

Synthesis and characterization of tetranuclear nickel(II) complex with a macrocyclic ligand

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Received 14 July 1994; revised and accepted 1 September 1994

A novel tetranuclear macrocyclic nickel(II) complex $[\text{Ni}_4\text{L}(\mu\text{-OAc})_2(\text{OAc})_4(\text{H}_2\text{O})_4]$ has been synthesized by the condensation of 2, 6-diformyl-4-methylphenol and triethylenetetramine in presence of nickel(II) perchlorate and excess sodium acetate. The complex has been characterized by its UV-vis, IR and FAB mass spectra along with magnetic susceptibility and conductivity data.

The literature survey revealed that extensive studies have been made on the metal complexes of the binucleating macrocyclic ligands¹⁻⁴ derived from 2, 6-diformyl-4-methylphenol and diamines. Recently Robson and coworkers⁵ have reported tetranuclear nickel(II) complexes of the macrocyclic Schiff base formed by condensing two molecules of 2, 6-bis(aminomethyl)-4-methylphenol with two molecules of 2, 6-diformyl-4-methylphenol. More recently Nag and coworkers⁶⁻¹⁰ have reported binuclear and tetranuclear nickel(II) complexes of macrocyclic ligands formed by the condensation of different types of diamines and 2, 6-diformyl-4-methylphenol. In continuation to our interest in macrocyclic nickel(II) complexes¹⁰, we report here the synthesis and characterization of a new tetranuclear nickel(II) complex of the formula $[\text{Ni}_4\text{L}(\mu\text{-OAc})_2(\text{OAc})_4(\text{H}_2\text{O})_4]$.

Experimental

All the chemicals used were of reagent grade and used as received. The solvents were purified by standard procedures. The infrared spectra were recorded on a Perkin Elmer 783 spectrophotometer using KBr discs and electronic spectra on a Shimadzu UV-160 spectrophotometer. The electrochemical data were obtained with a BAS 100B electrochemistry system. A three-electrode assembly (BAS) comprising of a Pt working electrode, a Pt auxiliary electrode and a saturated calomel reference electrode was used. Tetraethylammonium perchlorate (0.1 mol

dm^{-3}) was used as the supporting electrolyte. The C, H and N analyses were performed on a Perkin Elmer 240C elemental analyzer. The conductivity measurements were carried out using a Philips PR 9500 conductivity bridge. Nickel was estimated gravimetrically as dimethylglyoximate. A Kratos MS 50 TC mass spectrometer was used for positive ion fast atom bombardment (FAB) in *o*-nitrobenzalcohol. The magnetic susceptibilities were measured on an EG & G PAR 155 vibrating sample magnetometer using $[\text{HgCo}(\text{NCS})_4]$ as the calibrant.

Synthesis of the complex

To a boiling methanol solution (60 ml) of 2, 6-diformyl-4-methyl phenol (0.328 g, 2 mmol) was added in succession, a methanol solution (30 ml) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.64 g, 4.5 mmol), an aqueous solution (3 ml) of NaOAc (0.74 g, 9 mmol) and a solution of triethylenetetramine (0.292 g, 2 mmol) in methanol (10 ml). The solution after refluxing for 3 h was cooled and filtered. The filtrate was evaporated to dryness on a rotary evaporator and the residue was extracted with boiling acetonitrile. The acetonitrile solution on concentration afforded the bright green complex which was recrystallized from methanol-acetonitrile. [Found: C, 42.05; H, 5.71; N, 8.95; Ni, 18.76%; Analysis Reqd, for $\text{C}_{43}\text{H}_{72}\text{N}_8\text{O}_{19}\text{Ni}_4$: C, 41.65; H, 5.81; N, 9.04; Ni, 18.95%].

Results and discussion

The complex is a non-electrolyte which indicates that all the six acetate ions are coordinately bound to the metal ions. The room temperature magnetic moment of the complex is 3.24 B.M. which is typical of high-spin octahedral nickel(II) complex. The IR spectrum shows a broad band at 3400 cm^{-1} due to the water molecules and a weak band at 3200 cm^{-1} due to the $\nu(\text{N}-\text{H})$ of the secondary amine. The absence of vibrations due to the NH_2 and CHO moieties of the reactants and the appearance of $\nu(\text{C}=\text{N})$ at 1640 cm^{-1} provides a clear evidence of the formation of the macrocyclic ring. The acetate bands in the complex are observed at 1570 ($\nu_{\text{OCO}}(\text{asym})$) and 1400 and 1330 cm^{-1} ($\nu_{\text{OCO}}(\text{sym})$). The magnitude of the differences between $\nu_{\text{OCO}}(\text{sym})$ and $\nu_{\text{OCO}}(\text{asym})$ stretches ($\Delta\nu$) indicate the presence of bridging ($\Delta\nu=170\text{ cm}^{-1}$) as well as monodentate ($\Delta\nu=240\text{ cm}^{-1}$) acetates.

The formation of a macrocyclic complex was further confirmed by the FAB mass spectrum (in

nitrobenzyl alcohol matrix) which shows a group of peaks from (m/e) 850 to 857 with the strongest peak at 852.5 assignable to $[\text{Ni}_4\text{L}(\text{H}_2\text{O})_4]^+$. The next group of peaks with the strongest one observed at (m/e) 834.5 can accordingly be assigned to $[\text{Ni}_4\text{L}(\text{H}_2\text{O})_3]^+$. Subsequent to this, prominent cluster of peaks are observable at (m/e) 792.5, 776.5 and 718.6 respectively. The group of peaks appear due to the presence of several isotopes of nickel [^{58}Ni (67.9%), ^{60}Ni (26.2%), ^{61}Ni (1.2%), ^{62}Ni (3.7%), ^{64}Ni (1.1%)].

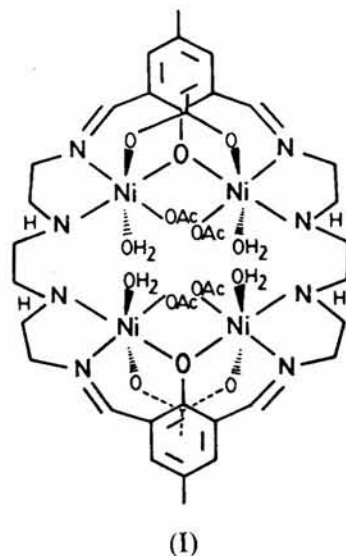
In methanol, the complex displays three absorption bands at 910 ($\epsilon = 35 \text{ M}^{-1} \text{ cm}^{-1}$), 600 ($\epsilon = 24.5 \text{ M}^{-1} \text{ cm}^{-1}$) and 385 nm ($\epsilon = 8500 \text{ M}^{-1} \text{ cm}^{-1}$), which may be ascribed to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ transitions for Ni^{2+} ions in O_h symmetry. A weak shoulder observed at 770 nm seems to be due to the spin-forbidden ${}^3A_{2g} \rightarrow {}^1E_g$ transition. The intensity of the band at 385 nm suggests that it is probably associated with a charge transfer process occurring in this region.

The redox behaviour of the complex studied by cyclic voltammetry in MeCN with a Pt electrode showed that both oxidation (+0.78 V *Vs* SCE) and reduction (-0.90 V *Vs* SCE) processes are irreversible in nature.

Although single crystals of the complex can be readily obtained from MeOH-MeCN solution, these crystals seem to contain more than one molecule of MeOH as solvent of crystallization which are immediately lost on isolation of the crystals from the mother liquor. It is due to this reason that we have so far been unable to determine the X-ray structure of the compound. Keeping in view the above findings, the following structure has been proposed for the tetranuclear nickel(II) complex (Structure I).

Acknowledgement

We are indebted to Prof. K Nag of this department for his interest and suggestions. We are also thankful



to the Department of Chemistry, Odense University, Denmark, for recording the FAB mass spectrum.

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