The Photochemical Preparation of Chromium(III) Mercaptides

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THE publication of a recent Paper[1] describing the mercaptides of cobalt, nickel, copper, and zinc(II) prompts us to communicate preliminary details of our studies on Cr^{III} mercaptides. Cr^{III} methylmercaptide was prepared by the photochemical oxidative decarbonylation of tricarbonylbenzenechromium in dry dimethyl disulphide, and is analogous to the preparation of Cr^{III} alkoxides.[2]

$$ArCr(CO)_3 \xrightarrow[h\nu]{Me_2S_2} Cr^{III}(SMe)_3 + Ar + 3CO$$

Chromium(III) methylmercaptide is a dark green involatile solid (m.p. > 250°), insoluble in organic solvents and with a faint disagreeable smell. Carbon and chromium analyses agree with the formula $Cr(SMe)_3$. The presence of methylmercaptide groups was confirmed by treatment with concentrated sulphuric acid, passage of the resultant gas into alcoholic sodium hydroxide, and addition of 2,4-dinitrochlorobenzene when golden yellow crystals of m.p. 127° (lit. 128°) were obtained.

The electronic spectrum measured in KBr discs and also by reflectance methods on the solid can be interpreted on the basis of an octahedral environment for Cr^{III} as follows:—

16,130 cm.$^{-1}$ [$^4A_{2g} - {}^4T_{2g}$],
23,800 cm.$^{-1}$ [$^4A_{2g} - {}^4T_{1g}(F)$]

the corresponding bands in the pure powder lie at 16,670 and 25,000 cm.$^{-1}$. The infrared spectrum measured in mulls, KBr (and CsBr) discs showed a weak band at 700 cm.$^{-1}$ which was assigned to a Cr–S–C stretch, a broad band at 490 cm.$^{-1}$ assigned tentatively to the Cr–S stretching frequency of the F_{1u} species (assuming octahedral Cr^{III}) and the band at 353 cm.$^{-1}$ to a S–Cr–S bending mode of the F_{1u} species; all other bands were consistent with the presence of methylmercaptide groups. The room temperature magnetic moment of 3·49 B.M. per Cr atom is lower than that of the spin-free value of 3·88 B.M. but considerably higher than 2·65 B.M. observed for the corresponding methoxide,[2] indicating a smaller antiferromagnetic interaction consistent with the larger size of the SMe bridging group compared with OMe. *X*-Ray powder photographs are very similar to those of Cr^{III} methoxide[2] with a very intense line at 7·8 Å corresponding to that at 7·1 Å in the methoxide and indicating a large unit cell as expected for the replacement of the OMe group by SMe.

Preparation of $Cr^{III}(SEt)_3$ by the above method yields a product with correct Cr analysis but slightly low carbon analysis (5%) as encountered in other alkoxides and mercaptides.[1-3] The infrared and electronic spectra and magnetochemical properties are consistent with the formulation $Cr(SEt)_3$; the compound is very similar in appearance to the methyl mercaptide.

Further studies are in progress on these compounds.

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[1] D. C. Bradley and C. H. Marsh, *Chem. and Ind.*, 1967, 361.
[2] D. A. Brown, D. Cunningham, and W. K. Glass, *Chem. Comm.*, 1966, 306.
[3] C. H. Brubaker and M. Wicholas, *J. Inorg. Nuclear Chem.*, 1965, **27**, 59.