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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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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 Co(hfac)$_2$·2H$_2$O, 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 Co(hfac)$_2$·2H$_2$O. 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 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 Co(hfac)$_2$·2H$_2$O.[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 CH$_2$Cl$_2$, 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 C$_{15}$H$_3$O$_6$F$_{18}$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° (~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 Co(hfac)$_2$·2H$_2$O.

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) 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 ~24,600 M^{-1} cm^{-1}), 350 (sh) mμ, and 600 mμ (ϵ ~225 M^{-1} cm^{-1}) (Cary Model 14 spectrophotometer; CH$_2$Cl$_2$ solution).

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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 Co(hfac)$_2$·2H$_2$O, but no detectable Co(hfac)$_3$, thus showing that the tris complex does not result from the initial decomposition of 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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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).

metal halides. These authors discussed infrared spectra obtained from the complexes and indicated that bonding between the metal and nitrogens is taking place. Similar complexes with rare earth halides have not been reported. It has become increasingly apparent that nitrogen-containing ligands will form complexes with rare earth salts.[4–7] As an extension of studies on rare earth chelates with an N–C–C–N linkage, rare earth–halide–8-aminoquinoline compounds were prepared. The infrared spectra from 4000 to 80 cm^{-1} are presented and discussed.

Experimental Section

Hydrated rare earth chloride was prepared by dissolution of the oxide in concentrated HCl and careful evaporation to dryness. 8-aminoquinoline, obtained from Eastman Organic Chemicals, was recrystallized from petroleum ether (bp 65–110°). The chloride and ligand, in a mole ratio of 1:2, are dissolved in separate, minimum volumes of absolute alcohol. The solutions are mixed and refluxed if necessary. The compounds are washed with benzene and dried at 110° for 2 hr. Rare earth 8-aminoquinoline bromides were similarly prepared using anhydrous rare earth bromide.

Table I tabulates the analytical data for the complexes. C, H, and N analysis was performed by standard microanalytical techniques. Rare earth was determined by titration with EDTA, and the halide, by gravimetric precipitation with silver ion.

The colors of the compounds ranged from gold to medium brown. The complexes are insoluble in typical organic solvents. They all decompose in water. Decomposition also occurs upon heating.

TABLE I

$Ln(8\text{-}NH_2Q)_2X_3 \cdot yH_2O$ COMPLEXES[a]

Ln	X	y		Analyses, % C	H	N	Ln	X
Nd	Cl	1	Calcd	38.82	3.26	10.06	25.90	19.16
			Found	40.27	3.32	10.70	25.30	17.47
Sm	Cl	2	Calcd	37.20	3.47	9.64	25.87	18.30
			Found	38.10	3.63	9.78	25.36	18.19
Eu	Cl	1	Calcd	38.29	3.21	9.92	26.91	18.84
			Found	38.20	3.39	9.98	25.90	18.04
Gd	Cl	1	Calcd	37.93	3.18	9.83	27.59	18.66
			Found	38.17	3.24	10.54	27.19	18.57
Dy	Cl	1	Calcd	37.58	3.15	9.74	28.25	18.49
			Found	37.49	3.38	9.73	27.34	18.11
Ho	Cl	2	Calcd	36.30	3.38	9.40	27.69	17.86
			Found	36.79	3.50	9.90	27.15	17.74
Er	Cl	1	Calcd	37.28	3.13	9.66	28.84	18.34
			Found	37.84	3.12	9.58	28.75	18.15
Tm	Cl	1	Calcd	37.17	3.12	9.63	29.04	18.28
			Found	38.47	3.06	10.29	28.52	17.53
Lu	Cl	4	Calcd	33.69	3.77	8.73	27.26	16.57
			Found	34.22	3.52	8.78	27.32	16.58
Nd	Br	4	Calcd	29.04	3.25	7.53	19.38	32.20
			Found	28.94	3.09	7.58	21.09	34.22
Gd	Br	4	Calcd	28.54	3.19	7.40	20.76	31.65
			Found	29.32	3.18	7.62	20.86	30.73

[a] $8\text{-}NH_2Q$: 8-aminoquinoline.

Results and Discussion

4000–650-Cm^{-1} Region.—Characteristic frequencies are listed in Table II. The NH_2 stretching vibrations increase in intensity and decrease in frequency upon coordination. This has been previously observed with related complexes in which coordination to an amino nitrogen takes place.[2,3,8–10] The NH_2 bending vibration shifts to lower frequency upon coordination,[9,10] although, owing to the complexity of the compounds, this may not be a pure vibration. The carbon to amino nitrogen stretching vibration (1333 cm^{-1})[3] also shifts to lower frequency upon chelation. In the 1000–1100-cm^{-1} region several new bands appear, the strongest at 1000 cm^{-1}.

TABLE II

CHARACTERISTIC FREQUENCIES (CM^{-1}) OBSERVED FOR THE 8-AMINOQUINOLINE COMPLEXES OF RARE EARTH CHLORIDES

	NH_2 str Asym	NH_2 str Sym	NH_2 bend[b]	NH_2[2] wag	$\nu(C\text{-}N)H_2$[3] str
$8\text{-}NH_2Q$[a]	3490	3390	. . .	. . .	. . .
$8\text{-}NH_2Q$	3440 m, b	3340 m, b	1613 m	. . .	1333 m
Nd	3190 m, b		1589 m	1009 m	1312 m
Sm	3315 m, b	3240 m, b	1598 m	1015 s	1324 m
Eu	3325 m, b	3254 m	1603 m	1016 s	1316 m
Gd	3330 m, b	3250 m	1598 m	1016 s	1316 m
Dy	3330 m, b	3245 m	1597 m	1017 s	1314 m
Ho	3315 w, b	3245 w, b	1595 m	1022 s	1316 m
Er	3336 w, vb	3246 w	1594 m	1021 s	1316 m
Tm	3260 m	3215 m	1588 sh	1020 m	1319 m
Lu	3330 m, b	3185 m, b	1574 m	1023 m	1320 m

[a] Spectrum taken in $CHCl_3$.[2] [b] Probably mixed with aromatic vibrations.

Upon chelation, the absorption at 1500 cm^{-1} becomes the most intense in the entire spectrum and a band at 1560 cm^{-1} also intensifies. These changes can be attributed to aromatic C=C and C=N vibrations indicating that metal bonding to the ring nitrogen is taking place. These observations, made in this region of the spectrum, confirm results obtained for related complexes with the transition metals.

650–80-Cm^{-1} Region.—From 650 to 300 cm^{-1} the spectra of the chelates and pure ligand are similar. Several new, weak to medium absorptions occur which can be attributed to coordinated water wag and the $M \rightarrow OH_2$ stretch.[11] All of the absorptions are broad.

Figure 1 records the absorptions for complexes and pure ligand below 300 cm^{-1}. The ligand itself exhibits six bands. In the compounds, two to three new strong bands appear between 220 and 250 cm^{-1}, where the ligand is free of absorptions. This is the region in which rare earth metal to nitrogen stretching vibrations have been assigned for other nitrogen ligand chelates.[7] Rare earth metal–chloride stretching vibrations have also been assigned at 240 cm^{-1}.[12] In addition, new bands are observed between 120 and 160 cm^{-1} in the spectra of the compounds. Here, again, the ligand is free of absorptions. A NMN bending vibration or a chelate ring vibration might be expected in this region, which would not be found in the spectrum of the pure ligand.

8-Aminoquinoline complexes of $NdBr_3$ and $GdBr_3$ have also been prepared. The spectra of the respective halide complexes have been compared below 300 cm^{-1}. The results indicate that the absorptions in the

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(4) S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

(5) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, **26**, 579 (1964).

(6) S. P. Sinha, *Z. Naturforsch.*, **20a**, 552 (1965).

(7) J. R. Ferraro, D. L. Kovacic, and L. J. Basile, *Inorg. Chem.*, **5**, 391 (1966).

(8) G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).

(9) M. A. J. Jungbauer and C. Curran, *Spectrochim. Acta*, **21**, 641 (1965).

(10) M. P. Coakley, *ibid.*, **21**, 1984 (1965).

(11) C. Postmus and J. R. Ferraro, submitted. Assignments are made for the infrared-active, coordinated water modes to rare earth metals.

(12) J. R. Ferraro, C. Cristallini, and I. Fox, *Inor . Nucl. Chem. Letters*, **1**, 25 (1965).

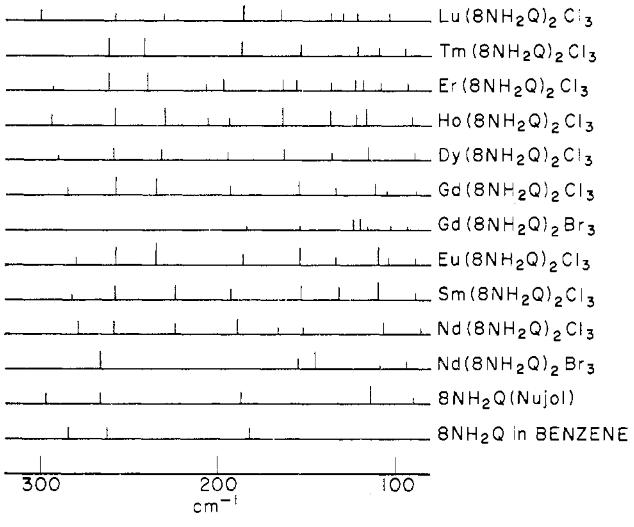

Figure 1.—Absorptions occurring from 300 to 80 cm^{-1} for 8-aminoquinoline–rare earth–halide complexes. Heights of lines indicate relative intensities of bands.

220–250-cm^{-1} region for the chlorides are not halide independent. Some shifts and losses of bands are observed. However, no systematic trend, such as the shifts to lower frequency expected for a metal–halide vibration, as one proceeds from the chloride to bromide, are found. Similar complications ensue in the 120–160-cm^{-1} region. As a result, unequivocal assignments for metal–ligand vibrations are impossible to make.

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New Rhodium Chelates of Hexafluoroacetylacetone

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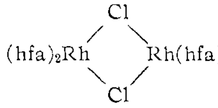
As part of a broad study[2] of volatile metal chelates, some novel complexes of rhodium(III) have been synthesized. Collman and co-workers[3] have described the synthesis of rhodium(III) hexafluoroacetylacetonate[4] from rhodium(III) nitrate and hexafluoroacetylacetone in basic aqueous solution. We have established that the reaction of rhodium(III) trichloride trihydrate with H(hfa) in anhydrous ethanol yields a mixed-ligand complex having the composition RhCl(hfa)$_2$·3H$_2$O. This compound, on vacuum sublimation, yielded a sublimate from which two other new compounds, I (brownish yellow crystals) and II (red crystals), were also isolated. Chemical analyses and infrared spectra indicate that both I and II are anhydrous and have the empirical formula RhCl(hfa)$_2$. Molecular weight measurements in carbon tetrachloride indicate that II is dimeric. On the basis of ^{19}F and ^{1}H nmr measurements on II, it was concluded that the rhodium ions are bridged through the two chloro groups, and should be formulated as



Experimental Section

Preparation of Rh(hfa)$_3$.—Rhodium(III) hexafluoroacetylacetonate was made by the method described by Collman, *et al.*,[3] except that RhCl$_3$·3H$_2$O was the starting material.

Preparation of RhCl(hfa)$_2$·3H$_2$O.—To 4 g of RhCl$_3$·3H$_2$O dissolved in 50 ml of absolute ethanol was added 11 ml of H(hfa) and the mixture was refluxed for about 4 hr. The resulting mixture was allowed to evaporate in a stream of dry air. When an almost dry solid was obtained, about 100 ml of water was added. Within 1 or 2 min a mustard-yellow, finely divided crystalline precipitate appeared. The ethanol must be removed as completely as possible; incomplete removal results in the formation of a black precipitate (presumably Rh) upon addition of water. The precipitate was separated by suction filtration, washed with water, and dried over Drierite (yield, 3.4 g or 36.9%).

The product turns brown-red at 126–129° and melts to a brown-red liquid at 129–131°. The compound is soluble in methanol, ethanol, ether, and acetone, almost insoluble in carbon tetrachloride, benzene, petroleum ether (bp 39–45°), and chloroform, and insoluble in water. Two measurements of the molecular weight in acetone yielded values of 618 and 622 (calculated, 607).

Anal. Calcd for RhCl(C$_5$HO$_2$F$_6$)$_2$·3H$_2$O: C, 19.80; H, 1.33; Cl, 5.85; F, 37.59. Found: C, 19.60, 19.81; H, 0.94, 0.90; Cl, 5.91, 6.01; F, 37.39, 37.65.

Vacuum Sublimation of RhCl(hfa)$_2$·3H$_2$O.—A 2.33-g sample of the compound was subjected to vacuum sublimation at 0.1 mm for 21 hr at 100 ± 2° (yield, 1.01 g). The sublimate was recrystallized from 100 ml of hot carbon tetrachloride (yield, *ca.* 0.4 g of brownish yellow, small, needle-shaped crystals, compound I). The product was again recrystallized from carbon tetrachloride. The combined fractions of mother liquor on concentration and prolonged cooling in a refrigerator for a few days deposited ruby-red crystals of larger size (compound II) along with a few crystals of I. The red crystals were hand-picked after each of several such crystallizations, and the collected crystals were finally recrystallized from carbon tetrachloride (yield, 0.4 g). I is soluble in carbon tetrachloride, ether, tetrahydrofuran, and acetone, almost insoluble in methanol, ethanol, chloroform, *p*-dioxane, nitromethane, and benzene, and insoluble in water. II is soluble in carbon tetrachloride (more soluble than I) and acetone, almost insoluble in ethanol, and insoluble in water. Two determinations of the molecular weight of II in carbon tetrachloride gave values of 1235 and 1254 (calculated for the dimer, 1105). The apparent molecular weight of I in acetone was determined to be 890 in one measurement and 907 in a second. The ultraviolet spectra of I, II, and Rh(hfa)$_3$ in cyclohexane are all very similar.

Anal. Calcd for Rh$_2$Cl$_2$(C$_5$HO$_2$F$_6$)$_4$: C, 21.74; H, 0.37; Cl, 6.42; F, 41.27. Calcd for RhCl(C$_5$HO$_2$F$_6$)$_2$·H$_2$O: C, 21.05; H, 0.71; Cl, 6.22; F, 39.96. Found (I): C, 20.36, 20.13; H, 0.40, 0.44; Cl, 6.67, 6.54; F, 40.24, 40.05. Found (II): C, 20.37, 20.11; H, 0.20, 0.15; Cl, 6.58, 6.50; F, 41.18, 41.41.

Alcoholic Silver Nitrate Tests.—No cloudiness or precipitate appeared immediately in any case when alcoholic silver nitrate was added to alcoholic solutions of RhCl(hfa)$_2$·3H$_2$O, compound I, or compound II. On prolonged standing a precipitate even-

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[1] Visiting Research Associate, Ohio State University Research Foundation.

[2] R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press Ltd., Oxford, 1965.

[3] J. P. Collman, R. L. Marshall, W. L. Young, and S. D. Goldby, *Inorg. Chem.*, **1**, 704 (1962).

[4] The parent ligand is the enol form of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, abbreviated hereafter as H(hfa); the anion as hfa.