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Molecular structures of nickel(II) monochelates of a racemic tridentate ligand and co-ligand induced structural variations

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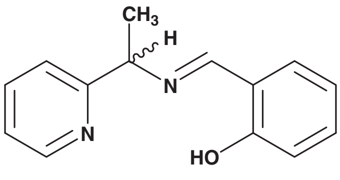
ABSTRACT

Using a racemic mixture of the tridentate ligand, (((2-pyridyl)ethylamine)methyl)phenolate ion (**L**$^-$) and $N_3{}^-$, NCS^-, $(NC)_2N^-$, OAc^- as coligands, complexes having the formula [Ni(**L**)(N_3)] (**1**), [Ni(**L**)(NCS)]$_2$ (**2**), [Ni_2(**L**)$_2$(OAc)(N(CN)$_2$)]$_n$ (**3**) were prepared and structurally characterized. In **1**, Ni(II) has a square planar geometry and phenolate oxygen is involved in dipolar $O_P^{\delta-}\cdots N^{\delta+}$ interaction with electrophilic central nitrogen atom of coordinated azide ion. Complex **2** is dimeric in nature and nickel(II) is penta-coordinated. Compounds **1** and **2** exist as centrosymmetric dimers made up of a pair of *R* and *S* enantiomers of **L**. In **3**, an acetate and phenoxo bridged dinickel complex is present which is further linked to a zigzag coordination polymer by the dicyanamide ion. In a given chain of **3**, both **L** have same enantiomeric form and either *RR* or *SS* dimers are repeated along the chain. The magnetic properties are described.

1. Introduction

Racemic crystallization is the most common occurrence when a solution containing a racemic mixture of an organic molecule is allowed to crystallize [1], however, a conglomerate crystallization may also take place [2–4]. Cocrystallization of a mixture of structurally similar isosteric molecules but opposites in their handedness, leads to racemate crystallization. The result is not a true racemate and hence is termed a quasiracemate [5–11]. A racemic mixture of a chiral ligand on coordination to a metal ion could also form racemate crystals having a centrosymmetric space group [12–15]. Construction of supramolecular helical chains based on a metal–organic framework using chiral and racemic organic ligands has been the theme of many investigations for a long time [16–24]. The metal complexes of tridentate ligands derived from salicylaldehyde and aliphatic/aromatic amines have a number of applications, which range from asymmetric catalysis to material sciences [25–28], biological model systems [29], molecule-based and single molecule magnets [30,31], energy transfer [32], cleavage of nucleic acids [33], etc. Small π-conjugated coligands like azido, cyano, dicyanamido, etc., in combination with other polydentate ligands, are being used for constructing inorganic magnetic materials [34–40].

We have been interested in the synthesis and coordination chemistry of ligands containing a pyridyl ring [41–43]. In that direction, the Schiff base **LH** having a chiral carbon and a 2-pyridyl ring was synthesized, which upon treatment with Ni(II) ions in the presence of the co-ligands N_3^-, SCN^-, $N(CN)_2^-$ and OAc^-, respectively, afforded racemic crystals of the formula [Ni(**L**)(N_3)], [Ni(**L**)(NCS)]$_2$ and [Ni_2(**L**)$_2$(OAc)(($NC)_2N$)]·(CH_3CN)·(H_2O). Herein we report the structural characterization of these three complexes that reveal the presence of rare occurrences of (a) involvement of the electrophilic central nitrogen atom of the coordinated azide in a $O_P^{\delta-}\cdots N^{\delta+}$ type dipolar interaction with the phenolate oxygen (b) existence of a distorted square-pyramidal coordination geometry around the Ni(II) ion and (c) a co-ligand dependent enantiomeric or conglomeric dimerization of the monochelates.



LH

2. Experimental

2.1. Materials and methods

X-ray crystallographic data were collected using a Bruker SMART APEX-CCD diffractometer with Mo Kα radiation (λ =

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0.71073 Å). The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied using the SAINT program [44,45]. All the structures were solved by direct methods using SHELXS-97 [46]. Non-hydrogen atoms located from the difference Fourier maps were refined anisotropically by full-matrix least-squares on F^2, using SHELXL-97 [46]. All hydrogen atoms were included in the calculated positions (except for the water of crystallization, O5 in **3**, for which hydrogen atoms could neither be added at calculated positions nor be located from FMAP) and refined isotropically using a riding model.

The temperature variations of zero field cooled (ZFC) magnetization (M) was measured using a Lakeshore model 7410 vibrating sample magnetometer under 200 G magnetic field in the temperature range 18–300 K. A helium exchange gas cooled top loading closed cycle helium refrigerator (CCR) was used to achieve temperature down to 18 K. The temperature dependent molar susceptibility data were fitted (after applying the diamagnetic corrections) using a non-linear least squares fit procedure to obtain the Curie–Weiss constant (θ) and the exchange integral (J). MATHSOL curvefitter (version 4.5.3 developed by Dr. Larry Nylund) was used for the curve fitting procedure.

2-Acetylpyridine, 2-hydroxybenzaldehyde, $NaN(CN)_2$, (Aldrich, USA); $NiCl_2{\cdot}6H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, KSCN, NaN_3 (Merck India Ltd.) and solvents were used as received without further purification. (*R*,*S*)-1-(2-pyridyl)ethylamine was prepared using the reported procedure [47,48].

Caution: Metal azide complexes are potentially explosive in the presence of organic ligands. They should be handled with care and prepared only in small quantities.

2.2. Syntheses

2.2.1. (R,S) 2-(1-(pyridin-2-yl)ethylimino)methyl)phenol (**LH**)

A mixture of 1-(2-pyridyl)ethylamine (4.5 g, 0.036 mol) and 2-hydroxybenzaldehyde (4.5 g, 0.036 mol) in 50 mL methanol was heated at reflux for 3 h. The solvent was removed in vacuo and the remaining yellow oil was triturated with a 1:1 methanol–water (10 mL) mixture. The resultant yellow oil was dried in desiccators over P_4O_{10} and was pure enough as inferred from the ^1H NMR spectrum, to be used without further purification. Yield: 7.0 g (86%). IR (KBr, cm^{-1}): 3445, 2975, 2930, 1630, 1589, 1460, 1277, 1207, 1150, 1130, 976, 755. 400 MHz ^1H NMR (δ (J, Hz), $CDCl_3$): 13.52 (OH, s), 8.55 (1H, d, 5.6), 8.51 (1H, s), 7.68 (1H, t, 7.8), 7.45 (1H, d, 7.6), 7.32 (1H, d, 8.4), 7.29 (1H, t, 6.0), 7.18 (1H, t, 6.2), 6.99 (1H, d, 8.4), 6.89 (1H, t, 7.4), 4.71 (1H, q, 6.8), 1.96 (3H, d, 6.8), 100 MHz ^{13}C NMR (δ, $CDCl_3$): 164.1, 161.7, 160.5, 148.4, 136.3, 131.9, 131.2, 121.8, 120.0, 118.3, 118.2, 116.4, 69.3, 22.7.

2.2.2. [Ni(**L**)(N$_3$)] (**1**)

To a methanol (10 mL) solution of $NiCl_2{\cdot}6H_2O$ (1.05 g, 4.0 mmol) was added **LH** (1 g, 4.0 mmol) dissolved in methanol (30 mL). To this mixture Et_3N (0.404 g, 4.0 mmol) was added and the resulting mixture was heated at reflux for 2 h. Solid sodium azide (0.3 g, 4.0 mmol) was added and reflux was continued for another 1 h. Red crystals of **1** deposited and were collected by suction filtration, washed with cold methanol and dried over $CaCl_2$. Yield: 1.0 g (78%). *Anal.* Calc. for $C_{14}H_{13}N_5ONi$: C, 51.58; H, 4.02; N, 21.48%. Found: C, 51.49; H, 4.00; N, 21.35. Selected IR (KBr, cm^{-1}) bands: 3430, 2980, 2932, 2035 (azide), 1614, 1568, 1449, 1357, 1096, 1033, 774, 760. UV–Vis [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 850(19); 745(12); 575(11); 390(2610); 282(6450).

2.2.3. [Ni(**L**)(NCS)]$_2$ (**2**)

To a methanol (10 mL) solution of $NiCl_2{\cdot}6H_2O$ (1.05 g, 4.0 mmol) was added **LH** (1 g, 4.0 mmol) dissolved in methanol (30 mL). To this mixture Et_3N (0.404 g, 4.0 mmol) was added and the resulting mixture was heated at reflux for 2 h. Solid potassium thiocyanate (0.430 g, 4.0 mmol) was added and reflux was continued for 1 h. The solvent was removed and the residue was dissolved in CH_3CN (30 mL) and the resulting solution was left undisturbed at room temperature. The green crystals deposited after a week were collected by suction filtration, washed with ice-cold methanol and dried over $CaCl_2$. Yield: 1.12 g (75%). *Anal.* Calc. for $C_{15}H_{13}N_3OSNi$: C, 52.67; H, 3.83; N, 12.29%. Found: C, 52.50; H, 3.82; N, 12.20. Selected IR (KBr, cm^{-1}) bands: 3430, 2924, 2088 (thiocyanate), 1633, 1600, 1540, 1446, 1402, 1301, 1025, 903, 750, 737. UV–Vis [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 630(470); 458(455); 375(10 240); 270(35 880).

2.2.4. [Ni$_2$(**L**)$_2$(OAc)((NC)$_2$N)]·(CH$_3$CN)·(H$_2$O) (**3**)

To a methanol (10 mL) solution of $Ni(OAc)_2{\cdot}4H_2O$ (0.990 g, 4.0 mmol) was added **LH** (1 g, 4.0 mmol) dissolved in methanol (30 mL). To this mixture Et_3N (0.404 g, 4.0 mmol) was added and the resulting mixture was stirred for 2 h. Solid sodium dicyanamide (0.356 g, 4.0 mmol) was added and the solution heated at reflux for 1 h. The solvent was removed and the green residue was washed with ice-cold methanol. Yield: 1.04 g (69%). Single crystals of **3** suitable for X-ray diffraction study were obtained by layering the CH_3CN solution of the crude green solid over dichloromethane. *Anal.* Calc. for $C_{34}H_{34}N_8O_5Ni_2$: C, 54.30; H, 4.56; N, 14.90%. Found: C, 54.17; H, 4.48; N, 14.87%. Selected IR (KBr, cm^{-1}) bands: 3430, 2277, 2170 (dicyanamide), 1643, 1594, 1410, 1327, 1050, 898, 764, 756. UV–Vis [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$), CH_3OH solution]: 842 (43); 746 (31); 573(25); 373(11 630); 281(16 050).

3. Molecular structures

The molecular structures of **1**–**3** were determined using single-crystal X-ray diffraction techniques. The crystal data and refinement parameters are listed in Table 1. Compound **1** crystallized in space group *C*2/*c*. The Ni(II) atom is bound by the meridionally coordinating tridentate ligand **L** and by a monodentate azide ligand. The bivalent nickel has a distorted square-planar geometry. **L** is bound to the Ni(II) atom by a five-membered and a six-membered chelate ring. The asymmetric carbon atom deviate from the otherwise nearly planar five-membered chelate ring, which is evident from the dihedral angle of 6.97° between the two planes C5C6N2 and C5N1Ni1N2. The six-membered chelate ring is slightly puckered and has an envelope form with the Ni1 being displaced out-of-plane, as is inferred from the dihedral angle of 8.83° between the planes formed by N2Ni1O1 and O1C14C9C8N2. The $Ni–N_P$ bond length is longer than $Ni–N_I$ bond (N_P = pyridyl-N; N_I = imine-N) and these two are shorter than the $Ni–N_A$ (N_A = azide-N).

The azide ligand is coordinated in the usual end-on bent fashion with the bending being uniquely towards the phenolic oxygen atom and is also out-of-plane from the donor atoms of **L** (the torsional angle between O1–Ni–N3 and Ni–N3–N4 is 15.28°). Significantly, the O1 atom of the phenol group is involved in a dipolar interaction (O1···N4 = 2.612(3) Å) with the central nitrogen atom of the coordinated azide group. It is pertinent to note that as per the valence structure of the N_3^- ion, the central nitrogen atom is electrophilic in nature [49] and hence the dipolar $O_P^{\delta-}\cdots N^{\delta+}$ interaction with the phenolate oxygen (O_P = phenolate-O) atom is explained. Probably this interaction partially compensates for the lack of O_P bridged dimerization as is observed in **2** and **3** (*vide infra*). Such a dipolar interaction can also be traced to a few other cases but they have longer non-bonded contacts (2.836(8)–3.333(4) Å) [50–52]. In another case an intermolecular dipolar