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Tetranuclear Metal Chelates of Nickel(II) with 1,2,5,6-Tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2, 4-hexadiene

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Tetrameric clusters of 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene with Ni(II) of the type $Ni_4L_2X_4 \cdot 12\ H_2O$ ($X = Cl^-, Br^-, I^-$ or NO_3^-) have been synthesised. Vibrational and electronic spectra suggest co-ordination of the ligand with the metal ions through nitrogen and oxygen atoms and each central ion is present in a tetragonal ligand field with chromophores NiN_4X_2 and each terminal nickel ion is present in an approxi- mately octahedral ligand field with the chromophores NiO_6.

INTRODUCTION

A series of cubane type tetrameric clusters of inckel(II) have been reported[1–4]. We have reported[5] earlier the dinuclear nickel(II) complexes with the ligand 1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene of the type $Ni_2L_2X_4$ ($X = Cl^-, Br^-, I^-$ or NO_3^-). The present paper deals with isolation and a structural elucidation of a few tetranuclear clusters of nickel(II) of the type $Ni_4L_2X_4, \cdot 12H_2O$ ($X = Cl^-, Br^-, I^-$ or NO_3^-).

EXPERIMENTAL

α-Benzil monoxime was prepared according to the procedure given in the literature[6, 7]. The ligand α-benzil azine dioxime was prepared as reported earlier[8] (m.p. 191°C).

Tetrahalo/nitrato bis(1,2,5,6,-tetraphenyl-3,4-diaza-1.6-dihydroxyimino-2,4-hexadiene) dinickel(II) $Ni_2L_2X_4$ ($X = Cl^-, Br^-, I^-$ or NO_3^-) complexes were prepared as reported earlier[5].

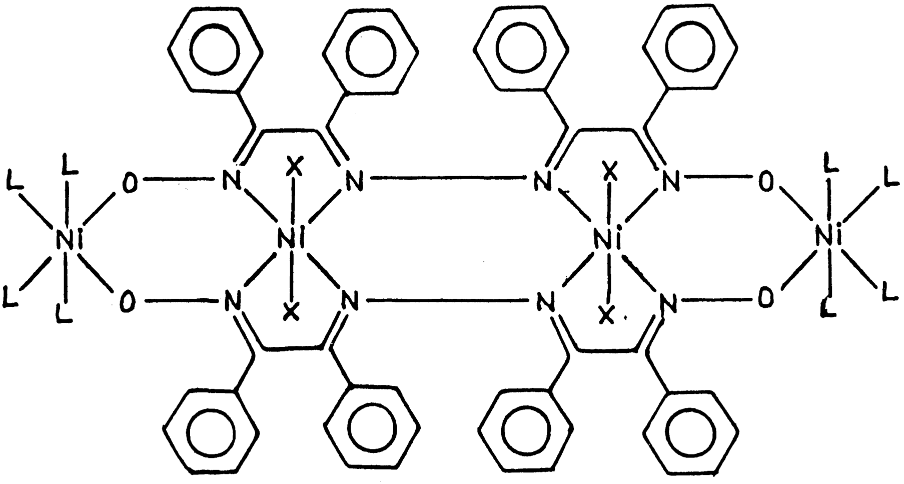
Preparation of Octaaquo-μ-[tetrachloro-bis(1,2,5,6-tetraphenyl-3,4-diaza-1,6-dihydroxyimino-2,4-hexadiene dinickel(II)] dinickel(II) tetrahydrate, $Ni_4L_2Cl_4 \cdot 12H_2O$

An ethanolic soution of $Ni_2L_2Cl_4$ was treated with nickel acetate in the molar ratio 1 : 2. The solution was allowed to crystallize by slow evaporation at room temperature on a water bath to give a brown crystalline product. The compound was filtered, washed first with ethanol and then with ether and analysed after drying *in vacuo.*

The bromo, iodo and nitrato complexes were prepared by similar methods.

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are presented in Table-I. The infrared spectra of the tetranuclear metal complexes have been examined in conjunction with the IR data of binuclear complexes. The first significant feature of the spectra of the tetranuclear complexes is the disapprearance of the —N—O—H deformation band in the region 1700–1650 cm^{-1} showing the existence of the ligand in its doubly charged anionic structure[9]. The IR spectrum of the complexes show a pair of bands of medium intensity occurring at 1525 and 1440 cm^{-1} which are believed to have arisen from C—N stretching vibration placed in two structural environments. The band found in high frequency region is ascribed to azine group and one that is observed in low frequency region to oxime groups[10, 11]. The complexes show a sharp band in the region 1000–980 cm^{-1} which arise due to N—O stretching vibration. Both the azine and oxime bands and NO bands appear at a lower frequency region as compared to the corresponding bands in the binuclear metal complexes. This shift of the structurally important C=N and NO bands to a lower frequency region in the tetrameric clusters demonstrates wider delocalisation of electronic charge due to the formation of new chelate rings. The above IR spectral data clearly suggest that the binuclear complexes are further co-ordinated to the metal ion through *cis* oxygen atoms and the complexes have been postulated to possess the structure (I)[9].



$L = H_2O, X + Cl^-, Br^-, I^-$ or NO_3^-

Fig. 1

Electronic Spectra

The complexes possess magnetic values within the range 2.60–2.80 B.M. per nickel ion at room temperature. The complexes show a group of three bands around 13,600, 15,600 and 18,200 cm^{-1} followed by a strong charge transfer band near 26,300 cm^{-1} implying tetragonal distortion of the crystal field around the central nickel(II) ions and approximately octahedral crystal field for the terminal nickel (ii) ions with chromophore NiN_4X_2 and NiO_6 respectively. The band near

13,600 cm^{-1} can be assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition for the terminal chromophores. The next two bands around 15,600, 18,200 cm^{-1} correspond to the two components in which the transition $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ of the octahedral field is split upon tetragonal distortion[9, 12].

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Sl No	Compounds	Found (Calcd) %			μ_{eff} (B.M.)
		Ni	Halogen	N	
1	$Ni_4L_2Cl_4 \cdot 12H_2O$	16.20 (16.62)	9.75 (10.09)	7.25 (7.99)	2.65
2	$Ni_4L_2Br_4 \cdot 12H_2O$	14.35 (14.75)	19.95 (20.18)	6.85 (7.06)	2.62
3	$Ni_4L_2I_4 \cdot 12H_2O$	12.85 (13.19)	28.35 (28.63)	5.65 (6.05)	2.60
4	$Ni_4L_2(NO_3)_4 \cdot 12H_2O$	15.10 (15.45)		10.75 (11.09)	2.80

L = Benzil azine dioxime.

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