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Studies on Some Metal Complexes of 4-Formyloxime-1,3-Diphenyl-2-Pyrazolin-5-one

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Chelates of VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one (FDPPZ) have been prepared and characterized on the basis of elemental analysis, conductivity, magnetic moment and spectral studies. The IR spectra suggest that the ligand shows bidentate behaviour. All chelates except Cr(III), Fe(III) and VO(II) have the general composition $M(FDPPZ)_2.2H_2O$, while Cr(III) and Fe(III) chelates have $M(FDPPZ)_3$ composition. The VO(II) chelates have $VO(FDPPZ)_2.H_2O$ composition. The ligand field parameters for VO(II), Cr(III), Co(II) and Ni(II) chelates are also calculated.

Key words: VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Chelates, 4-Formyloxime-1,3-diphenyl-2-pyrazolin-5-one.

In continuation of our work on metal chelates of 4-substituted-2-pyrazolin-5-ones[1–7] we report here synthesis and characterization of VO(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one (FDPPZ).

EXPERIMENTAL

All chemicals used were of reagent grade (BDH). 1,3-Diphenyl-2-pyrazolin-5-one[8] (m.p., reported 137°C, found 137°C) and 4-formyl-1,3-diphenyl-2-pyrazolin-5-one (m.p., reported 140-143°C, found 141°C) was prepared by reported methods[8]. 4-Formyloxime-1,3-diphenyl-2-pyrazolin-5-one (m.p. 101°C) was prepared[9] as follows: A mixture of 4-formyl-1,3-diphenyl-2-pyrazolin-5-one (0.01 mole in 20 mL ethanol), hydroxylamine hydrochloride (0.01 mole), sodium acetate (0.01 mole) was refluxed for 1 h on a water bath. The resulting mixture was then poured into ice-water (500 mL) with constant stirring. The isolated solid was then filtered, washed with water and dried in air.

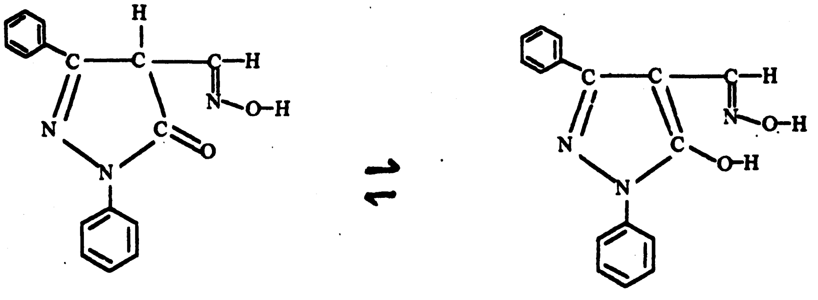
The following general procedure was used in the preparation of all the chelates. For the preparation of chelates of Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal acetates were used. $VOSO_4.H_2O$ and $FeCl_3$ (anhydrous) were used for the preparation of VO(II) and Fe(III) chelates respectively. Metal salts were dissolved in double distilled water. Hot ligand solution (in ethanol) in slight excess over the metal ligand ratio 1 : 3 for Cr(III) and Fe(III) chelates and 1 : 2 metal-ligand ratio for all other chelates, was added to it dropwise and with constant stirring. To the resulting mixture about 1 g of sodium acetate was added and then the mixture was refluxed for 2 h. The product thus obtained was filtered and washed several times with hot water, followed by ethanol and finally dried in air.

The chelates were analyzed for metal content using literature methods[10]. Carbon, hydrogen and nitrogen were analyzed on Carlo Erba 1108 instrument. Molar conductances in 10^{-3} M DMF solutions of chelates were measured on an Equiptronics EQ-660 digital conductivity meter using a calibrated cell at room temperature. Room temperature magnetic susceptibility measurements were made on a Sartorius Semimicro Gouy balance using $Hg[Co(NCS)_4]$ as calibrant and diamagnetic corrections were made using Pascal's constants. The FT-IR spectra were recorded on a Shimadzu 8201 PC FT-IR spectrophotometer using KBr pellets. The electronic spectra in DMF solution were recorded on a Perkin-Elmer Lambda-19 UV-visible Spectrophotometer at SICART, Vidyanagar.

RESULTS AND DISCUSSION

The physical and analytical data are presented in Table-1. The elemental analysis reveals 1 : 3 (metal : ligand) stoichiometry for Cr(III) and Fe(III) chelates and 1 : 2 (metal : ligand) stoichiometry for all other chelates. The conductance data of the chelates in 10^{-3} M DMF solutions indicate that they are non-electrolytes.

The ligand 4-formyloxime-1,3-diphenyl-2-pyrazolin-5-one (FDPPZ) used in the present work may have following tautomeric forms (I) and (II):



[I] [II]

4-Formyloxime-1,3-diphenyl-2-pyrazolin-5-one

The IR spectrum of free ligand shows medium broad band with some structures in the region 3450–2700 cm^{-1}, which may be due to ν(O—H) of oxime + ν(O—H) of 5-hydroxyl group of pyrazoline ring[11, 12]. The observed low value of ν(O—H) suggests the presence of intramolecular or intermolecular hydrogen bonding[13] in ligand and also suggest the presence of enol form (structure-II) of ligand at least in the solid state. The IR spectrum of ligand shows band at *ca.* 1330 cm^{-1}, which may be due to ν(C—O).[13, 14] The ν(C—O) frequency is raised by 8–37 cm^{-1} in the spectra of complexes compared to the position in ligand. This suggests the involvement of 5-hydroxyl group of pyrazoline ring on coordination[11, 13]. The IR spectrum of ligand shows a band at *ca.* 1028 cm^{-1}, which may be due to ν(N—O) of oximino group. The infrared spectra of all complexes show ν(N—O) of oximino group in the region 1030-1026 cm^{-1}. This observation is similar to our previous finding[13] and also ruled out the involvement of proton of oximino hydroxyl group on coordination. The infrared spectrum of ligand shows a band at *ca.* 1689 cm^{-1}, which may be due to ν(C═N) (oxime). The IR spectra of all the complexes show downshift in ν(C═N) (oxime) by 9–49 cm^{-1} . This may be due to coordinate bond formation through nitrogen of oximino group[12]. The infrared spectra of ligand show band at 1600 cm^{-1}, may be due to ν(C═N) (pyrazoline ring)[15, 16] this band remains almost unchange in all metal complexes. This indicates that ring nitrogen-2 does not take part in coordination. The possibility of coordination for ring nitrogen-1 to metal ion is ruled out by zwitter ion mechanism[17, 18]. The overtone of ν(C═N) is expected to occur at about 3100 cm^{-1}, but is not seen in the spectra, because of the broad nature of ν(O—H).[11]

The examination of infrared spectra of VO(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) show broad band in the region 3400–3200 cm^{-1}. This suggests the presence of coordinated water molecule or molecules in the complexes[14]. This is supported by additional band appearing in the range 864–800 cm^{-1} for O—H (wagging) deformation[11]. This is in accordance with TG analysis.

The VO(II) chelate shows a band at *ca.* 960 cm^{-1}, due to ν(V═O), suggesting the presence of monomeric (V═O) group[19]. The conclusive evidence of bonding of ligand FDPPZ to metal ion is indicated by the appearance of bands[20] due to ν(M—O) at 574–502 cm^{-1} and ν(M—N) at 490–450 cm^{-1}.

The magnetic moment of VO(II) chelate is 1.68 B.M., which is slightly less than spin only value. This may be due to the anti ferromagnetic exchange coupling between the pair of vanadyl ions as suggested by Ballhausen[21] and Zelenstove[22]. The electronic spectrum of VO(II) chelate shows bands at 9871, 21834 and 28328 cm^{-1}. These may be assigned to $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ transition respectively. Making the use of transition energies, various parameters such as $Dt = 572\ cm^{-1}$, $Dq^{XY} = 2183\ cm^{-1}$, $Dq^{XY} = 2183\ cm^{-1}$, $Dq^{Z} = 1182\ cm^{-1}$, $DT = 7753\ cm^{-1}$, $DQ = 50858\ cm^{-1}$, $DQ^{XY} = 60032\ cm^{-1}$, $DQ^{Z} = 32510\ cm^{-1}$ and ratio DT/DQ = 0.1524 have been evaluated. The ratio DT/DQ suggests the VO(II) chelate[23] is moderately distorted. DQ^{XY} and DQ^{Z} suggest that the field along XY plane is stronger compared to that along Z-axis.

The room temperature magnetic moment for Cr(III) chelate is 3.68 B.M. T'he low μ_{eff} for chelate may be due to positive spin-orbit coupling and small magnetic anisotropy irrespective of nature of the bond involved[24]. The electronic spectra of Cr(III) shows bands at 18116, 21367 and 27397cm^{-1} which may be assigned to $^4B_{1g} \rightarrow {}^4E_g$, $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4E_g, A_{2g}$ transition respectively[23]. An attempt has been made to calculate $Dt = 371 cm^{-1}$, $Dq^{XY} = 2136\ cm^{-1}$ and $Dq^{Z} = 1487\ cm^{-1}$ using reported method[25]. The absolute ligand field parameter $DQ = 52782\ cm^{-1}$, $DT = 5027\ cm^{-1}$, $DQ^{XY} = 58718\ cm^{-1}$ and $DQ^{Z} = 40910\ cm^{-1}$ have been evaluated[26]. The value of the ratio DT/DQ = 0.09524 suggests that Cr(FDPPZ)$_3$ is moderately distorted[27].

The magnetic moment of Mn(II) chelate is 5.80 B.M., which suggests high spin octahedral environment[28, 29]. The electronic spectrum of Mn(FDPPZ)$_2$(H$_2$O)$_2$ shows band at 17241 and 21505 cm^{-1}, which may be assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g(G)}$ and $^6A_{1g} \rightarrow {}^4T_{1g}\,E_g$ respectively in an octahedral field[28].

The magnetic moment of Fe(III) chelate is higher than required range for an octahedral structure. The electronic spectrum of Fe(FDPPZ)$_3$ shows band at 17391, 19230 and 22123 cm^{-1}, which may be assigned to transitions $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4T_{1g}, E_g$ respectively[29, 30].

The magnetic moment for Co(II) chelate is 4.78 B.M., which is in the range required for high spin octahedral structure. The electronic spectra of high spin octahedral Co(II) chelate shows band at 9328 and 17699 cm^{-1}. The former band may be due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$ and the latter band may be due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions[31]. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ transition is two electron transition and thus is expected to be much weaker. In the present study ν_2 transition remains almost unobserved. ν_2 transition (19817 cm^{-1}) was calculated by band fitting procedure[32]. The observed transition energies were used to calculate 10Dq ≈ 10437 cm^{-1}, B = 632 cm^{-1}, $\beta = 0.65$, $\nu_2^{calc}/\nu_1 = 2.12$ ratio also suggests octahedral geometry for the chelate[32].

The room temperature magnetic moment for Ni(II) chelate is 3.10 B.M. which is in the range required for an octahedral stereochemistty[33, 34]. The electronic spectra of Ni(II) chelate shows[35] ν_1 : $^3A_{2g} \rightarrow {}^3T_{2g}$, band at 8539 and 8934 cm^{-1}, ν_2 : $^3A_{2g} \rightarrow {}^3T_{1g}$ band at 17825 and 21739 cm^{-1} and ν_3 : $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ band at 28011 cm^{-1}.

The ν_1 and ν_2 bands of Ni(II) chelate are broad unsymmetrical weak bands. It shows splitting into two components. The splitting of ν_1 and ν_2 bands suggests the presence of tetragonal distortion[23] in the Ni(II) chelate. The lowering in symmetry is not reflected in ν_3 band. The $\nu_2/\nu_1 = 2.08$ is greater than the range required for an octahedral stereochemistry[36]. The splitting energy of ν_1 and ν_2 bands can be used to calculate[23, 36] DT = 51 cm^{-1}, DS = 1988 cm^{-1}, Dq^{XY} = 853 cm^{-1}, Dq^{Z} = 763 cm^{-1}. An attempt has also been made to calculate DT = 691 cm^{-1}, DS = 13916 cm^{-1}, DQ^{XY} = 23440 cm^{-1}, DQ^{Z} = 20992 cm^{-1} and DT/DQ = 0.0305. The ratio DT/DQ provides a measure of tetragonal distortion in the chelate.

The magnetic moment for Cu(II) chelate corresponds to one-unpaired electron[37]. The electronic spectrum of Cu(II) chelate shows bands at 12903 and 17762 cm^{-1}, which presumbly contains d-d transition[38]. Absence of any band below 10000 cm^{-1}, rules out the possibility of tetrahedral structure for chelate[39]. The former band may be due to $^2B_{1g} \rightarrow {}^4A_{1g}(\nu_1)$ and the latter may be due to $^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2)$ transition for octahedral strcuture[40, 41]. The $^2B_{1g} \rightarrow {}^2E_g(\nu_3)$ transition remained unresolved in the Cu(II) chelate. The high energy band shown at 28169 cm^{-1} might be charge transfer in origin. An approximate value of 10 Dq = 11311 cm^{-1} has been obtained from the splitting energies[38, 41].

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF LIGAND AND ITS METAL CHELATES

Compound (Colour)	% Analysis, found (calcd.)				λ_m (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (B.M.)
	M	C	H	N		
FDPPZ	—	69.09	4.76	14.60	—	—
(Turmeric yellow)		(68.81)	(4.66)	(15.05)		
$VO(FDPPZ)_2H_2O$	8.07	59.61	3.96	13.17	3.75	1.68
(Reddish brown)	(7.95)	{59.91)	(4.06)	(13.10)		
$Cr(FDPPZ)_3$	5.98	64.95	4.14	13.98	8.62	3.68
(Light brown)	(5.87)	(65.01)	(4.06)	(14.22)		
$Mn(FDPPZ)_2(H_2O)_2$	8.77	60.05	4.40	12.94	3.86	5.80
(Brown)	(8.49)	(59.35)	(4.32)	(12.98)		
$Fe(FDPPZ)_3$	6.54	65.03	4.09	14.65	10.27	6.05
(Dark brown)	(6.27)	(64.73)	(4.04)	(14.15)		
$Co(FDPPZ)_2(H_2O)_2$	8.80	58.95	4.46	12.70	4.25	4.78
(Brown)	(9.05)	(58.99)	(4.29)	(12.90)		
$Ni(FDPPZ)_2(H_2O)_2$	8.78	58.77	4.24	12.68	4.89	3.10
(Brown)	(9.02)	(58.87)	(4.30)	(12.91)		
$Cu(FDPPZ)_2(H_2O)_2$	10.01	58.34	4.56	13.04	3.42	1.90
(Light brown)	(9.69)	(58.54)	(4.26)	(12.81)		
$Zn(FDPPZ)_2(H_2O)_2$	10.36	58.48	4.50	12.65	5.16	—
(Magenta)	(9.95)	(58.41)	(4.26)	(12.78)		

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