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Preparation and Properties of New Metal Complexes with Binucleating Ligands Containing Oxygen and Sulphur

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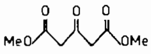
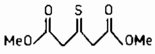
A study on metal complexes with binucleating ligands containing similar or dissimilar coordination sites has been undertaken for some time past, where the ligands used [1–4] have nitrogen and oxygen as donor atoms. We have now extended our interest to analogous systems with ligands containing sulphur. The ligands, HL_A and HL_B, have been prepared according to the literature [5].

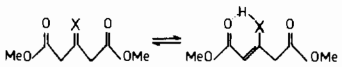


HL_A



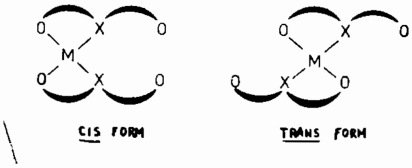
HL_B

Physico-chemical data show that for the ligands a keto–enolic equilibrium is operating; we have not found evidence for the presence of the bis-enolic form.



The ir spectrum of L_A has a broad band at 3200 cm^{-1} (νOH), at 1740 cm^{-1} (νC=O, ester), a shoulder at 1725 cm^{-1} (νC=O, ketonic), and two bands at 1660 cm^{-1} (νC=O···H) and 1630 cm^{-1} (νC=C). The ir spectrum of L_B has bands at 2455 cm^{-1} (νS–H), 1750 cm^{-1} (νC=O, esther), 1710 cm^{-1} (νC=O, ketonic), 1690 cm^{-1} (νC=O···H), 1605 cm^{-1} (νC=C), and 1180 cm^{-1} (νC=S). The ^{1}H nmr spectra in $CDCl_3$ [HL_A: 15.5 ppm (OH), 5.1 ppm (C=CH), 3.63 ppm (OCH_3), 3.45 ppm (CH_2); HL_B: 6.50 ppm (SH), 5.94 ppm (C=CH), 3.63 ppm (OCH_3), 3.34 ppm (CH_2)] confirm the presence of the two tautomeric forms. However the keto form is predominant in HL_A (87%), while the intramolecularly *cis*-enethiol tautomer is in HL_B (80%).

Mononuclear copper(II) and nickel(II) complexes are easily obtained by reacting copper(II) or nickel(II) acetate with the ligand in the presence of LiOH in ethanol solution. For the complexes both the *cis* and the *trans* forms are possible:



The elemental analyses are in good agreement with these formulations: $Cu(L_A)_2$, found C = 41.04%, H = 4.27%; calc. C = 41.02%, H = 4.39%. $Ni(L_A)_2(H_2O)_2$, found C = 38.91%, H = 4.52%; calc. C = 38.29%, H $\mp$ 4.56%. $Cu(L_B)_2$, found C = 37.83%, H = 4.27%; calc. C = 38.05%, H = 4.10%. $Ni(L_B)_2$, found C = 38.51%, H = 4.28%; calc. C = 38.47%, H = 4.15%.

Their infrared spectra in KBr pellets or nujol mull show a strong band at about 1720 cm^{-1} which can be assigned to the stretching frequency νC=O of the $-COOCH_3$ group not involved in the coordination. The bands relative to the νC=C and νC=O lie in the 1500–1600 cm^{-1} region. Electronic spectra were recorded in KBr pellets. The bands in the 500–700 nm range for the copper(II) complexes can be assigned to d–d transitions. Magnetic moments are 1.80 BM for $Cu(L_A)_2$ and 1.76 BM for $Cu(L_B)_2$. A square planar geometry around the copper ion can be proposed for these complexes. The electronic spectrum of $Ni(L_A)_2(H_2O)_2$ and the magnetic moment of 3.23 BM (at room temperature) suggest an octahedral configuration around the nickel ion. On the contrary $Ni(L_B)_2$ is diamagnetic and shows two d–d

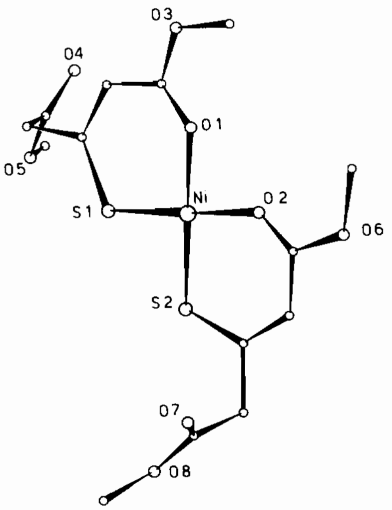


Fig. 1. Chelation of two ligand units to form a *cis*-geometrical isomer.

transition bands at 660 and 495 nm suggesting a square planar configuration. Ni(L_B)$_2$ was dissolved in hot ethanol and after few days red crystals suitable for an X-ray investigation were obtained.

The X-ray analysis, based on diffractometer data, shows that Ni(L_B)$_2$ crystallizes in the monoclinic system, space group $P2_1/n$, with a = 21.97(2), b = 8.21(1), c = 10.44(1) Å, and β = 101.87(3)° for Z = 4. The crystal data were recorded with a Philips PW1100 single crystal automatic difractometer with graphite monochromated Mo-Kα radiation. Solution of the structure was achieved by heavy atom Patterson and Fourier methods. The actual refinement converges to R = 8%.

As shown in Fig. 1, two ligand units are chelated to form the *cis*-geometrical isomer of the complex in which the nickel ion is essentially square-planar. The Ni–S and Ni–O bond distances (2.14 and 1.88 Å respectively) suggest the presence of double bond character. The nickel atom is also weakly bonded with oxygen atoms from two adjacent molecules.

We have tried to prepare binuclear complexes by using a large excess of the metal ions copper(II) or nickel(II); from the reaction mixtures only mononuclear chelates or complexes of unknown composition have been obtained. Further studies are in progress in this field.

References

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