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Transition metal complexes of indane 1,2,3-trione trioxime

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Abstract

Complexes of iron(III), cobalt(III), nickel(II), copper(II) and palladium(II) with new trioxime *i.e.*, indane-1,2,3-trione trioxime (ITT) have been prepared and characterised. Bonding in all complexes takes place *via* nitrogen atom of the oxime group Iron(III) complex is paramagnetic while cobalt(III), nickel(II), copper(II) and palladium(II) complexes are diamagnetic All the complexes prepared have been characterised by elemental analysis, conductance, IR and electronic spectral studies Copper complex is dimeric while other remaining complexes are monomeric.

Key words: Synthesis, characterisation, transition metal complexes.

1. Introduction

Oximes have good chelating properties and hence are exploited as analytical reagents for separation and determination of many metal ions. They exhibit insecticidal, miticidal and nematocidal activities[1]. They were employed as antidotes against organophosphorous poisons[2]. Further, vicinal α-dioximes have been used as chelating reagents for transition metal ions. Recently, 2,3,4-pentanetrionetrioxime (PTT) has been introduced as an analytical reagent for palladium[3]. The presence of an additional oxime group greatly increases the solubility of PTT in water. Considering the potential use of transition metal ions in biological systems and the growing importance of oximes as chelating agents, we have investigated complex formation between transition metal ions and the trioxime of indane 1, 2, 3-trione (ITT).

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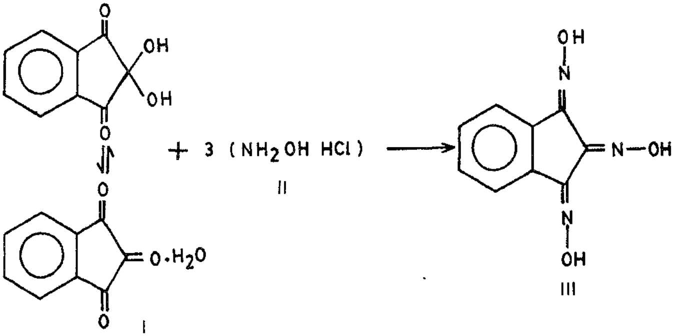
2. Experimental

2.1. *Preparation of indane 1,2,3-trione trioxime*

A solution of sodium hydroxide (5%, 50 ml) was added to a mixture of ninhydrin (I) (0.02 mol) dissolved in 50 ml of ethanol and hydroxylamine hydrochloride(II) (0.06 mol) dissolved in 50 ml of deionised water. The reaction mixture was heated under reflux for 30 min. A light yellow product separated on cooling the reaction mixture which was separated by filtration *in vacuo* and recrystallised from absolute ethanol, m.p. 169–171°C. ITT(III) was characterised on the basis of its infrared spectrum and its purity was confirmed by elemental analyses (Found: C, 52.88; H, 3.31; N, 19.01; Calc. for $C_9H_7N_3O_3$: C, 52.70; H, 3.45; N, 20.47%) and mass spectral data (measured mass of the parent peak correspond to 205). A solution of the reagent (1×10^{-2} M) was prepared in 30% aqueous dimethylformamide medium; the solution was stable for two days when stored in an amber bottle.



2.2. *Preparation of complexes*

Equimolar (1×10^{-2} M) metal salt solution (50 ml) and reagent (ITT) solution (100 ml) were taken in a 500-ml beaker containing 50 ml of sodium acetate–acetic acid buffer (pH 4.0) and 100 ml of methanol. The precipitate obtained was digested on a hot water bath for 1 h and separated by filtration *in vacuo*, followed by washing with hot water and methanol.

The metal salts, $FeCl_3$, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $PdCl_2$ used were of AR grade. Cobalt(III) complex was prepared in the presence of 2% ammonium persulphate $[(NH_4)_2S_2O_8]$ and 2M ammonia solution. The complexes were obtained as crystalline solids and were dried at 100°C to constant weight.

2.3. *Physical measurements*

Analyses and spectral measurements were carried out as described elsewhere[4].

Magnetic susceptibility and magnetisation measurements were obtained using a vibrating sample magnetometer (VSM) operating at field strength of 3 to 8 kilo gauss. VSM was calibrated *versus* the saturation moment of ultrapure (99.99%) Ni metal[5] and against the susceptibility of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$[6], the two calibrations agreed to within 2%.

A Beckmann DU-2 spectrophotometer equipped with 1.0 cm quartz cells and an ELICO pH meter (Model LI-120) were used in the present study.

3. Results and discussion

3.1. *Study of ligand (ITT)*

The absorption spectra of 8×10^{-5} M ITT at various pH values show bathochromic shift (257 to 275 nm) in acid and alkaline media (fig. 1). The pK value (9.4) was calculated from the variation of absorbance with pH by Phillips and Merritt's method[7].

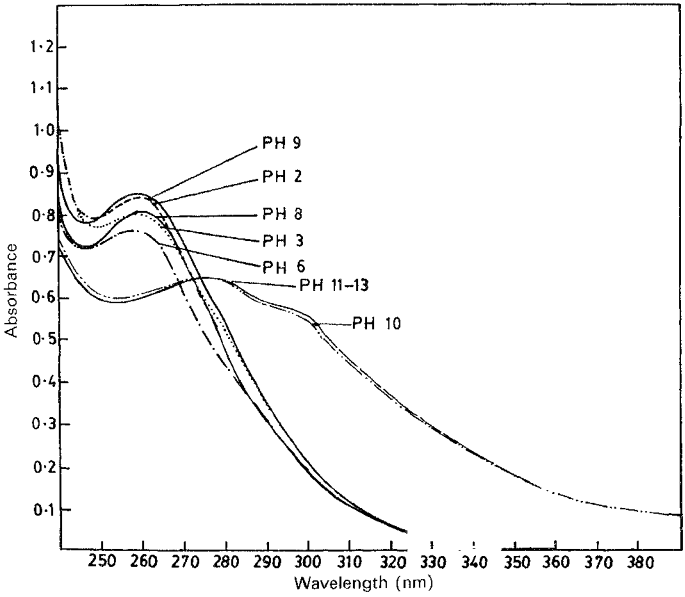


FIG. 1. Absorption spectra of ITT at different pH values.

The reactions of various cations with ITT were tested at different pH values. The characteristics of the most important complexes are summarised in Table I. The data from appropriate spectra were obtained in the presence of excess (20-fold molar) of the reagent to metal ion and pH values which facilitate the formation of different complexes. The compositions of complexes were determined by Job's continuous variation method[8] and molar ratio method (Tables I and II).

Room-temperature magnetic moment of iron(III) complex (1.92 BM) suggests that the complex is of d^5 low-spin type[9,10]. The electronic spectra of the complex shows four bands at 15,400, 19,000, 22,000 and 30,760 cm^{-1}. The assignment of the d–d transition is rather difficult. The strong highest energy band may arise due to the charge-transfer from ligand to metal. The first and third weak low-energy bands are assigned to two spin-forbidden transitions. The electronic spectral bands suggest distorted tetrahedral geometry for iron complex.

The palladium complex is diamagnetic at room temperature. Four bands are observed in the electronic spectra of the complex at 15,600; 23,800; 31,250 and 35,700 cm^{-1}. The first low-energy spin-allowed band (15,600 cm^{-1}) has been assigned to the transition $b_{2g}(xy) \rightarrow b_{1g}(dx^2 - y^2)$ *i.e.* ${}^1A_{1g} \rightarrow {}^1A_{2g}$ comparable to the transition assigned by

Table I
Characteristics of ITT complexes in solution

Metal ion	Colour	pH	λ_{max}	M:L	Molar absorptivity $L\,mol^{-1}\,cm^{-1}$
Fe(III)	Brown	5.0	305	1:1	7.8×10^3
Co(II)	Yellow	5.5	320	1:3	5.3×10^4
	Brownish-green*	5.5	400	1:1	2.6×10^4
Ni(II)	Yellow	5.0	310	1:1	8.7×10^3
	Orange-red	9.0	420		3.0×10^3
Cu(II)	Yellow	4.5	320	1:1	7.6×10^3
Pd(II)	Brown	4.0	320	1:1	1.5×10^4

*In the presence of 4 ml of 0.4% periodate.

Table II
Analytical data for the complexes of indane-1,2,3-trione trioxime (LH_3)

Complex	Colour	Yield	C%		H%		N%		Cl%		Metal %	
		(%)	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[FeLH_3Cl_2]Cl$	Brown	66	29.42	30.64	1.90	1.92	11.44	11.38	28.95	29.25	15.21	15.50
$[Co(LH_2)_2(H_2O)_2]Cl$	Brownish-green	35	39.97	40.50	2.96	2.92	15.54	15.45	6.56	7.10	10.90	10.25
$[NiLH_3Cl_2]$	Red	62	32.28	33.12	2.09	2.10	12.55	12.45	21.68	20.85	17.55	17.55
$[Cu_2(LH_3)_2Cl_2]Cl_2$	Dark-green	65	31.82	30.90	2.06	2.05	12.37	12.35	20.88	20.35	18.71	18.20
$[PdLH_3Cl_2]$	Red	67	28.25	29.15	1.83	1.85	10.98	10.56	18.55	18.65	27.84	26.50

Jorgensen[11], although in $PdCl_4^{2-}$ this transition is observed at 17,600 cm^{-1}. The red shift is due to the spectrochemical difference between the ligand (ITT) and the chloride ligand. The second (23,800 cm^{-1}) and the third (31,250 cm^{-1}) band are spin-allowed transitions which may probably arise due to

$$[a_{1g}(z^2) \rightarrow b_{1g}(x^2 - y^2) \text{ i.e., } {}^1A_{1g} \rightarrow {}^1B_{1g}]$$

and

$$[eg(xz, yz) \rightarrow b_{1g}(x^2 - y^2) \text{ i.e., } {}^1A_{1g} \rightarrow {}^1E_{1g}],$$

respectively. The highest energy band at 35,700 cm^{-1} may be assigned to charge-transfer from ligand to metal.

For the diamagnetic nickel(II) complex, no band in the visible region is observed except for intense band around 30,000 cm^{-1}. For the square-planar, nickel(II) compounds, the band arising from ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition usually occurs at about 20,000 cm^{-1} and the shift of this band to a much higher energy region may be due to the coupling of the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ band with the charge-transfer band[11].

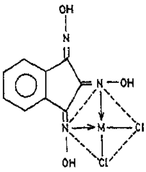
Copper(II) complex shows broad band at 15,500 cm^{-1} assignable to ${}^2B_{1g} \rightarrow {}^2E_g$ transition in terms of square-planar stereochemistry. The absence of any band below 10,000 cm^{-1} eliminates the possibility of tetrahedral or pseudotetrahedral environment in this complex[12]. The subnormal room temperature μeff value (0.95 BM) of copper complex may be explained in terms of metal–metal interaction in the dimers formed through halogen bridging resulting in the formation of $[Cu_2(LH_3)_2Cl_2]$ chromophore.

The reaction of cobalt(II) chloride hexahydrate with ITT in the presence of ammonium persulphate yielded a brownish-green compound of formula $Co(ITT)_2(H_2O)_2Cl$. Its molar conductance in dimethylformamide (50) shows that it behaves as a uni-univalent electrolyte in this solvent. Formulation as $[Co(LH_2)_2(H_2O)_2]Cl$ is therefore indicated. A deep brownish-green colour and diamagnetism of complex suggest that it is an octahedral cobalt complex. The electronic spectrum (in DMF) of the $[Co(LH_2)_2(H_2O)_2]Cl$ displays a band at 15,380 cm^{-1} which can be assigned as the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of O_h point group.

The molar conductance values of iron(III) and copper complexes in dimethylformamide, respectively, are 15 and 20 ohm^{-1} cm^2 mol^{-1}, and suggest 1:1 ionic nature of complexes.

The infrared spectra of complexes show three bands around 1560, 1180 and 940 cm^{-1} which do not appear in the spectrum of ITT(III). The band at 1560 cm^{-1} is attributed to the asymmetric νC=N stretching vibration and other bands to N–O stretching modes[13]. A broad band in the spectrum of ITT at 3285 cm^{-1} is assignable to νOH involved in strong hydrogen bonding. All the complexes exhibit a sharp band at 3420 cm^{-1} assigned to νOH of the oxime group.

A salient feature of the spectra of the ligand is a strong and sharp band at 1715 cm^{-1} which has been assigned to O–H deformation vibration of the NOH group[13]. This assignment is further strengthened since this band appears and the intensity is not lowered in all complexes where OH bands are not broken in the formation of the metal complexes. The coordination through nitrogen atom of NOH group is further substantiated by the appearance of additional M–N vibrations in the regions 500–430 cm^{-1} in the far IR spectra



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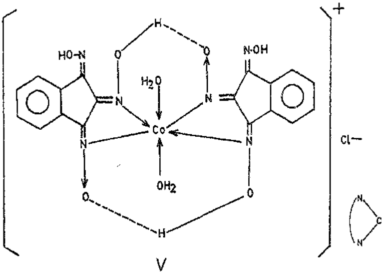

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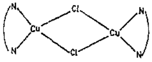

VI

of the complexes. In all the complexes (except cobalt) two M–Cl vibrations are observed at about 360 and 260 cm^{-1} suggesting the *cis*-arrangement of chlorine atoms with respect to each other.

The thermal decomposition behaviour of metal complexes has been examined. The complexes are generally stable up to 200°C. The residue value (weight) obtained in TG analysis corresponds to the respective metal oxides.

Based on analytical data, physico-chemical and spectral studies structure(IV) is assigned to iron(III), nickel(II) and palladium(II) complexes, the cobalt complex $[Co(LH_2)_2(H_2O)_2]Cl$ is assigned the octahedral structure(V) and the copper complex, the dimeric structure (VI).

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