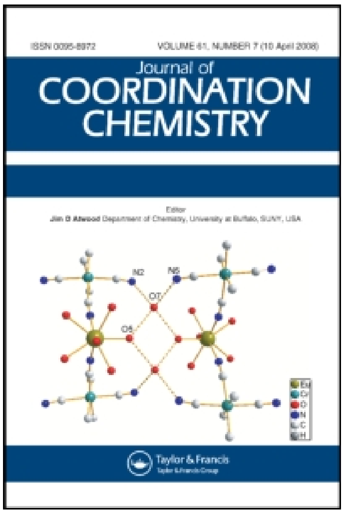

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STRUCTURE, MAGNETIC AND SPECTRAL PROPERTIES OF ETHYL PHOSPHITE NITRATE TRI(1,10-PHENANTHROLINE) NICKEL(II) SOLVATE TRIHYDRATE: $[Ni(PHEN)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$

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The compound, $[Ni(phen)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$, was obtained by the reaction of $Ni(NO_3)_2$, $C_2H_5OP(OH)_2$ and 1,10-phenanthroline in 95% EtOH solution, and was characterized using IR and UV spectra and magnetic susceptibility measurements over the temperature range 75–300 K. The red crystal is triclinic of space group $P\bar{1}$, with lattice parameters $a = 12.462(3)$, $b = 13.416(3)$, $c = 13.422(3)$ Å, $\alpha = 75.88(3)$, $\beta = 64.75(3)$, $\gamma = 65.87(3)°$, and $Z = 2$. The coordinated cation contains a six-coordinate nickel atom chelated by three phenanthroline ligands, resulting in a distorted octahedral arrangement with the six Ni–N distances ranging from 2.086(2) to 2.113(3) Å. In addition to the nickel coordination complex, there are two anions, NO_3^- and $C_2H_5OP(O)O^-$, and three water molecules which complete the crystal structure. In the solid state, the title compound forms a three dimensional network structure through hydrogen bonds. The intermolecular hydrogen bonds connect the $[Ni(phen)_3]^{2+}$, NO_3^-, $C_2H_5OP(O)O^-$ and H_2O molecules.

Keywords: Nickel complexes; 1,10-phenanthroline ligand; Hydrogen bond network

INTRODUCTION

Metal complexes of the type $[M(LL)_3]^{n+}$, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents that can recognize and cleave DNA [1,2]. The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing easy access for understanding DNA-bonding and cleavage [3]. The interaction of the optically active tri(phenanthroline)–Ni(II)

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complex ion, $[Ni(phen)_3]^{+2}$, with different polyelectrolytes in the dilute aqueous solution has been studied [4]. In this paper, we describe the crystal structure of ethyl phosphite nitrate tri(1,10-phenanthroline) nickel(II) solvate trihydrate, $[Ni(phen)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$, and discuss its IR, UV and magnetic properties.

EXPERIMENTAL

Physical Measurements

Elemental analysis was performed using a PE-240C elemental analyzer. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. Ultraviolet spectra were recorded on a Shimadzu UV-240 spectrophotometer. Magnetic measurements were carried out on a CHAN-2000 Faraday balance with $Ni(en)_3S_2O_3$ as a standard at a magnetic field of 6000 G. The resulting susceptibility was corrected for underlying diamagnetism.

Preparation of $[Ni(phen)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$

The reagents $Ni(NO_3)_2 \cdot 6H_2O$ (A.R.), and phen (A.R.) were commercially available. $C_2H_5OP(OH)_2$ was prepared using a literature method [5]. To a warm solution of phen (2.97 g, 15 mmol) in EtOH (50 mL) was added $[Ni(NO_3)_2 \cdot 6H_2O]$ (1.45 g, 5 mmol) and $C_2H_5OP(OH)_2$ (1.2 g, 10 mmol). The mixture was refluxed for 20 min and the red solution was filtered. Upon slow evaporation of the solvent at room temperature, a red crystalline solid appeared several weeks later and was separated by filtration. The C, H and N contents were determined by elemental analysis (Found: C, 54.16; H, 4.12; N, 10.48%. Calcd. C, 54.65; H, 4.20; N, 10.78%).

Crystallographic Data Collection and Solution of Structure

Crystallographic data for $[Ni(phen)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$, are summarized in Table I. The selected crystal was mounted on a Siemens P4 diffractometer. Reflection data were measured at 293 K, using graphite monochromated MoK_α ($\lambda = 0.71073$ Å) radiation and a ω-2θ scan mode. Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using SHELXTL5 [6].

The structure was solved by direct methods using SHELXS97 [7]. Non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method [8]. Hydrogen atoms were placed in calculated positions and were assigned fixed isotropic thermal parameters of 1.2 times the equivalent isotropic U of the atom to which it is attached and allowed to ride on the respective parent atom. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-squares cycle gave $R = 0.0396$, $R_w = 0.1308$ for 6477 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0797P)^2 + 0.9292P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Table for X-Ray Crystallography* [9].

TABLE I Summary of crystallographic results for the title compound

Color/shape	Red/prism
Empirical formula	$C_{38}H_{35}N_7NiO_9P$
Formula weight	823.41
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 12.462$ (3) Å, $b = 13.416$ (3) Å, $c = 13.422$ (3) Å $\alpha = 75.88$ (3). $\beta = 64.75$ (3). $\gamma = 65.87$ (3).
Volume	1845.7 (6)A^3
Z, Calculated density	2, 1.482 Mg/m^3
Absorption coefficient	0.636 mm^{-1}
F(000)	854
Crystal size	0.3 × 0.3 × 0.2 mm
Theta range for data collection	1.67–24.97°
Limiting indices	$0 \le h \le 14,\ -14 \le k \le 15,$ $-14 \le l \le 15$
Reflections collected/unique	6809/6477 [R(int) = 0.0125]
Completeness to theta = 24.97	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6477/0/505
Goodness-of-fit on F^2	1.166
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0396$, $wR2 = 0.1308$
R indices (all data)	$R1 = 0.0551$, $wR2 = 0.1393$
Largest diff. peak and hole	0.578 and − 0.351 eA^{-3}

RESULTS AND DISCUSSION

Spectroscopic Properties

IR and UV data support the conclusion that the reaction of $Ni(NO_3)_2$, $C_2H_5OP(OH)_2$ and phenanthroline yield the ethyl phosphite nitrate tris(1,10-phenanthroline) nickel(II) complex. The solution ultraviolet spectrum of the title compound in EtOH exhibits three intense bands at 205, 227 and 268 nm. These bands belong to π–π* or n–π* orbital transitions of the phen ligand [10]. The weak band at 295 nm is due to a charge-transfer transition. The *d–d* band at 222 nm might be taken as evidence for octahedral nickel(II) complexes, while the parent four-coordinate nickel(II) complexes show the *d–d* band at 400 nm [11]. The IR spectrum exhibits characteristic strong bands at 1584 (C=C), 1514, 1423 (C=N), 850 ($\nu_{C\text{-}H}$ benzene ring) and 720 cm^{-1} ($\nu_{C\text{-}H}$ pyridine ring) for the coordinated phen ligands [12]. The bands at 1514 and 1423 cm^{-1} are shifted from their positions for the free ligand (1503 and 1420 cm^{-1}), indicating nitrogen coordination. The bands at 1354 and 1052 cm^{-1} are characteristic absorptions of the nitrate anion [13]. The bands at 2880, 2330, 1201 and 539 cm^{-1} belong to the ethyl phosphite anion. A medium absorption band at 1569 cm^{-1} may be assigned to non-coordinated water, consistent with the results of crystal structure determinations mentioned below.

Magnetic Properties

The room-temperature magnetic moment of $[Ni(phen)_3]NO_3 \cdot C_2H_5OP(O)O \cdot 3H_2O$ is in the range normally found for octahedral nickel(II) complexes. The magnetic susceptibility of the title compound as a function of temperature is shown in Fig. 1.

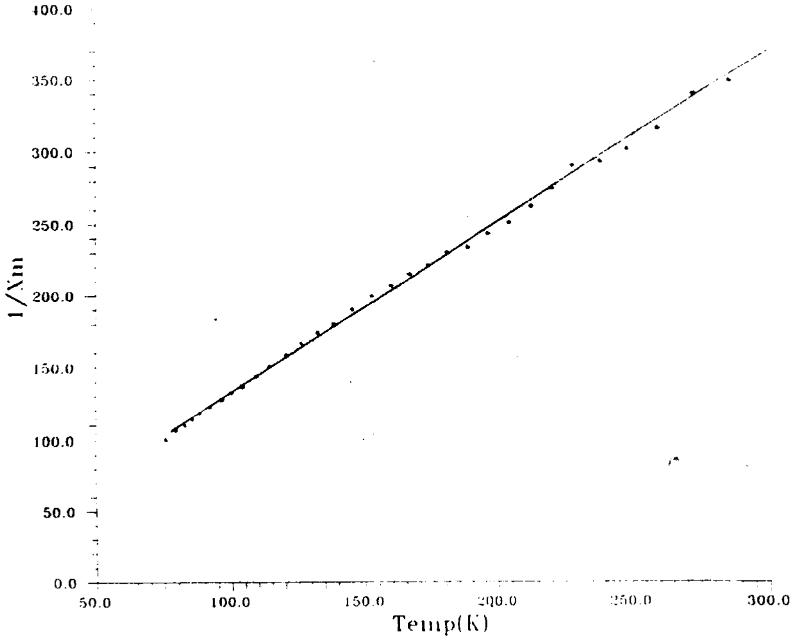

FIGURE 1 Inverse molar susceptibility *vs*. temperature for the title compound in the range 75–300 K.

The straight line is a least-squares fit to the data. The complex obeys the Curie–Weiss Law, with $X_m = C/(T-\theta)$ ($C = 0.8282$ and $\theta = -9.0483$ K, derived from the straight line). The corresponding value of μ_{eff} (300K) calculated from the slope, is 2.56 B.M., which is within with the range normally found for octahedral nickel(II) complexes [14]. The decrease of the effective magnetic moment is from 2.56 HB at room temperature to 2.45 HB at 75 K; the negative Weiss constant may also indicate the presence of a weak antiferromagnetic interaction.

Description of the Structure of $[\text{Ni(phen)}_3]\text{NO}_3 \cdot \text{C}_2\text{H}_5\text{OP(O)O} \cdot 3\text{H}_2\text{O}$

Figure 2 shows a perspective view of the title compound with the atom numbering scheme. Selected bond lengths (Å) and bond angles (°) are presented in Table II. The title compound crystallized with one $[\text{Ni(phen)}_3]^{2+}$ cation, one nitrate and one ethyl phosphite anion, and three molecules of water. There is no evidence of covalent bonding interactions between anions and cations, however, there are close contacts, probably indicative of hydrogen bonding between the hydrate molecules and anions, and also between the oxygen atoms of two anions and surrounding phenanthroline carbon atoms. The Ni atom exhibits a slightly distorted octahedral geometry in which the Ni atom is coordinated to six nitrogen atoms from three phenanthroline molecules. The Ni atom is 0.109(3) Å out of the plane defined by N1, N2 and N5. The Ni–N bond lengths are normal. One $[\text{Ni(phen)}_3]^{2+}$ contains a six-coordinate nickel atom chelated by three phen ligands with the Ni–N bond distance ranging from 2.086(2) to 2.113(3) Å in good agreement with previous reported structures [15–17]. The three

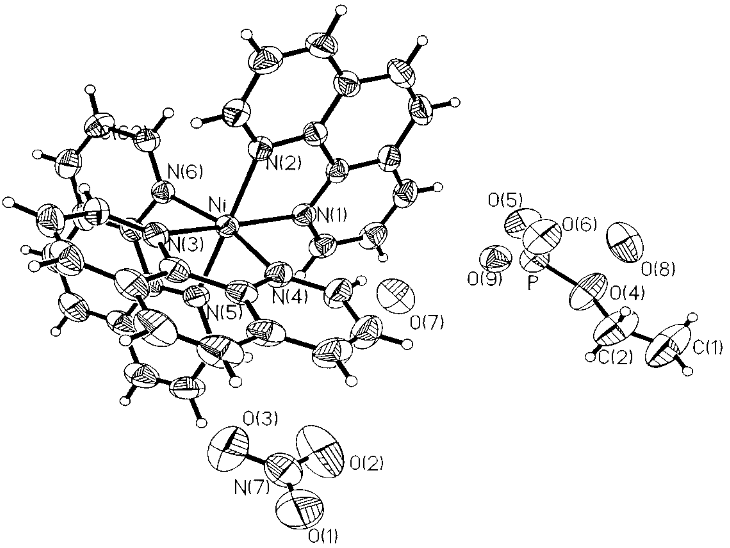

FIGURE 2 Molecular structure for the title compound with the atom numbering scheme.

TABLE II Selected bond length (Å), possible hydrogen bonds (Å) and bond angles (°) of the title compound

Ni–N(4)	2.086(2)
Ni–N(6)	2.090(2)
Ni–N(1)	2.093(2)
Ni–N(2)	2.096(2)
Ni–N(3)	2.102(2)
Ni–N(5)	2.113(3)
N(1)–C(15)	1.353(4)
C(14)–C(15)	1.435(4)
C(2)–C(1)	1.437(8)
N(4)–Ni–N(6)	167.49(9)
N(4)–Ni–N(1)	93.2(1)
N(6)–Ni–N(1)	96.65(9)
N(4)–Ni–N(2)	93.7(1)
N(6)–Ni–N(2)	95.6(1)
N(1)–Ni–N(2)	79.6(1)
N(4)–Ni–N(3)	79.8(1)
N(6)–Ni–N(3)	91.3(1)
N(1)–Ni–N(3)	170.1(1)
N(2)–Ni–N(3)	93.8(1)
N(4)–Ni–N(5)	92.1(1)
N(6)–Ni–N(5)	79.4(1)
N(1)–Ni–N(5)	95.1(1)
N(2)–Ni–N(5)	172.3(9)
N(3)–Ni–N(5)	92.2(1)

phen ligands are bonded to nickel, forming five-member chelate rings. The bite angles between the three phenanthroline chelate rings and the nickel atom are similar [79.6(1)°, 79.8(1)° and 79.4(1)° for angles N1–Ni–N2, N3–Ni–N4 and N5–Ni–N6, respectively]. However, there are significant deviations from linearity for the *trans* atoms with angles N1–Ni–N3, N2–Ni–N5 and N4–Ni–N6 at 170.1(1)°, 172.3(9)° and 167.5(9)° respectively owing to the rigidity of the phen ligand [18]. Therefore, in this report, the bite angles should not be taken as an indication of distortion with the phen ligand itself. Rather the bite angle appears to correlate well with the metal-to-N-atom distance; 82.6(4)° and 1.978(3) Å in $[Fe(phen)_3]^{2+}$ [19], 81.0(2)° and 2.050(10) Å in $[Cr(phen)_3]^{3+}$ [20], 78.1(3)° and 2.13(1) Å in $[Co(phen)_3]^{3-}$ [21], 70.2(2)° and 2.400(6) Å in $[Hg(phen)_3]^{2+}$ [22], 79.5(1)° and 2.097(2) Å in this study. This can be described by the equation $y = -29.818x + 141.75$, where y represents the bite angle and x is the metal-to-N-atom bond distance.

The bond distances of C–N and C–C in the title compound fall within the range of the literature values [23]. The three aromatic ring systems in each phen are coplanar within experimental error. The dihedral angles between the two phen ligands are 72.89°, 83.62° and 83.96°, respectively. The three lattice water molecules [O(7), O(8) and O(9)] with the oxygen atom of the two anions [O(3), O(5) and O(6)] form a hydrogen-bonded network; the donor and acceptor distances are $O(7){-}H\cdots O(3)$ $(1-x,\ 1-y,\ 1-z)$ 3.1013(4) Å, $O(7){-}H\cdots O(9)$ $(x,\ y,\ z)$ 2.8394(4) Å, $O(6)\cdots H{-}O(8)$ $(-x,\ 1-y,\ -z)$ 2.8456 Å and $O(5)\cdots H{-}O(9)$ (x, y, z) 2.8040 Å. Other short intermolecular contacts observed in this structure are $C(34){-}H\cdots O(2)$ $(1-x,\ -y,\ 1-z)$ and $C(91){-}H\cdots O(8)$ (x, y, z) with contact distances of 3.2626(3) Å and 3.2148(3) Å, respectively. In the solid state, the intermolecular hydrogen bonds connect the $[Ni(phen)_3]^{2+}$, H_2O moieties and nitrate and ethyl phosphite anions.

Acknowledgements

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