

Bis[*N*-methyl-1-(methylimino)-9-phenaleneaminato]nickel(II)

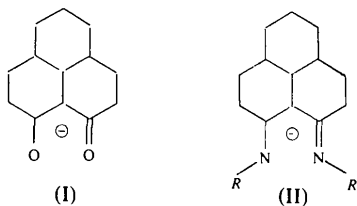
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Abstract. $C_{30}H_{26}N_4Ni$, $M_r = 501.28$, orthorhombic, $Pbcn$, $a = 18.556$ (3), $b = 10.356$ (2), $c = 12.030$ (2) Å (293 K), $Z = 4$, $D_c = 1.440$, $D_m = 1.44$ Mg m⁻³, $\mu(Mo K\alpha) = 0.868$ mm⁻¹. Full-matrix least-squares refinement with isotropic thermal parameters for H atoms and anisotropic parameters for all other atoms gave $R = 0.064$ and $R_w = 0.059$ for 211 variables and 1171 data [$I \geq 3\sigma(I)$]. The molecule has exact C_2 and approximate D_{2d} symmetry with distorted tetrahedral coordination of the Ni atom.

Introduction. 1,9-Diheterosubstituted phenalenes have potential as bidentate ligands able to confer unusual properties in their complexes with transition metals. The anion of 1-hydroxy-9-phenalene, (I), is strongly chelating and readily forms planar $M(L-L)_2$ and octahedral $M(L-L)_2X_2$, $M(L-L)_3$ complexes ($X = H_2O$, C_5H_5N) with a variety of divalent and trivalent metal ions (Demura, Kawato, Kanatomi & Murase, 1975). Nitrogen and sulphur donor analogues of (I) and (II) have recently been synthesized (Franz & Martin, 1978; Martin, 1981) and their complexes with a variety of electron-rich transition metals investigated. Bite angles for these ligands (*ca* 90°) might be expected to favour planar coordination of d^8 metal ions but the preference of bulky substituents on the donor atoms (as in II) will generally result in tetrahedral coordination. In the title complex, which was prepared by the method of Franz & Martin (1979), the R groups in (II) are both methyls.



Crystals grown from dichloromethane solution are acicular, orthorhombic, with well developed faces

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{110} and {001}. Crystals appear dark green in reflected light but powdered samples are orange-brown. The crystal used for data collection had dimensions 0.026 [$\perp(110)$] \times 0.040 [$\perp(\bar{1}10)$] \times 0.250 [$\perp(001)$] mm.

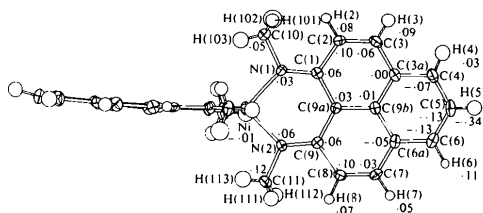
Reflection intensities were recorded on a Picker FACS-1 diffractometer in the θ - 2θ continuous scan mode (scan velocity 2° min⁻¹ 2θ , 2×10 s background counts at scan extremes, $3 < 2\theta < 55^\circ$, Mo $K\alpha$ radiation, graphite-crystal monochromator, $T = 293 \pm 1$ K, $+h,+k,+l$ forms recorded, 3139 reflections). Unit-cell dimensions were derived from the least-squares analysis of the setting angles of 12 well centred reflections with $35 < 2\theta < 45^\circ$ (Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, $T = 293 \pm 1$ K). Standard reflection intensities (three, indices: 400, 020 and 002) did not vary significantly during data collection. Reflection data with $I \geq 3\sigma(I)$ and with background imbalance $\Delta < 3\sigma(\Delta)$ were accepted and reduced to $|F_o|$ and $\sigma(F_o)$ values with an instrumental uncertainty constant $\rho = 0.04$ assumed (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). Data were also corrected for absorption (de Meulenaer & Tompa, 1965), but not for extinction: transmission factors ranged from 0.956 to 0.984. Because of the small crystal size the statistical counting precision is proportionately low and only 1183 (of 3139) reflections satisfied the acceptance criteria. The statistical R factor (R_s) for these reflections (Robertson & Whimp, 1975) was 0.056. The systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$) and Laue group (mmm) uniquely define the orthorhombic space group $Pbcn$ (No. 60). With $Z = 4$, molecules are constrained to have either exact C_i or exact C_2 symmetry. In the present instance the molecule has exact C_2 symmetry.

Coordinates for all non-H atoms were determined using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) and refined by full-matrix least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \{\sigma(F_o)\}^{-2}$. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). H atoms were located from a difference Fourier synthesis. In the final scattering model all non-H atoms were refined with anisotropic thermal parameters and

Table 1. Final atomic coordinates and isotropic thermal parameters

	x	y	z	B_{eq}^* (Å ²)
Ni	0.0	0.6273 (1)	0.75	3.9
N(1)	0.0628 (3)	0.7271 (5)	0.6569 (4)	3.3
N(2)	0.0790 (3)	0.5289 (5)	0.8069 (5)	3.5
C(1)	0.1342 (3)	0.7208 (6)	0.6467 (5)	3.0
C(2)	0.1706 (4)	0.8055 (7)	0.5694 (6)	3.7
C(3)	0.2428 (4)	0.8094 (8)	0.5593 (6)	4.3
C(3a)	0.2878 (3)	0.7278 (6)	0.6224 (6)	4.7
C(4)	0.3631 (4)	0.7353 (9)	0.6125 (8)	5.3
C(5)	0.4065 (4)	0.6569 (9)	0.6743 (8)	4.6
C(6)	0.3771 (3)	0.5702 (8)	0.7475 (8)	3.9
C(6a)	0.3024 (3)	0.5583 (7)	0.7602 (7)	3.9
C(7)	0.2713 (4)	0.4655 (7)	0.8297 (7)	3.0
C(8)	0.1997 (4)	0.4536 (7)	0.8410 (6)	2.9
C(9)	0.1492 (3)	0.5395 (6)	0.7872 (5)	3.5
C(9a)	0.1779 (3)	0.6342 (6)	0.7109 (5)	3.5
C(9b)	0.2556 (3)	0.6400 (7)	0.6968 (5)	3.1
C(10)	0.0221 (4)	0.8189 (10)	0.5892 (9)	4.5
C(11)	0.0548 (5)	0.4278 (9)	0.8841 (9)	4.9
B				
H(2)	0.140 (3)	0.867 (5)	0.529 (4)	3 (1)
H(3)	0.262 (3)	0.866 (6)	0.508 (5)	5 (2)
H(4)	0.378 (3)	0.794 (8)	0.560 (7)	6 (2)
H(5)	0.454 (4)	0.675 (7)	0.676 (6)	6 (2)
H(6)	0.407 (2)	0.510 (5)	0.788 (4)	2 (1)
H(7)	0.303 (3)	0.410 (5)	0.866 (4)	2 (1)
H(8)	0.184 (3)	0.393 (5)	0.897 (4)	2 (1)
H(101)	0.037 (3)	0.907 (6)	0.596 (5)	5 (2)
H(102)	0.031 (4)	0.801 (8)	0.507 (7)	9 (3)
H(103)	-0.024 (4)	0.800 (8)	0.610 (6)	6 (2)
H(111)	0.073 (4)	0.442 (7)	0.960 (6)	6 (2)
H(112)	0.074 (3)	0.336 (7)	0.861 (5)	5 (2)
H(113)	0.009 (4)	0.430 (6)	0.886 (6)	7 (2)

$$* B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$



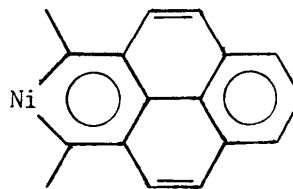
covalent ligands, is sterically precluded by the presence of the methyl substituents on the donor nitrogen groups. The molecule lies on a crystallographic twofold axis through the Ni atom and perpendicular to the long axis of the molecule. The Ni(*L*-*L*) moieties are slightly bowed (Fig. 1) and the angle between the Ni(*L*-*L*) planes is 84.7°. The mean Ni-N distance [1.916 (4) Å] is closer to the value expected for planar rather than tetrahedral nickel with donor imino sets, e.g. 1.896 (3) Å in planar bis- μ -[1,1,1,16,16,16-hexafluoro-4,13-dimethyl-2,15-bis(trifluoromethyl)-5,12-diazahexadeca-4,12-diene-2,15-diolato]dinickel(II) (Martin, Payne & Willis, 1978), *cf.* 1.974 (4) Å mean in tetrahedral bis[*N*-(3-methoxysalicylidene)isopropyliminato]nickel(II) (Ashida, Iwata, Yamane, Kakudo, Takeuchi & Yamada, 1976).

The tetrahedral coordination by N₄ donor groups is accompanied by a near-planar array of short intramolecular Ni-H contacts. The Ni...H distances [mean 2.56 Å; to H(103), H(113)] are within the range commonly ascribed to non-primary valence contacts (Bennett, Donaldson, Mason & Hitchcock, 1975). Bond angles at N(1), N(2) and at C(10), C(11) [N-C-H (contacting) = 104 (4)° mean] provide no evidence for attractive Ni...H interactions and the observed contacts must be, primarily, a consequence of non-bonding interactions to the other methyl H atoms. Nevertheless, the existence of these short Ni...H contacts may well serve to confer added stability to the complex by completing, *via* a predominantly electrostatic interaction, an 18-electron potential field about the metal ion (Bennett *et al.*, 1975; Robertson & Whimp, 1982).

To within experimental error the Ni(*L*-*L*) moieties have mirror symmetry about the Ni-C(5) vector. Differences between 'mirror' equivalent bond length and angle pairs (24 pairs not including H) in no case exceed twice the standard deviation of the difference. Differences are distributed about equally above and below their estimated probable errors and a probability plot of $\Delta i/\sigma(\delta i)$ has unit slope and zero intercept (Svensson, Abrahams, Bernstein & Haddon, 1979). Both observations are consistent with the e.s.d.'s having been accurately estimated.

The bond-length pattern in the phenalene moiety shows considerable similarity to that in 1-hydroxy-9-phenalene (Svensson *et al.*, 1979). The C-N distances [mean 1.330 (5) Å; similar to those in pyridine rings] and the short C(2)-C(3)/C(7)-C(8)

distances are both consistent with substantial structural contributions from the resonance form:



Extensive delocalization over the metallocycle ring would also account for the unusual shortness of the Ni-N bonds.

References

- ASHIDA, T., IWATA, S., YAMANE, T., KAKUDO, M., TAKEUCHI, A. & YAMADA, S. (1976). *Bull. Chem. Soc. Jpn.*, **49**, 3502-3506.
- BENNETT, M. J., DONALDSON, P. B., MASON, R. & HITCHCOCK, P. B. (1975). *Inorg. Chim. Acta*, **12**, L9-L10.
- BUSING, W. R. & LEVY, H. A. (1957). *J. Chem. Phys.* **26**, 563-568.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197-204.
- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOLFSON, M. M. (1973). *Acta Cryst.* **A29**, 231-234.
- DEMURA, Y., KAWATO, T., KANATOMI, H. & MURASE, I. (1975). *Bull. Chem. Soc. Jpn.*, **48**, 2820-2824.
- FRANZ, K. D. & MARTIN, R. L. (1978). *Tetrahedron*, **34**, 2147-2151.
- FRANZ, K. D. & MARTIN, R. L. (1979). Unpublished results. *International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- MCLAUGHLIN, G. M., TAYLOR, D. & WHIMP, P. O. (1977). *The ANUCRYS Structure Determination Package*, Research School of Chemistry, Australian National Univ., PO Box 4, Canberra, ACT 2600.
- MARTIN, J. W. L., PAYNE, N. C. & WILLIS, C. J. (1978). *Inorg. Chem.* **17**, 3467-3484.
- MARTIN, R. L. (1981). *Coord. Chem.* **20**, 255-265.
- MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014-1018.
- ROBERTSON, G. B. & WHIMP, P. O. (1975). *J. Am. Chem. Soc.* **97**, 1051-1059.
- ROBERTSON, G. B. & WHIMP, P. O. (1982). *Aust. J. Chem.* To be submitted.
- SVENSSON, C., ABRAHAMS, S. C., BERNSTEIN, J. L. & HADDON, R. C. (1979). *J. Am. Chem. Soc.* **101**, 5759-5764.