NICKEL(II) COMPLEXES OF 6-METHYLPYRIDINE-2-ALDOXIME

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WE recently reported the far infrared and electronic spectra of mono- and *bis*-complexes of copper (II) with pyridine-2-aldoxime (HPOX) and HMPX, and discussed these data in terms of the electronic and geometric structures of the complexes[1]. The nickel (II) complexes studied have been mainly restricted to complexes of HPOX[2,3] HMPX[3] and 4, 6-dimethyl-*s*-triazine-2-aldoxime[3]. We have now carried out a detailed study of the nickel (II) complexes of HMPX.

Nickel (II), salts, sodium iodide (all reagent grade), 6-*m*-ethylpyridine-2-aldoxime (HMPX) were used without further purification. [Ni(HMPX)$_2$Cl$_2$] and [Ni(HMPX)$_2$Br$_2$] were prepared as described previously[3].

Diiodo-*bis* (6-methylpyridine-2-aldoxime) nickel (II) : Ni(HMPX)$_2$(NO$_3$)$_2$ was prepared by the quantitative treatment of Ni(NO$_3$)$_2$.6H$_2$O and HMPX in ethanol. A suspension of green crystals of Ni(HMPX)$_2$(NO$_3$)$_2$ (0·01 mol) in ethanol when treated with an ethanolic solution (0·02 mol) of NaI gave a greenish blue solid which was filtered, washed with water to remove NaNO$_3$, and finally with ethanol and then dried *in vacuo* over KOH.

Diffuse reflectance spectra at room temperature were recorded on a Cary Model 14-Spectrophotometer equipped with a diffuse reflectance accessory using magnesium oxide as reference. The infrared spectra of the ligand and its complexes in Nujol mulls have been made on Perkin-Elmer infracord spectrophotometer. Magnetic measurements were obtained by the standard Gouy balance, calibrated with mercury tetrathiocyanatocobaltate (II). Metal and halogen analyses were by the authors and C, H and N were by Micro-analytical laboratory, I.I.T., Kanpur. Analytical data are given in Table I.

The magnetic susceptibilities (Table I) observed by these compounds are in good agreement with previous work and are consistent with those reported for distorted octahedral compounds[4].

The reflectance spectra of [Ni(HMPX)$_2$X$_2$] (X = Cl, Br or I) complexes exhibit the features associated with [Ni(en)$_2$Cl$_2$] (en = ethylenediamine) complex, which has shown to possess a dimeric chlorine-bridged structure in which the nickel (II) atoms tre in a *cis*-octahedral environment[5]. Therefore, the bands observed at *ca.* 9·7, *ca.* 10·6 and *ca.* 11·6 kK in [Ni(HMPX)$_2$X$_2$] can be assigned to the $^3A_2 \rightarrow {}^3B_1$, $^3A_2 \rightarrow {}^3B_2$ and $^3A_2 \rightarrow {}^3A_1$ transitions, all of which arises from the splitting of the ν_1 band (O$_h$ symmetry) when the symmetry is lowered to C_2v. The bands observed at *ca.* 15·6 and *ca.* 16·9 kK. can be assigned to the $^3A_2 \rightarrow {}^3A_2$, $^3B_1$ and $^3A_2 \rightarrow {}^3B_2$ transitions, which arises from the ν_2 band (O$_h$ symmetry). These assignments differ from those of Krause *et al.*[3], who assumed a *trans*-octahedral structure (D$_{4h}$) for these complexes. The transitions arising from the ν_3 band (O$_h$ symmetry) are obscured by very intense charge transfer bands in the spectra of these complexes.

A partial assignment of the bands observed for HMPX and its nickel (II) complexes is given in Table II. The i.r. spectrum of HMPX differs from the conventional oximes, which shows a band at *ca.* 3250 cm^{-1}. This band is replaced by multiple bands between 3194 and 2791 cm^{-1}. This implies a much stronger hydrogen bonding than in other oxides. The strong bands observed at 1515 and 980 cm^{-1} in HMPX can be assigned to —C=N (acyclic) and N—O stretching vibration whereas the band observed at 820 cm^{-1} can be assigned to

TABLE I
Analytical and magnetic results

Compound	Calc. (%)					Found (%)					μ_{eff} (B.M.) at 298 °K
	Metal	C	h	N	X	Metal	C	h	N	X	
Ni(C$_7$H$_8$N$_2$O)$_2$Cl$_2$	14·62	41·8	4·52	14·0	17·6	15·10	42·12	4·70	14·31	17·91	3·19
Ni(C$_7$H$_8$N$_2$O)$_2$Br$_2$	11·96	34·3	3·29	11·4	32·5	12·20	34·49	3·36	11·61	32·60	3·15
Ni(C$_7$H$_8$N$_2$O)$_2$I$_2$	10·04	28·74	2·73	9·5	43·44	11·10	28·79	2·81	9·60	43·54	3·12

TABLE II
I.R. absorption bands due to $-C=N$, $N-O$, *and Ring Vibrations* $I - IV$ (cm^{-1})

Compound	$-C=N$	$-N-O$	Ring I	Ring II	Ring III	Ring IV
HMPX	1515 (s)	980 (s)	1585 (s)	1564 (s)	1479 (m)	1436 (s)
Ni(HMPX)₂ Cl₂	1632 (w, b)	1039 (s)	1612 (s)	1563 (w)	1477 (s)	1426 (m)
Ni(HMPX)₂ Br₂	1629 (m)	1042 (s)	1595 (s)	1565 (w)	1490 (s)	1443 (m)
Ni(HMPX)₂ I₂	1630 (sh)	1048 (s)	1598 (s)	1562 (w)	1482 (s)	1438 (w)

the out-of-plane wag of the hydrogen bonded oxime proton. Rings bands appear at 1585, 1564, 1479 and 1436 cm⁻¹ in the free HMPX. However, the nickel (II) complexes exhibit the $-C=N$ band above 1600 cm⁻¹ and N—O band at *ca.* 1075 cm⁻¹. Similar band positions in the spectra of nickel, platinum and palladium complexes of HPOX, has previously been reported[7]. Therefore, these data indicate that oxime proton is not hydrolysed in [Ni(HMPX)₂X₂] complexes and there is a contribution from the $-C=N-OH$ grouping in these complexes.

In the region 450–200 cm⁻¹ HMPX exhibits absorption bands at 403s, 387m and 217m, whereas the nickel (II) complexes have absorption bands at *ca.* 425m, 417s, 344m, 321m, 278m and 230m cm⁻¹. Since, there are no terminal Ni-X bands, no ν Ni–X vibrations will be expected above 200 cm⁻¹ [8]. The relatively low frequencies assigned to these ν Ni–X vibrations would be consistent with a halogen bridging structure, although ν Ni-X stretching frequencies occur over a wide range and some terminal ν Ni-X frequencies have been reported. The very low-symmetry of these complexes should lead to the observations of upto four infrared active metal-nitrogen stretching vibrations. Two strong bands lie at *ca.* 350 cm⁻¹ and 280 cm⁻¹, whilst a weaker

band lies at *ca.* 300 cm⁻¹, these are therefore assigned as ν Ni–N vibrations.

In conclusion, reflectance and i.r. spectra indicate a *cis*-dimeric structure for [Ni(HMPX)₂X₂] (X = Cl, Br or I). Dimeric structures of this type have been found to occur extensively in complexes of nickel (II) halides with ethylenediamine and related ligands.

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NANNOPLANKTON PRODUCTION IN VELLAR ESTUARY

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ABSTRACT

Nanroplankton and netplankton primary production were estimated at 3 stations in Vellar estuary during premonsoon and monsoon months of 1974. On the average nannoplankters were responsible for 71·1% of total production in the estuary. Irrespective of surface or bottom, the nannoplankters contributed between 40 and 100% (mean 64·4%) at Station I, 50 and 100% (mean 67·7%) at Station II and 26·8 and 100% (mean 80·7%) at Station III, to the total primary production. Salinity was the chief ecological factor that influenced nannoplankton production in the Vellar estuary.

INTRODUCTION

STUDIES made in various biotopes[1-12], showed that nannoplankton formed the major source of primary production. Nannoplankters play a

significant part in marine as well as estuarine food chain; they form the main source of food for microzooplankton[13,14] and larvae of most of the benthic animals[15-17]. The present paper records