

## Thin Layer Chromatographic Behaviour of Piperidine-1-carbodithioates of Nickel(II), Copper(II), Zinc(II), Cobalt(III), Chromium(III), Manganese(III) & Iron(III)

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Thin layer chromatographic behaviour of piperidine-1-carbodithioates (Pip. dte) of Cr(III), Mn(III), Fe(III), Co(III), Ni(II), Cu(II) and Zn(II) has been studied on silica gel G layers and the results compared with those of diethyl dithiocarbamates (Die. dte). Pip. dte chelates afford better resolution than the corresponding Die. dte chelates. Migratory behaviour of these chelates has been correlated with some of their structural parameters.

Reports on thin layer chromatographic studies of neutral metal dithiocarbamates derived from heterocyclic amines are less frequent<sup>1</sup> than those derived from acyclic N,N-dialkylamines (particularly diethylamine)<sup>2,3</sup>. From equally basic cyclic piperidine and acyclic diethylamine metal dithiocarbamates with different physico-chemical properties have been prepared<sup>4,5</sup>. As an attempt to harness these differences to achieve better analytical separations, TLC behaviour of piperidine-1-carbodithioates (Pip. dte) of Ni(II), Cu(II), Zn(II), Co(III), Cr(III), Mn(III) and Fe(III) has been studied on silica gel layers. Galik's<sup>6</sup> theoretical treatment for diethyl dithiocarbamates (Die. dte) has been applied to explain the migratory behaviour of these chelates. The influence of electronic configuration of the central metal ion, the 'thioureide' bond order and molecular geometry around central metal ions on the migratory behaviour of these chelates are discussed.

### Materials and Methods

Sodium piperidine-1-carbodithioate was prepared as reported in literature<sup>7,8</sup>. Sodium diethyl dithiocarbamate (Fluka) was used as such. Chelates were prepared by metathetical reactions between ligand and metal salt solutions in water/ethanol in appropriate molar ratios<sup>4,9</sup>. Neutral chelates were purified by repeated crystallisations from chloroform. All reagents and chemicals employed were of analytical grade.

Freshly prepared chloroform solutions of the chelates were spotted 2 cm above the solvent surface on  $0.25 \pm 0.01$  mm thick silica gel G layers (BDH), which were activated at  $125^\circ$  for 45 min. Chromatograms were developed by allowing the solvent front to move up by 12 cm in pre-equilibrated (with eluent vapours) closed chambers at constant humidity.

### Results and Discussion

Pip. dte chelates (2) show generally differential and restricted migration than the corresponding Die. dte (1) chelates (Table 1). The increased electron density on N-atom of 'thioureide' bond, the absorbing site of these chelates, enhances the adsorption of the dithiocarbamate molecule. In Pip. dte (2) the rigid



heterocyclic ring restricts the flow of electron from N to C atom and then to donor sites via conjugation<sup>10</sup>. The electron density thus accumulated on N-atom makes Pip. dte to adsorb strongly than Die. dte. With simple solvents as mobile phases (Table 1) bis- and tris-chelates get resolved readily. Unlike the Ni(II) Die. dte, which moves parallel to Cu(II), Zn(II) and Co(III) Die. dte chelates, Ni(II) Pip. dte chelate does not migrate at all. The migratory order of Pip. dte chelates with simple mobile phases is:  $Zn \geq Cu > Cr > Co > Fe$ . Spectrophotometry after chromatographic separation and elution of these coloured chelates shows that the chromatographic stabilities of these chelates are in the order:  $Co > Cr > Cu > Ni > Zn > Fe > Mn$ . Fe(III) and Mn(III) dithiocarbamates are not recovered quantitatively after resolution because of their instability<sup>11</sup> on thin layers. For binary and ternary mobile phases (Table 1) also the same migratory behaviour and stability trend are observed.

The variation of mobility with filling-up of the *d*-orbitals of metal ions is shown in Fig 1. Bivalent metal chelates with filled or nearly filled *d*-orbitals show greater mobility than the trivalent metal chelates with half-filled or partially filled *d*-orbitals. In general, mobility decreases with increase in number of spin free

Table 1— $hR_f$  Values with Simple/Binary/Ternary Mobile Phases

Chelate	Cr(III)	Mn(III)	Fe(III)	Co(III)	Ni(II)	Cu(II)	Zn(II)
<i>Eluent: benzene</i>							
Pip. dtc	57	26	41	44	0	71	71
Die. dtc	62	56	52	54	59	76	75
<i>Toluene</i>							
Pip. dtc	32	16	20	22	0	55	60
Die. dtc	43	35	29	29	44	64	71
<i>Xylene</i>							
Pip. dtc	20	17	14	15	0	38	53
Die. dtc	25	21	19	19	29	44	60
<i>Chloroform-cyclohexane (1:1)</i>							
Pip. dtc	38	20	23	27	0	44	54
Die. dtc	51	33	32	30	33	49	58
<i>Chloroform-cyclohexane-diethylamine (30:65:5, v/v)</i>							
Pip. dtc	53	47	Dec.	58	0	46	41
Die. dtc	58	53	Dec.	61	66	53	47
<i>Benzene-cyclohexane-diethylamine (60:35:5, v/v)</i>							
Pip. dtc	61	50	Dec.	51	0	60	50
Die. dtc	73	68	Dec.	60	53	63	53

$hR_f = R_f \times 100$ ; Dec. decomposes

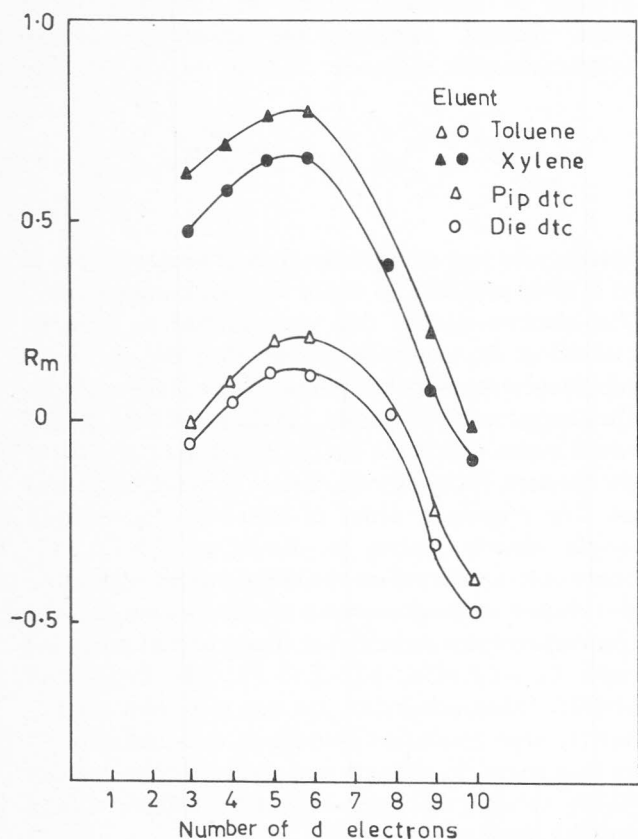


Fig. 1— $R_m$  versus number of electrons in  $d$ -orbital of central metal ion of the dithiocarbamate molecule.

electrons in  $d$ -orbitals; Fe(III) chelate with five unpaired electrons<sup>12</sup> is slow moving and Zn(II) chelate with no spin free electron is fast moving. Mn(III),

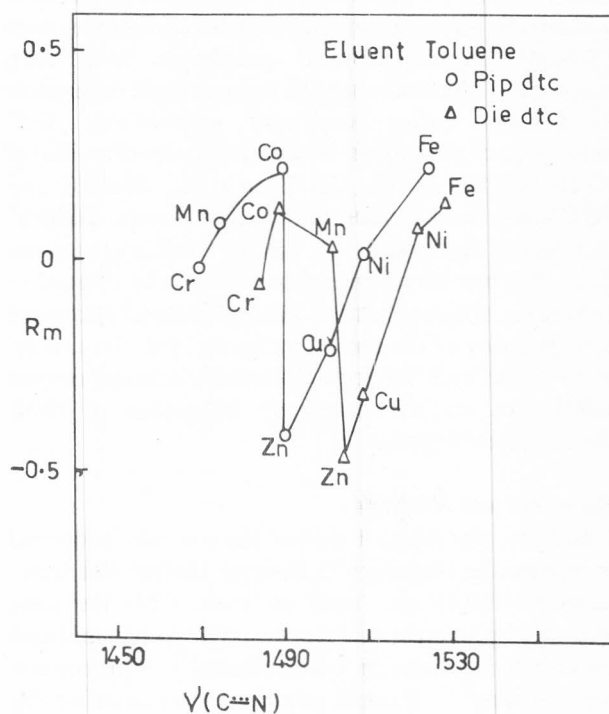


Fig. 2— $R_m$  versus  $v(N \equiv C)$  of dithiocarbamate molecules.

Cr(III) and Cu(II) chelates with 4,3,1 spin free electrons respectively show intermediate migratory behaviour.

$R_m$  versus  $\log X_s$  plots—In accordance with their restricted migration, Pip. dtc chelates show greater slopes than the corresponding Die. dtc chelates (Table 2). Slopes of trivalent and bivalent metal chelates are approximately in the order 3:2 indicating strong

Table 2—Slopes of  $R_m$  versus  $\log X_s$  Linear Plots of Piperidine-1-carbodithioates

Eluent system	Cr(III)	Mn(III)	Fe(III)	Co(III)	Cu(II)	Zn(II)
Chloroform + cyclohexane	4.44	4.00	4.00	3.62	2.22	2.35
(Same for Die. dtc)	(2.50)	(3.08)	(2.67)	(2.94)	(2.35)	(2.22)
Chloroform + carbon tetrachloride	2.27	2.85	2.11	2.22	1.11	1.17
Chloroform + benzene	0.83	1.08	0.79	0.77	0.46	0.49
Chloroform + cyclohexane + diethylamine	1.11	1.12	—	1.21	0.71	0.63
(Same for Die. dtc)	(1.25)	(1.11)	—	(1.25)	(0.71)	(0.71)
Benzene + cyclohexane	3.88	2.91	3.81	3.64	2.28	2.11
Benzene + carbon tetrachloride	3.00	1.57	2.96	2.33	2.00	2.00
Benzene + cyclohexane + diethylamine	1.25	1.18	—	1.33	0.40	0.65
(Same for Die. dtc)	(1.18)	(1.18)	—	(1.11)	(0.87)	(0.61)

$R_m = \log(1/R_f - 1)$ ,  $X_s$  = Fraction of more polar (active) solvent in the eluent (v/v).

adsorption of trivalent metal chelates through three dithiocarbamate moieties. Since the charge density on N-atom determines the extent of adsorption of chelates on adsorbent surface, the influence of N-alkyl substituent and the electronic configuration of the central metal ion are significant in addition to the number of dithiocarbamate groups.

The 'thioureide' bond order ( $N \cdots C$ )<sup>5,13</sup> is an approximate measure of the charge density on N-atom; so also is the influence of central metal ion on the adsorption characteristics of these chelate molecules with the same N-alkyl substituent (piperidyl group). The  $\nu(N \cdots C)$  of Pip. dtc chelates occur at lower wave number than those of the corresponding Die. dtc chelates because of the restricted electron release from piperidine ring. Contrary to the general expectation bis- and tris-chelates individually show increased mobility with decrease in  $\nu(N \cdots C)$  (Fig. 2). The  $\nu(N \cdots C)$ , in general follow the order<sup>12,13</sup>: square planar > tetrahedral > octahedral > distorted octahedral with respect to different molecular geometries. The mobilities of the chelates are found to decrease in the same order. Hence, in addition to charge density perturbations on N-atom, molecular geometry is also found to affect the migratory behaviour to a significant extent.

When the polarity of the eluent is increased, the adsorption of the chelate molecules diminishes resulting in enhanced migration and low slope values (Table 2).

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