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2,4 - Dihydroxybenzaldehyde oxime - formaldehyde polymer as a polymeric ligand

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Polychelates of Cu(II), Ni(II), Co(II), Zn(II), oxovanadium(IV) and dioxouranium(VI) with 2,4-dihydroxybenzaldehyde oxime (2,4-DBO)-formaldehyde (F) polymer (2,4-DBO-F) have been prepared. Elemental analyses of the polychelates indicate a metal: ligand ratio of 1:2. The structures of the complexes have been assigned on the basis of their elemental analyses, IR spectral, magnetic moment and reflectance spectral data.

Attempts to prepare coordination polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Polymeric ligands prepared by condensing formaldehyde with salicylic acid or resorcylic acid have been used as selective ion exchange reagents for the extraction of uranyl ion from solution[1]. Chelates of oxalic acid catalysed salicylaldehyde - formaldehyde polymer and *p*-amino salicylic acid - formaldehyde polymer with various metal ions have been reported[2,3]. Chelating polymers have been prepared by condensing *p*-chloro- and *p*-bromosalicyclic acids with formaldehyde. Their polychelates were also prepared and characterized[4,5]. This prompted us to try to prepare polymeric chelating ligand which would be able to form complexes with a variety of transition metals. This note describes the preparation and characterization of polychelates of the polymer derived from 2,4-dihydroxybenzaldehyde oxime and formaldehyde (2,4-DBO-F)[6].

Experimental

All the chemicals used were either of AR grade or chemically pure grade. DMF and methanol were used after distillation. 2,4-Dihydroxybenzaldehyde oxime was prepared following a known method[7].

Analyses of C,H and N were carried out on a Coleman C,H and N analyzer. IR spectra in KBr disks were recorded on a Perkin-Elmer-983 spectrophotometer. The metals were estimated by standard EDTA titration after decomposing the polychelates. The magnetic susceptibilities of the complexes were determined at room temperature by the Gouy method. Electronic spectra were recorded on a Beckman DK-2A spectrophotometer. Thermograms were recorded on a Du Pont Thermal Analyzer - 951.

Preparation of polymer

2,4-DBO (15.3 g, 0.1 mol) and oxalic acid (1% w/w of 2,4-DBO) dissolved in water were heated on a water-bath for 1 hr and then polymerized with 37% formaldehyde (0.1 mol). The contents were refluxed with stirring at 85-87°C for 6 hr on a water-bath. The solid yellow product obtained was filtered, washed with a large amount of boiling water and dried. Dried polymer was soxhlet-extracted with solvent ether to remove unreacted 2,4-DBO. The polymer was purified by reprecipitation from DMF with water and dried at 60°C. The molecular weight of 2,4-DBO-F polymer was found to be 3150 g/mol.

Preparation of polychelates

2,4-DBO-F polymer (0.01 mol) was dissolved in 30 ml of DMF-methanol mixture (1:1). To this solution, a solution of metal acetate (0.005 mol) in 30 ml of DMF-methanol mixture (1:1) was added dropwise with constant stirring. After the addition of metal ion solution, the reaction mixture was digested for 30 min on a water-bath. The solid product thus separated was filtered, washed with DMF - methanol mixture (1:1) and hot distilled water. The product was dried at 60°C for 24 hr.

Results and discussion

All the polychelates are coloured and amorphous in nature. They are insoluble in common organic solvents. The elemental analyses shown in Table 1 agree with a 1:2 (metal : ligand) stoichiometry.

IR spectral studies

IR spectrum of the polymer shows a broad band in the region 3280-3600 cm^{-1} due to νOH mode. While this band remains unchanged in the spectra of polychelates, a sharper but weaker band present at 2720 cm^{-1} (assigned to H-bonded νOH of the phenolic group in the *or-*

Table 1 – Analytical, magnetic moment and reflectance spectral data of polychelates

Polychelates	Found (Calc.), %				$\mu_{eff.}$ (BM)	Electronic transitions (cm^{-1})	Assignment
	C	H	N	Metal			
2,4-DBO-F	58.10	4.12	8.46	—	—	—	—
	(58.18)	(4.24)	(8.48)				
$[Cu(2,4\text{-}DBO\text{-}F)_2]_n$	51.20	3.40	7.02	16.20	1.64	15,625	$^2B_{1g} \rightarrow {}^2A_{1g}$
	(49.04)	(3.06)	(7.15)	(16.23)		25,000	Charge-transfer
$[Ni(2,4\text{-}DBO\text{-}F)_2.2H_2O]_n$	48.10	3.90	6.50	13.85	3.15	9,615	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	(45.42)	(3.78)	(6.62)	(13.89)		15,411	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
						25,108	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$[Co(2,4\text{-}DBO\text{-}F)_2]_n$	50.08	3.30	7.12	15.12	3.83	8,810	$^4A_2 \rightarrow {}^4T_1(F)$
	(49.62)	(3.10)	(7.23)	(15.23)		16,077	$^4A_2 \rightarrow {}^4T_1(P)$
						24,691	Charge-transfer
$[VO(2,4\text{-}DBO\text{-}F)_2.H_2O]_n$	47.52	3.42	6.49	13.00	1.75	11,160	$^2B_2 \rightarrow {}^2E$
	(46.49)	(3.15)	(6.78)	(12.34)		17,100	$^2B_2 \rightarrow {}^2B_1$
						24,330	$^2B_2 \rightarrow {}^2A_1$
$[UO_2(2,4\text{-}DBO\text{-}F)_2]_n$	33.60	1.89	4.23	40.55	Diamagnetic	20,610	$^1\Sigma_g^+ \rightarrow {}^3\pi_u$
	(32.10)	(2.00)	(4.68)	(39.80)		24,520	Charge-transfer
$[Zn(2,4\text{-}DBO\text{-}F)_2]_n$	50.82	3.22	6.92	16.65	Diamagnetic	—	—
	(48.81)	(3.05)	(7.12)	(16.62)			

tho position) disappears from the spectra of polychelates.

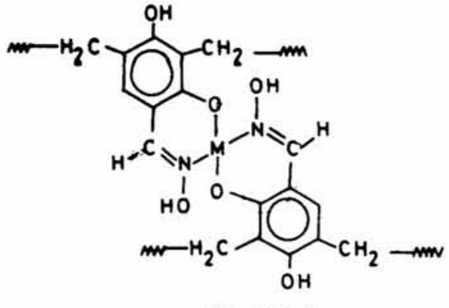
This indicates the replacement of hydrogen of the phenolic OH group (2-position) by metal ions. The lowering of $\nu C=N$ band by 10 cm^{-1} in the polychelates suggests coordination of metal ions through nitrogen of the oximino group. The increase in $N-O$ stretching frequency by 30 to 50 cm^{-1} confirms the coordination through nitrogen of the oximino group[8]. In oxovanadium(IV) and dioxouranium(VI) polychelates, sharp bands at 970 and 925 cm^{-1} are assigned to the $\nu(V=O)$ and $\nu(U=O)$ modes respectively[9,10]. The band around 550 cm^{-1} corresponds to the $\nu(M-N)$ vibration[11].

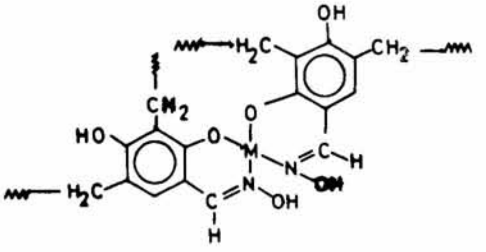
Magnetic and reflectance spectral studies

The magnetic moment and reflectance spectral data of polychelates are shown in Table 1. The magnetic moment of Cu(II) polychelate is 1.64 BM which is lower than expected and this may be due to weak exchange coupling. The reflectance spectrum of Cu(II) polychelate exhibits two bands in the expected region for square-planar Cu(II)[12]. The Ni(II) polychelate shows a magnetic moment of 3.15 BM which is close to the range (2.8 to 3.3 BM) observed for octahedral stereochemistry[13]. The reflectance spectrum of Ni(II) polychelate shows three bands in the expected region for octahedral geometry[14]. This structure is further confirmed by the ratio ν_2/ν_1 which is 1.67, close to the value expected for octahedral structure[15]. The Co(II) polychelate has a magnetic moment of 3.83 BM which is consistent with the spin-only value for three unpaired electrons in a tetrahedral environment[16]. Its reflectance spectrum shows three bands in the region expected for tetrahedral geometry[17]. The magnetic moment in oxovanadium(IV) polychelate is 1.75 BM which is normally observed for octahedral symmetry[18]. Reflectance spectra show three bands in the region expected for octahedral stereochemistry[19,20]. The Zn(II) and dioxouranium(VI) polychelates are found to be diamagnetic as expected. The reflectance spectrum of dioxouranium(VI) polychelate exhibits two absorption bands in the region expected for octahedral stereochemistry[21]. On the basis of IR and reflectance spectra, magnetic measurements, elemental analyses and the structure of the polymer (2,4-DBO-F) discussed earlier[6], it appears that chelation involves the two donor groups from different polymeric chains, as shown in structure A and B.

Thermal study

Voges[22] has reported that the thermal stability of a polymer is higher than that of its polychelates because of hydrogen bonding in the former. Our results also show that 2,4-DBO-F is more stable than the polychelates, and the order of stabilities has been found to be: 2,4-DBO-F > Ni chelate > Cu chelate > Mn chelate > UO_2 chelate > Zn chelate > VO chelate > Co chelate.


Structure A


Structure B

The removal of water above 150°C in case of Ni(II) and Mn(II) polychelates indicates the presence of two coordinated water molecules whereas oxovanadium(IV) polychelate has one coordinated water molecule[23].

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