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trans-Bis(*N*-ethylethane-1,2-diamine)-dinitronickel(II)

INAMUR RAHAMAN LASKAR,^a GOLAM MOSTAFA,^b DEBASIS DAS,^a KEN-ICHI OKAMOTO^c AND N. RAY CHAUDHURI^a

^aDepartment of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India,

^bDepartment of Physics, Krishnath College, Berhampore 742 101, India, and ^cDepartment of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan. E-mail: icnrc@mahendra.iacs.res.in

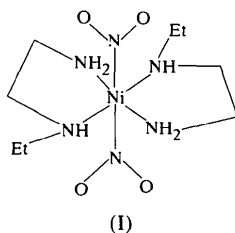
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Abstract

The title compound, [Ni(NO₂)₂(C₄H₁₂N₂)₂], was synthesized and characterized by X-ray crystallography. The Ni^{II} atom lies on an inversion centre and thus has a *trans*-octahedral coordination.

Comment

Substitution present in ethane-1,2-diamine or its analogues plays an interesting role in the coordination mode of ambidentate nitrite ions to nickel(II). It is observed that electronic factors favour the nitro coordination whereas steric factors favour in general (*a*) monodentate nitrito coordination and (*b*), in some cases, directs the nitrite ion to act as a chelating ligand. For instance, reactions of nickel(II) nitrite with ethane-1,2-diamine/*N*-methylethane-1,2-diamine/*N,N'*-dimethylethane-1,2-diamine generates a *trans*-dinitro complex species (Porai-Koshits & Minacheva, 1964; Finney *et al.*, 1981*a*; Drew *et al.*, 1964); whereas *N,N'*-diethylethane-1,2-diamine (dmen; Finney *et al.*, 1981*b*) generate *cis*-(nitrito-*O,O'*)-bis(dmen)nickel(II) nitrite. Therefore, it is difficult to predict the mode of coordination of the nitrite ion on the basis of the substituent present on the diamine unless the particular compound is characterized by X-ray crystallography. During our ongoing research program to understand the mode of coordination of the nitrite ion to nickel(II), we synthesized the title compound, *trans*-bis(*N*-ethylethane-1,2-diamine)dinitronickel(II), (I), and report here its synthesis and structure determination.



As shown in Fig. 1, the coordination polyhedron at the Ni atom is best described as a distorted octahedron, with four ligand N atoms belonging to the diamine ligands (N1, N2 and their centrosymmetrically related atoms) defining the equatorial plane and the remaining two N atoms belonging to the nitro groups (N3 and its centrosymmetric counterpart) in *trans*-axial positions. The Ni—N distances [2.071 (2) and 2.154 (2) Å] are consistent with corresponding values for octahedral nickel systems. The crystal packing is stabilized by extensive hydrogen-bonding interactions involving the amine N atoms and O atoms.

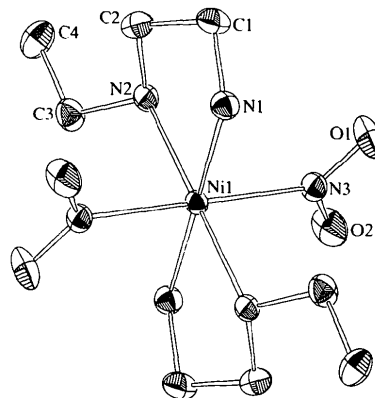


Fig. 1. ORTEP (Zsolnai, 1995) view (50% probability level) of (I) showing the atom-numbering scheme.

Experimental

The title compound was synthesized by adding the diamine ligand (2 mmol) to an ethanolic suspension (10 ml) of potassium hexanitronickelate(II) monohydrate (1 mmol). The resulting dark-green solution was kept in a CaCl₂ desiccator (yield 81%). After a few days, a brown complex was obtained in crystalline form.

Crystal data

[Ni(NO₂)₂(C₄H₁₂N₂)₂]

M_r = 327.02

Triclinic

P $\bar{1}$

a = 6.952 (2) Å

b = 8.909 (3) Å

c = 6.531 (2) Å

α = 94.76 (3)°

β = 111.03 (2)°

γ = 73.74 (2)°

V = 362.4 (2) Å³

Z = 1

D_x = 1.498 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 14.7–15.0°

μ = 1.359 mm⁻¹

T = 296.2 K

Prism

0.25 × 0.25 × 0.13 mm

Brown

Data collection

Rigaku AFC-7S diffractometer

1555 reflections with *I* > 1.5σ(*I*)

ω -2 θ scans
 Absorption correction:
 empirical σ scans (North
et al., 1968)
 $T_{\min} = 0.745$, $T_{\max} = 0.838$
 1800 measured reflections
 1663 independent reflections

$R_{\text{int}} = 0.012$
 $\theta_{\max} = 27.49^\circ$
 $h = 0 \rightarrow 9$
 $k = -10 \rightarrow 11$
 $l = -8 \rightarrow 7$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.12%

Refinement

Refinement on F^2
 $R = 0.029$
 $wR = 0.039$
 $S = 1.122$
 1555 reflections
 89 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o)$
 $+ 0.00063|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.049$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Ni1—N1	2.071 (2)	N1—C1	1.472 (3)
Ni1—N2	2.154 (2)	N2—C2	1.467 (3)
Ni1—N3	2.151 (2)	N2—C3	1.473 (4)
O1—N3	1.237 (3)	C1—C2	1.514 (4)
O2—N3	1.239 (3)	C3—C4	1.513 (4)
N1—Ni1—N2	82.84 (8)	N2—Ni1—N3'	89.99 (7)
N1—Ni1—N3	91.16 (8)	N1—C1—C2	109.3 (2)
N1—Ni1—N2'	97.16 (8)	N2—C2—C1	108.99 (17)
N1—Ni1—N3'	88.84 (8)	N2—C3—C4	115.5 (2)
N2—Ni1—N3	90.01 (7)		

Symmetry code: (i) $2 - x, -y, 2 - z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots O2'	0.95	2.29	2.920 (3)	123
N1—H2 \cdots O1''	0.95	2.30	3.104 (3)	142
N2—H3 \cdots O1'''	0.95	2.48	3.340 (2)	150
N2—H3 \cdots O2''''	0.95	2.24	3.118 (3)	154

Symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $1 - x, -y, 2 - z$; (iii) $2 - x, -y, 3 - z$.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1997). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1116). Services for accessing these data are described at the back of the journal.

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Bis(guanidinium) hexachlorostannate(IV)

HIROYUKI ISHIDA,^a YOSHIHIRO FURUKAWA^b AND SETSUO KASHINO^a

^aDepartment of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan, and ^bFaculty of School Education, Hiroshima University, Higashi-Hiroshima 739-8524, Japan. E-mail: ishidah@cc.okayama-u.ac.jp

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Abstract

The title complex, $(\text{CH}_6\text{N}_3)_2[\text{SnCl}_6]$, consists of planar $[\text{C}(\text{NH}_2)_3]^+$ ions and a slightly distorted $[\text{SnCl}_6]^{2-}$ octahedron connected by weak $\text{N—H}\cdots\text{Cl}$ hydrogen bonds, forming parallel sheets in the crystal.

Comment

The molecular motion of the guanidinium ion in $(\text{CH}_6\text{N}_3)_2[\text{SnCl}_6]$, (I), was studied by solid-state ^1H NMR (Furukawa & Nakamura, 1986). The 120° reorientational jumps of the cation about its C_3 axis were found to occur above room temperature. The activation energy for this motion is 52 kJ mol^{-1} , which is much larger than those of 4.2 – 10.0 kJ mol^{-1} for the reorientational motions accompanied by breaking the $\text{N—H}\cdots\text{Cl}$ hydrogen bonds in A_2SnCl_6 complexes [$\text{A} = \text{NH}_4$, CH_3NH_3 and $(\text{CH}_3)_3\text{CNH}_3$; Strange & Terenzi, 1972; Ikeda *et al.*, 1976; Ishida *et al.*, 1992].

