

# **SPECTROPHOTOMETRIC ANALYSIS, THERMAL ANALYSIS AND GRAVIMETRIC DETERMINATION OF SOME METAL IONS WITH OXIME AND SCHIFF'S BASE DERIVATIVES OF N-FUROYLPHENYLHYDROXYLAMINE**

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## **Abstract**

The oxime and Schiff's base of N-furoylphenylhydroxylamine form complexes with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ . These complexes were studied by means of the UV – Vis. spectra of nujol mulls, electron spin resonance (ESR) spectra and magnetic susceptibility to determine their stereochemistry. The complexes were characterized via elemental analyses, molar conductivities and thermogravimetric analyses. Organic reagents were used for the gravimetric determination of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  through the precipitation of their complexes. The compounds were also used for separation of a binary mixture of  $\text{Cu}^{2+}$  and  $\text{Cu}^{2+}$ . Interferences were studied.

**Keywords:** analyses of metal chelates, determination of stereochemistry

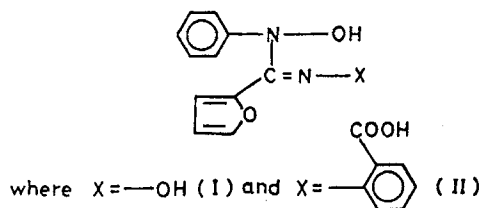
## **Introduction**

Hydroxamic acid derivatives have been used as analytical reagents for the analysis of many metal ions [1–5]. The coordination phenomena occurring in oximes and Schiff's bases of hydroxamic acid derivatives, and also the formation of stable metal complexes have been investigated by many authors [6, 7].

In the present work, the complexes were isolated in the solid state and characterized by means of spectral magnetic measurements and elemental and thermogravimetric analyses. The organic reagents were used for the gravimetric determination of metal ions after quantitative precipitation of the metal chelates.

## **Experimental**

The oxime (I) and Schiff's base (II) of N-furoylphenylhydroxylamine were prepared [7, 8] with the general formula:



The solid complexes were prepared by mixing a hot solution (0.01 mol) of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Fe}^{3+}$  chloride with the appropriate amount of the organic reagents sufficient to form 1:1 or 1:2 ( $M:L$ ) complexes in the case of divalent cations and also 1:3 ( $M:L$ ) complexes in the case of trivalent cations. The reaction mixture was then refluxed on a water bath for 2 h. The solid complexes separated out from the mixture, and were filtered off, washed with dry ethanol and dried over dried silica gel (yield in the range 78.5–91.7%). They were subjected to elemental micro analyses for C, H, N, metal and chloride ion content. The results were in good agreement with those calculated for the suggested formulae. The molar conductivities are listed in Table 1. Their structures were confirmed by spectroscopic techniques and thermogravimetric analysis. The structures of the solid chelates were previously suggested by the IR and  $^1\text{H}$  NMR spectra [9].

To determine the metal ion content [10], the solid complexes were digested with conc.  $\text{HNO}_3$ , and then diluted to a measured volume. The determination was performed by EDTA titration. The analysis of the solution for its chloride ion content was performed by Volhard's method [11].

Physical measurements and apparatus were as detailed earlier [7, 12, 13].

## Results and discussion

The absorption spectra and magnetic moments of the complexes are given in Table 1. The electronic absorption spectra of the ligands and their solid complexes with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Fe}^{3+}$  were measured in dimethylformamide (DMF), and also for solid complexes dispersed in nujol mull [14] (Table 1). The visible spectra indicate that the CT bands for the ligands (281–309 nm) are red-shifted on complexation. The  $\text{Co}^{2+}$  complexes exhibit a band at 400–428 nm, assigned to the  $^4A_{2g} \rightarrow ^4T_{1g}$  (F) transition, which indicates an octahedral structure [15]; transformation takes place through the coordination of two solvent molecules (DMF), leading to the six-coordinated complex. The observed magnetic moments of these cobalt complexes are 4.26–4.55 B.M. at room temperature. The  $\text{Cu}^{2+}$  complexes exhibit a broad band at 605–640 nm, assigned to the  $^2E_g \rightarrow ^2T_{2g}$  transition, which indicates square planar geometry. The magnetic moments of the copper complexes were found to be 1.78–1.96 B.M. a  $\text{dsp}^2$  hybrid orbital being involved. The  $\text{Zn}^{2+}$  complexes exhibit a shoulder at 455–480 nm, assigned to the  $^2B_{1g} \rightarrow ^1A_{1g}$  transition. This may be ascribed to square planar geometry. The  $\text{Fe}^{3+}$  complexes exhibit a band at 510–533 nm, which may be as-

Table 1 Cumulative data for spectrophotometric, magnetic susceptibilities and molar conductance studies of the metal chelates with organic reagents

Compound	CT transition		<i>d-d</i> transition				g value	$\mu_{\text{eff}}$ (B.M.)	$\Lambda_m /$ $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$
	DMF	Nujol mull	DMF	Nujol mull	$\lambda_{\text{nm}}$				
	$\lambda_{\text{nm}}$	$\lambda_{\text{nm}}$	$\lambda_{\text{nm}}$	$\lambda_{\text{nm}}$	$\lambda_{\text{nm}}$				
Ligand I	290	281	—	—	—	—	—	—	
[CoL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	316	290	403	416	—	—	4.42	21.2	
[CoL <sub>2</sub> ·2H <sub>2</sub> O]	305	287	400	408	—	—	4.26	9.4	
[CuL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	323	319	619	632	—	—	1.87	21.8	
					2.2814				
[CuL <sub>2</sub> ·2H <sub>2</sub> O]	318	311	605	611	—	—	1.81	12.3	
[ZnL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	298	287	468	480	—	—	—	20.3	
[ZnL <sub>2</sub> ·2H <sub>2</sub> O]	295	284	460	471	—	—	—	6.2	
[FeL·Cl <sub>2</sub> ·2H <sub>2</sub> O]·H <sub>2</sub> O	327	321	525	533	—	—	5.90	24.5	
					4.2023				
					2.0682				
[FeL <sub>3</sub> ]·2H <sub>2</sub> O	318	312	514	519	—	—	5.66	9.3	
Ligand II	309	294	—	—	—	—	—	—	
[CoL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	316	304	419	428	—	—	4.55	19.8	
[CoL <sub>2</sub> ·2H <sub>2</sub> O]	312	300	410	422	—	—	4.36	8.1	
[CuL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	323	327	630	640	—	—	1.96	20.2	
					2.1639				
					2.2648				
[CuL <sub>2</sub> ·2H <sub>2</sub> O]	318	319	621	633	—	—	1.78	10.8	
[ZnL·Cl·H <sub>2</sub> O]·H <sub>2</sub> O	312	311	466	475	—	—	—	18.1	
[ZnL <sub>2</sub> ·2H <sub>2</sub> O]	315	310	455	462	—	—	—	4.6	
[FeL·Cl <sub>2</sub> ·2H <sub>2</sub> O]·H <sub>2</sub> O	342	331	521	528	—	—	5.72	23.6	
					4.2891				
					2.1872				
[FeL <sub>3</sub> ]·2H <sub>2</sub> O	324	318	510	518	—	—	5.53	8.6	

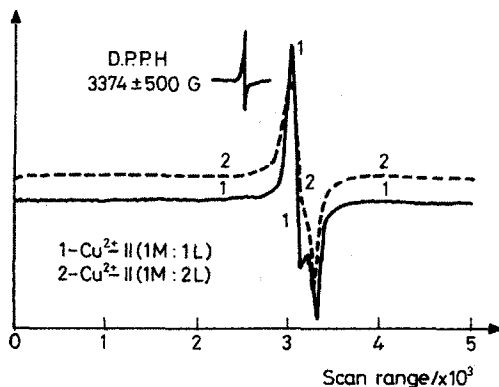


Fig. 1 ESR spectra of  $\text{Cu}^{2+}$ -chelates with ligand II

signed to the  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) transition in octahedral geometry of the complexes. The observed magnetic moments of the  $\text{Fe}^{3+}$  complexes are 5.53–5.90 B.M. Thus, the complexes formed have octahedral geometry involving  $d^2sp^3$  hybridization in the  $\text{Fe}^{3+}$  ion.

The ESR spectra of the  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  or  $\text{Fe}^{3+}$  complexes, measured at room temperature, exhibit an intense broad signal and no obvious hyperfine structure for the  $\text{Cu}^{2+}$  complexes (Fig. 1). The  $g_{\text{eff}}$  values of the chelates are given in Table 1. The data in Table 1 may indicate elongated octahedral geometry for the  $\text{Co}^{2+}$ , square planar geometry around the  $\text{Cu}^{2+}$  and elongated octahedral geometry for the  $\text{Fe}^{3+}$ . The positive contribution to the  $g_{\text{eff}}$  value over that for a free electron ( $g=2.0023$ ) may indicate an increase in the covalent nature of the bonding between the metal ion and the ligand molecule [16]. The magnitude of covalent bonding varies according to the nature of the ligand and the metal ion in the complex.

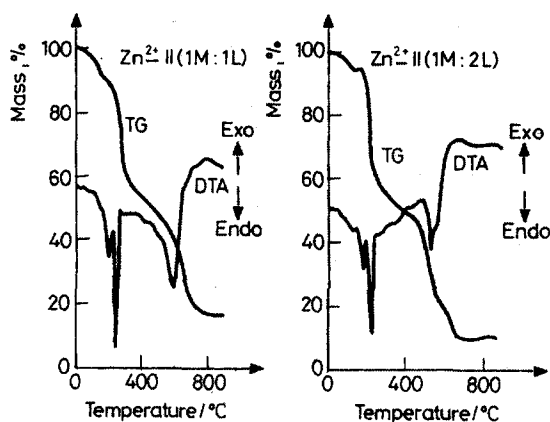


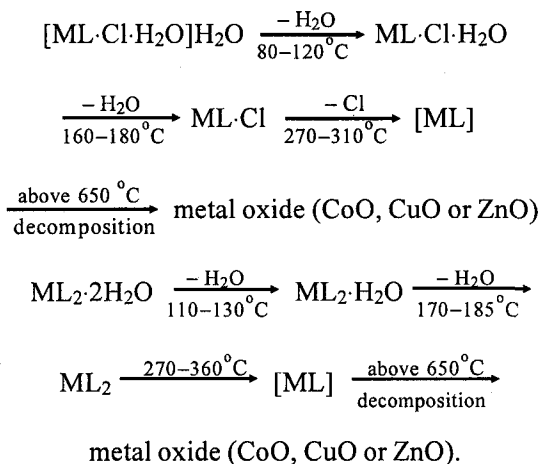
Fig. 2 Thermoanalytical curves of  $\text{Zn}^{2+}$ -chelates with ligand II

Table 2 Thermogravimetric analysis of the solid complexes

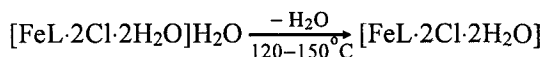
Complex	Ratio <i>M/L</i>	TG				DTA		
		Metallic residue/ %		%M		No <sub>H<sub>2</sub>O</sub>	<i>T</i> <sub>decomp</sub> / °C	$\Delta E_a$ / kJ mol <sup>-1</sup>
		calcd.	found	calcd.	found			
Co <sup>+2</sup> -I	1:2	14.0	11.0	11.13	11.0	2	535	37.39
Cu <sup>+2</sup> -I	1:2	15.0	12.0	11.90	12.0	2	398	121.88
Zn <sup>+2</sup> -I	1:1	23.2	18.6	18.47	10.18	2	425	36.35
	1:2	15.2	12.2	12.2	6.72	2	380	33.24
Fe <sup>+3</sup> -I	1:1	17.5	13.6	14.03	13.58	3	475	37.4
Co <sup>+2</sup> -II	1:1	16.8	13.2	13.05	7.98	2	520	23.54
	1:2	10.3	8.1	7.99	4.89	2	355	14.20
Cu <sup>+2</sup> -II	1:1	17.6	14.1	13.93	7.9	2	570	84.76
	1:2	10.6	8.5	8.56	4.85	2	495	51.46
Zn <sup>+2</sup> -II	1:1	17.4	14.0	14.27	7.86	2	585	91.41
	1:2	11.0	8.8	8.79	4.84	2	525	33.24
Fe <sup>+3</sup> -II	1:1	14.0	10.9	11.12	10.76	3	560	83.10
	1:2	7.0	5.4	5.29	3.41	2	500	10.38

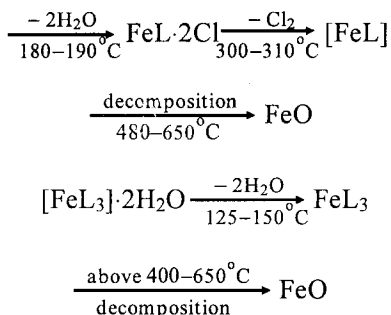
The molar conductivities ( $\Lambda_m$ ) of  $1 \times 10^{-3}$  M solutions of the metal complexes in DMF at  $25^\circ\text{C}$  are in the range  $4.6 - 24.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , i.e. the complexes behave as non-electrolytes. Accordingly, the chloride ions contribute to the coordination sphere in the complexes under investigation.

The thermogravimetric analyses of some of the solid complexes were performed in nitrogen atmosphere (Fig. 2). The loss in mass was measured from ambient temperature up to  $900^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . Each inflection in the TG curve is accompanied by an endothermic peak in the DTA curve, corresponding to certain phase transitions. From the TG curves of the  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  complexes, the loss in mass of each chelate was used to calculate the number of water molecules (Table 2). The metal content was confirmed by calculating it from the residual mass, after complete decomposition of the chelates to the corresponding metal oxide, the method described in [17] being applied (Table 2). According to the literature [18], water eliminated below  $120^\circ\text{C}$  can be regarded as crystal water, whereas water eliminated above  $150^\circ\text{C}$  is water coordinated to the metal ion in the chelates. The coordinated chloride ion is volatilized within the range  $270-325^\circ\text{C}$ . Above  $335^\circ\text{C}$ , decomposition of the complex species takes place with an inflection over the range  $380-580^\circ\text{C}$  in the range 30–55 wt%, indicating the transformation of another type of complex at this temperature. The formation of metal oxides starts above  $600^\circ\text{C}$  for the complexes. The final inflection shown by the 1:1 solid chelate in the 16.8–23.2 wt% range corresponds to the metal oxide residue, whereas for the 1:2 chelate it occurs at 11.0–15.2 wt% for the  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  complexes. The thermal degradation of the  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  complexes can be represented as follows:



The thermal degradation of the  $\text{Fe}^{3+}$  complexes can be postulated as follows:





The DTA curves of the metal complexes are characterized by the presence of an endothermic peak in the temperature range 80–220 °C. This is the temperature range in which water molecules are expelled. The DTA curves (Fig. 2) show several endothermic peaks at  $\approx 600^{\circ}\text{C}$ , which are due to the decomposition of the anhydrous complexes (ML) to the metal oxide in the experiments carried out by using a nitrogen atmosphere. The energies of activation ( $E_a$ ) of the thermal decomposition of the complexes are evaluated from the thermal curves (Table 2) as given in a previous work [19]. Generally, the reaction follows first-order kinetics. Arrhenius plots were constructed (Fig. 3) and  $E_a$  was obtained from the slope.

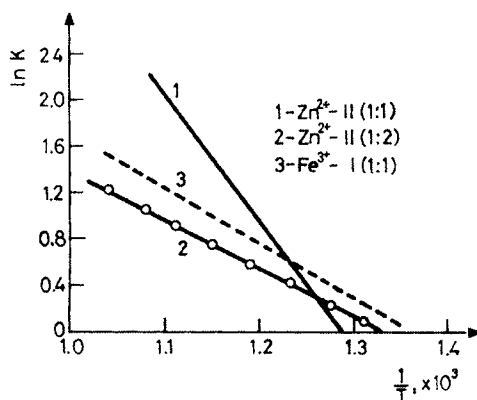


Fig. 3 Arrhenius plots constructed from DTA curves of some solid complexes

### Gravimetric determination of $\text{Co}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$

The organic ligands were used as reagents for the precipitation of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  complexes by using a buffer solution of 10% sodium acetate and dilute HCl to adjust the  $p\text{H}$  to the corresponding values for  $\text{Co}^{2+}$ =6.0–6.8,  $\text{Cu}^{2+}$ =4.0–5.5 and  $\text{Fe}^{3+}$ =3.0–3.8. The complex precipitate was filtered off on a G-4 sintered glass crucible, washed with hot distilled water, dried at  $120^{\circ}\text{C}$  to constant mass

and kept in a desiccator over dry calcium chloride. To determine the quantity of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , the precipitate was ignited at  $750^\circ\text{C}$  to yield the oxides (Table 3). The free ligands I and II are colourless while the complexes exhibit distinct colours, e.g. pale-brown complexes of  $\text{Co}^{2+}$ , greenish-yellow complexes of  $\text{Cu}^{2+}$  and red complexes of  $\text{Fe}^{3+}$ .

**Table 3** Determination of metal ion as oxide

Complex	Wt. taken		Wt. of oxide		Wt. found	% Error $\pm$
	mg					
$\text{Co}^{2+}$ -I	26.22		68.00		26.16	0.13
$\text{Co}^{2+}$ -II	25.17		66.50		25.32	0.12
$\text{Cu}^{2+}$ -I	58.50		74.61		58.57	0.10
$\text{Cu}^{2+}$ -II	53.81		68.82		53.90	0.21
$\text{Fe}^{3+}$ -I	29.94		34.83		29.70	0.80
$\text{Fe}^{3+}$ -II	18.71		21.75		18.55	0.85

### *Gravimetric determination of $\text{Co}^{2+}$ in presence of $\text{Cu}^{2+}$*

A mixture containing known amounts of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  was diluted to 80 ml with distilled water. A 10% buffer solution of sodium acetate and dilute HCl was then added to adjust the *pH* to about 4.8. The solution was heated to boiling and copper was precipitated by the gradual addition of the organic reagent I or II (30 ml of  $1 \times 10^{-2}$  M solution). The precipitate of the  $\text{Cu}^{2+}$  complex was heated on a water bath for 2 h with occasional stirring, filtered through a No. 4 sintered glass crucible, washed well with hot distilled water and dried at  $110\text{--}120^\circ\text{C}$  to constant mass. The copper content of the precipitate was calculated by multiplying the mass of the precipitate by the chemical factor. Before the subsequent determination of  $\text{Co}^{2+}$ , 10 ml of 2% hydroxylamine hydrochloride was added. The

**Table 4** Determination of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions in a mixture

Mixture No.	Taken			Found			% Error	
	mg						$\text{Cu}^{2+}$	$\text{Co}^{2+}$
	$\text{Cu}^{2+}$	+	$\text{Co}^{2+}$	$\text{Cu}^{2+}$	+	$\text{Co}^{2+}$		
1	33.10		26.21	32.97		26.30	0.14	0.10
2	27.80		28.32	27.64		28.36	0.20	0.08
3	30.44		29.35	30.58		29.31	0.15	0.10
4	39.71		31.46	39.62		31.48	0.13	0.04



$\text{Co}^{2+}$  in solution was then determined as described above after adjusting the buffer solution to  $\text{pH} \approx 6.5$ . A known mass of the precipitate of the metal complex was ignited to the metal oxide. The metal content was calculated by multiplying the mass of the metal oxide by the chemical factor. The metal ion concentration in the separated complex was determined after igniting a known mass of the complex, dissolving the remaining metal oxide in conc.  $\text{HNO}_3$  and removing the excess  $\text{HNO}_3$  by evaporation. The metal ion was then determined compleximetrically [10]. Table 4 indicates that  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  can be separated quantitatively, and hence they can be determined separately.

The average error for several determinations by gravimetric methods was found to be less than 0.99%.

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