

## Binuclear Metal Complexes of 1-Hydroxy-5-carboxylato-1,4-diaza-2-methyl-3-phenyl-1,3-pentadiene with Bivalent Transition Metal Ions

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Binuclear complexes of the type  $[M(\text{CAMPE})(\text{H}_2\text{O})_2]_2$  where  $\text{H}_2\text{CAMPE}$  stands for 1-hydroxy-5-carboxylato-1,4-diaza-2-methyl-3-phenyl-1,3-pentadiene and is the Schiff base derived from glycine and 1-phenyl-1,2-propanedione-2-oxime and  $M = \text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  or  $\text{Ag}^{2+}$  have been synthesized; physical and spectroscopic analyses indicate a binuclear structure for the complexes with metal ions in an octahedral environment, where the ligand coordinates to the metal centre through azomethine nitrogen, oxime and carboxylate oxygen.

### INTRODUCTION

The Schiff bases derived from ketoximes and amino acids have received only scanty attention<sup>1</sup>. This type of ligand is potentially polydentate capable of forming five- or six-membered metal chelate rings. We report here the results pertaining to the investigation of such a ligand,  $\text{H}_2\text{CAMPE}$ , and its metal complexes with a number of metal ions. The complexes have been characterized with particular reference to the ligand moieties in metal complexes.

### EXPERIMENTAL

1-Phenyl-1,2-propanedione-2-oxime and glycine were Aldrich (G.R.) quality reagents. Commercial solvents were used without further purification.

The ligand was prepared by condensing 1-phenyl-1,2-propanedione-2-oxime with glycine in 1 : 1 molar ratio in ethyl alcohol. As glycine is insoluble in ethanol it was first dissolved in a minimum volume of water and then added to the oxime. The resulting mixture was treated under reflux on a water bath for 3 h after which the volume was nearly halved. On cooling the solution, needle-shaped crystals separated. These were removed by filtration, washed with cold ethanol and ether and then dried over fused  $\text{CaCl}_2$ .

All the complexes were prepared in an identical method, either from the Schiff base and metal acetates or by template synthesis. However, in both the cases, complexes of the same stoichiometry were isolated. In this paper we describe the template method.

In a typical reaction, 1-phenyl-1,2-propanedione-2-oxime and the metal acetates dissolved in ethanol (1:1 molar ratio) were boiled under reflux till a clear solution was obtained. To this mixture glycine dissolved in minimum volume of water was added. The reaction mixture was further boiled under reflux for another 3 h and coloured precipitates were obtained. They were filtered and washed several times with H<sub>2</sub>O and finally with ethanol.

Infrared spectra were recorded on a Perkin-Elmer-983 spectrophotometer in KBr pellets and the reflectance spectra of the complexes were recorded with Cary-2390 spectrophotometer. TGA was carried out with a Netzch simultaneous recording TGA-DTA thermoanalyser-429, by heating the complexes up to 900°C at a rate of 10°C min<sup>-1</sup> in air and by taking 50–100 mg of the sample in each case. Metal and nitrogen contents were determined by standard methods. Conductance was measured in 10<sup>-3</sup> M dioxane solution of the complexes using a Toshniwal conductivity bridge. Room temperature magnetic susceptibility measurements were carried out on solid samples by Gouy method.

## RESULTS AND DISCUSSION

The analytical data of the complexes are presented in Table-1. All the complexes are stable under normal conditions and have high melting points. They are insoluble in common organic solvents, but are soluble in polar solvents such as DMF and dioxane. Low molar conductances in dioxane indicate their non-electrolytic nature.

TABLE-1  
ANALYTICAL DATA OF THE LIGAND, H<sub>2</sub>CAMPE AND ITS METAL COMPLEXES

Ligand/Complexes	Colour	m.p./Decomp. (°C)	Found (Calcd.) %			
			M	C	H	N
H <sub>2</sub> CAMPE	Cream	225	—	60.00 (62.26)	4.98 (4.24)	12.90 (13.20)
[Cu(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	Light green	> 260	9.95 (10.0)	41.30 (41.56)	4.44 (4.40)	8.76 (8.81)
[Ni(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	Grey	> 250	9.35 (9.38)	42.10 (42.21)	4.29 (4.48)	8.88 (8.95)
[Co(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	Pink	> 250	9.43 (9.40)	42.09 (42.18)	4.19 (4.47)	8.68 (8.94)
[Ag(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	Brown	> 250	14.80 (14.90)	36.23 (36.46)	3.77 (3.86)	7.45 (7.73)

*Infrared spectra:* A band of medium intensity at 3435 cm<sup>-1</sup> in the infrared spectrum of the ligand H<sub>2</sub>CAMPE has been assigned to ν(O—H). A broad band in the 3250–2350 cm<sup>-1</sup> region and two other bands at 1620 and 1400 cm<sup>-1</sup> are

due to  $\nu(\text{N—H})$ , antisymmetric and symmetric vibrations of the carboxylate group respectively. The broadness and large separation value *i.e.*  $\Delta\nu(\text{COO})$  indicate the presence of strong hydrogen bonding between the carboxylate and the amine<sup>1-4</sup>. The bands at 1650 and 1010  $\text{cm}^{-1}$  arise due to  $\nu(\text{C=N})$  and  $\nu(\text{N—O})$  respectively. In the infrared spectra of the complexes a broad band at 3420  $\text{cm}^{-1}$  supported by another band at 850  $\text{cm}^{-1}$  indicates the presence of co-ordinated water molecules<sup>2,3</sup>. In the spectra of the complexes  $\Delta\nu(\text{COO})$  is observed invariably by more than 150  $\text{cm}^{-1}$ , proving adequately that the carboxylate group acts in an unidentate manner<sup>4</sup>. The ligand band due to  $\nu(\text{C=N})$  undergoes downward shift and appears as a band of medium intensity at 1630  $\text{cm}^{-1}$  in the spectra of the complexes suggesting the participation of the azomethine group in complexation.

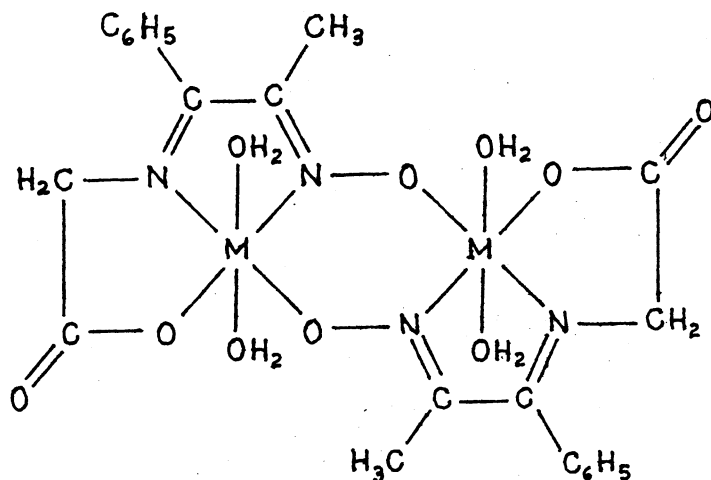
Further, the band due to  $\nu(\text{N—O})$  shows an upward shift and appears as a strong band at 1410  $\text{cm}^{-1}$  supporting coordination of the oxime group<sup>5,6</sup>. Additional bands in the 530–310  $\text{cm}^{-1}$  and 460–440  $\text{cm}^{-1}$  region are attributable to  $\nu(\text{M—O})$  and  $\nu(\text{M—N})$  respectively<sup>7,8</sup>.

*Thermal analysis:* Since the infrared spectra of the complexes indicate the presence of coordinated water molecules, thermal analyses of the complexes were undertaken in order to ascertain their nature. Rapid loss in weight corresponding to two molecules of water (Table-2) in a single step in the thermogram of the complexes accompanied by sharp endothermic peaks at the same temperature in the DTA curve suggests the presence of two molecules of water coordinated to the metal ion<sup>9</sup>.

TABLE-2  
THERMAL STABILITY OF THE COMPLEXES

Complexes	Wt. loss (180–230°C) Found (Calcd) %	Temp. (°C) Commencement of decomp.	Temp. (°C) Completion of decomp.	Wt. of residue Found (Calcd) (%)
[Cu(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	11.32 (11.33)	185	875	24.98 (25.04)
[Ni(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	11.49 (11.51)	235	813	23.79 (23.89)
[Co(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	11.56 (11.50)	218	790	23.88 (23.94)
[Ag(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	9.83 (9.94)	—	—	32.00 (32.04)

*Electronic spectra:* The electronic spectral data (Table-3) and the magnetic moment values suggest an approximately octahedral stereochemistry for cobalt(II) and nickel(II) complexes<sup>10-15</sup> and distorted octahedral geometry around copper(II) and silver(II) ions. Subnormal magnetic moment values of these complexes can be ascribed to the partial quenching of paramagnetism due to antiferromagnetic metal-metal interactions in a bimetallic structure (I).

Fig. 1.  $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Ag}^{2+}$ TABLE-3  
MAGNETIC AND SPECTRAL DATA OF THE COMPLEXES

Complexes ( $\mu_{\text{eff}}$ in B.M.)	Band position ( $\text{cm}^{-1}$ )	Assignments	10 Dq	B	C	F <sub>4</sub>	F <sub>2</sub>	$\beta$
[Cu(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> (1.61)	19230 30330	${}^2E_g \rightarrow {}^2T_{2g}$ CT band	—	—	—	—	—	—
[Ni(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> (2.37)	13157 20408 28570	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ CT band	1248	879	4139.0	118.1	14.70	0.84
[Co(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> (2.83)	11764 27544 31250	${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ CT band	789.8	877.5	4065.4	116.2	24.58	0.93
[Ag(CAMPE)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> (1.63)	28170	CT band	—	—	—	—	—	—

During complexation, the protons from the carboxylic group as well as the  $\nu(\text{N}-\text{OH})$  are abstracted by the metal ions with the formation of a neutral complex. Magnetic moment values, infrared and electronic spectral band positions, high melting points and sparingly soluble nature in common organic solvents support the binuclear structure.

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