Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) Complexes of 4'-Nitrobenzylidene-2-Hydroxy-3,5-Dinitroaniline

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Abstract. Complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with 4'-nitrobenzylidene-2-hydroxy-3,5-dinitroaniline (hereafter abbreviated as *nhd*) have been prepared and characterized by their microanalyses, molar conductance, magnetic susceptibility, electronic and IR spectra. The donor sites of the ligand have been derived from the results of infrared spectra.

1. Introduction

In our previous paper, we have reported on the preparation and studies of some transition metal complexes of 4'-dimethylaminobenzylidene-2-hydroxy-3,5-dinitroaniline[1-3]. In this paper we report the synthesis, characterization and explosive properties of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of 4'-nitrobenzylidene-2-hydroxy-3,5-dinitroaniline. Our studies are mainly confined to physical properties, conductance, magnetic moment, electronic spectra, infrared spectra and explosive properties.

2. Experimental

All the chemicals used were of BDH (AR) grade. 4'-nitrobenzylidene-2-hydroxy-3,5-dinitroaniline (Fig. 1) was prepared by refluxing picramic acid and *p*-nitrobenzaldehyde in 1 : 1 molar ratio at 100° for about 3-4 hours in' ethanol. The whole mixture was concentrated, cooled, filtered and washed with ethanol to give desired product, m.p. 228°. Metal *p*-nitrobenzylidene picramates were prepared following the method as reported earlier[1-3]. The analytical results are listed in Table 1.

Physical measurements were carried out following the method reported earlier[4].

The explosive properties (Explosion Delay, Explosion Temperature, Activation Energy and Explosion Pressure) were measured in a way similar to that described earlier[1-3]. Curves obtained by plotting Explosion Delay (D_E) against $1/T$ are given in figures 2a and 2b.
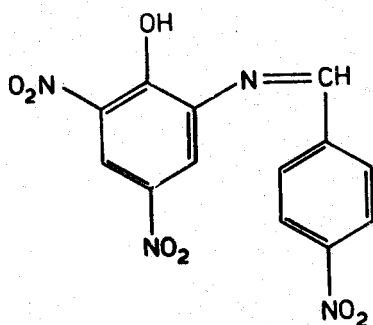
Figure 1. Structural formula of the ligand.

Table 1. Analytical and magnetic moment data

Complex*	Metal (%)	Nitrogen (%)	H_2O (%)	$\mu_{eff.}$ (BM)
Fe (nhd . $H_2O)_2$	7.4 (7.0)	14.0 (14.2)	4.7 (4.6)	4.98
Co (nhd . $H_2O)_2$	7.5 (7.4)	14.1 (14.1)	4.8 (4.5)	4.75
Ni (nhd . $H_2O)_2$	7.3 (7.4)	14.3 (14.1)	4.8 (4.5)	3.36
Cu (nhd . $H_2O)_2$	7.7 (8.0)	14.0 (14.0)	5.0 (4.5)	1.98
Zn (nhd . $H_2O)_2$	8.0 (8.2)	13.8 (14.0)	4.0 (4.5)	Diamagnetic
Cd (nhd . $H_2O)_2$	13.3 (13.3)	13.1 (13.2)	4.2 (4.2)	Diamagnetic
Hg (nhd . $H_2O)_2$	21.3 (21.5)	12.1 (12.0)	3.8 (3.9)	Diamagnetic

*Satisfactory carbon and hydrogen analyses were obtained for all complexes. Calculated values are given in parentheses.
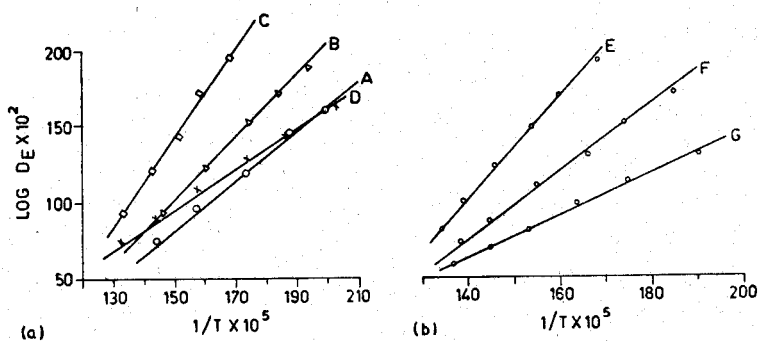

Figure 2(a). Variation of log D_E against absolute temperature: A = Fe(II) complex, B = Co(II) complex, C = Ni(II) complex, and D = Cu(II) complex.

Figure 2(b). Variation of log D_E against absolute temperature: E = Zn(II) complex, F = Cd(II) complex and G = Hg(II) complex.

3. Results and Discussion

The stoichiometries of the complexes are confirmed by elemental analyses reported in Table 1. The complexes are non-electrolytes in acetone/ethanol. This clearly indicates coordination of benzylidene anion. The absence of anions in the above complexes indicates the formation of covalent bond between phenolic oxygen and the metal. The loss of water molecules between 140–200° shows that the water molecules are coordinated and not lattice held.

The corrected magnetic moment data (Table 1), electronic spectral bands, their positions, spectral parameters and IR frequencies (Table 2) indicates high-spin octahedral geometry for all the complexes under study.

Table 2. Electronic spectral bands, parameters and IR frequency of the ligand and complexes

Complex	Bands (cm^{-1})	Assignments	Dq (cm^{-1})	B' (cm^{-1})	β	ν_2/ν_1
Fe (nhd . H$_2$O)$_2$	11000	$^5T_{2g} \rightarrow {}^5E_g(D)$	—	—	—	—
Co (nhd . H$_2$O)$_2$	8500	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$				
	17000	$^4T_{1g} \rightarrow {}^4A_{2g}(F) (\nu_2)$	850	1050	—	2.18
	18500	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) (\nu_3)$				
Ni (nhd . H$_2$O)$_2$	10050–10950	$^3A_{2g} \rightarrow {}^3T_{2g} (\nu_1)$				
	17350–17895	$^3A_{2g} \rightarrow {}^3T_{1g}(F) (\nu_2)$	960	1100	0.96	1.67
	27000–29000	$^3A_{2g} \rightarrow {}^3T_{1g}(P) (\nu_3)$				
Cu (nhd . H$_2$O)$_2$	16540	$^2E_g \rightarrow {}^2T_{2g}$	—	—	—	—
M* (nhd . H$_2$O)$_2$	25000–26000	Charge transfer and/ or intraligand transition				

M* = *Zn* (II), *Cd* (II) and *Hg* (II)

IR (cm^{-1}) : *nhd* = 1660 ($-N=C$), 3475 (Phenolic *OH*)
M(*nhd.*H$_2$O)$_2$ = 1620–1630 ($-N=C$), 650–880 (Coordinated water)[5,6]
(M = Fe(II), *Co*(II), *Ni*(II), *Cu*(II), *Zn*(II), *Cd*(II) and *Hg*(II))

On the basis of ionization potential, ionic radii and metal-oxygen bond dissociation energy data, it may be concluded that the thermal stability increases as the ionic radius decrease or ionization potential increases. This has been established by various workers[7-9].

On the basis of the bond dissociation energies[10,11] of different linkages present in the metal benzylidene picramate, it may be suggested that the initial stage in the explosion reaction is the breaking of the $N-O$ linkage[12,13] of the $-NO_2$ group directly linked to the benzene nucleus. This then enables the oxygen which was linked wholly to nitrogen to be consumed for the complete oxidation of carbon and hydrogen obtained from ring rupture and thus produces a large amount of heat.

It is obvious from Table 3, all the parameters related to explosion properties viz. Explosion Delay, Explosion Temperature, Explosion Pressure and Activation Energy increase with the increase in the number of nitro groups. This has also been established by Agrawal and Agrawal[14] and corroborated by the author[15]. The Oxygen Balance[16] for *p*-nitrobenzylidene picramate of bivalent iron, cobalt, nickel, copper, zinc, cadmium

and mercury will have the same value of -78.33. The value of Oxygen Balance for the corresponding p-dimethyl-aminobenzylidene picramates of these metal works out to -85.14. The high values of Oxygen Balance in the former cases compared to the latter ones explains the higher values of Explosion Pressure in the former cases.

Table 3. Explosion delay, explosion temperature, activation energy and explosion pressure of the complexes

Density of Mercury = 13.595 g/ml; Gravitational acceleration (g) = (980.665 cm Sec²)

Complex	Explosion dely at 593°K (Sec)	Explosion temp. for explosion delay of 10 Sec. (K)	Activation energy (KJ/mole)	Explosion pressure* (bath temp. 623±2°K) (nm⁻² × 10³)
Fe (nhd . H₂O)₂	12.9	617±2	56.90	18.40
	25.7	671±2	67.92	22.66
	97.7	741±2	110.00	26.40
	15.9	649±2	87.54	15.20
	97.7	719±2	99.53	14.57
	25.1	622±2	71.80	11.97
	12.7	602±2	59.35	12.26

*The explosion pressure was obtained by taking 10 mg of the explosive materials.

A comparison of the data of Explosion Delay, Explosion Temperature and Activation Energy of p-nitribenzylidene picramates of iron, cobalt, nickel, copper, zinc, cadmium and mercury with those of the corresponding picramates studied by Agrawal and Agrawal[17-19] shows that the formers are thermally less stable. This may be attributed to the easy fission of $-N = C$ bond in comparison to $-N-H$ bond due to bigger size of benzylidene moiety.

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