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Synthetic, Structural, Thermal and Electrical Properties of Some Transition Metal Polymeric Chelates of Bis(mercaptoacetamido)diaminobutane

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Polymeric chelates of bis(mercaptoacetamido)-1,4-diaminobutane (BMADB) with manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) ions have been synthesized and characterized by elemental analysis, magnetic moment, infrared, electronic spectra and thermal analysis. In the present investigation the ligand BMADB exhibits bis-bidentate character and coordinates symmetrically with metal through nitrogen of amido and sulfur of mercapto groups. The thermogravimetric studies indicate a two stage decomposition and the presence of water molecules. Thermal data have been analyzed by Freeman-Carroll and Sharp-Wentworth methods and various kinetic and thermodynamic parameters have also been evaluated. Comparable values of parameters indicate common decomposition reaction mode in all chelates. Their d.c. electrical conductivity in pellet form over a wide range of temperatures have also been studied.

Key words: polymeric chelates, magnetic, spectral, TGA and electrical conductivity

Organic compounds possessing mercaptoamide $NHCOCH_2SH$ functional set have been reported to have noteworthy biological, industrial and analytical applications [1]. Further they have been found to be potential coordinating centers, yielding complexes of great industrial and biochemical importance [2]. The first row transition metals are very well known for their ability to form wide range of coordination complexes, in which octahedral, tetrahedral and square-planar stereochemistry predominate. Chelate polymers having good thermal stability and catalytic activity prompted the development of polymeric material from both polymeric and monomeric ligands. Such metal ions with polymeric systems may also possess unusual electrical properties. Though chelate polymers are known for long time, the studies on transition metal polymeric chelates and their electrical conductivity have been initiated only recently [3,4]. An industrially useful semiconducting material has been reported, since delocalized electrons and conjugation impart semiconducting properties [5].

In this work we report the synthesis of the chelate polymers of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with bis(mercaptoacetamido)-1,4-diaminobutane (BMADB), their structural, thermal and electrical properties.

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EXPERIMENTAL

Manganese(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate, zinc(II) acetate dihydrate and cadmium(II) chloride monohydrate were obtained from British Drug House. Mercapto acetic acid and 1,4-diaminobutane were purchased from E. Merck (India) and solvents were used after distillation.

Synthesis of ligand BMADB: Mercaptoacetic acid (0.2 mol) in 25 ml of dry methanol was taken in the round bottom flask and few drops of concentrated H_2SO_4 were also added as a catalyst. The mixture was refluxed on water bath for about 45 minutes and then the solution of 1,4-diaminobutane (0.1 mol) in 25 ml of methanol was added to it with constant stirring and reaction mixture was refluxed for another 30 minutes. A pale white solid which precipitated on cooling was filtered under suction, washed with water and methanol and crystallized from DMF and dried *in vacuo* over $CaCl_2$. Purity of the ligand was checked by TLC, IR and elemental analysis. The crystallized ligand showed the expected elemental analysis. Yield: 75%, m.p.165°.

Synthesis of chelates: All the chelate polymers were isolated by the following general method. Equimolar quantities of metal acetates (Cd(II) chloride) and ligand BMADB were dissolved separately in minimum quantity of DMF (20–40 ml). Both the solutions were filtered and mixed in hot conditions.The reaction mixture was refluxed for further 4–5 h on an oil bath, while refluxing a slow steam of N_2 gas was passed in the solution. The coloured products obtained with different metals were filtered, washed thoroughly with DMF, absolute ethanol followed by acetone to remove the excess of unreacted ligand and metal acetate and dried in an electric oven at 80° and kept in vacuum desiccator over $CaCl_2$. All the chelates are found to be insoluble in water and most of the polar and non-polar organic solvents and hence normal methods of charactarization such as ^1H NMR and electronic spectra in solution cannot be applied. The metal and sulfur content in each polymer were determined by standard methods [6]. Carbon, hydrogen and nitrogen analysis were obtained from microanalytical unit C.D.R.I. Lucknow [7]. The magnetic measurements were carried out by Gouy method at room temperature using $Hg[Co(NCS)_4]$ as the calibrant. The diffuse reflectance measurements were recorded on photoacoustic spectrophotometer (PAS) using $BaSO_4$ as the calibrant. The IR spectra were recorded in KBr pellets on Perkin-Elmer 577 spectrophotometer. Thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 thermobalance in air with 10^0 min^{-1} heating rate. D.C. electrical conductivity was measured over 313–498 K range by voltage drop method using d.c. microvoltmeter [7].

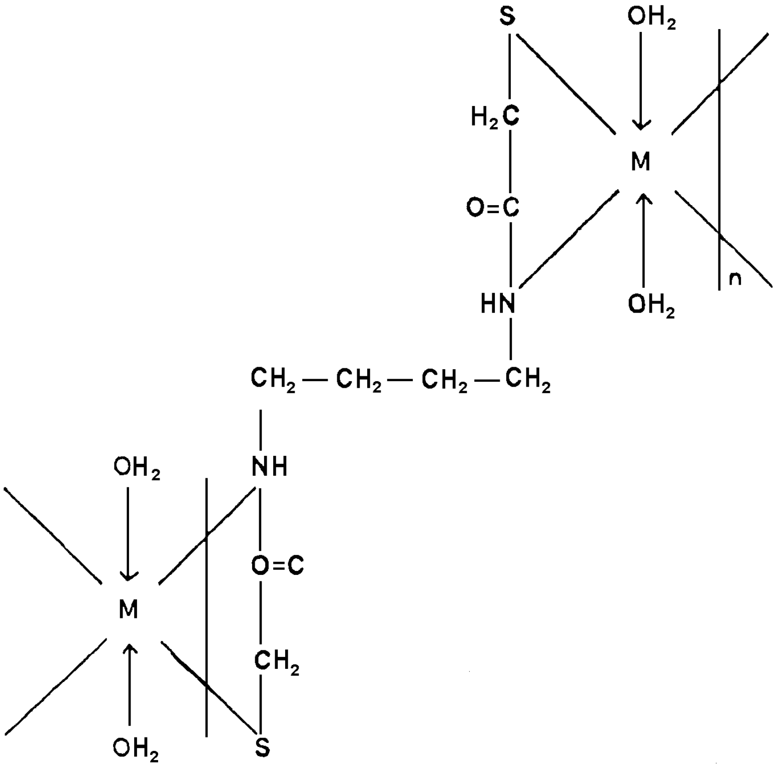
RESULTS AND DISCUSSION

All the chelates are coloured amorphous solids, air-stable, non-hygroscopic and insoluble in water and common organic polar and non-polar solvents indicating their polymeric nature. All the chelates gave satisfactory C, H, N, S and M analyses and revealed that all the chelate polymers have general formula $[ML]_n$. The reaction pathway for synthesis of chelate polymers is shown in Scheme 1.

The IR spectrum of BMADB exhibits a band at 3330 cm^{-1}, which may be assigned to NH stretch, which is shifted to a lower frequency region by 10–20 cm^{-1} in the chelates, indicating the involvement of amido nitrogen on coordination [8]. The medium strong band of ligand appearing at 1630 cm^{-1} due to C=O stretching remains at same position in all complexes, suggesting the non-participation of oxygen of C=O in the coordination [9]. The medium strong band at 2620 cm^{-1}, due to SH group in the free ligand, disappears in the metal chelates indicating the deprotonation of the SH group and the formation of M–S bond [10]. The shifting of band at 1470 cm^{-1}, due to $S–CH_2$ to lower wavenumber (1420 cm^{-1}), also supports the formation of M–S bond by the replacement of SH proton [11]. The bands observed in the range 2650–2950 cm^{-1} are attributed to aliphatic asymmetric stretching of methylene group [12]. The appearance of new bands in the regions 410–560 and 340–360 cm^{-1} are assigned to M–N and M–S vibrations in chelates respectively, confirming the coordination through the deprotonation of thiol sulfur and amido nitrogen [13]. The broad band, observed in all chelates except Cd(II) at around 3400–3500 cm^{-1}, is due to ν OH of water molecules. In the spectra of Co(II) and Ni(II) chelates, additional peaks in the range of 1569–1585 cm^{-1} and 700 cm^{-1} have been observed, which are attributed to the presence of coordinated water molecules, further confirmed by TGA.

Scheme 1

$$H_2N\text{-}(CH_2)_4\text{-}NH_2 \quad + \quad 2SH.CH_2.COOH \xrightarrow[M[CH_3COO]_2\cdot nH_2O]{H_2SO_4/MeOH}$$



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).
For Mn(II), Cu(II), Zn(II) and Cd(II) coordinated H_2O molecules absent

The electronic spectra of Mn(II) chelate exhibit three bands at 19993, 21230 and 23255 cm^{-1}, due to $^6A_1 \rightarrow {}^4T_1$ (G), $^6A_1 \rightarrow {}^4T_2$ (G) and $^6A_1 \rightarrow {}^4A_1$, ^4E (G) transitions respectively, suggesting the tetrahedral environment around Mn(II) ion [14]. The magnetic moment value (5.12 B.M.) of Mn(II) chelate also favours the tetrahedral geometry. The diffuse reflectance spectra of Co(II) chelate exhibits the d-d bands at 8800, 17730 and 23310 cm^{-1} due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively, in conformity with octahedral stereochemistry around Co(II) ion. The magnetic moment of Co(II) chelate (5.30 B.M.) is also indicative of high spin octahedral structure [15]. Since spin only value for three unpaired electron is only 3.99 B.M., the high value in the present case may be attributed to a high orbital contribution [16]. The magnetic moment of Ni(II) chelate (3.10 B.M.) is in agreement with an octahedral geometry [11]. The slightly higher value than the spin only value (2.83 B.M.) may be due to either the paramagnetic interaction in the clusters or to Jahn-Teller distortion or both these factors. The electronic spectra of Ni(II) chelate exhibit three bands at 11000, 16583 and 23255 cm^{-1} due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively indicative of octahedral geometry [17]. The electronic spectra of Cu(II) chelate show three bands at 16584, 19083 and 23310 cm^{-1} due to $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{2g} \rightarrow {}^2E_g$ and C.T. transitions respectively, suggesting planar geometry [18]. The magnetic moment (1.87 B.M.) of Cu(II) chelate is slightly higher than the spin only value for single unpaired electron [19]. The Zn(II) and Cd(II) chelates are found to be diamagnetic as expected for d^{10} ion system and may have tetrahedral geometry [19,20].

The study of the thermal behaviour of all the polymers in air provides information about its thermal stability and nature of degradation of products at various temperatures. Thermal decomposition results revealed that all the chelates decompose gradually. The elimination of lattice and coordinated water molecules takes place in the first stage. In the present study Co(II) and Ni(II) polymers exhibit the weight loss near 170–190°C equal to 8.91% and 9.52% (calcd. 10.91% and 10.87%) respectively, which corresponds to two coordinated water molecules per repeating unit of chelates [21]. Then, a continuous mass loss is observed up to 540°C, indicating the decomposition of the organic part of the chelates. Above this temperature, TG curve attains the constant level corresponding to metal oxides Co_3O_4 (22.11% found, 24.32% calcd.) and NiO (22.01% found, 22.56% calcd.). In the case of Mn(II), Cu(II) and Zn(Il) polychelates the weight loss at about 110–130°C equals to 5.23, 4.98 and 4.90% (calcd. 5.85, 5.69 and 5.60%) respectively, corresponds to one water molecule [22]. The decomposition is completed at 520–590°C, forming Mn_3O_4, CuO and ZnO. In the Cd(II) polymer there are neither lattice nor coordinated water molecules. This chelate is stable up to 220°C and then exhibits a gradual mass loss up to 530°C, which may be due to thermo-oxidative degradation and formation of volatile products from the polymer melt and residue left as metal oxides [23,24].

The thermal activation energy has been calculated by both Freeman-Carroll [25] and Sharp-Wentworth [26] methods and the values obtained are given in Table 1. It is

Table 1. Thermal and electrical data of BMADB chelates.

Compound	Decomp. Temp.	Activation energy* ($Kcalmol^{-1}$)		–Δ S	Δ F	Z	–S*	Order of reaction	Elect. conductivity (σ)	Activation Energy
	(°C)	FC*	SW*	cal K^{-1} mol^{-1}	k cal mol^{-1}	S^{-1}	k cal $K^{-1}mol^{-1}$	(n)	$ohm^{-1}cm^{-1}$(K)	(Ea)eV
$\{[Mn(BMADB)]\cdot H_2O\}_n$	390	6.86	6.86	63.88	26.21	31.10	53.20	0.50	8.45×10^{-6} (373) 3.70×10^{-2} (453)	1.02
$[Co(BMADB)]\cdot H_2O]_n$	290	7.11	6.23	63.12	26.24	39.88	48.95	0.50	9.90×10^{-5} (373) 2.38×10^{-2} (453)	0.93
$[Ni(BMADB)]\cdot H_2O]_n$	300	6.59	6.23	76.77	29.85	34.24	53.01	0.50	2.84×10^{-8} (373) 5.42×10^{-4} (453)	0.80
$\{[Cu(BMADB)]\cdot H_2O\}_n$	320	6.86	7.62	70.06	28.08	42.21	56.60	0.50	2.66×10^{-3} (373) 6.26×10^{-2} (453)	0.79
$\{[Zn(BMADB)]H_2O\}_n$	380	9.14	9.97	70.40	30.48	30.76	48.63	0.50	1.13×10^{-3} (373) 1.02×10^{-1} (453)	0.75
$\{[Cd(BMADB)]H_2O\}_n$	370	7.40	7.48	72.88	29.48	28.81	53.35	0.55	3.46×10^{-2} (373) 2.67×10^{-2} (453)	0.34

* FC: Freeman-Caroll, *SW: Sharp-Wentworth.

seen that the degradation of polychelate at elevated temperature is a complex process. The thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), apparent entropy (S^*) and frequency factor (Z) have also been calculated using transition state theory and the values are nearly same for each chelate, which indicates a similar type of reaction in all polychelate (Table 1). The negative value of ΔS indicates that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal. The lower values of the frequency factor suggest that the decomposition reaction of the polychelate can be classified as the slow reaction [27].

The d. c. electrical conductivity of all chelate polymers were measured over a wide range of temperatures in a pellet form and the values are given in Table 1, including the activation energies. The resistance values of the pellets of the sample, ranging from room temperature to 225°C, were converted into conductivities (σ). Generally, the diameter of the pellet remained constant, since the same die was used and the thickness varied according to the amount of sample pressed. In all cases, the plots of log σ *versus* 1/T are linear, indicating that these polychelates are semiconducting. In the electrical conduction domain, the temperature dependence of electrical conductivity obeys the equation [28] $\sigma = \sigma_0 \exp(-Ea / kT)$. From the analysis of our results, it can be assumed that the difference in electrical properties of the polychelates studied are determined mainly by their chemical structure [29]. Activation energy of electrical conduction of chelates has been found to be increased in the order Cd < Zn < Cu < Ni < Co < Mn. The small activation energy observed may be attributed to the interaction between the electrons of d-orbitals of the cations and π-orbitals of the ligand. This interaction will localize the π-electronic charge on the ligand molecule [30].

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