

*Acetyl isothiocyanate* — Acetyl isothiocyanate was prepared by the reaction of potassium thiocyanate (vacuum dried) and acetyl chloride in benzene (~50 ml). The reaction mixture was refluxed for 6 hr under a fractionation column. Volatile fractions up to about 130° were slowly distilled out and rejected. The second fraction (130-33°) contained acetyl isothiocyanate as a yellow liquid having pungent smell. It was collected in 80% yield. The product was redistilled before use (Found: N, 13.80. Calc. for CH<sub>3</sub>CONCS: 13.86%).

*Reaction between triethyltin isopropoxide and acetyl cyanide* — A mixture of triethyltin isopropoxide (2.52 g, 0.009 mole) and acetyl cyanide (0.66 g, 0.009 mole) in cyclohexane (~40 ml) was refluxed for 2 hr. Removal of solvent under reduced pressure gave a white crystalline solid, which sublimed at 130-35°/0.5 mm (72% yield) (Found: Sn, 51.51; N, 5.82. Calc. for Et<sub>3</sub>SnCN: Sn, 51.22; N, 6.04%).

Other reactions of trialkyl- and dialkyltin isopropoxides with acetyl cyanide and thiocyanate have been carried out similarly and the results are summarized in Table 1.

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### Some Penta-coordinated Adducts of Cu(II)-β-Isopropyltropolonate with α- & γ-Picolines, Pyridine, Diethylamine & Imidazole

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The adduct formation of Cu(II)-β-isopropyltropolonate with some bases has been studied spectrophotometrically in benzene solution. All the bases form 1:1 adducts in which copper exhibits penta-coordination. The equilibrium constants have been obtained using a computer programme and the stability order for adduct formation is: γ-picoline > pyridine > diethylamine > imidazole > α-picoline.

WE have previously investigated the base adducts of Ni(II) and Co(II) β-isopropyltropolonates using an NMR technique<sup>1,2</sup>. Because of unfavourable relaxation time, the corresponding Cu(II) adducts could not be studied in a similar manner. Adduct formation with bases like pyridine, γ-picoline, α-picoline, imidazole and diethylamine was therefore studied by a spectrophotometric method and the results are described in the present note.

β-Isopropyltropolone (IPT) and imidazole (Koch-Light) were used as such. The other bases, α- and γ-picoline, pyridine (all BDH, LR) and diethylamine (Eastman) were stored overnight over sodium hydroxide pellets and distilled before use.

Cu(II)-β-isopropyltropolonate was prepared by slowly mixing 1 mole of copper acetate in 50% ethanol with slight excess of IPT (2 moles) in ethanol. The compound precipitated as green crystals after a few hours and was recrystallized from benzene-pet. ether.

The base adducts were obtained by slow recrystallization from the solution of the parent compound in the relevant base. However, only the γ-picoline adduct was found to be sufficiently stable in the solid state for use in physical measurements.

The electronic spectra in the range 400-800 nm were recorded on a Hitachi model 200-10 spectrophotometer while the infrared spectra of IPT, Cu(IPT)<sub>2</sub> and its γ-picoline adduct in KBr were obtained on a Perkin-Elmer spectrophotometer, model 21. The molecular weight determinations were made on a Hitachi apparatus.

Cu(IPT)<sub>2</sub> in benzene exhibits a broad absorption maximum at about 675 nm. Addition of bases brings about a bathochromic as well as a hyperchromic effect and the family of absorption spectra for increasing base concentration pass through an isobestic point at 598 nm.

Since  $\epsilon_a$ , the extinction coefficient of the adduct could not be obtained with certainty from experimental data,  $\epsilon_a$  along with the equilibrium constant for the adduct forming reaction was obtained by the method of Graddon<sup>3</sup>. The absorbance  $D$  at a particular wavelength for a given base concentration is given by

$$D = D_c + D_a$$

where  $D_c$  and  $D_a$  are the absorbances of the parent complex and the adduct respectively. Now if  $C$  is the total concentration of the parent complex and  $x$  be the amount of the adduct formed,

$$\epsilon \cdot C = \epsilon_0(C-x) + \epsilon_a x$$

where  $\epsilon_0$  and  $\epsilon_a$  are the extinction coefficients of the parent complex and the adduct respectively and  $\epsilon$  the observed value at a given base concentration, so that

$$x = \frac{C(\epsilon - \epsilon_0)}{\epsilon_a - \epsilon_0}$$

and the equilibrium constants  $\beta_1$  and  $\beta_2$  for the 1:1 and 1:2 adducts are given by

$$\beta_1 = \frac{x}{(C-x)(b-x)} \quad \text{and} \quad \beta_2 = \frac{x}{(C-x)(b-2x)^2}$$

where  $b$  is the concentration of the base added. Using a suitable computer programme, the trial

TABLE 1 — EQUILIBRIUM CONSTANTS OF ADDUCT FORMING REACTIONS OF  $\text{Cu}(\text{IPT})_2$  WITH BASES

Base	$pK^8$	$\lambda_{\text{max}}$ nm	$\epsilon_0$	$\epsilon_a$	$\beta_1$
Pyridine	5.18	700	54.0	97.0	$7.73 \pm 0.10$
$\gamma$ -Picoline	6.08	700	54.0	103.0	$9.12 \pm 0.15$
$\alpha$ -Picoline	6.20	690	53.0	95.0	$3.53 \pm 0.20$
Diethylamine	10.90	695	53.6	111.0	$4.46 \pm 0.20$
Imidazole	7.12	690	53.4	100.0	$3.73 \pm 0.20$

value of  $\epsilon_a$  was varied at intervals of unity to yield  $\alpha$  and  $\beta$  values, the true value being selected on the basis of constancy of  $\beta$  s for all the data points (different base additions). It turned out that reasonably constant  $\beta$  values were obtained for a 1:1 stoichiometry. The existence of mono-adducts in which  $\text{Cu}(\text{II})$  is penta-coordinated was further confirmed by elemental analysis and molecular weight determination for the isolated  $\gamma$ -picoline adduct (Calc. C, 64.6; H, 6.0; N, 2.9; mol. wt 483. Found: C, 64.4; H, 5.9; N, 2.6%; mol. wt 470).

Further, the IR spectrum of the adduct exhibits a strong band at  $1575 \text{ cm}^{-1}$  characteristics of the coordinated  $\text{C}=\text{O}$  while there is no absorption in  $1600\text{--}1800 \text{ cm}^{-1}$  region for any free  $\text{C}=\text{O}$ . This rules out the possibility of opening up of one of the chelate rings in the parent complex to accommodate the base molecule and thus maintain the original four-fold coordination<sup>3</sup>.

Penta-coordination is not uncommon in  $\text{Cu}(\text{II})$  complexes and a large number of such penta-coordinated adducts of  $\text{Cu}(\text{II})$ - $\beta$ -diketones have been reported<sup>4-7</sup>.

The  $\epsilon_a$  values and equilibrium constants for the adduct forming reactions along with the  $pK$  values for the bases are summarized in Table 1. The observed  $\beta$  values are rather small and do not follow the basicity order of the amines used in the present study. The order observed is  $\gamma$ -picoline > pyridine > diethylamine > imidazole >  $\alpha$ -picoline.

The weaker affinity of  $\alpha$ -picoline is probably the result of steric hindrance by the methyl group adjacent to the basic nitrogen, whereas the stronger affinity of  $\gamma$ -picoline and pyridine can arise from resonance contribution to bonding.

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## Complexes of $\text{Mn}(\text{II})$ , $\text{Fe}(\text{II})$ , $\text{Co}(\text{II})$ , $\text{Ni}(\text{II})$ & $\text{Cu}(\text{II})$ with Naphthalene-1-sulphonic Acid

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Complexes of the type  $\text{M}(\text{ANSO})_2 \cdot 2\text{H}_2\text{O}$  where  $\text{M} = \text{Mn}(\text{II})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  or  $\text{Cu}(\text{II})$  and  $\text{ANSO} = \text{naphthalene-1-sulphonic acid}$  have been prepared and characterized on the basis of elemental analyses, spectral, magnetic moment and thermogravimetric measurements. IR spectral data suggest that the ligand, in all these complexes, acts as a bidentate chelating agent coordinating through two oxygen atoms. The magnetic moment data show that the complexes are hexa-coordinated spin-free complexes. Octahedral structure is assigned to them on the basis of their electronic spectra.

EVENTHOUGH alkyl and aryl sulphonic acids are comparatively less stable and weakly acidic, stable complexes of bivalent metal ions have been reported with methanesulphonic acid<sup>1</sup>, trifluoromethanesulphonic acid<sup>2</sup> and benzene- and *p*-toluenesulphonic acids<sup>3,4</sup>. These acids generally act as bidentate ligands, coordinating through two oxygen atoms<sup>4,5</sup>. Coordination through sulphur or only one oxygen atom<sup>6</sup> is also known. Bivalent metal ion complexes of naphthalene sulphonic acid have not been studied although its reactivity and salt formation with  $\text{Fe}(\text{III})$ ,  $\text{Ce}(\text{IV})$ ,  $\text{Th}(\text{IV})$ ,  $\text{U}(\text{IV})$  and  $\text{Sn}(\text{IV})$  have been described<sup>7</sup>.

Preparation and characterization of  $\text{Mn}(\text{II})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Cu}(\text{II})$  complexes with naphthalene-1-sulphonic acid are described in this note.

Reagent grade (BDH) metal(II) chlorides or acetates were used. Naphthalene-1-sulphonic acid was prepared as reported in the literature<sup>8</sup> with a slight modification, and recrystallized from hot water containing a little HCl in colourless needles, m.p.  $84^\circ$ .

*Preparation of the complexes: General method*—To a solution of metal(II) chloride or acetate (10 mmoles) in water (50 ml) was added, with stirring, sodium naphthalene-1-sulphinate (21 mmoles) in water (20 ml). The reaction mixture was allowed to stand for 3 hr and the separated crystalline complex filtered, washed with water followed by THF (20 ml) and dried *in vacuo*.

In the case of  $\text{Ni}(\text{II})$  complex the reaction mixture was kept overnight.

$\text{Fe}(\text{II})$  complex was prepared from AR ferrous ammonium sulphate and the product separated from the reaction mixture only after the addition of THF (30 ml) to it.

Characterization data of the complexes are presented in Table 1. The complexes have very low solubility in water and common organic solvents, except DMSO, which may be attributed to their polymeric nature. The solubility in DMSO may be due to the adduct formation.