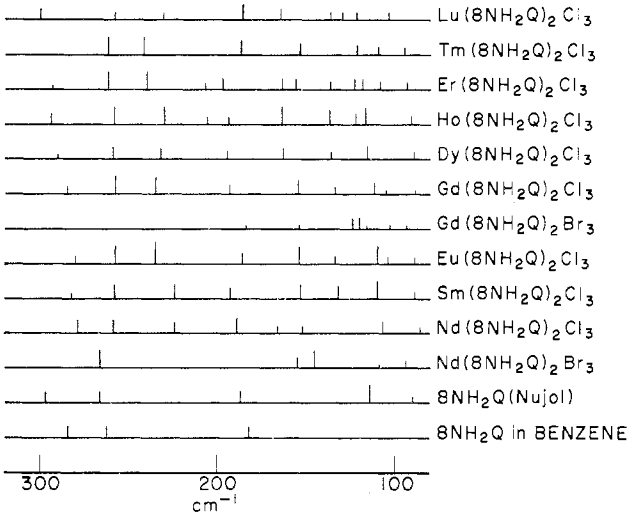


Figure 1.—Absorptions occurring from 300 to 80 cm^{-1} for 8-aminoquinoline–rare earth–halide complexes. Heights of lines indicate relative intensities of bands.

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.

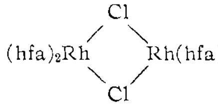
CONTRIBUTION FROM THE
AEROSPACE RESEARCH LABORATORIES,
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

New Rhodium Chelates of Hexafluoroacetylacetone

BY S. C. CHATTORAJ[1] AND R. E. SIEVERS

Received August 25, 1966

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-

---

[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.

tually formed in each test. This indicates that the chloride ion is in the coordination sphere in all three compounds.

Infrared Spectra.—Spectra were taken with a Perkin-Elmer 521 grating infrared spectrophotometer in Nujol and in Fluorlube oil LG 160 (Fisher Scientific Co.) mulls between sodium chloride and potassium iodide plates.

Nmr Spectra.—Proton nmr spectra were measured at 60 Mc at 37° sample temperature on a Varian Associates Model A-60 spectrometer using tetramethylsilane as internal standard. The ^{19}F spectra were obtained at 40 Mc on a Varian Associates Model V-4300-2 high-resolution spectrometer with a magnetic field of ~9906 gauss. Trifluoroacetic acid was used as an external reference standard.

Discussion

Infrared Spectra.—The presence of several bands, some of them broad, in the region 3650–3000 cm^{-1} (Table I) confirms the hydrated nature of the compound, $RhCl(hfa)_2 \cdot 3H_2O$. The very broad nature of the band at 2850 cm^{-1} for the hydrated chelate and its absence in the other anhydrous chelates suggests that it may not be due to C–H stretch but may be due to O–H stretching altered by some type of hydrogen bonding. There is a fairly weak but sharp peak at 3132–3140 cm^{-1}, present in all of the compounds including $Rh(hfa)_3$, which is known to be anhydrous. The detection of this peak in the tris complex is significant for it suggests that a similar band found in this region for compound I is probably not due to the presence of water, but due instead to C–H stretching. This absorption is somewhat high for a C–H stretch; however, hexafluoroacetylacetone has a sharp, fairly strong peak at 3125 cm^{-1} and a weak absorption band at 3140 cm^{-1} was found for the copper chelate of 2-furoylperfluorobutyrylmethane.[5] In accordance with the discussion of Nakamoto[6] the highest frequency bands in the carbonyl region have been tentatively assigned to C$\overset{...}{-}$C stretching, although it must be recognized that the C$\overset{...}{-}$C and C$\overset{...}{-}$O stretching frequencies are difficult to distinguish in this region.

Molecular Weights.—The experimentally determined molecular weight for the compound $RhCl(hfa)_2 \cdot 3H_2O$ is satisfactorily close to its calculated value. Compound I gives molecular weight values that are anomalously low for a dimer, but still lie much closer to the value calculated for a dimer than that for a monomer. Evidence based on nmr data suggests that a reaction takes place when this compound is dissolved in acetone. Because of the limited solubility of I in carbon tetrachloride, its molecular weight could not be determined in this solvent or in others suitable for molecular weight determinations. The values for II indicate that it is dimeric in carbon tetrachloride.

Nmr Spectra and Structural Implications.—In the data presented in Table II the proton peaks due to the solvents have been excluded. Only one proton peak was observed for each of the compounds; this occurred in the region assigned to C–H protons in hfa complexes by earlier investigators.[3,7] For the hydrated complex, $RhCl(hfa)_2 \cdot 3H_2O$, one might expect a proton peak due to water. The absence of such a peak may be due to rapid proton exchange with the solvent. The hydrated rhodium complex and compound I are insufficiently soluble in carbon tetrachloride to permit spectra to be obtained; therefore, acetone was used as a solvent for these compounds. Proton nmr spectra of acetone solutions were taken within a few minutes after the solutions were made and again 24 hr later. Only in the case of I was a reaction detected. The peak observed initially was missing after about 20 min and a new peak had appeared in its place. Fortunately, II is sufficiently soluble in a nonpolar, inert solvent (CCl_4) to permit meaningful and defini-

TABLE I

INFRARED ABSORPTION OF RHODIUM–hfa CHELATES IN THE 4000–650-CM^{-1} REGION[a]

				CC str	CO str			CC str CF_3str	CF_3 str		CH in-plane bend			CH out-of-plane bend C–CF_3 str		
$RhCl(hfa)_2 \cdot 3H_2O$	3650 w, sp 3513 b 3416 b ~3200 w, vb	3140 w, sp	2850 w, vb	1625	1604	1554 1526 w	1433	1345	1260	1210	1153	1102		827 806	750 w	714
I, $Rh_2Cl_2(hfa)_4$(?)		3135 w, sp (3050 b)		1623	1602	1567 sh 1551 1525	1432	1340	1267 1255 1245 sh	1205 1192 sh	1153	1100	952 w, sp	824 807	(762) 749	703
II, $Rh_2Cl_2(hfa)_4$		3132 w, sp (3050 b)		1625	1601	1570 w 1553 1526	1437	1342	1258 1236	1210 1184	1151	1105	950 w, sp	827 807	750	707
$Rh(hfa)_3$	(3196)	3135 w, sp (3050 b) 3130 sh		1627 sh	1597	1554 1528	1450 1423	1342	1271 1256	1215 1182	1150	1106	(955)	826 814	768 w 753	714 705

[a] b, broad; sh, shoulder; sp, sharp; v, very; w, weak. Very weak or doubtful bands are enclosed in parentheses.

TABLE II

PROTON NMR SPECTRA OF RHODIUM–hfa CHELATES

Compound	Solvent	C–H proton peak, ppm
$RhCl(hfa)_2 \cdot 3H_2O$	Methanol	−6.60
	Acetone	−6.70
I, $Rh_2Cl_2(hfa)_4$(?)	Acetone	−6.94[a] (−6.70)[b]
II, $Rh_2Cl_2(hfa)_4$	Carbon tetrachloride	−6.54
$Rh(hfa)_3$	Carbon tetrachloride	−6.58
	Acetone	−6.93

[a] This peak, although always seen in freshly prepared solutions, disappeared after the compound had stood in acetone for *ca.* 20 min at 35° in the nmr probe. [b] This peak, not present initially, appeared after *ca.* 20 min; it was still present after 24 hr.

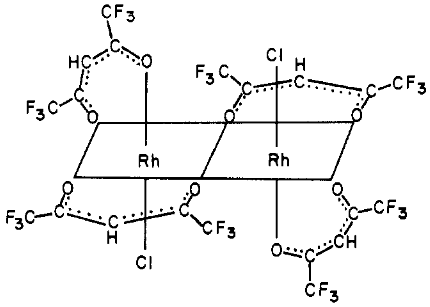
---

(5) H. F. Holtzclaw and J. P. Collman, *J. Am. Chem. Soc.*, **79**, 3318 (1957).

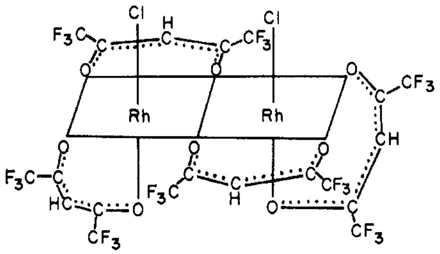
(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

(7) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 806 (1966).

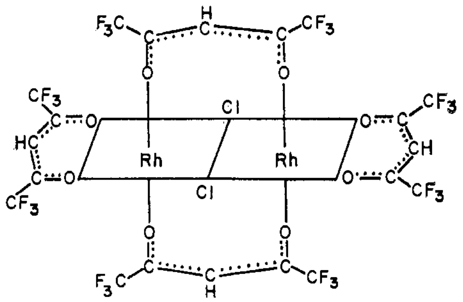
tive structural evidence to be obtained. The molecular weight measurements coupled with the silver nitrate test indicate that II is a dimer with the chloride ions in the coordination sphere. These facts, taken together with the nmr data, permit consideration of the structural aspects in a little more detail. Rhodium(III) complexes are normally six-coordinate.[8] Assuming the expected coordination number of six for Rh(III), one can propose several possible structures (I–VI). Structure I is analogous to the one proposed for the tetramer of cobalt(II) acetylacetonate by Cotton and Elder.[9] This may easily be seen if one considers only the two central cobalt atoms and substitutes a chloro group in place of each of two terminal bridging acetylacetonate moieties. Structure II is merely the *cis* form of structure I. Structures III, V, and VI are chloro-bridged compounds; binuclear rhodium(III) complexes having two bridging chloro groups are known.[10] Structure IV is illustrative of Rh–C bonding of the type described by Parshall and Jones.[11] Examination of all the structures (I–VI) reveals that structures I–IV have two different types of protons while structures V and VI have only one type of proton. If structure IV were correct, the proton magnetic resonance spectra might be expected to show multiple peaks due to ^{103}Rh–H spin–spin splitting of protons attached to the rhodium-bonded carbons. Furthermore, the proton peaks might be expected to shift to significantly higher fields. Parshall and Jones[11] observed that the protons on carbons bonded to rhodium were shifted to *ca.* −3.2 ppm.



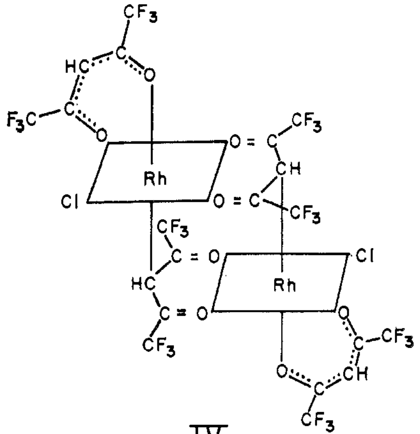
I



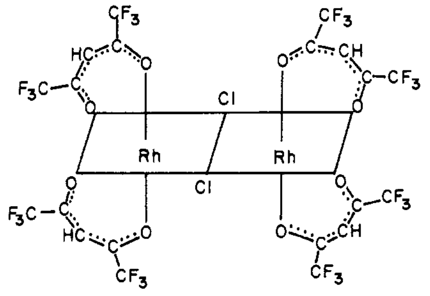
II



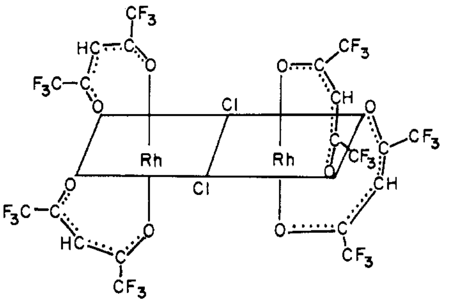
III



IV



V



VI

As expected, the nmr data on Rh(hfa)$_3$ in carbon tetrachloride exhibit a single proton peak at −6.59 ppm. Likewise, the ^{19}F spectrum contains only one peak, which appears at −5.46 ppm relative to an external reference capillary of trifluoroacetic acid. For compound II a single resonance peak appears at −6.54 ppm, but two peaks of equal area are found in the

---

[8] J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).

[9] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965).

[10] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 2508 (1964).

[11] G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, **87**, 5356 (1965).

fluorine resonance spectrum at −5.42 and −5.27 ppm, respectively. The nmr evidence, therefore, tends to rule out structures I–IV[12] but is entirely consistent with what one would expect for either structure V or structure VI. It should be mentioned here that it is possible that either of these two structures may also be the correct structure for compound I, but this could not be confirmed because of the solvent problem mentioned earlier. The simultaneous formation of I and II under the same experimental conditions in approximately the same amounts and the close similarity of infrared spectra lead us to suspect that these compounds may, in fact, be the two expected geometrical isomers.

It may be noted that a compound having structure V is optically inactive while one with structure VI will exist as optical isomers. A successful resolution of either compound I or II may indicate which structure is correct.

Acknowledgments.—We are grateful to J. S. Smith, for obtaining some of the infrared spectra. The fluorine nmr spectra were measured by Messrs. John Strobel and John Pustinger. This research was supported in part by the ARL In-House Independent Laboratory Research Fund.

[12] The absence of multiple peaks cannot, of course, be taken as positive proof that only a single proton environment exists. The proton peak width at half peak height is 1.3 cps, similar to other β-diketonates known to contain a single proton environment. From experience with numerous other β-diketonate complexes having nonequivalent protons, it is considered extremely unlikely that protons in dissimilar rings would have exactly the same magnetic environment. Furthermore, substitution and isomerization reactions are known to occur extremely slowly with respect to proton relaxation rates, so the existence of equilibria that would average the environments may be discounted.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CALIFORNIA STATE COLLEGE AT FRESNO,
FRESNO, CALIFORNIA 93726

The Separation of Nonelectrolytic Geometric Isomers of Platinum(II) by Thin Layer Chromatography

BY GEORGE B. KAUFFMAN AND BARRETT W. BENSON

Received August 26, 1966

The use of thin layer chromatography as an important separative, diagnostic, and preparative technique is well established, especially in the organic and biochemical areas. Its application to inorganic compounds, however, has been much less extensive and has been limited primarily to the separation of the common cations and anions.[1–3]

Syntheses of coordination compounds frequently produce more than one isomer,[4] and, consequently, rapid, efficient, and reliable methods for separating the resulting mixtures are desirable. A recent study describing the separation of a number of electrolytic geometric isomers of ammines and amines of cobalt(III) by thin layer chromatography[5] prompts us to report our results of a similar study of nonelectrolytic isomers. The present paper, then, describes the separation by thin layer chromatography of a number of nonelectrolytic geometric isomers of platinum(II) (square-planar configuration) which we had separated previously by column chromatography.[6] In addition, the separation of two pairs of binuclear platinum(II) isomers [*sym*-di-μ-ethylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II) and *sym*-di-μ-*p*-nitrophenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II)] for which column chromatography had proven inadequate (see footnote 36 of ref 6) is here reported.

Experimental Section

Isomers.—Dichlorobis(diethyl sulfide)platinum(II),[7] dichlorobis(tri-*n*-butylphosphine)platinum(II),[8] dichlorodipyridineplatinum(II),[9] *sym*-di-μ-phenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II),[10] *sym*-di-μ-ethylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II),[10] and *sym*-di-μ-*p*-nitrophenylthio-dichlorobis(tri-*n*-propylphosphine)diplatinum(II)[10] were prepared according to the literature references given. Both the *cis* and *trans* forms of each of these compounds were characterized by elemental analyses, melting points, physical properties, and chemical reactions.[6]

Chromatography.—Microscope slides (75 × 25 mm) were thoroughly cleaned with detergent, rinsed with distilled water, and coated with a slurry consisting of 1 part of Silica Gel G (Kensington Scientific Corp., Oakland, Calif.) in 3 parts of a 1:1 by volume mixture of methanol and redistilled methylene chloride.[11] The plates were air dried for 10–20 min and activated by drying for 1 hr at 110° just prior to use.

Saturated solutions of the *cis* isomer, the *trans* isomer, and a 1:1 by weight mixture of both isomers, all in redistilled methylene chloride, were applied side by side along the origin of the plate, resulting in three distinct spots. After the plate had been air dried for 2–3 min, it was placed in a small screw-cap jar containing the solvent and was developed by the ascending technique.[1] When the solvent had attained a height of *ca.* 6 cm, the plate was removed from the developing chamber and was air dried. The positions of the isomers were detected as intense yellow-brown spots by placing the developed and dried plate in a screw-cap jar containing a few iodine crystals.[1] The mixed samples were found to have separated into two spots. The isomers which were thus separated from the mixtures were identified by comparison with the R_f values obtained for the pure isomers.

---

[1] J. M. Bobbitt, "Thin-Layer Chromatography," Reinhold Publishing Corp., New York, N. Y., 1963.

[2] E. Stahl, "Thin-Layer Chromatography," Academic Press Inc., New York, N. Y., 1965.

[3] E. J. Goller, *J. Chem. Educ.*, **42**, 442 (1965), and references therein.

[4] R. G. Wilkins and M. J. G. Williams in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 197.

[5] L. F. Druding and R. B. Hagel, *Anal. Chem.*, **38**, 478 (1966), and references therein.

[6] G. B. Kauffman, R. P. Pinnell, and L. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962).

[7] G. B. Kauffman and D. O. Cowan, *Inorg. Syn.*, **6**, 211 (1960).

[8] G. B. Kauffman and L. A. Teter, *ibid.*, **7**, 243 (1963).

[9] G. B. Kauffman, *ibid.*, **7**, 249 (1963).

[10] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953); 2807 (1960). Samples of these isomers were kindly furnished by Drs. J. Chatt, P. G. Owston, and F. A. Hart of Imperial Chemical Industries, Ltd.

[11] The use of a mixture of organic solvents rather than water as the slurry medium aids in maintaining a uniform suspension, yields an even layer thickness (*ca.* 200 μ) when poured directly onto the slides, and requires less time for evaporation of the solvent prior to activation. Separation of the various isomer pairs was shown to be independent of the slight variations in layer thickness obtained by this method.