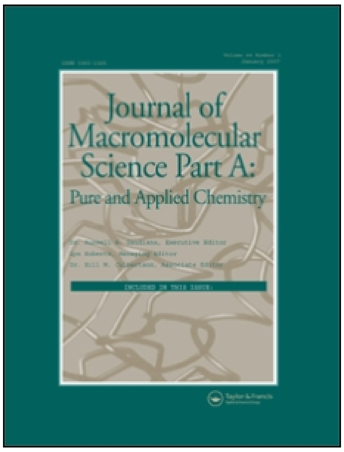

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Spectral, Thermal, and Magnetic Properties of Chelate Polymers

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Spectral, Thermal, and Magnetic Properties of Chelate Polymers

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ABSTRACT

Polychelates of VO(II), Mn(II), Zn(II), Cr(III), and Fe(III) with the bis-oxime of 5,5'-methylene-bis-salicylaldehyde have been prepared and are characterized on the basis of their elemental analyses, IR, diffuse reflectance spectra, magnetic moments, and thermogravimetric analyses. Except for VO(II), the other metal ions form octahedral polychelates. VO(II) forms a square-pyramidal coordination polymer. The Zn(II) polychelate has the highest thermal stability.

INTRODUCTION

Monomeric complexes of several oximes such as dimethylglyoxime, salicylaldoxime, α-benzoinoxime, acetoxime, and α-benzaldoxime have been extensively studied. However, very little systematic work seems to have been done on bis-oximes as ligands in forming polymeric complexes. There are, however, numerous reports of the preparation of polymeric chelates using monomeric ligand. Trent'ev el al. have prepared and studied the polychelates of bis-aldehyde and its anils [1]. Subnormal magnetic moments of the polychelates of Co(II), Mn(II), Fe(III) and Cr(III) with 5,5'-thiosalicylic acid have been reported by Nigam et al. [2]. Rastogi and others have reported the polychelates of 3,3'-diamino-4,4'-dihydroxy sulfone [3]. They have studied their IR, electronic spectral, and magnetic properties. In the present study we have used the bis-oxime of 5,5'-methylene-bis-salicylaldehyde as a polychelating agent. It can be seen from the geometry of the ligand that the donor atoms on the rings are widely separated, so that metal ions can act as bridges between the ligands, giving polychelates. Here we report the preparation of its polychelates with VO(II), Mn(II), Zn(II), Cr(III), and Fe(III). We have also studied their IR, diffuse reflectance, magnetic, and thermal properties.

EXPERIMENTAL

Materials

Salicylaldehyde (B.D.H.) was used after distillation. Metal chlorides used for the preparation of polychelates were obtained from B.D.H. Vanadyl sulfate (B.D.H.) was used to prepare its polychelates. Absolute alcohol was obtained from Alembic Co. Ltd.

5,5'-Methylene-bis-salicylaldehyde was obtained by the method of Marvel et al. [4]. Its bis-oxime (mp 222° C) was prepared by the aqueous ethanolic alkali method [5].

Preparation of Polychelates

Ligand and metal salt solutions were prepared in absolute alcohol. The ligand solution in slight excess over the metal:ligand ratio of 1:1 was added to the metal solution with constant stirring. About 500 mg of sodium acetate was added to the refluxed solution. The precipitated metal chelate was filtered and dried in an oven at 70° C. The polychelates were insoluble in all common organic solvents. They were purified by extraction with water and then with alcohol. They were dried in vacuum at 50° C for about 24 h.

Measurements

Magnetic measurements were made on Sartorious semi-micro Gouy balance at room temperature (30° C). The diffuse reflectance measurements were made on a Beckman-DU spectrophotometer. The IR spectra were recorded on a Perkin-Elmer spectrophotometer in a Nujol mull. The TG thermograms were recorded on a DuPont (U.S.A.) analyzer.

The metal content in each polychelate was determined by independent gravimetric and volumetric methods. Carbon, nitrogen and hydrogen analysis were made on an University C–H–N analyzer. Chloride content in Fe(III) and Cr(III) polychelates was determined by the Carius method. The water content in each polychelates was estimated from the thermograms.

RESULTS AND DISCUSSION

The polychelates are found to be insoluble in all common organic solvents and therefore their characterization by such conventional methods as osmometry and viscometry was not possible. The analytical data given in Table 1 suggest 1:1 (metal:ligand) stoichiometry for the polychelates.

The symmetry of V(IV) polychelate containing VO group cannot be higher than C_{2v}. For such a five-coordinate chelate, three bands below 30,000 cm^{-1} at room temperature are expected [6]. In the present case we have observed the following three bands which suggest a square pyramidal ligand field around V(IV):

$^2E \longleftarrow {}^2B_2$	11,430 cm^{-1}
$^2B_1 \longleftarrow {}^2B_2$	16,390 cm^{-1}
$^2A_1 \longleftarrow {}^2B_2$	21,280 cm^{-1}

By comparing the pyridine spectra of the polychelate with the above data, some evidence on the nature of bonding in the polychelate is available. All bands in the solid spectra are shifted to higher energy when they are recorded in pyridine. It is now safe to assume that the pyridine occupied the vacant axial site to give a six-coordinated compound and that the solid has a five-coordinated structure [7].

The reflectance spectra for Mn(II) polychelate show three bands and suggest an octahedral structure. They can be assigned to the following transitions [8]:

$^4T_{1g} \longleftarrow {}^6A_{1g}$	~17,000 cm^{-1}
$^4T_{2g} \longleftarrow {}^6A_{1g}$	~21,000 cm^{-1}
$^4A_{1g}, {}^4E_g \longleftarrow {}^6A_{1g}$	~25,000 cm^{-1}

The solution spectra of the six-coordinated aquo complex of iron(III) [9] and that of the polychelate of iron(III) are found to be quite comparable, suggesting an octahedral structure for the polychelate of iron(III). The observed transitions may be assigned as follows:

TABLE 1. Analytical Data for the Polychelates

	Analysis[a] (%)			
Compound	C	N	Cl	M
$C_{15}H_{14}O_4N_2$	62.48 (62.93)	9.77 (9.78)	-	-
$[VO(C_{15}H_{12}O_4N_2)].H_2O$	47.23 (48.66)	7.32 (7.57)	-	11.92 13.76
$[Mn(C_{15}H_{12}O_4N_2)(H_2O)_2]$	49.37 (48.01)	7.28 (7.46)	-	15.20 (14.64)
$[Zn(C_{15}H_{12}O_4N_2)].H_2O$	46.88 (48.73)	7.63 (7.58)	-	18.22 (17.68)
$[Fe(C_{15}H_{12}O_4N_2)(Cl)(H_2O)].H_2O$	44.22 (43.77)	6.63 (6.81)	8.53 (8.61)	14.20 (13.57)
$[Cr(C_{15}H_{12}O_4N_2)(Cl)(H_2O)].H_2O$	46.12 (44.18)	7.20 (6.87)	8.76 (8.69)	13.20 (12.75)

[a] Theoretical values are given in parentheses.

${}^4T_{1g} \leftarrow {}^6A_{1g}$	11,980; 12,900; 14,080 cm^{-1}
${}^4T_{2g} \leftarrow {}^6A_{1g}$	18,020; 20,000 cm^{-1}
${}^4A_{1g}$, ${}^4Eg \leftarrow {}^6A_{1g}$	22,730 cm^{-1}
${}^4T_{1g} \leftarrow {}^6A_{1g}$	25,000; 27,030 cm^{-1}

The Cr(III) polychelate in its reflectance spectra shows two bands at 17,200 and 24,500 cm^{-1}. Six-coordinate Cr(III) gives three spin-allowed transitions [10]. The third higher energy band usually occurs above 30,000 cm^{-1}. Considering the octahedral stereochemistry for the Cr(III) polychelate, we have calculated the ν_3 band by band-fitting methods [11]. It is 38,345 cm^{-1}. The calculated B value is found to be 744 cm^{-1}.

Magnetic susceptibility data (Table 2) show subnormal magnetic moments, indicating the presence of metal-metal interactions [12]. Zn(II) polychelate is found to be diamagnetic.

The IR spectral data for the ligand and its polychelates are given

TABLE 2. Infrared Data in cm^{-1}[a]

Bis-oxime of 5,5'-methylene-bis-salicylaldehyde	VO(II)	Mn(II)	Zn(II)	Fe(III)	Cr(III)
3325 s,vbr	3370 w,br 3150 w,s	3575 w,s	3250 m,vbr	3350 w,vbr 3150 w,s	3275 w,br
1640 m,s	1600 w,s	1600 w,s	1600 s,s	1630 sh	1630 sh
1305 m,s	-	-	-	-	-
1005 s,s	1015 s,br 970 s,s	1025 sh	1010 s,s	1020 m,br	1020 s,br

[a] s,s, = strong, sharp; s,vbr = strong, very broad; m,s = medium, sharp; w,br = weak, broad; sh = shoulder.

TABLE 3. Color, Magnetic Moment,

Compound	Color	Magnetic moment (B.M.)	Transition[a] energies (cm^{-1})
$C_{15}H_{14}O_4N_2$	Colorless	-	-
$[VO(C_{15}H_{12}O_4N_2)].H_2O$	Black	1.04	11430 (12050) 16390 (19610) 21280 (23530)
$[Mn(C_{15}H_{12}O_4N_2)(H_2O)_2]$	Dark green	5.43	16560, 18180 21050, 23810 24960
$[Zn(C_{15}H_{12}O_4N_2)]H_2O$	White	Diamagnetic	-
$[Fe(C_{15}H_{12}O_4N_2)(Cl)(H_2O)].H_2O$	Black	4.55	11980, 12900 14080, 18020 20000, 22730 25000, 27030
$[Cr(C_{15}H_{12}O_4N_2)(Cl)(H_2O)].H_2O$	Green	3.58	17240, 24670

[a] Transition energies in pyridine are given in parentheses.

in Table 2. The spectra of polychelates are found to be comparable with each other, but are definitely different from that of the ligand. The sharp and strong bands observed for the ligand in the range 900-1300 cm^{-1} are not found with the polychelates; rather, we observe a weak and very broad bands in this region. The ligand shows a strong and broad band in the region 3150-3340 cm^{-1}. This broadening of the band might be because of the overlapping of the stretching mode of OH of the oximino group with that of phenolic O–H. The band at 1305 cm^{-1} may be assigned to phenolic O–H band deformation. This band is not seen in the IR spectra of polychelates, indicating the loss of the phenolic proton on coordination. However, a weak and very broad band is observed in the range 3150-3575 cm^{-1}. This might be assigned to the water present in the polychelates as well as to the –OH of the oximino group. This reveals that the coordination to metal would have occurred through the nitrogen atom of the oximino group and the proton of the hydroxyl group is not removed. Some evidence for such a coordination is also available from examination of the C=N vibrations. In ligand C=N stretching occurs at 1640 cm^{-1}, while in polychelates

Electronic Spectral, and Thermal Data

Decomposition temperature (°C)	Energy of activation E* (kcal/mol)		Order of reaction n	
	Freeman-Anderson	Broido	Freeman-Anderson	Broido
241	15.88	13.42	2.30	2
344	18.42	13.48	2.50	2
372	24.32	22.26	2.50	2
425	12.30	9.20	2.62	2
265	11.05	15.35	2.56	2
370	12.57	8.95	2.38	2

this vibration occurs at lower frequency. This observation confirms the nitrogen coordination. A very strong band at 1005 cm^{-1} observed in the ligand spectra may be assigned to C—O stretching vibrations of the hydrogen-bonded ring system [13]. In polychelates this band is found to shift to the higher frequency side. The vanadyl polychelate shows a sharp and very strong band at 970 cm^{-1}, suggesting the presence of the V=O group [14].

Examination of the TG thermograms of polychelates shows the presence of water molecule(s). The losses in weight of the Zn(II) and VO(II) polychelates, 4.5% at 150 and 250°C, respectively, correspond to the presence of 1 mol of water per mole of polychelate. Mn(II) polychelate loses 10% of its weight at 250°C. This weight loss corresponds to 2 mol of water per mole of polychelate. The trivalent Fe and Cr polychelates lose 10 and 8.3%, respectively, of their weight at 250°C. This weight loss corresponds to two water molecules. However, this loss occurs during a wide range of temperatures, indicating the presence of different types of water molecules; viz., water of crystallization and water of coordination. The weight loss corresponding to the former is complete at 150°C and that of the latter is complete at 250°C.

The decomposition temperatures (Table 3) calculated from the TG thermograms show the following thermal stability orders: Zn(II) > Mn(II) > VO(II) and Cr(III) > Fe(III). It was also possible to calculate the energy of activation and order of reaction for all the polychelates using Freeman-Anderson's and Broido's method [15]. The results are given in Table 3.

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