

analysis. The infrared spectra are characterized by a band in the region  $1720-1690\text{ cm}^{-1}$  which is due to the  $\delta\text{C}=\text{O}$  group.

### Experimental

All melting points were uncorrected. The IR spectra were recorded on a spectrophotometer, (Pye Unicam SP 200 G), using KBr discs.

#### Synthesis of Schiff bases (1a-h)

These compounds were prepared according to standard procedure<sup>4</sup>.

#### Synthesis of N-oxidopyridines (2a-h)

The schiff base (1a-h) (0.02 mol) in glacial acetic acid (25 ml) was treated with hydrogen peroxide (10 ml). The reaction mixture was heated at reflux temperature for about 3 hr and left to stand at room temperature for 24 hr. On concentration and cooling the precipitated product was filtered off, washed with petroleum ether, then with dilute alcohol and dried. The results are given in table 1.

#### Synthesis of N-oxidopyridylthiazolidinones (3a-h)

A mixture of mercaptoacetic acid (0.015 mol) and the N-oxidopyridine derivatives (2a-h) (0.01 mol) in dry benzene (50 ml) was refluxed for 4 hr and stirred over periods of time ranging from 6 to 24 hr. The product which precipitated was filtered off and crystallized from the proper solvent. The results are shown in table 2.

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## PYRIDINE COMPLEXES OF NICKEL (II) AND COPPER (II) CONTAINING ORTHOPHOSPHATE ION/ ORTHOPHOSPHORIC ACID

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METAL complexes containing orthophosphate ion can be expected to show interesting coordination modes in view of the multivalent and multidentate nature of the orthophosphate ion. Very little work has been reported on such complexes so far<sup>1,2</sup>. When chlorides of Ni(II) and Co(II) were reacted with pyridine in the presence of orthophosphoric acid  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  and  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$  (py = pyridine) were obtained. Some structural aspects of these complexes have been investigated.

All chemicals used were of A. R. grade. The reactions were carried out in dry alcohol to minimise the water content of the medium and thereby to possibly prevent coordination of water.  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  was prepared by adding solutions of pyridine (40 mmol in 20 ml) and  $\text{H}_3\text{PO}_4$  (20 mmol in 20 ml) to  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solution (10 mmol in 20 ml) simultaneously. The green precipitate  $[\text{Ni}(\text{py})_2\text{Cl}_2]$  formed in the initial stages of addition of reactants was filtered off and to the filtrate the remaining pyridine and  $\text{H}_3\text{PO}_4$  were added. The pale blue compound precipitated out was filtered, washed and dried in vacuum ( $10^{-2}$  torr). Yield 1.6 g; Anal. found: Ni, 10.06; P, 10.47; N, 9.70; Calcd. for  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$ : Ni, 10.31; P, 10.87; N, 9.84.  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$  was prepared by a similar method. The mixture of pale green and yellow compounds precipitated out initially was filtered off and on further addition of pyridine and  $\text{H}_3\text{PO}_4$  to the filtrate a blue precipitate was obtained, which was filtered, washed and dried in vacuo. Yield, 3.5 g; Anal. found: Cu, 18.79; P, 4.90; Cl, 20.50; N, 8.18; C, 35.10; H, 3.47; Calcd. for  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot 0.5\text{H}_3\text{PO}_4$ : Cu, 18.61; P, 4.53; Cl, 20.76; N, 8.20; C, 35.15; H, 3.37. The above complexes were not soluble in common organic solvents. They were stable in air and melted with decomposition at  $190-225^\circ\text{C}$ .

The electronic absorption spectra of the complexes (nujol mulls) in the visible and near IR regions were recorded on a Cary-14 spectrophotometer. The magnetic susceptibilities were measured by the Gouy method using  $\text{HgCo}(\text{CNS})_4$  as standard.

The IR spectrum of  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  (nujol mulls) showed two bands at  $262\text{ cm}^{-1}(\text{m})$  and  $230\text{ cm}^{-1}(\text{s})$  in the region of  $200-300\text{ cm}^{-1}$  where metal-ligand stretching modes are expected. The IR active metal-

ligand stretching modes for the different possible chromophores namely  $\text{NiN}_4$  ( $T_d$ ,  $D_{4h}$ ),  $\text{NiN}_4\text{O}$  ( $C_{2v}$ ,  $C_{4v}$ ) and  $\text{NiN}_4\text{O}_2$  ( $C_{2v}$ ,  $D_{4h}$ ) were derived by the method described by Cotton<sup>3</sup> and on this basis the spectrum conforms to octahedral coordination to Ni(II) with the two  $\text{H}_2\text{PO}_4^-$  ions in the axial positions [ $D_{4h}$ , one  $\nu_{\text{Ni-N}}$  (Eu) and one  $\nu_{\text{Ni-O}}$  ( $A_{2u}$ )]. The bands at  $262\text{ cm}^{-1}$ (m) and  $230\text{ cm}^{-1}$ (s) were attributed to Ni-O stretching<sup>4</sup> and Ni-N stretching<sup>5</sup> modes respectively. The spectral features of coordinated pyridine were similar to those for related complexes<sup>6</sup>. The absorption bands due to  $\text{H}_2\text{PO}_4^-$  were noticed at the following frequencies ( $\text{cm}^{-1}$ ): 2850 (br,m), 2400 (br,m), 1250 (m), 1175 (vs), 1100 (s), 1050 (m), 958 (sh), 950 (s), 890 (m), 880 (sh), 850 (sh), 535 (sh), 525 (s), 505 (w), 400 (w), 385 (w) and 350 (w). These bands were shifted<sup>7</sup> to different extents relative to those of non-coordinated  $\text{H}_2\text{PO}_4^-$ .

The electronic absorption spectrum of the complex showed five  $d-d$  transition bands at  $26,670\text{ cm}^{-1}$ ,  $16,130\text{ cm}^{-1}$ ,  $13,890\text{ cm}^{-1}$  (shoulder on the  $16,130\text{ cm}^{-1}$  band),  $8930\text{ cm}^{-1}$  (br) and  $10,640\text{ cm}^{-1}$  (shoulder on the  $8930\text{ cm}^{-1}$  band). The broad band at  $8930\text{ cm}^{-1}$  showed a spike at  $8416\text{ cm}^{-1}$  which is attributed to  $\text{H}_2\text{PO}_4^-$  ( $8405\text{ cm}^{-1}$  in  $\text{KH}_2\text{PO}_4$ ). The spectrum of  $\text{Ni}(\text{py})_4(\text{H}_2\text{PO}_4)_2$  is characteristic of trans-octahedral complexes like  $\text{Ni}(\text{py})_4\text{X}_2$ <sup>8,9</sup> ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) thereby substantiating axial coordination of  $\text{H}_2\text{PO}_4^-$  ion as revealed by IR results. It appears from the electronic spectrum that the ligand field due to  $\text{H}_2\text{PO}_4^-$  is comparable to that of halide ions. The lack of solubility of the complex in organic solvents possibly indicates extensive intermolecular hydrogen bonding.

The magnetic moment of the complex (3.26 B.M.) is in the range expected for octahedral complexes<sup>10</sup>.

The IR spectrum of  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$  in the region of  $300-200\text{ cm}^{-1}$  (metal-nitrogen and metal-halogen stretching modes) was similar to that reported for  $\text{Cu}(\text{py})_2\text{Cl}_2$ <sup>11</sup> and therefore  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$  is also very likely to have a chlorine-bridged distorted polymeric octahedral structure as for  $\text{Cu}(\text{py})_2\text{Cl}_2$ <sup>11</sup>, with  $\text{H}_3\text{PO}_4$  remaining uncoordinated in the lattice. The x-ray powder diffraction patterns of  $\text{Cu}(\text{py})_2\text{Cl}_2 \cdot \text{O} \cdot \text{O} \cdot 5\text{H}_3\text{PO}_4$  and  $\text{Cu}(\text{py})_2\text{Cl}_2$  were conspicuously different as expected. The room temperature magnetic moment of the complex (1.82 B.M.) is in the expected range<sup>10</sup>.

As no Cu(II) complexes with coordinated orthophosphate ion have been obtained in the present work, alternative routes should be explored to obtain such complexes.

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#### HYDRAZINE CARBOTHIOAMIDE, 2-[(4-HYDROXY-3-METHOXY PHENYL) METHYLENE], AS A SELECTIVE REAGENT FOR THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II)

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GHUHA-SIRCAR *et al.*<sup>1</sup> have prepared hydrazine carbothioamide-2-[(4-hydroxy-3-methoxy phenyl) methylene], [HCHMM] and used as a colour reagent for a few metal ions in inorganic analysis. A survey of chemical literature shows that no attempt has been made to use HCHMM as spectrophotometric reagent for cobalt(II). The present investigation deals with the study of the colour reaction of HCHMM with cobalt(II) for the rapid spectrophotometric determination of cobalt(II). The proposed method offers the advantages of simplicity, rapidity, sensitivity and selectivity