

Synthesis and Physico-Chemical Studies on Metal Complexes of some Bisazo phenyl β -Diketone Derivatives

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Summary: Mn^{2+} , Fe^{3+} , Co^{2+} , Cu^{2+} , and Zn^{2+} complexes with some m- and p-bisazo-phenyl-di-(β -diketone) derivatives have been prepared of the type (M:L) or (2M:L) and then investigated. Their chemical constitution and molecular structure are determined on the basis of conductometric titration, molar conductance, elemental and thermogravimetric analysis, IR, 1H NMR, ESR and electronic absorption spectra. The bonding of metal ions to the ligand takes place through the coordination of O in the C=O group and O in the enolic groups by proton displacement in 1:1 or 2:1 complexes. The coordination polyhedron is completed by water and solvent molecules to give tetrahedral or octahedral shapes. Titration technique is used to calculate the proton-ligand and metal-ligand stability constants in 70% (v/v) aqueous dioxane media.

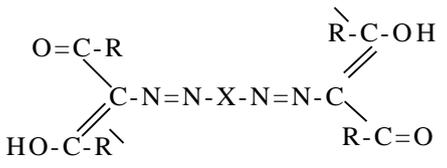
Introduction

The coordination phenomena occurring with azo dyes have been investigated by many authors⁽¹⁻⁸⁾. Many of these compounds act as mordant dyes for different fibers⁽⁹⁻¹¹⁾. A large number of azo compounds have been used in the field of analytical chemistry⁽¹²⁻¹⁶⁾.

This work aimed to synthesize and characterize some transition metal complexes of bisazophenyl- β -diketone derivatives.

Experimental

The bisazo compounds were prepared as reported previously⁽⁶⁻¹⁷⁾. The ligands have the following structure.

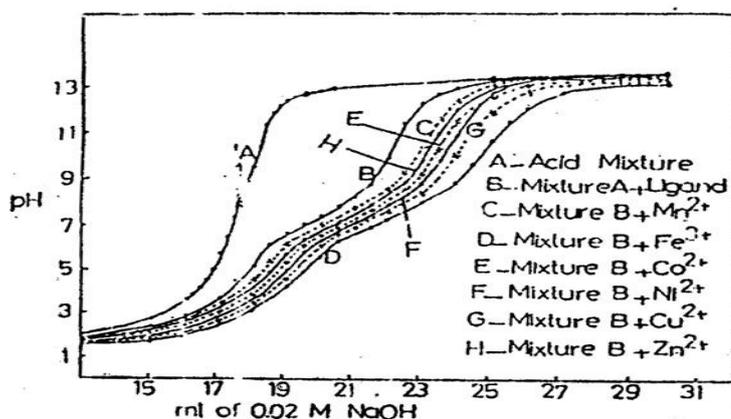
	Comp.	X	R	R ¹
Ia	m-phenylene	Me	Me	Me
Jb	m-phenylene	Me	Ph	Ph
Jc	m-phenylene	Ph	Ph	Ph
Ha	p-phenylene	Me	Me	Me
Hb	p-phenylene	Me	Ph	Ph

Stock solutions of ligands (dioxane 0.01 M) and transition metal chloride (bidistilled water 0.1 M) were prepared.

The solid chelates were prepped by mixing hot saturated aqueous solution of 0.01 mole of Mn²⁺, Fe³⁺, Co²⁺ or Zn²⁺ chloride with the requisite amount of each ligand in dioxane as solvent so as to form 1:1 or 2:1 (M: L) chelates. The reaction mixture was then refluxed on a water bath for \approx 6 hrs. The solid complexes separated on standing were filtered off, washed with ethyl alcohol, dried and then subjected to elemental analysis.

For pH titration (Fig. 1) the following mixtures were prepared:

Fig. 1: Titration curves for Ib and its metal complexes.



(A) 5 ml NaClO_4 (1.0 M) and 5 ml HClO_4 (0.1 M);

(B) Mixture (A) + 25 ml (1×10^{-3} M, ligand,

(C) To (H) mixture (B) + 2 ml of 2.5×10^{-3} M metal ion total volume of all mixtures was made up to 50 ml with aqueous dioxane (70% v/v).

The pH values were measured using Orion research model 601A/Digital Ionalyzer. Molar conductance measurements were carried out on a YSI 32 conductivity bridge. Elemental analysis (Table 1) was carried out by recommended standard methods (19). Thermogravimetric analysis (TGA) were performed by using 951-thermogravimetric analyzer Du-pont-instrument "U.S.A" at rate of 10°C per minute. IR spectra of the ligands and their chelates were recorded in the solid state using the KBr disc technique on a Beckman 4220 IR spectrophotometer. ^1H NMR spectra of the diamagnetic complexes were obtained on a Varian EM 390-90 MHz spectrometer. ESR spectra were studied for some solid complexes using the Varian E-109 ESR spectrometer. Electromic absorption spectra were measured for the complexes in the solid state as nujol mull and in DMF solution using Shimadzu 240 spectrophotometer.

Results and discussion

Studies in solution

The stoichiometries of the complexes were first determined by conductometric titration, where a steady increase in conductance occurs with increase of the volume of the ligand added which is due to the liberation of easily mobile H^+ ion of the enolic (OH) group through the formation of covalent bond between oxygen of enolic (OH) group and metal ion in a six membered ring fashion. The three breaks at $[L]/[M]$ ratios of $\frac{1}{2}$, 1 and 2 indicate the existence of 2:1, 1:1 and 1:2 (M:L) complex species in solution.

The proton-ligand ionization $\log K^1_H$, $\log K^2_H$ and metal-ligand formation constants $\log B_1$ and $\log B_2$ of the bisazo dyes under investigation were determined by the method of Irving and Rossotti [18] as well as that of Mushran et al. (24) by the half-integral (i.e. at $n_A = 0.5, 1.5$) method using the n_A vs pH curves. The values of $\log K^1_H$ and $\log K^2_H$ of the ligands Ia, Ib, Ic, IIa and IIb amount to 10.86 and 6.2; 8.5 and 5.7; 7.55 and 5.11; 11.85 and 7.3; 9.65 and 5.85 respectively, indicating that the proton ionization constants of the ligands decrease in the order IIa > Ia > IIb > Ib > Ic, which is due to the effect of the relative position of the N=N groups and also the substitution of methyl group by phenyl ring in the molecules. The formation curves of the metal complexes as n vs pL curve, used to obtain $\log \beta_1$, and $\log \beta_2$ ($\log \beta_1 = \log K_1$ and $\log \beta_2 = \log K_1 K_2$) indicate that the formation constant of the metal complexes decreased in the order IIa > Ia > IIb > Ic > Ib. which is due to the change of electron donating CH_3 group by electron accepting Ph group in the structure of these ligands. The over all formation constant of metal complexes decreased in the order $Fe^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$. This can be explained on the basis that the stability increases with decreased size of the cations, its charge and also with increased number of 3d-electrons, except for Zn^{2+} .

Studies of the composition and structure of the solid complexes:

Data of elemental analysis for metal ion, chloride ion and water content show a satisfactory agreement with the proposed formulae. The molar conductance values of the solid complexes in DMF medium lies in the range $62-63 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for all chelates of 1:1 and 2:1 (M:L) ratios which indicate clearly the ionic nature of these chelates and also that the chloride ion is present outside the coordination sphere. This was detected by the precipitation of AgCl on addition of AgNO₃.

The thermogravimetric analysis (TGA) curves of the Co²⁺ and Zn²⁺ chelates denote the loss of physically bound water molecules from the crystal lattice at 75-100 °C, whereas at higher temperature 120-200 °C there is a loss of one or two water molecules in (1:1 or 2:1 M:L ratios) that are coordinated to the metal ions of the chelates. The TGA curves show at the range 240-750 °C a clear weight loss of about 52-82% having inflection within 350-400 °C. This range of temperature represents the decomposition of the organic part of the chelates. The final constancy of the 1:1 solid chelate lied at 27.8%; from TGA curve. The percentage of water molecules and metal ions in the chelates were calculated, (Table 1).

The bands observed at 3400, 3360, 3480 and 3440 cm⁻¹, assigned to $\nu(\text{OH})$, in the spectra of the free ligands Ia, b, c and IIa, b, are broadened; their positions are shifted to higher or lower wave number (20-400 cm⁻¹), except Zn²⁺ Ib (2:1) chelate where this band disappeared. This behavior may be attributed to the participation of the enolic OH group of the bisazo β -diketones in chelation with the metal ion. The bending δ_{OH} bands at 1365, 1358, 1328, 368 and 1360 cm⁻¹ of the free ligand exhibit a shift of 4-12 cm⁻¹ to lower or higher wave numbers on complexation. This behaviour is due to the liberation of the enolic OH group of ligand from hydrogen bonded OH-group through chelation with metal ions. The $\nu_{\text{C=O}}$ bands at 1648, 1675, 1644, 1640 and 1672

cm^{-1} of the free ligands exhibit a shift of $10\text{-}65\text{ cm}^{-1}$ to lower or higher wave numbers on complexation which may be taken as an evidence for the participation of the C=O group in coordination (25). The $\nu(\text{N}=\text{N})$ band at $1418, 1400, 1415$ and 1425 cm^{-1} of the free ligands are not or little shifted to lower or higher wavenumbers on complexation ($3\text{-}8\text{ cm}^{-1}$). This indicates that the N = N group does not contribute to chelation. The $\nu(\text{C}-\text{O})$ band at $1127, 1125, 1153, 1028$ and 1052 cm^{-1} of the free ligands exhibit a shift of $5\text{-}62\text{ cm}^{-1}$ to lower or higher wave numbers on complexation. Thus, the chelation occurs through the carbonyl and enol -oxygen atoms from the ligand. The new bands appearing in the range of $370\text{-}360\text{ cm}^{-1}$ are assigned to $\nu_{\text{M}-\text{O}}$ (21).

The $^1\text{H NMR}$ spectra of ligands Ia, b, c and IIa, b were compared with those of its Zn^{2+} -chelates in CDCl_3 , DMSO or mixed CDCl_3 and DMSO at M:L ratios of 2:1 and 1:1. The signal of the protons of the enolic OH groups of free ligands Ia, b, c, and IIa, b are found at $14.68, 14.74, 13.55, 14.98$ and 8.2 ppm respectively, disappear in the presence of D_2O . It is weak and shifted to higher field ($0.04\text{-}1.58$ ppm) upon chelation, except the Zn^{2+} -Ic chelate (2:1) ratio where it disappeared. The aromatic protons resonate at $6.25\text{-}8.10$ ppm for free ligand Ia, b, c and IIa, b. Chelation causes shift to upfield, accompanied by an obvious decrease of their intensities and broadening of their envelope, indicating the formation of a covalent bond between the zinc ions and the oxygen atom of the enolic OH group. In the most of the spectra of Zn^{2+} -chelates a new signal is observed at $3.7\text{-}4.0$ ppm, which is due to, water molecules coordinated to zinc ion in the complex. The signal of the proton of enolic OH group of Zn^{2+} -Ib chelate, was removed after deuteration, indicating the contribution of enol in addition to keto forms of the ligand to chelation.

The ESR spectra of Mn^{2+} , Fe^{3+} , Co^{2+} and Cu^{2+} chelates of (2M:IL) ratio measured at room temperature, exhibited intense broad signals with hyperfine structure, the g_{eff} -values of the chelates are as follows:

The Mn^{2+} -Ia $g = 2.0142$; Fe^{3+} -Ia ($g_1 = 2.0476, g_2 = 4.2931$); Co^{2+} -Ia. $g_1 = 2.0057$; Cu^{2+} -Ia ($g_1 = 2.0219, g_2 = 4.4342$); Co^{2+} -IIa ($g_1 = 2.2122, g_2 = 2.557$)

and Cu^{2+} -Ib ($g_1 = 2.2178$, $g_2 = 25638$). The values indicate tetrahedral geometry around Mn^{2+} and Co^{2+} complexes, square planar geometry around Cu^{2+} complexes and elongated octahedral geometry for Fe^{3+} complexes. The positive deviation in the g_{eff} values for all metal complexes over that of a free electron (2.0023) may indicate an increased covalent nature of the bonding between the metal ion and the ligand (22).

The electronic absorption spectra of all metal chelates (Fig. 2) showed a blue shift for the CT band in comparison to that of the free-ligands, this together with change in color of the complexes indicate complex formation. This may be due to the coordination through the C=O and covalent bond through OH enolic groups with metal ion in case of 1:1 and 2:1 (M: 1) chelates. The position of the absorption bands in DMF solutions of the metal chelates is different from that in the solid state of nujol mull technique. This may be due to the fact that the environment around the metal ion in the chelates is different in

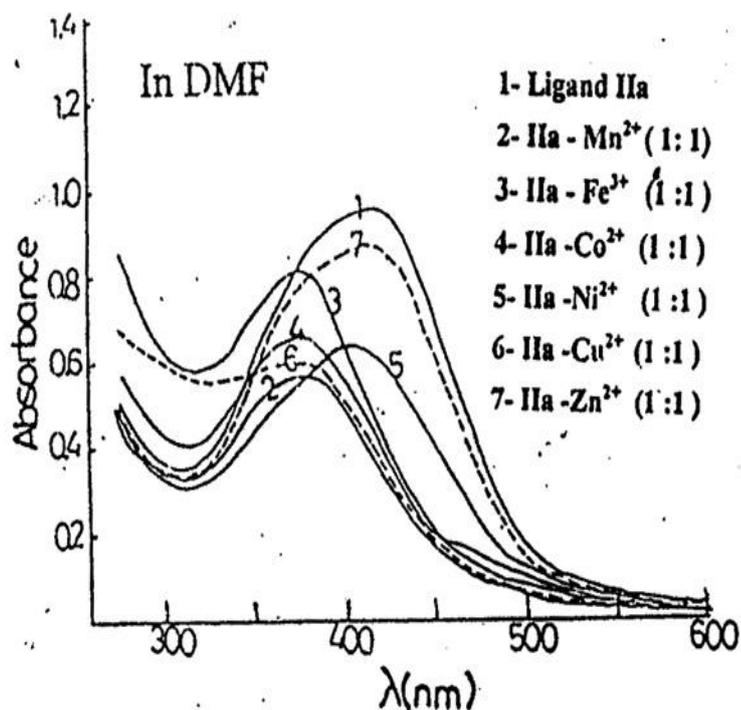
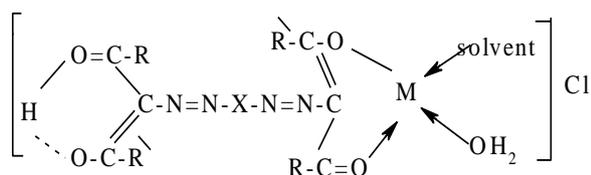


Fig. 2: Electronic absorption spectra of IIa and its metal chelat

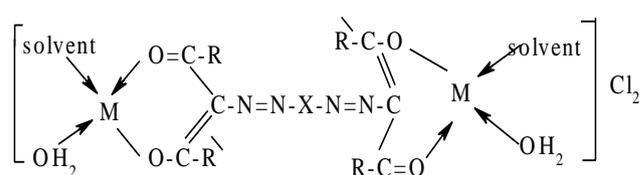
the solid state than in DMF solution. The new weak absorption band which appeared at 16949 cm^{-1} can be assigned to a transition within the framework as all the $d \rightarrow d$ transition is spin forbidden for high-spin metal ions. The above analytical data agree satisfactorily with the expected formulae represented as given below:



[1M:1L] ratio

M = Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}

(for X,R and R see experimental part)



[2M:1L] ratio

M = Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}

Solvent = dioxane or DMF

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Table 1. Elemental analysis, molar conductance and formation constants for some chelates (1M:1L)

Chelate	Ratio	Metal %		Chloride %		Water %		Λ_m	$\log \beta_1$	$\log \beta_2$
		Calc.	Fou.	Calc.	Fou.	Calc.	Fou.			
(Mn-Ia.H ₂ O)Cl	1:1	12.52	12.00	8.08	7.30	4.10	4.00	71	6.1	9.5
(Mn ₂ -Ia ₂ . H ₂ O)Cl ₂	2:1	20.08	19.80	12.96	12.82	6.58	6.47	158	---	---
(FeIb.H ₂ O)Cl ₂	1:1	9.05	9.00	11.49	11.40	5.83	6.00	184	6.0	9.9
(Fe ₂ -Ib. 4H ₂ O)Cl ₄	2:1	14.32	14.30	18.18	18.14	9.23	10.10	358	---	---
(Ni-IIa.H ₂ O)Cl	1:1	13.27	13.00	8.01	7.76	4.07	4.00	100	9.2	14.56
(Ni ₂ -IIa.H ₂ O)Cl ₂	2:1	21.17	20.80	12.78	12.00	6.49	6.32	187	---	---

