

**PREPARATION AND CHARACTERISATION OF BIS (PICROLONATE)  
TRANSITION METAL(II) DIHYDRATE AND TRIS (PICROLONATE)  
LANTHANIDE(III) TRIHYDRATE COMPLEXES**

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The complexes of picrolonic acid with the divalent Mn, Fe, Co, Ni, Cu and Zn and the trivalent La, Nd, Eu, Gd, Dy and Er were prepared. The compounds were characterised by the chemical and thermal analyses and IR. The electronic spectra and magnetic data suggest the octahedral structure for the metal(II) complexes. Neutral complexes of the general formula  $MP_2 \cdot 2H_2O$  and  $MP_3 \cdot 3H_2O$  were isolated for the metal(II) and metal(III) ions respectively (P = picrolonate ion). Coordination of the ligand with the metal ion occurs through the carbonyl and adjacent nitro-group.

### INTRODUCTION

The successful use of picrolonic acid in analytical chemistry was reviewed in our previous work[1]. We reported on the strong acid character of the compound in terms of its structure and we also studied the conductivity of its alkali metal salts in water and in dimethylsulfoxide[1]. It may be expected that the picrolonate ion, will be sufficiently weak and leads to formation of weak complexes, which may be beneficial in lanthanide separation processes. The present work is an attempt to study the coordination chemistry of picrolonic acid with the divalent ions of Fe, Mn, Co, Ni, Cu and Zn and with the trivalent ions of La, Nd, Eu, Gd, Dy and Er.

### EXPERIMENTAL

(i) *Picrolonic Acid*. The purification of the commercially available picrolonic acid was described in the previous work[1].

(ii) *Preparation of the Metal Complexes*. The metal(II) complexes were generally prepared as follows: A solution of 10 mmole of the metal chloride in 50 ml water was added to 20 mmole of the hot alcoholic solution of the ligand. A fine crystalline product was separated on cooling, it was washed with hot ethanol and ether and dried to constant weight *in vacuo* ( $P_2O_5$ ).

The lanthanides complexes were prepared in a similar way using 1.33 mmole of lanthanide nitrate and 5 mmole of the ligand.

(iii) *Physical Measurements*. The IR of the ligand and its complexes as KBr discs were recorded on Beckman

4220 IR spectrophotometer. The electronic spectra of the solid complexes were measured in nujoll mull on a manual Unicam SP 600 spectrophotometer in the range 25000-10000  $cm^{-1}$ . The magnetic susceptibility measurements of the complexes were done at room temperature using a Gouy balance. The diamagnetic corrections were considered in calculations[2]. The thermal measurements of the samples were recorded on a Du Pont thermal analyser Model 990, DSC cell in the temperature range 25-550°. The rate of heating was 2 and 5°/minute.

### RESULTS AND DISCUSSION

The analytical data of the complexes agree with the general formula  $M(II)P_2 \cdot 2H_2O$  and  $M(III)P_3 \cdot 3H_2O$ , (M(II), Fe, Mn, Co, Ni, Cu and Zn; M(III), La, Nd, Eu, Gd, Dy and Er.) e.g.,  $FeP_2 \cdot 2H_2O$ : C, 38.96; N, 17.80; M, 9.18; calc., C, 38.85; N, 18.13; M, 9.04 and  $LaP_3 \cdot 3H_2O$ : C, 36.40; N, 17.20; M, 13.90; calc., C, 36.67; N, 17.10; M, 14.14. The analyses of the other compounds are also satisfactory.

The DTA curves of the lanthanide complexes show three endothermic peaks at  $120 \pm 5$ ,  $150 \pm 5$  and  $220 \pm 5^\circ$  corresponding to the stepwise dehydration of the three water molecules. In case of the metal(II) complexes, dehydration of the two water molecules occurs at  $170 \pm 20^\circ$ . The exothermic peak in the range  $285-325^\circ$  could be related to the decomposition process of the complexes.

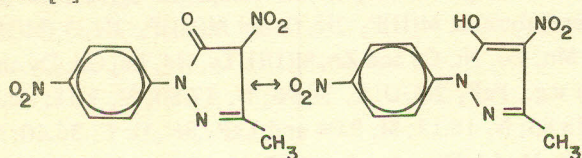
The IR spectrum of picrolonic acid[1] was compared with that of its metal complexes. In all the complexes, the ligand  $\nu(C=O)$  at  $1660 cm^{-1}$  is only shifted to  $1650 \pm 5$ , which indicates the coordination of the carbonyl oxygen with the metal ion. We have also found in the previous



Table 1. Magnetic and electronic spectra data for the metal(II) picrolonates.

Compound	$\mu_{\text{eff}}$ (B.M)	d-d transition ( $\text{cm}^{-1}$ )	Assignment
MnP <sub>2</sub> .2H <sub>2</sub> O	5.70		
FeP <sub>2</sub> .2H <sub>2</sub> O	5.24	10750 (b)	$5T_{2g} \rightarrow 5E_g$
CoP <sub>2</sub> .2H <sub>2</sub> O	4.67	18180 (sh)	$4T_{1g}(F) \rightarrow 4T_{1g}(P)$
		16390 (sh)	$4T_{1g}(F) \rightarrow 4A_{2g}(F)$
		10305	$4T_{1g}(F) \rightarrow 4T_{2g}(F)$
NiP <sub>2</sub> .2H <sub>2</sub> O	3.30	16665	$3A_{2g} \rightarrow 3T_{1g}(F)$
		13330 (sh)	$3A_{2g} \rightarrow 1E_g(D)$
		12345 (sh)	$3A_{2g} \rightarrow 1E_g(G)$
		10525 (sh)	$3A_{2g} \rightarrow 3T_{2g}(F)$
CuP <sub>2</sub> .2H <sub>2</sub> O	2.04	16665-11110(b)	$2B_{1g} \rightarrow 2B_{2g}$
		10525 (sh)	$2B_{1g} \rightarrow 2A_{1g}$

work[1] and in the current work[4] on the synthesis of some condensation products of picrolonic acid with amino-triazole derivatives, that picrolonic acid and its ion exist in the keto-form. Joshi and Jain had, however, reported that the acid can be represented by the two tautomeric forms[3].



In spite of the complex nature of the spectra in the absorption region of the nitro-group, the bonding of the latter with the metal ion could be indicated by the splitting of the ligand bands at 1500 and 1350  $\text{cm}^{-1}$ . The splitting is presumably attributed to the superimposed frequencies of  $\nu_{\text{as}}(\text{NO}_2) + \nu(\text{C}=\text{C})$  and  $\nu_{\text{s}}(\text{NO}_2) + \delta_{\text{s}}(\text{C}-\text{CH}_3)$  respectively.

The magnetic moments and electronic spectra data for the metal(II) picrolonates are listed in Table 1. A high-spin octahedral structure is suggested for iron[6], cobalt and nickel complexes, while that of copper is a tetragonal distorted one[7,8]. The magnetic moment of MnP<sub>2</sub>.2H<sub>2</sub>O indicates only the high-spin character of the compound. No conclusion about the stereochemistry of the complex

could be drawn from either the magnetism or the electronic spectrum. The characteristic multiple band of the high-spin octahedral or tetrahedral Mn(II) compounds[7] is assumed to be screened by the broad charge transfer absorption in the region greater than 20000  $\text{cm}^{-1}$ . We may reasonably however, propose an octahedral environment for the six-coordinate manganese on the basis of the bidentate mode of bonding of the picrolonate ion.

An octahedral environment is also proposed for the six-coordinate ZnP<sub>2</sub>.2H<sub>2</sub>O.

The analysis, in addition to the bidentate character of the picrolonate ion, suggest that, the lanthanide ions tend to expand their coordination number to 9, which is consistent with the fact that the coordination number of these ions can be as high as ten[9].

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