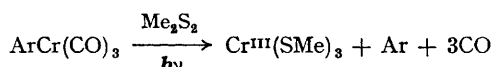


The Photochemical Preparation of Chromium(III) Mercaptides

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THE publication of a recent Paper¹ 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 tricarbonylbenzene-chromium in dry dimethyl disulphide, and is analogous to the preparation of Cr^{III} alkoxides.²



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:—

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

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,³ 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} methoxide³ 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.