

First structural characterisation of nitro–nitrito linkage isomers of nickel(II): synthesis and single crystal structures of $[\text{NiL}_2(\text{NO}_2)_2]$ and $[\text{NiL}_2(\text{ONO})_2]$ [$\text{L} = 1\text{-}(2\text{-aminoethyl})\text{piperidine}$]

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The linkage isomers *trans*-bis[1-(2-aminoethyl)piperidine]dinitronickel(II) (brown) **1** and *trans*-bis[1-(2-aminoethyl)piperidine]dinitritonickel(II) (blue) **2** have been synthesized and characterised by X-ray single crystal structure analysis.

The nitrite ion is a well known ambidentate ligand, capable of binding through the N or O atoms. There are nine different ways in which the nitrite ion can function as a ligand. Out of these nine modes eight have been confirmed by X-ray crystallography.¹ These different modes of binding lead to the linkage isomerism in the nitrite complexes. The best known examples are the nitro and nitrito monodentate linkage isomers formed by cobalt(III), rhodium(III), iridium(III) and platinum(IV).² In all of these complexes the nitrito isomers are thermodynamically unstable and are only formed because of the unusual reaction kinetics and relatively inert nature of these metal ions.

The existence of nitro–nitrito linkage isomers has also been postulated for several nickel(II) nitrite amine complexes.^{3–6} It has also been suggested that there is a general trend for the nitrite to co-ordinate *via* oxygen when the ligands carry bulky substituents.¹ However, to the best of our knowledge there is no genuine report of monodentate nitro–nitrito linkage isomerism in the nickel(II) complexes. The existence of such isomerism was suggested later to be due to different kind of linkage isomerism. As for examples, the red nitro complex $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ on heating at *ca.* 120 °C changes to a blue form and it was suggested initially that this blue form is probably the nitrito isomer of the molecule.⁶ Now, it seems more likely that the blue form contains one chelating and one non-bonded ionic nitrite.⁷ The blue form of $\text{Ni}(N,N'\text{-meen})_2(\text{NO}_2)_2$ ($N,N'\text{-meen} = N,N'\text{-dimethylethane-1,2-diamine}$) also possesses similar structure.⁸ The existence of a mixture of both the forms of $\text{Ni}(\text{C}_9\text{H}_7\text{N})_4(\text{NO}_2)_2$ ($\text{C}_9\text{H}_7\text{N} = \text{isoquinoline}$) has been reported only on the basis of IR spectra,⁹ but no attempt was made to separate the isomers. Thus in all of the systems reported so far, neither the isomerism was confirmed by X-ray single crystal analysis, nor even both the pure isomers were isolated in stable form.

We report here the syntheses of both monodentate nitro and nitrito isomers of nickel(II) complexes of 1-(2-aminoethyl)piperidine. This is the first example where both the isomers are stable and their structures have been characterised by X-ray single crystal analysis.

Experimental

Materials

High purity (98%) 1-(2-aminoethyl)piperidine (L) was purchased from Aldrich Chemical Company Inc. and used as

received. Potassium hexanitronickelate(II) monohydrate was prepared as usual.⁴

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyser and nickel(II) content was estimated gravimetrically.¹⁰ Infrared spectra (4000–400 cm^{-1}) were taken at 27 °C using a Perkin-Elmer IR 783 spectrometer where KBr was used as medium, electronic spectra (1400–200 nm) at 27 °C using a Hitachi UV-VIS-NIR model U-3410 spectrometer where Nujol was used as a medium as well as a reference. The magnetic susceptibility was measured at 27 °C using an EG and G PAR 155 vibrating sample magnetometer, where $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a reference material and diamagnetic corrections were made using Pascal's constants. Molar conductances were measured using a Systronics 304 conductivity meter, where the cell constant was calibrated with 0.02 M KCl solution and dry methanol was used as solvent.

Preparations

The complexes $\text{NiL}_2(\text{NO}_2)_2$ **1** (brown) and $\text{NiL}_2(\text{ONO})_2$ **2** (blue) were synthesized by adding a methanolic solution (5 cm^3) of the diamine (2 mmol) to a methanolic suspension (10 cm^3) of potassium hexanitronickelate(II) monohydrate (1 mmol). The resulting dark green solution was kept in a CaCl_2 desiccator (yield 81%). After a few days a mixture of brown and blue crystals was obtained which was easily separable by tweezers [Found for **1**: C, 41.1; H, 7.7; N, 20.7; Ni, 14.3. Calc. for $\text{C}_{14}\text{H}_{32}\text{N}_6\text{NiO}_4$: C, 41.3; H, 7.9; N, 20.7; Ni, 14.4. μ_{eff} 2.97 μ_{B} . λ_{max} (Nujol) 1195, 847 and 495 nm. Found for **2**: C, 41.2; H, 7.8; N, 20.7; Ni, 14.3%. μ_{eff} 2.98 μ_{B} . λ_{max} (Nujol) 1194, 899 and 581 nm].

Crystallography

All measurements of complexes **1** and **2** were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). Cell constants and the orientation matrix for data collection were determined by least-squares refinement using the setting angles of 25 and 24 carefully centred reflections in the range $29.54 < 2\theta < 29.99^\circ$ for **1** and $28.07 < 2\theta < 29.97^\circ$ for **2**. Crystal data collection and structure solution parameters for complexes are summarised in Table 2.

Table 1 Electronic absorption maxima of the complexes **1** and **2**

Compound	Medium	$\tilde{\nu}_{\max}/\text{cm}^{-1}$ ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$)
1	Mull	20,186; 11,805; 8,369 (sh)
2	Mull	17,224; 11,130; 8,374 (sh)
1	CH ₃ OH (0.001 M)	16,000 (11.2); 9,615 (7.6)
2	CH ₃ OH (0.001 M)	16,000 (13.4); 9,615 (8.8)
1	CH ₂ Cl ₂ (0.02 M)	20,619 (70.3); 10,256 (40.8)
2	CH ₂ Cl ₂ (0.02 M)	20,619 (88.6); 10,256 (52.4)

The structure was solved by direct methods¹¹ and expanded using Fourier techniques.¹² The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1516 for **1**, 1558 for **2** observed reflections [$I > 1.50\sigma(I)$] and 133 for **1**, 116 for **2** variable parameters and converged with unweighted and weighted agreement factors of $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.046$ for **1**, 0.036 for **2**, and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.065$ for **1**, 0.064 for **2**. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.96 and $-1.04 \text{ e } \text{\AA}^{-3}$ for **1**, 0.47 and $-0.47 \text{ e } \text{\AA}^{-3}$ for **2**, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.¹³ Anomalous dispersion effects were included in F_{calc} ,¹⁴ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁵ The values for the mass attenuation coefficients are those of Creagh and Hubbel.¹⁶ All calculations were performed using the TEXSAN¹⁷ crystallographic software package.

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Results and discussion

Infrared spectra

The shifts exhibited by the asymmetric and symmetric stretching frequencies are used to indicate the mode of bonding of the nitrite group, *i.e.* whether it co-ordinates through the nitrogen atom (nitro complex) or through the oxygen atom (nitrito complex).^{18–21} In the present paper IR bands for the nitrite groups were identified by comparison of the nitrite complexes with the nickel thiocyanate and nickel halide analogues. The bands due to ν_{asym} , ν_{sym} and δ of nitrite appear at 1360, 1285 and 815 cm^{-1} , respectively for $\text{NiL}_2(\text{NO}_2)_2$ and at 1385, 1138 and 820 cm^{-1} , respectively for $\text{NiL}_2(\text{ONO})_2$. In the case of the nitro complex, both $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ are shifted to higher frequencies as compared to the free nitrite ion.^{19,22} In the nitrito complexes, $\nu_{\text{asym}}(\text{NO}_2)$ lies at higher and $\nu_{\text{sym}}(\text{NO}_2)$ at lower values than the free ion frequencies.^{2,23} The bands at 815 and 820 cm^{-1} are assigned to the bending mode of the nitro and nitrito complexes, respectively.

Far-IR spectra

There are two additional bands obtained for the nitro complex compared to the nitrite complex in the far-IR region. The bands obtained at 354 and 521 cm^{-1} , assigned for Ni–N stretching mode and wagging mode (ρ_w),^{21,24} respectively, are clear evidence for the nitro complexes.

Electronic spectra and electrolytic conductance

The electronic spectral bands of complexes **1** and **2** in mull, methanol and dichloromethane are listed in Table 1. The **1** (brown) and **2** (blue) species on dissolution in methanol (or ethanol) give light green solutions the electronic spectra of which are identical and very similar to those of the nitrito isomer. On the other hand, in dichloromethane (or in chloroform) both the isomers produce pink solutions whose electronic spectra correspond to those of the nitro isomer. The measurement of electrolytic conductance of the isomers shows that they are non-conducting in dichloromethane ($\Lambda_m = 6.2 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$),

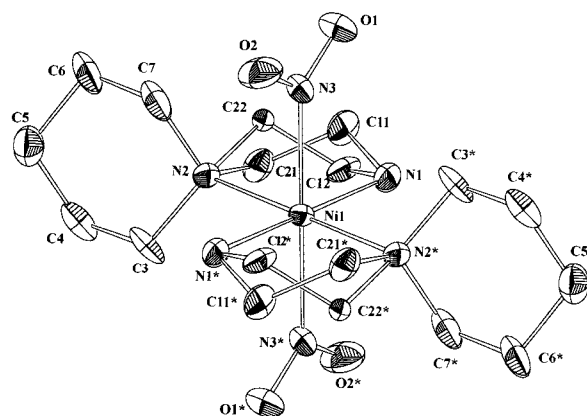


Fig. 1 An ORTEP diagram of complex **1** showing two positions of the disordered dimethylene bridge (occupancies 75% for C11, C21, 25% for C12, C22). Atomic displacement ellipsoids are drawn at 50% probability (atoms related *via* the inversion centres are labelled with asterisks).

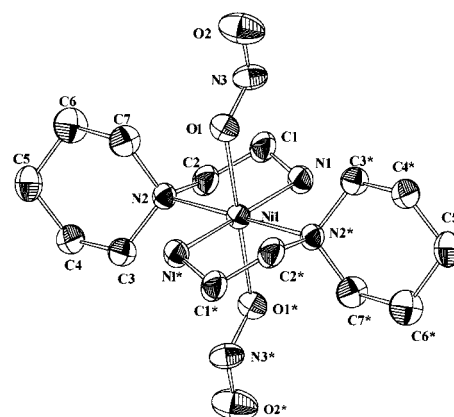
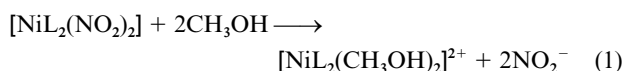


Fig. 2 An ORTEP diagram of complex **2**. Ellipsoids are drawn at 50% probability (atoms related *via* the inversion centres are labelled with asterisks).

whereas they are 1:1 electrolytes in methanol ($\Lambda_m = 110.5 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The higher conductance value in methanol may be attributed to the contribution of solvated species as in eqn. (1).



Thus, from the above results it is evident that in inert solvents such as chloroform or dichloromethane the nitro form is stabilised. On the other hand, in co-ordinating solvents such as methanol or ethanol the stable form is either the nitrito isomer or its solvated species. This is also corroborated by the ratio of the weights of the brown and blue isomers obtained by slow evaporation of the corresponding saturated solutions (*ca.* 5:1 for dichloromethane; *ca.* 3:1 for methanol).

Crystal structures

The ORTEP²⁵ diagrams of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are presented in Table 3. The non-bonding and hydrogen bonding contacts are presented in Table 4. Both the structures consist of discrete $\text{NiL}_2(\text{NO}_2)_2$ molecules. The nickel atoms at the inversion centre are coplanar with four ligand nitrogen atoms (N1, N2 and their centrosymmetrically related ones). The geometry around Ni^{II} is distorted octahedral. The difference between the compounds lies in the co-ordinating atom of the nitrite with nickel(II): N in the case of **1** and O in the case

Table 2 Crystallographic data for complexes **1** and **2**

	1	2
Empirical formula	C ₁₄ H ₃₂ N ₆ NiO ₄	C ₁₄ H ₃₂ N ₆ NiO ₄
Formula weight	407.14	407.14
Crystal colour, habit	Brown, prismatic	Blue, prismatic
Crystal dimensions/mm	0.13 × 0.25 × 0.35	0.25 × 0.38 × 0.50
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>Pbca</i> (no. 61)
<i>a</i> /Å	9.689(7)	9.73(5)
<i>b</i> /Å	8.348(6)	19.98(4)
<i>c</i> /Å	11.912(6)	9.50(5)
β /°	109.00(4)	
<i>V</i> /Å ³	911.0(9)	1835.6(6)
<i>Z</i>	2	4
<i>D</i> _f /g cm ⁻³	1.484	1.473
<i>F</i> (000)	436.00	872.00
μ (Mo-K α)/cm ⁻¹	10.98	10.89
<i>T</i> /°C	23.0	23.0
No. reflections measured	total 2372 unique 2247 (<i>R</i> _{int} = 0.036)	total 2432

Table 3 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	2
Ni1–N1	2.056(3)	2.077(2)
Ni1–N2	2.253(3)	2.242(2)
Ni1–N3	2.10(3)	—
Ni1–O1	—	2.116(2)
N1–Ni1–N2	83.1(1)	83.4(7)
N1–Ni1–N3	91.1(1)	—
N2–Ni1–N3	90.7(1)	—
O1–Ni1–N1	—	94.7(7)
O1–Ni1–N2	—	93.6(7)

Table 4 Hydrogen bonding (*) and non-bonding contacts (distances in Å and angles in °) for complexes **1** and **2**

D–H...A	D–H	H...A	D...A	D–H...A
Complex 1				
N1–H321...O1 ^{I*}	0.950(1)	2.429(1)	3.030(1)	120.98(4)
N1–H312...O2 ^{II*}	0.950(1)	2.326(1)	2.934(2)	121.33(4)
N1–H311...O1 ^{III*}	0.950(1)	2.395(1)	3.222(2)	145.21(4)
N1–H321...O2 ^{III*}	0.950(1)	2.499(1)	3.290(2)	140.73(4)
N1–H311...N3 ^I	0.950(1)	2.906(2)	3.004(2)	86.63(4)
N1–H321...N3 ^I	0.950(1)	2.747(2)	3.004(2)	96.31(4)
C7–H9...N3 ^I	0.950(1)	2.954(1)	3.025(2)	85.12(4)
C7–H10...N3 ^I	0.950(1)	2.568(2)	3.025(2)	109.84(4)
C11–H111...O1 ^I	0.950(1)	2.586(2)	3.209(2)	123.54(6)
C3–H1...N3 ^{II}	0.950(1)	2.536(1)	3.073(2)	115.97(5)
C12–H122...O2 ^{II}	0.950(1)	2.361(1)	3.041(1)	127.91(4)
N1–H312...N3 ^{II}	0.950(1)	2.679(1)	2.945(1)	96.69(4)
N1–H322...O2 ^{II}	0.950(1)	2.604(1)	2.934(2)	100.82(4)
N1–H322...N3 ^{II}	0.950(1)	2.860(1)	2.945(1)	85.64(6)
Complex 2				
N1–H1...O1 ^I	0.950(1)	2.995(1)	3.084(1)	86.42(2)
N1–H1...N3 ^I	0.950(1)	2.699(1)	3.060(1)	103.48(2)
C7–H15...O1 ^I	0.950(1)	2.847(1)	3.036(1)	92.15(1)
C7–H16...O1 ^I	0.950(1)	2.667(1)	3.036(1)	103.91(1)
N1–H1...O2 ^{IV}	0.950(1)	2.802(1)	3.136(1)	101.89(1)
N1–H2...O2 ^{IV*}	0.950(1)	2.603(0)	3.136(1)	115.94(1)
N1–H2...O1 ^V	0.950(1)	2.581(1)	2.840(1)	95.93(2)
C3–H7...O1 ^V	0.950(1)	2.511(1)	3.069(1)	117.73(2)
Symmetry codes: I <i>x</i> , <i>y</i> , <i>z</i> ; II $-x + 2$, $-y$, $-z + 2$; III $-x + 2$, $+y + \frac{1}{2}$, $-z + \frac{1}{2} + 2$; IV $-x + \frac{1}{2}$, $-y$, $+z - \frac{1}{2}$; V $-x + 1$, $-y$, $-z + 1$.				

of **2**. So the structures correspond to two genuine linkage isomers. The Ni–N (amine) distances ranging between 2.072 and 2.252 Å are consistent with the corresponding values observed

in similar systems.^{26–28} The discrepancy between the two Ni–N distances is a consequence of the steric constraints introduced by the bulky piperidine group. Another difference between the two molecules is that the five membered chelate rings are disordered over two conformations in **1** whereas in **2** they are not disordered.

Conclusion

As we have discussed earlier in the series of complexes of general formula Ni(diamine)₂(NO₂)₂ formed by substituted ethylenediamines, it is apparent that there is a general trend for the nitrite to co-ordinate *via* nitrogen when little interligand steric crowding is expected, but *via* oxygen when the ligands carry bulky substituents. In the present complexes the bulkiness of the piperidine group is such that the factors favouring the nitro and nitrito co-ordination are about equally balanced and syntheses of both the isomers become possible.

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