E* map). After a few cycles of least-squares refinement the H atoms could be included from a difference electron density synthesis. The parameter refinement was performed by the cascade least-squares method (Sheldrick, 1983), anisotropic atomic displacement parameters of the non-H atoms were refined, least-squares refinement on $|F|$, 245 parameters, $w = 1/\sigma^2(|F|)$ based on counting statistics, $R = 0.138$, $wR = 0.042$, $S = 1.38$; max. $\Delta/\sigma = 0.1$, the ten largest peaks in the final difference electron density synthesis were between 0.74 and 0.33 e Å⁻³. All calculations and drawings

Table 1. Positional and equivalent isotropic displacement parameters (\AA^2) with e.s.d.'s in parentheses
$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
C01	1-0772 (5)	0-5829 (4)	0-4455 (5)	0-044 (3)
C02	1-0511 (6)	0-5733 (4)	0-3262 (5)	0-054 (4)
C03	1-1400 (5)	0-5190 (4)	0-2956 (5)	0-063 (4)
C04	1-2498 (6)	0-4772 (4)	0-3750 (5)	0-068 (4)
C05	1-2799 (6)	0-4845 (4)	0-4965 (5)	0-060 (4)
C06	1-1929 (5)	0-5372 (3)	0-5325 (5)	0-048 (3)
C07	1-2270 (6)	0-5432 (4)	0-6524 (5)	0-058 (4)
C08	1-3368 (6)	0-4993 (4)	0-7314 (6)	0-071 (4)
C09	1-4205 (6)	0-4472 (4)	0-6956 (6)	0-073 (5)
C10	1-3920 (6)	0-4405 (4)	0-5796 (6)	0-077 (5)
C11	0-9931 (5)	0-6385 (3)	0-4799 (4)	0-042 (3)
C12	0-8179 (5)	0-7447 (4)	0-4527 (5)	0-042 (3)
C13	0-7152 (6)	0-7879 (4)	0-3596 (5)	0-051 (4)
C14	0-6372 (6)	0-8506 (4)	0-3852 (5)	0-065 (4)
C15	0-6602 (6)	0-8700 (4)	0-4989 (5)	0-066 (4)
C16	0-7591 (6)	0-8257 (4)	0-5885 (5)	0-063 (4)
C17	0-8407 (6)	0-7633 (4)	0-5667 (5)	0-055 (4)
C18	0-6950 (6)	0-6321 (4)	0-0152 (5)	0-076 (5)
C19	0-6431 (6)	0-6470 (5)	-0-1148 (5)	0-088 (5)
C20	0-7600 (6)	0-6782 (4)	-0-1464 (4)	0-078 (4)
C21	0-8288 (6)	0-7564 (4)	-0-0774 (5)	0-082 (4)
C22	0-8767 (6)	0-7402 (4)	-0-0518 (5)	0-071 (4)
N1	0-8925 (4)	0-6852 (3)	0-4110 (3)	0-043 (2)
N2	0-7648 (5)	0-7079 (3)	0-0851 (4)	0-062 (3)
Ni1	0-8301 (1)	0-6897 (1)	0-2515 (1)	0-051 (1)
O1	0-9538 (4)	0-6124 (3)	0-2420 (3)	0-058 (3)
O2	0-6992 (4)	0-7677 (3)	0-2518 (3)	0-059 (2)

were performed on a NOVA 3/12 computer with the *SHELXTL* programs (Sheldrick, 1983); the scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). The final atomic positional parameters are given in Table 1, and bond lengths and angles in Table 2.* The difference between R and wR is relatively large, because we took all reflections into account, which were larger than their e.s.d.'s calculated from counting statistics.

Discussion. Fig. 1 shows the structure of the molecule. The monodentate and the tridentate ligands are coordinated to nickel(II). The configuration of the Ni atom is a distorted square plane. The crystal structure consists of discrete molecules (Fig. 2).

In Table 3 the bond lengths of several complexes of N -substituted salicylaldimines are compared with our values. The Ni—O distances of 1.830 and 1.804 \AA found by us agree with the values in these square-planar coordinated complexes. The Ni—N1 bond length of 1.848 \AA , however, is definitely shorter than Ni—N2 and others from the literature. The

* Lists of structure factors, anisotropic atomic displacement parameters, H-atom coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53303 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

C01—C02	1.422 (8)	C13—O2	1.334 (6)
C01—C06	1.458 (6)	C13—C14	1.388 (8)
C01—C11	1.416 (8)	C14—C15	1.384 (8)
C02—O1	1.296 (5)	C15—C16	1.377 (6)
C02—C03	1.415 (8)	C16—C17	1.388 (8)
C03—C04	1.356 (6)	C18—N2	1.478 (7)
C04—C05	1.435 (8)	C18—C19	1.522 (7)
C05—C06	1.424 (8)	C19—C20	1.507 (9)
C05—C10	1.405 (7)	C20—C21	1.501 (7)
C06—C07	1.407 (7)	C21—C22	1.520 (7)
C07—C08	1.370 (7)	C22—N2	1.477 (8)
C08—C09	1.390 (10)	N1—Ni1	1.848 (4)
C09—C10	1.370 (9)	N2—Ni1	1.947 (4)
C11—N1	1.292 (5)	Ni1—O2	1.830 (4)
C12—N1	1.434 (7)	Ni1—O1	1.804 (4)
C12—C13	1.410 (6)	Ni1—O2	1.830 (4)
C12—C17	1.386 (7)		
C02—C01—C06	119.9 (5)	C14—C13—O2	123.2 (4)
C02—C01—C11	119.9 (4)	C13—C14—C15	120.7 (4)
C06—C01—C11	120.1 (5)	C14—C15—C16	120.4 (5)
C01—C02—C03	118.2 (4)	C15—C16—C17	120.7 (5)
C01—C02—O1	125.2 (5)	C12—C17—C16	118.6 (4)
C03—C02—O1	116.6 (5)	C19—C18—N2	113.7 (5)
C02—C03—C04	122.9 (5)	C18—C19—C20	110.2 (4)
C03—C04—C05	120.9 (5)	C19—C20—C21	111.3 (5)
C04—C05—C06	118.8 (4)	C20—C21—C22	111.4 (4)
C04—C05—C10	121.5 (6)	C21—C22—N2	113.1 (4)
C06—C05—C10	119.7 (5)	C11—N1—C12	122.3 (4)
C01—C06—C05	119.2 (5)	C11—N1—Ni1	126.6 (4)
C01—C06—C07	123.8 (5)	C12—N1—Ni1	111.1 (3)
C05—C06—C07	116.9 (4)	C18—N2—C22	111.4 (4)
C06—C07—C08	122.0 (6)	C18—N2—Ni1	113.9 (3)
C07—C08—C09	120.8 (6)	C22—N2—Ni1	111.7 (3)
C08—C09—C10	119.0 (5)	N1—Ni1—O2	88.3 (2)
C05—C10—C09	121.6 (6)	N1—Ni1—N2	173.8 (2)
C01—C11—N1	125.4 (5)	N1—Ni1—O1	95.1 (2)
C13—C12—C17	121.5 (5)	N2—Ni1—O1	89.1 (2)
C13—C12—N1	110.6 (4)	N2—Ni1—O2	87.6 (2)
C17—C12—N1	127.9 (4)	O1—Ni1—O2	176.6 (1)
C12—C13—C14	118.0 (5)	C02—O1—Ni1	127.8 (4)
C12—C13—O2	118.7 (5)	C13—O2—Ni1	111.2 (3)

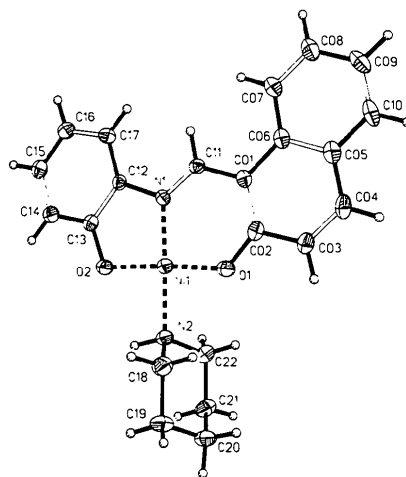


Fig. 1. Molecular structure, showing 30% probability thermal ellipsoids for the non-H atoms and the atom-numbering scheme.

reason for this is that the two oxygens, coordinated to the Ni atom, are drawing the whole ligand and therefore also the N atom towards the Ni atom.

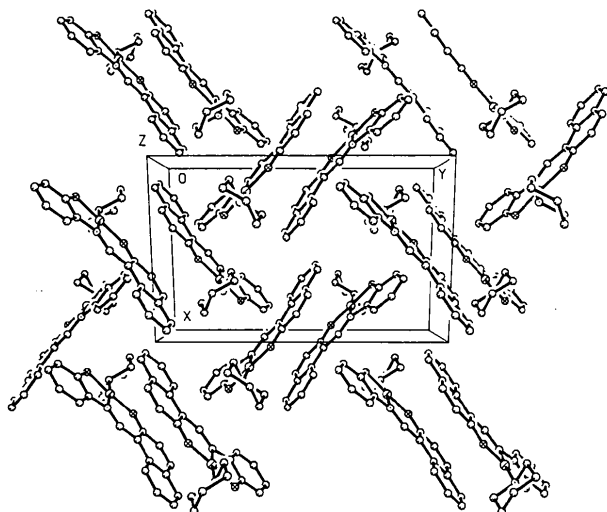


Fig. 2. View of the crystal structure, viewed parallel to the *z* axis.

An inquiry of the Cambridge Structural Database (1989) for octahedrally coordinated Ni^{II} ions resulted in 104 compounds with Ni—O and/or Ni—N bonds. The average Ni—O and Ni—N distances are 2.084 and 2.110 Å, respectively. They are significantly longer than in the square-planar configuration.

The coordination of the ligands around the Ni atom is fairly planar, and the bonding angles of the ligands are between 87.6 and 95.1°. The Ni atom is 0.033 Å out of the plane of its ligands. The angles between the planar organic groups are smaller than 8°. The Ni atom deviates from these planes by less than 0.165 Å.

The piperidine ring has an almost ideal chair conformation: the perpendicular distances of the two

Table 3. Bond lengths (Å) in some nickel(II) complexes

	(I)	(II)	(III)	(IV)	
C01—C02	1.402 (6)	1.401 (7)	1.397 (5)	1.427 (6)	1.422 (8)
C01—C11	1.430 (5)	1.429 (4)	1.429 (4)	1.446 (6)	1.416 (8)
C02—O1	1.323 (5)	1.318 (5)	1.305 (4)	1.332 (5)	1.296 (5)
C11—N1	1.298 (5)	1.302 (5)	1.297 (4)	1.279 (6)	1.292 (5)
C12—C13					1.410 (6)
C12—N1					1.434 (7)
C13—O2					1.334 (6)
Ni1—N1	1.913 (4)	1.918 (4)	1.912 (3)	1.941 (3)	1.848 (4)
Ni1—N2					1.947 (4)
Ni1—O1	1.829 (2)	1.828 (2)	1.832 (2)	1.828 (3)	1.804 (4)
Ni1—O2					1.830 (4)

(I) Bis{*N*-[(1,3-dioxolan-2-yl)methyl]salicylaldiminato}nickel(II); (II) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-2-hydroxy-1-naphthaldiminato}nickel(II); (III) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-3-hydroxy-2-naphthaldiminato}nickel(II) (Fernandes-G., Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987); (IV) present work.

para positioned chair atoms from the plane of the other four atoms of the six-membered ring are between 0.608 and 0.650 Å. The ideal theoretical value is 0.726 Å.

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Structure of μ -Pyrazine-bis[(diethylenetriamine-*N,N',N''*)(diperchlorato-*O*)copper(II)]

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Abstract. [Cu₂(ClO₄)₄(C₄H₁₃N₃)₂(C₄H₄N₂)], *M_r* = 76.54 (5)^o, *V* = 690.0 (7) Å³, *F*(000) = 1648, *Z* = 1, 811.1, triclinic, *P* $\bar{1}$, *a* = 7.204 (4), *b* = 7.814 (5), *c* = 12.612 (5) Å, α = 87.90 (4), β = 89.08 (4), γ = 20.76 cm⁻¹, room temperature, *R* = 0.052 for 2489