

IR spectra, elemental analysis and other properties (Table 1) are in good agreement with the formulae suggested for the derivatives. The IR spectra of these compounds also indicate that the linkage between the cyclopentadienyl and indenyl rings and the metal atom has the character of delocalized  $\pi$ -bonds<sup>9,10</sup> and the nitro and nitrito groups are attached to the metal by covalent  $\sigma$ -bonds.

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### Di-(*p*-chlorophenyl)dithiophosphinato Derivatives of Fe(III), Co(III) & Ru(III)

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Spectral studies in the infrared and visible regions and the magnetic studies over a temperature range (80° to 300°K) of M(III) (M = Fe, Co, Ru) derivatives of di(*p*-chlorophenyl)dithiophosphinic acid (CldtpiH) have been investigated. These complexes have been assigned octahedral stereochemistry and *Dq*, *B* and  $\beta$  values computed wherever possible. A novel mixed complex of Co(III) containing Cldtpi<sup>-</sup> and dimethylglyoximate anion (Dmg<sup>-</sup>) has been characterized.

THE electron spin resonance, magnetic and spectroscopic studies of dichlorophenyldithiophosphinato (Cldtpi<sup>-</sup>) complexes of some transition metals were reported<sup>1,2</sup> earlier. The reducing property of this ligand and the stabilization of Co(II) in Co(Cldtpi)<sub>2</sub> which is in contrast to the behaviour of other dithio ligands such as dithiophosphates, dithiocarbamates and xanthates were noted. Therefore, the synthesis of Fe(III) and Co(III) complexes of this ligand are of interest and are reported here together with a novel mixed complex of Co(III) containing Cldtpi<sup>-</sup> and dimethylglyoximate anion (Dmg<sup>-</sup>). The complex of Ru(III) is included for comparison with iron.

*Fe(Cldtpi)*<sub>3</sub>—A concentrated aqueous solution of ferric chloride was neutralized with sodium carbonate and after filtration treated with a slight excess of Na(Cldtpi) in water. The required complex came down as a black precipitate, and was washed with water and dried *in vacuo* (Found S, 18.92; Fe, 5.60. C<sub>36</sub>H<sub>24</sub>Cl<sub>6</sub>FeP<sub>3</sub>S<sub>6</sub> requires S, 19.05; Fe, 5.53%).

The room temperature magnetic moment of 5.85 BM indicated a *d<sup>5</sup>* high spin configuration and the measurements carried over a temperature range of 80° to 300°K indicated the ground state to be <sup>6</sup>A<sub>1</sub> in an octahedral stereochemistry and no spin equilibrium. The electronic spectrum, which is similar to that of other dithio complexes is dominated by intense charge transfer bands with bands at 16600, 18900 and 23500 cm<sup>-1</sup>. A slight bathochromic shift of the absorption bands is noticed as the ligand field strength decreases from xanthate to dithiophosphinate. However, no major change in the nature of the spectra is observed between the low spin Fe(ethyl xanthate)<sub>3</sub> to the high spin Fe(Cldtpi)<sub>3</sub>.

*Ru(Cldtpi)*<sub>3</sub>—Ruthenium trichloride trihydrate (0.5 g) in water (10 ml) was mixed with an aq. solution of Na(Cldtpi) (2 g) and the violet solution so obtained allowed to stand overnight. The deep violet compound which was obtained, was repeatedly washed with water and dried (Found: S, 18.3. C<sub>36</sub>H<sub>24</sub>Cl<sub>6</sub>P<sub>3</sub>RuS<sub>6</sub> requires S, 18.23%).

The complex is stable in air unlike Fe(III) complex and is sparingly soluble in methanol. It is highly soluble in benzene and is monomeric, like other Ru(III) complexes<sup>3</sup>. The electronic spectrum exhibited bands around 18400, 22300 and 24200 cm<sup>-1</sup> (*sh*). The shift of the bands to lower frequency in comparison<sup>3</sup> to the spectrum of tris (diethyldithiophosphato)ruthenium(III) [Ru(Et<sub>2</sub>dtP)<sub>3</sub>], is due to the lower position of dithiophosphinates in the spectrochemical series. The band around 18400 cm<sup>-1</sup> have been assigned to the transition<sup>4</sup> *t<sub>2g</sub>* → *e<sub>g</sub>*. The magnetic moments at 293°K and 83°K were 1.70 and 1.62 BM respectively. The value of 1.70 BM is lower than 2.1 BM expected for a six coordinate Ru(III) complex. This might be due to factors<sup>5</sup> such as axial distortion, extensive *t<sub>2g</sub>* electron delocalization, mixing with higher energy components of the <sup>2</sup>*I* term or may be due to quenching of the orbital angular momentum by spin orbit coupling which removes the degeneracy of <sup>2</sup>*T<sub>2g</sub>* ground state.

*Co(Cldtpi)*<sub>3</sub>—Aqueous solutions of sodium cobaltinitrite and Na(Cldtpi) were mixed together and the required brown complex immediately precipitated. It was washed with water and dried under vacuum (Found: S, 18.72; Co, 5.74. C<sub>36</sub>H<sub>24</sub>Cl<sub>6</sub>CoP<sub>3</sub>S<sub>6</sub> requires S, 18.99; Co, 5.81%).

The complex is quite stable unlike Co(Et<sub>2</sub>PS<sub>2</sub>)<sub>3</sub> which decomposed even under nitrogen atmosphere<sup>6</sup>. The diamagnetic nature of the compound is indicative of *d<sup>6</sup>* low spin system. The solid state and solution electronic spectra of freshly prepared samples are similar exhibiting bands at 12600 (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>) and 17900 (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>). Based on available data<sup>7</sup>, the complex can be assigned an octahedral geometry. The ligand field parameters *Dq*, *B* and  $\beta$  were calculated as 1392 cm<sup>-1</sup>, 331 cm<sup>-1</sup> and 0.32 respectively.

*Co(Cldtpi)*<sub>2</sub>(Dmg)—Cobalt chloride hexahydrate dissolved in methanol and a filtered solution of dimethylglyoxime in methanol were mixed together and air was bubbled through the solution for 3 hr. To this a methanolic solution of CldtpiH was added

dropwise with vigorous stirring. After slight evaporation the required brown precipitate separated out, which was filtered, washed with methanol and dried *in vacuo* (Found: S, 15.8; Co, 7.25; N, 3.45.  $C_{28}H_{22}Cl_4CoN_2O_2P_2S_4$  requires S, 15.64; Co, 7.31; N, 3.24%).

The brown complex is diamagnetic, indicating a low spin Co(III) system. A broad moderately intense band at  $1510\text{ cm}^{-1}$  in the IR spectrum may be ascribed to  $\nu C=N$ , which is slightly lower than is usually observed for the other dimethylglyoximate complexes of trivalent ions<sup>8</sup>. The two medium strong bands at  $1075$  and  $1235\text{ cm}^{-1}$ , assigned to the  $\nu N-O$  are due to unequal N-O linkages. This is in conformity with the X-ray studies of Ni(II) and Cu(II) complexes of dimethylglyoxime<sup>8</sup>. A weak band around  $865\text{ cm}^{-1}$  could be due to OH deformation vibration. The spectrum of the complex in the visible region indicated a broad band with peaks around  $19200$  and  $20600\text{ cm}^{-1}$ , and a shoulder at  $14900\text{ cm}^{-1}$ . The split band around  $20000\text{ cm}^{-1}$  may be due to  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transition in an octahedral symmetry with splitting occurring due to the spectrochemical differences between the ligands coordinated to the metal atom.

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**Studies on Ion Association: Stabilities of Azido Complexes of Ni(II), Zn(II) & Cd(II)**

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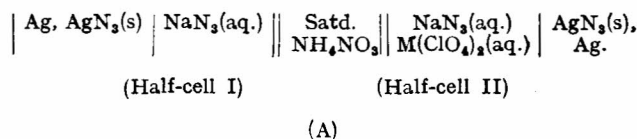
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The association constants of monoazido complexes,  $MN_3^+$ , for M = Ni(II), Zn(II) and Cd(II) have been determined potentiometrically using silver-silver azide electrode. The results have been compared with those of monothiocyanato and monoselenocyanato complexes. Inner-sphere bonding is indicated in the complexes.

**THERMODYNAMICS** of formation of thiocyanato and selenocyanato complexes of some bi- and trivalent metal ions have been studied by Das and coworkers<sup>1-3</sup>. It was thought useful to extend the work to another pseudo-halide ion,  $N_3^-$ . The present paper reports the stability constants of azido complexes of Ni(II), Zn(II) and Cd(II) at  $25^\circ$  determined by potentiometric method using silver-silver azide electrode.

Stock solution of metal perchlorates were prepared by dissolving the corresponding carbonates (AR) in dilute perchloric acid (Merck, GR) and were estimated by standard gravimetric procedures. Sodium azide (Reidel) was crystallized twice before use.

Silver-silver azide electrodes, prepared by the method of Taylor and Nims<sup>4</sup>, were equilibrated in the cell solutions for 48 hr before use. The electrode set-up has been described in a previous paper and was kept in an air-thermostat ( $25^\circ \pm 1^\circ$ ). E.m.f. measurements were made with a OSAW potentiometer (model 30071) in conjunction with a multiflex galvanometer.



The cell of the type (A) was set up.

It has been observed earlier that in such a cell the small liquid-junction potential which may be existing does not seriously vitiate stability constant result<sup>1</sup>. The e.m.f. of the cell is given by the expression

$$E = \frac{RT}{F} \ln \frac{a(I)}{a(II)} \quad \dots(1)$$

where *a* represents the activity of the  $N_3^-$  ion. *a*(I) being known from the concentration and activity coefficient of  $N_3^-$  in half-cell I, *a*(II) were easily calculated from Eq. (1). Concentrations of different species in equilibrium [ $M^{2+}$ ,  $N_3^-$ ,  $MN_3^+$ ,  $M(N_3)_2$ ] in the half-cell II were calculated by a series of approximations and refinements as detailed in our earlier work<sup>1</sup>. Both  $K_1$  and approximate value of  $K_2$

$$K_1 = \frac{[MN_3^+]}{[M^{2+}][N_3^-]} \cdot \frac{1}{f_{++}} \quad \dots(2)$$

and

$$K_2 = \frac{[M(N_3)_2]}{[MN_3^+][N_3^-]} \cdot \frac{1}{f_{\pm}^2} \quad \dots(3)$$

(assuming activity coefficients of species of similar charge to be equal) were calculated using Eqs. (2) and (3) respectively and the values are presented in Table 1. The activity coefficients of the ions in the solutions were calculated from the ionic strengths with the help of Davies equation<sup>5</sup>.

A comparison can be made of our results with those found in the literature. Gerding<sup>6</sup> has calorimetrically determined the free-energy, enthalpy and entropy changes of formation of the azido complexes of Cd(II) in 3M solution of sodium perchlorate at  $25^\circ$ . The  $\Delta G$  of formation of  $CdN_3^+$  was found to be  $-9.25\text{ kJ mole}^{-1}$  against our thermodynamic value,  $\Delta G^\circ = -13.5\text{ kJ mole}^{-1}$ , at zero ionic strength (calculated from the relationship:  $\Delta G^\circ = -RT \ln K$ ). It is difficult to compare the two results as, in very high ionic strength, it is not possible to evaluate the activity coefficient terms. However, qualitatively one expects lower stability at higher ionic strength in agreement with our findings.