Preparation and Properties of Anhydrous Rhodium(II) Acetate and Some Adducts Thereof[1]

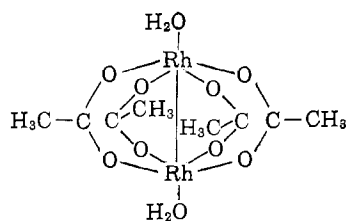By SUSAN A. JOHNSON, H. R. HUNT, AND H. M. NEUMANN

The synthesis of anhydrous rhodium(II) acetate is described. Solid [Rh(OOCCH₃)₂]₂ forms stable 1:2 adducts (*i.e.*, 1 dimer:2 ligands) with water, tetrahydrofuran, acetonitrile, dimethyl sulfoxide, dimethyl sulfide, trimethylamine, ammonia, nitric oxide, and ethylenediamine. All but the last of these revert to [Rh(OOCCH₃)₂]₂ at 120°. Adducts of pyridine (1:2) and o-phenanthroline (1:1) were obtained by precipitation from solution. The properties of [Rh(OOCCH₃)₂]₂ are described and spectral data for it and its several adducts are presented.

In the course of work aimed at the preparation of rhodium(III) complexes from hydrous Rh(III) hydroxide, it was observed that a green crystalline material, analysis of which corresponds to the empirical formula Rh(OOCCH₃)₂, is formed when Rh(OH)₃·H₂O reacts with acetic acid either in ethanol or in glacial acetic acid. A related compound, Rh(OOCCH₃)₂·H₂O, has been reported by Chernyaev and co-workers[2] as the product of the reaction of (NH₄)₃[RhCl₆] and acetic acid in ethanol, but complete details of their work do not seem to have been published.

An X-ray investigation[3] of Rh(OOCCH₃)₂·H₂O has shown that the compound has the same dimeric structure as the hydrated copper(II)[4] and chromium(II)[5] acetates. The structures of the latter two com-

pounds have been of much interest because of the existence of a metal–metal bond in them.

Relatively little work has been done on the unstable [Cr(OOCCH₃)₂H₂O]₂; however, [Cu(OOCCH₃)₂H₂O]₂ and related compounds have been the subjects of extensive investigation. Magnetic[6] and spectrophotometric[7] evidence seems to indicate a dimeric structure for a whole series of hydrated and anhydrous cupric alkanoates, [Cu(OOCR)₂(H₂O)₀ or ₁]₂. It is also believed that in organic solvents the terminal positions may be occupied by such molecules as the solvent itself, *e.g.*, ethanol and dioxane, free alkanoic acid, or

pyridine.[8] The pyridine adduct, [Cu(OOCCH₃)₂py]₂, has been isolated and shown by X-ray to retain the basic copper acetate structure.[9,10] Electron paramagnetic measurements show that a quinoline adduct, [Cu(OOCCH₃)₂NC₉H₇]₂, also is dimeric.[11]

In this paper the preparations of anhydrous rhodium(II) acetate and its several adducts are described.

Experimental

Synthesis of Compounds. Rhodium(II) Acetate Dimer.— A suspension of 10.0 g. of Rh(OH)₃·H₂O in 400 ml. of glacial acetic acid dissolved upon refluxing for 18 hr. to give a deep emerald-green solution. Most of the acetic acid was evaporated on a steam bath; remaining traces were removed by heating the residue at 120° for 1 hr. The residue was then extracted with boiling acetone until the extract was colorless rather than bluish green. The extract was quickly passed through a fritted glass filter, concentrated on a steam bath to ¹/₃ its original volume, and placed in the freezing compartment of a refrigerator for 18 hr. The resulting large dark green crystals were collected on a filter, washed with small portions of ice-cold acetone, and dried at 110°. When first collected, the product is the weak adduct [Rh(OOCCH₃)₂(CH₃)₂CO]₂; however, acetone is lost fairly readily at room temperature and immediately in the drying oven; yield, 6.2 g. (48%).

Anal. Calcd. for Rh(OOCCH₃)₂: C, 21.74; H, 2.74; Rh, 46.5. Found: C, 22.00; H, 2.73; Rh, 46.5.

The residue remaining after acetone extraction, a greenish brown, water-soluble crystalline material, may in turn be converted in about 50% yield to [Rh(OOCCH₃)₂]₂ by treating it with fresh glacial acetic acid and proceding as outlined above.

Rhodium(II) acetate is soluble in a wide variety of solvents including water, tetrahydrofuran, ethanol, acetone, acetic acid, acetonitrile, dimethyl sulfoxide, nitromethane, and triethyl phosphate. It is believed that terminal positions in the coordination sphere are occupied by solvent molecules, although several of the "adducts" are insufficiently stable to exist in the solid state at room temperature. Rhodium(II) acetate is insoluble in ether, benzene, and carbon tetrachloride.

Adducts.—Although it was possible to isolate adducts of [Rh(OOCCH₃)₂]₂ and various molecular and anionic ligands from water, ethanol, or acetone solution, these adducts were generally impure. A more satisfactory method of preparing many adducts was to treat solid [Rh(OOCCH₃)₂]₂ with a slight excess of the pure gaseous or liquid potential ligand.

(1) This research was supported by the National Science Foundation under Grant NSF-G19753.

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The following general method was used for investigating adduct formation with liquid materials: Approximately 75 mg. of finely powdered [Rh(OOCCH$_3$)$_2$]$_2$ was placed in a microcrucible and covered with several drops of the potential ligand. The excess liquid was allowed to evaporate; the crucible was then weighed and placed under vacuum for 1 hr., after which its weight was again determined. If no appreciable weight loss took place upon evacuation the adduct formed (if any) was considered stable. By this method it was found that [Rh(OOCCH$_3$)$_2$]$_2$ forms stable 1:2 adducts (*i.e.*, 1 dimer : 2 ligands) with H$_2$O, tetrahydrofuran (THF), CH$_3$CN, dimethyl sulfoxide (DMSO), (CH$_3$)$_2$S, and (CH$_3$)$_3$N; no evidence for solid compound formation was found with CH$_3$CH$_2$OH, (CH$_3$)$_2$CO, CH$_3$NO$_2$, or (CH$_3$-CH$_2$)$_3$PO$_4$; acetic acid formed an adduct of intermediate stability—the acid was lost slowly in air or under vacuum.

Each adduct was then heated in an oven at 120° until constant weight was achieved; in every case the terminal ligands were completely removed and [Rh(OOCCH$_3$)$_2$]$_2$ recovered unchanged as evidenced by spectral and analytical data. The process was then repeated to make certain no further decomposition had taken place.

Dropwise addition of pyridine to a concentrated solution of [Rh(OOCCH$_3$)$_2$]$_2$ in ethanol resulted in precipitation of the extremely insoluble [Rh(OOCCH$_3$)$_2$py]$_2$ in sufficiently pure form. The product was collected on a filter, washed with ethanol and ether, and air-dried.

Reaction of [Rh(OOCCH$_3$)$_2$]$_2$ with a gaseous material was carried out by passing a stream of the gas over a microcrucible containing about 75 mg. of the finely powdered complex until constant weight was achieved. Ammonia is absorbed extremely rapidly, nitric oxide considerably more slowly. Ethylenediamine (en) was carried on a stream of air at room temperature after treatment with the liquid or the hot vapor was found to result in reactions other than simple adduct formation. The samples were then weighed and placed under vacuum for 1 hr. Ammonia, NO, and en formed stable 1:2 adducts; CO and H$_2$S did not react. Upon heating at 120°, [Rh(OOCCH$_3$)$_2$NH$_3$]$_2$ and [Rh(OOCCH$_3$)$_2$NO]$_2$ revert to [Rh(OOCCH$_3$)$_2$]$_2$; some decomposition may occur in the latter case, as a second treatment with NO gave an adduct of slightly improper stoichiometry. The addition of en is not reversible; heating produced a greenish yellow substance of unknown nature which continued to lose weight, at 120°, over an extended period of time. It is not unlikely that chelation of the amine takes place with resultant disruption of the acetate bridging structure.

o-Phenanthroline (phen) reacts with [Rh(OOCCH$_3$)$_2$]$_2$ in acetone at 0° to give a deep olive-green solution from which a small amount of olive-green powder precipitates. This is presumably an adduct of [Rh(OOCCH$_3$)$_2$]$_2$ and phen; from the Rh analysis it appears that the stoichiometry is 1:1. *Anal.* Calcd. for [Rh(OOCCH$_3$)$_2$(phen)$_{0.5}$]: Rh, 33.0. Calcd. for [Rh(OOCCH$_3$)$_2$phen]$_2$: Rh, 25.7. Found: Rh, 32.7, 32.8. The complex loses no weight when heated at 120° for several hours. The color of the solution continues to change slowly from olive-green to brown to red-orange, the same color observed in the preparation of [Rh(phen)$_3$]$^{3+}$ which will be described in a later publication. It seems reasonable to assume that the color change takes place when excess phen attacks the acetate bridging structure of the original adduct.

A complete list of adducts with colors and analytical data is given in Table I.

Rhodium(II) Trifluoroacetate Dimer.—[Rh(OOCCH$_3$)$_2$]$_2$ (0.25 g.) was twice dissolved in 25 ml. of CF$_3$COOH and evaporated to dryness on a steam bath. The residue was dried briefly at 110°. It was then dissolved in acetone, passed through a fritted glass filter, and allowed to crystallize slowly upon evaporation of the solvent. The product was collected on a filter and dried at 110°.

Anal. Calcd. for Rh(OOCCF$_3$)$_2$: Rh, 31.3. Found: Rh, 31.1, 31.0.

The solubility of [Rh(OOCCF$_3$)$_2$]$_2$ in the previously mentioned solvents is much greater than that of [Rh(OOCCH$_3$)$_2$]$_2$; quali-

TABLE I
ADDUCTS OF DIMERIC RHODIUM(II) ACETATE

Ligand	Color of adduct	Calcd.	Gain	Loss
H$_2$O	Green	7.5	7.4, 7.4	7.5, 7.4
THF	Green	24.6	24.4, 24.3	24.5, 24.4
CH$_3$CN	Violet	15.6	15.1, 15.4	15.3, 15.2
DMSO	Orange	26.1	26.3, 26.5	26.3, 26.4
(CH$_3$)$_2$S	Rose-red	21.9	21.0, 21.0	21.0, 21.0
(CH$_3$)$_3$N	Pink	21.1	21.0, 21.2	21.1, 21.2
CH$_3$COOH	Green	21.4	20.4[b]	20.4
py	Rose-red	26.4	[c]	26.4; 26.6
NH$_3$	Wine-red	7.1	7.1, 7.0, 7.2	7.2, 7.2, 7.2
NO	Dark brown	11.9	11.5; 11.9	11.4; 11.8
en	Pink	21.4	21.6; 22.7	[d]
phen	Olive-green	...	[e]	[d]

Per cent ligand in adduct—Found[a]

[a] Results separated by a comma represent successive determinations upon a single sample; those separated by a semicolon represent independent measurements upon separate samples. [b] CH$_3$COOH lost slowly under conditions of experiment. [c] Prepared in ethanol solution. [d] Does not revert to [Rh(OOCCH$_3$)$_2$]$_2$ upon heating. [e] Prepared in acetone solution.

tative observations indicate similar behavior in formation of adducts. While [Rh(OOCCH$_3$)$_2$]$_2$ ignites readily upon heating over a flame, [Rh(OOCCF$_3$)$_2$]$_2$ sublimes somewhere above 250° and ignites at a higher temperature.

Absorption Spectra.—Visible–ultraviolet spectra of [Rh-(OOCCH$_3$)$_2$]$_2$ and most of its adducts were determined on a Cary Model 14 recording spectrophotometer. Details of the spectra of [Rh(OOCCH$_3$)$_2$]$_2$ in a variety of solvents and in various aqueous salt solutions are summarized in Table II.

Infrared spectra were examined in both KBr disks and Nujol mulls on a Beckman IR8 spectrophotometer.

TABLE II
VISIBLE–NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF DIMERIC RHODIUM(II) ACETATE IN VARIOUS MEDIA

Medium		λ, mμ	ε	λ, mμ	ε
H$_2$O		587	230	447	94
CH$_3$CH$_2$OH		590	210	446	98
(CH$_3$)$_2$CO		603	260	440	115
THF		597	235	441	110
CH$_3$COOH		592	255	442	100
DMSO		500	275	...	...
CH$_3$CN		552	235	437	125
NaCl	0.67 *M*	596	210	454	110
	2.0 *M*	602	225	456	130
NaBr	0.67 *M*	608	210	453	125
	2.0 *M*	612[a]	215	454	140
NaI	0.67 *M*	619	265	...	...
	2.0 *M*	623	275	...	...
NaCNS	0.67 *M*	580	310	sh[b]	
	2.0 *M*	577	315	sh	
NaNO$_2$	0.67 *M*	509	275	...	...
	2.0 *M*	505	295	...	...
NH$_3$[c]	0.67 *M*	530	310	sh	

[a] Compares with λ = 613 in KBr disk where bromide ions may occupy terminal positions. [b] sh, shoulder. [c] The solubility of adducts formed with py and en was so small as to preclude measurement of their visible–ultraviolet spectra.

Discussion

The mechanism of the reduction of Rh(III) in acetic acid is of interest in that it apparently involves the oxidation of the latter as evidenced by the evolution of

CO_2 during the course of the reaction. While the exact nature of the Rh-containing by-product is unknown, it is presumably a Rh(III) compound; it is readily converted into rhodium(III) chloride by treatment with hydrochloric acid.

The infrared spectrum of $[Rh(OOCCH_3)_2]_2$ is similar to those of the anhydrous Cu(II) and Cr(II) acetates. The degree of separation of the symmetric and asymmetric C–O stretching frequencies in a substance where acetate functions as a bidentate bridging group is expected not to be grossly different from that observed for free acetate ion. The following C–O stretching frequencies have been reported: $[Cr(OOCCH_3)_2]_2$, 1422, 1571 cm.$^{-1}$ ($\Delta = 149$ cm.$^{-1}$); $[Cu(OOCCH_3)_2]_2$, 1420, 1591 cm.$^{-1}$ ($\Delta = 171$ cm.$^{-1}$)[12]; $NaOOCCH_3$, 1422, 1575 cm.$^{-1}$ ($\Delta = 153$ cm.$^{-1}$).[13] Observed for $[Rh(OOCCH_3)_2]_2$ are 1433, 1588 cm.$^{-1}$ ($\Delta = 155$ cm.$^{-1}$). In contrast, for $[Co(NH_3)_5OOCCH_3](ClO_4)_2$, where acetate is a unidentate ligand and a divergence of the two C–O bands is thus predicted, the frequencies 1380, 1603 cm.$^{-1}$ ($\Delta = 223$ cm.$^{-1}$) have been reported.[14]

The adduct of $[Rh(OOCCH_3)_2]_2$ and dimethyl sulfoxide is interesting in that it appears that the ligand is bonded to the metal through sulfur. Pointing to this conclusion are (1) the striking difference in color of $[Rh(OOCCH_3)_2DMSO]_2$, orange, and the oxygen-liganded adducts (e.g., those of H_2O, THF, and CH_3-COOH), all of which are green or bluish green, and (2) the position of the S–O stretching frequency in its infrared spectrum. The S–O stretching frequency of complexes in which the ligand is bonded through oxygen should appear at a lower frequency than that of free DMSO (1055 cm.$^{-1}$), at a higher frequency when the ligand is sulfur-bonded. Among a wide variety of transition metal–DMSO complexes, two, $PdCl_2 \cdot 2DMSO$ ($\nu_{S-O} = 1116$ cm.$^{-1}$) and $PtCl_2 \cdot 2DMSO$ ($\nu_{S-O} = 1157$ and/or 1134 cm.$^{-1}$), have been shown by this criterion to involve metal–sulfur bonding.[15] An intense absorption band appears at 1086 cm.$^{-1}$ in the infrared spectrum of $[Rh(OOCCH_3)DMSO]_2$; this is presumably the S–O stretching frequency. A somewhat less intense band at 1014 cm.$^{-1}$ is believed, by analogy to a band at

1022 cm.$^{-1}$ for $PdCl_2 \cdot 2DMSO$, to be due to CH_3 rocking.

The adduct of $[Rh(OOCCH_3)_2]_2$ and NO exhibits infrared bands at 1800 (m) and 1710 (s) cm.$^{-1}$; these are within the 1940–1660 cm.$^{-1}$ stretching region considered typical of complexes involving donation from NO^+,[16] rather than in the region of 1200–1000 cm.$^{-1}$ typical of complexes involving the NO^- ion.[17]

While no pure salts containing ionic derivatives of $[Rh(OOCCH_3)_2]_2$ were obtained, evidence of the existence in aqueous solution of adducts with anions was obtained by observing spectrophotometrically the effect of concentrated solutions of various sodium salts upon the spectrum of $[Rh(OOCCH_3)_2H_2O]_2$. Such solutions are presumed to be equilibrium mixtures containing appreciable concentrations of $[Rh(OOCCH_3)_2$-$X]_2^{-2}$, where X^- is the anion in question. It may be noted that the displacement of the principal visible absorption band follows the usual spectrochemical series for increasing d-orbital splitting: $I^- < Br^- < Cl^- < H_2O < NCS^- < NH_3 < NO_2^-$.

The acetate bridging structure in $[Cu(OOCCH_3)_2$-$H_2O]_2$ breaks down fairly readily; the complex is known to ionize in aqueous solution[18] and is destroyed by strong acids and bases. On the other hand, rhodium-(II) acetate appears (from spectrophotometric measurements) to be stable indefinitely in aqueous solutions and in a variety of organic solvents. However, the cage structure is destroyed quite readily by strong acids; an indication of this behavior is the fact that the product of the evaporation of a solution of $[Rh(OO$-$CCH_3)_2]_2$ in CF_3COOH is $[Rh(OOCCF_3)_2]_2$.

Chernyaev and co-workers[2] state that $[Rh(OO$-$CCH_3)_2H_2O]_2$ appears to undergo no reactions other than the reversible substitution of various ligands for water. Indeed the hydrate reacts very rapidly in aqueous solution with a wide variety of ligands (Table II). However, our spectrophotometric observations indicate a further, slower, reaction of the adduct with an excess of any of several nucleophilic reagents. Presumably the acetate cage structure is being destroyed in this slower reaction. Such reactions, if carried out in an inert atmosphere, may make possible the syntheses of a wider variety of rhodium(II) complexes than are known presently.

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