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Structural Investigation of a Nickel(II) Complex Containing a New Type of Terdentate Ligand with a Planar NNN Donor Set and Both Uni- and Bi-dentate Nitrato-groups. *X*-Ray Analysis of 2,6-Bis-(phenyliminoethyl)-pyridine(dinitrato)nickel(II)

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Summary Spectral and crystallographic data are presented for the title nickel(II) complex containing a new terdentate ligand with a planar NNN donor set and both unidentate and almost symmetrically bidentate nitrato-groups.

THE synthesis and versatility of some new terdentate NNN donor ligands derived from 2,6-diacetylpyridine have recently been reported.[1] As part of our study of the co-ordinating ability of these 2,6-diacetylpyridinebis(imines), we have isolated some nitrato-derivatives of the 2,6-bis-(1-phenyliminoethyl)pyridine ligand ($L{=}C_{21}H_{19}N_3$) that display a variety of nitrato-bonding types.[2] The complexes $[LM(NO_3)_2]$ ($M{=}Ni^{II}$, Zn^{II}) are of particular interest since few metal species are suggested[3] to contain both unidentate and symmetrically bidentate nitrato-groups. In the series of related complexes $[(C_5H_5N)_3M(NO_3)_2]$ ($M = Co^{II}$, Cu^{II}, Zn^{II}), *X*-ray structural studies[4] have shown that one nitrato-group is unidentate whereas distinct but differing degrees of asymmetry occur in the bidentate nitrato–metal bonding. The seven-co-ordinate vanadium(V) complex $[VO(NO_3)_3MeCN]$ is the only complex in which both unidentate and almost symmetrically bidentate (V–O bond length differences 0·02, 0·05 Å) nitrato-bonding has been previously established.[5] We report here the crystal structure of the complex $[LNi(NO_3)_2]$ which contains a new terdentate NNN donor ligand and both unidentate and almost symmetrically bidentate nitrato-groups.

The dark red-brown crystals of $C_{21}H_{19}N_5NiO_6$ are monoclinic, space group $P2_1/c$, $a = 11{\cdot}037(2)$, $b = 14{\cdot}662(4)$, $c = 16{\cdot}039(3)$ Å, $\beta = 122{\cdot}66(1)^\circ$; $Z = 4$. The structure was solved by the heavy-atom method using 2148 observed reflections $[I > 3\sigma(I)]$ measured on a Hilger and Watts automatic diffractometer with graphite-monochromatized Mo-K_α radiation. Refinement by block-diagonal least-squares techniques, using anisotropic thermal parameters for the nonhydrogen atoms and with hydrogen atoms in calculated positions with isotropic thermal parameters, gave a final R value of 0·040 over the observed reflexions.

The nickel co-ordination is distorted from regular octahedral (Figure) by the bite of the NNN terdentate ligand. The plane formed by atoms N(1), Ni, O(41), O(42) makes a dihedral angle of 89·9° with the plane formed by the Ni atom and the NNN donor set of the terdentate ligand. The nickel six-co-ordination is completed by unidentate [Ni–O(51), 2·027(5) Å] and near symmetrical bidentate [Ni–O(41), 2·138(5); Ni–O(42), 2·070(4) Å] nitrato-groups. The degree of symmetrical character is reflected in the Ni–O(41)–N(4) and Ni–O(42)–N(4) angles, 90·1(4) and 93·1(3)°, respectively (unidentate co-ordination would give 110°[2]), as well as in the N(4)–O(41) and N(4)–O(42) bond lengths of 1·271(5) and 1·276(8) Å which are not significantly different. The small degree of asymmetry is also reflected in the Ni–O(41) and Ni–O(42) bond length difference (0·068 Å) when compared to the Co–O bond length differences (0·104 Å) in [$(C_5H_5N)_3Co(NO_3)_2$] whose bidentate nitrato-group exhibits the least amount of asymmetry in the series quoted in ref. 4.

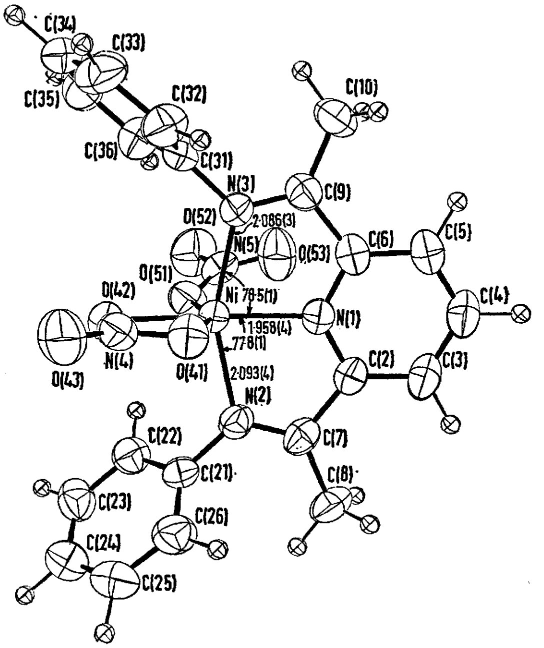

FIGURE. A view of the 2,6-bis-(1-phenyliminoethyl)pyridine (dinitrato)nickel(II) molecule. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms have been included with isotropic B values of 1·0 Å.[2]

The $LNi(NO_3)_2$ complex gave $\mu_{eff} = 3{\cdot}17$ B.M., $\Lambda_M = 27\ \Omega^{-1}\ cm^2$ (indicating partial dissociation in nitromethane) and solid state electronic spectral bands at 11,500, 12,700 (broad d) and 20,000 cm^{-1} assignable to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ in a pseudo-octahedral field. I.r. bands at 1502 cm^{-1} (shoulder at 1512 cm^{-1}) and 1272 cm^{-1} can be assigned to N–O stretching frequencies of the bidentate nitrato-group while bands at 1455 and 1298 cm^{-1} are attributed to the unidentate nitrato-group.[2,3]

The related compound of formulation [$LNiBr(NO_3)$] [$\mu_{eff} = 3{\cdot}21$ B.M., $\Lambda_M = 9\ \Omega\ cm^2$ and solid state electronic spectral bands at 11,250, 12,100, (broad d) and 19,200 cm^{-1}] shows only the i.r. bands characteristic of bidentate nitrato-groups at 1485 and 1280 cm^{-1}. The terdentate behaviour of the NNN donor ligand is indicated by the typical pattern in the $C\underline{\cdots}N$ region of the i.r. spectra of all [LMX_2] and related [ML_2][BF_4]$_2$ complexes (two bands at *ca.* 1640 and 1590 cm^{-1}) and the downfield shift of the singlet methyl resonance in the ^1H n.m.r. spectra of the analogous zinc complexes [δ 2·63 for $LZn(NO_3)_2$ in nitromethane].[1]

Correlation of i.r. and Raman spectral data (depolarization ratios and intensities of N–O bands) of several related complexes is being undertaken to establish the generality of the structure proved for [$LNi(NO_3)_2$].

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