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Coordination Compounds with Biomimetic N_2S_2 Donor Ligands, II: Synthesis and Characterization of Group II-B Metal Complexes of Benzil Dithiosemicarbazone

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Complexes of benzil dithiosemicarbazone (BDTSC) with zinc (II), cadmium (II) and mercury (II) have been prepared and characterized on the basis of elemental analyses, conductivity and infrared spectral studies. IR spectral data suggest that BDTSC acts as dibasic quadridentate ligand in all complexes, the bonding sites being the two enolic sulphur and two azomethine nitrogen atoms to have $M-N_2S_2$ coordination core. Hence Zn-BDTSC may be regarded as structural model for the proposed active centre present in TF IIIA. Only Cd-BDTSC forms bipyridyl adduct.

Although transition metal complexes[1-6] with ligands containing N_2O_2 and N_2S_2 donor atoms have been studied extensively, group II-B metal chelates with N_2S_2 ligating atoms and serving as model compounds have received little attention. Recently transcription factor IIIA is discovered as zinc cysteine protein[7-9] and known to contain ZnS_2N_2 core which displays a structural role in creating nine binding fingers which enables the protein to bind to DNA. In view of importance of group II-B metal complexes with ligands possessing N_2S_2 donor atoms, we considered worthwhile for the synthesis and characterization of zinc, cadmium and mercury (II) complex with benzil dithiosemicarbazone (BDTSC).

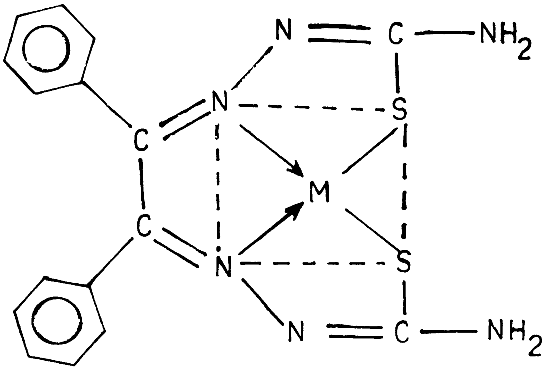
BDTSC was prepared as described earlier[5]. Metal complexes were prepared by refluxing a reaction mixture containing metal salt solution (100 ml of 0.01 M prepared in deionised water), BDTSC (100 ml of 0.01 M prepared in hot methanol) and NaOH (3 ml of 0.1 M prepared in methanol) for 30 min. The reaction mixture was cooled and the complex precipitated filtered off, washed with 1 : 1 hot aqueous methanol and dried at 80°C in electric air oven. The metal salts ($ZnCl_2$, $Cd(CH_3COO)_2$ and $HgCl_2$) used were of AR grade.

Elemental analyses indicate the formation of 1 : 1 (M: BDTSC) complexes of molecular formula [M(BDTSC)]. All complexes decompose in the 210–280°C temperature range. These complexes are soluble in DMF and DMSO and found to be non-electrolytes in former solvent.

In infrared spectrum of BDTSC highest frequency band observed at 3422 cm^{-1} is assigned to the assymetric stretching vibration of terminal $-NH_2$

group. The other bands at 3380 and 3229 cm^{-1} are due to the superimposed form of symmetric (NH) bands of amino and imino groups. The band at 3380 cm^{-1} in the spectrum of BDTSC has been assigned to secondary -NH group[10] absent in all complexes. The IR spectra of metal chelates show the presence of highest band around 3440 cm^{-1} indicating the non-participation of terminal nitrogen atom in coordination. In the spectrum of BDTSC a strong and sharp band is located at 1605 cm^{-1} assignable to amide I and NH_2 bend[11]. In all complexes a new band is observed at 1570 ± 5 cm^{-1} due to the participation of azomethine nitrogen atom in chelation. In the spectra of all complexes, new bands are observed at 1610 ± 5 cm^{-1} attributable to the contribution of terminal NH_2 or >C=N– groups that are in thiol form. Strong and sharp bands are observed at 1295 and 747 cm^{-1} due to νC=S vibration in the infrared spectrum of BDTSC. These bands disappear in all metal complexes and instead new bands arise around 645 cm^{-1} characteristic of νC–S vibration formed in complexes[12]. The absence of bands in the ligand spectrum in the 2800–2650 cm^{-1} region indicates that BDTSC remains in thione form in solid state. These facts are compatible with the enolization of the NH–CS–NH_2 group in the ligand to form –N=CSH–NH_2, which then loses the thiol protons to form a covalent bond between metal and sulphur. Metal ligand vibrations are difficult to assign on empirical basis, since their frequencies are sensitive to both metal and ligand and often couples with low frequency modes in metal complexes. However coordination through sulphur atom is further corroborated[13] by the appearance of M–S vibration in the region 325–337 cm^{-1} in far-infrared spectra of metal complexes.

The observed magnetic moment value (1.8 BM) and elctronic spectra (weak bands in the region 10000–12000 cm^{-1}) for Co-BDTSC suggest squareplanar (or distorted tetrahedral) stereochemistry[14]. The structures of diamagnetic and spectroscopically silent metal complexes (for *e.g.*, Zn complexes) have been solved by studying cooresponding cobalt complexes of the same ligand. Then the present complexes are expected to have the configuration with that of Co-BDTSC complex. Based on the above discussion squareplanar geometry (I) is assigned for the present complexes.



(I)

where M = Zn(II), Cd(II), or Hg(II)

Several attempts have been made (by us) for the preparation of pyridine and bipyridine adducts of Zn-BDTSC and HG-BDTSC and got parent compound, possibly due to the preference of zinc and mercury to remain in tetragonal geometry. However, Cd-BDTSC gives an adduct [1 : 1 (Co-BDTSC): bpy] with 2,2′-bipyridyl (bpy) to give 6-coordinate complex. This adduct has been characterized by its infrared spectrum (1629 and 1596 cm^{-1} due to >C=N– skeletal vibrations of bpy ring present in the adduct].

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