TABLE 1—ANALYTICAL AND PHYSICAL DATA OF METAL BENZILATE COMPLEXES

| Compd.* | Colour | M.p. °C | Analysis % : Found/(Calcd.) | | $\mu_{eff}$ B.M. | $\Lambda_M$ $\Omega^{-1}$ cm$^2$ |
|---|---|---|---|---|---|---|
| | | | Metal | N | | |
| CoL$_2$Q$_2$ | Blue | 158 | 7.45 (7.65) | 3.25 (3.63) | 4.6 | 8.6 |
| CoL$_2$ ($\beta$-pic)$_4$ | Pink | 162 | 7.12 (6.66) | 5.89 (6.33) | 5.1 | 6.2 |
| NiL$_2$Q$_4$ | Green | 165 | 7.38 (7.62) | 3.36 (3.63) | 3.1 | 5.8 |
| NiL$_2$($\beta$-pic)$_4$ | Green | 168 | 6.21 (6.64) | 5.95 (6.33) | 3.2 | 8.8 |
| Cu L$_2$Q$_2$ | Blue | 146 | 8 41 (8.22) | 3.46 (3.61) | 1.79 | 10.2 |
| Cu L$_2$($\beta$-pic)$_2$ | Blue | 149 | 9.25 (9.03) | 3.62 (3 98) | 1.8 | 9 6 |
| Zn L$_2$Q$_2$ | White | 154 | 8 62 (8.41) | 3.71 (3.60) | – | 10.5 |
| Zn L$_2$($\beta$-pic)$_2$ | White | 156 | 8.85 (9.23) | 3.71 (3.98) | – | 9.8 |

* L – Benzilate, Q – Quinoline, B – (pic) – 3 methyl pyridine.

## Results and Discussion

All the complexes are crystalline having fairly low melting point and are soluble in common organic solvents. Acetone solution of the compounds have low molar conductance values indicating their non-electrolytic nature.

In the infrared spectra, benzilic acid[4] has the $\nu_{C=O}$ band at 1 650 cm$^{-1}$, which shifts to lower frequency region in metal benzilates at 1 625 – 1 630 cm$^{-1}$. In the base adducts, this band shifts slightly to the higher frequency region at 1 635 – 1 640 cm$^{-1}$ due to coordination of the $\sigma$-bonding nitrogen bases to the metal ion. In addition, most of the bands due to the free nitrogen ligand either shift or are modified, indicating bonding to the metal ion. This has been corroborated by the observation[5] of $\nu_{M-O}$ and $\nu_{M-N}$ at 465 and 385 cm$^{-1}$, respectively.

In the visible electronic spectra, Co$^{II}$-benzilate complex with quinoline exhibits one intense band at 16.0 kK assignable[6] to $4A_2 \rightarrow 4T_1$ (P) transition. On the basis of the position and intensity of the absorption band and magnetic moment data, this complex has presumably a tetrahedral configuration which is supported by $\mu_{eff} = 4.6$ B.M. The other cobalt complex has bands around 19.5 and 20.0 kK regions attributable[7] to $4T_{1g}$ (F) → $4T_{1g}$ (P) transition, suggesting a possible octahedral geometry of the complex. In case of Ni$^{II}$ complexes, bands are observed in the regions 9.6 – 9.8, 13.5 – 13.8 and 24.8 – 25.2 kK due to $3A_{2g}$ (F) → $3T_{2g}$ (F) → $3T_{1g}$ (F), → $3T_{1g}$ (P) transitions, respectively suggesting[8] an octahedral environment around the metal ion in conformity with the magnetic moment values 3.1 – 3.2 B.M. Cu$^{II}$ complexes have a broad absorption band in the regions 18.4 – 18.6 kK, indicating[9] a four coordinated square-planar configuration. $\mu_{eff}$ for Cu$^{II}$ complex was in the normal range 1.79 – 1.80 B.M. Zn$^{II}$ complexes are presumed to be tetrahedral on the basis of their analysis, conductance and infrared spectral data.

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## A Study on the Thermal Decomposition of some Metal Dithiocarbamate Complexes†

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THERMAL decomposition of nickel(II), zinc(II), cadmium(II), chromium(III) and cobalt(III) complexes with N-methylbenzyldithiocarbamate and morpholine-4-carbodithioate has been studied by

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Venkappayya and Brown[1]. On investigation of thermal properties of iron(III) and several other metal dithiocarbamate complexes, it was found that a few of these were volatile at elevated temperatures[2] and others decomposed on heating[3]. We report here the results of thermal studies on the metal dithiocarbamate complexes with cyclohexyldithiocarbamate (CHDTC), dicyclohexyldithiocarbamate (DCHDTC), methylanilinedithiocarbamate (MADTC), anilinedithiocarbamate (ADTC) and diphenyldithiocarbamate (DPDTC) ligands.

## Experimental

The ligands CHDTC, DCHDTC, MADTC, ADTC and DPDTC were prepared as their sodium salts by the interaction of carbon disulphide with the respective amines at 5° in presence of sodium hydroxide. The metal dithiocarbamate complexes were prepared by the interaction of an aqueous solution of the ligands with the respective metal salts[4]. 1 : 2 metal–ligand stoichiometry for the complexes of $Ni^{II}$, $Cu^{II}$, $Zn^{II}$, $Cd^{II}$ and $Hg^{II}$ and 1 : 3 stoichiometry for the complexes of $Fe^{III}$, $Co^{III}$ and $Mn^{III}$ were established from elemental analysis[5,6].

Details of analytical and other physical studies on these complexes are reported elsewhere[4,7,8]. TGA studies were carried out using a Stanton thermobalance under static conditions in air (using 100 mg of the sample) to observe thermal behaviour and to determine the decomposition temperature of the complexes. The heating rate of the furnace was 6° per min. Decomposition temperatures as discerned from the thermograms are indicated in Table 1. The highest temperature attained is 600° except in the case of Ni–DPDTC complex where it is 750°.

## Results and Discussion

The sodium salts of all the ligands used were found to decompose at around 180–185°. Metal complexes with dithiocarbamates (having a hydrogen atom attached to the nitrogen in the ligand), i.e. the dithiocarbamates derived from primary amine (aniline, cyclohexylamine) decompose differently from the metal complexes with that derived from secondary amine, which do not have a hydrogen atom attached to the nitrogen in the ligand (e.g. dicyclohexylamine, N-methylaniline). In the former case, decomposition of the metal complexes is through the evolution of $H_2S$, formation of isothiocyanate and sulphide before the final formation of the metal oxide, sometimes contaminated with smaller quantities of sulphides and sulphates. In the latter case, evolution of $H_2S$ and formation of isothiocyanate could not be detected. Thus the presence of H atom on the nitrogen seems to facilitate loss of $H_2S$ and the formation of isothiocyanate as intermediate products during the thermal decomposition. In both the cases, the final decomposition to the metal oxide stage proceeded through the intermediate formation of metal sulphide, which indicated the breaking of C–S linkage during thermal degradation of the complexes. Thus it seems that the M–S bond remains intact during the initial stage of decomposition.

In general, there appears to be difference in thermal stabilities of the two sets of complexes also. Metal complexes with the dithiocarbamates having a hydrogen attached to the nitrogen, start decomposing at a lower temperature than those without such hydrogen. In $Ni^{II}$ complexes, this difference is much larger than that with the corresponding $Co^{III}$ complexes. The much bulkier dicyclohexyl moiety appears to influence the thermal stability of the metal complexes, i.e. the bulkier ligands were also less likely to give volatile complexes.

TABLE 1—RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF DITHIOCARBAMATE COMPLEXES

| Compd. | Ligand (LH) | Initial decomp. temp °C | Decomp. temp. range °C | Inorganic residue |
|---|---|---|---|---|
| Fe(L)₃ | DCHDTC | 230 | 230–350 | $Fe_2O_3$ + $FeSO_4$ |
| | MADTC | 200 | 200–320 | $Fe_2O_3$ + FeS |
| Co(L)₃ | CHDTC | 150 | 150–200 | $Co_3O_4$ + $CoSO_4$ |
| | DCHDTC | 180 | 180–340 | $Co_3O_4$ + $CoSO_4$ |
| | MADTC | 130 | 130–250 | $Co_3O_4$ + $CoSO_4$ |
| | ADTC | 120 | 120–300 | $Co_3O_4$ + $CoSO_4$ |
| Ni(L)₂ | CHDTC | 120 | 120–320 | NiO + $NiSO_4$ |
| | DCHDTC | 250 | 250–550 | NiO |
| | MADTC | 150 | 150–330 | NiO |
| | ADTC | 130 | 130–320 | NiO (contaminated with $NiSO_4$) |
| NiL | DPDTC | 77 | 77–300 | |
| | DPDTC | 400 | 400–520 | NiO |
| Cu(L)₂ | CHDTC | 120 | 120–280 | CuO |
| | DCHDTC | 180 | 180–300 | CuO |
| | MADTC | 140 | 140–320 | CuO |
| | ADTC | 120 | 120–320 | CuO (contaminated with CuS, $CuSO_4$) |
| Zn(L)₂ | CHDTC | 200 | 200–440 | ZnO + ZnS + $ZnSO_4$ |
| | DCHDTC | 140 | 140–340 | ZnO + ZnS |
| Cd(L)₂ | CHDTC | 120 | 120–160 | CdO + CdS |
| | DCHDTC | 180 | 180–300 | CdO + CdS |
| Hg(L)₂ | CHDTC | 135 | 135–180 | All are highly volatile in the course of decomposition |
| | DCHDTC | 140 | 140–300 | |
| | MADTC | 130 | 130–300 | |
| | ADTC | 60 | 80–200 | |
| | DPDTC | 120 | 120–280 | |
| Mn(L)₃ | CHDTC | 130 | 130–290 | $Mn_3O_4$ + $MnSO_4$ |
| | DCHDTC | 120 | 120–300 | $Mn_3O_4$ |
| | MADTC | 115 | 115–300 | $Mn_3O_4$ |
| | ADTC | 120 | 120–300 | $Mn_3O_4$ |

The thermal decomposition pattern of $Ni(DPDTC)_2$ was different from other complexes and it proceeded through the formation of intermediate 1 : 1 complex, viz. Ni.DPDTC. Stoichiometry of this complex was confirmed by an independent chemical analysis of the sample. The weight of the final residue left at 750° almost corresponds with the weight expected for pure NiO.

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## Rhenium. Part-XVIII. Isothiocyanato Complexes of Quadrivalent Rhenium

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THE present communication describes the reaction between $K_2[ReI_6]$ and KSCN in methanol in which two complex ions having essentially the same composition, viz. $[Re(NCS)_6]^{2-}$ were obtained. While one of these has been fully characterised as hexaisothiocyanatorhenate(IV)[1,2], the other has been tentatively formulated as a dimer, $[Re_2(NSC)_{12}]^{4-}$.

## Experimental

A concentrated solution (60 ml) of $K_2[ReI_6]$ (3 g, 0.0029 mol) and excess of KSCN (3.6 g, 0.037 mol) in methanol (25 ml) was boiled for 0.5 h. The mixture was dried by evaporation, and then extracted with diethyl ether (75 ml) leaving a residue ($\sim 2$ g). The extract was evaporated and dissolved in water (5 ml). The complex $Cs_2[Re(NCS)_6]$ precipitated on addition of CsCl (5 g, 0.029 mol). The precipitate was washed with ice-cold water, extracted with acetone and the extract dried over fused calcium chloride. Elemental analysis (Table 1) gave Cs, Re and NCS ratio as 2 : 1 : 6.

$Cs_4[Re_2(NCS)_{12}]$ : The residue ($\sim 2$ g) left after extraction with diethyl ether was dissolved in water (5 ml) and precipitated with CsCl (5 g, 0 029 mol). The precipitate was washed with ice-cold water followed by extraction with acetone and drying over fused calcium chloride. Elemental analysis (Table 1) gave Cs, Re and NCS ratio as 2 : 1 : 6. A thallium salt (Table 1) precipitated when a concentrated solution of the caesium salt (0.4 g, 0.00025 mol) was treated with $TlNO_3$ (0.4 g, 0.0015 mol) in water.

## Results and Discussion

All the complexes are dark red-brown, almost black. The two caesium salts are moderately soluble in methanol, ethanol and water, but highly soluble in acetone. The thallium salt is highly soluble in acetone, but insoluble in water, methanol and ethanol. The aqueous solutions of $Cs_2[Re(NCS)_6]$ and $Cs_4[Re_2(NCS)_{12}]$ appear reddish brown and brown black, respectively.

The room temperature magnetic moment value of $Cs_2[Re(NCS)_6]$ (Table 1) agrees with those of other salts of $[Re(NCS)_6]^{2-}$ reported earlier[1-3]. The much lower magnetic moment values of $Cs_4[Re_2(NCS)_{12}]$ and $Tl_4[Re_2(NCS)_{12}]$ (Table 1) are indicative of their dinuclear nature involving thiocyanate bridging and/or Re—Re interaction, the latter being well known[4] in $Re^{III}$ and $Re^{IV}$.

TABLE 1—ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

| Compd. | Analysis % : Found/(Calcd ) | | | | $\mu_{eff}$* | $\nu_{CN}$ cm$^{-1}$ |
|---|---|---|---|---|---|---|
| | Re | S | N | Cs/Tl | | |
| $Cs_2[Re(NCS)_6]$ | 22 8 (23.3) | 23 8 (24.0) | 10.6 (10.5) | 33.2 (33.2) | 3.10 | 2 020 |
| $Cs_4[Re_2(NCS)_{12}]$ | 22.7 (23.3) | 24.1 (24 0) | 10.5 (10.5) | 33.4 (33.2) | 1.04a | 2 055 |
| $Tl_4[Re_2(NCS)_{12}]$ | 19.4 (19.7) | 20.3 (20.4) | 8.8 (8.9) | 42.9 (43.3) | 1.09a | 2 055 |

*At 298 K.
a Magnetic moment per rhenium.