

Complexes of 4-Formyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one with Oxovanadium(IV), Chromium(III), Manganese(II), Cobalt(II), Nickel(II), Copper(II) & Zinc (II)

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Structural studies on the oxovanadium(IV), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates of 4-formyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one are reported. The chelates have been isolated in the solid state and characterized by elemental analyses, spectral (visible reflectance and infrared) data, room temperature magnetic moment and conductivity measurements. All the chelates except oxovanadium(IV) chelate are assigned octahedral geometry. The oxovanadium(IV) chelate is probably square-pyramidal.

Preparation and characterization of the oxovanadium(IV), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) chelates of 4-formyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one (FOP) are described in this note. The probable structures of the chelates have been assigned on the basis of elemental analyses, magnetic susceptibility data, diffuse reflectance spectra, IR and conductivity measurements.

The ligand FOP (m.p. 171.5°C) was prepared following the literature method¹. Metal nitrates were used for the preparation of the chelates, except for the

oxovanadium(IV) and Mn(II) chelates for which vanadyl sulphate and manganese chloride were used. All the chemicals used were of reagent grade.

All the chelates, except the Mn(II) chelates, were prepared by refluxing the required quantities of ligand and metal salts in absolute ethanol. In the case of Mn(II) chelate, sodium acetate (1.0 g) was added to the refluxing solution prepared as above. The separated solid was filtered, washed with water, ethanol and finally with ether and dried.

The chelates were analysed for carbon, hydrogen and nitrogen by the Coleman analyser. Except for the oxovanadium(IV) and Cr(III) chelates, the metal contents were determined by independent gravimetric and volumetric methods, while for the former chelates only gravimetric (oxide) method was used. Magnetic susceptibility measurements were made on a Sartorius semi-micro Gouy balance. The diffuse reflectance measurements were made on a Beckman DU spectrophotometer. The IR spectra were recorded on a Carl-Zeiss Model UR-10 spectrophotometer in KBr. The conductances were measured on a Toshniwal digital conductometer.

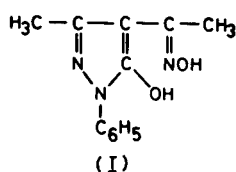
The elemental analyses (Table 1) reveal 1:3 (metal:ligand) stoichiometry for the Cr(III) chelate and 1:2 for all the other chelates. The electrolytic conductance measurements in DMF (7.63-9.07 ohm⁻¹cm²mol⁻¹) show that the chelates are non-electrolytes.

The infrared spectrum of the ligand shows a medium broad band at ~ 3150 cm⁻¹, which may be due to νOH

Table 1 – Analytical and Magnetic Moment Data of the Chelates

Compound	m.p. (°C)	Found (Calc.) (%)				μ_{eff} (B.M.)
		Metal	C	H	N	
[VO(FOP) ₂] ₂ H ₂ O	130	8.82 (8.86)	51.00 (51.06)	4.01 (4.26)	16.83 (16.25)	1.75
Cr(FOP) ₃ H ₂ O	139	7.40 (7.24)	55.11 (55.15)	4.15 (4.46)	16.06 (17.55)	3.47
Mn(FOP) ₂ (H ₂ O) ₂	143	10.78 (10.52)	50.84 (50.47)	4.83 (4.59)	15.89 (16.06)	6.04
Co(FOP) ₂ (H ₂ O) ₂	149	10.89 (11.18)	50.00 (50.10)	4.34 (4.55)	15.80 (15.94)	4.85
Ni(FOP) ₂ (H ₂ O) ₂	147	10.83 (11.14)	50.83 (50.12)	4.12 (4.56)	15.74 (15.95)	3.06
Cu(FOP) ₂ (H ₂ O) ₂	136	11.81 (11.95)	46.98 (46.67)	4.32 (4.52)	15.99 (15.80)	1.85
Zn(FOP) ₂ (H ₂ O) ₂	158	12.02 (12.26)	50.04 (49.49)	4.31 (4.50)	16.18 (15.75)	--

the oximino group as well as that of the 5-OH group (see structure I).



The observed lowering may be due to the presence of intra- or inter-molecular hydrogen bonding². All the chelates contain water molecule(s) and show a broad band in the region 3200-3400 cm^{-1} , which may be due to νOH of water or oximino or 5-OH of the ligand. The $\nu\text{N}-\text{O}$ (1016 cm^{-1}) of the ligand does not undergo any change in the chelates indicating retention of the oximino proton and hence dissociation of the 5-OH proton on coordination.^{3,4} The ligand as well as the chelates show a band at $\sim 1600 \text{cm}^{-1}$ which may be assigned to δOH . The intensity of this band is weakened in the chelates, may be due to deprotonation of the 5-OH group. The chelates also show a band at 1632 cm^{-1} due to $\nu\text{C}=\text{N}$ (cyclic), suggesting non-participation of the cyclic nitrogen in coordination. The ligand shows $\nu\text{C}=\text{N}$ (oxime) at 1596 cm^{-1} , which is considerably lowered ($\Delta\nu = 50 \text{cm}^{-1}$) in all the chelates, indicating coordination through oximino nitrogen atom. A weak band observed in the ligand spectrum at 1180 may be due to $\nu\text{C}-\text{O}$ ⁵. On coordination, this band does not show any marked shift.

The diffuse electronic spectrum of oxovanadium(IV) complex shows four bands at 10695, 13513, 15384 and 24390 cm^{-1} . The last three high energy bands may be assigned to the $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a$ transitions, respectively, considering C_4 symmetry for the chelate^{6,7}. The low energy band may be due to lowering of symmetry⁸. The observed magnetic moment (1.75 B.M.) of the chelate is consistent with the presence of one unpaired electron.¹⁰

The diffuse reflectance spectrum of the Cr(III) chelate shows bands at 12345, 16528 and 22988 cm^{-1} . The former low energy band may be due to spin-forbidden ${}^4A_{2g} \rightarrow {}^2E_g$ transition.¹¹ The latter two bands may be due to the ${}^4A_{2g} \rightarrow {}^4T_{2g}(\nu_1)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(\nu_2)$ transitions, respectively, considering an octahedral stereochemistry for the chelate¹². The calculated value of the transition energy corresponding to the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition comes to be 36100 cm^{-1} , which occurs in the region where ligand shows absorption. The calculated value (0.733) of β_{55} is significantly lower than unity, indicating π -type of interaction between Cr(III) and ligand^{11,12}. The magnetic moment value (3.47 B.M.) is slightly lower than required¹³.

The spectrum of the Mn(II) chelate shows bands at 17391, 20408, and 25000 cm^{-1} , which may be assigned to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$, $\rightarrow {}^4T_{2g}$ and $\rightarrow {}^4E_g$, ${}^4A_{1g}$ transitions, respectively, on the basis of an octahedral structure for the chelate¹⁴. The observed magnetic moment of 6.04 B.M. is in the range required for high-spin octahedral structure¹⁵.

Co(II) chelate shows two bands at 8403 and 20000 cm^{-1} in its diffuse reflectance spectrum. In an octahedral stereochemistry, they may be assigned to the ${}^4T_{1g} \rightarrow {}^4T_{2g}(\nu_1)$ and $\rightarrow {}^4T_{1g}(P)$ transitions, respectively¹⁶. The values of $10Dq$ (9419 cm^{-1}), B_{35} (845 cm^{-1}) and β_{35} (0.75) have been calculated. The magnetic moment (4.85 B.M.) of the chelate is in the range required for octahedral structure¹⁷.

The diffuse electronic spectrum of the Ni(II) chelate shows bands at 9523, 17094 and 22980 cm^{-1} . These bands in an octahedral structure may be assigned to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$, $\rightarrow {}^3T_{1g}$ and $\rightarrow {}^3T_{1g}(P)$ transitions, respectively.¹⁸ The ν_2/ν_1 ratio (1.80) is as required for the octahedral structure¹². The magnetic moment (3.06 B.M.) is in the required range¹⁹.

The Cu(II) chelate shows strong and broad absorption in the region 16130-12500 cm^{-1} . This band is observed as a doublet showing structures at 13333 and 15625 cm^{-1} . These may be due to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, on the basis of a distorted octahedral structure for the chelate²⁰. An intense band at 22471 cm^{-1} may be of charge-transfer type. The magnetic moment (1.85 B.M.) of the chelate is as required for the presence of one unpaired electron²¹.

The Zn(II) chelate shows an intense band at 25000 cm^{-1} . This may be due to intra-ligand or charge-transfer transition.²²

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