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Synthesis and Sterochemical Studies of Some New Chelate Polymers

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ABSTRACT

The polychelates of bivalent metal ions such as copper, nickel, cobalt, manganese, and zinc have been synthesized from polymeric ligands derived from 4,4'-dihydroxy-3,3'-diacetyl biphenyl and 4,4'-diamino diphenyl methane. Elemental, magnetic susceptibility, visible and IR spectra, and thermal properties have been studied. The analytical data suggest the general formula $(ML)_n$ for the polychelates. The polychelates are quite stable but insoluble in common organic solvents.

INTRODUCTION

At the present time development of new polymeric chelates has been stimulated due to their good thermal stability and catalytic action in connection with chemical reactions in biological materials. Such polymers can be obtained by an insertion of an inorganic component into the polymer. The polychelates derived from poly-Schiff bases have been reported by many workers [1-3]. Metal complexes containing tetradentate ligands offer several stereochemical forms depending on the number of methylene groups in the central chelate ring [4]. This prospect has been the subject of numerous investiga-

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tions with both transition and nontransition metal ions [5-7]. K. C. Patel et al. [1] has prepared the polychelates derived from 4,4'-dihydroxy-3,3'-diacetyl biphenyl (DABP) with p-phenylene diamine and thiosemicarbazide and studied electrical properties and magnetic moment. In the present communication, we report the polychelates of transition metal ions formed by DABP with 4,4'-diamine diphenyl methane (DDM) along with their physicochemical properties. An attempt has been made to characterize these compounds by elemental analysis, magnetic behavior at room temperature, diffuse reflectance spectra, infrared spectra, and thermal analysis.

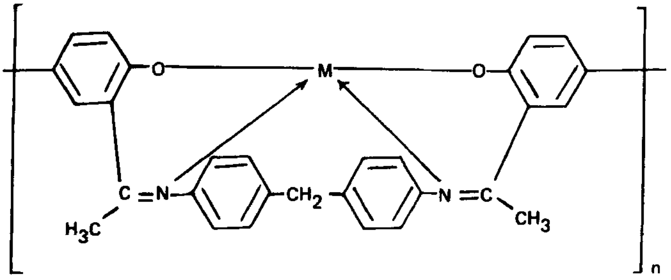
EXPERIMENTAL

Materials

DDM was received from Merk-Schuchardt Co. DABP was prepared by a known procedure [8]. The solvents, ethanol, DMF, and methanol were purified by double distillation. The ligand was prepared by the following procedure.

The hydroxy ketone (DABP) and aromatic diamine (DDM) were dissolved separately in ethanol in a 1:2 stoichiometric ratio and mixed. The reaction mixture was refluxed for 10 h. It was cooled, and the yellow-colored PSB was separated out. It was filtered, washed with ethanol, and dried. It was insoluble in common organic solvents but found soluble in DMF, DMSO, and H_2SO_4. The polymeric Schiff base so prepared may act as a quadridentate ligand through two oxygen and two nitrogen donors.

To prepare polychelates, equimolar quantities of metal acetates and ligand were dissolved in DMF separately and mixed. The reaction mixture was refluxed for 6 h. The hot solution was poured into crushed ice. The precipitates were allowed to settle, then filtered, washed with hot water, and dried. The polychelates were insoluble in common organic solvents and were purified by Soxhlet extraction in methanol to remove impurities and dried. The nature of bonding of the ligand to the metal ion (M = Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) is shown below.



Measurements

C, H, and N analyses were made with a Coleman C-H-N analyzer. The metal content was determined by the EDTA titration technique after decomposition of the polychelates. The magnetic susceptibility of the polychelates was measured by the Gouy method at room temperature. IR spectra were scanned in KBr on a Carl Zeiss Jean UR-10 spectrophotometer. Diffuse reflectance spectra were recorded on a Beckman Du spectrophotometer. TG analysis was carried out on a Linseis thermogravimetric analyzer in air at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The possible coordination modes in all compounds can be determined by coordination number, geometry of the metal centers, and their IR spectra. From elemental analysis it was revealed that all compounds have a 1:1 metal-to-ligand stoichiometry (Table 1) with the general formula $[ML]_n$.

The magnetic moment of copper(II) polychelate is 1.85 BM, which is in the range expected for the spin-only value of one unpaired electron (1.73 BM) for Cu(II) derivatives involving planar geometry [9]. The excess of magnetic moment may be due to an orbital contribution [10]. Nickel(II) polychelate exhibits a magnetic moment of 2.88 BM which is close to the spin-only value for two unpaired electrons (2.83 BM) in an octahedral or distorted octahedral configuration [11]. The magnetic moment value for cobalt(II) polychelate (3.89 BM) is consistent with the spin-only value for three unpaired electrons in a tetrahedral environment [12]. Manganese(II) polychelate shows a magnetic moment of 5.85 BM, which is in agreement with the spin-only value of 5.92 BM for an octahedral Mn(II) environment [13]. Zinc(II) polychelate is diamagnetic because there is no unpaired electron.

Electronic spectra provide much more detailed information about the stereochemistry. In most cases, square planar Cu(II) complexes possess a single broad band, making the assignment of individual electronic transitions difficult. We have observed three transitions at 22 720, 19 800, and 15 500 cm^{-1}. The band at 22 720 cm^{-1} is due to charge transfer from ligand to metal ion [14]. The other two bands are d-d transitions for which a planar structure has been proposed [15]. The electronic spectrum of Ni(II) exhibits four transitions at 22 720, 13 790, 9 800, and 8 890 cm^{-1}. The positions of these transitions are consistent with octahedral stereochemistry [16]. The ν_1 transition is found to split into two bands (9 800 and 8 890 cm^{-1}) which are assigned to the transition arising from the splitting of the $^3T_{2g}$ (F) [17]. The ν_3 transition is observed at 22 720 cm^{-1} and is mixed with the charge transfer band. The transitions are

TABLE 1. Analytical Data and Other Physical Properties

Compound	Color		Elemental analysis M, %	C, %	H, %	N, %	MW of repeating unit
DABP DDM	Yellow	Calculated	-	80.57	5.55	6.47	432.27
		Found	-	81.50	5.10	5.86	
[Cu DABP DDM]	Dark brown	Calculated	12.85	70.53	4.45	5.67	493.81
		Found	11.45	71.10	4.90	5.10	
[Ni DABP DDM $2H_2O$] H_2O	Brown	Calculated	10.81	64.14	5.15	5.15	542.97
		Found	10.10	63.80	4.85	4.77	
[Co DABP DDM]	Brown	Calculated	11.61	68.66	4.33	5.52	507.20
		Found	10.80	69.55	5.15	4.89	
[Mn DABP DDM $2H_2O$] H_2O	Dark brown	Calculated	10.18	64.59	5.19	5.19	539.20
		Found	9.28	65.85	4.80	4.65	
[Zn DABP DDM]	Brown	Calculated	13.19	70.26	4.43	5.64	495.65
		Found	13.00	69.15	5.35	5.10	

$$^{3}A_{2g}\,(F) \longrightarrow {}^{3}T_{2g}\,(F) = \nu_1 \begin{cases} \nearrow 9\ 800\ \text{cm}^{-1} \\ \searrow 8\ 890\ \text{cm}^{-1} \end{cases}$$

$$\longrightarrow {}^{3}T_{1g}\,(F) = \nu_2 \longrightarrow 13\ 790\ \text{cm}^{-1}$$

$$\longrightarrow {}^{3}T_{1g}\,(P) = \nu_3 \longrightarrow 22\ 720\ \text{cm}^{-1}$$

The Racah parameter, B_{35}, is calculated by using the Konig equation [18]:

$$B_{35} = \nu_2 + \nu_3 - 3\nu_1/15$$

Transition energies ν_2 and ν_3 are calculated [18] by using B_{35} obtained from the above equation:

$$\nu_{2,3} = \frac{1}{2}\,(15B + 30Dq) \pm \frac{1}{2}\,[(15B - 10Dq)^2 + 12B\cdot 10Dq]^{1/2}$$

The value of ν_1 corresponds to 10Dq, which is calculated using the following known equation [18]:

$$\nu_1 = 10Dq = \frac{1}{3}\,(\nu_2 + \nu_3) - 5B$$

Various spectral parameters are calculated by known methods [17, 19]:

$\nu_2/\nu_1 = 1.55$, $Dt = 104.5\ \text{cm}^{-1}$, $B_{35} = 657.0\ \text{cm}^{-1}$

$\beta_{35} = 0.608$, $Dq_{av} = 797.3\ \text{cm}^{-1}$, $Dq = 888.8\ \text{cm}^{-1}$

L.F.S.E. = 30.28 kcal/mol

The diffuse reflectance spectrum of the cobalt(II) polychelate shows transitions at 9 090, 16 660, and 21 505 cm^{-1}. First, two transitions ν_2 and ν_3 can be assigned to tetrahedral geometry and the third transition has been assigned to charge-transfer and internal ligand transition [20]. The transition energies ν_1, ν_2, and ν_3 have been calculated using

TABLE 2. Electronic Spectral Data and Magnetic Moment

Compound	Energies, cm^{-1}		Assignment	μ_{eff} (BM)
	Observed	Calculated		
[Cu DABP DDM]	15 500	-	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1.85
	19 800	-	$\longrightarrow {}^2Eg$	
	22 720		Charge transfer	
[Ni DABP DDM $2H_2O$] H_2O	8 890	8 888	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$	2.88
	9 800			
	13 790	14 046	$\longrightarrow {}^3T_{1g}(F)$	
	22 720	22 472	$\longrightarrow {}^3T_{1g}(P)$	
[Co DABP DDM]	-	4 196	$^4A_2 \longrightarrow {}^4T_2(F)$	3.89
	9 090	9 866	$\longrightarrow {}^4T_1(F)$	
	16 660	15 890	$\longrightarrow {}^4T_1(P)$	
	21 505	-	Charge transfer	
[Mn DABP DDM $2H_2O$] H_2O	15 260	-	$^6A_1(S) \longrightarrow {}^4T_{1g}(G)$	5.85
	20 880	-	$\longrightarrow {}^4T_{2g}(G)$	
	22 990	-	$\longrightarrow {}^4A_{1g}, {}^4E_g(G)$	

the equation applied for nickel(II) polychelate (Table 2). The value of B_{35} is calculated by following the Konig relation [18]:

$$B_{35} = \frac{1}{510}\left[7(\nu_2 + \nu_3) \pm \{49(\nu_2 + \nu_3)^2 + 680(\nu_2 - \nu_3)^2\}^{1/2}\right]$$

The values of B_{35}, β_{35} and L.F.S.E. are 877.9 cm^{-1}, 0.7838, and 14.39 kcal/mol, respectively.

The electronic spectrum of the Mn(II) polychelate exhibits three weak bands at the expected positions for an octahedral environment. The band at 15 260 cm^{-1} is attributed to the $^6A_1(S) \rightarrow {}^4T_{1g}(G)$ transition, the band at 20 880 cm^{-1} to the $^6A_1(S) \rightarrow {}^4T_{2g}(G)$ transition, and the band at 22 990 cm^{-1} to the $^6A_1(S) \rightarrow {}^4T_{1g}, {}^4E_g(G)$ transition.

The IR spectra (Fig. 1) provide important information about the bonding site through comparison of the spectra of the ligand and the

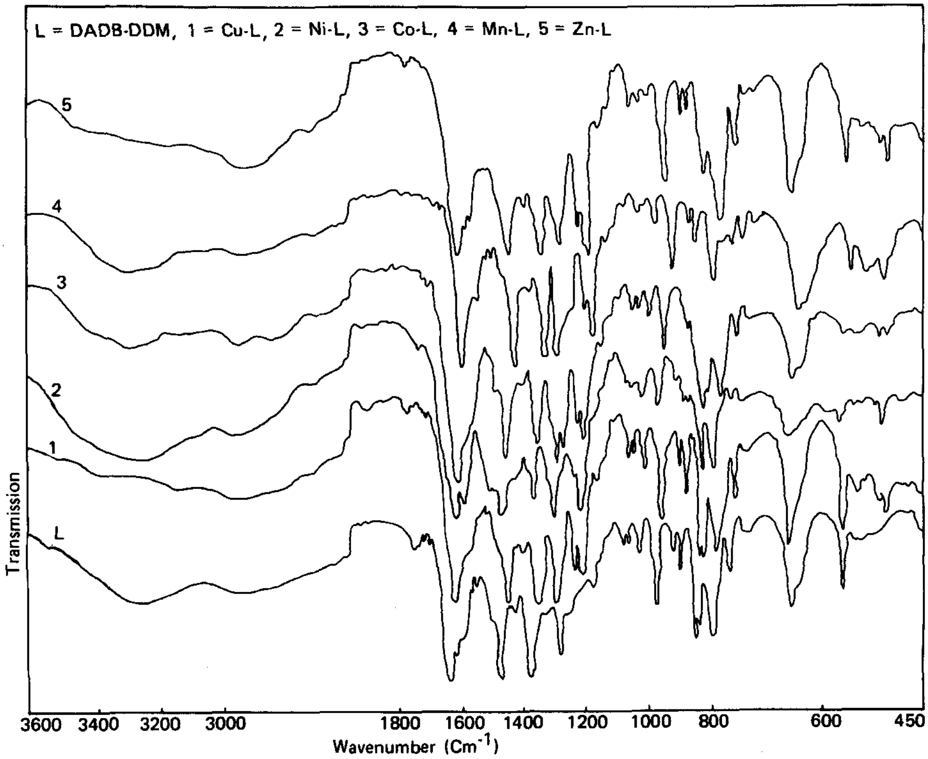


FIG. 1. Infrared spectra of DABP-DDM and polychelates.

TABLE 3. Results of Thermogravimetric Analysis for PSB and Its Polychelates

Compound	Decomposition point, °C	Temperature, °C						E_a, kcal/mol
		100	200	300	400	500	600	
		% Weight loss						
DABP DDM	200-330 440-600	0.0	0.0	43.00	43.00	63.00	90.00	10.12, 28.36
[Cu DABP DDM]	225	0.0	0.0	67.00	74.00	75.00	75.00	26.45
[Ni DABP DDM $2H_2O$] H_2O	280	0.0	9.0	13.50	76.00	80.00	81.50	15.64
[Co DABP DDM]	225-300 375-510	0.0	0.0	28.00	34.50	74.50	89.50	13.53, 15.33
[Mn DABP DDM $2H_2O$] H_2O	250	1.0	9.0	35.50	70.50	82.50	91.00	18.4
[Zn DABP DDM]	225	0.0	1.5	37.50	52.50	68.50	85.00	17.78

polymeric chelates. Chelation through the azomethine group causes a negative shift [21] by 10-40 cm^{-1}. The ligand exhibits phenolic C–O stretching at 1 280 cm^{-1}. On chelation, this band is raised to a higher wavenumber, indicating that oxygen is involved in bonding [22]. Ni(II) and Mn(II) polychelates exhibit bands in the 795-820 and 1 605-1 610 cm^{-1} regions. These bands are attributed to coordinated water [23], and this is confirmed from thermogravimetric analysis.

Table 3 describes the weight loss at different temperatures as calculated from the respective TGA curves. Goodwin et al. [2] reported the thermal stability order for the polychelates to be Ni > Cu > Co. Marvel et al. [3] reported the thermal stability order at 250°C to be Ni > Co > Cu. We have observed the same order at 300°C as observed by Marvel et al.

The water molecules (lattice or coordinated) were estimated by determining the amount of decomposition residue at 200°C. The activation energy was calculated by the Broido method [24] and is summarized in Table 3.

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