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Physicochemical Investigations on the Complexation of Dithiolterephthalic Acid with Heavy Metal Ions. V. Infrared Spectra of Complexes with Zinc(II), Cadmium(II), Mercury(II), Lead(II), and Copper(II)

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Complexes of dithiolterephthalic acid with Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, and Cu^{2+} have been prepared in aqueous unbuffered medium. Infra red spectrum of the solid compounds were scanned (4000-650 cm^{-1}) and analysed for determining the mode of complex formation and structure elucidation. The study has evidence the coordination of metal through the sulphydryl group. The shifts in the carboxylate frequencies as a function of M show that the order of strength of metal-ligand cordination is $Zn > Cd > Hg$. The presence of ionic $-COS^-$ group in the case of disodium salt of dithiolterephthalic acid and linear polymer structures for Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, and Cu^{II} complexes have been suggested.

Dithiolterephtalic acid, which figures prominently in the discussion of organo-sulphur compounds, has significant industrial and pharmaceutical importance. Interesting results pertinent to its polarographic behaviour[1] and interaction with various metal ions have already been reported, in which 1:1 complex formation has been concluded electrometrically.[2-5] The present investigation has been carried out to obtain further information about metal ion interaction with the dithiolterephtalic acid. Salient features of intra red spectra of the ligand and complexes formed–Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, and Cu^{II} ions with dithiolterephthalic acid–are reported.

Experimental Section

All reagent were of analytical grade. Dithiolterephthalic acid was obtained as gift sample from Evan's Chemetics, Inc., New York. It is an insoluble compound and its disodium salt was prepared by digesting known weight of dithiol with requisite amount of NaOH, which took about 3-4 days.

Infra red spectra of solids were recorded with Perkin Elmer infracord (Model 137-E) in nujol mulls using kBr optics. The results have been summarised in Table I.

Preparation of dithiolterephthalic acid complexes of divalent ions. To a 50 ml solution 0.05 M in inorganic salt was added, with gradual stirring, 50 ml solution 0.05 M in disodiumdithiolterephthalate. The resultiyng precipitate was filtered, washed and sucked dry in vacuum. The filtrate was collected and examined polarographically for –SH group and metal-ion, their absence in the filtrate indicated the complete interaction between the reactants. Under similar conditions the metal ion and ligand were mixed in a 1:2 molar ratio and again the filtrate was examined polarographically. The presence of one mole of ligand in the filtrate ruled out the possibility of 1:2 complex formation.

Results and Discussion

The infrared spectra of the compounds have been discussed regionwise and tentative band assignments were made on the basis of the existing literature.[6-8] The spectra of the compounds were recorded in nujol mulls.

2910-2880 cm^{-1} Region. This region has been assigned to νC–H in nujol, which is overlapped with νC–H arising from C–H stretching vibrations of the ligand. As the spectra of ligand and metal complexes are recorded in nujol it is, therefore, difficult to distinguish between the νC–H arising from nujol or from the phenyl ring.

2470 cm^{-1} Region. Most of the thiols show absorption around 2600-2550 cm^{-1}, assigned to νS–H. The aryl as well as the alkyl thiols show weak intensity absorption bands in practically the same region *i.e.* 2600-2500 cm^{-1}. But the presence of the $>C=O$ group attached to –SH shows marked hydrogen bonding properties[9] (inter or intramolecular

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(1) Pandey A.V. and Mittal M.L., *Indian J. Chemistry*, 9, 449 (1971).

(2) Pandey A.V. and Mittal M.L., *Zeit. fur Naturforschung*, (1971) (in press).

(3) Pandey A.V., and Mittal M.L., *Monatschefte fur Chemie.*, (1971) (communicated).

(4) Mittal M.L. and Pandey A.V., *Experientia*, (1971) (communicated).

(5) Mittal M.L. and Pandey A.V., *Zeit. anorg. und allegem. chemie* (1971) (communicated).

(6) Cross A.D., Introduction to Practical Infrared Spectroscopy. 2nd Edn., Butterworth and Co., 1964.

(7) Roberts J.D. and Caserio M.C., « Basic Principles of Organic Chemistry ». W.A. Benjamin, Inc., 1964, pp. 747-754.

(8) Bellamy L.J., « Infrared Spectra of Complex Molecules » 2nd. Ed., John Wiley and Sons, Inc., New York, N.Y., 1958.

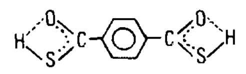
(9) Bellamy L.J., « Advances in Infrared group frequencies » Methuen and Co. Ltd., 1968.

Table I. Absorption bands of dithiolterephthalic acid and its metal complexes.

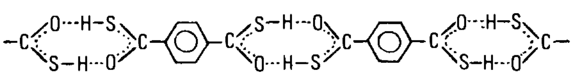
A Dithiol terephthalic acid.	B Di sodium salt	C ZnL	D HgL	E PbL	F CuL	G CdL	Band assignment
2897s	2894s	2890s	2890s	2913m	2897s	2899s	νC—H
2470w	—	—	—	—	—	—	νS—H
1685s	1547m	1528s	1679m	1687m	1685m	1587s.b	νC=O
1657sh	—	—	—	—	—	—	Intramolecular hydrogen bonding.
1492w	1458m	1461vw	1456s	1451vw	1454m	1464w	$\nu_{as}COS^-$
1391w	1366m	1369w	1369s	1365m	1367w	1389m.b	ν_sCOS^-
1192s	1190m	1210s	1190m	1185s	1280vwb	1205s	ρC—H+1:4φring substitution.
1107vw	1123vw	1125vw	—	—	1188w	—	
980m	1007vwb	951m	—	1000vw	—	1000s.b	δC—H+1:4φring substitution.
867m.b	940w	837s	882vw	889wb	—	—	

The following abbreviations were used: s = strong, m = medium, w = weak, vw = very weak, Sh = shoulder and b = broad. L = Ligand molecule.

hydrogen bonds). The infrared spectrum of the dithiolterephthalic acid shows absorption around 2470 cm^{-1} (w) which has been tentatively assigned to νS–H. This value is much less than what might be expected from the unchelated dithiol. The down shift of 80 cm^{-1} in νS-H reveals the presence of inter or intramolecular hydrogen bonds in the ligand.



Intermolecular hidrogen bonded ligand.



Intramolecular hydrogen bonded ligand.

The insolubility of dithiolterephthalic acid in various organic solvents has precluded further spectral studies as to the nature of the hydrogen bonds.

The disodium salt of dithiolterephthalic acid shows no absorption in the region 2600-2470 cm^{-1} which is indicative of the absence of –SH group in the disodium salt.

Further, the infrared spectra of Zn^{II}, Cd^{II}, Hg^{II}, Pb^{II}, and Cu^{II} complexes of dithiolterephthalic acid show the disappearance of –SH stretching frequencies suggesting that the complexation is taking place through the sulphur atom of –SH group.

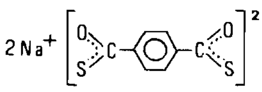
1685-1540 cm^{-1} Region. The absorption bond in the spectrum of dithiolterephthalic acid around 1685 cm^{-1}, assigned to νC=O, shows the presence of the unionised –COSH group. The appearance of a shoulder at 1657 cm^{-1} substantiates the existence of inter or intramolecular hydrogen bonding.

In the case of the disodium salt of the ligand the absorption band, occurred at 1685 cm^{-1}, shifts to 1547 cm^{-1} (m) which may be due to the νC=O arised from –COS$^-$ group.

Further, the cordination through the carbonyl oxygen has been indicated by the decrease in νC=O in zinc,, cadmium, and mercury complexes; this shows the presenec of four-coordinated metal. However, in case of lead and copper complexes there is no significant change in νC=O (Table I), which means that they are two-coordinated derivatives.

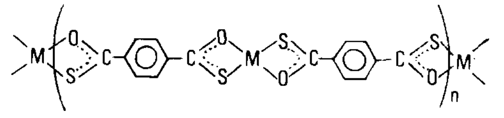
The frequencies lower than 1500 cm^{-1} have been originated from the asymmetric and symmetric stretching of –COS$^-$ (1490-1350 cm^{-1}) and in-plane (φ) and ouf-of-plane (δ) deformation as well as phenyl ring vibrations (1:4 substitution).

In view of the above the following tentative structures of the disodium salt of dithiolterephthalic acid and the metal complexes have been proposed:

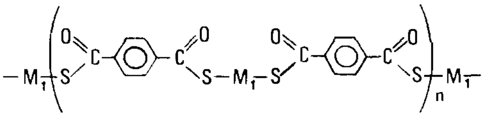


(B)

Ion-pair formation in disodium dithiolterephthalate



Linear polymer (where M = Zn, Cd, Hg; represented in Table I by C, G, and D)



Linear polymer (where M$_I$ = Pb, Cu; represented in Table I by E and F).

The formation of an ion-pair in case of disodium dithioelterephthalate has been further shown by its solubility and appreciable electrical conductivity in aqueous medium.

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