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Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) chelates of nitrogen, oxygen and sulphur donor ligands

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Abstract

Two monobasic tridentates, namely *o*-(*N*-α-furfuraldimino)phenol (HFP) and *o*-(*N*-thiophene-2-aldimino)phenol (HTP) and their bivalent metal chelates were synthesised and studied by physicochemical techniques. Potentiometric studies were carried out in 30%(v/v) dioxane-water media ($\mu = 0.01$, 0.05 and 0.1 M $NaClO_4$) at 25, 35 and 45°C. The solid metal chelates were characterised by molecular mass, elemental analysis, conductance, magnetic, thermal and spectral analyses and were assigned 1:2(metal-ligand) stoichiometry, in which the bivalent metals showed six coordination number. Some spectral parameters were also evaluated.

Key words: Bivalent chelates, physicochemical investigation of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II), Irving-Williams rule.

1. Introduction

A perusal of the literature[1-2] has shown that no work has been done so far on *o*-(*N*-α-furfuraldimino)phenol (HFP) and *o*-(*N*-thiophene-2-aldimino)phenol (HTP) and their bivalent metal chelates. Hence the same was undertaken and the present communication reports its findings.

2. Experimental

o-(*N*-α-furfuraldimino)phenol (HFP) and *o*-(*N*-thiophene-2-aldimino)phenol (HTP) were synthesised by refluxing equimolar ethanolic solution of *o*-aminophenol with furfuraldehyde or thiophene-2-aldehyde in presence of $CH_3COONa + CH_3COOH$. The brownish yellow ppt. formed was filtered and dried in vacuum.

The authenticity and purity of the compounds were established by elemental analysis, molecular mass, ^1H NMR and IR spectra. m.p. 157° (HFP) and 120°C (HTP). For HFP found: C, 70.52; H, 4.75; N, 7.38; calc. for ($C_{11}H_9NO_2$) C, 70.59; H, 4.81; N, 7.49%; for HTP found: C, 64.93; H, 4.38; N, 6.85; S, 15.71; calc. for ($C_{11}H_9NSO$) C, 65.03; H, 4.43; N, 6.90; S, 15.76%.

The metal nitrates (BDH) and other solvents were reagent grade chemicals.

The following general procedure was used for preparation of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) complexes. HFP or HTP (0.01 mole) was dissolved in 30–50 ml of 80% ethanol. A solution of metal(II) acetate (0.005 mole) in 10–15 ml of 80% ethanol was prepared. Ligand and metal-ion solution were mixed and refluxed in nitrogen atmosphere, on a steam-bath for 3–4 h. The crystalline solid obtained was filtered, washed with ethanol and recrystallised from acetone. 80–87% yield was obtained.

The C, H, N and S were determined microanalytically and the metal content in the complexes was estimated[3] by EDTA titrations after destroying the organic part first with aqua regia and then with concentrated H_2SO_4.

A digital pH meter Type DPH-77 (Unitec) equipped with a glass-calomel electrode assembly was used to determine the pH. The potentiometric studies were carried out by the Calvin-Bjerrum pH titration technique[4] at 25, 35 and 45°C in 30% (v/v) dioxane-water media ($\mu = 0.05$, 0.01 and 0.1 M $NaClO_4$) and pH values were corrected for partially aqueous media[5]. Molecular mass was determined ebulliometrically in dioxane. Magnetic measurements at room temperature were made on a Gouy-magnetic balance using $Hg[Co(NCS)_4]$ as the calibrant.

A VEB Carl-Zeiss Jena, VSU-2P spectrophotometer was used to record the electronic spectra. The IR spectra in Nujol were recorded on a Perkin-Elmer spectrophotometer using KBr pelletes. The ^1H NMR spectra in $CdCl_3$/TMS were recorded on a Varian Model Em-390.

3. Results and discussion

The pK^H of HFP and HTP were found to be 5.85 and 5.08 at 25°; 5.61 and 4.79 at 35°; 5.37 and 4.54 at 45°C, respectively ($\mu = 0.1$ M $NaClO_4$). These values suggested the monoprotic nature of the ligands. The pK^H values of HFP and HTP decreased with increasing temperature. The formation curves of the metal-ligand systems were obtained by plotting $\bar{n}$ v/s $-\log[A^-]$ and it attained maxima at $\bar{n} \approx 2$, indicating formation of 1:1 and 1:2 M(II)-HFP or M(II)-HTP complexes. The values of stability constants obtained were further refined by various computational methods[6] (Interpolation at various $\bar{n}$ values, correction terms, convergence formula and successive approximation method, etc.) and the stabilities of these chelates were found to follow the order Cu(II) > Ni(II) > Co(II) > Mn(II) > Cr(II) in agreement with Irving-Williams rule[7].

The values of ΔG^0, ΔH^0 and ΔS^0 were evaluated using Gibbs-Helmholtz equation (Table I). Log β_0 values decreased with increasing ionic strength of the medium, in agreement with Huckel equation. The stability decreased with increasing temperature.

The negative value of ΔH^0 suggested the exothermic nature of reactions and positive value of ΔS^0 suggested favourable chelation reactions.

The data were also analysed in terms of Harned's relation[8] $[(pK^H - ct^2) = -2\cot +$

Table I
Thermodynamic parameters of the bivalent metal chelates of *o*-(*N*-α-furfuraldimino)phenol (HFP) and *o*-(*N*-thiophene-2-aldimino)phenol (HTP)

Metal ion	$\log \beta_o$			$-\Delta G^0$ KJ moles^{-1}			$-\Delta H^0$ KJ mole^{-1} at 35°C	ΔS^0 JK^{-1} mole^{-1} at 35°C
	25°	35°	45°	25°	35°	45°		
Cr(II)	8.54 (7.84)	8.45 (7.65)	8.24 (7.50)	48.73 (44.74)	49.83 (45.12)	50.17 (45.67)	27.22 (30.85)	73.40 (46.33)
Mn(II)	8.84 (8.15)	8.60 (7.94)	8.44 (7.75)	50.44 (46.51)	50.72 (46.83)	51.39 (47.19)	36.29 (36.29)	46.85 (34.22)
Co(II)	9.45 (8.68)	9.23 (8.48)	9.10 (8.35)	53.92 (49.53)	54.43 (50.01)	55.41 (50.84)	31.75 (29.94)	73.63 (65.16)
Ni(II)	9.85 (9.04)	9.60 (8.79)	9.35 (8.60)	56.20 (51.58)	56.62 (51.84)	56.93 (52.37)	45.36 (39.92)	36.56 (38.70)
Cu(II)	10.86 (9.35)	9.87 (9.10)	9.70 (8.90)	57.40 (53.35)	58.21 (53.66)	59.06 (54.19)	32.66 (40.83)	82.95 (41.66)

In terms of Harned's equation, pK^H at 35°, 5.61 (4.79); $pK^H_m = 2.41$ (0.46) and $\theta = 252.86$ (294.29).

Values in parentheses are those of HTP chelates.

$(pK^H_m - c\theta^2)]$ and the value θ, pK^H and pK^H_m were evaluated (Table I). The ΔH^0 values, obtained by Harned's and Gibbs-Helmholtz equations were found in agreement.

3.1. *Solid chelates*

Based on elemental analysis and molecular mass (Table II), it is determined that the solid metal chelates possess 1:2 (metal-ligand) stoichiometry.

The molar conductance in DMSO was found in the range 3.2 to 6.8 Ω^{-1} cm^2 mol^{-1} suggesting non-electrolytic nature of the metal chelates.

The magnetic moments of Cr(II), Mn(II), Co(II) and Ni(II) complexes (Table II) indicate their octahedral stereochemistry[9,10]. In the case of Cu(II) complexes the observed magnetic moments suggest a distorted octahedral geometry in terms of Jahn-Teller effect.

The electronic spectra (Table III) typical for octahedral coordination, observed for Cr(II) complexes, corresponded to the transition $^5E_g \rightarrow {}^5T_{2g}$.

The spectra of Mn(II) complexes, which corresponded to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^6A_{1g}(S) \rightarrow {}^4T_{2g}$ and $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ *viz.* ν_1, ν_2 and ν_3, respectively, were characteristic of octahedral geometry around the metal ion.

The electronic spectra of Co(II) complexes gave three distinct transitions—$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ν_1; $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ν_2 and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$, ν_3. These bands were typical for high-spin octahedral Co(II) complexes. The splitting of ν_3 band into two or more compounds in Co(II) complexes was due to lifting of degeneracy of $^4T_{1g}$ level either by the

Table II

Molecular mass, elemental analysis and magnetic moment of bivalent metal chelates of HFP ($C_{11}H_9NO_2$) and HTP ($C_{11}H_9NSO$)

Composition	Molecular mass		% Elemental analysis										μ_{eff} B.M. at 308°K
			Metal		Carbon		Hydrogen		Nitrogen		Sulphur		
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
$C_{11}H_9NO_2$	174	186	—	—	70.52	70.59	4.75	4.81	7.38	7.49	—	—	—
$(C_{11}H_9NSO)$	(196)	(203)	—	—	(64.93)	(65.03)	(4.38)	(4.43)	(6.83)	(6.90)	(15.71)	(15.76)	—
$Cr(C_{11}H_8NO_2)_2$	411	424	12.16	12.26	62.18	62.26	3.71	3.77	6.53	6.60	—	—	4.88
$[Cr(C_{11}H_8NSO)_2]$	(451)	(456)	(11.29)	(11.40)	(57.81)	(57.90)	(3.43)	(3.51)	(6.08)	(6.14)	(13.97)	(14.04)	(4.80)
$Mn(C_{11}H_8NO_2)_2$	414	427	12.73	12.88	61.74	61.83	3.68	3.75	6.47	6.56	—	—	5.89
$[Mn(C_{11}H_8NSO)_2]$	(453)	(459)	(11.82)	(11.98)	(57.46)	(57.52)	(3.40)	(3.49)	(6.02)	(6.10)	(13.84)	(13.94)	(5.84)
$Co(C_{11}H_8NO_2)_2$	420	431	13.60	13.69	61.17	61.25	3.64	3.71	6.38	6.50	—	—	4.76
$[Co(C_{11}H_8NSO)_2]$	(457)	(463)	(12.64)	(12.74)	(56.93)	(57.02)	(3.37)	(3.46)	(5.97)	(6.05)	(13.76)	(13.82)	(4.81)
$Ni(C_{11}H_8NO_2)_2$	421	431	13.55	13.69	61.10	61.25	3.62	3.71	6.35	6.50	—	—	3.45
$[Ni(C_{11}H_8NSO)_2]$	(455)	(463)	(12.61)	(12.74)	(56.90)	(57.02)	(3.35)	(3.46)	(5.90)	(6.05)	(13.69)	(13.82)	(3.28)
$Cu(C_{11}H_8NO_2)_2$	424	436	14.59	14.68	60.47	60.55	3.55	3.67	6.27	6.42	—	—	1.87
$[Cu(C_{11}H_8NSO)_2]$	(459)	(468)	(13.56)	(13.68)	(56.33)	(56.41)	(3.25)	(3.42)	(5.79)	(5.98)	(13.59)	(13.68)	(1.80)

Values in parentheses are those of HTP chelates.

Table III
Electronic spectral data of the bivalent metal chelates of *o*-(*N*-α-furfuraldimino)phenol (HFP) and *o*-(*N*-thiophene-2-aldimino)phenol (HTP)

Composition	ε mole^{-1} cm^{-1}	Band maxima	D_0 cm^{-1}	B	β	δ	C	F_4	F_2	ν_2/ν_1	LFSE KJ mole^{-1}
$[Cr(C_{11}H_8NO_2)_2]$	52 (44)	15600 (15340)									
$[Mn(C_{11}H_8NO_2)_2]$	65 (53)	18500 (16700)	1210 (1120)	880 (798.67)	.9263 (.8407)	.0795 (.1895)	3942.40 (3578.04)	112.64 (102.23)	1443.2 (1309.82)	1.2162 (1.2293)	
	80 (68)	22500 (20530)									
	91 (78)	27000 (25050)									
$[Co(C_{11}H_8NO_2)_2]$	68 (63)	8800 (8750)	805.07 (875)	955.85 (855)	.9844 (.8805)	.0159 (.1357)	4425.59 (3958.65)	126.45 (113.10)	1558.10 (1420.52)	2.3037 (2.1451)	57.63 (62.64)
	84 (78)	17870 (18770)									
	97 (95)	20620 (20350)									
$[Ni(C_{11}H_8NO_2)_2]$	72 (69)	10350 (10240)	1030 (1024)	923.33 (825.33)	.8549 (.7642)	.1697 (.3086)	4348.88 (3887.30)	124.25 (111.07)	1544.58 (1380.66)	1.7198 (1.6309)	147.47 (146.41)
	89 (93)	17800 (16700)									
	105 (98)	26950 (26400)									
$[Cu(C_{11}H_8NO_2)_2]$	121 (118)	12270 (13570)	1227 (1357)								87.84 (97.14)
		26570 (25670)									

Values in parentheses are those of HTP chelates.

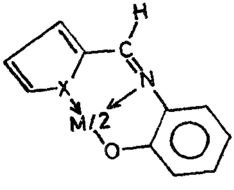
spin-orbital coupling or by the presence of a low-symmetry component in the ligand field. However, the ν_2/ν_1 ratio (2.15–2.30) also confirmed the octahedral geometry.

Spectra of the Ni(II) complexes were typical of octahedrally[9] coordinated Ni(II) in as much as they exhibited three d—d transition bands *viz.* $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ corresponding to ν_1, ν_2 and ν_3 bands. These spectral data were utilised to compute the important ligand field parameters $10\,Dq$, B and λ using the ligand field theory of spin-allowed transitions in d^8-configuration. The high values of $10\,Dq$ and B are consistent with the nitrogen coordination of the azomethine group[11]. The ratio of ν_2/ν_1 lies between 1.72 and 1.63 as expected for octahedral Ni(II) complexes.

The spectra of Cu(II) complexes corresponded to the transitions, $^2E_g \rightarrow {}^2T_{2g}$ and $C \rightarrow T$ (charge-transfer band). The broadness of the bands and their positions indicated tetragonally distorted octahedral symmetry for these complexes.

Comparison of the IR spectra of the ligand with those of their bivalent metal chelates indicated coordination of the ligand through azomethine nitrogen, phenolic oxygen besides furfural ring oxygen and thiophene-2-aldehyde ring sulphur in HFP and HTP, respectively. In the IR spectra of HFP and HTP two bands were observed in the ranges 3460–3470 cm^{-1} and 1620–1630 cm^{-1} assignable to $\nu_{\mathrm{OH...N}}$ (hydrogen-bonded OH) and $\nu_{\mathrm{C=N}}$.

The band in the region 3460–3470 cm^{-1} disappeared in the metal chelates indicating deprotonation due to chelation. $\nu_{\mathrm{C-O}}$ shift of the phenolic (1105 cm^{-1}) as obtained towards the higher region ($\sim$25 cm^{-1}) suggested the bonding between metal and phenolic oxygen atom. The band in the region 1620–1630 cm^{-1} was shifted to lower region 1600–1610 cm^{-1} in the complexes indicating coordination through azomethine nitrogen. The new broad bands around 540 cm^{-1} and 295 cm^{-1} in the IR spectra of the [M(FP)$_2$] and [M(TP)$_2$] complexes arose due to M—O and M—S stretches, respectively. Such bands were also observed in similar complexes with Schiff base and oxime suggesting coordination of the furan ring oxygen and thiophene ring sulphur. The shift in the M—O and M—S[12] frequencies to higher wave number with increasing atomic number of bivalent metals suggested increased covalent character of the metal-ligand bond. The sharp band in the range 400–425 cm^{-1} in the complexes was assignable to $\nu_{\mathrm{M-N}}$ vibrations. The absence of an



where M = Cr(II), Mn(II), Co(II), Ni(II) or Cu(II)
when X = O, it represents [M(FP)$_2$]
and X = S, it represents [M(TP)$_2$]

FIG. 1. Structure of bivalent metal chelates of HFP and HTP.

IR band in the range 250–100 cm^{-1} indicated the non-existence of M—M bond in the complexes.

To summarise the ^{1}H NMR spectral findings it can be stated that the signals due to —OH protons of the ligands HFP and HTP at δ 8.15 and 8.38 ppm, respectively, were found absent in the spectra of the corresponding metal chelates, suggesting their replacement by the metal atoms on complexation.

The results obtained conclusively indicate hexa-coordinated octahedral geometry for the bivalent metal chelates of HFP and HTP (fig. 1) except the Cu(II) chelates which possess distorted octahedral stereochemistry.

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