N-bonded isomer. This shift should, however, be counterbalanced by the lower ligand field strength of $-SCN^-$ relative to $-NCS^-$.[18]

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New Complexes of Dirhodium(II)

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The species $Rh_2(CO_3)_4^{4-}$ forms when CO_3^{2-} in slight excess reacts with Rh_2^{4+}(aq). It is readily produced in good yield also by the reaction of CO_3^{2-} with $Rh_2(OAc)_4$. Solids containing the anion have been prepared and characterized. On treatment with acid, CO_2 is slowly released. The stage $Rh_2(CO_3H)_2^{2+}$ has been characterized in solution but we did not find it possible to prepare the aquo ion by heating the carbonato complex with acid. The complex $Rh_2(SO_4)_4^{4-}$ also has been prepared as have salts containing the species. On treatment with Ba^{2+}, $Ba_2Rh_2(SO_4)_4$ is precipitated, and the aquo ion is not formed.

Rhodium(III) in analogy to Co(III) forms a wide variety of complexes including many with saturated ligands, which are stable enough, at least in the kinetic sense, to be readily characterizable. But the coordination chemistry of Rh(II), in contrast to that of Co(II), is still highly circumscribed. Until the discovery of Rh_2^{4+}(aq),[1] the only example of Rh(II) in combination with saturated ligands was $Rh_2(OAc)_4$,[2] and from this example it was not clear to what extent the Rh–Rh bond owed its stability to the fact that OAc^- acts in a bridging capacity to unite the Rh(II) centers—thus note that Cr(II) is monomeric as the aquo ion but dimeric when combined with an equivalent amount of acetate. The existence of Rh_2^{4+}(aq) makes it clear that direct Rh–Rh interactions are important in the chemistry of aquorhodium(II), but the work of Maspero, *et al.*, did leave open the possibility that significant amounts of Rh^{2+} are in labile equilibrium with Rh_2^{4+}(aq).

The experiments to be described were undertaken in an effort to find a convenient route to preparing Rh_2^{4+}(aq) at relatively high concentration, so that the aquo ion could be studied intensively. Though they failed in this purpose they did reveal some new substitution chemistry of the Rh_2^{4+} unit. In particular, a new series of complexes in which CO_3^{2-} plays a role similar to that of OAc^- in $Rh_2(OAc)_4$ was found. Though there is an obvious analogy between CO_3^{2-} and OAc^-, this analogy has until now not been exploited in the extensive series of complexes of the type $M_2(OAc)_4$ which have been prepared.[17] But there are significant differences between the carbonato and acetato series in that only the former includes anionic species and in that CO_3^{2-} is expected to be removed from the coordination sphere much more readily than is OAc^- by acid.

Experimental Section

Materials. All chemicals were of the highest purity commonly available. Water used as reaction medium was redistilled from alkaline potassium permanganate in an all-glass still. Argon (99.995% pure), purchased from Liquid Carbonic, was freed of oxygen by passing the gas through a tower containing amalgamated zinc and a solution of chromous ion in 0.50 *M* acid. Ion-exchange resins were purchased from Bio-Rad. For anion exchange, Ag 1-X2, 200–400 mesh chloride form was used. This was pretreated by washing with saturated sodium chloride solution and excess water. For cation exchange, AG 50W-X2, 200–400 mesh hydrogen ion form was used. This resin was pretreated as described by Deutsch[3] except that 3% peroxide was used instead of 30%. The resin was stored in the acid form, under water and in the dark, until use. It was then rinsed with the strongest eluting agent to be used and with quantities of water.

Preparation of Anhydrous Tetra-μ-acetato-dirhodium(II). Hydrated rhodium trichloride (Engelhard Industries) was refluxed in a mixture of glacial acetic acid and ethanol following Rempel, *et al.*[4] Yields ranged from 70 to 85%.

Preparation of the Aquodirhodium(II) Cation. The procedure of Maspero, *et al.*,[1] was followed, care being taken to exclude oxygen. Only platinum needles were used in syringe transfers and residence time on the cation-exchange resin was minimized.

Instrumentation and Analysis. Ultraviolet and visible spectra were recorded on Cary 14 and 15 spectrophotometers. Infrared spectra were measured on Perkin-Elmer 457 and 621 machines. Magnetic susceptibilities were measured on solid samples by the Faraday method using the Ventron Corp. Model 7600 system with Model 7570 variable-temperature accessory. For liquid samples the nmr method of Evans[5] was used, as modified by Bailey.[6]

All microanalyses were performed by the Stanford Microanalytical Laboratory. Even though the decomposition temperature was at 940°, it was found necessary to add vanadium pentoxide as a catalyst to obtain reproducible and meaningful carbon analyses with carbonate complexes of rhodium.

Cyclic Voltammetry. For cyclic voltammetry a saturated calomel electrode was placed in a cell compartment connected by a partially fused glass frit to a degassed cell compartment containing platinum auxiliary and indicator electrodes and the solution of interest. The necessary electronics were constructed by Glenn M. Tom out of conventional operational amplifier circuitry, and voltammagrams were displayed on Houston Instument's Omnigraphic 200 X-Y recorder.

Results and Discussion

The Carbonato Complex. When a freshly prepared solution of Rh_2^{4+}(aq) is added under an inert atmosphere to a solution containing excess carbonate ion, the solution immediately changes from wintergreen to dark blue. With an appropriate cation, such as Na^+ or K^+, a purple solid is precipitated and it may be collected on a fritted filter. The solid appears wet. When it is air-dried or washed with methanol and air-dried, it changes into a blue solid having the infrared spectrum shown in Figure 1. (This differs in some details from that of the purple solid, which is a higher hydrate.) The identical material can be prepared by the following more convenient route. Approximately 0.5 g of anhydrous tetra-μ-acetato-dirhodium(II) is suspended in 10 ml of 2 *M* sodium carbonate solution. The solution is heated to near boiling and held at 100° for 10–15 min. Upon cooling and filtering, a solid forms. The resulting precipitate is washed with water until it just begins to dissolve, thus removing excess carbonate. The solid then is redissolved in water, reprecipitated with either methanol, sodium carbonate, or sodium chloride, washed with small amounts of water, rinsed with methanol and ether, and air-dried. Yields are greater than 90%.

Analyses for the various preparations of the carbonato complex are shown in Table I. It is found that they correspond

Table I. Analyses for Carbonate Complexes of Dirhodium(II)

		% M		% Rh		% C		% H	
Compd	M	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Na_4[Rh_2(CO_3)_4]\cdot 2.5H_2O$	Na	15.8	15.8	35.3	33.1	8.23	8.19	0.86	0.71
$Na_4[Rh_2(CO_3)_4]\cdot 2.5H_2O$	Na	15.8	16.3	35.3	35.4	8.23	8.39	0.86	0.87
$K_4[Rh_2(CO_3)_4]\cdot 2.5H_2O$	K	24.2	24.9	31.8	31.9	7.42	7.80	0.77	0.78
$Cs_4[Rh_2(CO_3)_4]\cdot 6.3H_2O$	Cs	48.8	49.0	18.9	18.8	4.40	4.35	1.15	1.17
$Cs_4[Rh_2(CO_3)_4]\cdot 7.5H_2O$	Cs	47.8	47.6	18.5	17.7	4.31	4.33	1.35	1.16

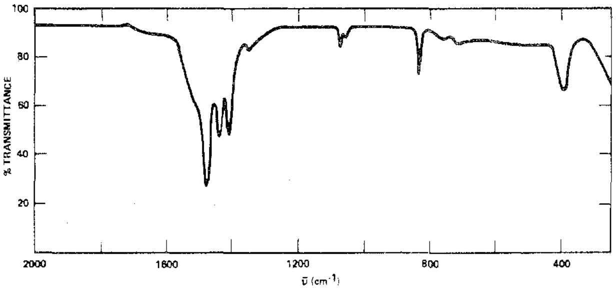

Figure 1. Infrared spectrum of blue $Na_4Rh_2(CO_3)_4\cdot 2.5H_2O$ in KBr.

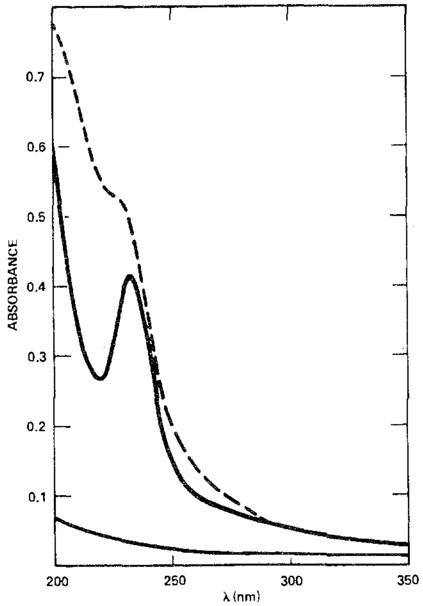

Figure 2. Ultraviolet spectrum of $Na_4Rh_2(CO_3)_4\cdot 2.5H_2O$, 3.68 × 10^{-5} *M*, in water (– – –) and in 1 *M* $HClO_4$ (——).

Table II. Susceptibilities by the Faraday Method

Compd	Temp, °C	$10^6\chi_{cor}$[a]
$Rh_2(OAc)_4$	22	72
	−54	88
	−93	72
	−123	74
	−132	93
	Av ± σ	80 ± 10[b]
$Na_4Rh_2(CO_3)_4\cdot 2.5H_2O$	21	533
	−59	419
	−94	476
	−123	609
	−128	469
	Av ± σ	501 ± 50
$(NH_4)_4Rh_2(SO_4)_4\cdot 4.5H_2O$ sample 1	22	48
	−61	417
	−96	83
	−126	171
	−132	170
	Av ± σ	178 ± 170
$(NH_4)_4Rh_2(SO_4)_4\cdot 4.5H_2O$ sample 2	24	173
	−62	405
	−103	371
	−134	60
	−143	193
	Av ± σ	240 ± 120

[a] χ_{cor} is the molar susceptibility per dimer corrected for ligand contributions in cgsu/mol as in A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York, N. Y., 1968. The value for one unpaired electron is 1250 × 10^{-6}. [b] Compares with the value 169 × 10^{-6} from ref 16 (recalculated).

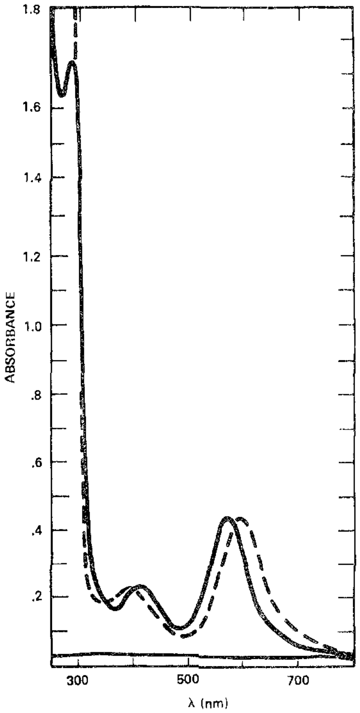

Figure 3. Visible spectrum of $Na_4Rh_2(CO_3)_4\cdot 2.5H_2O$, 2.01 × 10^{-3} *M*, in water (– – –) and in 1 *M* $HClO_4$ (——).

well to the formula $M_4[Rh_2(CO_3)_4]$ if we allow for variable extents of hydration by H_2O. Potentiometric titration with Ce(IV) shows the average oxidation state of Rh in the compound to be 2.0 ± 0.1. The cesium salt is very slow to precipitate (~2 days); the ammonium salt is unstable.

The compounds are essentially diamagnetic (small temperature-independent paramagnetism)—*cf.* Table II. The ultraviolet and visible spectra shown in Figures 2 and 3 resemble those of $Rh_2(OAc)_4$ and the aquo ion Rh_2^{4+}. Beer's law is followed over a 50-fold concentration range. On the basis of the analyses and observations just stated, it seems reasonable to formulate the solid as containing the anion $Rh_2(CO_3)_4^{4-}$.

The disposition of the CO_3^{2-} ions about the Rh_2^{4+} unit is not settled by any observations we have made. In all likelihood, they bridge the Rh–Rh bond as the anions do in $Rh_2(OAc)_4$. The lines in the infrared spectrum attributable to CO_3^{2-} are different from those exhibited by monodentate carbonate, by bidentate carbonate in tetraamminecarbonatocobalt(III),[7] and in μ-carbonato-bis(pentaamminecobalt(III).[8] These observations are consistent with the formulation of the complex as $Rh_2(CO_3)_4^{4-}$ in which the CO_3^{2-} is proposed as being structurally different from that in any of the comparison species. The resistance of the CO_3^{2-} to acid hydrolysis (*vide infra*) also indicates that the carbonate is not bound in Rh_2^{4+}

Table III. Ultraviolet and Visible Absorption Maxima for Dirhodium(II) Species

Species	λ, nm (ε, molar extinctions per dimer)	Medium
$Rh_2(OAc)_4$	585 (241),[a] 440 (106),[a] 250 (sh, 4 × 10^3),[b] 218 (1.7 × 10^4),[b] 587 (230),[c] 443 (94)[c]	H_2O
$Rh_2{}^{4+}(aq)$	648 (93),[a] 402 (126), 250 (1.97 × 10^4),[d] 630 (79.8),[e] 412 (118), 250 (2.12 × 10^4)	3 *M* $HClO_4$
$Na_4Rh_2(CO_3)_4 \cdot 2.5H_2O$	575 (217),[a] 414 (105), 265 (870), 234 (1.06 × 10^4), 595 (216),[a] 394 (102)	1 *M* $HClO_4$ H_2O
Di-μ-bicarbonato-dirhodium(II)	629 (91),[a] 433 (107), 376 (142), 248 (2.01 × 10^4)	1 *M* $HClO_4$
$(NH_4)_4Rh_2(SO_4)_4 \cdot 4.5H_2O$	625 (128),[a] 415 (65), 297 (408), 243 (1.66 × 10^4)	1 *M* $HClO_4$

[a] This work. [b] L. Dubicki and R. L. Martin, *Inorg. Chem.*, 9, 673 (1970). sh = shoulder. [c] Reference 2. [d] 1 *M* $HClO_4$. [e] Reference 1.

in the way it is in tetraamminecarbonatocobalt(III), which readily yields CO_2 on being acidified.

On adding excess acid, an immediate change in spectrum is observed (*cf.* Figures 2 and 3) which is reversed if the solution is neutralized quickly. When only slightly more than an equivalent amount for complete protonation is added and the solution is quickly evaporated to dryness, an unstable purple powder is left, which then decomposes to a green-purple product. When an acidified solution (4 mol of proton/mol of $Rh_2(CO_3)_4{}^{4-}$) is quickly placed on either a cation- or an anion-exchange resin, the colored species does not adhere. The ion-exchange behavior shows that a neutral species is formed on acidification. From the fact that this can be reconverted to the starting material by adding alkali, we can take this to be tetra-μ-bicarbonato-dirhodium(II).

The species does undergo aquation within a matter of minutes as evidenced by a gradual change in spectrum and by the evolution of gas. However, no significant concentration of a 1+ species is formed, and the first readily characterizable stage in the aquation yields a 2+ species.

When the sodium salt (*ca.* 10^{-2} *M* in Rh(II)) is added to 1 *M* perchloric acid and heated on a steam bath for 15 min, the purple solution turns green and the slow evolution of gas is observed. If the solution then is diluted and passed onto a cation-exchange resin, a bright green band forms. This band is eluted slowly with 0.5 *M* acid and more quickly with 1 *M* acid. This behavior is indicative of a species with a 2+ charge. Excess sodium carbonate reconverts the product ion to the parent carbonato dimer. Solutions, when titrated potentiometrically with ceric ion in 1 *M* sulfuric acid to rhodium(III), were found to consume 2.08, 2.14, and 2.26 equiv/dimer showing that the oxidation state of rhodium remains 2+. The spectrum, the characteristics of which are summarized in Table III, greatly resembles that of the di-μ-acetato-dirhodium(II) ion.[9] On increasing the pH by the dropwise addition of 1 *M* sodium hydroxide to between 4 and 5, most of the colored solute is precipitated as a green gel-like solid that can be dried to a powder after washing with methanol and ether. The solid was always found to contain rhodium and carbon in a 1:1 ratio. The solid on dissolution does not produce a solution identical with the initial one. The species in solution at low pH is taken to be the hydrated di-μ-bicarbonato-dirhodium(II) cation. It is fairly air stable, being oxidized only over a period of days. The solid obtained from the solution on raising the pH proved to be difficult to characterize. According to the analysis, it can be formulated as a hydrated di-μ-carbonato-dirhodium species, but the behavior suggests that condensation occurs when the precipitate forms.

When an acidic solution of the hydrated di-μ-bicarbonato-dirhodium(II) cation was heated in the absence of oxygen even for long periods of time, the aquo ion was never observed. Experiments were done with a variety of acids including $H_2B_{12}Cl_{12}$,[10] perchloric, sulfuric, fluoroboric, hexafluorophosphoric, *p*-toluenesulfonic, and trifluoromethylsulfonic acid, neat or dilute, and with temperatures ranging from ambient to 100°, for short or long periods of time (up to 1 week with concentrated sulfuric acid), all without leading to the aquo dimer in significant amounts. Small amounts of a species elutable slowly from a cation-exchange column with 1 *M* $HClO_4$ were encountered. This is probably a 3+ species. Conditions drastic enough to produce $Rh_2{}^{4+}(aq)$ were found to lead to elementary Rh and Rh(III).

A remarkable feature of the observations is the exceptional stability of the species containing two carbonate units per dimer. These ligands can occupy only four of the eight equatorial positions on the $Rh_2{}^{4+}$ units. Exploratory experiments with anions such as oxalate or fumarate being added showed that they readily substitute into the dimeric species, but the work was not carried far enough to lead to the identification of products.

Investigation of a saturated solution of tetra-μ-carbonato-dirhodate(II) in 0.1 *M* sodium tosylate by cyclic voltammetry reveals a reversible wave at 0.498 V *vs.* nhe (88-mV peak to peak separation). If a small excess of *p*-toluenesulfonic acid is added, the wave shifts to 1.022 V (94-mV separation). This wave is indicative of a one-electron oxidation, as in the case of rhodium acetate.[9] In the potentiometric oxidation, a colored intermediate is observed that rapidly decays. The oxidation consumes 2 equiv of Ce(IV)/dimer and shows no break at the 1-equiv point, indicating that the intermediate decays rapidly on the time scale of the titration. In following the oxidation spectrophotometrically a maximum intensity for the spectrum of the intermediate is observed after 1 equiv of Ce(IV)/Rh(II) is added. The spectrum consists of two maxima in the visible region (755 and 505 nm), to be compared with 570 and 410 nm observed for hydrated tetra-μ-bicarbonato-dirhodium(II). The ultraviolet region is obscured by Ce(III). No reversible waves are observed in doing cyclic voltammetry on the product solution nor would any be expected if Rh(II) were completely oxidized to Rh(III).

The Sulfato Complex. Maspero, *et al.*,[1] reported that the aquorhodium(II) species is eluted much more freely with sulfuric acid than with noncomplexing acids. Ziolkowski[11] noted that on adding sulfuric acid to solutions of the aquo dimer, the visible spectrum changes slightly. We find that both the ultraviolet and the visible spectra are sensitive to the concentration of sulfate and to the time the sulfate is allowed to remain in contact with the aquo dimer.

Repeated attempts to isolate solids from solutions of the aquo dimer in various concentrations of sulfuric acid failed. The solutions are sensitive to oxidation by air and to disproportionation upon rotary evaporation. Organic solvents added to the solutions did not produce precipitates and solutions prepared using mixtures of various sulfate salts and sulfuric acid also failed to yield solids, even on cooling to −10°.

A solid containing what we believe to be the tetrasulfatodirhodium(II) cation was obtained by the following procedure. The aquodirhodium(II) cation was produced[1] and charged onto a cation-exchange column. It was eluted under an inert atmosphere with 2 *M* $(NH_4)_2SO_4$. The solution was reduced to a solid by rotary evaporation and pumped on until it was quite dry. The resulting solid was washed onto a glass

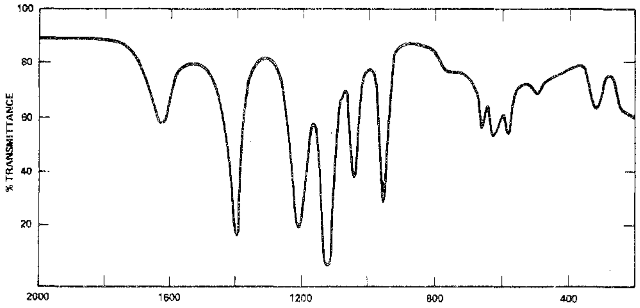

Figure 4. Infrared spectrum of $(NH_4)_4Rh_2(SO_4)_4 \cdot 4.5H_2O$ in KBr.

frit with acetone, where it was stirred with a mixture of 70 parts of water to 30 parts of acetone by volume and filtered. The solid was rinsed with acetone and then air-dried. The yields were about 70%.

Anal. Calcd for $(NH_4)_4RH_2(SO_4)_2 \cdot 4.5H_2O$: Rh, 27.6; S, 17.1; N, 7.5; H, 3.35. Found: Rh, 26.7; S, 17.5; N, 7.6; H, 3.26. These analyses are typical except in the feature that somewhat variable amounts of water appeared to be present in different batches. All samples showed evidence of slight contamination by $(NH_4)_2SO_4$. Alternate syntheses using the acetato or carbonato dimers as starting materials failed.

The main features of the uv and visible spectra are summarized in Table III. Measurements of magnetic susceptibility, reported in Table II, show some scatter, but indicate that the compound exhibits a small temperature-independent paramagnetism. The similarity of the spectra to those of other dirhodium species shows, as prior experience would lead us to expect, that unit Rh_2^{4+} is retained in the sulfate complex.

The infrared spectrum of $(NH_4)_4Rh_2(SO_4)_4 \cdot 4.5H_2O$ is shown in Figure 4. The ν_3 mode of free sulfate is split into three bands at 1210, 1110, and 1040 cm^{-1}. The ν_4 mode is also clearly separated into three bands just above 600 cm^{-1}. Such splitting is compatible with C_{2v} site symmetry for the sulfate ions in the complexes, but this site symmetry is compatible with either of the two binding modes possible for SO_4^{2-}.

When investigated by cyclic voltammetry, the sulfato complex behaves similarly to the acetato and carbonato dimers. An oxidation wave is observed at 1.112 V (60-mV separation) in 0.2 *M* sulfuric acid. The position of this redox wave is slightly medium dependent. In 0.2 *M* sodium tosylate, it is found at 1.132 V (100-mV separation) and it shifts to 1.102 V (80-mV separation) when the solution is made about 0.2 *M* in *p*-toluenesulfonic acid. By analogy to the other cases, this redox process also is taken to be a one-electron oxidation. Since Rh_2^{4+}(aq) does not show a similar wave, the experiments prove that sulfate is actually coordinated to Rh_2^{4+} in the systems just described. They furthermore show that SO_4^{2-} stabilizes the Rh_2^{4+} unit, and this suggests that the anion occupies a bridging position. The structures of solids containing $Mo_2(SO_4)_4^{4-}$ [12] and $Mo_2(SO_4)_4^{3-}$ [13] have been determined and both ions have been shown to contain SO_4^{2-} in bridging positions.

In the case of the molybdenum sulfate dimer, barium ion strips off the sulfate ions to produce aquomolybdenum(II). The addition under argon of excess barium ion in 1 *M* perchloric acid to freshly saturated solutions of the rhodium sulfate dimer precipitates a pale blue-white powder, removing all colored species from solution. When barium carbonate is added directly to a neutral solution of the blue-green sulfate dimer, all colored species precipitate as a pale purplish solid (mixed with excess barium carbonate) that turns to blue as it dries.

Observations on Rh_2^{4+}(aq). The foregoing account shows that the approach neither through $Rh_2(CO_3)_4^{4-}$ nor through $Rh_2(SO_4)_4^{4-}$ brought us to our originial preparative goal of having a convenient way to obtain Rh_2^{4+}(aq) at high concentration. We found, however, that following the method of Maspero and Taube[1] and using 3 *M* $HClO_4$ as eluting medium, Rh_2^{4+} at the 0.02 *M* level was readily obtained. We find that Beer's law in the visible range is accurately obeyed over a 100-fold range of dilution of such a solution, and it is unlikely, therefore, that significant concentrations of Rh^{2+}(aq) are present, at least at the concentrated end of this range.

Since the report on Rh_2^{4+} was published, several events have occurred which have changed the perspective on the nature of the species. Among these is the reinvestigation[14] of the structure of $Rh_2(OAc)_4$, the new Rh–Rh distance of 2.386 Å being regarded as in accord with a triple bond.[15] The general similarity of the spectra for Rh_2^{4+}(aq) and $Rh_2(OAc)_4$ argues for similar electronic structures for the two species.

In the interim, also, the magnetic susceptibility of $Rh_2(OAc)_4$ was determined, and it was found to show a small temperature-independent paramagnetism.[16] Thus the small paramagnetism reported[1] for Rh_2^{4+}(aq) based on a measurement at a single temperature can be dismissed as being caused by the effect that gives rise to paramagnetism in $Rh_2(OAc)_4$ (or $Rh_2(CO_3)_4^{4-}$ or $Rh_2(SO_4)_4^{4-}$). A solution of Rh_2^{4+}(aq) was prepared in the course of present work to check the earlier measurements of magnetic susceptibility. Our measurements checked that reported[1] within experimental error but did not improve on the eariler measurement. The measurement performed by Maspero and Taube on a solution of the dirhodium cation eluted from a cation-exchange column with sulfuric acid also agrees within experimental error with our value for the solid sulfate dimer.

A large number of anions were tried as precipitants for Rh_2^{4+}(aq), including PF_6^-, $B(C_6H_5)_4^-$, BF_4^-, $B_{10}H_{10}^{2-}$, $B_{12}Cl_{12}^{2-}$, and $Fe(CN)_6^{4-}$, but none yielded a solid, even with cooling, using high concentrations of the precipitating anion and using mixed-solvent systems. On subjecting Rh_2^{4+}(aq) to extreme conditions in the presence of putative precipitating ions, disproportionation to Rh(s) and Rh(III) often ensues. The disproportionation is catalyzed by Cl^- and Br^-, and by I^- as well, with the difference in the latter case that reduction to Rh is eventually complete. Fluoride ion removes color from a solution of Rh_2^{4+}(aq) but forms no precipitate.

Hydrogen gas reduces Rh_2^{4+}(aq) to metal. Oxygen (from air) produces a highly charged (>3+) species showing an absorption peak at 398 nm (ϵ 222 based on molarity of dimer). The species slowly hydrolyzes, and after 1 or 2 days, some $Rh(H_2O)_6^{3+}$ can be separated using a cation-exchange resin. Treating the freshly prepared product of the reaction of O_2 with Rh_2^{4+}(aq) with Cr^{2+} regenerates Rh_2^{4+}(aq). All of the observations can be understood on the basis that $[(H_2O)_5RhOORh(H_2O)_5]^{4+}$ is the intermediate formed when Rh_2^{4+}(aq) reacts with O_2.

Acknowledgment. This work was initiated under AEC support and was completed under NSF Grant GP24726XI.

Registry No. $Na_4[Rh_2(CO_3)_4]$, 53078-66-3; $K_4[Rh_2(CO_3)_4]$, 53078-64-1; $Cs_4[Rh_2(CO_3)_4]$, 53078-65-2; $(NH_4)_4Rh_2(SO_4)_4$, 53078-62-9; $Rh_2(OAc)_4$, 15956-28-2; Rh_2^{4+}(ag), 12396-17-7.

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Infrared and Raman Studies of Alkali Metal Atom Matrix Reactions with Fluorine. Vibrational Spectrum of the $M^+F_2^-$ Species

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Argon matrix reactions of alkali metal atoms with fluorine have been studied using laser Raman and infrared spectroscopy. Raman signals appropriate for the ν_1 intraionic $(F\leftrightarrow F)^-$ mode in the $M^+F_2^-$ species have been observed to show an alkali metal effect due to interaction with the ν_2 interionic $M^+\leftrightarrow F_2^-$ mode. Infrared spectra revealed several ν_2 assignments for the $M^+F_2^-$ molecules and intense sharp bands due to the MF and $(MF)_2$ species.

Introduction

The fluorine molecular anion, F_2^-, was first observed in radiation-damaged salts by electron spin resonance spectroscopy. In 1955, Känzig[1] postulated the existence of F_2^- in γ-irradiated LiF at 77°K. In later work, Delbecq, *et al.*[2], reproduced the Känzig results on F_2^-, while Vande Kieft and Gilliam[3] produced the F_2^- species by irradiation of alkali metal bifluoride salts ($M^+HF_2^-$). Balint-Kurti and Karplus[4] have performed potential energy surface calculations for the reaction

$$Li + F_2 \rightarrow LiF_2 \rightarrow LiF + F \tag{1}$$

Even though this reaction is exothermic by approximately 100 kcal/mol, there is a stable intermediate, isosceles triangular $Li^+F_2^-$, which has a maximum calculated well depth of about 40 kcal/mol. Recently, Ham and Chang[5] have attributed the chemiluminescence arising from dilute gas mixtures of sodium and fluorine to NaF_2. Very recently, Martinez de Pinillos and Weltner[6] have obtained electron spin resonance evidence for F_2^- from alkaline earth metal atom–F_2 matrix reactions.

The possibility of observing such a potentially unstable intermediate species as $M^+F_2^-$ was greatly enhanced by the stabilizing effect of an Ar matrix. The reaction intermediate produced during condensation of alkali atoms and F_2 was trapped in the rare gas lattice and kept available for spectroscopic examination. This provided a look at the mechanism of an elementary chemical reaction, the combination of two elements to form the alkali halide molecule. Here follows a detailed vibrational spectroscopic study of alkali metal atom–molecular fluorine matrix reactions.

Experimental Section

The 15°K cryogenic refrigeration and vacuum apparatus for infrared[7,8] and Raman[9,10] studies of alkali metal atom matrix reactions has been described previously. The techniques for handling the alkali metals for producing atomic beams have also been reported. Evaporation temperatures appropriate to 0.5–1.0 μ of alkali metal vapor pressure were used.[8]

Fluorine was handled in a passivated stainless steel vacuum system constructed with "swaglok" fittings and Nupro SS-4BK valves. Pressures were measured with an Ashcroft vacuum gauge with a stainless steel Bourdon tube. Fluorine (Allied Chemical) obtained from the Naval Research Laboratory in small stainless steel cans was passed through a stainless steel U tube immersed in liquid nitrogen before use. In some cases the F_2 can was cooled to 77°K before the sample was withdrawn. Argon (Air Products, 99.995%) matrix samples were prepared using standard techniques.[11]

For infrared experiments, gas spray-on rates were initially 1 mmol/hr slowly increasing to 2 mmol/hr when alkali metal atom codeposition was started. Sample formation was monitored by infrared survey scans and stopped after 10–20 hr when the sample transmission reached 30–40%. Calibration spectra, run at 8 or 3.2 cm^{-1}/min on a Beckman IR-12 filter–grating spectrophotometer, are accurate to ± 0.5 cm^{-1}.

Raman experiments employed gas deposition for 3–5 hr at 3 mmol/hr with metal atoms for all but the first hour. Raman spectra were recorded on a Spex Ramalog using Coherent Radiation Model 52G argon and krypton ion lasers. Dielectric filters (Corion Instrument Corp.) were used to remove undesired laser plasma emission from recorded spectra. Raman signals were calibrated by superimposing emission lines on each side of the band during an actual running scan, which gives an accuracy of 0.5 to 1.0 cm^{-1} depending upon the half-bandwidth.

Results

The infrared and Raman spectra of each alkali metal–fluorine–argon matrix combination will be treated in turn. The Ar–F_2 samples were diluted 50:1 for Raman studies and 100:1 for infrared experiments, unless otherwise stated. As expected, the frequency regions for alkali fluorides trapped in solid argon were void of signals in the Raman work. The Raman signals shifted about 460 cm^{-1} were unstable with respect to laser photolysis; the Na–F_2 reaction intermediate, which had a half-life of approximately 25 min, was the most photolytically stable new species observed. Further, these signals exhibited faster degradation than the 892-cm^{-1} F_2 band, which has been shown to undergo photolytic dissociation with the blue Ar^+ laser lines and to react in solid Kr and Xe to form KrF_2 and XeF_2, respectively.[12]

The infrared spectra were unexpectedly complex due to fluorine-carried impurities and alkali fluoride aggregates. Impurity bands will be identified where possible in the appropriate tables but will otherwise not be mentioned. Infrared surveys were taken with purified and unpurified F_2 in the matrix without alkali metal, which provided a check on the impurity signals.

Lithium. Raman spectra involving either Li isotope yielded identical signals, within experimental error: the F_2 signal shifted 892.2 ± 0.5 cm^{-1} from the laser source and a band of moderate intensity at 452.0 ± 1.0 cm^{-1} (^6Li) or 451.6 ± 0.8 cm^{-1} (^7Li). This band is contrasted in Figure 1 with the analogous signals produced by the other alkali metal species. No other band was observed in any Li–F_2 Raman experiment.

The infrared scans of ^6Li–F_2 reaction products showed a strong doublet at 891.8 (0.32) and 886.6 cm^{-1} (0.53) (optical