

Chromium(III) Dithiocarbamates—A Thin Layer Chromatographic Study & Characterisation of Some New Binuclear Mixed Ligand Dithiocarbamates

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When chromium(III) dithiocarbamates are prepared from chromium(VI) species by reduction and complexation with excess ligand, new mixed ligand binuclear dithiocarbamates $[\text{Cr}_2\text{O}(\text{dtc})_4\text{tds}]$ are formed along with mononuclear chelates $[\text{Cr}(\text{dtc})_3]$, where dtc = dithiocarbamate anion and tds = thiuram disulphide. These new complexes are characterised by different physical methods after separation from mononuclear chelates by preparative column chromatography.

Chromium(III) dithiocarbamates of different types have been characterised by a number of workers¹⁻⁵. Preparation of these chelates is relatively difficult³ because of the chemical inertness of Cr(III) species in aqueous medium towards ligand exchange reaction. This led previous workers^{2,4} to prepare these chelates by simultaneous reduction and complexation from labile Cr(VI) species. Ballschmitter⁶ has reported the resolution of Cr(III) diethyl dithiocarbamates into two spots on silica gel layers. Formation of Cr(IV) dithiocarbamates has also been reported⁷ during oxidation of Cr(III) chelates. While the present work was in progress Sinha and coworkers⁴ reported and characterised some insoluble Cr(III) mixed ligand dithiocarbamates. Our TLC studies showed that Cr(III) dithiocarbamates prepared from Cr(VI) species at pH 4.8 invariably resolved into two spots. The new species formed along with the simple tris-chelates have been separated in preparative columns of silica gel and characterised by different physicochemical techniques.

Materials and Methods

Sodium salts of the ligands were prepared by mixing carbon disulphide, amine and sodium hydroxide solution in 1:1:1 molar ratio at 0°C in ethereal medium. Dithiocarbamates (dtc) of Cr(III) and Co(III) were prepared as reported earlier^{8,9} and recrystallised from chloroform.

All the reagents and solvents employed were of AR grade. Silica gel (BDH) was employed for thin layers and for preparative columns.

Preparation of mixed ligand Cr(III) dithiocarbamates

Sodium salt of the ligand in water (6%, w/v) was added to an aqueous solution of $\text{Cr}_2\text{O}_7^{2-}$ in 1:5 molar proportion at pH 4.8 (maintained with acetate buffer). The chloroform extract of the violet coloured

complexes was charged into a preparative column of silica gel (60-120 mesh) and eluted with chloroform. Fast moving violet coloured mononuclear chelates were eluted first followed by slow moving greenish violet mixed ligand binuclear chelates. The collected fractions were freed from solvent by evaporation and the solid obtained was recrystallised from chloroform and characterised.

Thin layer chromatography

Chromatographic migratory studies were made by allowing the solvent front to move up by 11 cm from the point of application of spots (uniformly above 1.5 cm from the lower end of the chromatostrips) on thin layers of silica gel (thickness 0.25 mm, activated at 100°C for 30 min) in closed glass chambers preequilibrated with solvent vapours.

Results and Discussion

Cr(III) chelates derived from Cr(VI) species invariably resolved into two spots on thin layers when weakly polar and non-polar were used as eluents (Table 1). The fast moving fraction corresponded to mononuclear tris-chelates as evidenced from their parallel migration with Cr(III) chelates prepared directly from CrCl_3 . The ratio of slopes of R_m versus $\log X_s$ plots of these fast and slow moving fractions is approximately of the order 3:4 (Table 1, Fig. 1). The migratory order of Cr(III) chelates derived from different amines is: Morph dtc < Dime dtc < Pip dtc < De dtc < Me ph dtc < Dipr dtc < Dibut dtc < Dibenz dtc.

Cr(III) chelates were separated quantitatively from bis-chelates of bivalent metal ions (synthetic mixtures) without much difficulty; however, their resolution from other tris-chelates was achieved only with certain dithiocarbamates and eluents. The parallel migrations

Table 1—The hR_f Values and Slopes of R_m versus $\log X_s$ Plots for Some Chromium(III) Dithiocarbamates

Mobile phase	Chelates with							
	A	B	C	D	E	F	G	H
	hR_f values							
<i>Fast moving fraction</i>								
Benzene	35.0	62.4	83.7	92.0	62.0	56.7	5.0	93.0
Toluene	22.5	43.0	69.0	91.3	51.0	32.7	4.1	88.4
Xylene	12.4	25.3	40.4	80.8	22.7	19.8	0	71.7
Chloroform	77.2	84.2	94.4	96.1	86.6	82.2	24.0	97.0
<i>Slow moving fraction</i>								
Benzene	6.0	5.9	16.3	32.0	13.0	8.0	0	46.0
Toluene	3.9	4.9	9.0	15.5	7.0	3.1	0	27.4
Xylene	0	0	5.8	9.6	0	0	0	11.1
Chloroform	29.7	40.5	68.7	84.3	54.6	33.6	16.0	82.0
	Slopes of R_m versus $\log X_s$ plots							
<i>Fast moving fraction</i>								
Benzene in carbon tetrachloride	1.78	1.63	1.82	2.33	1.55	2.22	—	2.22
Chloroform in carbon tetrachloride	1.80	1.91	2.22	1.95	2.12	1.51	—	1.70
<i>Slow moving fraction</i>								
Benzene in carbon tetrachloride	2.96	2.08	2.40	3.33	1.55	3.00	—	2.94
Chloroform in carbon tetrachloride	2.76	2.22	2.65	2.29	2.22	2.27	—	2.22
<i>Cobalt(III) chelates</i>								
Benzene in carbon tetrachloride	1.09	1.63	1.86	1.60	1.56	2.33	—	2.16
Chloroform in carbon tetrachloride	1.91	1.95	2.29	1.67	2.22	2.22	—	1.54

A = dimethyl dithiocarbamate; B = diethyl dithiocarbamate; C = di-*n*-propyl dithiocarbamate; D = di-*n*-butyl dithiocarbamate; E = *N*-methyl-*N*-phenyl dithiocarbamate; F = 1-piperidyl carbodithioate; G = morpholine-4-carbodithioate; H = dibenzyl dithiocarbamate.

observed for Co(III) and Cr(III) chelates indicate their similar molecular geometry⁹. This is verified by similar slopes (Table 1 and Fig. 1) of R_m versus $\log X_s$ plots for these chelates.

Our chromatographic investigations with dithiocarbamates of a number of transition elements indicate¹⁰ that dtc moiety gets adsorbed on hydroxyl groups of silica gel surface via H-bond formation through the lone pair of electrons available on N-atom. This is supported by the correlation of migratory order with $\nu(\text{C}\cdots\text{N})$ frequencies. TLC migration is found to increase (Table 1) with decreasing IR $\nu(\text{C}\cdots\text{N})$ frequencies. This observed decrease in IR frequencies is a measure of decreased hyperconjugation with N- α -CH₂ protons due to bulky and massive N-alkyl substituents¹¹. The increased inductive effect of alkyl groups and the electron conjugation with N-C-S group delocalises the electron density at N-atom resulting in the decreased availability of lone pair on N-atom for adsorption. From this fact and also following the arguments of Galik¹², it may be concluded that the fast

and slow moving fractions get adsorbed on adsorbent surface with 3 and 4 adsorbing centres respectively. The parallel migration of the slow moving fraction along with the adjacently spotted tris-chelate, on development with polar mobile phases like acetonitrile, tetrahydrofuran and DMSO etc., showed the conversion of the slow moving species into fast moving species.

Characterisation of slow moving species

Complexation of Cr(VI) species preceded by its reduction to Cr(III) in the presence of excess ligand is quantitative in the pH range 4.5-4.8 (acetate buffer). Slow moving fractions are formed with all types of dithiocarbamates, though the proportions decreased with increase in ligand concentration.

Results of elemental analyses of fast moving and slow moving fractions are presented in Table 2. For slow moving species the composition corresponds to the general formula $[\text{Cr}_2\text{O}(\text{dtc})_6]$, a binuclear molecule with oxygen bridge as evident from the

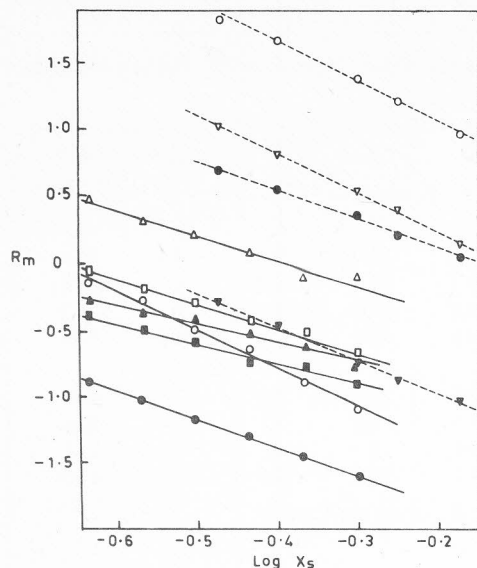


Fig. 1—Plots of R_m versus $\log X_s$ values [Mobile phases: benzene in CCl_4 , dotted line; ethyl acetate in CCl_4 , solid line. Δ , \square , \circ , ∇ = mononuclear species; \blacktriangle , \blacksquare , \bullet , \blacktriangledown = binuclear species; \triangle , \blacktriangle = dimethyl dithiocarbamate; \square , \blacksquare = diethyl dithiocarbamate; \circ , \bullet = 1-piperidyl carbodithioate; ∇ , \blacktriangledown = dibenzyl dithiocarbamate]

decreased magnetic moments¹³ (Table 2). Molecular weight measurements also confirm their dimeric nature (Table 2). Conductivity studies in acetonitrile [Λ_M (ohms⁻¹ mol⁻¹ cm²) in the range 4 to 10] indicate that these species are neutral and non-conducting.

IR spectral studies†

The characteristic absorbance of thioureide

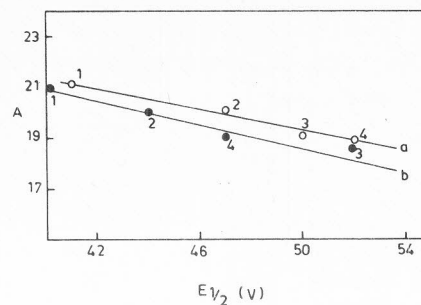


Fig. 2—Plot of A (in Hz) versus $E_{1/2}$ (in V) [1=(Morph)dtc; 2=(Pip)dtc; 3=(Dime) dtc; and 4=Me.ph.dtc; a=slow moving fraction (binuclear species); b=fast moving fraction (mononuclear species)]

bond^{14,15}, i.e. $\nu(\text{C}\cdots\text{N})$ in the region 1500-1475 cm^{-1} shifts to higher frequencies in binuclear species. Correspondingly $\nu(\text{C}\cdots\text{S})$ absorption¹⁶ in the region 940-1000 cm^{-1} shifts to lower frequencies. $\nu(\text{C}-\text{N})$ frequencies in the region 1275-1390 cm^{-1} for mononuclear tris-chelates also shift to higher energy regions for binuclear complexes. The latter chelates show split absorbance peaks for $\nu(\text{C}\cdots\text{N})$, $\nu(\text{C}-\text{N})$, and $\nu(\text{C}\cdots\text{S})$. This indicates the presence of nonequally bonded dtc moieties in these complexes¹⁷. Similarly strong, sharp but split absorptions in the range 830-890 cm^{-1} , characteristic of $\nu(\text{C}-\text{S})$ are also observed¹⁸. But these are absent in fast moving mononuclear chelates. This again indicates the presence of monodentate or otherwise nonequally bonded dtc moiety in the binuclear complex in addition to the normal bidentate dtc moiety. The weak

Table 2—Analytical Data and Some Physical Properties of the Complexes

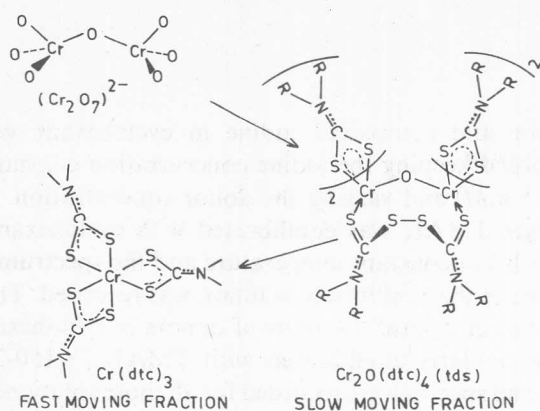
Compound	m.p. (°C)	Mol. wt. found ^a (calc.)	μ_{eff}^b	Found (calc.), %				
				Cr	N	S	C	H
[Cr(dimedtc) ₃]	148	421.3 (412.6)	3.78	12.58 (12.60)	10.22 (10.19)	46.71 (46.62)	26.21 (26.19)	4.22 (4.39)
[Cr ₂ O(dimedtc) ₄ tds]	280	812.0 (841.3)	4.87	12.41 (12.36)	9.97 (9.99)	45.78 (45.73)	25.72 (25.70)	4.28 (4.31)
[Cr(dedtc) ₃]	200	511.2 (496.8)	3.87	10.42 (10.47)	8.63 (8.46)	38.82 (38.73)	36.55 (36.26)	5.88 (6.09)
[Cr ₂ O(dedtc) ₄ tds]	250	980.0 (1009.6)	4.83	10.35 (10.31)	8.28 (8.33)	38.11 (38.12)	35.75 (35.70)	5.81 (5.99)
[Cr(pip dtc) ₃]	200	540.2 (532.8)	3.17	9.71 (9.76)	7.91 (7.89)	36.33 (36.12)	40.43 (40.57)	5.61 (5.67)
[Cr ₂ O(pip dtc) ₄ tds]	220	1019.0 (1081.6)	4.59	9.65 (9.62)	7.68 (7.77)	35.59 (35.57)	40.42 (39.91)	5.48 (5.59)
[Cr(morph dtc) ₃]	155	552.2 (538.7)	3.01	9.55 (9.65)	7.90 (7.81)	35.82 (35.72)	33.35 (33.44)	4.41 (4.49)
[Cr ₂ O(morph dtc) ₄ tds]	300	1002.0 (1093.5)	4.22	9.57 (9.55)	7.51 (7.69)	35.22 (35.18)	33.10 (32.95)	4.38 (4.43)

^a Molecular weight determination by cryoscopic method in benzene

^b Magnetic measurement by Guoy's balance at 28°C

^c Elemental analyses C and H by Perkin Elmer 240 B elemental analyzer; N by micro Kjeldahl method; S by microgravimetry as BaSO_4 ; Cr by spectrophotometry with diphenyl carbazide.

† Detailed IR spectral data for mono- and bi-nuclear chelates can be had from the authors on request.



(Chart 1).

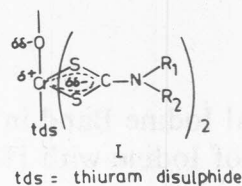
absorptions in the region $470\text{--}480\text{ cm}^{-1}$ indicate the presence of $-\text{S}-\text{S}-$ (disulphide) linkage^{19,20}. In addition, weak signals observed at $560\text{--}660\text{ cm}^{-1}$ correspond to $\nu(\text{Cr}-\text{S})$, $\nu(\text{Cr}-\text{O})$ and chelate ring deformation vibrations^{21,23}. From these facts it may be concluded that a thioammonium disulphide moiety is present in binuclear complexes as a bridge between two Cr(III) centres (Chart 1).

Electronic spectra and single electron reduction potentials

The electronic spectra of mono- and bi-nuclear Cr(III) dithiocarbamates are similar except for the shift of the 20.4 kK band of binuclear chelates to higher energy regions ($\sim 0.5\text{ kK}$) relative to mononuclear chelates. Likewise, the single electron reduction potentials $[\text{Cr}(\text{dtc})_3 + e^- \rightleftharpoons \text{Cr}(\text{dtc})_3^-]$ are more or less similar for both mono- and bi-nuclear chelates, though the latter show relatively more negative $E_{1/2}$ values (upto about 0.1 V).

NMR studies

The NMR $\text{N}-\alpha-\text{CH}_2$ interaction coefficients³ A (in Hz) [from $\Delta H = -A h g \beta H S(S+1)/3 g_N \beta_N k_B T$] are found to vary uniformly with $E_{1/2}$ values for Cr(III) dithiocarbamates like those for Fe(III) and Mn(III) chelates²⁴. For dialkyl derivatives, irrespective of the length of the N-alkyl chain, A remains almost the same, though $E_{1/2}$ varies from -0.41 to -0.62 V depending on the crystal field strength. This constancy in A -values is due to the bulky alkyl substituents making p_z orbital of N-atom non-coplanar with $\alpha-\text{CH}_2$ protons. But for cyclic (piperidyl and morpholy) and less bulky (dimethyl and methylphenyl) groups, which provide less steric hindrance, A -values decrease linearly with $E_{1/2}$ (Fig. 2). The unpaired $3d$ -electron density in Cr(III) binuclear complexes delocalises through conjugated ligand systems. This delocalisation increases as the crystal field strength increases. If the N-atom p_z orbital is coplanar with H ls



orbital, the extent of this delocalisation may be measured from the electron spin density on N-atom and its interaction with $-\text{CH}_2$ protons. For binuclear complexes having greater crystal field due to CrS_5O core, the canonical form (I) contributes more due to greater degree of metal electron delocalisation. Thus the compound becomes difficult to reduce and moves hardly on silica gel layers due to decreased positive charge on N-atom. From these facts, the redox process may be inferred to take place through N-atom rather than the Cr atom as observed earlier³. Though the CrS_6 core is non-labile on the NMR time scale, lability and some relaxation mechanisms are created through the tetragonal distortion of octahedral symmetry in CrS_5O core.

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