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Synthesis, IR and electronic spectroscopic and X-ray single crystal structural analysis of *cis*-[Ni(ipren)$_2$(NO$_3$)](NO$_3$) (ipren = *N*-isopropylethane-1,2-diamine)

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Abstract—The deep blue complex [Ni(ipren)$_2$(NO$_3$)](NO$_3$) has been synthesized, which is proposed to have *cis*-octahedral geometry on the basis of IR and electronic spectral studies and confirmed by single crystal X-ray analysis. © 1997 Elsevier Science Ltd

Keywords: N-isopropylethane-1,2-diamine; nitratobis(N-isopropylethane-1,2-diamine)nickel(II)nitrate; nickel(II)diamine complex; single crystal X-ray analysis of nickel(II)complex; *cis*-octahedral geometry of nickel(II); vibrational spectra of nickel(II).

Octahedral bis(diamine)nickel(II) nitrate complexes attract special attention from the coordination chemists as they have either *cis* or *trans*-configuration depending upon not only the nature of the diamine but also on the coordination mode of the nitrate ions. Determination of the exact configuration is essential to understand the reaction mechanism for the formation of the complex as well as the mode of coordination of the nitrate ions and the diamines. A few such complexes have been reported [1–5] to be synthesized and in most cases configurations have been suggested from electronic and IR-spectroscopic studies. Recently, one such complex has been reported to be characterized by X-ray single crystal structural analysis, where one of the nitrate ions along with two molecules of the diamine are coordinated in a *cis*-bidentate fashion [6]. Here, we report the synthesis, IR- and electronic spectral studies and X-ray single crystal structural analysis of octahedral bis(N-isopropylethane-1,2-diamine)nickel(II) nitrate.

EXPERIMENTAL

High purity *N*-isopropylethane-1,2-diamine (ipren) was purchased from Aldrich Chemical Company Inc. and used as received. The instruments used for recording the IR and electronic spectra (UV-Visible and near-IR regions), elemental analyses, magnetic susceptibility and molar conductance measurements were as reported earlier [7].

Preparation of the complex

Cis-[Ni(ipren)$_2$(NO$_3$)](NO$_3$) was synthesized by adding the butanolic solution (5 cm^3) of the diamine (2 mmol) to the butanolic solution (10 cm^3) of anhydrous nickel(II)nitrate (1 mmol), obtained by refluxing Ni(NO$_3$)$_2$·6H$_2$O in 2,2-dimethoxypropane. The resulting mixture was refluxed for 10–15 min and was kept in a CaCl$_2$-desiccator. After a few days, fine deep blue crystals were separated out, which were filtered and washed with butanol and dried in a CaCl$_2$-desiccator. Found: C, 31.1; H, 7.2; N, 21.9; Ni, 15.2. Calc.

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Table 1. Crystallographic data for $[Ni(ipren)_2(NO_3)](NO_3)$[a]

Formula	$NiC_{10}H_{28}N_6O_6$
Colour	Deep blue
Formula weight	386.7
Crystal system	Monoclinic
Space Group	$P2_1/c$
a (Å)	11.959(1)
b (Å)	12.946(1)
c (Å)	12.585(1)
β (°)	109.49(1)
V (Å^3)	1836.8(3)
Z	4
ρ_{calcd} (g cm^{-3})	1.400
F(000)	824.0
μ(Mo-K_α) (mm^{-1})	1.09
Unique reflections	3202
Observed reflections $[I \geqslant 2\sigma(I)]$	2620
$R1$[b], $wR2$[c]	0.053, 0.171
Weighting parameters (A, B)[d]	0.1086, 1.63
Goodness-of-fit (S[e])	1.121
Maximum Δ/e.s.d	0.414
Final Δρ, max/min (eÅ^{-3})	0.52/−0.50

[a] = 23°C.

[b] $R1 = \Sigma||F_0|-|F_c||/\Sigma F_0$.

[c] $wR2 = [\Sigma\{w(F_0^2-F_c^2)^2\}/\Sigma\{w(F_0^2)^2\}]^{1/2}$.

[d] $w = 1/[\sigma^2(F_0^2)+(AP)^2+BP]$, where $P = (F_0^2+2F_c^2)/3$.

[e] $S = [\Sigma\{w(F_0^2-F_c^2)^2\}/(N-P)]^{1/2}$, where N is the number of data and P is the total number of parameters refined.

for $NiC_{10}H_{28}N_6O_6$: C, 31.0; H, 7.2; N, 21.7; Ni, 15.2%. $\mu_{eff} = 3.1$ B.M. λ_{max}(Nujol) = 974, 593 and 373 nm, $\Delta = 92\Omega^{-1}$ cm^2 dm^{-3}).

X-ray diffraction structural study

Single crystals suitable for X-ray analysis were obtained by recrystallization of the complex from acetonitrile-butanol mixture (1 : 1).

A single crystal of the title complex was mounted on an Enraf-Nonius CAD4 diffractometer. Lattice parameters were determined by least-squares refinement of the angular settings of 25 well-centred reflections. Crystal data are summerised in Table 1. Intensity data were collected using Mo $K\alpha$ radiation (λ = 0.71073 Å) with the ω-2θ scan mode. The stability of the crystal was measured by monitoring three standard reflections every hour. Data were corrected for Lorentz, polarization and absorption (T_{min}/T_{max} is 0.724/0.995) [8].

The structure was solved by a combination of the Patterson and Fourier methods and refined through full-matrix least-squares calculations (SHELXL 93). Anisotropic refinements were carried out for all non-hydrogen atoms (disordered methyl carbon atom C(4B) with occupancy 0.3 was treated isotropically). The hydrogen atoms, except those attached with the disordered methyl group, were located from the difference Fourier maps and refined with isotropic thermal parameters. Complex neutral atom scattering factors [9] were used throughout. All calculations were carried out using SHELXS 86 [10], SHELXL 93 [11], PARST [12] and ORTEP II [13] programs. Selected bond distances and angles are listed in Table 2.

RESULTS AND DISCUSSION

The complex, $Ni(ipren)_2(NO_3)_2$ is deep blue in colour and its composition was determined by elemental analyses. IR-spectral study (KBr) shows that the diamine is chelated in the complex [14,15]. The magnetic and electronic spectral data reveal that the complex possesses octahedral geometry, in which both NO_3^- ions may be coordinated in a monodentate fashion or one of them is coordinated in a *cis*-bidentate fashion while the other remains uncoordinated. The actual mode of coordination has been investigated by IR-spectral (Nujol) study in the region of 1700–1800 cm^{-1} where, the combination band of the ν_1-symmetric stretching and the doubly degenerate in-plane bending mode of the nitrate ions in metallic complexes have been assigned [1–5]. The complex exhibits three peaks at 1770, 1750 and 1720 cm^{-1}, (Fig. 1). The peak at 1750 cm^{-1} indicates the presence of free NO_3^- ion. The large separation (50 cm^{-1}) between the other two peaks (1770 and 1720 cm^{-1}) suggests that the other NO_3^- ion is coordinated in a *cis*-bidentate fashion. Thus, the complex is nitrato bis(N-isopropylethane-1,2-diamine)nickel(II) nitrate. The electronic spectrum (mull) in the near-IR region has been studied to strengthen the above view. It is observed that the complex exhibits no splitting of its *d-d* band in that region (Fig. 2) which corroborates the *cis*-configuration in the complex [3–5,16]. The molar conductance ($92\Omega^{-1}$ cm^2 dm^{-3}, in dry methanol) corresponds to a 1 : 1 electrolyte in agreement with the proposed structure of the complex.

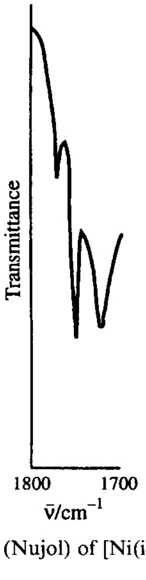

Fig. 1. IR-spectrum (Nujol) of $[Ni(ipren)_2(NO_3)](NO_3)$.

Table 2. Selected bond distances (Å) and angles (°)

Ni—N(1)	2.054(4)	N(1)—Ni—N(5)	106.7(2)
Ni—N(2)	2.142(4)	N(1)—Ni—N(2)	82.4(2)
Ni—N(4)	2.144(4)	N(1)—Ni—O(1)	99.6(2)
Ni—N(5)	2.072(4)	N(1)—Ni—O(2)	159.5(2)
Ni—O(1)	2.135(3)	N(1)—Ni—N(4)	91.0(2)
Ni—O(2)	2.160(3)	N(2)—Ni—N(5)	92.2(2)
N(1)—C(1)	1.462(8)	N(2)—Ni—N(4)	169.9(2)
N(2)—C(2)	1.471(8)	N(2)—Ni—O(1)	91.5(2)
N(2)—C(3)	1.508(8)	N(2)—Ni—O(2)	96.4(2)
N(3)—O(3)	1.232(5)	N(4)—Ni—N(5)	82.3(2)
N(3)—O(1)	1.263(5)	N(4)—Ni—O(1)	97.2(1)
N(3)—O(2)	1.258(5)	N(4)—Ni—O(2)	92.5(2)
N(4)—C(7)	1.485(6)	N(5)—Ni—O(1)	153.7(2)
N(4)—C(8)	1.493(7)	N(5)—Ni—O(2)	93.8(2)
N(5)—C(6)	1.467(7)	O(1)—Ni—O(2)	59.9(1)
		C(1)—N(1)—Ni	111.5(4)
		C(2)—N(2)—Ni	104.6(3)
		C(2)—N(2)—C(3)	116.7(6)
		C(3)—N(2)—Ni	123.0(5)
		C(6)—N(5)—Ni	110.5(3)
		C(7)—N(4)—C(8)	112.7(4)
		C(7)—N(4)—Ni	104.2(3)
		C(8)—N(4)—Ni	129.0(3)
		O(1)—N(3)—O(2)	116.6(4)
		O(1)—N(3)—O(3)	121.3(4)
		O(2)—N(3)—O(3)	122.0(4)

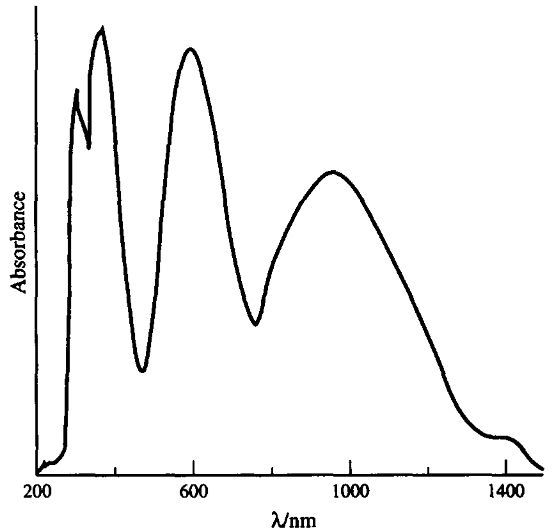

Fig. 2. Electronic spectrum (Nujol) of [Ni(ipren)$_2$(NO$_3$)](NO$_3$).

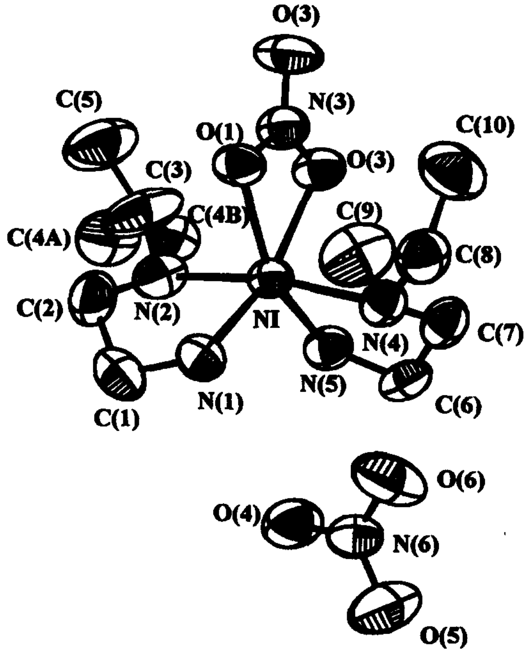

Fig. 3. ORTEP-plot, [Ni(ipren)$_2$(NO$_3$)](NO$_3$) with atom numbering scheme.

An ORTEP view of the complex with the atom numbering scheme is shown in Fig. 3. The crystal structure consists of discrete [Ni(ipren)$_2$(NO$_3$)] cations with approximate C2 symmetry and (NO$_3$) anions. The coordination polyhedron around the metal centre is best described as a distorted octahedron with the two O atoms [O(1), O(2)] of the *cis*-bidentate nitrate group and the two N atoms [N(1), N(5)] of the diamines defining an equatorial plane and the remaining two N atoms [N(2), N(4)] are in axial positions; Ni being displaced by 0.004(2) Å towards N(4). The five membered chelate rings, Ni—N(1)—C(1)—C(2)—N(2) and Ni—N(4)—

C(7)—C(6)—N(5) display open-envelope geometries with the flap atoms C(2) and C(7), 0.644(9) and 0.636(7) Å, respectively, away from the least-squares planes through the remaining endocyclic atoms. The dihedral angle between the planar parts of the chelate rings is 77.0(2)°. The Ni—O, Ni—N distances (Table 2) are consistent with the corresponding values for octahedral nickel(II)-diamine/nitrato-diamine complexes [6,17]. The crystal packing is stabilized by an extensive network of hydrogen bonds involving the amine N atoms of the cation and nitrate O atoms of the anion.

The structure of the complex proposed from IR and electronic spectral studies was thus confirmed by single crystal X-ray analysis. It is noteworthy that the diamine, *N*-propylethane-1,2-diamine, which is isomeric to (ipren) produces *cis* as well as *trans*-species with nickel(II) nitrate [18]. Several attempts to prepare *trans*-species with (ipren) failed. This is likely to be due to the severe steric effect of the bulkier isopropyl groups.

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