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Coordination Polymers of Be(II), Zn(II), Cd(II) and UO_2(VI) with Terephthalaldehyde bis-(4-phenylthiosemicarbazone) as a Ligand

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Introduction

In earlier communications (MAURYA et al 1978a, 1978b) the syntheses and characterizations of neutral chelates of several bivalent metal ions with 4-phenylthiosemicarbazide, and coordination polymers of Co(II), Ni(II), and Cu(II) involving Schiff base obtained by condensation with terephthalaldehyde have been described. In this communication, the polymeric chelates of beryllium(II), zinc(II), cadmium(II), and uranyl(VI) with the Schiff base (terephthalaldehyde bis-(4-phenylthiosemicarbazone; TPBPTS) are being reported.

Experimental

TPBPTS was prepared as reported earlier (MAURYA et al 1978). $BeSO_4.4H_2O$, $Zn(CH_3COO)_2.2H_2O$, $Cd(CH_3COO)_2.2H_2O$ (all BDH), and $UO_2(CH_3COO)_2.2H_2O$ (Baker AnalaR), and solvents of reagent grade were employed.

1.08 g of TPBPTS dissolved in 100 ml hot dimethylformamide was added slowly to an equivalent amount of metal salt solution also in dimethylformamide. The mixture was refluxed at 130° for ca 2h and left overnight. The separated solid was filtered, washed successively with dimethylformamide and ethanol, till the filtrate was colourless. The product was finally washed with ether, and dried over calcium chloride under reduced pressure.

The compounds are powdery in appearance, insoluble in water and in common organic solvents viz. ethanol, acetone, benzene, nitrobenzene, chloroform, dimethylformamide, and dimethylsulphoxide. The colour, temperature of decomposition, and analytical data of the complexes are as follows :

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TABLE 1

Colour, Temperature of Decomposition, and Composition of the Complexes

Empirical formula	Colour	Dec. temp. (°C)	Elemental analyses (%) Found (calc.) M	C	H	N
$BeC_{22}H_{18}N_6S_2$	Yellow	280	1.9 (2.1)	61.0 (60.1)	4.0 (4.1)	19.9 (19.1)
$ZnC_{22}H_{18}N_6S_2$	Red	360	13.0 (13.1)	54.1 (53.3)	4.1 (3.6)	17.5 (17.1)
$CdC_{22}H_{18}N_6S_2$	Yellow	280	20.3 (20.7)	49.3 (48.7)	3.7 (3.3)	16.9 (15.5)
$UO_2C_{22}H_{18}N_6S_2$	Yellow	260	32.5 (34.1)	38.1 (37.8)	3.0 (2.6)	13.1 (12.0)

The i.r. spectra were recorded using KBr pellets. The compounds were heated upto 800° at a rate of 10° min^{-1} for thermogravimetry.

Results and Discussion

The complexes correspond to the general formula: $-(ML)_n-$ (where M = metal ion, L = $C_{22}H_{18}N_6S_2$, and n = degree of polymerization). The thermal stability data show that the decomposition of the complexes starts at 280° (Be), 360° (Zn), 280° (Cd) and 260° (UO_2), and the complete decomposition of the ligand takes place at ~640° with the formation of the metal oxides.

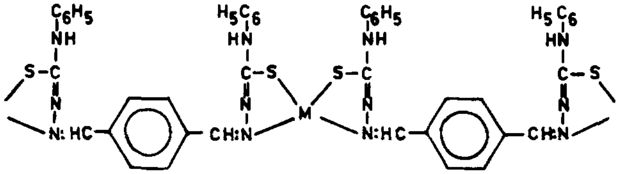
The strong absorption bands near 3480 and 3440 in the i.r. spectra (wave numbers expressed in cm^{-1}) of both the ligand and the complexes are due to the N-H stretching vibrations (Table 2). The intense band at 1680 may be assigned to C=N stretching vibration in the free ligand. It shows a positive shift towards the higher frequency region in the spectra of the metal - complexes (an additional band is observed near 1700). This may be due to the presence of one free C=N group, while the other one is coordinated to the metal ion. The shifting of the band towards higher frequency region indicates the increase in bond order of the coordinated C=N group due to the back donation of the pi-electrons by the metals (BURGER et al 1965, BURGER 1966). The spectrum of the ligand shows the bands at 1480 and 1430 which are assigned to C=S and N-C-N stretching. These bands are absent in the spectra of the complexes due to a likely change of C=S to C-S and N-C-N to N-C=N on complexation (ALI and BOSE 1977, CHAKRAVARTY and DRINKARD 1960, MURCU and DIMA 1968).

TABLE 2

I.r. spectra of TPBPTS and the complexes

TPBPTS	Be(II)	Zn(II)	Cd(II)	UO_2(VI)	Assignments
3480	3480	3480	3480	3475)	νN-H
3440	3430	3435	3440	3440)	
1680	1690	1695	1710	1695)	νC=N
	1675	1685	1680	1675)	
1480	....	....	....	....)	νC=S &
1430	....	....	....	....)	νN-C-N
....	650	625	630	635	νM-N
....	580	545	545	540	νM-S

It is thus evident that TPBPTS acts as tetradentate chelating agent coordinating through the thiolo sulphur and nitrogen of the (C=N) group of the Schiff base. Polymerization is achieved since steric factors prevent the coordination of all the donor groups to a single metal ion, and the metal ion acts as a bridging unit between two donor groups of the ligand. Thus the polymeric chain grows through the consecutive TPBPTS-metal linkage. The polymeric chelate (I) is neutral, since the protons from the SH groups remain ionized.



I. Polymeric metal-complex

The geometry of the ligand, the extreme insolubility of the complexes, and the thermal stability data indicate the polymeric nature of the complexes, as noted in some other coordination polymers (MAURYA et al 1977, 1978; BANERJIE and DEY 1979).

Summary

Polymeric metal-complexes $-(ML)_n-$, of Be(II), Zn(II), Cd(II) and UO_2(VI) with terephthalaldehyde bis-(4-phenylthiosemicarbazone) (TPBPTS) have been synthesized, and the composition, structure, and thermal stability are described. The complexes are coloured, powdery, and insoluble in water

and in common organic solvents. TPBPTS molecules act as tetradentate chelating agent, coordinating through the thiolo sulphur and nitrogen of the C=N group of the Schiff base. The metal ion acts as a bridging unit between two donor groups of the ligand, and the polymeric chain grows through consecutive TPBPTS-metal linkage. The order of thermal stability is : Zn > Be > Cd > UO_2.

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