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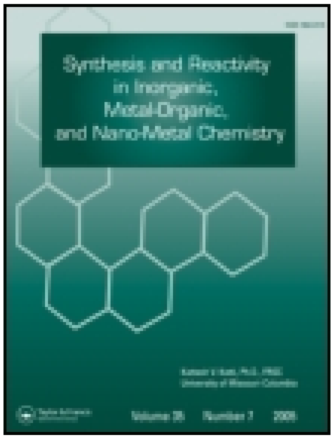

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COORDINATION CHAIN POLYMERS OF SOME TRANSITION METALS WITH SCHIFF BASE

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COORDINATION CHAIN POLYMERS OF SOME TRANSITION METALS WITH SCHIFF BASE

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ABSTRACT

The Schiff base derived from terephthalaldehyde and *o*-aminophenol is known as N,N′-di(*o*-hydroxyphenyl)terephthalaldehydediimine and is termed here as H_2SB. The polychelates of this Schiff base having the general formula $[M(SB)(H_2O)_2]_n$ [where $M = Mn(II)$, Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] have been synthesized and characterized on the basis of elemental analyses, infrared spectra, electronic spectra, magnetic measurements and thermogravimetric analyses. The Schiff base act as uninegative bidentate ligand and bonding occurs through the hydroxyl oxygen and nitrogen atoms. An octahedral geometry has been assigned to all of the prepared polychelates.

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INTRODUCTION

The study of polychelates or coordination polymers is of recent interest. The coordination polymers of terephthalaldehyde containing Schiff bases have been prepared by Dey *et al*[1]. The present communication describes the synthesis of the Schiff base of terephthalaldehyde and *o*-aminophenol, which is capable of being bidentate and should form linear polymers when allowed to react with suitable metal ions like Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The structures of the polymeric metal chelates were established on the basis of elemental analyses, infrared spectra, electronic spectra, magnetic and thermogravimetric measurements.

The suggested structure of N,N′-di(*o*-hydroxyphenyl)terephthalaldehydediimine) (H_2SB) is shown in Fig. 1.

EXPERIMENTAL

The chemicals employed were of analytical grade and were used without further purification.

Synthesis of the Ligand

An ethanolic solution (100 mL) of terephthalaldehyde (1.34 g, 1 mmol) and an ethanolic solution (200 mL) of *o*-aminophenol (2.18 g, 2 mmol) were mixed and a yellow crystalline solid was obtained immediately. The mixture was heated on a water bath for one hour. The ligand was filtered, washed successively with water and ethanol and dried in air. They are insoluble in common organic solvents like benzene, chloroform, and acetone but soluble in dimethylformamide.

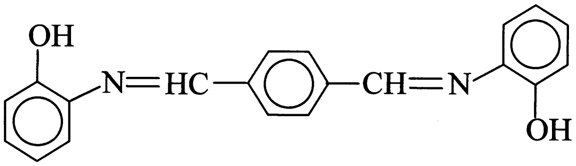


Figure 1. Suggested structure of the ligand.

Synthesis of the Complexes

The solution of metal acetate (2 mmol) in dimethyl formamide (100 mL) was added slowly to a dimethyl formamide solution (100 mL) of the ligand (0.6 g, 2 mmol) in 1:1 molar ratio. The mixture was heated for ten hours at 120 °C to ensure complete precipitation and then allowed to cool overnight at room temperature. The obtained metal chelates were filtered, washed with dimethyl formamide and dried in air. The polymeric chelates are insoluble in all common organic solvents like acetone, ethanol, chloroform, methanol, benzene and dimethylformamide.

Analytical Procedures

The chelates were analyzed for the metal contents by the EDTA titration technique[2]. The magnetic moment were obtained by Gouy's method using mercury tetrathiocyanatocobaltate(II) as a calibrant ($\chi_g = 6.44 \times 10^{-6}$ c.g.s. units at 20 °C). Diamagnetic corrections were made using Pascal's constant. The infrared spectra were recorded on a FT-IR Nicolet 400 D spectrophotometer. The electronic spectra were measured on a Beckman DK-2A spectrophotometer using MgO as reference. Nitrogen, carbon and hydrogen were analysed with an Heraeus C, H, N analyzer (Germany). A 951 Du Pont analyzer (Germany) was used for thermogravimetric analyses. The experiment was started by heating the system at a constant rate of 10 °C per minute. Samples supplied by the Mettler company were used for calibration of the thermobalance.

RESULTS AND DISCUSSION

The analytical data of the ligand and complexes and some physical properties are listed in Table I. The reaction to form the complexes may be represented as follows:

$$M(CH_3COO)_2 + H_2SB \longrightarrow [MSB(H_2O)_2]_n + 2\ CH_3COOH$$

$$H_2SB = N,N'\text{-di}(o\text{-hydroxyphenyl})\text{terephthalaldehydediimine}$$

$$M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), \text{and } Cd(II).$$

The nature of the ligand, high thermal stability and metal-ligand ratio (1:1) and insolubility of the complexes in common organic solvents suggest their polymeric nature[3]. The insolubility of the complexes in common

Table I. Analytical Data of the Chelates

Compound[a]	Empirical Formula	Yield %	% Found (calculated) M	C	H	N	μ_{off} (B.M.)	M.p. (°C)
H_2SB	$C_{20}H_{16}O_2N_2$	67	–	75.90 (75.94)	5.02 (5.06)	8.80 (8.86)	–	108
$[MnSB(H_2O)_2]_n$	$C_{20}H_{18}MnO_4N_2$	38	13.30 (13.55)	59.30 (59.27)	4.42 (4.44)	6.95 (6.91)	6.10	above 350
$[CoSB(H_2O)_2]_n$	$C_{20}H_{18}CoO_4N_2$	25	14.15 (14.40)	58.74 (58.69)	4.35 (4.40)	6.82 (6.84)	4.38	above 350
$[NiSB(H_2O)_2]_n$	$C_{20}H_{18}NiO_4N_2$	22	14.19 (14.36)	58.79 (58.72)	4.40 (4.14)	6.89 (6.85)	2.84	above 350
$[CuSB(H_2O)_2]_n$	$C_{20}H_{18}CuO_4N_2$	14	15.29 (15.35)	58.09 (58.04)	4.42 (4.35)	6.38 (6.77)	1.88	above 350
$[ZnSB(H_2O)_2]_n$	$C_{20}H_{18}ZnO_4N_2$	15	15.68 (15.72)	57.69 (57.78)	4.28 (4.33)	6.71 (6.75)	–	above 350
$[CdSB(H_2O)_2]_n$	$C_{20}H_{18}CdO_4N_2$	20	24.10 (24.30)	51.96 (51.90)	3.87 (3.89)	6.09 (6.05)	–	above 350

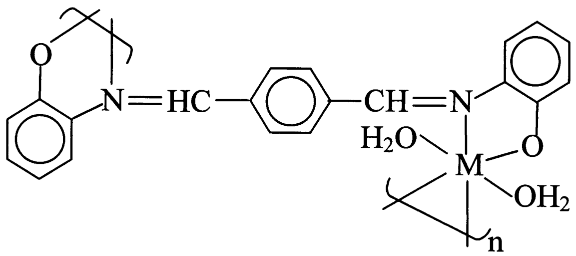
[a] H_2SB = N,N′-di(*o*-hydroxyphenyl)terephthalaldehydediimine.

organic solvents does not permit a determination of the molecular weights but indicate a polymeric nature. It is suggested that the compounds are coordination chain polymers[4,5]. Elemental analyses, physical properties and infrared data provide good evidence that the compounds are polymeric. The analytical data indicate that the polychelates have the general formula $[MSB(H_2O)_2]_n$.

The probable structure of the complexes shown in Fig. 2.

Magnetic Measurements

The magnetic measurement data are presented in Table I. The magnetic moment value of the Cu(II) chelate (1.88 B.M.) is slightly higher than the spin-only value (1.73 B.M.) expected for one unpaired electron, which offers the possibility of an octahedral geometry[6]. The effective magnetic moment of the Ni(II) chelate is (2.84 B.M.) indicating that this chelate is also having an octahedral structure[7]. The observed magnetic moment of the Co(II) chelate (4.38 B.M.) is in good agreement with high-spin octahedral geometry[8]. The magnetic moment value for the Mn(II) chelate is 6.1 B.M., which is slightly greater than spin-only value 5.92 B.M., but within the limits of spin-free values for five unpaired electrons, indicating that the chelates are high-spin six-coordinated[9]. The magnetic moment determination shows that the Zn(II) and Cd(II) chelates are diamagnetic.



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Figure 2. Suggested structure of $[MSB(H_2O)_2]_n$.

Electronic Spectra

The electronic spectra of the chelates were recorded in the solid state. The nickel(II) chelate gave three bands at 10,525, 16,970 and 25,000 cm^{-1} corresponding to the transitions $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)(\nu_3)$, respectively. The values of the ligand field splitting energy (10 Dq), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β) and ratio ν_2/ν_1 are presented in Table II and are consistent with the values for an octahedral geometry. The electronic spectra of the manganese(II) chelate show three weak bands at 14,600, 20,000 and 25,600 cm^{-1} which have been assigned to the transitions $^6A_{1g}\rightarrow{}^4T_{1g}(^4G)$, $^6A_{1g}\rightarrow{}^4T_{2g}(^4G)$ and $^6A_{1g}(F)\rightarrow{}^4A_{1g}$, ^4E_g (^4G), respectively, in an octahedral field of the manganese(II) ion. The electronic spectra of the cobalt(II) chelate show three bands at 9,090, 18,348 and 19,230 cm^{-1} which have been assigned to the transitions $^4T_{1g}(F)\rightarrow{}^4T_{2g}$, $^4T_{1g}(F)\rightarrow{}^4A_{2g}$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$, respectively. The values of the ligand field splitting energy (10 Dq), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β) and ratio ν_2/ν_1 are presented in Table II and are consistent with the values for an octahedral structure. The electronic spectra of the copper(II) chelate[10] exhibit a band at 16,500 cm^{-1} assigned to the $^2E_g\rightarrow{}^2T_{2g}$ transition considering an octahedral geometry. A strong charge transfer band is observed at 24,500 cm^{-1}.

Thermogravimetric Analyses

It has been observed that all the chelates show a loss in weight corresponding to two water molecules in the range 150 to 180 °C, indicating that these water molecules are coordinated to the metal ion[11]. The TG curves indicate that above 180 °C the compounds start to loose mass with partial evaporation of the Schiff base. In the temperature range 180 to 450 °C the Schiff base molecules are lost. In all of the cases the final products

Table II. Reflectance Spectral Data of the Co(II) and Ni(II) Complexes

	Observed Band (cm^{-1})							
Compound	ν_1	ν_2	ν_3	ν_2/ν_1	B	β	β°	10 Dq
$[CoSB(H_2O)_2]_n$	9,090	18,348	19,230	2.01	751.45	0.773	22.7	10,221
$[NiSB(H_2O)_2]_n$	10,525	16,970	25,000	1.61	693.00	0.672	32.7	10,525

Table III. Infrared Spectral Data of the Polychelates (cm^{-1})[a]

Compound	v(O-H)	v(M-O)	v(C-O)	v(M-N)	v(C=N)
H_2SB	3375 s	–	1380 s	–	1625 s
$[MnSB(H_2O)_2]_n$	3430 b	410 m	1400 s	440 m	1605 w
$[CoSB(H_2O)_2]_n$	3415 b	405 m	1390 s	430 s	1600 w
$[NiSB(H_2O)_2]_n$	3420 b	405 m	1387 s	445 w	1595 w
$[CuSB(H_2O)_2]_n$	3425 b	415 m	1384 s	435 s	1595 w
$[ZnSB(H_2O)_2]_n$	3440 b	410 m	1406 s	440 m	1602 w
$[CdSB(H_2O)_2]_n$	3425 b	420 m	1391 s	425 s	1605 w

[a] b = broad, m = medium, s = strong, w = weak.

are metal oxides. These results are in good accordance with the composition of the complexes.

Infrared Spectra

The important infrared spectra of the chelates and their assignments are presented in Table III. The spectra of H_2SB show a medium intense band at 2700 cm^{-1} due to intramolecularly hydrogen bonded v(OH)[12]. The infrared spectra of the Schiff base show a weak band at 3200–3600 cm^{-1} which is assigned to hydrogen bonded O-H stretching. This band becomes broader on chelation. The spectra of the chelates exhibit a broad band in the region of 3300–3400 cm^{-1} suggesting the presence of water molecule[13,14]. The weak bands around 860 and 700 cm^{-1} are assigned as OH stretching, rocking and wagging vibrations, respectively[15]. The presence of coordinated water molecules is also confirmed by elemental analyses and thermogravimetric analyses. The characteristic bands appearing at 1590–1630 and 1380–1410 cm^{-1} may be assigned to C=N and phenolic C-O stretching vibrations, respectively[16,17]. The ligand shows the C=N stretching band at 1625 cm^{-1} which shifts to 1595–1610 cm^{-1} in the chelates indicating the involvement of the azomethine nitrogen in coordination[16]. The band appearing at about 410 cm^{-1} is v(M-O)[18]. The band appearing at about 450 cm^{-1} is v(M-N)[19].

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REFERENCES

1. Singh, B.; Banerjie, V.; Agarwala, B.V.; Dey, A.K. Coordination Chain Polymers of Schiff Base Derived From *o*-Aminobenzoicacid and Terephthalaldehyde. J. Ind. Chem. Soc. **1980**, *57*, 365–367.
2. Vogel, A.I. *A Text Book of Quantitative Inorganic Analysis*; Longmans Green: London, 1962.
3. Dwivedi, D.K.; Shukla, R.K.; Shukla, B.K. Coordination Polymers of Lanthanum(III) acetate Isatin Oxalydihydrazone. Acta Cienc. Indica Chem. **1991**, *17c* (4), 383–386. Chem. Abstr. **1992**, *117*, 142241n.
4. Korshak, V.V.; Vinogradora, S.V.; Artemora, V.S. Some Polymers of Quinizarin and Metals. Vysokomolekul. Soidin. **1960**, *2*, 492–497. Chem. Abstr. **1961**, *55*, 3104c.
5. Coble, H.D.; Holtzclaw, H.F. (Jr.). Chelate Polymers of Copper(II) with Various Dihydroxy Quinoid Ligands. J. Inorg. Nucl. Chem. **1974**, *36*, 1049–1053.
6. Patel, B.K.; Patel, M.M. Synthesis and Characterization of some New Chelate Polymers. J. Ind. Chem. Soc. **1990**, *67*, 186–188.
7. Sharma, C.L.; Islam, M.S. Characterization of Mixed Ligand Complex of Cobalt(II) and Nickel(II) With Diphenic Acid as Primary and Heterocyclic Bases as Secondary Ligands. Synth. React. Inorg. Met.-Org. Chem. **1986**, *16* (4), 553–563.
8. Cotton, F.A.; Goodgame, M. Magnetic Investigation of Spin-free Cobaltous Complex. J. Phys. Chem. **1961**, *65*, 191–192. Chem. Abstr. **1961**, *55*, 26655i.
9. Sahu, B.K.; Mahapatra, B.K. Mixed Ligand Complexes of Mn(II) and Cd(II) Dithiocarbamate with Nitrogen Donors. J. Ind. Chem. Soc. **1979**, *56*, 825–826.
10. Sacconi, L.; Champdini, M.; Campigli, U. Magnetic Investigation of some Tetracoordinated Nickel(II) and Copper(II) Complexes Between 80 and 300 °K. Inorg. Chem. **1965**, *4*, 407–409.
11. Nakolacv, M.A.; Longvineuko, V.A.; Mychino, C.T. *Thermal Analyses*; Academic Press: New York, 1969; Vol. 2, 779.
12. Basseler, G.C.; Silverstein, R.M. *Spectrophotometric Identification of Organic Compounds*; 3rd Edn.; Wiley: New York, 1992; 111.
13. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York, 1975.
14. Percy, G.C. Infrared Spectra of Nickel(II) and Cobalt(II) N-Salicylideneglycinates. J. Inorg. Nucl. Chem. **1975**, *37*, 2071–2073.
15. Fuzita, L.; Nakamoto, K.; Kobayashi, M. Infrared Spectra of Metallic Complexes II. The Absorption Bands of Coordinated Water in Aquo Complexes. J. Amer. Chem. Soc. **1956**, *78*, 3963–3965.

16. Freedman, H.H. Interamolecular H-Bonds. A Spectroscopic Study of the Hydrogen Bond Between Hydrogen and Nitrogen. J. Amer. Chem. Soc. **1961**, *83*, 2900–2905.
17. Hadzi, D.; Prevorsek, D. Infrared Absorption Bands Associated with the NH Group. III. Hydroxamic Acids and Derivatives. Spectrochim. Acta. **1957**, *10*, 38–51. Chem. Abstr. **1958**, *52*, 9766i.
18. Ferraro. I.R. *Low Frequency Vibrations of Inorganic and Coordination Compounds*; Plenum Press, 1971.
19. Siddiqi, K.S.; Arjamand, F.; Tabassum, S.; Zaidi, S.A.A. Heterometallic Complexes of N_2S_2 Macrocyclic Ligands With Group IV Tetrachlorides and Bistrimethylsilye-amine. Main Group Metal Chem. **1994**, *17* (9), 619–622. Chem. Abstr. **1995**, *123*, 46620p.

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