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Metal Complexes of N^1 (4-Chloro)- Phenyl-N^4- (3,5-Dinitro) - Benzoyl- Thiosemicarbazide

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Abstract

This paper deals with sunthesis of N^{l}-(4-Chloro)–phenyl-N^{l}-(3,5-dinitro)-benzoylthiosemicarbarbazide (CDTS) and complex formation with CDTS employing Fe (II), Co (II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and UO_2 (VI) metal ions The complexes are coloured, voluminous, powdery solids, in- Soluble in water and in organic solvents. CDTS complexes have a composition $(ML2H_2O)_n$ where M=Mn (II)Co (II), Ni (II) Cu(II) and Zn (II) and $(ML)_m$ for M=Cd (II), Pb (II) and UO_2(VI).

Introduction

The synthesis of transition metal complexes of ithiosemicarbazides and thiosemicarbazones of 2-pyridinaldehyde isatin, 1- methyl isatin, pyruvic acid, salicylaldehyde, methyl pyruvate, 8-quinonilaldehyde, acetone, cyclohexanone and 3-ethoxy-2-oxobutananone, and is characterized with them by thermal, X-ray, magnetic and spectral have been studies by Drunkard and Chakravarti prepared bis-thiosemicarbazone of terathalaldehyde and naphthazarin and synthesized their polymeric Zn (II) and Ni (II) complexes. The coordination polymers of isophthalaldehyde-bis- (thiosemicarbzone) and terphthalaldehyde–bis thioseimicarbazone with Cd (II) and Hg (II) were prepared by Murcu and Dima and the thermal stability and semiconducting properties of complexes were studied. 4-phenul thiosemicarbazide was used to synthesize thiozolidones by Saha et al. Saha and Trivedi and its salicylaldehyde derivative was used to study the complex formation with VO(IV), CU(II) and Ni(II) using potentiometry. Jain et al. studied the magnetic and spectral properties of Cu (II) complexes of ά pyridylthiosemicarbazide and predicted sqare planar or distorted octahedral symmetry for the metal in the complexes. Recently, 4-phenylamidothiosemicarbazide has been synthesized and its Ru (III), Rh(III), Pd(III), Os(VIII) and Pt (II)complexes has been reported. The synthesis and characterization of the complexes of Mn (II), Fe(II),Co(II), Ni(II),Cu(II), Zn(II), Pb(II), Cd(II) and UO2 (VI) with $N^{1'}$(4-chlorophenyl)-$N^{4'(}$3,5 dinitrobenzoyl)- thiosemicarbazide have been carried out. The Complexes of thiosemicarbazides with tranisition metal ions were first reported by Jensen and the complexes were characterized through study of the i.r. and electronic spectra and it was concluded that they may be either square planar ionic complexes or neutral chelates. Coordination occurs through terminal nitrogen and the thioketo sulphur in the case of ionic complexes, while in the case of neutral complexes, thioenolic sulphur atoms are involved. The worker Mashima and of Wailes and Suprunochuk, on i.r. spectra of thiosemicarbazide complexes kindled renewed interest on thiosemicarbazide and its derivatives as potential bidentate heteroligands. Some of them were tried for their medicinal use, and it was found that there is significant correlation between the antitumour activity of a group of heterocyclic aldehyde-thiosemicarbazones in animal systems and their metal chelating properties.

Experimental-

Synthesis of 4-Chlorophenylisothiocyanate;

To a mixture containing 24cm^{3}of carbondisulphide and 40 cm^{3}of ethanol, 45cm^{3}of chloroaniline was added; the mixture cooled in ice and 41 cm^{3}of liquor ammonia (sp.gr=0.88) was added dropwise with constant stirring. The temperature has a tendency to rise but there was taken that the temperature remained below 15^0. A milky suspension was obtained, which on standing the clear solution yielded a little ether. The crystalline solid was dissolved in 1500 cm^{3}of water and a solution of 87 g lead nitrate in 175 cm^{3}of water was added slowly, when a curdy white precipitate of lead dithiocarbonate separate out. This mixture was steam distilled, when 4-chlorophenyl isothiocyanate passed into the distillate and was collected in a receiver containing 5 cm^3 of N-sulphuric acid. The compound which is volatile with steam condenses to a solid in the condenser, from where it was removed, periodically, by stopping the flow of cold water around the condenser. The product was filtered, washed with water and dried at room temperature to yield shining white amorphous solid, m.p, 60.^{0}

Synthesis of N^1 (4-chlorophenyl)-N^4-(3,5diintrobenzoyl) thiosemicarbazide

A solution of 9.04 g of 3,5- dinitrobenzoylhydrazide in 100 cm^{3}of hot acetone was added, drop wise , to a 50 cm^{3}solution of 4-chlorophenyl- isothiocynate (8.56g.) in acetone, and was refluxed for Ca 4h. The thiosemicarbazide which separated out as a voluminous white solid, was filtered and washed with acetone and ether alternatively, and dried in vacuum over fused calcium chloride. The purity of the shining white compound was checked by TLC, Yield, 87%m.p.155^0, Found C, 38.00; H, 2.30; N, 15-88(%), Calculated for $C_{14} H_{10}O_5CI$, C, 38.10; H, 2-27; N, 15-69 (%) The compound was found to be insoluble in water and also in common organic solvents (ethanol, acetone, benzene, chloroform, carbontetra chloride, ether etc.) except in DMF and DMSO.

Synthesis of Metal Complexes of N^1-(4-Chlorophenyl)-N^4-(3,5-dinitrobenzoyl)-thiosemicarbazide (BDT):

The Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and UO_2(VI) acetates, $FeSO_4$ $(NH_4)_2SO_4$. $6H_2O$, DMF and all other chemicals required were of reagent grade. The metal complexes were prepared by adding a solution of 0.01 mole metal salt in 100 cm^{3}hot DMF to 0.01 mole of the legand (CDTS), also in hot DMF. The mixture was refluxed for ca 4h., the coloured products, separating out, were washed several times with hot DMS and dried. The complexes are coloured, amorphous solids, insoluble in organic solvents viz. ethanol, acetone, benzene, chloroform, carbontetrachloride, carbon disulphide, DMF,DMSO etc. the color of the amourphous compound are noted in the following table.

Table-1

Metal Complexes	Colour	M(%) obs (calc)	C(%) obs (calc)	H(%) obs (calc)	N(%) obs (calc)
$(Mn.L.2H_2O)_n$	Light Red	11.2 (11.4)	34.5 (34.7)	2.6 (2.8)	14.1 (14.5)
$(Fe.L.2H_2O)_n$	Green	11.3 (11.5)	34.5 (34.7)	2.2 (2.5)	14.2 (14.4)
$(Co.L.2H_2o)_n$	Red Brown	11.8 (12.0)	34.1 (34.1)	2.2 (2.5)	14.2 (14.3)
$(Ni.L.2H_2O)n$	Grey	11.9 (12.0)	34.1 (34.4)	2.2 (2.5)	14.1 (14.3)
$(Cu. L.2H_2O)n$	Dark Green	11.6 (11.8)	31.2 (31.2)	2.1 (2.2)	13.1 (13.0)
$(Zn.L .2H_2O)n$	Yellow	12.9 (13.1)	33.9 (34.0)	2.2 (2.5)	14.0 (14.2)
$(Cd.L)_n$	Dirty Green	22.1 (22.2)	33.0 (33.2)	1.4 (1.6)	13.6 (13.8)

$(Pb.L)_n$	Brown	34.2 (34.5)	27.9 (28.0)	1.1 (1.3)	11.4 (11.6)
$(UO_2)_n$	Brown	35.7 (35.9)	25.1 (25.3)	1.0 (1.2)	10.3 (10.5)

Results and Discussion

The metal ligand ratio 1:1 and the possibility of the association of two water molecules with one metal ion , in the axes o Mn(II), Fe(II), Co(II),Ni(II), Cu(II) and Zn (II) are indicated from analytical data while in the cases of Cd(II),Pb(II) and UO_2(VI)complexes no water association is in indicated. The presence of NH group may be attributed to the presence of a band at 3535 cm^{-1} in the spectrum of BDTS. CH stretching band is indicated at 3020 and 3010 cm^{-1} and a very sharp band at 1705 cm^{-1} for $\upsilon_{c=0}$. The band at 1530 cm^{-1} shows the presence of N-C-N linkage and a band at 1080 cm^{-1} may be due to C-N-H group in BDTS. The three bands at 935, 925 and 915 cm^{-1} are due to $\delta_{C\text{-}H}$ of trisubstitued benzene ring. C=S group corresponds to the the band at 1440 cm^{-1} and a band at.1320 cm^{-1} shows the presence of NH-C=S stretching in BDTS. A prominent extra band at 715 cm^{-1} is due to NO_2 substituednts present in the benzene ring. The identification of N-C-N, CS-NH-Ar, and NH.C=S frequencies in the spectrum indicates the formation of CDTS form the interactants in the coupling reaction.

The comparative study of i.r. spectra of CDTS and its metal complexes reveals the enolization and or thioenolization in theligand at the stage of complexation. A positive shift more than 50 cm^{-1} for U_{N-N} in the bands of complexes compared to the ligand is indicative of bidentate nature of N-N suggests the polymeric nature of the complexes the drs of the complexes which envolve metal capable of undergoing d-d transition indicate an octahedral geometry.

The magnetic studies evaluation of magnetic moments of the complexes show That Zn (II), Cd(II),Pb(II) and UO_2 (VI)complexes are diamagnetic where as Mn(II), Co(II), Ni(II) and Cu(II) complexes with CDTS are paramagnetic. The complexes are visualized as polymeric with octahedral symmetry of metal ion in the cases of Fe(II),Mn(II),Co(II),Ni(II),Cu(II) and Zn(II) and with tetrahedral symmetry for Cd(II), Pb(II), and UO_2(VI). The tg analyses show that (i) the coordination polymers are more stable to heat than those thje ligand; (ii) the decomposition of complexes is accompanied by explosion and evolution of sulphuretted gases. The order of thermal stability for CDTS complexes are UO_2(Vi)<PB(II)= Ni(II)<Co(II)<Fe (II)<Cd(II)= Cu(II)<Mn(II)<Zn(II).

The Thermal studies of metal complexes of thiosemicarbazides, with 4-phenyl thiosemicarbazide, 4-phenyl 1- solicylidene thiosmi-carbazide, 1-(2,4-dinitrobenzoyl) thiosemicarbazide, ά-pyridyl- thiosemicarbazide and thiosemicarbazide as ligand have been studied the thermal stability of Ni (II), Co(II), Cu(II), Zn(II), Cd(II) and UO2(VI) complexes with 4-phenylthiosemicarbazide. The association water in the coordination sphere of the metal ion in CDTH complexes is rervealed by the loss of the same at higher temperature range (125^0-185^0) where as the temperature of decomposition of the metal complexes are also noted. The CDTS complex decomposes with a smell which may be probably, due to evolution of sulphuretted gases. The decomposition of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and UO_2 (VI) complexes was accumpnied by explosion, while no explosion was observed in the cases of Cd(II) and Pb(II) complexes.

References:

1. Campbell, M.J.M. : Coord. Chem. Rev.,15, 279(1975)
2. Drinkard, W.C. Jr. and Chakravarty, D.N. : WADC. Tech. ept. No. 59/761, 232(1960)

3. Murcu, M., Dima and Basu, G. : ca 74,126516u) (1971), Rom, 52, 349 (cl.0083) 05 Oct, 1970, Appl. 04 Apr. 1968, 2 pp
4. Shah, I.D. and Trivedi, J.P. : J. Indian Chem. Soc., 40, 869 (1963)
5. Saha, N. and Gayen, N.C. : Indian J. Chem., 14A, 878 (1976)
6. Jain, C.L., Saxena. R.C.; Saxena, B.S. and Gupta, L.R. : Curr.Sci., 47, 330 (1978)
7. Iskandar, M.F.; Soyed, L.El.; Sadeek, S. and Toleb, M.A. : Trans. Met. Chem., 5,168 (1980)
8. Maurya, P.L.; Agarwal, B.V. and Dey, A.K. : Inorg. Nucl. Chem. Let., 13 145 (1977) Indian J. Chem., 16A258 (1978)
9. Pandey, U.N. : J. Indian Chem. Soc., 54 579 (1977)
10. Pandey, U.N. : J. Indian Chem. Soc., 55, 645 (1978)
11. Poddar, S.N. and Sahoo, B. : J. Indian Chem. Soc., 47, 255(1970)
12. Jensen, K.A. and Madeen, E.R. : Z. Anorg. Allag. Chem., 219, 6 (1934)
13. Jensen, K.A. : Z. Anorg. Anorg. Allg. Chem., 221, 6 (1934)
14. Jensen, K.A. : Z. Anorg. Allg. Chem., 229, 265 (1964)
15. Mashima, M. : Bull. Chem. Soc. Japan, 37, 974 (1964)
16. Wiles, D.M. and Suprunchuk, J. : Canadian. J. Chem., 47, 271 (1969)
17. Dash, B. and Mahapatra, S.K. : J. Inorg. Nucl. Chem., 27, 271 (1975)
18. Dutta, N.K. and Chakdar, N.C. : J. Inorg. Nucl. Chem., 22, 2303 (1970)
19. Dutta, R.L. and Hussain, M.J. : Orient Indian Res., 44, 635 (1980)
20. Furlani, C. and Furlani, A. : J. Inorg. Nucl. Chem., 23, 51 (1961)
21. Ferguson, J.; Wood, D.L. and Knox, K. : J. Chem. Phys., 39, 881 (1963)
22. Tripathi, S.C.; Srivastava, S.C. Shrimal; A.K. and Singh, O.P. : Trans. Met. Chem., 9, 478 (1984)