

Studies on Coordination Polymers: Part I—Polymeric Complexes of α -Dipyridyl Disulphide with Nickel(II)

(MRS) P R SHUKLA*, B B AWASTHI &
(MISS) RACHNA RASTOGI

Department of Chemistry, University of Lucknow
Lucknow 226 007

and

GOPAL NARAIN

Department of Chemistry, University of Saugar
Sagar 470 003

Received 12 December 1983; revised and accepted 8 June 1984

Twelve polymeric complexes of nickel(II) have been obtained using a new ligand, α -dipyridyl disulphide (L). The complex cation possesses the general formula $[-NiL-]_n^{2n+}$; the various anions used are Cl^- , NO_3^- , CH_3COO^- , SO_4^{2-} , $[Fe(CN)_5NO]^{2-}$ and $C_4H_4O_4^{2-}$. The complexes are assigned planar structures on the basis of analytical, magnetic and spectral studies. α -Dipyridyl disulphide acts as a tetradentate chelating agent coordinating through both the sulphur atoms and pyridine nitrogens. Steric factors prevent the coordination of all four donors to the same metal ion and hence polymeric complexes are formed. Treatment of these planar complexes with additional donors such as pyridine, picoline (am) or diamines (dam), results in the formation of polymeric octahedral complexes of the type $[-NiLAm_2 \text{ or } dam-]_n^{2n+}$.

A large number of polymeric complexes in which sulphur and nitrogen donors are present have been characterised and studied¹⁻⁵. In the present note we report the synthesis of some planar polymeric complexes prepared from a tetradentate ligand, α -dipyridyl disulphide, containing two sulphur and two nitrogen donor atoms. These complexes change to octahedral polymeric forms on treatment with additional ligands.

Preparation of α -dipyridyl disulphide— α -Mercaptopyridine (0.5 g)⁶ was dissolved in 4.50 ml of 25% sodium hydroxide solution and iodine (0.6 g) dissolved in 25 ml of 10% potassium iodide solution was added dropwise. At the first appearance of a reddish colour, the solid which had separated out gradually was filtered and washed with water. The crude disulphide was recrystallised from petroleum ether, m.p. = 57-58°C; yield = 80%.

Synthesis of complexes of type $[-Ni(L)-]_n^{2n+}$ —To a suspension of appropriate nickel salt solution (0.01 M) in 50 ml of xylene, ligand (2.2 g, 0.01 M) was added and the solution was refluxed on a sand bath for 12 hr. The reaction mixture was distilled off and the complexes were crystallised from the solution using petroleum ether - methanol mixture and dried.

Synthesis of complexes of type $[-NiLAm_2 \text{ or } dam-]_n^{2n+}$ —The parent chloride complex (3.49 g, 0.01 M) was suspended in 50 ml xylene and treated with pyridine (1.58 ml, 0.02 M), picoline (1.89 ml, 0.02 M), ethylenediamine (1.20 ml, 0.01 M) or propylenediamine (1.49 ml, 0.01 M). The solution was refluxed for 15 hr and the solvent was then distilled off. The complex was crystallised using petroleum ether (50-60°C).

The analytical data of parent complexes (Table 1) agree with the general formulae $[-NiL-]_n(Cl, CH_3COO \text{ or } NO_3)_{2n}$ or $[-NiL-]_n[C_4H_4O_4, SO_4 \text{ or } Fe(CN)_5NO]_n$. The IR spectrum of free ligand (band positions in cm^{-1}) exhibits characteristic absorptions in the ranges 1650-1370, 1350-1000 and 800-700 assignable to mixed $>C=C$, $>C=N-$ and ring stretches, in-plane or out-of-plane CH deformations and ring deformations respectively. In addition, a strong band arising from the $\nu(CS)$ vibration appears at 940 cm^{-1} . In the spectra of complexes either all or some of the pyridine vibrations appear but at slightly higher than usual positions indicating the coordination of pyridine nitrogen⁷. The strong band at 940 cm^{-1} is normally split in two components one at 960 ± 10 and the other at $735 \pm 5\text{ cm}^{-1}$, if only one sulphur atom is coordinated. In the present complexes, however, only a weak band appears at 735 cm^{-1} . The complete disappearance of 940 cm^{-1} band in complexes is probably due to the formation of polymeric structures through the involvement of both sulphur atoms in coordination, as found for other similar complexes⁸. The coordination through nitrogen and sulphur is further confirmed by the occurrence of new bands at 430 and 290 cm^{-1} which may be assigned to Ni-S and Ni-N stretches, respectively^{9,10}. It is thus clear that the ligand acts as a tetradentate chelating agent, coordinating through both pyridine nitrogen and sulphur atoms. Polymeric complexes (structure I) are expected to be formed as the steric factors prevent the coordination of all the donor groups to the same metal ion.

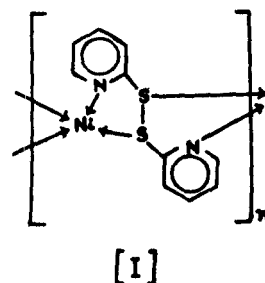


Table 1—Analytical and Magnetic Moment Data of Complexes

Formula	Colour	Found, % (Calc.)			$\mu_{\text{eff.}}$ (B.M.)
		M	N	S	
$[-\text{NiL}-]_n(\text{Cl})_{2n}$	Yellow	15.82 (16.77)	7.50 (8.00)	33.94 (34.33)	0.69
$[-\text{NiL}-]_n(\text{NO}_3)_{2n}$	Brown	14.92 (14.56)	13.02 (13.90)	29.20 (29.80)	0.53
$[-\text{NiL}-]_n(\text{CH}_3\text{COO})_{2n}$	Greenish yellow	14.52 (15.48)	7.26 (7.06)	41.95 (42.39)	0.695
$[-\text{NiL}-]_n(\text{SO}_4)_n$	Green	14.98 (15.57)	7.02 (7.43)	30.95 (31.87)	0.47
$[-\text{NiL}-]_n[\text{FeCN}_5\text{NO}]_n$	Brown	12.02 (11.86)	21.92 (22.64)	35.90 (36.40)	1.029
$[-\text{NiL}-]_n(\text{C}_4\text{H}_4\text{O}_4)_n$	Greenish yellow	14.00 (14.86)	7.50 (7.09)	41.96 (42.56)	0.56
$[-\text{NiL}(\text{C}_5\text{H}_5\text{N})_2-]_n(\text{Cl})_{2n}$	Green	12.32 (11.55)	10.95 (11.03)	46.92 (47.27)	3.036
$[-\text{NiL}(\alpha-\text{C}_6\text{H}_7\text{N})_2-]_n(\text{Cl})_{2n}$	Dark brown	12.36 (11.64)	10.90 (11.10)	53.00 (52.41)	2.97
$[-\text{NiL}(\beta-\text{C}_6\text{H}_7\text{N})_2-]_n(\text{Cl})_{2n}$	Dark brown	13.0 (11.64)	11.65 (11.10)	51.90 (52.41)	3.15
$[-\text{NiL}(\gamma-\text{C}_6\text{H}_7\text{N})_2-]_n(\text{Cl})_{2n}$	Brown	11.00 (11.64)	10.60 (11.10)	53.00 (52.41)	3.07
$[-\text{Ni}(\text{C}_2\text{H}_5\text{N}_2)-]_n(\text{Cl})_{2n}$	Pink	14.28 (15.36)	25.10 (26.20)	37.05 (37.7)	2.89
$[-\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)-]_n(\text{Cl})_{2n}$	Pink	15.2 (14.82)	7.65 (7.07)	39.80 (38.43)	2.86

The polymeric nature of the complexes is also inferred from the fact that these, in general, are insoluble in water and common organic solvents. Measurements of conductance in the form of very dilute solutions in DMF give large values showing the electrolytic nature of the complexes.

The $\mu_{\text{eff.}}$ values of the parent complexes are around 0.70 B.M. corresponding to spin-paired singlet ($^1A_{1g}$) state of the ion in complexes, which is also confirmed by the electronic spectra where the ν_2 and ν_3 transitions of planar geometry are seen at 14.00 and 22.00 kK¹¹. The electronic spectra of mixed complexes show bands at 10.00, 16.50 and 23.50 kK which correspond to the transitions $^3A_{2g} \rightarrow ^3T_{2g}(\nu_1)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow ^3T_{1g}(F)(\nu_3)$ respectively. The ν_2/ν_1 ratio is around 1.60. The magnetic moment values (2.86-3.15 B.M.) together with the drs data show the polymeric octahedral geometry for the complexes with the spin free triplet ($^3A_{2g}$) state.

We thank the Head, Chemistry Department, Lucknow University, Lucknow for providing

necessary laboratory facilities. Two of us (B.B.A. and R.R.) are thankful to the CSIR and UGC, New Delhi respectively for the award of junior research fellowships. We are also thankful to Dr. Y.D. Kulkarni, Lucknow University, for his help in the synthesis of the ligand.

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