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Synthesis and characterization of $[NiL_2(OCOCF_3)_2]$ [L = 1-(2-aminoethyl) piperidine]: thermochromism and X-ray single crystal structure analysis

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Abstract—The complex $[NiL_2(OCOCF_3)_2]$ (**1**) [L = 1-(2-aminoethyl) piperidine] has been synthesized. Single crystal X-ray structure analysis of **1** reveals a *trans*-octahedral geometry having an N_4O_2 chromophore. **1** upon heating undergoes an irreversible endothermic phase transition (194–215°C; $\Delta H = 11.2\ \mathrm{kJ\ mol^{-1}}$) accompanied by a blue to reddish pink colour change retaining its *trans*-configuration. The thermochromism is proposed to be due to a decrease of in-plane ligand field strength resulting from conformational changes of the diamine chelate rings. © 1997 Elsevier Science Ltd

Keywords: thermochromism; X-ray single crystal analysis of nickel(II) complex; conformational isomerism; nickel(II) trifluoroacetate; 1-(2-aminoethyl)piperidine; nickel(II) diamine complex.

The thermochromic behaviour of $[NiL_2X_2]$, (where L = ethane-1, 2-diamine or its N-/C-alkyl/phenyl substituted derivatives, X a monovalent anion) is well documented in the literature [1–8]. The thermochromism in C-substituted diamine complexes of nickel(II) is a consequence of configurational changes (*cis*↔*trans*/octahedral↔square planar) and routine IR, electronic spectroscopy and magnetic susceptibility studies are sufficient to characterize the configurational isomers. For the analogous N-substituted diamine complexes, the thermochromic phenomenon is assumed to be due to a decreased strength of the in-plane ligand field resulting in conformational changes in the diamine chelate rings, and routine physicochemical methods, as stated above, are often not enough to characterize the conformational isomers. Second moment study at variable temperature is a useful tool to explain the decreased in-plane ligand field strength resulting from the onset of dynamic disorder of the chelate rings. The anions, beside the diamines, play a vital role in the thermochromism of these complexes. The less easily polarizable anions such as ClO_4^-, BF_4^- or $CF_3CO_2^-$, which have the capability of undergoing rotational reorientation and forming hydrogen bonds with the amino groups are more prone to exhibit thermochromism due to conformational isomerism compared to the easily polarizable anions like Br^- or I^-. The thermochromic phenomenon in nickel(II) amine system using anions as ClO_4^- or BF_4^- is documented [2] whereas, the similar study with $CF_3CO_2^-$ is rare. Here, we report the synthesis, and characterization of $[NiL_2(OCOCF_3)_2]$ (**1**), (L = 1-(2-aminoethyl) piperidine), thermochromism and X-ray single crystal structure analysis of (**1**).

EXPERIMENTAL

Materials

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

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and used as received. All other chemicals used were of AR grade.

Physical measurements

The thermal analysis (TG-DTA) was carried out on a Shimadzu DT-30 thermal analyser in dynamic atmosphere of dinitrogen (flow rate: 30cm^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 of phase transition was calculated using a Perkin-Elmer DSC-7 differential scanning calorimeter with indium metal as calibrant (rate of heating 10°C min^{-1}). The instruments used for recording the IR spectra (KBr disc at ambient), electronic spectra (Nujol mull at ambient), elemental analyses and effective magnetic moments at room temperature (22°C) were as reported earlier [6].

Preparation of $[NiL_2(OCOCF_3)_2]$ (**1**)

The complex was prepared by adding the diamine (L) (2 mmol) dropwise to nickel(II) trifluroacetate hexahydrate (1 mmol) dissolved in acetonitrile (10 cm^3). The blue complex separated immediately, was filtered, washed with isopropanol and dried in a $CaCl_2$-desiccator. Found: C, 39.8 H, 5.9; N, 10.1, Ni, 10.8. Calc. for $C_{18}H_{32}N_4O_4F_6Ni$: C, 39.9; H, 5.9; N, 10.3; Ni, 10.8% μ_{eff} = 3.1 B. M.; λ_{max} = 1204, 929, 594 and 363 nm.

X-ray diffraction structural study of $[NiL_2(OCOCF_3)_2]$ (**1**)

Single crystals suitable for X-ray analysis were obtained by recrystallization of (**1**) from ethanol. A single crystal of (1) was mounted on an Enraf-Nonius CAD 4 diffractometer. Lattice parameters were determined by least-squares refinement of the angular setting of 25 well-centred reflections. Crystal data are summarised in Table 1. Intensity data were collected using Mo-Kα radiation (λ = 0.71073 Å) with ω-2θ scan mode. Three control reflections monitored at regular intervals during the X-ray exposures indicated no significant variation in the intensities. Data were corrected for Lorentz and polarisation effects. An empirical absorption correction [9] based on ψ scan was applied (T_{min}/T_{max} 0.737/0.998).

The structure was solved by combination of the

Table 1. Crystal data for complexes 1 and 2

	1	**2**
Formula	$C_{18}H_{32}N_4F_6O_4Ni$	$C_{18}H_{32}N_4F_6O_4Ni$
Colour	Blue	Reddish-pink
Formula weight(fw)	541.19	541.19
Crystal system	Orthorhombic	Monoclinic
Space group	*P cab*	
a (Å)	10.242 (2)	13.025 (5)
b (Å)	11.954 (3)	11.565 (5)
c (Å)	19.022 (3)	15.830 (7)
β (°)		96.40 (1)
V (Å)	2328.9 (8)	2369 (2)
Z	4	4
Radiation λ (Å)	Mo-$K\alpha$ (0.71073)	Cu-$K\alpha$ (1.5418)
F(000)	1128	
μ(mm^{-1})	0.913	
Dc(g cm^{-3})	1.543	
Crystal size (mm)	0.60 × 0.40 × 0.25	
θ range (°)	$2 < \theta < 27.5$	
Unique reflections	2588	
Observed reflections $[I > 2\sigma(I)]$	1894	
$R1^a$ $\omega R2^b$	0.0436, 0.1137	
Weighting parameters (A, B)	0.0636, 4.49	
Goodness-of-fit(^{d}s)	0.834	
Maximum Δ/esd	0.287	
Final $\Delta\rho$, max/min (e Å^{-3})	0.38/−0.67	

$^aR1 = \Sigma\|F_o 1 - 1F_c\|/\Sigma|F_o|$

$^b\omega R2 = [\Sigma\{\omega(F_o^2 - F_c^2)^2\}/\Sigma\{\omega(F_o^2)^2\}]^{1/2}$

$\omega = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$

$^d s = [\Sigma\{\omega(F_o^2 - F_c^2)^2\}/(N - P)]^{1/2}$, where *N* is the number of data and *P* is the total number of parameters refined.

Table 2. Selected bond lengths [Å] and angles (°) in $[NiL_2(OCOCF_3)_2]$ (**1**)

Ni—N(1)	2.061(3)	Ni—N(2)	2.238(2)
Ni—O(1)	2.104(2)	O(1)—C(8)	1.243(3)
N(1)—C(1)	1.482(8)	N(1)—C(1A)	1.483(10)
N(2)—C(2)	1.461(6)	N(2)—C(2A)	1.531(8)
C(1)—C(2)	1.537(10)	C(1A)—C(2A)	1.481(13)
N(2)—C(3)	1.468(6)	N(2)—C(7)	1.473(4)
C(8)—C(9)	1.538(4)	C(8)—O(2)	1.226(3)
C(9)—F(1)	1.317(4)	C(9)—F(2)	1.320(4)
C(9)—F(3)	1.295(4)		

N(1)—Ni—N(2)	82.4(1)	N(1)—Ni—O(1)	94.7(1)
N(2)—Ni—O(1)	92.2(1)	Ni—O(1)—C(8)	133.4(2)
Ni—N(1)—C(1)	110.8(3)	Ni—N(1)—C(1A)	107.8(4)
Ni—N(2)—C(2)	101.6(2)	Ni—N(2)—C(2A)	103.9(3)
C(3)—N(2)—C(7)	108.0(3)	O(1)—C(8)—O(2)	130.5(2)
O(1)—C(8)—C(9)	113.3(2)	O(2)—C(8)—C(9)	116.1(2)
C(8)—C(9)—F(1)	113.3(2)	C(8)—C(9)—F(2)	110.1(2)
C(8)—C(9)—F(3)	114.7(3)	F(1)—C(9)—F(2)	105.4(3)
F(1)—C(9)—F(3)	106.6(3)	F(2)—C(9)—F(3)	106.1(3)

Patterson and Fourier methods and refined through full matrix least-squares calculations (SHELXL 93). Two of the diamine carbon atoms [C(1) and C(2)] were disordered over two sites with occupancy factors 0.55 and 0.45 respectively. Anisotropic refinements were carried out for all non-hydrogen atoms. The hydrogen atoms located from difference Fourier maps were treated isotropically. All calculations were carried out on a DEC alpha computer, Department of Physics, Jadavpur University using SHELXS 86 [10], SHELXL 93 [11], PARST [12] and ORTEP [13] programs. Selected bond distances and angles of (**1**) are given in Table 2.

RESULTS AND DISCUSSION

The composition of the title complex $[NiL_2(OCOCF_3)_2]$ (**1**) [(where L = 1-(2-aminoethyl) piperidine] has been confirmed by elemental analyses. The IR-spectrum (KBr) of (**1**) suggests that the diamines are chelated [14,15]. The magnetic susceptibility and electronic spectral (in Nujol) data are typical to octahedral nickel(II) complexes. Thus it may be assumed that the Ni^{II} centre in complex (**1**) should have octahedral geometry with an N_4O_2 chromophore. The blue complex $[NiL_2(OCOCF_3)_2]$ (**1**) on heating undergoes an irreversible endothermic phase transition (194–215°C; $\Delta H = 11.2$ kJ mol^{-1}, Fig. 1) and transforms to a reddish-pink complex $[NiL_2(OCOCF_3)_2]$ (**2**) without any mass loss in the TG-curve (Fig. 1). Complex (**2**) is stable in the open atmosphere and reverts to (**1**) on crystallization from $CH_3OH/EtOH/CH_3CN$ etc. The magnetic susceptibility and electronic spectral (in Nujol) data of the reddish-pink species in the solid state correspond to octahedral nickel(II). As the counter anion, $CF_3CO_2^-$, has only one option to coordinate with nickel(II) (through its negatively charged oxygen) it may be inferred that no chromophoric change around nickel(II) is associated with the transition. Both (**1**) and (**2**) exhibit two bands in the near-IR region in their corresponding electronic spectra (in Nujol) (1204 and 929 nm; and 1191 and 935 nm respectively) suggesting *trans*-octahedral configuration in them [16]. Thus, complex (**1**) undergoes a phase transition with retention of the *trans*-configuration. So, configurational isomerism (octahedral↔square planar/*cis*↔*trans*) is not likely to be responsible for the colour change. However, (**1**) and (**2**) show marked differences in their IR-spectral band positions in the regions of 3350–3100, 1600, 1400–1300 and 950–850 cm^{-}, where $\gamma(NH_2)$, δ (NH_2), $\rho_w(CH_2)$ and skeletal vibrations appear. The differences in IR and X-ray powder

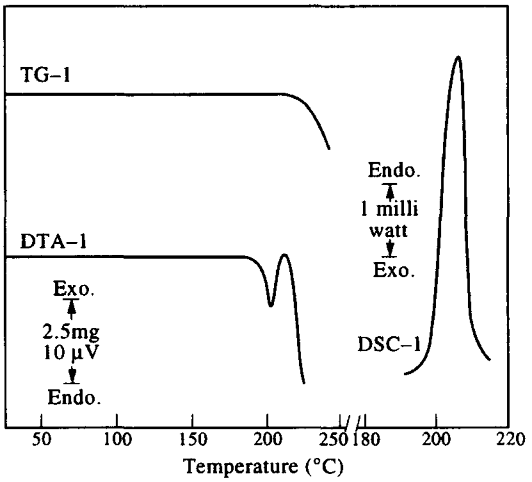

Fig. 1. TG-DTA (sample weight = 12.35 mg) and DSC (sample weight = 7.83 mg) curves of $[NiL_2(OCOCF_3)_2]$ (**1**).

diffraction patterns of (**1**) and (**2**) are in agreement to those observed in related conformational isomers [6,7]. Thus, the thermochromism exhibited by complex (**1**) is likely to be due to the conformational changes of the diamine chelate rings. The second moment of the complex at variable temperature could not be measured as the phase transition and decomposition temperatures are very close (Fig. 1).

Description of the structure of $[NiL_2(OCOCF_3)_2]$ (**1**)

An ORTEP view of the complex with atom numbering scheme is shown in Fig. 2. With the metal atoms lying at the centres of inversion, the crystallographic asymmetric units consist of half molecules. The nickel atom is octahedrally coordinated in which four ligand nitrogen atoms [N(1), N(2) and their centrosymmetrically related ones] define an equatorial plane, two oxygen atoms of the trifluroacetate groups coordinate in *trans*-axial positions. The in-plane distortion is introduced by ligand bite angle N(1)—Ni—N(2) 82.4(1)°. The Ni-N/O distances ranging between 2.061(3) and 2.238(2) Å are consistent with the corresponding values observed in similar systems [17–19]. The discrepancy between the two Ni—N distances (Table 2) is a consequence of the steric constraints introduced by the bulky piperidine group. The five-numbered chelate rings, disordered over two orientations Ni—N(1)—C(1)—C(2)—N(2) and Ni—N(1)—C(1A)—C(2A)—N(2), display open-envelope geometries with the flap atoms C(2) and C(1A) 0.669(9) and 0.652(12) Å, respectively, away from the least-squares planes through the remaining endocyclic atoms. The dihedral angle between the planar parts of the two orientations of the chelate ring is 1.0(2)°. The six-membered piperidine ring adopts a chair conformation with C(4) 0.614(9) Å above and C(7) 0.614(7) Å below the least-squares plane defined by the other four ring atoms. Except the hydrogen bonding between one of the amine nitrogen atoms and trifluroacetate oxygen atom [N(1)—H2····O(2) 3.006(3) Å] the crystal packing in the complex is stabilized by van der Waal's forces.

X-ray powder diffraction study of $[NiL_2(OCOCF_3)_2]$ (**2**)

Since all attempts to obtain suitable single crystals of (**2**) failed, the complex was examined by X-ray powder diffraction. Accurate d_{hkl} spacing (Å) were obtained from the powder patterns recorded on a Seifert XRD-3000P diffractometer at 22°C operating at 30 KV and 30 mA with 2° min^{-1} scan rate. The results are summarized in Tables 1 and 3, respectively.

The initial cell parameters of complex (**2**) have been determined from the powder diffraction data and accurate lattice parameters were obtained by least-squares refinement [20]. Though it is difficult to comment on the mechanism of phase transition (**1**→**2**) from the X-ray powder data (Table 3) the following observations are noteworthy. There is no drastic change in the cell volume (Table 1) and complex (**2**) belongs to the monoclinic system, a lower symmetry one, compared to the orthorhombic system in (**1**). The *h*0*l* and 0*k*0 data containing lines with *h*, *l*, *h*+*l* and *k* odd indicate absence of any glide plane or screw axis. With the disappearance of two diad axes in (**1**), the likely space group of complex (**2**) is *P*2, *Pm* with two molecules per asymmetric unit or *P*2/*m* with the

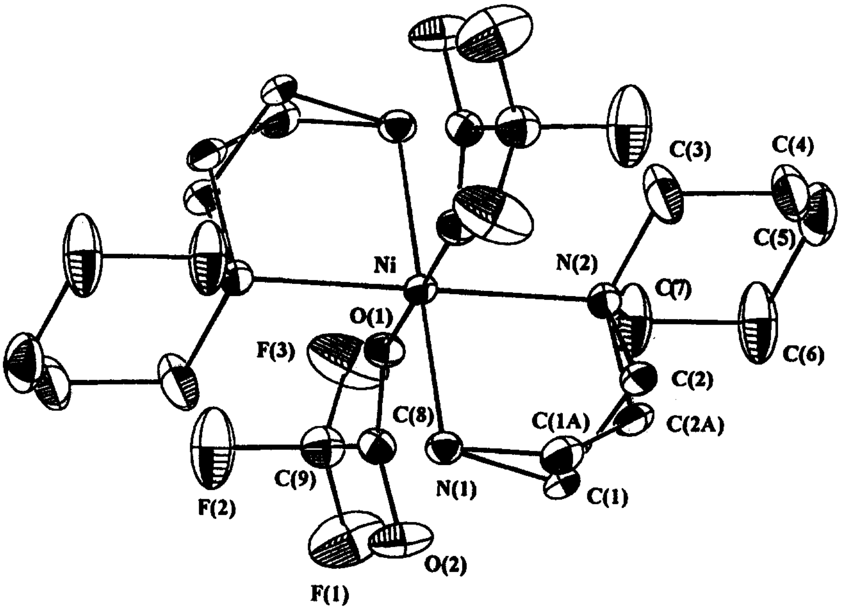

Fig. 2. ORTEP plot of $[NiL_2(OCOCF_3)_2]$ (**1**) with atom numbering scheme.

Table 3. X-ray powder diffraction data for $[NiL_2(OCOCF_3)_2]$ (**2**), (λ = 1.5418 Å)

d_{obs} (Å)	d_{cal} (Å)	h	k	l	I/I_o (%)
12.888	12.942	1	0	0	23
10.642	10.594	−1	0	1	25
9.313	9.317	0	1	1	95
8.626	8.626	1	1	0	100
7.859	7.866	2	0	0	24
7.066	7.082	−1	0	2	29
6.553	6.504	0	1	2	70
6.399	6.412	1	0	2	20
6.016	6.039	−1	1	2	37
5.769	5.763	2	0	1	17
5.472	5.488	−2	1	1	15
5.249	5.244	0	0	3	87
4.943	4.938	1	2	1	23
4.486	4.479	−1	2	2	80
4.298	4.294	1	2	2	44
4.083	4.082	2	2	1	49
3.970	3.974	−3	0	2	43
3.862	3.855	0	3	0	13
3.760	3.759	−3	1	2	28
3.611	3.617	3	0	2	12
3.462	3.462	0	3	2	13
3.378	3.377	−3	1	3	14
3.148	3.146	0	0	5	16
3.082	3.083	−3	0	4	12
3.011	3.010	−4	1	2	15
2.961	2.963	−2	0	5	10
2.871	2.870	−2	1	5	13
2.729	2.731	2	3	3	17
2.679	2.677	−1	4	2	14
2.608	2.608	−2	3	4	22
2.547	2.545	−5	0	2	17
2.490	2.489	3	2	4	28
2.390	2.391	4	2	3	18
2.328	2.329	−5	2	2	20
2.282	2.282	−5	0	4	11
2.211	2.211	−4	2	5	14
2.143	2.142	−6	0	2	14
2.119	2.120	−2	5	2	10
2.073	2.074	1	5	3	17
2.001	2.001	2	3	6	14

molecules distributed in the general equivalent positions.

CONCLUSIONS

The thermochromism in $[NiL_2(OCOCF_3)_2]$ (**1**) is most likely due to a decreased in-plane ligand field strength resulting from the conformational changes of the diamine chelate rings.

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