First report on thermally induced nitro → nitrito(*O*,*O*) linkage isomerization in diamine complexes of nickel(II) in the solid state: X-ray single crystal structural analyses of nitro and nitrito isomers

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The brown nitro isomer, *trans*-[$NiL_2(NO_2)_2$], **1** (L = *N*,*N*′-dipropyl-1,2-diaminoethane), was synthesized by adding L to a suspension of $K_4[Ni(NO_2)_6] \cdot H_2O$ in methanol. Complex **1** is metastable at *ca.* 298 K and transforms slowly to the greenish blue nitrito(*O*,*O*) isomer, *cis*-[$NiL_2(O_2N)$](NO_2), **2**. This transformation is accelerated with increasing temperature and slowed down on lowering the temperature (<283 K). Complex **2** shows a reversible phase transition, **2** ↔ **3** (cooling: $\Delta H = 8.150 \pm 0.004$ kJ mol^{-1}; 266–255 K; heating: $\Delta H = -7.960 \pm 0.003$ kJ mol^{-1}; 257–268 K), whereas complex **1** does not exhibit any such transition. The structures of **1**, **2** and **3** have been characterized by X-ray single crystal structure analyses, which reveal that **1** and **2**/**3** are nitro and nitrito(*O*,*O*) linkage isomers, respectively. Complexes **2** and **3** have essentially similar structures and their reversible transformation is supposed to be due to the change in thermal motion of the side chains on variation of temperature.

The versatile coordinating ability of the nitrite ion attracted much interest from chemists, who explored its chemistry in the early days of coordination chemistry. Several interesting reports in the literature concern the nickel(II) nitrite system,[1–9] which reveal that the mode of nitrite coordination is largely influenced by the nature of the neighboring ligand, temperature and solvent. To study the factors responsible for the various modes of NO_2^- coordination in nickel(II) complexes, the system best suited for our initial investigations seemed to be $NiL_2(NO_2)_2$ (L = 1,2-diaminoethane and its derivatives) as the 1,2-diaminoethane ligand may be tuned sterically, as well as electronically, by changing substituents on N and/or C. In the present work we have chosen *N*,*N*′-dipropyl-1,2-diaminoethane as the diamine ligand L. The chemistry of nickel(II) nitrite with *N*,*N*′-dimethyl-1,2-diaminoethane (*N*,*N*′-dmen)[8] and *N*,*N*′-diethyl-1,2-diaminoethane (*N*,*N*′-deen)[2,4a] is very interesting. The *trans*-dinitro complex can only be characterized for *N*,*N*′-dmen in the solid state as well as in solution, whereas *N*,*N*′-deen yields a nitrito(*O*,*O*) complex in the solid state. This nitrito(*O*,*O*) species exhibits a nitro–nitrito(*O*,*O*) equilibrium in different solvents. But the nitro form cannot be isolated in the solid state. Appropriate tuning of the bulkiness of the substituent may allow the linkage isomers to be isolated in the solid state, just as we reported the first structurally characterized nitro and nitrito linkage isomers of nickel(II) with 1-(2-aminoethyl)piperidine as the ligand, whose isomers are not interconvertible in the solid state.[10] Here, we present the first report on thermally induced nitro → nitrito(*O*,*O*) linkage isomerization in diamine complexes of nickel(II) in the solid state, a (more) disordered ↔ (less) disordered phase transition of the nitrito(*O*,*O*) isomer in the solid state and their X-ray single crystal structure analyses.

Experimental

Materials and measurements

High purity (98%) *N*,*N*′-dipropyl-1,2-diaminoethane (L) was purchased from Lancaster Chemical Company Inc. and used as received. Potassium hexanitronickelate(II) monohydrate was prepared in the usual way.[4b] Solvents were dried according to standard procedures and distilled before use.

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer and the nickel(II) content was estimated gravimetrically.[11] IR spectra (4000–600 cm^{-1}) were taken as Nujol and hexachlorobutadiene mulls using a Jasco FT-IR (model 300E) spectrometer. Electronic spectra (1400–200 nm) were obtained using a Hitachi UV-VIS-NIR (model U-3410) spectrometer where Nujol was used as a medium as well as a reference. The magnetic susceptibilities were measured using an EG&G PAR 155 vibrating sample magnetometer and diamagnetic corrections were made using Pascal's constants.[12] All the physicochemical studies of **1** and **2** were performed at 278 and 298 K, respectively. The thermal analyses (TG-DTA) were carried out on a Shimadzu DT-30 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 cm^3 min^{-1}). The sample (particle size within 150–200 mesh) was heated in a platinum crucible at a rate of 10 °C min^{-1} with inert alumina as reference. The enthalpy change for the phase transition was calculated using

Table 1 Crystal data and refinement details for complexes **1**, **2** and **3**

	1	**2**	**3**
Formula	$C_{16}H_{40}N_6NiO_4$	$C_{16}H_{40}N_6NiO_4$	$C_{16}H_{40}N_6NiO_4$
FW	439.25	439.25	439.25
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	7.4721(10)	10.2830(9)	10.3131(7)
b/Å	7.5310(10)	19.467(2)	19.2548(12)
c/Å	11.0761(9)	12.124(2)	12.0523(8)
α/°	93.42(1)	90	90
β/°	102.04(1)	95.40(1)	96.47(1)
γ/°	100.49(1)	90	90
U/Å^3	596.29(12)	2416.2(4)	2378.1(3)
Z	1	4	4
μ/cm^{-1}	8.43	8.32	8.00
No. meas. reflect.	4723	4466	6836
No. indep. reflect. (R_{int})	2486(0.085)	4219(0.029)	3995(0.024)
R^a	0.0795	0.0521	0.0404
$R_w{}^b$	0.2150	0.1088	0.1095
T/K	278(2)	293(2)	258(2)

[a] $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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

	1		**2**	**3**
Ni–N1	2.117(5)	Ni–N1	2.130(4)	2.133(2)
Ni–N2	2.119(5)	Ni–N2	2.102(4)	2.104(2)
Ni–N3	2.134(4)	Ni–N3	2.126(4)	2.126(2)
		Ni–N4	2.100(4)	2.108(2)
		Ni–O1	2.127(3)	2.134(2)
		Ni–O2	2.129(3)	2.127(2)
N1–Ni–N2	83.0(2)	N2–Ni–N1	84.21(9)	84.20(9)
N1–Ni–N3	91.0(2)	N2–Ni–N4	99.78(8)	99.77(8)
N2–Ni–N3	87.7(2)	N2–Ni–N3	92.84(8)	92.85(8)
N1*–Ni–N1	180.0	N4–Ni–N3	83.87(8)	83.86(9)
N2–Ni–N2*	180.0	N4–Ni–N1	92.28(9)	92.27(9)
N3–Ni–N3*	180.0	N3–Ni–N1	174.70(8)	174.69(8)
		N2–Ni–O2	100.15(8)	100.17(8)
		N4–Ni–O2	160.01(8)	160.00(8)
		N3–Ni–O2	93.66(8)	93.66(8)
		N2–Ni–O1	158.82(8)	158.83(8)
		N4–Ni–O1	101.34(8)	101.33(8)
		N3–Ni–O1	91.10(8)	91.09(8)
		O2–Ni–O1	58.80(7)	58.79(8)
		N1–Ni–O1	93.24(8)	93.24(9)
		O2–Ni–N1	91.20(8)	91.21(9)
		O3–N6–O4	114.3(14)	122.4(4)

Table 3 Hydrogen bonding in complexes **1**, **2** and **3**

D–H···A	H···A/Å	D···A/Å	∠D–H···A/°
1			
N1–H1···O2A^{i}	2.399(10)	3.018(10)	125.3(6)
N2–H2···O2^{i}	2.335(14)	3.033(14)	133.5(6)
C1–H1B···O2^{ii}	2.189(14)	2.996(14)	139.8(8)
C2–H2B···O1A^{iii}	2.193(9)	2.982(10)	137.5(6)
C6A–H62A···O2A^{ii}	2.443(10)	3.197(10)	134.4(5)
C8A–H83A···O2A^{ii}	2.209(10)	3.088(10)	151.7(5)
2			
N1–H1···N6^{i}	2.339(12)	3.203(11)	158.3(5)
N2–H2···O4^{ii}	2.197(9)	3.094(9)	168.7(5)
N3–H3···O3^{ii}	2.169(7)	3.050(7)	162.4(5)
N4–H4···O3^{i}	2.179(7)	3.065(7)	164.2(4)
C2–H2A···O3^{i}	2.554(8)	3.459(8)	155.3(6)
C5–H5C···O1^{i}	2.468(14)	3.090(11	127.4(12)
3			
N1–H1···N6^{i}	2.327(4)	3.206(4)	162.4(2)
N2–H2···O^{iii}	2.147(4)	3.047(4)	170.2(3)
N3–H3···O3^{iii}	2.129(4)	3.016(4)	164.6(2)
N4–H4···O3^{i}	2.196(4)	3.072(4)	161.3(3)
C2–H2A···O3^{i}	2.570(4)	3.468(4)	153.8(4)

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

a Perkin-Elmer (model DSC-7) differential scanning calorimeter with indium metal as a calibrant (heating rate: 10 °C min^{-1}).

Preparations

***trans*-[NiL$_2$(NO$_2$)$_2$] (brown), 1.** This complex was synthesized by adding a methanolic solution (5 cm^3) of the diamine (2 mmol) to a suspension (10 cm^3) of potassium hexanitronickelate(II) monohydrate (1 mmol) in methanol at ambient temperature (298 K). The resulting solution was kept in a $CaCl_2$ desiccator. After a few days, brown crystals were separated out, filtered, washed with methanol and preserved at < 283 K. Yield 80%. **1** was also obtained in solvents other than methanol: ethanol, propanol, *n*-butanol, chloroform, dicholoromethane, benzene, acetone, *etc.* Anal. calc. for $C_{16}H_{40}N_6NiO_4$: C, 43.8; H, 9.1; N, 19.1; Ni, 13.4%. Found: C, 43.7; H, 9.0; N, 19.1; Ni 13.3%. μ_{eff} 2.98 BM at 278 K. λ_{max} (Nujol; 278 K) 1321, 1177, 659, 421 nm. Single crystals suitable for X-ray data collection were prepared by slow evaporation of the methanolic solution of **1** at *ca.* 278 K.

***cis*-[NiL$_2$(O$_2$N)](NO$_2$) (greenish blue), 2.** This complex was synthesized in the solid state by keeping complex **1** at *ca.* 298 K for a few days. The rate of conversion is accelerated with increasing temperature (100% conversion within 5 days at 298 K). Anal. calc. for $C_{16}H_{40}N_6NiO_4$: C, 43.8; H, 9.1; N, 19.1; Ni, 13.4%. Found: C, 43.7; H, 9.0; N, 19.1; Ni 13.3%. μ_{eff} 2.98 BM at 298 K. λ_{max} (Nujol; 298 K) 1340, 725 and 491 nm. Single crystals suitable for X-ray data collection were obtained by keeping the single crystals of **1** at *ca.* 298 K for 5 days.

X-Ray crystallography

Suitable single crystals of the complexes **1** and **2** were mounted on a Siemens CCD system for data collection. Crystal data for complex **1** was collected at 278(2) K, while this was done for **2** at 293(2) and 258(2) K to obtain the data for complex **2** and its low temperature phase analog, **3**. Intensity data were collected in the $\omega - 2\theta$ scan mode using graphite monochromated Mo-Kα radiation (0.71073 Å). The intensity data were corrected for Lorentz and polarization effects.[13] The empirical absorption corrections were based on ψ-scans. The structure was solved by Patterson methods, followed by Fourier syntheses, and refined through full-matrix least-squares calculations. During the refinement the crystal structures of **1** and **2** were found to be disordered. In complex **1**, each of the carbon atoms of the four *N*-substituted propyl groups as well as the oxygen atoms of the NO_2 groups are distributed over two positions (C3, C3A; C4, C4A; C5, C5A; C6, C6A; C7, C7A; C8, C8A and O1, O1A, O2, O2A) with a site occupancy ratio of 0.6 : 0.4 in each case. In complex **2**, each carbon atom of the two *N*-substituted propyl groups is distributed over two positions (C5, C5A; C6, C6A; C7, C7A; C11, C11A; C12, C12A; C13, C13A) with a site occupancy ratio of 0.6:0.4 in each case. Anisotropic full-matrix refinements based on F^2 were carried out for all non-hydrogen atoms. The located hydrogen atoms, with isotropic thermal parameters 1.2 times U_{eq} of the atom to which they were attached were treated as fixed contributors to the final structure factor calculations. Complex neutral atom scattering factors[14] were used throughout the refinement. All calculations were carried out using SHELXS 86,[15] SHELXL 93,[16] PLATON 99[17] and ZORTEP[18] programs. Selected crystallographic data for complexes **1**, **2** and **3** are displayed in Table 1 while selected bond lengths and bond angles of the three complexes are presented in Table 2. The H-bonding and nonbonding contacts of **2** and **3** are listed in Table 3.

CCDC reference numbers 153398–153400. See http://www.rsc.org/suppdata/nj/b0/b008254f/ for crystallographic data in CIF or other electronic format.

Results and discussion

The study of the complexation reaction upon adding *N*,*N*′-dipropyl-1,2-diaminoethane (L) to a suspension of $K_4[Ni(NO_2)_6]\cdot H_2O$ in different solvents like methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, chloroform, dichloromethane, benzene and acetone reveals that a brown complex **1** with composition $NiL_2(NO_2)_2$ is formed, irrespective of the nature of the solvent used. On keeping **1** in a desiccator or in open atmosphere it gradually transforms to a greenish-blue form, **2**. This transformation is accelerated with increasing temperature[19] and once the greenish-blue species is formed it never reverts back. However, the brown form may be preserved by storage at <283 K. On heating complex **2** undergoes decomposition at *ca.* 421 K without showing any phase transition. However, it exhibits a phase transition on cooling ($\Delta H = 8.150 \pm 0.004$ kJ mol^{-1}; 266–255 K) that reverts back on heating ($\Delta H = -7.960 \pm 0.003$ kJ mol^{-1}; 257–268 K). Complex **1** does not show any such phase transition on cooling.

Freshly prepared brown **1** exhibits IR spectral bands at 1336, 1304 and 813 cm^{-1} [10,20] assigned as ν_{as}, ν_s and δ bands characteristic of nitro coordination, whereas the greenish-blue **2** shows the corresponding IR spectral bands at 1270, 1205 and 840 cm^{-1}, characteristic of nitrito(*O*,*O*) coordination. Magnetic susceptibility measurements and electronic spectral studies (Nujol) reveal that nickel(II) is in an octahedral configuration in both complexes. Complex **2** does not show any splitting of the d–d bands in the NIR region suggesting a *trans* configuration, whereas complex **1** exhibits further splitting of d–d bands in the NIR region indicating *cis* configurations.[21] From the routine physicochemical studies it may be inferred that complexes **1** and **2** are linkage isomers, but it is difficult to comment on complex **3** as we could not measure the IR, electronic spectrum and magnetic susceptibility at 258 K. However, we have been able to collect single crystal X-ray data.

Description of the structures for complexes 1, 2 and 3

The solution of the crystal structure of complex **1** reveals that it consists of discrete $NiL_2(NO_2)_2$ molecules. A ZORTEP view of complex **1** with two positions for each of the disordered propyl groups and the atom numbering scheme is shown in Fig. 1. The nickel atom occupies the inversion center. The coordination polyhedron of the metal atom is a distorted octahedron. The four nitrogen atoms, N1, N2 and N1*, N2* (* designates the centro-symmetrically related atoms) of the bidentate diamine ligand define the equatorial plane and two nitrogen atoms, N3 and N3*, of the NO_2 group coordinate in *trans* axial positions. The N3–Ni–N3* axis is nearly orthogonal to the equatorial plane [angle range: 87.7(2) to 91.0(2)°]. In-plane distortion is introduced by a ligand bite angle, N1–Ni–N2, of 83.0(2)°. The Ni–N bond distances of the equatorial plane are similar [Ni–N1 2.117(5); Ni–N2 2.119(5) Å] and are shorter than the axial Ni–N3 distance [2.134(4) Å]. The Ni–N(amine) distances are consistent with corresponding values observed in similar systems, whereas the Ni–N(nitro) distances are longer compared to similar systems,[8,16] which reveals that the approach of the nitro groups is severely hindered. The five-membered chelate ring N1–C1–C2–N2–Ni displays an open envelope geometry with the C1 atom on the flap, 0.611 Å away from the least-squares plane through the remaining endocyclic atoms. The conformation of the diamine chelate ring is $\delta\lambda$ as the molecule has a center of inversion.

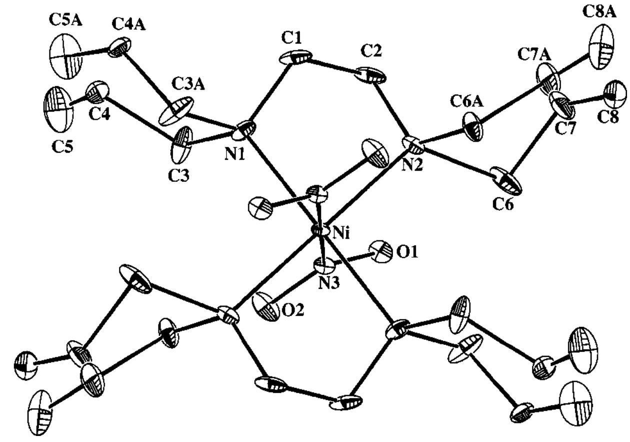

Fig. 1 ZORTEP diagram of *trans*-$[NiL_2(NO_2)_2]$, **1**, showing the two orientations of the four disordered propyl groups at 50% probability levels.

The ZORTEP views of complex **2**, showing two positions of the disordered propyl groups, and complex **3**, with the atom numbering scheme, are depicted in Fig. 2 and 3, respectively. Both of them have similar structures, consisting of discrete $[NiL_2(O_2N)]$ cations and NO_2 anions. Hence, a general description of the structures of **2** and **3** will be given. The ligand moieties (L and NO_2) are monometallic and bidentate.

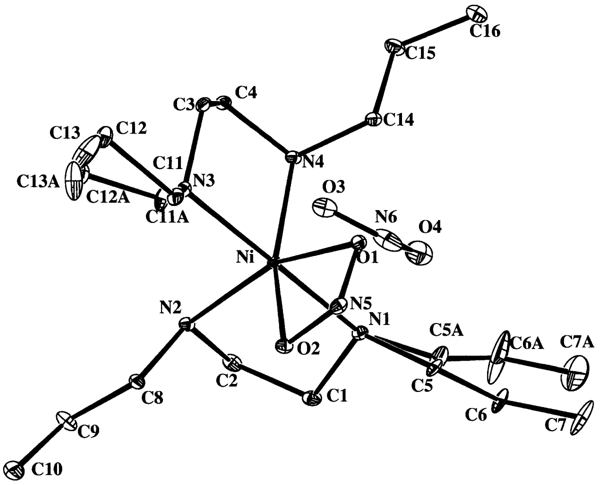

Fig. 2 ZORTEP diagram of *cis*-$[NiL_2(O_2N)](NO_2)$, **2**, showing the two orientations of two disordered propyl groups at 50% probability levels.

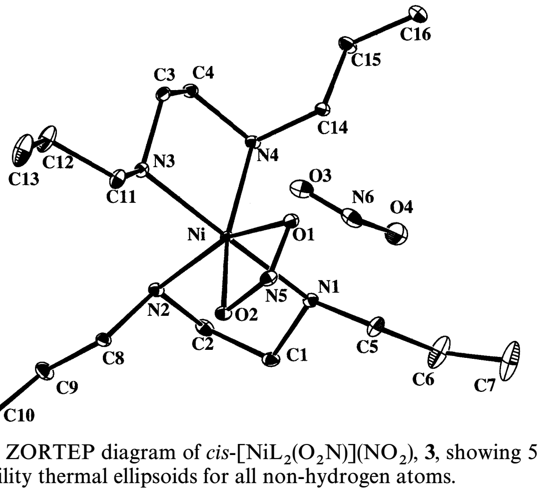

Fig. 3 ZORTEP diagram of *cis*-$[NiL_2(O_2N)](NO_2)$, **3**, showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Table 4 Coordination modes of the nitrite ion in nickel(II) nitrite complexes of diamines

Diamine[a]	Complex	Coord. type	Evidence[b]	Ref.
$NH_2CH_2CH_2NH_2$ (en)	$[Ni(en)_2(NO_2)_2]$	*trans*-Dinitro	x	2
$NH_2CH_2CH_2NH_2$ (en)	$[Ni(en)_2(NO_2)_2]\cdot H_2O$	*cis*-Dinitro	x	5
$NH_2CH_2CH_2NH_2$ (en)	$[Ni(en)_2(O_2N)]NO_2$	Chelating	i	4*c*
$MeNHCH_2CH_2NH_2$ (men)	$[Ni(men)_2(NO_2)_2]$	*trans*-Dinitro	i	22
$EtNHCH_2CH_2NH_2$ (een)	$[Ni(een)_2(NO_2)_2]$	*trans*-Dinitro	x	23
$MeNHCH_2CH_2NHMe$ (*N*,*N*′-dimen)	$[Ni(N,N'\text{-dmen})_2(NO_2)]\cdot H_2O$	*trans*-Dinitro	x	8
$EtNHCH_2CH_2NHEt$ (*N*,*N*′-dieen)	$[Ni(N,N'\text{-dieen})_2(NO_2)_2]$	*trans*-Dinitro	e	4*a*
$EtNHCH_2CH_2NHEt$ (*N*,*N*′-dieen)	$[Ni(N,N'\text{-dieen})_2(O_2N)]NO_2$	Chelating	x	6
$(Me)_2NCH_2CH_2NH_2$ (*N*,*N*-dimen)	$[Ni(N,N\text{-dimen})_2(ONO)_2]$	*trans*-Dinitrito	x	1, 8
$(Et)_2NCH_2CH_2NH_2$ (*N*,*N*-dieen)	$[Ni(N,N\text{-dieen})_2(ONO)_2]$	*trans*-Dinitrito	i, e	7
$(Me)_2NCH_2CH_2N(Me)_2$ (*N*,*N*,*N*′,*N*′-tetmen)	$[Ni(N,N,N',N'\text{-tetmen})(O_2N)_2]$	Chelating	x	8
$NH_2CH(Ph)CH(Ph)NH_2$ (m-stien)	$[Ni(\text{m-stien})_2(O_2N)]NO_2$	Chelating	x	8
$NH_2C(Me)_2CH_2NH_2$ (ibn)	$[Ni(ibn)_2(NO_2)_2]$	*cis*-Dinitro	x	24

[a] Me = methyl; Et = ethyl; Ph = phenyl. [b] x = single crystal structure; i = infrared; e = electronic spectra.

The coordination polyhedron around the metal is best described as a distorted octahedron. Two nitrogen atoms (N2 and N4) of the diamines and two oxygen atoms (O1 and O2) of the *cis*-bidentate nitrite group define the equatorial plane and the remaining two nitrogen atoms (N1, N3) of the diamine ligand are in axial positions [N1–Ni–N3: 174.70(8)° for **2** and 174.69(8)° for **3**]. The N1–Ni–N3 axis deviates largely from orthogonality to the equatorial plane [angle ranges: 83.87(8) to 93.66(8)° for **2** and 83.86(9) to 93.66(8)° for **3**]. The Ni–N bond distances of the equatorial plane are similar [Ni–N2: 2.102(4) Å for **2**; 2.104(2) Å for **3** and Ni–N4: 2.100(4) Å for **2**; 2.108(2) Å for **3**]. As usual, the axial Ni–N distances are longer [Ni–N1: 2.130(4) Å for **2**; 2.133(2) Å for **3** and Ni–N3: 2.126(4) Å for **2**; 2.126(2) Å for **3**]. Similar types of bond distances in **1** are longer. The Ni–O distances [Ni–O1 2.127(3) Å for **2**; 2.134(2) Å for **3** and Ni–O2: 2.129(3) Å for **2**; 2.127(2) Å for **3**] are consistent with those of corresponding nickel(II) diamine-nitrite systems.[2,4a,16] The five-membered chelate rings, Ni–N1–C1–C2–N2 and Ni–N3–C3–C4–N4, display open envelope geometries with the flap atoms, C1 and C3 (0.402 and 0.403 Å for **2**; 0.454 and 0.430 Å for **3**, respectively), away from the least-squares plane through the remaining endocyclic atoms.

In complexes **1**, **2** and **3**, the overall chelate ring conformations and the crystal packing are stabilized by hydrogen bonding networks (Table 3). Crystallographic analyses prove unambiguously that complexes **1** and **2**/**3** are linkage isomers. The structures of **2** and **3** are essentially the same and the only differences are minor reductions in disorder brought about by reduced thermal motion of the side chains.

From the above discussion it is clear that complex **1** is an N-bonded nitro species, metastable at *ca.* 298 K and that may be preserved by storage below 283 K. This indicates that the nitro complex is still thermodynamically unstable at lower temperatures but that the kinetics are controlled. Complex **1** undergoes a solid-state rearrangement reaction to produce the nitrito(*O*,*O*) linkage isomer **2**, which at low temperature transforms to a more ordered species, **3**. The solid-state transformations, **1** → **2** and **2** ↔ **3**, are unique as the single crystals of **2** and **3** were synthesized in the solid state (*vide infra*) from the parent crystals, **1** and **2**, respectively.

Table 4 presents the coordination modes of the nitrite ion in nickel(II) nitrite complexes of 1,2-diaminoethane and its derivatives reported earlier.[2,4a,c,8,22–24] It is evident that N-bonded nitro complexes are preferred when little steric bulk is present on the 1,2-diaminoethane moiety, whereas O-bonded (preferably with *N*,*N*-dialkyl substituted diamines as the ligand[1,8]) or O,O-chelated (preferably with *N*,*N*′-dialkyl substituted diamines as the ligand[6]) coordination are obtained with increasing bulkiness of the diamine substituent. It is of note that we prepared the complexes cited in Table 4 and carried out their simultaneous TG-DTA experiments in the solid state. But none of them showed thermally induced isomerizations or phase transitions. The above facts reveal that propyl groups exert the optimum bulkiness for causing thermally induced linkage isomerization and a phase transition leading to a more ordered species in the nickel(II) nitro system in the solid state.

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