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Probing the Binding Fashion in Coordination Compounds of D-Block Metals with Versatile Dithiocarbamate N and S Containing Ligand

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ABSTRACT. The synthesis of sulfur and nitrogen (S and N) containing dithiocarbamate ligand derived from 1-naphthylylamine as well as its coordination compounds with d-block metals of first series have been described. These synthesized compounds were characterized through elemental analysis, conductometric measurements and IR spectral studies. The analytical data showed that the stoichiometry should be 1:2 and 1:3 for the compounds of the types ML_2 {M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)} and $M'L_3$ {M'=Cr(III) and Fe(III)}, respectively. The conductometric measurements indicated that the compounds are non-ionic in nature. The bidentate nature of dithiocarbamate moiety was confirmed on the basis of FT-IR spectral analysis.

Keywords: Transition metal; Dithiocarbamate; Metal complex.

INTRODUCTION

Chemistry stands at the basis of many innovations and often has been a driver for change in science and technology, even though its innovation accomplishments are often not highly visible, nor well recognized. This paper intends to draw attention to selection of a class of compounds-dithiocarbamate, which strongly believes that it could help Smart Cities to achieve some of their objectives. Dithiocarbamate, with their insecticidal, herbicidal, and fungicidal properties, have a wide range of applications.[1] Because of their high biological activity, dithiocarbamate compounds are also used in medicine and rubber industries. Extensive literature survey approved that dithiocarbamate could be a versatile chelating ligand, which readily forms a wide variety of stable complexes with all transition metal ions through its two donor sulfur (S) atoms.[1] This trend displays interesting and often quite novel properties for the complex structures. The dithiocarbamate ligand offers great synthetic flexibility and well developed chemistry in the family of S donor ligands.[2-4] In extension of previous studies of S and nitrogen (N) containing ligands,[5-14] this current work deals with the synthesis and characterization of coordination compounds of d-block metals of first series with dithiocarbamate ligand derived from 1-naphthylylamine. It is done to observe the coordination behavior of the dithiocarbamate moiety as well as some other physicochemical properties of the compounds. This work aims to show the scientific potency of dithiocarbamate to form new complexes for novel applications.

MATERIALS AND METHODS

1-Naphthylamine, carbon disulfide (CS_2), sodium hydroxide (NaOH), salts of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) (all E. Merck) were used as received. Solvents (all BDH) were purified by standard methods before use.[15] Elemental analyses of the complexes for carbon, hydrogen and nitrogen were performed at semi-micro scale by the Regional Sophisticated Instrumentation Centre (R.S.I.C.), Central Drug Research Institute (C.D.R.I.), Lucknow (U.P.), India. Sulfur was estimated gravimetrically by known procedure.[16] Infrared spectra in the region of 4000-200 cm^{-1} were recorded in Nujol mull on Perkin Elmer Model 1620 Fourier-Transform Infrared (FT-IR) spectrophotometer by Jamia Millia Islamia University, Delhi, India. Conductometric measurements were done on Systronics 321 Conductivity Bridge. The metal

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dithiocarbamate complexes could be synthesized by one of the following standard and reliable methods.[17]

(a) *Insertion Reaction Method*: This method involves direct insertion of a –CS2 group in the presence of an amine and the metal salt (MXn where n=2 or 3).

$n\mathrm{RNH_2} + n\mathrm{CS_2} + \mathrm{MX}_n \rightarrow (\mathrm{RHNCS_2})_n\mathrm{M} + n\mathrm{HX}$

(b) *Replacement Reaction Method*: This method involves replacement reaction using the sodium salt of the dithiocarbamate with metal salt.

$n(\mathrm{RHNCS_2})\mathrm{Na} + \mathrm{MX}_n \rightarrow (\mathrm{RHNCS_2})_n\mathrm{M} + n\mathrm{NaX}$

Since the sodium salts of dithiocarbamate of 1-naphthylamine were readily synthesized, the replacement reaction method was adopted for the synthesis. Amine, carbon disulfide and sodium hydroxide were taken in 1:1:1 molar ratio respectively. To an ethanol 0.1 M solutions of amine (14.3 g 1-naphthylamine), carbon disulfide (0.1 mol, 6.03 ml) and aqueous solution of sodium hydroxide (0.1 mol, 4.0 g) were added drop-wise with continuous stirring. The reaction mixture was stirred for about 1 h. On completion of the reaction, sodium dithiocarbamate of 1-naphthylamine was obtained as soluble in DMF.

The metal dithiocarbamate was synthesized as follows: In a molar ratio 1:2, the 0.01 M solutions of metal salts (1.2594 g $\mathrm{MnCl_2}$, 1.2994 g $\mathrm{CoCl_2}$, 1.2972 g $\mathrm{NiCl_2}$, 1.3466 g $\mathrm{CuCl_2}$ and 1.3636 g $\mathrm{ZnCl_2}$) were added to sodium dithiocarbamate dissolved in DMF (4.82 g sodium 1-naphthylamine dithiocarbamate) at room temperature. In a molar ratio 1:3, 0.01 M solutions of metal salts (1.5850 g $\mathrm{CrCl_3}$ and 1.6234 g $\mathrm{FeCl_3}$) were added to 0.03 M solutions of sodium 1-naphthylamine dithiocarbamate (7.23 g). The reaction mixture was stirred for 1 h. The solid thus formed was washed with diethyl ether and dried in air.

Table 1: Analytical data and other physical properties of 1-naphthylamine dithiocarbamate complexes.

Compounds (Formula Wt.)	Yield (%)	M.P. (^{o}C)	Color	Λ_m ohm^{-1}cm^{2}mol^{-1}	Found (Calculated)%				
					C	H	N	S	M
1. Na(1-NA dtc)	67	290	Light violet	----	54.65	3.32	5.82	26.50	------
(241)					(54.77)	(3.31)	(5.80)	(26.55)	------
2. Cr(1-NA dtc)$_3$	58	240	Blue-Green	0.0065	56.17	3.38	5.98	27.09	7.38
(705.99)					(56.09)	(3.40)	(5.95)	(27.20)	(7.36)
3. Mn(1-NA dtc)$_2$	65	235	Yellow	0.0560	53.68	3.28	5.67	26.14	11.23
(490.94)					(53.78)	(3.26)	(5.70)	(26.07)	(11.19)
4. Fe(1-NA dtc)$_3$	66	260	Brown	0.0978	55.87	3.35	5.88	27.01	7.89
(709.85)					(55.79)	(3.38)	(5.92)	(27.05)	(7.86)
5. Co(1-NA dtc)$_2$	72	280	Black	0.0678	53.26	3.20	5.68	26.00	11.86
(494.93)					(53.35)	(3.23)	(5.66)	(25.86)	(11.90)
6. Ni(1-NA dtc)$_2$	68	220	Dark-Green	0.0985	53.49	3.21	5.64	25.84	11.82
(494.71)					(53.38)	(3.23)	(5.65)	(25.88)	(11.86)
7. Cu(1-NA dtc)$_2$	69	250	Black	----	52.76	3.18	5.62	25.74	12.70
(499.55)					(52.85)	(3.20)	(5.61)	(25.62)	(12.72)
8. Zn(1-NA dtc)$_2$	73	210	Gray	0.0672	52.76	3.22	5.56	25.40	13.06
(501.37)					(52.66)	(3.19)	(5.58)	(25.53)	(13.04)

RESULTS AND DISCUSSION

The replacement reaction method yielded compounds of high purity, which was supported by their elemental analysis (Table 1). The colorful compounds were air and moisture stable at room temperature. These complexes were found to have melting points ranging from 210 to 290oC. The metal to ligand ratio for manganese, cobalt, nickel, copper and zinc was 1:2 and that for chromium and iron was 1:3. The molar conductivity value should be 65-90 ohm^{-1}cm^{2}mol^{-1} for 1:1 electrolytes.[18] The low molar conductance values of 10^{-3} M solutions of these complexes in DMF at room temperature lying in the 0.0065-10 ohm^{-1}cm^{2}mol^{-1} range confirmed the non-electrolytic behavior of all the complexes. The conductance of Cu(II) complexes of 1-naphthylamine could not be measured due to their very low solubility in nitrobenzene.

The evidence regarding bonding and structures of these complexes has been deduced after thoroughly examining the observed frequencies characteristic of dithiocarbamate group in their infrared spectra. The IR spectra of solid complexes (Table 2) showed well-resolved and sharp bands. The characteristic frequencies arising from dithiocarbamate can be examined by comparing the observed spectra reported for the free dithiocarbamate ion (dithiocarbamic acid) and those of complexes. The free dithiocarbamate ion, as it exists in ionic compound, is expected to show IR active fundamental bands. It is expected that if there exists an increased cation-anion interaction in these dithiocarbamate compounds, as has been observed in covalent compounds, the results show that the vibrational frequencies are very much affected and undergo a positive shift.

Table 2: IR spectral data of 1-naphthylamine dithiocarbamate complexes.

Complexes	*ν*(C-N) cm^{-1}	*ν*(C-S) cm^{-1}	*ν*(M-S) cm^{-1}
1. Na(1-NA dtc)	1465	1010	------
2. Cr(1-NA dtc)$_3$	1470	1010	440
3. Mn(1-NA dtc)$_2$	1470	1010	455
4. Fe(1-NA dtc)$_3$	1470	1010	450
5. Co(1-NA dtc)$_2$	1470	1010	476
6. Ni(1-NA dtc)$_2$	1475	1005	490, 420
7. Cu(1-NA dtc)$_2$	1470	1010	465, 425
8. Zn(1-NA dtc)$_2$	1470	1002	430

The dithiocarbamate group being flexidentate ligand, can coordinate symmetrically involving both the sulfur atoms as well as unsymmetrically involving only one sulfur atom in complexation. The frequency modes *ν*(C-N) and *ν*(C-S) are diagnostic factors for the nature of dithiocarbamate moiety whether it is acting as monodentate or bidentate. The monodentate or bidentate nature of dithiocarbamate group in the ligand is reflected in the *ν*(C-S) stretching frequency.[19, 20] In the case of bidentate behavior, a single strong band appears in the region 950-1050 cm^{-1}, while a doublet is expected in the region around 1000 cm^{-1} for the monodentate one. It is further reflected that the strong band appearing near 1500 cm^{-1} in the infrared spectra of the ligands can be assigned to the thioureide group, S=C-N^{-}.[21] The energy of this band lies intermediate to the stretching frequency associated with C-N bond (1250-1350 cm^{-1}) and C=N bond (1640-1690 cm^{-1}) and can best be explained as a vibration of a polar C=N^{+} bond.[22] Thus the thioureide band near 1500 cm^{-1} implies a considerable double bond character in the SC-NRR' bond. In general, *ν*(C-N) frequency shows a blue shift in the complexes as compared to the respective dithiocarbamate ligand as compared to the respective dithiocarbamate ligands, if the dithiocarbamate group behaves as a bidentate ligand. For a monodentate dithiocarbamate moiety, this frequency should exhibit either no change in position or undergo a red shift with respect to the corresponding free ligand frequency. The *ν*(C-N) frequency in these complexes occurred in the region 1465-1475 cm^{-1}. Since these frequency modes lie in between those associated with single C-N and double C=N bonds hence the partial double bond character of thioureide bond was confirmed1 for all the complexes studied. The *ν*(C-S) mode for these complexes was observed in the region 1002-1010 cm^{-1}. The absorption bands occurring in the wave number range 420-490 cm^{-1} for these complexes were attributed to *ν*(M-S) stretching frequency.[23]

CONCLUSION

This work has been done to synthesize S and N containing dithiocarbamate ligand derived from 1-naphthylylamine as well as its coordination compounds with d-block metals of first series have been described. In the light of all these experimental data as well as theoretical facts it could be concluded that that this dithiocarbamate ligand showing bidentate nature, formed four membered chelate rings in complexation with metals. The metal (M) was observed to be tetra-coordinated in ML$_2$ type chelates and in M'L$_3$ type, it was hexa-coordinated. The analytical data showed that the stoichiometry should be 1:2 and 1:3 for the compounds of the types ML$_2$ {M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)} and M'L$_3$ {M'=Cr(III) and Fe(III)}, respectively. The conductometric measurements indicated that the compounds are non-ionic in nature.

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REFERENCES

1. Hulanicki A. Complexation reactions of dithiocarbamates. Talanta 1967;14:1371-1392.
2. Halls DJ. The properties of dithiocarbamates a review. Microchimica Acta 1969;57:62-77.
3. Alison JM, Stephenson TA. Metal complexes of sulphur ligands. Part III. Reaction of platinum (II) NN-dialkyldithiocarbamates, O-ethyl dithiocarbonate (xanthate), and OO′-diethyl dithiophosphate with tertiary phosphines.

J. Chem. Soc. Dalton Trans. 1973:254-263.

4. Willemse J, Cras JA, Steggerda JJ, Keijzers CP. Dithiocarbamates of transition group elements in “unusual” oxidation states. In Electrons in Oxygen-and Sulphur-Containing Ligands 1976 (pp. 83-126). Springer, Berlin, Heidelberg.
5. Tarique M, Aslam MO. Bi and Trivalent transition metal complexes of dithiocarbamates derived from 2, 6-diacetyl pyridine. Orient. J. Chem. 2008;24:267-270.
6. Tarique M. Coordination aspects of dimethyldithiocarbamate ligand towards the first series transition metal ions. Chem. Sci. Trans. 2012;1:257-260.
7. Tarique M, Aslam M. Comparative study on the IR spectra of some transition metal dithiocarbamates. Biosci. Biotechnol. Res. Asia 2008;5:833-836.
8. Tarique M, Aslam M. Physico-chemical study of complexes of some 3d-series transition metals with piperazine 1,4-dicarbodithioate. Orien. J. Chem. 2009;25:207-210.
9. Tarique M, Aslam M. Studies on coordination compounds of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with butyldithiocarbamate ligand. Asian J. Exp. Chem. 2009;4:46-48.
10. Tarique M, Aslam M. Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) chelates with S and N containing ligand diisopropyl-dithiocarbamate. Asian J. Exp. Chem. 2009;4:87-89.
11. Tarique M, Aslam M. Synthesis and characterization of some transition metal complexes of dithiocarbamate ligand derived from p-toluidine. Asian J. Chem. 2010;22:2031-2034.
12. Tarique M, Aslam M. Investigation on transition metal complexes with sulphur and nitrogen containing ligand derived from diethylamine. Asian J. Chem. 2010;22:2465-2467.
13. Tarique M. Cr(III),Mn(II),Fe(III),Co(II),Ni(II),Cu(II) and Zn(II) complexes with diisobutyl-dithiocarbamato ligand. E. J. Chem. 2011;8: 2020-2023.
14. Tarique M. Coordination aspects of dimethyl-dithiocarbamate ligand towards the first series transition metal ions. Chem. Sci. Trans. 2012;1:257-260.
15. Vogel AI. Text Book of Practical Organic Chemistry, ELBS and Longmans Green Co. Ltd., 1968.
16. Vogel A. I.; A Text Book of Quantitative Inorganic Analysis, Ed. III, ELBS and Longmans, London, 1960.
17. Siddiqi KS, Khan P, Khan S, Siddiqi MR, Zaidi SA. Transition metal complexes of a-naphthylamine dithiocarbamate. Croatica Chem. Acta 1982;55:271-276.
18. Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. Coordinat. Chem. Rev. 1971;7:81-122.
19. Druce PM, Kingston BM, Lappert MF, Spalding TR, Srivastava RC. Metallocene halides. Part I. Synthesis, spectra, and redistribution equilibria of di-π-cyclopentadienyldihalogeno-titanium (IV),-zirconium-(IV), and-hafnium (IV). J. Chem. Soc. A 1969;2106-2110.
20. Srivastava TN, Kumar V. Some triorganotin (IV) dithiocarbamates. J. Organometal. Chem. 1976;107:55-61.
21. Bhatt A, Sengupta SK, Pandey OP. Mono- and bis(cyclopentadienyl)hafnium(IV) derivatives with heterocyclic dithiocarbamates. Indian J. Chem. A 2001,40:994-998.
22. Chatt J, Duncanson LA, Venanzi LM. Electronic structures of dithiocarbamates and xanthates. Nature 1956;177:1042-1043.
23. Kwoka W, Moyer RO, Lindsay R. Alkylenebisdithiocarbamates of oxovanadium (IV), chromium (III), and manganese (II). J. Inorg. Nucl. Chem. 1975;37:1889-1892.

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