

Synthesis, Characterization & Toxicity of Group (IV) Metal Dithiocarbamates

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Group(IV) metal dithiocarbamates of the types $(\text{RHNC}_2)_4\text{M}$ and $(\text{RNCS}_2)_4\text{M}$ where $\text{R} = \text{N-phenyl-}\alpha\text{-naphthylamines}$, 2-aminobenzothiazole, benzidine and 2,4-tolylenediamine; $\text{M} = \text{Si(IV)}$, Ge(IV) , Sn(IV) , Ti(IV) and Zr(IV) have been synthesized. Molar conductances of metal dithiocarbamates in ethanol suggest their covalent nature. An octahedral geometry has tentatively been proposed for these metal chelates. Toxicity of the compounds has been studied against houseflies, cockroaches and fungi. The % mortality in terms of LD_{50} and % inhibition has been evaluated. The metal derivatives have been found to be slightly more toxic than the free dithiocarbamates. The toxicity of dithiocarbamates against insects shows an ascending order $\text{NPdte} < \text{TCdte} \approx \text{MBdte} < \text{AMdte}$, while their fungitoxicity follows the reverse trend.

Dithiocarbamates are well known chelating agents and biocides^{1,2}. In continuation of our earlier work on complexes of group(IV) metal ions, we are reporting here the preparation, characterization and toxicity studies on complexes of N-phenyl- α -naphthylamine-, 2-aminobenzothiazole-, benzidine- and 2, 4-tolylenediamine dithiocarbamates with some group (IV) elements. Their antifungal activities have been investigated against the fungi *Aspergillus flavus*, *Aspergillus niger* and *Alternaria pori*.

N-Phenyl- α -naphthylamine, benzidine, 2-amino-benzothiazole, 2, 4-tolylenediamine (AR, BDH), carbon disulphide (BDH), SiCl_4 , SnCl_4 , TiCl_4 , ZrCl_4 (BDH) and GeCl_4 (Koch Light) were used as such. The IR spectra ($250\text{-}4000\text{ cm}^{-1}$) were recorded in mull and KBr on a Beckman spectrophotometer. The NMR spectrum was recorded on Varian A60 D instrument. The conductivity measurements were made on an Elico conductivity bridge type CM-82T. The molecular weights were determined by viscosity measurements.

Synthesis of the complexes

The reaction mixture containing amine, CS_2 and MCl_4 (4:4:1) was vigorously stirred at room temperature and allowed to stand overnight when a solid product was obtained. It was washed with ethanol and dried *in vacuo*.

Toxicity studies

Experiments were done on houseflies and cockroaches. Equal number of individuals in five sets were taken and allowed to feed on dithiocarbamates mixed in a palatable base in different concentrations ranging from 8 to 12 ppm (w/w). A control set was also run simultaneously and the test insects were kept under observation. The % mortality was recorded after 24 and 96 hr.

To investigate the fungitoxicity three sets of experiments were done on *A. flavus*, *A. niger* and *Alternaria pori* alongwith a control set. A 1-2% solution of dithiocarbamate in water was sprayed on fungus colony and the area both in the control and in the treated set was separately measured. The % inhibition was calculated from the area of the affected portion.

The prepared metal dithiocarbamates (Table 1) are stable at room temperature and decompose between 60 and 310°C . The molar conductances of 10^{-3} M solutions in ethanol ($0.1\text{-}0.25\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$) show that the complexes are non-electrolytes.

The proton NMR spectra of the free dithiocarbamates derived from various amines have been recorded in deuterated DMSO. The spectra have been compared with those of the parent compounds. It is known that in secondary and primary amines the NH proton signals depend on the extent of exchange rate. If the rate of exchange is slow the NH peak is broadened as a consequence of decoupling with CH protons. It, however, gives a broad singlet. In the present work, the sodium salts of the dithiocarbamates showed only a singlet corresponding to NH proton in the region δ 3-5 ppm except in N-phenyl- α -naphthylamine dithiocarbamate. The resonance signals due to phenyl protons lie in the range δ 6.8-7.6 while the signal for methyl protons in the case of 2, 4-tolylenediamine dithiocarbamate appears at δ 4.5.

It is well known that a symmetrically bound dithiocarbamate exhibits only one band around 1000 cm^{-1} and a splitting of this band ($1000 \pm 70\text{ cm}^{-1}$) indicates the presence of an unsymmetrical dithiocarbamate³. If the CS_2 absorptions are not coupled with or overlapped by other bands, the criterion of Bonati and Ugo⁴ can be used to determine the nature of bonding of the dithiocarbamate group. In the present case, two absorption bands have been observed in the region $1000 \pm 70\text{ cm}^{-1}$ which show the splitting of (C-S) band. The third band is far below the range of $\nu(\text{C}=\text{S})$. It is believed that one of the two bands in the

Table 1—Analytical Data, Melting Points and Molecular Weights of Dithiocarbamates of Group (IV) Elements

Dithiocarbamate	m.p. (°C)	Found (Calc.)				
		%C	%H	%N	%S	Molec. wt
(C ₁₆ H ₁₂ NCSS)Na	62	64.30 (64.32)	3.80 (3.81)	4.39 (4.41)	20.18 (20.20)	316.55 (317.41)
(C ₁₆ H ₁₂ NCSS) ₄ Si	60	67.68 (67.70)	4.00 (4.01)	4.60 (4.64)	21.24 (21.27)	1204.70 (1205.73)
(C ₁₆ H ₁₂ NCSS) ₄ Ge	90	65.30 (65.32)	3.84 (3.86)	4.45 (4.48)	20.48 (20.51)	1248.20 (1250.24)
(C ₁₆ H ₁₂ NCSS) ₄ Sn	120	63.01 (63.00)	3.70 (3.73)	4.30 (4.32)	19.75 (19.78)	1294.31 (1296.34)
(C ₁₆ H ₁₂ NCSS) ₄ Ti	230	66.62 (66.64)	3.92 (3.94)	4.55 (4.57)	20.90 (20.93)	1224.50 (1225.55)
(C ₁₆ H ₁₂ NCSS) ₄ Zr	70	64.33 (64.36)	3.80 (3.81)	4.40 (4.41)	20.19 (20.21)	1267.86 (1268.87)
(C ₇ H ₅ N ₂ SCSS)Na	120	38.67 (38.69)	2.01 (2.02)	11.22 (11.27)	38.70 (38.73)	247.30 (248.32)
(C ₇ H ₅ N ₂ SCSS) ₄ Si	85	41.32 (41.35)	2.14 (2.16)	12.03 (12.05)	41.37 (41.40)	928.50 (929.35)
(C ₇ H ₅ N ₂ SCSS) ₄ Ge	250	39.42 (39.46)	2.03 (2.07)	11.47 (11.50)	39.47 (39.50)	975.23 (973.86)
(C ₇ H ₅ N ₂ SCSS) ₄ Sn	200	37.63 (37.68)	1.92 (1.97)	10.93 (10.98)	37.69 (37.72)	1018.33 (1019.96)
(C ₇ H ₅ N ₂ SCSS) ₄ Ti	270	40.46 (40.49)	2.10 (2.12)	11.70 (11.79)	40.50 (40.53)	948.19 (949.17)
(C ₇ H ₅ N ₂ SCSS) ₄ Zr	100	38.70 (38.72)	2.02 (2.03)	11.25 (11.28)	38.74 (38.76)	991.74 (992.49)
(C ₁₂ H ₁₁ N ₂ CSS)Na	d.310	50.28 (50.30)	3.54 (3.57)	18.01 (18.04)	20.63 (20.66)	309.66 (310.38)
(C ₁₂ H ₁₁ N ₂ CSS) ₄ Si	135	52.23 (52.29)	3.70 (3.71)	9.38 (9.41)	32.19 (32.21)	1193.20 (1194.19)
(C ₁₂ H ₁₁ N ₂ CSS) ₄ Ge	220	50.38 (50.41)	3.56 (3.58)	9.04 (9.08)	31.06 (31.06)	1238.00 (1238.70)
(C ₁₂ H ₁₁ N ₂ CSS) ₄ Sn	200	48.55 (48.60)	3.41 (3.45)	8.73 (8.75)	29.90 (29.94)	1283.00 (1284.80)
(C ₁₂ H ₁₁ N ₂ CSS) ₄ Ti	300	51.40 (51.44)	3.62 (3.65)	9.22 (9.26)	31.65 (31.69)	1213.50 (1214.01)
(C ₁₂ H ₁₁ N ₂ CSS) ₄ Zr	290	49.62 (49.64)	3.50 (3.52)	8.90 (8.94)	30.55 (30.60)	1256.40 (1257.33)
(C ₇ H ₉ N ₂ CSS)Na	200	43.58 (43.61)	4.05 (4.09)	12.65 (12.71)	29.07 (29.10)	219.50 (220.30)
(C ₇ H ₉ N ₂ CSS) ₄ Si	160	47.00 (47.02)	4.42 (4.44)	13.68 (13.70)	31.35 (31.38)	816.50 (817.27)
(C ₇ H ₉ N ₂ CSS) ₄ Ge	d.220	44.58 (44.60)	4.20 (4.21)	12.97 (13.00)	29.72 (29.76)	860.32 (861.77)
(C ₇ H ₉ N ₂ CSS) ₄ Sn	190	42.43 (42.46)	3.95 (3.99)	12.30 (12.34)	28.38 (28.40)	906.37 (907.87)
(C ₇ H ₉ N ₂ CSS) ₄ Ti	180	45.89 (45.91)	4.30 (4.33)	13.35 (13.38)	30.60 (30.64)	836.05 (837.08)
(C ₇ H ₉ N ₂ CSS) ₄ Zr	180	43.60 (43.65)	4.09 (4.12)	12.68 (12.72)	29.08 (29.13)	880.49 (880.40)

region $1000 \pm 70 \text{ cm}^{-1}$ is due to symmetrically bonded dithiocarbamate group which is overlapped by the split bands assignable to unsymmetrically bonded dithiocarbamate. It is, therefore, tempting to assume that the metal ions may be hexacoordinated although an octacoordinated group (IV) metal is not

unprecedented⁵. We have observed the $\nu(\text{C}-\text{N})$ mode in the range $1440\text{--}1490 \text{ cm}^{-1}$ which is intermediate between carbon-nitrogen double bond ($1690\text{--}1640 \text{ cm}^{-1}$) and carbon-nitrogen single bond ($1360\text{--}1250 \text{ cm}^{-1}$) showing a partial double bond character. In the far IR region metal-sulphur stretching frequency has

Table 2—% Mortality of Houseflies, Cockroaches at Different Concentrations of Dithiocarbamates

Ligand/Complex	Log conc. in ppm × 100	% Mortality ligand/ complex	Probit value	LD ₅₀ in ppm ligand/ complex
HOUSEFLIES				
Na.NPdtc/Complex	2.90	20/30	4.1584/4.4756	10.47/10
	2.95	30/40	4.4756/4.7467	
	3.00	40/50	4.7467/5.0000	
	3.04	60/60	5.2533/5.2533	
	3.07	80/80	5.8416/5.8416	
Na.AMdtc/Complex	2.90	20/20	4.1584/4.1584	10.96/9.55
	2.95	30/40	4.4756/4.7467	
	3.00	40/60	4.7467/5.2533	
	3.04	50/70	5.0000/5.5244	
	3.07	70/80	5.5244/5.8416	
Na.MBdtc/Complex	2.90	10/30	3.7184/4.4756	11.22/9.77
	2.95	20/40	4.1584/4.7467	
	3.00	30/60	4.4756/5.2533	
	3.04	40/80	4.7467/5.8416	
	3.07	60/100	5.2533/ —	
Na.TCdtc/Complex	2.90	10/30	3.7184/4.4756	11.22/9.77
	2.95	20/40	4.1584/4.7467	
	3.00	30/60	4.4756/5.2533	
	3.04	40/80	4.7467/5.8416	
	3.07	60/100	5.2533/ —	
COCKROACHES				
Na.NPdtc/Complex	2.90	20/30	4.1584/4.4756	10.00/8.94
	2.95	30/50	4.4756/5.0000	
	3.00	50/60	5.0000/5.2533	
	3.04	60/80	5.2533/5.8416	
	3.07	80/100	5.8416/ —	
Na.AMdtc/Complex	2.90	30/50	4.4756/5.0000	10.00/7.94
	2.95	40/60	4.7467/5.2533	
	3.00	50/70	5.0000/5.5244	
	3.04	60/80	5.2533/5.8416	
	3.07	80/100	5.8416/ —	
Na.MBdtc/Complex	2.90	20/30	4.4584/4.4756	10.96/10.0
	2.95	30/40	4.4756/4.7467	
	3.00	40/50	4.7467/5.0000	
	3.04	50/60	5.0000/5.2533	
	3.07	60/70	5.2533/5.5244	
Na.TCdtc/Complex	2.90	20/30	4.1584/4.4756	10.96/10.0
	2.95	30/40	4.4756/4.7467	
	3.00	40/50	4.7467/5.0000	
	3.04	50/60	5.0000/5.2533	
	3.07	60/80	5.2533/5.8416	

been assigned to a band appearing in the range 350–540 cm^{-1} ; the band is absent in the spectra of the free ligands.

The toxicity of various dithiocarbamates^{6–8} is due to the presence of CS_2 group. In order to determine the

toxicities of the present compounds, experiments were done on houseflies and cockroaches. The % mortality of the insects was plotted against concentration of the compound in ppm (w/w) which gave a sigmoid curve. Since it was not a straight line, the data pertaining to

Table 3—% Inhibition Data of Dithiocarbamate Complexes of Group(IV) Metal Halides

[(a) <i>A. Flavus</i> , (b) <i>A. niger</i> , (c) <i>Alternaria pori</i>]		
Ligand/complex	Concentration (%)	Inhibition (%)
(a)Na.NPdte/Complex	1	50/54
	1.5	54/58
	2	58/60
Na.AMdte/Complex	1	58/60
	1.5	60/62
	2	62/64
Na.MBdte/Complex	1	55/60
	1.5	57/62
	2	60/64
Na.TCdte/Complex	1	56/60
	1.5	58/62
	2	60/64
(b) Na.NPdte/Complex	1	51/55
	1.5	53/59
	2	55/61
Na.AMdte/Complex	1	59/61
	1.5	62/63
	2	64/64
Na.MBdte/Complex	1	54/58
	1.5	56/60
	2	57/61
Na.TCdte/Complex	1	55/57
	1.5	57/60
	2	59/62
(c)Na.NPdte/Complex	1	49/52
	1.5	51/54
	2	53/57
Na.AMdte/Complex	1	57/61
	1.5	59/63
	2	61/64
Na.MBdte/Complex	1	54/57
	1.5	56/59
	2	57/63
Na.TCdte/Complex	1	54/57
	1.5	57/60
	2	59/62

percentage kill were transformed into probit which were plotted against log concentration in ppm $\times 100$. A perpendicular drawn from probit 5 yielded LD_{50} (Table 2). It is evident from LD_{50} values that the dithiocarbamates are slightly less toxic than their metal derivatives. The toxicity decreases in the order: AMdte > NPdte > MBdte $\approx$ TCdte.

The antifungal activities of the dithiocarbamates and their complexes were evaluated (Table 3) against the fungi *A. flavus*, *A. niger* and *Alternaria pori* at three different concentrations, viz., 1%, 1.5% and 2%. The area of the fungus colony in the control and the treated set was measured after 96 hr. All the compounds tested against fungi appeared to be growth inhibitor precluding the formation of spores and further development of fungus colony. It is worth mentioning that toxicities of the compounds for insects are different from those observed for fungi. The antifungal activity follows the order: NPdte < AMdte $\approx$ MBdte $\approx$ TCdte.

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