Oxidation of Dithiocarbamate Ligands to Positive Ions

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Summary Halogenation of dithiocarbamato-complexes of iron, cobalt, antimony, and copper gives compounds in which the dithiocarbamate is oxidised to a positive ion, presumably with an *s*-tetrathian ring, and the metals are present in halogenated negative ions.

A COMPOUND of composition $Fe(dtc)Cl_4$(dtc = *NN*-diethyldithiocarbamato), formed as a greenish yellow product from the reaction of $FeCl_3$ and *NNN'N'*-tetraethylthiuram disulphide was reported by Tamminen and Hjelt.[1] They assumed one of the chlorine atoms to be bound to a sulphur atom of the dithiocarbamato-group. We found that the same compound could be formed by the reaction of $Fe(dtc)_3$ or $Fe(dtc)_2Cl$ with chlorine in chloroform as solvent, while the corresponding bromo-compound $Fe(dtc)Br_4$ could be prepared from $Fe(dtc)_3$ or $Fe(dtc)_2Br$ and Br_2.

Satisfactory analytical data were obtained for the formulae $FeCl_4C_5H_{10}NS_2$ and $FeBr_4C_5H_{10}NS_2$.

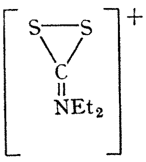
Magnetic susceptibility measurements show both products to have a magnetic moment of 5·92 B.M. at 298° K as well as at 83° K.

From the Mössbauer spectrum of $Fe(dtc)Cl_4$ the isomer shift [0·90 mm./sec. relative to $Na_4Fe(CN)_6$] and the quadrupole splitting (0·22 mm./sec.) are found to be equal to those for $(Et_4N)^+FeCl_4^-$.

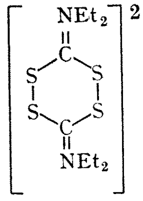
In the i.r. spectra there is no evidence for Fe–S or S–Cl vibration bands. The Fe–Cl stretching vibration is found at 386 cm.$^{-1}$ compared with 378 cm.$^{-1}$ in $(Et_4N)^+FeCl_4^-$ while the absorption band of $Fe(dtc)Br_4$ at 296 cm.$^{-1}$ corresponds with the one for Fe–Br at 290 cm.$^{-1}$ in $(Et_4N)^+ FeBr_4^-$.[2]

Magnetic and spectroscopic measurements indicate that the compounds $Fe(dtc)Cl_4$ and $Fe(dtc)Br_4$ contain $FeCl_4^-$ and $FeBr_4^-$ ions, respectively. The unit dtc must then be present in a positive ion.

Since a monomeric ion (I) should be unstable because of considerable ring strain a dimeric dipositive ion (II) with a *s*-tetrathian ring is assumed to be present. The very high C=N stretching frequency, found at 1568 cm.$^{-1}$ is in accordance with this assumption.



(I)



(II)

A dithiocarbamato-complex is obtained by reducing the compounds by the method of Tamminen and Hjelt.[1]

Because of decomposition in polar solvents, no electric conductance data are available.

Strong support is further given by the successful synthesis of $CoCl_4(dtc)_2$ and $SbCl_6(dtc)$, which can be prepared in a similar manner to $FeCl_4(dtc)$.† The results of spectroscopic and magnetic measurements suggest they have the same dipositive *s*-tetrathian ion and $CoCl_4^{2-}$ and $SbCl_6^-$ ions respectively. The compounds $Cu(dtc)Cl_3$ and $Cu(dtc)Br_3$, which we reported recently[3] are now considered to be composed of the dipositive ion and a halogenocuprate(II) ion.[4]

The oxidation of the dithiocarbamato-anion to a positive

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† The compound $SbCl_6(dtc)$ can also be prepared from NO $SbCl_6$ and Na(dtc) in chloroform.

ion, no longer co-ordinated to the metal is similar to the behaviour of the dithioacetylacetone group, which can be oxidised to a dithiolium cation.[5]

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