The Nature of the Product from the Reaction between Octacarbonyldicobalt and Bis(trifluoromethyl)dithieten

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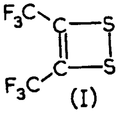
IN 1963 one of us[1] reported the reaction between $Co_2(CO)_8$ and bis(trifluoromethyl)dithieten (I) to give a volatile black solid of empirical composition $C_4F_6S_2CoCO$. We now present evidence for the formulation of this substance as the trimer $[(CF_3)_2C_2S_2Co(CO)]_3$ (II).

The ion at highest *m/e* in the mass spectrum of the black crystals occurs at *m/e* 939, corresponding to the ion $C_{12}F_{18}S_6Co_3(CO)_3^+$, the expected parent ion for the trimer (II). Furthermore, ions at *m/e* 911, 883, and 855 are observed, corresponding to the ions $C_{12}F_{18}S_6Co_3(CO)_n$ ($n = 2$, 1, and 0, respectively) resulting from the stepwise loss of carbonyl groups from the parent ion.[2] Also observed is an intense ion at *m/e* 758, apparently $C_{12}F_{16}S_6Co_2^+$, and a relatively intense metastable ion at *m/e* 672 indicating the reaction

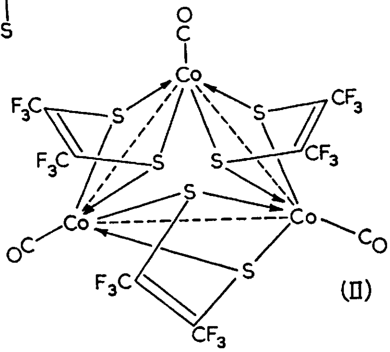
$$C_{12}F_{18}S_6Co_3^+ \rightarrow C_{12}F_{16}S_6Co_2^+ + CoF_2$$

with loss of a neutral metal fluoride fragment to be a favoured pathway for further fragmentation.

The trimeric formulation $[(CF_3)_2C_2S_2Co(CO)]_3$ (II) thus indicated by mass spectrometry has an odd number of electrons and would be expected to be paramagnetic. Magnetic susceptibility measurements[3] on this material indicate it indeed to be paramagnetic with a molar susceptibility at 23° of $+1138 = 10^{-6}$ cm.^{3}/mole corresponding (after diamagnetic corrections) to 1·84 B.M., approximately that expected for one unpaired electron.



(I)



(II)

The formation of a trinuclear complex from bis(trifluoromethyl)dithieten (I) and $Co_2(CO)_8$ is hardly surprising since other trinuclear sulphur derivatives of cobalt carbonyl such as $Co_3(CO)_6$-$S_2CH_2 \cdot C_6H_5$ and $Co_3(CO)_9S$ are known.[4,5] The last compound, like $[(CF_3)_2C_2S_2Co(CO)]_3$, (II) exhibits

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the expected paramagnetism for one unpaired electron.

A compound which should be closely related to (II) is the black solid of empirical composition $C_4F_6S_2FeNO$ obtained from $Hg[Fe(CO)_3NO]_2$ and bis(trifluoromethyl)dithieten (I).[6] The highest *m/e* ion in the mass spectrum of this substance occurs at *m/e* 936, corresponding to the trimer $[(CF_3)_2C_2S_2Fe(NO)]_3$. Furthermore, other ions are observed corresponding to losses of up to three nitrosyl groups and/or one fluorine atom from this parent ion. However, another series of ions occurs at *m/e* 772, 742, 712, 682, and 652, corresponding to $(C_4F_6S_2)_2Fe_3S(NO)_n$ (n = 4, 3, 2, 1, and 0, respectively) indicating a second component to be $[(CF_3)_2C_2S_2]_2Fe_3S(NO)_4$. Thus the reaction of bis(trifluoromethyl)dithieten with $Hg[Fe(CO)_3NO]_2$ appears to be more complex than that with $Co_2(CO)_8$.

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[1] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1587.

[2] For a discussion of the mass spectra of some polynuclear metal carbonyl derivatives see: R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 2075.

[3] These measurements were carried out at ambient temperature by the Faraday method.

[4] E. Klumpp, L. Markó, and G. Bor, *Chem. Ber.*, 1964, **97**, 926.

[5] L. Markó, G. Bor, E. Klumpp, B. Markó, and G. Almasy, *Chem. Ber.*, 1963, **96**, 955.

[6] R. B. King, *Inorg. Chem.*, 1963, **2**, 1275.