Rapid Communication

First example of a double stranded helicate with square-planar coordination for the metal

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Reaction of dichlorobis(benzildihydrazone)Ni(II) with biacetylmonoxime in 1:4 molar proportion generates diamagnetic Ni_2L_2 where LH_2 (H = dissociable oximato proton) is HO-N=C(CH$_3$)-C(CH$_3$)=N-N=C(C$_6$H$_5$)-C(C$_6$H$_5$)=N-N=C(CH$_3$)-C(CH$_3$)=N-OH. Our molecular mechanics calculations show that Ni_2L_2 is an unprecedented double stranded homotopic helicate with the metal ion having a square-planar N_4 coordination.

Helical transition metal complexes initially received attention because of their structural similarity to nucleic acids and proteins. Later the interest has shifted towards development and understanding of self-processes in supramolecular chemistry[1-5]. A number of helicates have been synthesised and characterised since 1987, although a helical structure was first proposed[6] in 1969 for a dinuclear Cu(II) complex by Harries and Mckenzi. In most of these complexes the ligands employed are polypyridines or combinations of pyridine and benzimidazole. Use of other ligands has so far been limited[7-14]. Moreover, with a few exceptions the metal ions in the known helicates are four-, six- or eight- coordinate[1]. In the four-coordinate helicates, the metal ions are invariably tetrahedral which tends to suggest that such a geometry is a prerequisite for generating a helicate of the metal ions which can have four coordination. In such cases, the ligands have been tailored to cater to this need. Interestingly, Pd(II), which normally prefers a square-planar disposition of the coordinating atoms, has been found to have distorted penta-coordination in its only known helicate[15]. Herein for the first time, we describe a double stranded helicate where the metal ion is in a square-planar geometry. The metal ion involved is Ni(II) and the ligand has azine and oximato N donor sites.

Experimental

GR grade NiCl$_2$.6H$_2$O, benzil and biacetyl monoxime were procured from Loba-Chemie Indoaustranal Co. (India), hydrazine hydrate (99-100%) from Qualigens (India) and CDCl$_3$ (99.9 atom % D) from Aldrich. All other chemicals were of AR grade. Nickel was estimated gravimetrically as the dimethylglyoximate. Microanalyses were performed using a Perkin-Elmer 2400II elemental analyser. IR spectra (KBr disc) were recorded on a Perkin-Elmer 783 spectrophotometer, UV/VIS spectra on a Shimadzu UV-160A spectrophotometer, FAB mass spectrum on a VG-ZAB-SE instrument and ^{1}H-NMR spectrum (in CDCl$_3$) by a Brucker DPX300 spectrometer. Magnetic susceptibility was measured by a PAR 155 Vibrating Sample Magnetometer fitted with a Walker Scientific magnet; the magnetometer was calibrated with Hg[Co(SCN)$_4$].

Synthesis of 3

Dichlorobis(benzildihydrazone)nickel(II) (0.36g, 0.6 mmol), prepared by a reported procedure[16], was taken in 30 cm^3 of dehydrated methanol and was heated to dissolve. To the hot faint green solution, three drops of triethyl amine and 0.24 g (2.4 mmol) of solid biacetylmonoxime were added and refluxed for 7 h during which period the reaction mixture turned wine red and a fluffy dark precipitate appeared. Then it was cooled to room temperature. The dark compound precipitated was filtered, washed with methanol till the filtrate became colourless and dried *in vacuo* over fused CaCl$_2$; yield, 0.09 g (32% based on Ni). The compound is analytically pure. It can be recrystallised from 1:1.5 chloroform-hexane mixture. Elemental analyses were consistent with the stoichiometry [C$_{44}$N$_{12}$H$_{44}$Ni$_2$O$_4$]$_2$ [Found : C, 57.26; N, 18.18; H, 4.72; Ni, 12.71. Calc. : C, 57.28; N, 18.23; H, 4.81; Ni, 12.74%]. IR (KBr): 1210 cm^{-1} [v(N-O)]. UV/VIS (CHCl$_3$) : λ/nm (ε/ dm^3 mol^{-1} cm^{-1}) :

Table I—Various data for molecular mechanics calculations (the numeral n beside an atomic symbol indicates the atom's sp^n hybridisation)

Stretching Interactions

Interaction	Bond length (A)	Force constant (kcal mol^{-1})	Bond Moment
Ni-N2	2.050	190	-0.30

Bond Angle Interaction

Interaction	Angle (°)	Force constant (kcal mol^{-1})
Ni-N2-C2	120	15.00
Ni-N2-O3	120	15.00
N2-Ni-N2	90	15.00

Bond Angle Substructures to overcome the unique labelling problem

For Structure A	For Structure B
Ni-N2-N2-Ni-N2=C2-C2=N2-N2-1 where the angle between atoms 3, 4 and 5 is ideally 180° and has a force constant of 15 kcal mol^{-1}	O3-N2-Ni-N2=C2-C2=N2(-O3)-3 where the angle between atoms 2, 3 and 4 is ideally 180° and has a force constant of 15 kcal mol^{-1}

Dihedral Interactions

All torsions around the metal ion were set to zero.

728 (33 400), 533 (10 000), 355 sh (20 100) and 261 (53 000). UV/VIS (nujoll) λ/nm : 740, 550, 380, 280.

Molecular mechanics calculations

All the MM calculations have been performed using MacroModel v5.5[17]. In order to model the coordination geometry of the nickel ions the AMBER* force field has been used with the additional parameters listed in Table 1. The bond angles around the nickel have been calculated using the bond valence approach and the unique labelling problem has been solved by using special substructures given in Table 1. Dihedral Monte Carlo (MC) multiple minimum searches[18] were undertaken to find all the low energy conformations. During the search procedure minimisation was continued until convergence was reached or until 1,000 iterations had been performed. The Polak-Ribiere conjugate gradient minimisation mode was used "*in vacuo*" with a derivative convergence criterion of 0.05 kJ mol^{-1}. Structures within 50 kJ mol^{-1} of the lowest energy minimum were kept and a usage di-

rected method[19] was used to select structures for subsequent MC steps. Two thousand MC steps were taken.

Results and discussion

In our attempt to generate **1** by refluxing dichlorobis(benzildihydrazone)Ni(II) (**2**) with biacetylmonoxime (BAMO) in 1:4 molar proportion in dry methanol [reaction (i)], we have obtained **3** which analyses as the mononuclear formulation NiL (molecular weight
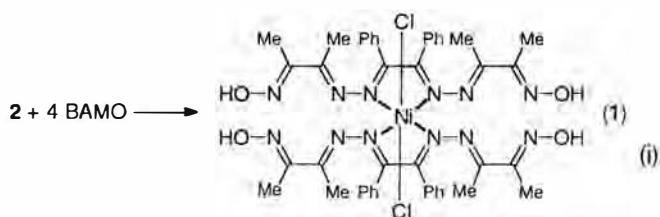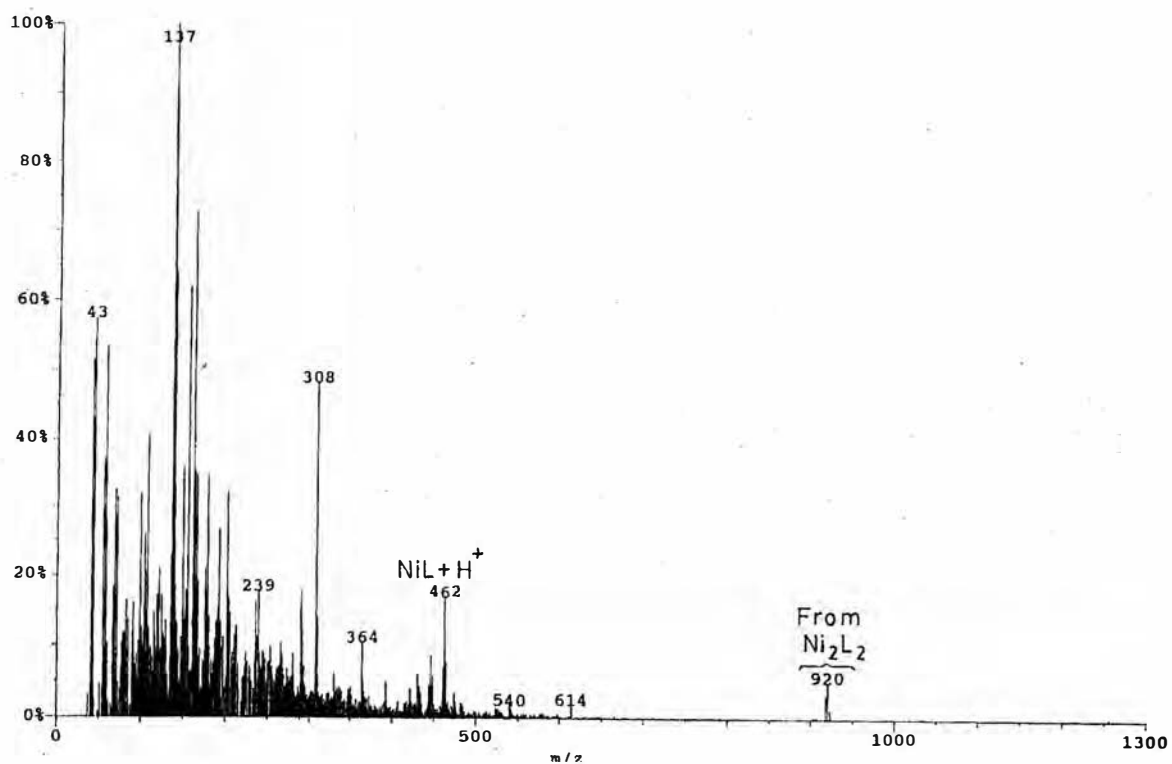
Fig. 1 — FAB mass spectrum of **3**

M_w = 460.87) where LH_2 (H = dissociable oximato proton) is $HO-N=C(CH_3)-C(CH_3)=N-N=C(C_6H_5)-C(C_6H_5)=N-N=C(CH_3)-C(CH_3)=N-OH$. We have found that the yield of **3** increases significantly when the reaction is carried out in presence of triethyl amine (see **Experimental** section for details). Our magnetic susceptibility measurements reveal that **3** is diamagnetic. Thus a square planar coordination is indicated for Ni(II) in **3**. Its FAB mass spectrum (Fig. 1) shows that it is actually

(a)
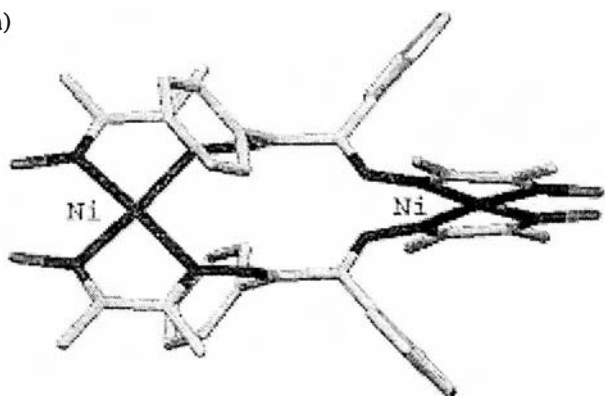
(b)
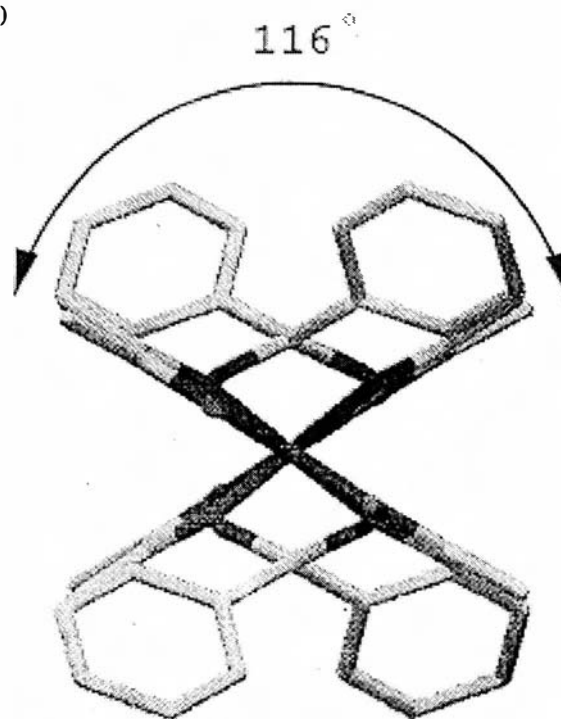
Fig. 2—Views of the global energy minimum structure of **3** as obtained by MM calculations. (a) as seen perpendicularly from the Ni-Ni axis and (b) as seen along the Ni-Ni axis.
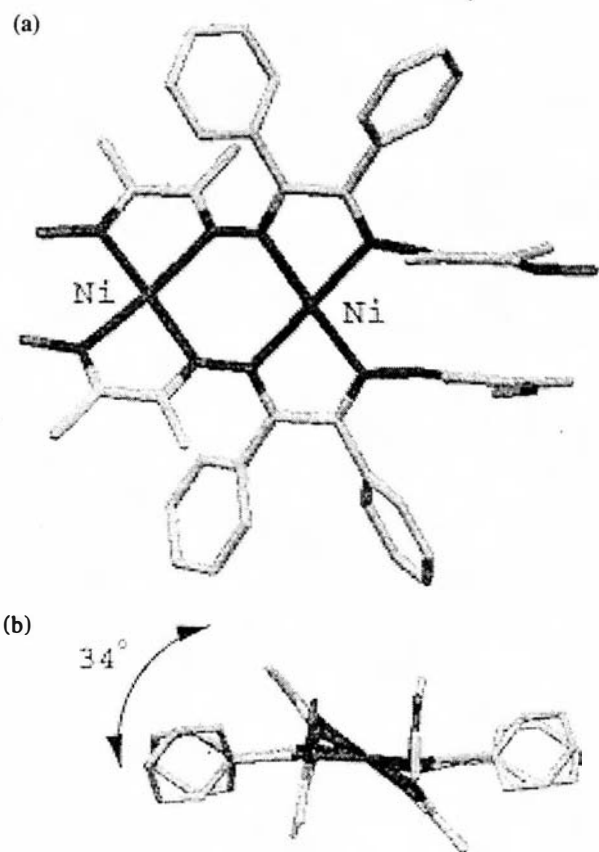
(a)

(b)

Fig. 3—Views of the global energy minimum conformation of the hypothetical structure **A** for **3** as obtained by MM calculations. (a) as seen perpendicularly from the Ni-Ni axis and (b) as seen along the Ni-Ni axis.

a dimer of the formulation Ni_2L_2 ($M_w = 921.75$). This suggests two possible structures for **3** — **A** where the two nickel atoms are juxtaposed and **B** where the two nickel atoms are terminally located. Our thin layer
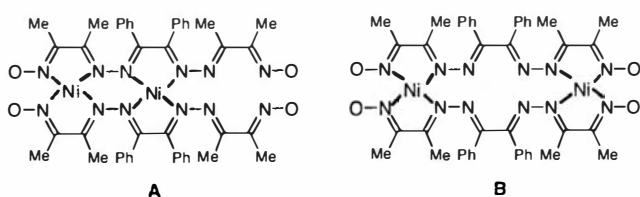
chromatographic investigation in chloroform shows that in reaction (i) a single species is formed. Since so far we have not been able to grow single crystals of **3**, we have taken recourse to Molecular Mechanics (MM) in order to examine its structure. Our MM calculations (see **Experimental** section for details) show that **B** is stabler than **A** by 157 kJ mol^{-1}. Accordingly, structure **B** is assigned to **3**. It is also revealed that **3** is a double stranded
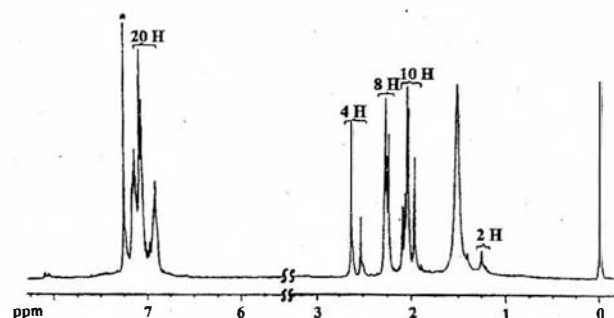

Fig. 4—A 300 MHz ^{1}H-NMR spectrum (reference: TMS) of **3** in deuterated chloroform. The peak marked by an asterisk is due to solvent and the broad peak around 1.53 ppm is due to water present in the solvent.

homotopic helical complex (Fig. 2). It may be noted as a point of academic interest that the hypothetical structure **A** is more or less planar (Fig. 3). An analysis of the reorganisation energy[20,21] indicates that it is the steric strain generated upon binding the nickel (II) ions that mostly accounts for the energy difference between the two structures. While the steric strain for structure **B** is only 6 kJ mol^{-1}, it is 151 kJ mol^{-1} for **A**.

The complex **3** displays a very strong charge transfer (CT) band around 730 nm giving rise to an intense blue colour in solution. A CT band at such a low energy, to our knowledge, is unknown for a square-planar Ni^{II}N$_4$ chromophore. The ^{1}H-NMR spectrum of **3** in CDCl$_3$ is shown in Fig. 4. The twenty phenyl protons appear in three groups in the region 6.90-7.26 ppm; twenty two of the twenty four methyl protons appear in several groups in the region 1.98-2.63 ppm and the other two methyl protons are shifted a bit upfield at 1.24 ppm. For a planar structure, normally one would expect two types of methyl signal for **3**. Thus, the multiple methyl signals observed in Fig. 4 possibly indicates that **3** has a structure more complicated than a planar one. Not unexpectedly, solution of **3** is not optically active.

Now in view of the structure of **3**, it is imperative to discuss its synthetic aspect[†]. In reaction (i), possibly **4** is formed first (Scheme 1). The ligand strands in **4** offer three N$_4$ compartments to the metal. The compartments are of two types. The central one is made up of all azine N atoms while the flanking ones are composed of two azine N and two oximato N atoms. **4** then

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[†] Interestingly, a direct reaction of NiCl$_2$.6H$_2$O with the preformed ligand LH$_2$ (obtained by successive condensation of diacetyl hydrazone oxime with benzil) does not give rise to **3**; it yields a dark red insoluble material containing nickel, the IR spectra of which displays a keto stretch indicating hydrolysis of LH$_2$.
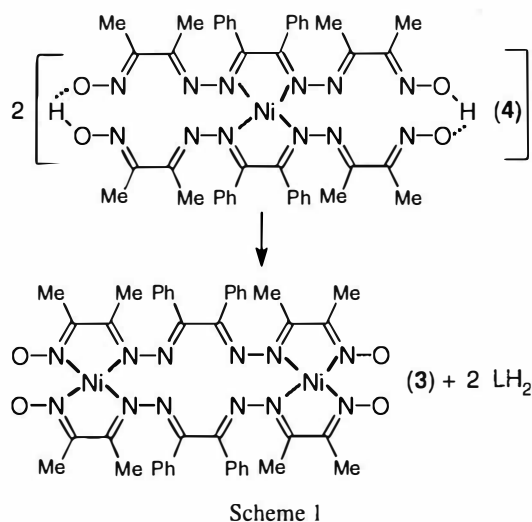
Scheme 1

disproportionates as shown in Scheme 1 to give rise to **3**. It is really interesting to note that the Ni atom leaves the central compartment in order to occupy the terminal ones. Such translocation of a metal ion is hitherto unprecedented. Switching of a metal ion from one type of compartment to another type in a two compartmental ligand with change in the oxidation state is, however, known[10].

Acknowledgement

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