IR SPECTRA STUDIES OF COORDINATION POLYMERS PREPARED BY UREA BISDITHIOCARBAMATES

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ABSTRACT

Dithiocarbamates (DTCs) have been a subject of major research in the past decade and a number of these compounds have been prepared. *A series of Coordination polymers were synthesized with Co (II), Ni (II), Zn (II), Pb (II), and Hg (II.) and their IR spectral shifting was studied. The disodium salts of bisdithiocarbamates had been prepared from urea, to prepare multidentate ligand. Elemental analysis, Electronic, Infrared (IR) spectroscopy evidenced the formation of coordination polymers and multidentate ligands. In present paper author wants to emphasize that Infrared spectral analysis is changing the geometry of a dithiocarbamate group from bidentate ligand to monodentate ligand by shifting many important bands.*

Keywords: Bisdithiocarbamates, Coordination Polymers, Infrared (IR) Spectroscopy, Multidentate Ligands,

I INTRODUCTION

Sulphur and nitrogen containing compounds act as multidentate ligands and usually produce coordination polymers with high thermal stability [1-4] and sometimes electrical conductivity due to the presence of heteroaromatic ring.[5-9] Dithiocarbamates are S , N containing Ligands which display a rich and varied coordination chemistry providing a wide range of transition and main group metal complexes many of which have important chemical and biological properties. [10] In the present paper synthesis and complexation behaviour of Ureabisdithiocarbamate reported towards various transition metal ions namely Co (II), Ni (II), Zn (II), Hg (II), and Pb (II) has been investigated. The characterization of the resulting complexes with IR spectral analysis and conclusive changing the geometry of a dithiocarbamate group from bidentate to monodentate shifts.

II EXPERIMENTAL

2.1 Materials

Acetates of Co (II), Ni (II), Hg (II) Pb (II) , Zn (II), and Cobalt (II) chloride and cobalt (II) sulphate of analytical quality products were used for the synthesis of metal complexes.

2.2 Preparation of Metal Complexes of Bisdithiocarbamates

Metal complexes of various bisdithiocarbamates were prepared by mixing of aqueous solutions of ligands and metal salts in equimolar ratio. For the coagulation of fine particles in every case, the mixture was stirred magnetically for 10 min and then kept overnight at room temperature, filtered, washed thoroughly with water and dried.

2.3 Measurements

IR spectra of metal complexes were recorded on a Perkin- Elmer spectrometer model 1430 in 4000-600 cm^{-1} range using KBr as dispersant.

III RESULTS AND DISCUSSION

The yield, colour and elemental analysis for various metal complexes of UBDT are reported in Table 1. The approximate yield all the complexes is 55-60 %. All the complexes are stable at room temperature, unaffected by atmospheric oxygen and moisture and are insoluble in water as well as common organic solvents. The complexes appeared to be amorphous even on microscopic examination. The complexes do not melt on heating up to 360^{o}C, however, many of them became black above 200^{o}C.

Usually the dithiocarbamate complexes have been reported to be crystalline compounds soluble in organic solvents and have well defined melting points. Although the results of elemental analysis for bisdithiocarbamate in the present study were reproducible but close agreement with the theoretical calculation based on assumed structures could not be obtained. This observation along with amorphous morphology and insoluble nature suggested the polymeric structure for these complexes which was expected for the multidentate ligands prepared.

Table 1: Physical and Analytical Data of Coordination Polymers of UBDT ^{a}

					Elemental Analysis found (Calculated)				
Complex	MOLECULAR FORMULA	COLOUR	MELTING POINT^{O}C	YIELD %	C %	H %	N %	S %	METAL %
CoAcUBDT	$C_{16}H_{20}N_4O_{14}Na_2Co_3$ ($L_2Ac_6Na_2Co_3$)	Dark purple	220^{b}	57	18.9 (19.2)	2.32 (2.00)	5.8 (5.6)	25.4 (25.6)	16.9 (17.7)
$CoCl_2$UBDT	$C_6H_4N_4O_2Na_2Co_3Cl_6$	Light purple	180^{b}	53	7.9 (8.4)	0.93 (0.46)	6.0 (6.6)	29.09 (30.01)	19.2 (20.6)

CoSO$_4$UBDT	$C_6H_4N_4O_{10}Na_2Co_3$ $H_2O(SO_4)_2$	Light purple	220^b	56	6.9 (7. 6)	1.50 (1.69)	5.8 (5.9)	32.15 (33.97)	18.3 (18.7)
NiAcUBDT	$C_{16}H_{20}N_4O_{14}Na_2Ni_3$ $L_2Ac_6Na_2Ni_3$	Light green	180^b	52	18.9 (19)	1.9 (2.0)	5.0 (5.6)	26.46 (25.70)	16.7 (17.4)
ZnAcUBDT	$C_{16}H_{20}N_4O_{14}Na_2Zn_3$ $L_2Ac_6Na_2Zn_3$	White	>360^{O}C	60	18.1 (18.8)	2.1 (1.9)	4.9 (5.5)	26.8 (25.1)	18.2 (19.3)
HgAcUBDT	$C_{16}H_{20}N_4O_{14}Na_2Hg_2$ $L_2Ac_6Hg_2Na_2$	Brown	>360	35	16.0 (15.7)	1.9 (1.6)	3.98 (4.58)	20.6 (20.9)	33.3 (32.8)
PbAcUBDT	$C_{14}H_{16}N_4O_{10}Na_2Pb_3$ $L_2Ac_4Na_2Pb_3$	White	>360	57	12.4 (12.6)	1.8 (1.2)	4.73 (4.23)	20.2 (19.3)	45.8 (46.9)

^{a} L = -SSCNHCONHCSS, Ac = CH_3COO^- ^{b} Does not melt but darken at the temperature mentioned

IV IR SPECTRAL ANALYSIS

The IR spectra of metal dithiocarbamate have been reported abundantly. [11-16] The IR data various metal complexes of UBDT are shows in Table 2 and Figure (2 and 3). Changing the geometry of a dithiocarbamate group from bidentate to monodentate shifts many important bands by 10-20 cm^{-1} and even in the case of unsymmetric bidentate ligand noticeable shifts occur in *v* C-N, *v* C- S and N- alkyl streching. v_{as}(CS) mode is thought to appear in 950—1050 cm^{-1} spectral region. In complexes containing mixed mono and bidentate bonding additional frequencies will be observed in the *v* C-N , *v* C- S and *v* C=S region.

A single symmetrical band suggests the presence of symmetrically-bonded (two equivalent CS bonds) ligands, while a split 1000 cm^{-1} band indicates asymmetrically bonded (two in equivalent CS bonds) ligands (unidentate or bidentate asymmetric).

The *v* (CN) for the thioamides appear at about 1500 cm^{-1} and the *v* (CN) for the UBDT under consideration is observed at about 1459 cm^{-1} was consistent with extensive electron delocalization rendering bond between nitrogen and carbonyl carbon equivalent to that between nitrogen and dithioate carbon. However, splitting of this band by more than 100 cm^{-1} is suggestive of coordination through oxygen as well as oxygen and the contribution of following canonicals structure predominates:

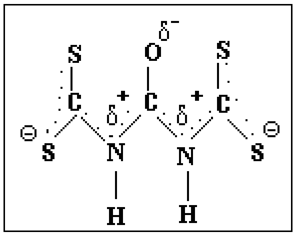

Fig. 1: Canonical Structure of UBDT

Table 2: IR Spectra Data of Coordination Polymers of UBDT [(a)]

Ligand Complex	***v*N-H+δO-H**	**δNH_2+*Vc*=O**	***v*C=N**	***v*C=S +SCN**	***v*C=S**	***v*C-S +NCO+C-N**
Co(II) AcUBDT	3485s, vbr	1690vw,sh	1490 vs 1413vs		830 m,sharp	687 m
Co (II)Cl_2UBDT	3443vs,vbr	1600sh	1490sh 1413sh	1070sh 977w	831 m,sharp	621 m,br
Co(II) SO_4UBDT	3489vs,vbr	1600sh	1475vs 1410sh		830 m,sharp	750 689
Ni (II) AcUBDT	3426mbr	1610sh	1490sh 1412.2s		843 w	700 w, br
Zn(II) AcUBDT	3412s,br	1600sh	1509vs 1386vs	953w	833 w, sharp	788 w 707w
Hg(II)AcUBDT	3421m,br	1615w,sh	1500sh 1405s	1029m	830 s, sharp	600 br
Pb(II)AcUBDT	3419m,br	1635 w	1425vs,br	1051w 992w	839 sharp	476 m

[(a)] vs = very strong, s = strong, vbr =very board, m= medium, sh = shoulder, vw = very weak

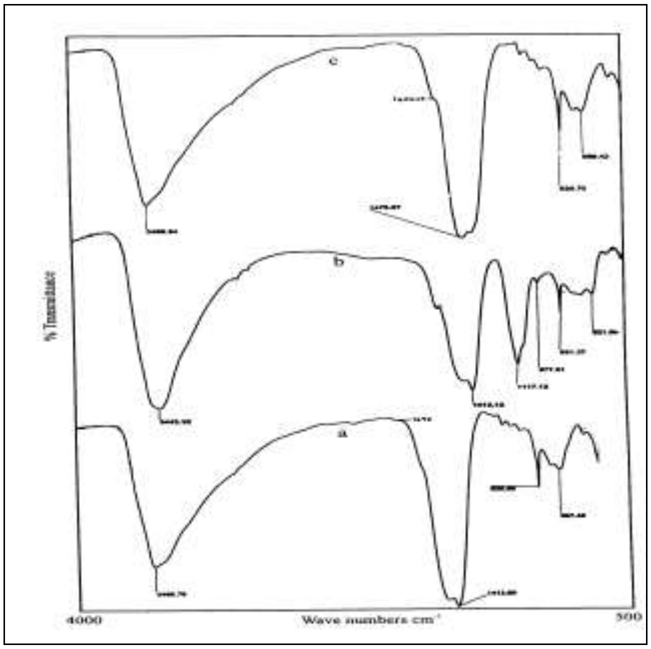

Fig. 2 : IR Spectra of (a) Co Ac UBDT (b) Co Cl_2 UBDT (c) Co SO_4 UBDT

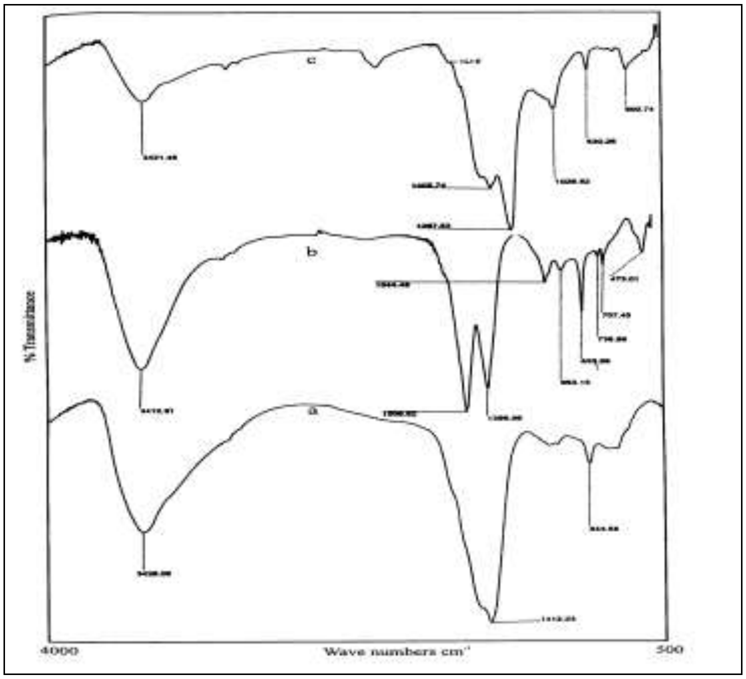

Fig. 3 : IR Spectra of (a) Zn Ac UBDT (b) Ni Ac UBDT (c) Hg Ac UBDT

The band at 1696 cm^{-1} in UBDT involves significant contribution from NH bending vibrations besides ν(C = O). This band either disappears or appears as a shoulder on broad thioamide II band suggesting coordination through nitrogen and carbonyl oxygen both.

A band at 1018 cm^{-1} has medium intensity and is broad, it may be assigned to asymmetric C—S stretching and a intense sharp band at 860 cm^{-1} may be assigned to symmetric C-S stretching. On complexation in most of the complexes the bands corresponding 1018 cm^{-1} band of UBDT appears with greatly decreased intensity, disappear in cobalt (II) acetate , cobalt (II) sulphate, and nickel (II) acetate complexes. Zinc (II) acetate and ceric sulphate complexes are shifted downward with weak absorption. In lead (II) acetate and mercuric (II) acetate complexes this band is shifted to slightly higher wavenumber with medium absorption in Hg (II) Ac UBDT and weak band show in Pb (II) Ac UBDT. However, the band at 860 cm^{-1} although experiences a downward shift but appears as a sharp band with slightly decreased intensity on complexation except for Ni (II) acetate complex where it is broader.

The intense bands due to carbonyl stretching get overlapped by δ OH from water molecules and disappears in all the complexes. Thus all these observations lead to conclude that all the donor atoms, *viz.*, O, N, and S are involved in coordination. Presence of water molecules in all the complexes is ruled out because the bands associated with water molecules are not observed in the IR spectra. Dithiocarbamate complexes can assume four structural geometries (Fig.4) :

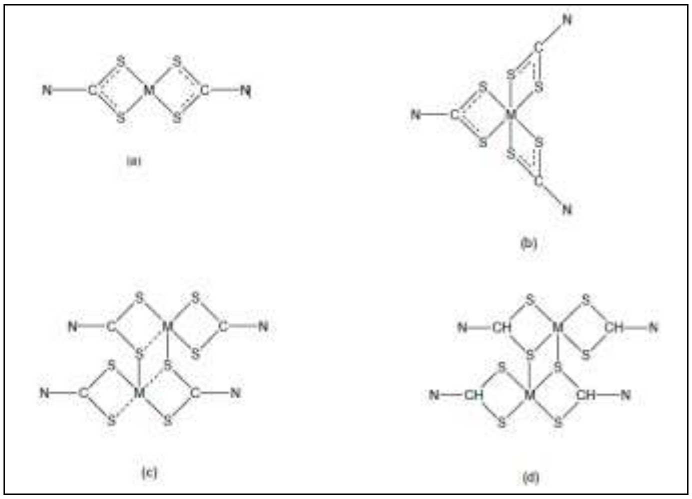

Fig.4: Dithiocarbamate complexes structural geometries

(a) The square planar coordination geometry

(b) The octahedral coordination geometry

(c) The four coordinate dimer

(d) The five coordinate dimer

V CONCLUSION

The various bisdithiocarbamate ligands exhibited excellent complexing ability towards various transition metal ions. The complexes obtained simply on mixing of the aqueous solutions of the respective ligands and metal ions were polymeric in nature, with high thermal stability.

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NOMENCLATURE

DTCs	Dithiocarbamates
UBDT	Ureabisdithiocarbamate
Co(II)AcUBDT	Cobaltacetatebisdithiocarbamate
Ni(II)AcUBDT	Nickelacetatebisdithiocarbamate
Hg(II)AcUBDT	Mercuricacetatebisdithiocarbamate
Zn(II) AcUBDT	Zincacetatebisdithiocarbamate
Co (II)Cl_2UBDT	Cobaltchloridebisdithiocarbamate
Co(II) SO_4UBDT	Cobaltsulphatebisdithiocarbamate

Bibliography Notes

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