[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

Cyclopentadienyl-nitric oxide-di-sulfur-manganese

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The reaction of sulfur with the compound $(C_5H_5)_3Mn_2(NO)_3$ gives a product with the empirical formula $C_5H_5MnNOS_2$. The properties and structure of this polymeric compound are discussed briefly.

The preparation of a compound $(C_5H_5)_3Mn_2(NO)_3$ by the reaction of nitric oxide with manganese cyclopentadienide, has been described previously.[2] This compound, which is best formulated as (π-cyclopentadienyl)-(σ-cyclopentadienyl)-manganese-μ-di-nitric oxide-(π-cyclopentadienyl) (nitric oxide)-manganese, has been found to react with sulfur in carbon disulfide to give a compound of empirical formula $C_5H_5MnNOS_2$.

Experimental

The starting material was prepared as before.[2] In a typical preparation of the sulfur derivative, 2 g. of $(C_5H_5)_3Mn_2(NO)_3$ was refluxed for two days under nitrogen with 0.5 g. of sulfur in 50 ml. of carbon disulfide. The solvent was removed and unreacted sulfur extracted from the residue by repeated extractions with boiling petroleum ether (~400 ml.). The residual brown powder was then crystallized from dichloromethane under nitrogen by chilling the solution to −78° and centrifuging the product; yield 0.84 g. (40% based on manganese content). The product forms opaque brown-black crystals with a metallic glance somewhat resembling pyrite. It decomposed on heating without melting. Although different quantities of sulfur have been used in the preparation, the product is always the same and several checking analyses have been made.

Anal. Calcd. for $C_5H_5MnNOS_2$: C, 28.0; H, 2.35; N, 6.54; S, 29.9; Mn, 25.66. Found: C, 29.90; H, 2.56; N, 6.6; S, 29.2; Mn, 25.70.

The solid is stable in air but the red brown solutions in organic solvents decompose slowly when exposed to air. The compound also decomposes when heated with acids, bases, mercuric chloride, mercury and iodine; no recognizable compound other than sulfur has been obtained in reactions. The compound is moderately soluble in polar organic solvents such as dichloromethane (~ 1 g./100 ml.), chloroform and tetrahydrofuran; it is insoluble in petroleum ether and carbon tetrachloride.

Using the method of isothermal distillation in dichloromethane, values for the molecular weight ranged from 700 to 1200; the irreproducibility of the values may be attributed to partial decomposition occurring during the several days necessary to obtain equilibrium. The most reliable values, obtained by a method of successive approximations, in which the weights of the sample and of the reference substance are adjusted so that little or no movement of the solvent columns occurs during the initial period gave values between 1100 and 1200.

Since the compound is diamagnetic, fivefold polymers are impossible and it is most likely that the compound is a hexamer $[C_5H_5MnNOS_2]_6$ (mol. wt. = 1284) or a mixture of this and a tetramer (mol. wt. = 856).

The infrared spectrum of the compound in a potassium bromide pressed disc showed the characteristic spectrum of the "sandwich bonded" or π-cyclopentadienyl ring,[3] with bands at 3085(w), 1430(m), 1360(w), 1120(w), 1067(m), 1060(w), 1023(w), 1007(m), 933(w), 855(m), 835(m), 822(vs) cm.$^{-1}$. In addition, there was a single very strong band at 1743 cm.$^{-1}$ attributable to a singly coördinated NO group,[2,3] and a strong band at 491 cm.$^{-1}$ with a shoulder at 485 cm.$^{-1}$. The spectra were measured in the sodium chloride region on a Perkin–Elmer double beam recording spectrophotometer, and with potassium bromide optics on a Perkin–Elmer single beam instrument.

The ultraviolet absorption spectrum measured in tetrahydrofuran solution on a Cary recording spectrophotometer consists of generally high absorption without distinct peaks in the region 2300-4000 Å. (ϵ 5–10,000).

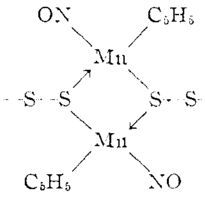
The compound was found to be diamagnetic by the Gouy method.

Discussion

While it is impossible with the data available to assign a structure for the compound, certain features that any model must satisfy can be specified.

(a) Only a single N–O stretching frequency is observed and hence only one NO group must be bonded to each manganese atom. (b) Each manganese atom must have a cyclopentadienyl ring bonded to it by a "sandwich bond." (c) The strong band at ~491 cm.$^{-1}$ strongly suggests the presence of linked sulfur atoms and this absorption is in the right range for S–S stretching frequencies.[4] (d) By analogy with other cyclopentadienyl compounds,[2,3] it would be desirable, but not essential, that the metal atom be allocated fourteen valence electrons.

Further, the manganese compound may be similar to the well known red salts of Roussin, in which two metal atoms probably are linked by two bridging sulfur atoms. While numerous models for the structure of $C_5H_5MnNOS_2$ involving metal to metal bonds and bridging sulfur atoms can be devised, it is impossible on the basis of the data available to decide on a particular model. Cyclic polymers based on the unit I linked through sulfur atoms, for example, would be in agreement with the data



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