

Charge Transfer & Metal Complexes of Dithiocarbamate Esters

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The charge transfer complexes of S-methyldithiocarbamate esters with iodine and their metal complexes with mercury(II), cadmium(II) and copper(II) chlorides have been investigated by means of infrared spectroscopy. Metal complexes of the general formula $M(\text{DTC-ester})_2\text{Cl}_2$ are obtained. The perturbation of the infrared band positions on complexation is discussed.

INTENSE current interest in metal complexes of dithiocarbamates stems from their novel structural¹ and electro-chemical properties³ and more recently their photoredox chemistry³. Additionally, metal dithiocarbamate complexes have been shown to be effective accelerators in the vulcanization of rubber⁴. The investigations on complexes of dithiocarbamate (DTC) esters are however scanty. Only mercuric chloride complexes of certain N,N-dialkyldithiocarbamate esters have been reported⁵. In an effort to evaluate the influence of S-methylation on the donor characteristics of dithiocarbamates, an investigation of charge transfer complexes with iodine of primary (S-methyldithiocarbamate, SMDTC), secondary (S-methyl-N-methyldithiocarbamate, MMDTC) and tertiary (S-methyl-N,N-dimethyldithiocarbamate, MDMDC) and metal complexes of these esters has been carried out. Complex formation between thioureas, thioamides and iodine has been the subject of several studies⁶⁻¹⁰. Similar investigations on dithiocarbamates are not available. Dithiocarbamate esters appeared to be well suited for further studies of charge transfer complexes with iodine by infrared spectral technique in non-polar solvents.

Materials and Methods

DTC esters, SMDTC, MMDTC and MDMDC were synthesized according to literature methods^{11,12}. The complexes were prepared by mixing ethanol solutions of the metal salt and the ligand. The complexes which separated out immediately were washed with ethanol and dried *in vacuo*. These complexes analysed for $M(\text{DTC-ester})_2\text{Cl}_2$.

Infrared spectra were recorded on a Perkin-Elmer model 599 in nujol or KBr for solid complexes and as thin film for liquids. The solution spectra using CCl_4 , CS_2 and CHCl_3 as solvents were recorded in the region 4000-500 cm^{-1} using conventional type cells with KBr windows of path length 0.2 to 0.5 mm. The spectra of charge transfer complexes of DTC esters were similarly obtained in CHCl_3 in the presence of slight excess of iodine. Solvents of Merck Uvasol grade and resublimed iodine (Merck) were used.

Results and Discussion

Charge transfer complexes with iodine — In Table 1 are listed some important IR bands† for the free DTC esters and the data for charge transfer complexes. The intense bands of SMDTC at 1350 and 878 cm^{-1} assignable¹³ chiefly to $\nu\text{C-N}$ and $\nu\text{C=S}$ respectively get further intensified and shift to 1380 and 860 cm^{-1} respectively in the iodine complex. Likewise for MMDTC, the frequency shifts of 20-60 cm^{-1} are found mainly for 1520, 1340 and 1050 absorptions. For MDMDC, the shifts in the positions of the analogous bands are too small and this may be traced to the extensively mixed nature of $\nu\text{C-N}$ and $\nu\text{C=S}$ in the tertiary ester¹⁴. The shift to higher frequency of $\nu\text{C-N}$ and to lower frequency of $\nu\text{C=S}$ reflects the increased C-N double bond character with consequent decrease in the C=S bond order on coordination of iodine to sulphur atom. This fact is further confirmed by the behaviour of νNH and νNH_2 . The νNH_2 and νNH of free SMDTC and MMDTC move to lower energy by 40 to 80 cm^{-1} in the charge transfer complexes. This decrease arises from the enhanced positive charge on nitrogen due to increased contribution from the charge-separated form $>\overset{+}{\text{N}}=\text{C}(\text{S}^-)\text{SCH}_3$ on complexation to iodine.

Metal complexes — Selected infrared frequencies of DTC esters and their metal complexes are shown in Table 2. The shifts in $\nu\text{C-N}$ and $\nu\text{C=S}$ of SMDTC parallel the spectral changes in the charge transfer complexes described previously. Somewhat larger downward shifts (130-160 cm^{-1}) in νNH_2 are observed, from the band positions of the free ligand in CHCl_3 . It arises from the differences in the nature of hydrogen bonding in the free ligand and in the metal complexes, besides owing to the effects of coordination. Unidentate coordination through the terminal sulphur of SMDTC may be suggested for copper(II) and mercury(II) complexes. $\nu\text{C=S}$ of the cadmium(II) complex behaves in an unexpected manner. It shifts to a higher frequency and occurs as a doublet at 880, 890 cm^{-1} . This suggests that in the cadmium(II) complex, bidentate chela-

†IR ν_{max} in cm^{-1} throughout the paper.

TABLE 1 — SOME IMPORTANT INFRARED BANDS (cm⁻¹) OF THE CHARGE TRANSFER COMPLEXES OF DTC ESTERS

SMDTC		MMDTC		MDMDTC		Assignment†
CHCl ₃	CHCl ₃ +I ₂	CHCl ₃	CHCl ₃ +I ₂	CHCl ₃	CHCl ₃ +I ₂	
3500	3460	3492	3410	—	—	ν(NH ₂ , NH) (free)
3380	3335	3408	3312	—	—	ν(NH ₂ , NH) (bonded)
1600	1600	1518	1538	1505	1508	δ(NH ₂ , NH) + ν(CN)
1350	1380	1345	1360	810	812	νCN, νC ^N N
878	860	1050	985	990	988	νC=S
738	740	986	990	730	740	νC ^S
625	630	632	635	573	570	νCS

†C^s, S-methyl carbon; and Cⁿ, N-methyl carbon.

TABLE 2 — SELECTED INFRARED FREQUENCIES OF SOME METAL COMPLEXES OF DTC ESTERS

Ligand	ν _{max} (cm ⁻¹)			Assignment
	Cu(II)	Cd(II)	Hg(II)	
COMPLEXES WITH SMDTC				
3378	3310	3340	3210	νNH ₂
3260	3255	3280	3260	
1617	1625	1630	1635	δNH ₂
1389	1394	1412	1395	νCN
851	840	880	846	νC=S
		890		
716	730	722	724	νS-CH ₃
621	630	600	633	νC-S
430	440	452	445	δC=S
COMPLEXES WITH MMDTC				
3260	3230	3235	3220	νNH
1519	1538	1550	1560	νCN(+δNH)
1349	1365	1370	1375	δNH(+νCN)
1034	990	995	980	νC=S
721	725	726	725	νS-CH ₃
	735			
620	575	650	628	νC-S
440	460	470	464	δC=S
COMPLEXES WITH MDMDTC				
1520	1536	1540	1555	νCN(+δNH)
988	970	960	972	νC=S
737	724	728	730	νS-CH ₃
575	570	560	575	νC-S
	555		558	

tion of SMDTC through the dithio group is possible.

Relatively larger decrease in νC=S of free MMDTC by nearly 45 cm⁻¹ is observed in the spectra of the metal complexes. The bands at 1519 and 1349 to which the amide νC-N contributes, substantially moves to higher frequency on complexation. The variations in νC-N and νC=S in the complexes follow the order, Cu < Cd < Hg. Concordant with the coordination of MMDTC through terminal sulphur, the δC=S at 440 is displaced to higher wavenumbers (to ~460-470) in the complexes, while νN-H registers an opposite trend.

In contrast to the charge transfer complex of MDMDTC with iodine where very little or no spectral

variations are observed, the spectra of the metal complexes show smaller but definite shifts for certain characteristic bands. The 988 and 575 bands of MDMDTC shift to lower frequency side by 15 to 30 cm⁻¹ in the spectra of metal complexes and reflect the contribution from νC=S. A similar shift but to higher frequency is noted for the absorption at 1520; some contribution from νC-N may be responsible for this upward shift. Analogous assignment for νC=S and νC-N is made in closely related N,N-dimethylthioacetamide¹⁵.

The spectra of all the metal complexes of DTC esters, excepting that of the cadmium(II) complex of SMDTC, show similar variations. Pseudo-tetrahedral stereochemistry may be suggested for these complexes; the cadmium(II) complex of SMDTC may possess octahedral geometry.

In conclusion, DTC esters appear to act as monodentate, bonding through the terminal sulphur. This is in accord with the findings of Brinkoff and Dautzenberg⁵ for the mercury(II) halide complexes of N,N-dialkyldithiocarbamate esters.

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