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The Reaction of Dicobalt Octacarbonyl with 1,1,1,5,5,5-Hexafluoropentane-2,4-dione. Tris(hexafluoroacetylacetonato)cobalt(III)[1]

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Received August 24, 1966

Conspicuously absent on the extensive list of hexafluoroacetylacetonato complexes of transition metals[2] is the tris diketonate of cobalt(III), Co(hfac)$_3$.[3] Since several β-diketonato complexes have been prepared from the metal carbonyls or carbonyl halides,[4,5] we investigated the reaction of dicobalt octacarbonyl and hexafluoroacetylacetone with a view to synthesizing the missing compound or, alternatively, a mixed carbonyl chelate of cobalt.

Dicobalt octacarbonyl reacts with 1,1,1,5,5,5-hexafluoropentane-2,4-dione under reflux conditions to yield $\mathrm{Co(hfac)_2\cdot 2H_2O}$, a known compound,[2] as the major product and Co(hfac)$_3$ in trace quantities (*ca.* 1%).[6,7] The deep green, crystalline tris complex is volatile and quite soluble in a variety of the more polar organic solvents. Noteworthy is the observation that, whereas the compound remains intact for at least 1 day in dry acetone, addition of water to these solutions causes immediate reduction to $\mathrm{Co(hfac)_2\cdot 2H_2O}$. Thus the inability to synthesize this complex successfully from cobalt carbonate and hexafluoroacetylacetone[6] may be due to the concomitant formation of water in which the tris diketonate is not stable. The mechanism of reduction of Co(hfac)$_3$ by water was not investigated.

Experimental Section

Dicobalt octacarbonyl was purchased from Alfa Inorganics, Inc., and hexafluoroacetylacetone was obtained from Columbia Organic Chemicals Co. All solvents, except petroleum ether (bp 65–110°), were analytical reagent grade. Davison commercial grade silica gel (100–200 mesh) was used for chromatography.

The proton magnetic resonance spectrum of the complex in deuterioacetone solution was recorded on a Varian HR 100 instrument using tetramethylsilane as an internal reference. The molecular weight (10^{-2} M solution in $\mathrm{CHCl_3}$) was determined using a Mechrolab Model 301-A osmometer. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Co(hfac)$_3$.—In a typical preparation, dicobalt octacarbonyl (3.0 g, 8.8 mmoles) was added to refluxing 1,1,1,-5,5,5-hexafluoropentane-2,4-dione (15.0 g, 72 mmoles), no attempt having been made to exclude air from the reaction flask.[8] The mixture was refluxed until the evolution of carbon monoxide had ceased (*ca.* 1 hr). The deep orange solution was then cooled to room temperature, transferred to a large beaker, and diluted with 400 ml of petroleum ether (bp 65–100°). The beaker was covered with a watch glass and allowed to stand in air for 48 hr. After this time orange crystals (8.5 g) were collected on a filter and identified by infrared spectroscopy as $\mathrm{Co(hfac)_2\cdot 2H_2O}$.[2] The red-green filtrate was evaporated to dryness in a stream of air. The residue was dissolved in dichloromethane (10 ml) and chromatographed on a silica gel column (25 × 2.5 cm). The chromatogram was developed with $\mathrm{CH_2Cl_2}$, and a green band was eluted using the same solvent, the orange band remaining on the column. The volume of the green eluate was reduced to 10 ml in a stream of air. Cooling to *ca.* −20° resulted in the separation of deep green crystals. The product (mp 93–94°) was collected on a filter and air dried. The yield was 0.1 g (1%).

Anal. Calcd for $\mathrm{C_{15}H_3O_6F_{18}Co}$: C, 26.49; H, 0.44; F, 50.29; mol wt, 680. Found: C, 26.37; H, 0.40; F, 50.23, mol wt, 744. The nmr spectrum showed a single proton signal at τ 4.05.

The compound sublimes at 45° ($\sim$0.1 mm). It is soluble in chloroform, dichloromethane, and acetone, but only slightly soluble in hexane. Its solutions in dry acetone appear to be stable for at least 1 day; however, addition of water causes an immediate change of the deep green color to red. The latter solution was shown (infrared spectroscopy) to contain the complex $\mathrm{Co(hfac)_2\cdot 2H_2O}$.

Infrared Spectrum of Co(hfac)$_3$.—Bands were observed at 3155 (w–m), 1629 (s), 1609 (s), 1574 (sh), 1559 (m–s), 1542 (sh), 1533 (m), 1451 (m–s), 1438 (sh), 1424 (s), 1355 (m–s), 1262 (vs), 1239 (vs), 1213 (vs), 1170 (vs), 1151 (vs), 1113 (vs), 962 (vw), 825 (w–m), 808 (s), 769 (w), 752 (m), 714 (m), 702 (m–s), 606 (m–s), 548 (w–m), 535 (w–m) $\mathrm{cm^{-1}}$ (Beckman Model IR-9 spectrophotometer; Nujol and hexachlorobutadiene mulls).

Ultraviolet–Visible Spectrum of Co(hfac)$_3$.—Absorption bands were observed at 290 mμ (ϵ $\sim$24,600 M^{-1} $\mathrm{cm^{-1}}$), 350 (sh) mμ, and 600 mμ (ϵ $\sim$225 M^{-1} $\mathrm{cm^{-1}}$) (Cary Model 14 spectrophotometer; $\mathrm{CH_2Cl_2}$ solution).

Acknowledgment.—The authors wish to acknowledge support of this work by the National Science Foundation.

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[1] This work was first reported in a paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 3, 1964.

[2] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963), and references therein.

[3] hfac = anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

[4] M. Kilner and A. Wojcicki, *Inorg. Chem.*, **4**, 591 (1965), and references therein.

[5] J. W. Fitch, III, and J. J. Lagowski, *ibid.*, **4**, 910 (1965).

[6] Under similar experimental conditions cobalt(II) carbonate and hexafluoroacetylacetone yield $\mathrm{Co(hfac)_2\cdot 2H_2O}$, but no detectable Co(hfac)$_3$, thus showing that the tris complex does not result from the initial decomposition of $\mathrm{Co_2(CO)_8}$ to the carbonate and the subsequent reaction of the latter with the acetylacetone.

[7] The compound Co(hfac)$_3$ has been recently prepared, but by a different method, by H. Veening, W. E. Bachman, and D. M. Wilkinson (private communication from H. V.).

[8] The reaction does not appear to proceed in the absence of air. The use of purified cobalt carbonyl (by sublimation) and the diketone (by distillation) does not increase the yield of Co(hfac)$_3$.

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Infrared Spectra of Complexes of 8-Aminoquinoline with Lanthanide Halides[1]

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Received August 24, 1966

Recently, Coakley[2] and Fanning and Taylor[3] prepared complexes of 8-aminoquinoline with transition

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[1] (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission; (b) presented in part at the 5th National SAS Meeting, Chicago, Ill., June 1966.

[2] M. P. Coakley, *Appl. Spectry.*, **18**, 149 (1964).

[3] J. C. Fanning and L. T. Taylor, *J. Inorg. Nucl. Chem.*, **27**, 2217 (1965).