

Linkage isomerism in 4-(2-aminoethyl)morpholine (L) complexes of nickel (II) nitrite: X-ray single crystal structure of *trans*-[NiL₂(NO₂)₂]

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Abstract

The linkage isomers *trans*-bis[4-(2-aminoethyl)morpholine]dinitronickel (II) (brown, **1a**) and *trans*-bis[4-(2-aminoethyl)morpholine]dinitritonickel (II) (blue-violet, **1b**) have been synthesized from solution. Complex **1a** is the major and thermodynamically controlled product, whereas, complex **1b** is minor and kinetically controlled product. The X-ray single crystal structure analysis of complex **1a** has been performed.

Keywords: Linkage isomerism; 4-(2-Aminoethyl)morpholine; Nickel (II) nitrite

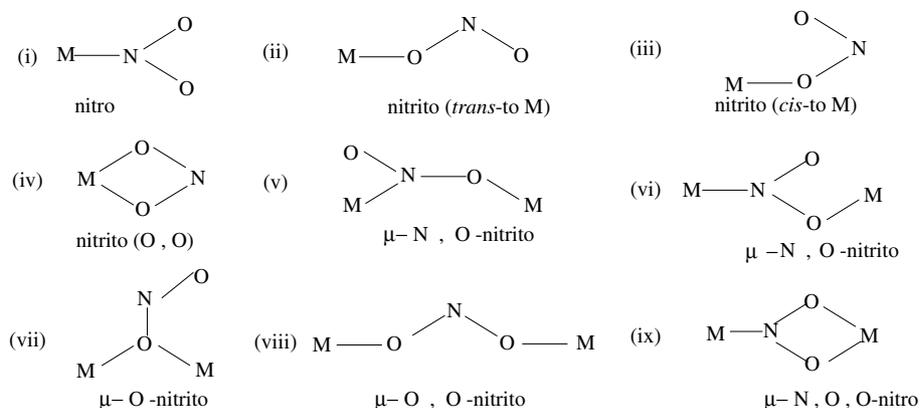
1. Introduction

Jorgensen first rationalized the ambidentate behavior of the nitrite ion as early as 1894 [1]. Since then several interesting reports of nitrite coordination have come in the literature, which reveal that there are nine different ways in which the nitrite ion may coordinate as a ligand (Scheme 1). These different modes of binding generate linkage isomerism in nitrite complexes. The most well know systems are the monodentate nitro and nitrito linkage isomers obtained with cobalt (III), nickel (II), copper (II), rhodium (III) and platinum (IV). The nitro–nitrito linkage isomerism in nickel (II) amine systems have been investigated by several groups of workers [2–11]. It has been suggested that a steric effect favors the binding of the nitrite ion through oxygen to yield the nitrito isomer, although they are thermodynamically unstable. In order to study the influences of steric and electronic factors on

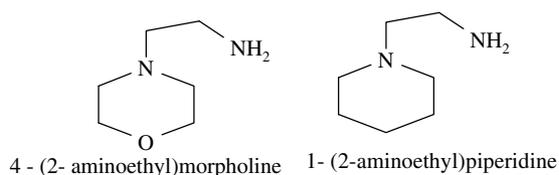
the mode of nitrite coordination in the nickel (II) system, the co-ligands that seem to be best suited are 1,2-diaminoethane and its derivatives, as different substituents may be tailored on the backbone of 1,2-diaminoethane to obtain the desired steric and electronic effects. For NiL₂(NO₂)₂, when L = *N,N'*-dimethyl-1,2-diaminoethane only the *trans*-dinitro species can be isolated in the solid state as well as in solution [9], when L = *N,N'*-diethyl-1,2-diaminoethane a nitrito(O,O) complex is obtained in the solid state which exhibits a nitro–nitrito(O,O) equilibrium in different solvents, though the nitro form cannot be isolated in the solid state [6a], and when L = *N,N'*-dipropyl-1,2-diaminoethane a metastable (at ca. 298 K) *trans*-dinitro species is formed which gradually transforms into the nitrito(O,O) species, and that *trans*-dinitro form may be preserved by keeping the species below 283 K [11d]. To date only one report of monodentate nitro and nitrito linkage isomers of nitrite complexes of nickel (II) has been cited in the literature, with L = 1-(2-aminoethyl)piperidine [11a]. The steric and electronic factors are just perfectly balanced in this case to generate the monodentate nitro as well

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Scheme 1. Nine possible modes of nitrite ion coordination to metal.



Scheme 2. Molecular structures of the ligands.

as the monodentate nitrito linkage isomers in the solid state. Therefore, the steric and electronic factors of the co-ligand may impart interesting findings in nitrite coordination. For the present study we have chosen 4-(2-aminoethyl)morpholine (Scheme 2) as the co-ligand, which should exert nearly equal steric and electronic effects in comparison with 1-(2-aminoethyl)piperidine (Scheme 2), with the view to obtain some interesting results. We report herein the synthesis and characterization of nitro and nitrito complexes of nickel (II) of 4-(2-aminoethyl)morpholine and the X-ray single crystal structure analysis of the nitro species.

2. Experimental

2.1. Materials

4-(2-Aminoethyl)morpholine was purchased from Aldrich Chemical Company Inc. and used as received. Potassium hexanitronickelate (II) monohydrate was prepared using a standard method [6b]. All other chemicals used were of AR grade.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer; the nickel (II) content was estimated gravimetrically [12]. The IR spectrum ($4000\text{--}400\text{ cm}^{-1}$) was taken at $27\text{ }^{\circ}\text{C}$ using a SHIMADZU FTIR-8400S and KBr

was used as the medium. The electronic spectrum ($1400\text{--}200\text{ nm}$) was obtained at $27\text{ }^{\circ}\text{C}$ using a SHIMADZU UV-3101PC, and Nujol was used as a medium as well as a reference. The magnetic susceptibility was measured at $27\text{ }^{\circ}\text{C}$ using an EG and G PAR 155 vibrating sample magnetometer, and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a reference material; diamagnetic corrections were made using Pascal's constants [13]. Molar conductances were measured using a Systronic 304 conductivity meter, where the cell constant was calibrated with 0.02 M KCl solution and dry dichloromethane was used as the solvent.

2.3. Synthesis of the complexes

The nitro $[\text{NiL}_2(\text{NO}_2)_2]$ (**1a**) and nitrito $[\text{NiL}_2(\text{ONO})_2]$ (**1b**) complexes were synthesized by adding the ligand L (2 mmol) in methanol (5 mL) dropwise to a methanolic suspension (10 mL) of potassium hexanitronickelate (II) monohydrate (1 mmol) with vigorous stirring. Initially a clear green solution was formed, but within a few minutes a blue-violet precipitate also appeared. After 1 h of stirring the mixture was filtered and the green colored filtrate part was kept in a CaCl_2 desiccator. After a few days, brown-colored crystals (**1a**) separated out from the green solution. Yield 65%. *Anal.* Calc. for $\text{C}_{12}\text{H}_{28}\text{N}_6\text{O}_6\text{Ni}$: C, 38.0; H, 7.4; N, 22.2; Ni, 15.5. Found: C, 38.0; H, 7.3; N, 22.1; Ni, 15.6%. $\mu_{\text{eff}} = 3.2\ \mu_{\text{M}}$. $\lambda_{\text{max}}(\text{Nujol}) = 1264, 1182, 535, 371\text{ nm}$. The blue-violet precipitate part was dissolved in excess methanol, and the resulting green colored solution was kept in a CaCl_2 desiccator. After a few days a blue-violet species was deposited at the side-walls of the beaker and brown crystals were formed at the bottom of the beaker. After crystallization of the blue-violet species, complex **1b** was isolated in pure form. Yield: 25%. *Anal.* Calc. for $\text{C}_{12}\text{H}_{28}\text{N}_6\text{O}_6\text{Ni}$: C, 38.0; H, 7.4; N, 22.2; Ni, 15.5%. Found: C, 38.1; H, 7.3; N, 22.0; Ni, 15.4%. $\mu_{\text{eff}} = 3.2\ \mu_{\text{M}}$. $\lambda_{\text{max}}(\text{Nujol}) = 1255, 1192, 588, 412\text{ nm}$.

2.4. X-ray data collection and structure determination

A single crystal suitable for X-ray data collection was mounted on Bruker SMART CCD diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation source. The program SMART [14] was used for collecting frames of data, indexing reflection and determination of lattice parameters, SAINT [14] for integration of the intensity of reflections and scaling, and SADABS [15] for absorption correction. A total 2977 reflections were measured and 2366 were assumed observed applying the condition $I > 2\sigma(I)$. The structure was solved by direct methods using the SHELXS-97 [16] computer program and refined by full-matrix least squares methods on F^2 , using the SHELXL-97 [17] program with anisotropic displacement parameters for all non-hydrogen atoms. Selected crystallographic data and refinement details are displayed in Table 1. Selected bond lengths and angles are given in Table 2.

3. Results and discussion

When a methanolic solution of L was added to a methanolic suspension of potassium hexanitronickelate (II) monohydrate, a blue-violet precipitate was formed within a few minutes, during the stirring. On filtration a green colored solution was obtained which on keeping yielded complex **1a**. After repeated crystallization of the

Table 1
Crystal data and structure refinement of complex **1a**

Empirical formula	C ₁₂ H ₂₈ N ₆ NiO ₆
Formula weight	411.09
<i>T</i> (K)	293
Mo K α	0.71073
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	7.1761(16)
<i>b</i> (Å)	8.0904(18)
<i>c</i> (Å)	8.3814(19)
α (°)	94.116(3)
β (°)	112.337(2)
γ (°)	101.296(3)
<i>V</i> (Å ³)	435.60(17)
<i>Z</i>	1
<i>D</i> _{calc} (Mg m ⁻³)	1.567
<i>F</i> (000)	218
μ (mm ⁻¹)	1.2
θ Range (°)	2.6–28.4
Reflection collected	2977
Independent reflection	2420
Reflection observed	2366 [$I > 2\sigma(I)$]
Goodness of-fit on F^2	1.07
<i>R</i> _{int}	0.013
<i>R</i>	0.0273
<i>wR</i>	0.0698

$$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.0177P], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

Table 2
Selected bond lengths (Å) and bond angles (°) of complex **1a**

Ni1–N1	2.069(3)
Ni1–N2	2.336(3)
Ni1–N3	2.032(4)
Ni1–N4	2.372(3)
Ni1–N5	2.135(3)
Ni1–N6	2.101(4)
O1–N5	1.197(5)
O2–N5	1.218(5)
O3–N6	1.276(6)
O4–N6	1.258(5)
N1–Ni1–N2	80.23(12)
N1–Ni1–N3	177.72(14)
N1–Ni1–N4	99.00(13)
N1–Ni1–N5	89.71(13)
N1–Ni1–N6	90.07(15)
N2–Ni1–N3	97.50(12)
N2–Ni1–N4	179.20(13)
N2–Ni1–N5	93.48(12)
N2–Ni1–N6	87.79(14)
N3–Ni1–N4	83.28(13)
N3–Ni1–N5	90.32(14)
N3–Ni1–N6	89.95(15)
N4–Ni1–N5	86.70(13)
N4–Ni1–N6	92.02(14)
N5–Ni1–N6	178.65(15)
O3–N6–O4	114.1(4)
O1–N5–O2	120.3(4)

blue-violet species, complex **1b** was obtained in the pure form. Complex **1a** was the major and thermodynamically controlled product, whereas complex **1b** was the minor and kinetically controlled product. The composition of the complexes **1a** (brown) and **1b** (blue-violet) have been assigned as NiL₂(NO₂)₂ on the basis of elemental analyses. Magnetic susceptibility measurements of **1a** and **1b** reveal that nickel (II) is in an octahedral configuration in both complexes and electronic spectral data of the complexes suggest that they have octahedral geometry around the nickel (II) centre. IR spectral studies are observed to be immensely helpful to elucidate the binding mode of the nitrite ion in its complexes. The three fundamental vibrational modes of the nitrite group (*C*_{2v} symmetry) are all IR active and the band positions are shifted upon coordination. The brown species **1a** exhibits IR bands at 1333, 1310 and 808 cm⁻¹ assigned to $\nu_{as}(\text{NO}_2)$, $\nu_s(\text{NO}_2)$ and $\delta(\text{NO}_2)$, respectively. Both $\nu_{as}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ are shifted to higher frequencies as compared to the free nitrite ion (1329 and 1264 cm⁻¹) suggesting that the nitrite ion is coordinated via the N atom [2,11a]. The blue-violet species **1b** shows two sets of bands for $\nu_{as}(\text{NO}_2)$ (1365 and 1331 cm⁻¹) and $\nu_s(\text{NO}_2)$ (1318 and 1304 cm⁻¹) in its IR spectrum. The complex **1b** may be either the monodentate nitrito species or the nitrito(O,O) species. Generally, nitrito species exhibit $\nu_{as}(\text{NO}_2)$ at a higher frequency (observed for **1b**) and $\nu_s(\text{NO}_2)$ at a lower frequency (not observed for **1b**) than the free nitrite ion frequencies [11a,18]. On the other hand, nitrito(O,O) species show a lowering of

both $\nu_{as}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ in comparison to free ion frequencies. Therefore, from the IR spectrum of **1b** it is difficult to assign the coordination mode of the nitrite ion in it. Now the electronic spectral and electrolytic conductance studies may impart some light on the mode of nitrite ion coordination especially in **1b**. Electronic spectral data indicate that both **1a** and **1b** possess octahedral geometry around nickel (II) and since they exhibit further splitting in the d-d band in the near-IR region they should have a *trans*-configuration [19]. The electrolytic conductance measurements in dichloromethane suggest that both **1a** and **1b** are non-conducting ($A_m = 7.1$ and $4.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for **1a** and **1b**, respectively). Since **1b** shows non-electrolytic behavior in non-coordinating solvents like dichloromethane it should be a nitrito species not the nitrito(O,O) species. From the above results it may be assumed that both **1a** and **1b** possess a *trans*-octahedral geometry, and **1a** and **1b** are, respectively, the nitro and nitrito linkage isomers.

The ORTEP view of complex **1a** with the atom numbering scheme has been depicted in Fig. 1. The selected bond lengths and bond angles are shown in Table 2. The hydrogen bonding is presented in Table 3. The structure consists of a discrete $\text{NiL}_2(\text{NO}_2)_2$ molecule and the nickel atom occupies an inversion center. The coordination polyhedron around the metal atom may be best described as a distorted octahedron. The four nitrogen atoms of the diamine part of the ligands (N1, N2 and their centrosymmetrically related atoms) define the equatorial plane and the two nitrogen atoms belonging to the nitro groups (N5 and its centrosymmetric counterpart) coordinate in *trans* axial positions. The Ni-N (amine) distances, ranging between 2.032(4) and 2.372(3) Å, are consistent with the corresponding values observed in similar systems. The discrepancy between the two Ni-N distances is a consequence of the steric constraints imposed by the bulky morpholine

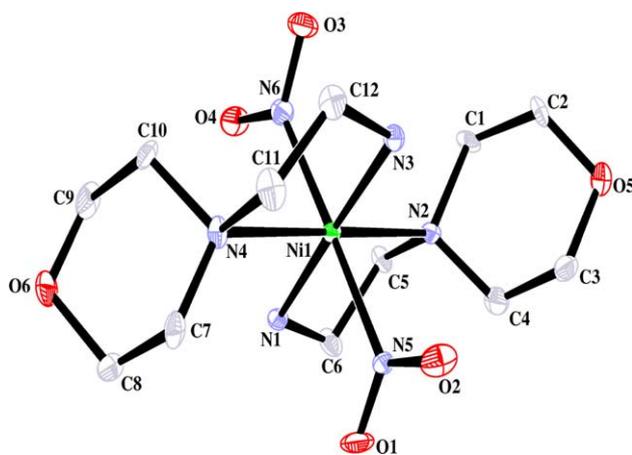


Fig. 1. ORTEP [21] diagram of *trans*- $[\text{NiL}_2(\text{NO}_2)_2]$ (**1a**) [L = 4-(2-aminoethyl)morpholine] with the atom numbering scheme. Ellipsoids are drawn at 50% probability.

Table 3
H-bonding list for complex **1a**

D-H...A	D-H	H...A	D...A	$\angle \text{D-H...A}$
N1-H1A...O1 ^a	0.9001	2.4179	2.869(5)	111.22
N1-H1A...O3 ^a	0.9001	2.2971	3.008(6)	135.77
N1-H1B...O4 ^b	0.9002	2.4179	2.979(5)	120.67
N1-H1B...O5 ^b	0.9002	2.3680	3.164(5)	147.41
N3-H3A...O2 ^c	0.8998	2.4347	2.973(5)	118.63
N3-H3A...O6 ^c	0.8998	2.4024	3.187(5)	145.74
N3-H3B...O1 ^d	0.9005	2.3904	3.085(6)	134.05
N3-H3B...O3 ^d	0.9005	2.4847	2.952(6)	112.73
C3-H3D...O3 ^e	0.9700	2.4708	3.398(6)	159.89
C4-H4B...N5 ^e	0.9709	2.6131	3.198(6)	118.94
C5-H5B...O4 ^e	0.9705	2.5920	3.330(5)	132.94
C9-H9A...O1 ^f	0.9700	2.5503	3.503(6)	167.43
C10-H10A...N6 ^f	0.9693	2.5664	3.155(7)	119.22

^a Symmetry codes: $1 + x, y, z$.

^b Symmetry codes: $x, y, -1 + z$.

^c Symmetry codes: $x, y, 1 + z$.

^d Symmetry codes: $-1 + x, y, z$.

^e Symmetry codes: $1 + x, y, 1 + z$.

^f Symmetry codes: $-1 + x, y, -1 + z$.

group. The crystal packing diagram of **1a**, done by using program PLATON99 [20], is shown in Fig. 2 which reveals a two dimensional infinite chain structure through a hydrogen bonding network.

The proposition made regarding the structure of complex **1a** and the coordination mode of the nitrite ions in it by routine physicochemical techniques have been established unambiguously through the X-ray single crystal structure analysis of **1a**. Our efforts to synthesize single crystals of **1b** yielded no results. However, routine physicochemical studies suggest that **1b** should be a monodentate nitrito species with a *trans*-octahedral

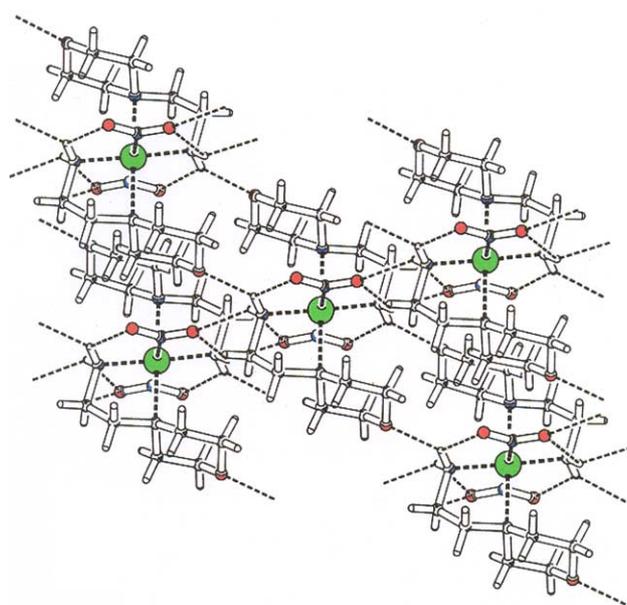


Fig. 2. Crystal packing diagram of *trans*- $[\text{NiL}_2(\text{NO}_2)_2]$ (**1a**) [L = 4-(2-aminoethyl)morpholine] and H-bonds (-----) in the crystal structure.

configuration. Therefore, the bulkiness of the morpholine moiety in the ligand 4-(2-aminoethyl)morpholine is just the optimum to stabilize both the nitro and nitrito isomers in the solid state as we observed earlier only in one case with the ligand 1-(2-aminoethyl)piperidine.

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Appendix A. Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition number CCDC 264274. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2005.04.039](https://doi.org/10.1016/j.poly.2005.04.039).

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