

## Complexes of Dibenzoyldisulphide with Metal Halides. Part III. Complexes of Dibenzoyldisulphide with Cobalt(II), Nickel(II), Manganese(II), Copper(II), Iron(III) and Chromium(III) Halides

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### Abstract

Adducts (1:1) of halides of cobalt(II), nickel(II), manganese(II), copper(II), iron(III) and chromium(III) with dibenzoyldisulphide have been isolated and characterized on the basis of elemental analysis, molar conductance, magnetic susceptibility, infra-red spectra, molecular weight and thermogravimetric analysis data.

### Introduction

Very little is known about the donor properties of dibenzoyldisulphide ( $Bz_2S_2$ ) which has two carbonyl groups and one sulphur–sulphur bond capable of acting as donor sites. On hydrolysis there is a cleavage of C–S bond rather than the S–S bond which indicates, that S–S bond is fairly stable in this molecule [1]. An attempt has been made to prepare some complexes of  $Bz_2S_2$  with nitrogen bases [2] but structural evidence is lacking. Some seven membered ring chelates of Zn, Cd and Mg(II) halides with  $Bz_2S_2$  have been isolated and characterized wherein both carbonyl oxygen atoms, in preference to the S–S system act as donor sites [3, 4]. Isolation and characterization of some chelates of  $Bz_2S_2$  with halides of Co(II), Ni(II), Mn(II), Cu(II), Fe(III) and Cr(III) are reported in the present studies.

### Experimental

Dibenzoyldisulphide ( $Bz_2S_2$ ) was prepared and purified by the standard method [5]. Anhydrous metal halides were prepared by the methods already reported in literature. All the complexes were prepared by refluxing equimolar quantities of both components in dry benzene, (both the components going into solution). The compounds were recovered

by adding an inert solvent such as petroleum ether. Their composition has been determined by elemental analysis according to the standard literature methods [6].

Molecular weights were determined using the Beckman method. Magnetic susceptibility measurements were carried out by the standard Guoy method using a permanent magnet and a sample tube calibrated with mercury(II) tetrathiocyanate cobalt(II) and the diamagnetic corrections were made by standard methods [7].

Infra-red spectra of the compounds were recorded on Perkin-Elmer models 337 and 621 grating IR spectrophotometers as mulls in nujol or hexachlorobutadiene between CsI plates.

Thermogravimetric analysis was carried out on a Stanton thermobalance Model TR-1. Thermograms were obtained on 300–400 mg samples at a heating rate of  $4^\circ \text{ min}^{-1}$ .

### Results and Discussion

Stoichiometric composition of these compounds was determined by elemental analysis and is reported in Table I. These compounds are fairly stable at room temperature and do not change their colours on exposure to moisture. They are soluble in the conventional organic solvents. Molar conductance values of the millimolar solutions in nitrobenzene show them to be non-electrolytes and rule out the possibility of the presence of ions of the type  $[MBz_4S_4]^{2+}$  and  $[MCl_4]^{2-}$ . Molecular weight determination in benzene and nitrobenzene suggests them to be monomers only.

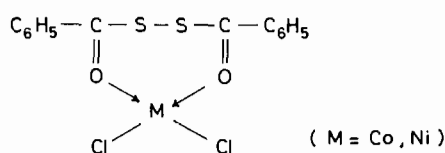
Infra-red spectrum of pure  $Bz_2S_2$  shows an intense absorption band at  $1670 \text{ cm}^{-1}$  and a weak band at  $1750 \text{ cm}^{-1}$  which are due to  $\nu(C=O)$ . It also shows one weak band at  $540 \text{ cm}^{-1}$  due to  $\nu(S-S)$  band and a sharp band at  $670 \text{ cm}^{-1}$  assigned to  $\nu(C-S)$  stretch-

TABLE I. Analytical Data of the Compounds of Dibenzoyldisulphide with Halides of Co(II), Ni(II), Cu(II), Mn(II), Fe(III) and Cr(III).

Compounds	Physical state and colour	m.pt. °C	$\mu_{\text{eff}}$ B.M.	Molar conductance $\text{ohm}^{-1} \text{cm}^2/\text{litre}$	M.Wt. in nitrobenzene	%Found			%Required		
						Sulphur	Halogen	Metal	Sulphur	Halogen	Metal
$\text{CoCl}_2 \cdot \text{Bz}_2\text{S}_2$	Solid blue	170	4.82	3.50	399.6	15.95	17.20	13.83	15.84	17.59	14.34
$\text{CoBr}_2 \cdot \text{Bz}_2\text{S}_2$	Solid blue	152	4.76	2.30	490.2	12.38	31.52	11.58	12.84	31.98	11.54
$\text{NiCl}_2 \cdot \text{Bz}_2\text{S}_2$	Solid brown	122	4.28	2.40	398.2	15.98	16.84	13.92	15.88	17.62	14.41
$\text{NiBr}_2 \cdot \text{Bz}_2\text{S}_2$	Solid brown	136	4.24	1.80	489.6	12.76	31.86	11.74	13.00	32.52	11.86
$\text{CuCl}_2 \cdot \text{Bz}_2\text{S}_2$	Solid blue	220	1.92	1.15	403.8	14.95	16.97	15.15	15.65	17.35	15.55
$\text{MnCl}_2 \cdot \text{Bz}_2\text{S}_2$	Solid white	133	5.94	1.20	394.7	15.85	17.36	13.52	16.04	17.75	13.75
$\text{FeCl}_3 \cdot \text{Bz}_2\text{S}_2$	Solid yellow	190	5.64	2.05	432.8	14.36	24.25	12.46	14.66	24.63	12.82
$\text{CrCl}_3 \cdot \text{Bz}_2\text{S}_2$	Solid green	171	3.60	0.88	428.6	14.45	24.14	11.85	14.79	24.62	12.02

ing mode [8, 9]. On complex formation there is a significant lowering of  $\nu(\text{C}=\text{O})$  while the other two important stretching modes due to S-S and C-S bands are not disturbed, suggesting that only carbonyl groups take part in bonding and the other two bonds namely (S-S) and (C-S) are intact after complex formation. In the case of adducts of cobalt(II) and nickel(II) halides the band originally present at  $1750 \text{ cm}^{-1}$  is shifted to  $1670 \text{ cm}^{-1}$  and the one present at  $1670 \text{ cm}^{-1}$  is shifted to  $1590 \text{ cm}^{-1}$  showing that, in preference to S-S group, coordination takes place at the carbonyl group oxygen atom. In addition a new band not present in the ligand and independent of the metal halide used makes its appearance at  $430 \text{ cm}^{-1}$  in the case of complexes of cobalt(II) halides and at  $410 \text{ cm}^{-1}$  in the case of nickel halide compounds. These bands may be assigned to metal-oxygen stretching modes. These findings are in good agreement with the observations that metal(II) oxygen stretching modes in tetrahedral environments are expected to be in the region  $400-500 \text{ cm}^{-1}$  [10, 11]. The other important stretching bands which lie in the far infra-red region are due to (Ni-Cl) and (Co-Cl) which are observed at  $284 \text{ cm}^{-1}$  and  $292 \text{ cm}^{-1}$  in these compounds. Similarly (Ni-Br) and (Co-Br) are observed at  $226$  and  $234 \text{ cm}^{-1}$ . These are in agreement with the reported values of the metal halogen stretching modes for tetrahedral symmetry reported in literature [12, 13].

The magnetic moment values of  $4.82 \text{ B.M.}$  at  $25^\circ \text{C}$  for the cobalt(II) complexes are much higher than  $3.88 \text{ B.M.}$ , the spin only value corresponding to three unpaired electrons. The values in the range  $4.2-4.8 \text{ B.M.}$  are generally observed for the tetrahedral stereochemistry with a  $^4\text{A}_2$  ground state term being proposed for Co(II) complexes. The magnetic moment value of  $4.28 \text{ B.M.}$  for Ni(II) complexes is in good agreement with the tetrahedral stereochemistry for which the values ranging from  $3.5$  to  $4.1 \text{ B.M.}$  are expected because of the orbital contribution of  $^3\text{T}_1$  ground state term [14]. In the light of the above observations, seven membered ring structures for these compounds may be proposed as below. These chelates seem to be quite stable.



In case of Mn(II) and Cu(II) chloride adducts with  $\text{Bz}_2\text{S}_2$  the absorption bands due to  $\nu(\text{C}=\text{O})$  originally present in the pure dibenzoyldisulphide at  $1750 \text{ cm}^{-1}$  and  $1670 \text{ cm}^{-1}$  are shifted to  $1655$ ,  $1645$  and  $1610$ ,  $1580 \text{ cm}^{-1}$  respectively which further indicates that in preference to S-S group,

coordination occurs at the carbonyl group oxygen atom. In addition to this, bands observed at  $410\text{ cm}^{-1}$  in case of Mn(II) and  $452\text{ cm}^{-1}$  in case of Cu(II) complexes may be assigned to metal-oxygen bonds as reported in literature [15].

The magnetic moment value of 5.94 B.M. for  $\text{MnCl}_2 \cdot \text{Bz}_2\text{S}_2$  complex is in good agreement with the high spin Mn(II) complexes having tetrahedral stereochemistry for which the spin only value of 5.92 B.M. is expected [16]. The magnetic susceptibility value of 1.92 B.M. obtained in case of  $\text{CuCl}_2 \cdot \text{Bz}_2\text{S}_2$  is very close to value 1.9 B.M. which is generally observed for the octahedral stereochemistry and thus a octahedral stereochemistry with  ${}^2E_g$  ground state term [17] may be proposed for  $\text{CuCl}_2 \cdot \text{Bz}_2\text{S}_2$  complex.

Similarly, anhydrous iron(III) and chromium(III) chloride, when refluxed with equimolar quantities of dibenzoyldisulphide in anhydrous benzene, form coloured crystalline compounds. Elemental analysis for metal, sulphur and chlorine (Table I) corresponds to the composition  $\text{FeCl}_3 \cdot \text{Bz}_2\text{S}_2$  (yellow) and  $\text{CrCl}_3 \cdot \text{Bz}_2\text{S}_2$  (green). These complexes are not so moisture sensitive and soluble in nitrobenzene. Infra-red spectra of these solutions in nitrobenzene indicate that during the dissolution, the carbonyl group is set free due to the co-ordination of a solvent molecule (a stronger base) in its place. The molar conductance and the molecular weights measurements of these compounds also suggest their monomeric nature.

In these complexes the carbonyl stretching frequencies at  $1750$  and  $1670\text{ cm}^{-1}$  originally present in the pure dibenzoyldisulphide is lowered to  $1665$  and  $1642\text{ cm}^{-1}$ ,  $1625$  and  $1610\text{ cm}^{-1}$  in the complexes  $\text{FeCl}_3 \cdot \text{Bz}_2\text{S}_2$  and  $\text{CrCl}_3 \cdot \text{Bz}_2\text{S}_2$ , respectively. Again the coordination is *via* the carbonyl group oxygens to the central metal ion [18]. The formation of a metal-oxygen bond is indicated by the appearance of new vibrational bands [ $\nu(\text{M}-\text{O}) + \nu(\text{C}-\text{C})$ ] at  $550\text{ cm}^{-1}$  and  $532\text{ cm}^{-1}$  in  $\text{CrCl}_3 \cdot \text{Bz}_2\text{S}_2$  and  $\text{FeCl}_3 \cdot \text{Bz}_2\text{S}_2$ , respectively [19]. These spectral observations thus indicate a bidentate nature of the ligand.

Measuring their magnetic susceptibility at room temperature from the following the complexes of chromium(III) are usually octahedral [7]. Under the action of octahedral crystal field, the ground state term of the chromium(III) ion is  ${}^4A_{2g}$ , and thus there is no orbital contribution towards the magnetic moment. The magnetic moment value, however, is expected to be reduced to 3.80 B.M. due to the action of spin-orbit coupling. The experimental value of 3.60 B.M. for  $\text{CrCl}_3 \cdot \text{Bz}_2\text{S}_2$  is low, and may be attributed to spin-orbit coupling only. The tendency of chromium(III) ion to attain hexaco-ordination has given rise to so many polynuclear complexes usually having hydroxide, carboxylate or chloride as bridging

groups [20, 21]. In these polymers there is a possibility of magnetic exchange between the neighbouring chromium(III) ions. This magnetic interaction may lead to intramolecular antiferromagnetic behaviour which is responsible for the lowering of magnetic moment values to as low as 3.41 B.M. [20]. The proposed co-ordination number six as well as the low magnetic moment value of 3.60 B.M. in our complex are consistent with a polymeric structure. The most-likely possibility is via chlorine bridges such that each chromium has two oxygen and four chlorine atoms in the co-ordination sphere.

In the case of iron(III) the cubic crystal field splits the  ${}^6S$  term into  ${}^6A_1$  from which there is no orbital contribution to the magnetic moment. Consequently, the magnetic moment for a magnetically dilute system is expected to be close to 5.92 B.M. (the spin only value), but the experimental value for  $\text{FeCl}_3 \cdot \text{Bz}_2\text{S}_2$  is only 5.64 B.M. The low magnetic moment of the complex may be explained on the basis of a polynuclear structure similar to that postulated for chromium(III). Such chlorine bridged polynuclear complexes are known in the literature [21].

Thermogravimetric analyses of all these adducts have also been carried out. All these compounds all show the same trend decomposition around  $140\text{--}150^\circ\text{C}$  to form benzoyl halides which volatilize leaving behind black metallic sulphides.

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