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Crystal and Molecular Structure of Tris(propane-1,3-diamine)nickel(II) Dinitrate Complex

IDA MARIA VEZZOSI*, ADRIANO BENEDETTI, MONICA SALADINI

Istituto di Chimica Generale e Inorganica, Università di Modena, Via Campi 183, 41100 Modena, Italy

LUIGI PIETRO BATTAGLIA and ANNA BONAMARTINI CORRADI

Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, Via D'Azeglio 85, 43100 Parma, Italy

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Abstract

The title compound, $[Ni(1,3\text{-pn})_3](NO_3)_2$, crystallizes in the orthorhombic space group *Pbca* with eight formula units in a cell of dimensions a = 17.146(8), b = 14.364(5) and c = 15.054(7). The structure was solved by the heavy-atom method and refined by least-squares calculations to R = 0.053 for 1439 counter data. It consists of discrete, slightly distorted octahedral $[Ni(1,3\text{-pn})_3]^{2+}$ cations and NO_3^- anions. One of the three six-membered chelate rings shows a pronounced flattening unusual chair conformation. Magnetic and spectroscopic data agree to a lower stability of six-membered chelate rings, compared to five-membered chelate ones.

Introduction

Comparison of the stability of metal–amine complexes as a function of chelate ring size, reported for solution complexes, has demonstrated that the complexes of propane-1,3-diamine are less stable than those of ethylenediamine [1–4], since there is a less favourable entropy change in the formation of the six-membered ring [3, 4]. This is also reflected in the large number and types of nickel(II) ethylenediamine complexes investigated in the solid state [5, 6]. In some cases these present very interesting properties, unusual for nickel(II) complexes [7, 8] despite the very few reports on nickel(II)–propanediamines [9–11].

Undertaking a systematic investigation to fill this gap, we report in this paper the synthesis and magnetic, spectroscopic and structural characterization of tris(propane-1,3-diamine)nickel(II) dinitrate complex.

Experimental

Preparation of the $Ni(1,3\text{-pn})_3(NO_3)_2$ Complex

By evaporating an alcoholic (methanolic or ethanolic) solution containing the nickel(II) salt and the amine in a metal-to-ligand molar ratio of 1:3, a microcrystalline compound was separated. The compound was recrystallized repeatedly until a well-crystallized violet product was obtained. *Anal.* Found: C, 26.70; H, 7.51; N, 27.74. Calcd. for $C_9H_{30}N_8O_6Ni$: C, 26.73; H, 7.48; N, 27.72%.

Physical Measurements

The room-temperature magnetic moment was measured by the Gouy method using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The electronic spectrum of the solid compound was recorded at room-temperature as mull transmission spectrum with a Shimadzu MPS 50L spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 180 Instrument as Nujol mull or KBr pellets in the 300–4000 cm^{-1} spectral range (no difference was observed among spectra obtained by these two different methods) and as polythene pellets in the 100–500 cm^{-1} range. Nitrogen, carbon and hydrogen were analysed with a Carlo Erba Analyser Instrument Mod. 1106.

X-Ray Structure Determination

A summary of the crystal data and details concerning the intensity data collection are given in Table I. The unit cell parameters were obtained at 20 °C by a least squares refinement of the angular setting of 12 high-angle reflections. Intensity data were collected on a Siemens AED single-crystal diffractometer and corrected for Lorentz and polarization effects; correction for absorption was deemed unnecessary in view of the small dimensions of the crystal. The Cu atom was located from a three-

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*Author to whom correspondence should be addressed.

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TABLE I. Summary of Crystal Data and Experimental Details.

Compound	$Ni(1,3\text{-}pn)_3(NO_3)_2$
Crystal system	orthorhombic
Space group	*Pbca*
a, Å	17.146(8)
b, Å	14.364(5)
c, Å	15.054(7)
F(000)	1728
F.W.	405.10
V, Å^3	3708(3)
Z	8
D_m, g cm^{-3}	1.43
D_c, g cm^{-3}	1.452
Radiation (λ, Å)	Cu-K$_\alpha$ (λ = 1.54178)
μ(Cu-K$_\alpha$), cm^{-1}	18.6
Crystal size, mm^3	0.13 × 0.20 × 0.42
Scan type	$\omega - 2\vartheta$
Scan speed, °/sec	0.02
Scan range, °	$1.2 + 0.3 \tan \vartheta$
2ϑ range, °	6–120
Reflections measured	3971
Unique reflections ($I > 2\sigma(I)$)	1439
R, R_w	0.053, 0.060
W	$1.40/(\Sigma^2 F + 0.0027F^2)$

dimensional Patterson map and the position parameters of the non-hydrogen atoms were deduced from successive Fourier syntheses. The refinements were performed by several cycles of full-matrix least-squares with isotropic and anisotropic thermal parameters; in the last cycle the hydrogen atoms were fixed at the calculated positions. The final *R* indices were $R = 0.053$ and $R_w = 0.060$. The functions minimized were: $R = \Sigma[|F_o| - |F_c|]/|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Scattering factors were taken from International Tables [12]. All the calculations were performed with the use of CYBER 76 of the Centro di Calcolo dell'Italia Nord Orientale, Bologna, with the SHELX system of programs [13] and the financial support of the University of Parma. Final atomic coordinates are listed in Table II.

Results and Discussion

Description of the Structure

The crystal structure consists of discrete, slightly distorted octahedral $[Ni(1,3\text{-}pn)_3]^{2+}$ cations and NO_3^- anions (Figs. 1 and 2). Bond distances and angles involving the nickel atom are reported in Table III. The Ni–N bonds show no significant differences and are in agreement with the values reported in the literature for nickel(II)–propane-1,3-diamine complexes [10, 11]. The distortion of the coordination polyhedron is well evaluated from the angles on the metal, which are in the range: *cis* angles 87.4(5)–95.8(6)°, *trans* angles 173.9(5)–177.1(5)°. The Ni–N–C angles present values close to the trigonal value (122(1), 121(1)°) in the ring involving N(1) and N(2), and very different from this value (116(1), 114(1)°; 128(1), 125(1)°) in the other two rings.

Some of the bond distances in the ligand molecules (Table III) show rather large displacements from the expected values, probably because of the high thermal motion of the atoms involved.

As can be seen from Table IV in which the torsion angles for each of the three six membered chelate rings are reported, the rings involving N(1)–N(2) and N(3)–N(4) are in the usual chair conformation found for this ligand [10, 14, 15], while that involving N(5)–N(6) shows a pronounced flattening with a significant enlargement of all the bond angles (Table III). The non-equivalent conformations of these chelate rings are unusual. In fact in propane-1,3-diamine–cobalt(II) complexes [16–18] and in a nickel(II) complex, also containing the $[Ni(1,3\text{-}pn)_3]^{2+}$ cation [10], all rings present chair conformations.

TABLE II. Final Fractional Coordinates (×10^4) with Esd's in Parentheses for $Ni(1,3pn)_3(NO_3)_2$.

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Ni	1715(1)	1223(1)	1944(1)	C6	756(15)	890(16)	298(16)
N1	2592(5)	1106(9)	937(8)	C7	713(11)	780(15)	3632(13)
N2	2493(7)	2094(9)	2665(8)	C8	1126(11)	−86(14)	3757(11)
N3	1216(6)	2447(7)	1349(7)	C9	1753(14)	−431(14)	3252(17)
N4	978(7)	416(9)	1093(8)	N7	−709(9)	−924(9)	2036(8)
N5	882(10)	1379(12)	2986(11)	O1	−615(6)	−78(9)	1998(8)
N6	2130(10)	11(11)	2591(10)	O2	−1356(8)	−1225(10)	2072(11)
C1	3429(7)	1132(12)	1154(11)	O3	−141(8)	−1417(9)	2041(9)
C2	3645(9)	1948(12)	1728(11)	N8	2656(8)	1370(11)	5106(12)
C3	3350(10)	1940(14)	2634(12)	O4	2391(7)	2074(8)	4744(6)
C4	430(14)	2336(22)	977(20)	O5	2549(9)	1163(9)	5865(11)
C5	238(14)	1670(18)	347(16)	O6	3044(10)	814(12)	4671(12)

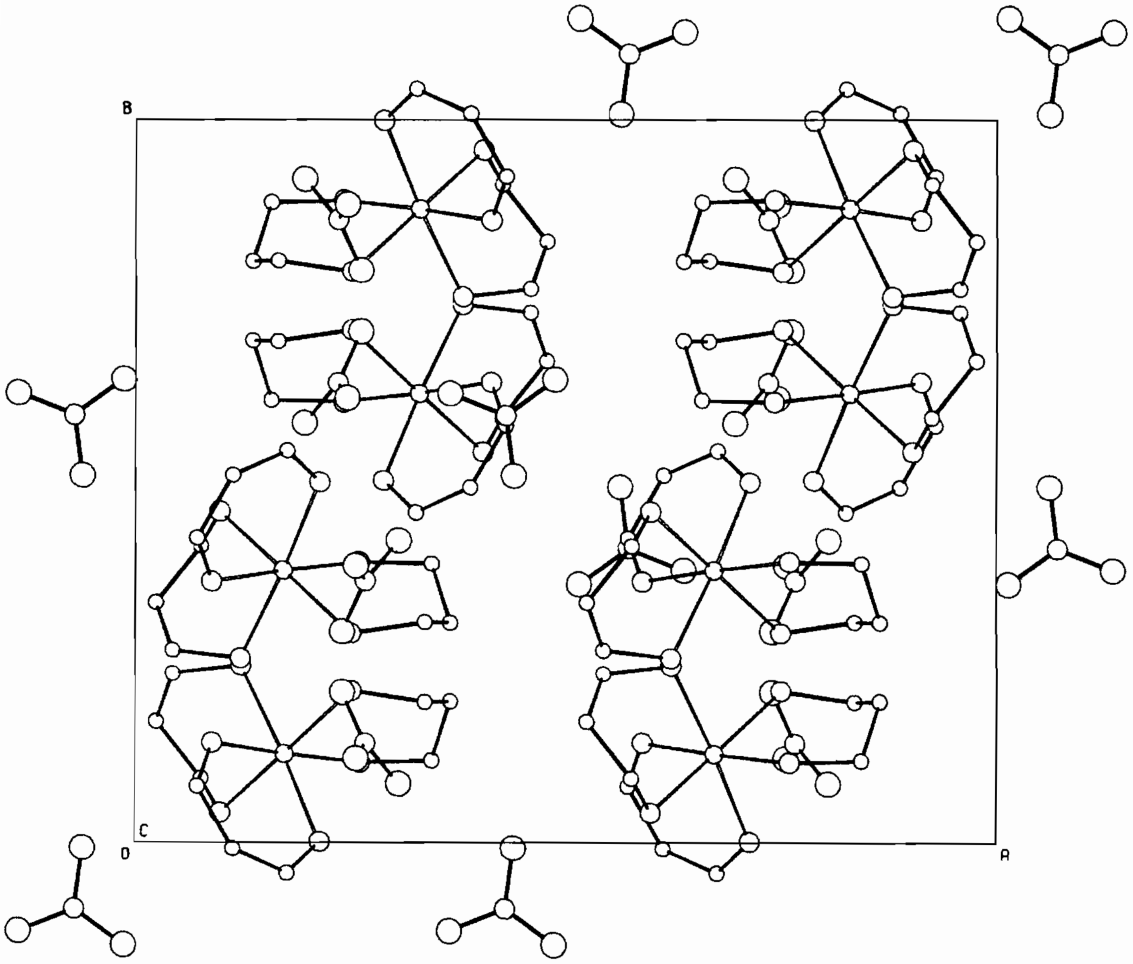

Fig. 1. Projection of the structure along the *c* axis.

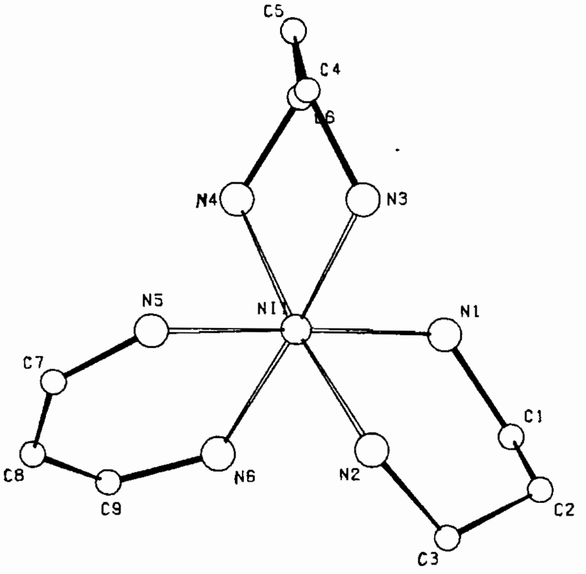

Fig. 2. The environment of the Ni atom.

Bond distances and angles in the nitrate ions show no abnormal features (Table III) and in particular these ions fully satisfy the planarity conditions.

The molecular packing is mainly determined by weak hydrogen bonds (Table VI). There are also present some significant van der Waals interactions, the shortest of which are quoted in Table III.

Magnetism and Ligand Field and Infrared Spectra (Table VI)

The magnetic moment is in the range expected for spin-free d^8 systems.

The reflectance spectrum shows the three bands characteristic of triplet ground-state Ni(II) with octahedral coordination. Band shapes and positions, assigned on the basis of O_h symmetry, and the D_q (ligand field parameter) and B (Racah parameter) calculated values are in the range found for octahedrally coordinated nickel(II) ethylenediamines having the NiN_6 choromophore [9, 19].

TABLE III. Bond Distances (Å) and Angles (°).

(a) Involving Ni atom

Ni–N(1)	2.14(1)	Ni–N(4)	2.14(1)
Ni–N(2)	2.13(1)	Ni–N(5)	2.13(2)
Ni–N(3)	2.15(1)	Ni–N(6)	2.12(2)
N(1)–Ni–N(2)	88.1(4)	N(2)–Ni–N(5)	89.0(6)
N(1)–Ni–N(3)	92.8(4)	N(2)–Ni–N(6)	92.2(6)
N(1)–Ni–N(4)	87.0(4)	N(3)–Ni–N(4)	87.6(4)
N(1)–Ni–N(5)	177.1(5)	N(3)–Ni–N(5)	87.4(5)
N(1)–Ni–N(6)	91.4(6)	N(3)–Ni–N(6)	175.7(5)
N(2)–Ni–N(3)	88.9(4)	N(4)–Ni–N(5)	95.8(6)
N(2)–Ni–N(4)	173.9(5)	N(4)–Ni–N(6)	91.6(6)
Ni–N(1)–C(1)	122(1)	N(5)–Ni–N(6)	88.5(6)
Ni–N(2)–C(3)	121(1)	Ni–N(4)–C(6)	114(1)
Ni–N(3)–C(4)	116(1)	Ni–N(5)–N(7)	128(1)
		Ni–N(6)–C(9)	125(1)

(b) Involving nitrate ions

N(7)–O(1)	1.23(2)	N(8)–O(4)	1.24(2)
N(7)–O(2)	1.19(2)	N(8)–O(5)	1.20(2)
N(7)–O(3)	1.20(2)	N(8)–O(6)	1.23(2)
O(1)–N(7)–O(2)	119(1)	O(4)–N(8)–O(5)	125(2)
O(1)–N(7)–O(3)	119(1)	O(4)–N(8)–O(6)	120(2)
O(2)–N(7)–O(3)	123(2)	O(5)–N(8)–O(6)	116(2)

(c) Involving the ligand molecules

N(1)–C(1)	1.47(2)	C(1)–C(2)	1.50(2)
N(2)–C(3)	1.49(2)	C(2)–C(3)	1.46(2)
N(3)–C(4)	1.47(3)	C(4)–C(5)	1.39(4)
N(4)–C(6)	1.43(3)	C(5)–C(6)	1.43(4)
N(5)–C(7)	1.33(3)	C(7)–C(8)	1.44(3)
N(6)–C(9)	1.35(3)	C(8)–C(9)	1.41(3)
N(1)–C(1)–C(2)	113(1)	C(4)–C(5)–C(6)	115(2)
C(1)–C(2)–C(3)	117(2)	N(4)–C(6)–C(5)	120(2)
N(2)–C(3)–C(2)	112(1)	N(5)–C(7)–C(8)	123(2)
N(3)–C(4)–C(5)	124(2)	C(7)–C(8)–C(9)	127(2)
		N(6)–C(9)–C(8)	127(2)

(d) Contacts less than 3.50 Å^{a}

N(3)···O(4^{i})	3.22(2)	N(3)···N(7^{iii})	3.48(2)
N(3)···O(5^{i})	3.12(2)	N(3)···O(3^{iii})	3.46(2)
N(1)···O(5^{ii})	3.27(2)	N(5)···O(3^{iii})	3.41(2)
N(4)···O(5^{ii})	3.41(2)	N(6)···O(2^{iv})	3.19(2)
N(4)···O(6^{ii})	3.24(2)	C(3)···O(1^{iv})	3.44(2)
N(2)···O(2^{iii})	3.13(2)	C(6)···O(6^{ii})	3.33(3)
		C(9)···O(2^{iv})	3.47(3)

^{a}i = x, 1/2 − y, z − 1/2; ii = 1/2 − x, $\bar{y}$, z − 1/2; iii = $\bar{x}$, 1/2 + y, 1/2 − z; iv = 1/2 + x, y, 1/2 − z.

The position and number of fundamental modes of nitrate groups agree on the presence of an ionic nitrate group [9]. In the far-infrared spectrum of the compound two new bands assignable to a Ni–N bond appear.

By comparing the physical data reported in Table V with those of Ni(en)$_3^{2+}$ cations [20] the main differences are observed in the positions of the Ni–N bands, at higher energies in the latter cations. This is consistent with the greater stability of five-membered chelate rings with respect to six-membered ones.

TABLE IV. Torsion Angles (°) in the Six-Membered Chelate Rings.

Ni–N(1)–C(1)–C(2)	−51(2)
N(1)–C(1)–C(2)–C(3)	68(2)
C(1)–C(2)–C(3)–N(2)	−71(2)
C(2)–C(3)–N(2)–Ni	56(2)
C(3)–N(2)–Ni–N(1)	−34(1)
N(2)–Ni–N(1)–C(1)	32(1)
Ni–N(3)–C(4)–C(5)	−55(3)
N(3)–C(4)–C(5)–C(6)	21(4)
C(4)–C(5)–C(6)–N(4)	49(3)
C(5)–C(6)–N(4)–Ni	−69(2)
C(6)–N(4)–Ni–N(3)	25(1)
N(4)–Ni–N(3)–C(4)	26(1)
Ni–N(5)–C(7)–C(8)	4(3)
N(5)–C(7)–C(8)–C(9)	1(3)
C(7)–C(8)–C(9)–N(6)	5(4)
C(8)–C(9)–N(6)–Ni	−15(3)
C(9)–N(6)–Ni–N(5)	14(2)
N(6)–Ni–N(5)–C(7)	−9(2)

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Supplementary Material Available

A listing of thermal parameters, calculated atomic coordinates of hydrogen atoms, weighted least-squares plane for the NO_3^- ions and final structure factors (11 pages) are available from the Editor.

TABLE V. Magnetism, Electronic and Infrared Spectra (cm^{-1}) and Ligand Field Parameters (cm^{-1}) of Ni(1,3-pn)$_3$(NO$_3$)$_2$.

μ_{eff}	3.16
$^3A_{2g} \rightarrow {}^3T_{2g}$	11300
$\rightarrow {}^3T_{1g}$(F)	18000
$\rightarrow {}^3T_{1g}$(P)	28600
Dq	1130
B	850
$\nu_1 + \nu_4$(NO$_3$)	1738w
ν_3(NO$_3$)	1370vsb
ν_2(NO$_3$)	819m
ν_4(NO$_3$)	712w
ν(Ni–N)	474ms 396w

TABLE VI. Possible Hydrogen Bonds and other Short Intermolecular Distances (Å and °).[a]

N(2)–H(9)	N(2)···O(4)	H(9)···O(4)	N(2)–H(9)···O(4)
1.08	3.14(2)	2.10	160
N(4)–H(19)	N(4)···O(1)	H(19)···O(1)	N(4)–H(19)···O(1)
1.08	3.13(2)	2.06	174
N(1)–H(1)	N(1)···O(4^{i})	H(1)···O(4^{i})	N(1)–H(1)···O(4^{i})
1.08	3.19(2)	2.12	171
N(6)–H(30)	N(6)···O(5^{ii})	H(30)···O(5^{ii})	N(6)–H(30)···O(5^{ii})
1.08	3.15(2)	2.09	164
N(3)–H(14)	N(3)···O(2^{iii})	H(14)···O(2^{iii})	N(3)–H(14)···O(2^{iii})
1.08	3.06	2.00	165

[a] i = x, 1/2 − y, z − 1/2; ii = 1/2 − x, $\bar{y}$, z − 1/2; iii = $\bar{x}$, 1/2 + y, 1/2 − z.

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