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Coordination Polymers. IV. Physicochemical Studies on Chelate Polymers of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) with a Schiff Base of 4,4'-(4,4'-Biphenylylene Bisazo)di-(salicylaldehyde) with m. Toluidine

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Coordination Polymers. IV. Physicochemical Studies on Chelate Polymers of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) with a Schiff Base of 4,4′-(4,4′-Biphenylylene Bisazo)di-(salicylaldehyde) with m-Toluidine

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ABSTRACT

Coordination polymers of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) with a Schiff base derived from 4,4′-(4,4′-biphenylylene bisazo)di(salicylaldehyde) and m-toluidine have been prepared. All the polychelates are dark colored and insoluble in common organic solvents. Magnetic susceptibility and electronic and IR spectra of the polychelates have been studied. All the polychelates except Cu(II) show octahedral structures while Cu(II) polychelate is suggested to be a square planar.

INTRODUCTION

The preparation and characterization of inorganic coordination polymers employing a great variety of ligands and metal ions have been extensively studied and reviewed [1]. Schiff bases are useful catenating ligands [2] and have been used in the synthesis of polymeric metal complexes. Coordination polymerizations of monomeric metal

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chelates via the reacting groups present in the ligands have been studied by Bailes and Calvin [3], Rau [4], and Marvel et al. [5]. In continuation of our earlier work [6], the polychelates of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) with the Schiff base derived from m-toluidine and 4,4'-(4,4'-biphenylylene bisazo)di(salicylaldehyde) are being reported here. We have also studied their IR, diffuse reflectance, and magnetic properties, and have made conductivity measurements.

EXPERIMENTAL

Materials

m-Toluidine and salicylaldehyde (BDH) were used after distillation. Benzidine from Samir Tech. Chem. Industry was used after recrystallization from hot water. Absolute ethanol was obtained from Alembic Co. Dimethyl formamide (DMF), obtained from SD's Lab. Chem. Industry, was used after distillation. Metal chlorides and ferrous ammonium sulfate were obtained from BDH.

Preparation of the Ligand

4,4'-(4,4'-Biphenylylene bisazo)di(salicylaldehyde) was prepared by the method reported earlier [7]. Its Schiff base was obtained by refluxing its solution in DMF with m-toluidine (1:2 mol ratio) for 2 h on a sand bath. The solid obtained on cooling was filtered, washed with DMF, and then with ethanol.

Preparation of Polychelates

The Schiff base (0.0025 mol) was dissolved and refluxed in about 100 mL DMF. To the refluxed ligand solution, the ethanolic metal chloride solution (0.0025 mol) was added slowly with constant stirring. An aqueous ethanolic solution of ferrous ammonium sulfate was used in the preparation of Fe(II) polychelate. To the resulting mixture about 2.0 g of sodium scetate was added and refluxed on a sand bath for ~2 h. The dark-colored solid was filtered, washed several times with hot water, followed by hot DMF, and then with ethanol. The product was dried in an oven at 45°C.

Measurements

All physicochemical measurements were made at room temperature (30°C). Magnetic measurements were made on Sartorius semimicro Gouy balance. The IR spectra were recorded on a Carl-Zeiss model

UR-10 Spectrophotometer in KBr. The diffuse reflectance and solution spectral measurements were made on a Beckman-DU Spectrophotometer. The conductances were measured on a Toshniwal Digital Conductometer.

For establishing the compositions of the polychelates, the metal content in each polychelate was determined by independent volumetric and gravimetric methods. Carbon and hydrogen analyses were made on Coleman analyzer. Chlorine in Cr(III) polychelate was estimated (4.94%; calc 4.85%) by the Carius method.

RESULTS AND DISCUSSION

The elemental analyses of the polychelates given in Table 1 suggest 1:1 (metal:ligand) stoichiometry for all the chelate polymers except copper(II) for which the ratio is 2:3. As all the polychelates were insoluble in common organic solvents, it was not possible to characterize them by conventional methods nor was it possible to determine their molar conductances. However, low values of specific conductances indicate that all the polychelates are nonelectrolyte in behavior. Moreover, a low value of specific conductance in the case of Cr(III) polychelate indicates chlorine coordination.

The diffuse electronic spectral and magnetic data of the polychelates are given in Table 2. The diffuse reflectance spectrum of the ligand shows two strong bands at 24,390 and 20,833 cm^{-1}. The former band may be due to $\pi \rightarrow \pi^*$ transition and the latter may be due to $n \rightarrow \pi^*$ transition according to the assignments for azobenzenes [8]. The high intensity of these bands and their large red shift compared to azobenzene may be attributed to extensive conjugation between rings and –N=N– groups, which lowers the energy of the π^* orbital [9].

The diffuse electronic spectrum of all the polychelates shows a strong band around 20,000-22,222 cm^{-1} which may be a ligand $n \rightarrow \pi^*$ band probably mixed with a charge transfer process [10]. Co(II) and Ni(II) polychelates show an additional band at ~25,000 cm^{-1} which may be due to ligand $\pi \rightarrow \pi^*$ transition. All the polychelates are suggested to have octahedral structure except Cu(II) polychelate which is suggested to have a square planar structure.

The diffuse electronic spectrum of Cr(III) polychelate exhibits bands at 12,500 and 15,384 cm^{-1}. The band at 15,384 cm^{-1} may be safely assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1) transition. The weak band at 12,500 cm^{-1} may be a spin forbidden in nature and corresponding to ${}^4A_{2g} \rightarrow {}^2E_g$ transition [11]. The room temperature magnetic moment (4.3 B.M.) of Cr(III) polychelate is a little higher than the spin-only value but still within the range required for octahedral stereochemistry [12].

The diffuse reflectance spectrum of Fe(II) polychelate shows bands at 8,696, 10,309, and 14,286 cm^{-1}. The bands at 10,309 and 14,286 cm^{-1}

TABLE 1. Analytical and Conductivity Data

Compound	Elemental analysis found (calc) (%)			Specific conductivity × 10^6 mho/cm
	C	H	M	
$[C_{40}H_{32}N_6O_2]$ ligand	76.43 (76.42)	5.96 (5.09)	-	-
$[(CrC_{40}H_{30}N_6O_2)(Cl)(H_2O)]$	65.3 (65.61)	4.74 (4.37)	7.2 (7.10)	1.2
$[(MnC_{40}H_{30}N_6O_2)(H_2O)_2]$	67.3 (66.95)	4.8 (4.74)	7.38 (7.66)	1.6
$[(FeC_{40}H_{30}N_6O_2)(H_2O)_2]$	66.40 (66.86)	4.77 (4.74)	7.6 (7.78)	1.2
$[(CoC_{40}H_{30}N_6O_2)(H_2O)_2]$	66.84 (66.59)	4.13 (4.72)	8.4 (8.18)	2.1
$[(NiC_{40}H_{30}N_6O_2)(H_2O)_2]$	66.35 (66.61)	4.09 (4.72)	8.03 (8.15)	1.8
$[Cu_2(C_{40}H_{30}N_6O_2)_3] . H_2O$	71.78 (71.18)	4.30 (4.55)	6.00 (6.28)	2.2

TABLE 2. Magnetic and Electronic Spectral Data

Compound	Magnetic moment (B.M.)	Transition energies (cm^{-1})			
$[(CrC_{40}H_{30}N_6O_2)(Cl)H_2O)]$	4.30	12,500;	15,384;	22,222	
$[(Mn(C_{40}H_{30}N_6O_2)(H_2O)_2]$	5.70	11,360;	17,857;	21,276	
$[(FeC_{40}H_{30}N_6O_2)(H_2O)_2]$	46.00	8,696;	10,309;	14,285;	21,739
$[(CoC_{40}H_{30}N_6O_2)(H_2O)_2]$	4.70	8,333;	10,929;	22,222;	25,000
$[(NiC_{40}H_{30}N_6O_2)(H_2O)_2]$	3.17	8,696;	10,256;	16,129;	25,000
$[Cu_2(C_{40}H_{30}N_6O_2)_3] . H_2O$	2.05	13,605;	20,000		

may be assigned to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition [13], while the low energy band at 8,696 cm^{-1} may be due to a low symmetry ligand field component [14]. Its magnetic moment per iron atom has been observed to be as high as 46 B.M. This large magnetic moment value indicates the ferromagnetic behavior of the chelate.

The diffuse reflectance spectrum of Mn(II) polychelate shows bands at 11,360 and 17,857 cm^{-1}, which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ transitions, respectively. The observed room temperature magnetic moment (5.7 B.M.) of Mn(II) polychelate is slightly less than that required for a high spin octahedral structure [15].

The diffuse electronic spectrum of Co(II) polychelate exhibits bands at 8,333 and 10,929 cm^{-1}, which may be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^2E_g$, respectively [16]. The magnetic moment of Co(II) polychelate is in the range required [17].

The electronic spectrum of Ni(II) polychelate shows bands at 8,696 (ν_1) and 16,129 (ν_2) cm^{-1}, which may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions, respectively [18]. The ν_1 band is found to be broad and unsymmetrical in structure at 10,256 cm^{-1}. This suggests the presence of a low symmetry component [18]. The ν_2/ν_1 ratio (ν_1 = 8,696 cm^{-1}) is found to be greater (1.85) than that required for the octahedral structure [18]. This suggests considerable distortion from the cubic field and therefore splitting of the ν_1 band. The most probable assignments of the split components (in D_4h symmetry) can be given as ${}^3B_{1g} \rightarrow {}^3E_g$ (8696 cm^{-1}) and ${}^3B_{1g} \rightarrow {}^3B_{2g}$ (10,256 cm^{-1}) [19, 20]. The amount of splitting in the ν_1 band can be taken as a measure (35/4 Dt) of the degree of distortion [21], and D_t = 178 cm^{-1} can be calculated. Using D_t (D_4h) and D_q^{xy} (1026 cm^{-1}), D_q^{z} is found to be 714 cm^{-1} [19]. This suggests that the field in the XY plane is stronger than that along the Z axis. The room temperature magnetic moment of Ni(II) polychelate is in the range required for six-coordinate spin-free Ni(II) [23, 24].

In the Cu(II) chelate the d-d transition occurs at rather relatively low energy (13,605 cm^{-1}) compared with those normally observed in square planer complexes [25, 26]. However, several square planar chelates show a band in the 13,000 to 14,000 cm^{-1} range [27]. This band arises probably due to a ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition [25]. In order to confirm the square planar structure of the Cu(II) polychelate, its pyridine spectrum was taken. It shows a band at ~15,000 cm^{-1}, indicating a distorted octahedral structure. This suggests pyridine coordination. The room temperature magnetic moment of the polychelate is 2.05 B.M.

Although much information is available in the literature concerning

TABLE 3. Infrared Spectral Data[a]

Ligand	Cr	Mn	Fe	Co	Ni	Cu
3370 Wbr	3366 Mbr	3380 Mbr	3358 Mbr	3383 Mbr	3383 Mbr	3391 Wbr
1616 SVS	1605 SVS	1605 SS	1605 SVS	1600 SVS	1604 SVS	1600 SVS
1592 SVS	1597 ShS	1595 ShS	1598 SS	1595 Shw	1595 ShS	1595 Shs
1283 SS	1288 Shm	1279 SS	1285 SS	1288 Sm	1279 Shm	1283 SS
1107 SVS	1112 SS	1108 SS	1110 SS	1112 SVS	1112 SVS	1112 SVS

[a] SVS = sharp very strong, sm = sharp medium, Mbr = medium broad, Wbr = weak broad, SS = sharp strong, shs = shoulder strong, shm = shoulder medium.

the IR spectra of imines, less is known about the polymeric azomethines and their polychelates. An attempt has been made to get an idea about the bonding by comparing the IR spectrum of the ligand with those of the polychelates. As all the compounds contain six aromatic rings, the interpretation of the C=C stretching region is rather complicated due to the overlap of several bands. However, some stray findings are indicated here. The important band frequencies are listed in Table 3.

The infrared spectrum of ligand shows a weak and broad absorption band at ~3,370 cm^{-1} which may be due to stretching vibrations of the phenolic hydroxyl group. The observed negative shift might be because of the presence of the intramolecular or intermolecular hydrogen bonding present in the molecule [28]. A weak or medium broad band observed in the spectra of the polychelates at ~3,400 cm^{-1} may be due to the presence of water molecule(s).

It is rather difficult to assign the bands due to $\nu_{C=N}$ as they can be confused with the bands due to $\nu_{N=N}$. Therefore, a very strong band at ~1,616 cm^{-1} with a weak band or shoulder at about 1,595 cm^{-1} shown by the ligand as well as by the polychelates might be due to $\nu_{N=N}$ and $\nu_{C=N}$ [7].

The ligand shows a strong band at 1,283 cm^{-1} which may be assigned to a hydrogen bonded O–H in-plane bending vibration [29]. However, all the polychelates show this band, which may be due to the presence of either coordinate water or water of crystallization.

A strong absorption at 1,107 cm^{-1} is shown by the ligand. It can be attributed to the phenolic C–O vibration of the hydrogen-bonded ring system of the ligand. This band is shifted slightly toward higher frequency on coordination, indicating that the oxygen of the hydroxy group of the Schiff base has taken part in coordination [30].

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REFERENCES

[1] N. Dunski and T. H. Crawford, J. Inorg. Nucl. Chem., 35, 2707 (1973).

[2] P. L. Maurya, B. V. Agarwala, and A. K. Dey, Makromol. Chem., 183, 511 (1982).

[3] R. H. Bailes and M. Calvin, J. Am. Chem. Soc., 69, 1886 (1947).

[4] P. L. Rau, Diss. Abstr., 16, 232 (1956).

[5] C. S. Marvel, L. F. Andrieth, J. Moeller, and J. C. Bailar, Jr.,

Wright Air Development Center, U.S.A., Techn. Rept. 58/51, Pt. III (1960). F. G. A. Stone and W. A. G. Graham, "Inorganic Polymers" Academic, New York, 1962, p. 508.
[6] M. S. Patil, N. R. Shah, A. K. Rana, A. M. Karampurwala, and J. R. Shah, J. Macromol. Sci.–Chem., A16(3), 737 (1981) and references therein.
[7] A. K. Rana, N. R. Shah, M. S. Patil, A. M. Karampurwala, and J. R. Shah, Makromol. Chem., 182, 3387 (1981).
[8] P. H. Gore and O. H. Wheeler, J. Org. Chem., 26, 3295 (1961).
[9] J. Griffiths, Colour and Constitution of Organic Molecules, Academic, Oxford, 1976.
[10] D. A. Baldwin, A. B. P. Lever, and R. V. Parish, Inorg. Chem., 8, 107 (1969).
[11] D. K. Rastogi and P. C. Jain, Indian J. Chem., 10, 100 (1972).
[12] E. Konig, E. Lindner, I. P. Lorenz, and G. Ritter, J. Inorg. Nucl. Chem., 33, 3305 (1971).
[13] C. P. Prabhakaran and C. C. Patel, Ibid., 34, 3485 (1972).
[14] B. N. Figgis, Introductions to Ligand Fields, Wiley-Interscience, New York, 1966.
[15] B. N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 157 (1964).
[16] K. S. Patel, J. Inorg. Nucl. Chem., 42, 1235 (1980).
[17] B. N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 187 (1964).
[18] D. K. Rastogi and K. C. Sharma, J. Inorg. Nucl. Chem., 36, 2219 (1974).
[19] A. B. P. Lever, Coord. Chem. Rev., 3, 119 (1968).
[20] B. Singh and R. Singh, J. Inorg. Nucl. Chem., 34, 3449 (1972).
[21] G. R. Brubacker and D. H. Busch, Inorg. Chem., 5, 2114 (1966).
[22] C. R. Hare and C. J. Ballhausen, J. Chem. Phys., 40, 788 (1964).
[23] P. D. Singh, N. K. Jha, and L. K. Mishra, J. Inorg. Nucl. Chem., 42, 282 (1980).
[24] N. Saha and N. C. Gayen, Indian J. Chem., 19A, 229 (1980).
[25] S. K. Mondal, D. S. Joardar, and K. Nag, Inorg. Chem., 17, 191 (1978).
[26] B. J. Hathaway, Coord. Chem. Rev., 5, 143 (1970).
[27] P. R. Blum, R. M. C. Wei, and S. E. Cummings, Inorg. Chem., 13, 450 (1974).
[28] H. H. Freedman, J. Am. Chem. Soc., 83, 2900 (1961).
[29] K. Ueno and A. E. Martell, J. Phy. Chem., 60, 1270 (1956).
[30] N. S. Biradar and V. H. Kulkarni, J. Inorg. Nucl. Chem., 33, 2451 (1971).

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