TABLE IV

Complex	Color	Mp, °C[a]		Mol wt	Analyses, %				
					C	H	N	O	Halogen
$[Ru(CO)_3Br_2]_2$	Yellow	...	Calcd	691	10.43	...	...	13.89	46.25
			Found	691[b]	10.45	...	...	13.93	45.78
$[Ru(CO)_3I_2]_2$	Yellow	...	Calcd	879	8.20	...	...	10.92	57.74
			Found	890[c]	8.40	...	...	10.85	56.91
$Ru(CO)_3Br_2(C_5H_5N)$	Ivory yellow	180	Calcd	424	22.67	1.19	3.30	11.32	37.70
			Found	445	22.57	1.17	3.29	11.13	36.90
$Ru(CO)_3Br_2$(3-pic)	Ivory yellow	149	Calcd	438	24.67	1.61	3.20	10.96	36.48
			Found	446	24.65	1.78	3.39	10.71	36.40
$Ru(CO)_3Br_2$(3,4-lut)	Ivory yellow	164	Calcd	452	26.57	2.00	3.10	10.62	35.35
			Found	483	26.56	2.12	3.17	10.84	35.90
$Ru(CO)_3I_2(C_5H_5N)$	Ivory yellow	143	Calcd	518	18.55	0.97	2.70	9.27	49.00
			Found	532	18.71	1.05	2.66	9.51	49.50

[a] Uncorrected values determined in evacuated tubes. [b] Determined by mass spectra. [c] Determined in $CHCl_3$ solution using a Mechrolab osmometer, Model 301 A.

distilled. Methyl isobutyl ketone was dried over anhydrous calcium sulfate and then distilled.

Thermal Decomposition of Ruthenium Tetracarbonyl Dihalides.—About 0.2 g (0.0005 mol) of the compounds $Ru(CO)_4X_2$ (X = Br, I), dissolved in 100 ml of chloroform or benzene, was allowed to react at 50°. The progress of the reaction was monitored by infrared spectroscopy. When no more $Ru(CO)_4X_2$ could be detected, the solution was cooled to room temperature and evaporated under reduced pressure. The products were precipitated by adding *n*-pentane, filtered, washed with *n*-pentane, and dried under high vacuum. The yields were practically quantitative. A further purification was effected by sublimation under high vacuum (120° and 10^{-3} mm). The yellow crystalline compounds $[Ru(CO)_3I_2]_2$ and $[Ru(CO)_3Br_2]_2$ have a different solubility in common organic solvents such as chloroform, 1,2-dichloroethane, benzene, toluene, nitromethane, nitrobenzene: $[Ru(CO)_3I_2]_2$ is very soluble in these solvents, whereas the analogous $[Ru(CO)_3Br_2]_2$ is only slightly soluble. They are insoluble in aliphatic hydrocarbons and decompose on being heated without melting. Infrared spectra, elemental analyses, and other data are given in Tables I and IV.

General Procedure for the Synthesis of $Ru(CO)_3X_2L$ (X = Br, I; L = Pyridine, 3-Picoline, 3,4-Lutidine).—$Ru(CO)_4X_2$ (0.0004 mol) and *ca.* 0.0005 mol of ligand dissolved in 50 ml of chloroform were allowed to react at room temperature. The conversion of $Ru(CO)_4X_2$ to $Ru(CO)_3X_2L$ was followed either spectroscopically or gas volumetrically. The conversion was practically complete within 20 min. The solution was then concentrated under reduced pressure and the product was precipitated by adding *n*-pentane. The ivory yellow crystalline compound was collected on a filter, washed with *n*-pentane, and dried under high vacuum. Purification was effected by recrystallization from chloroform–pentane (1:5). All the compounds are soluble in organic solvents such as chloroform, carbonte trachloride, benzene, and toluene and insoluble in aliphatic hydrocarbons. Infrared spectra, elemental analyses, and other data are given in Tables I and IV.

Kinetic Studies.—The rates of reaction 1 were followed by recording the decrease in intensity of the high-frequency CO stretching absorption of the $Ru(CO)_4X_2$ complexes at about 2170 cm^{-1}. The reactions were carried out under nitrogen in an aluminum-wrapped vessel fitted with a serum cap. A constant-temperature bath was used to maintain the temperature within 0.1°. The concentration of $Ru(CO)_4X_2$ was in the range 3.2×10^{-3}–12×10^{-3} *M*. At appropriate time intervals aliquots were withdrawn from the reaction vessel with a syringe and transferred into a 1-mm infrared cell, and their infrared spectra were measured against a reference containing only the solvent. Anywhere between 15 and 20 measurements were made during a period of 3 or 4 half-lives. All reactions proceeded to completion and the spectra at infinite time were in good agreement with those of the known products independently prepared. The pseudo-first-order rate constants were reproducible to 5% or better. More details about this method have been given previously.[16] Measurements were performed on a Perkin-Elmer Model 621 spectrophotometer. A general nonlinear least-squares program was used to calculate the activation parameters.

Acknowledgments.—We wish to thank the Italian National Research Council (CNR, Rome) for financial support.

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The Metal–Metal Bond in Binuclear Rhodium(II) Acetate Monohydrate[1]

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Rhodium(II) acetate monohydrate is isostructural with binuclear copper(II) acetate monohydrate[2] and the published[2] Rh–Rh separation of 2.45 Å suggests significant Rh–Rh bonding [Rh–Rh = 2.69 Å in rhodium metal]. Many adducts of the type $Rh(CH_3CO_2)_2L$ have been prepared.[3-5] In most cases it is probable that these adducts are binuclear with the addends L terminally coordinated to rhodium atoms bridged by the acetate cage. This is consistent with the analytical data, diamagnetism, and electronic spectra.[3-5] The visible spectra of Rh(II) acetate and of some of its adducts have been reported but not interpreted.[3]

The visible spectra usually consist of two main absorptions: band I at ~600 mμ and band II at ~450 mμ (*cf.* Figure 1). Band II is relatively insensitive to terminal ligands while band I is particularly sensitive

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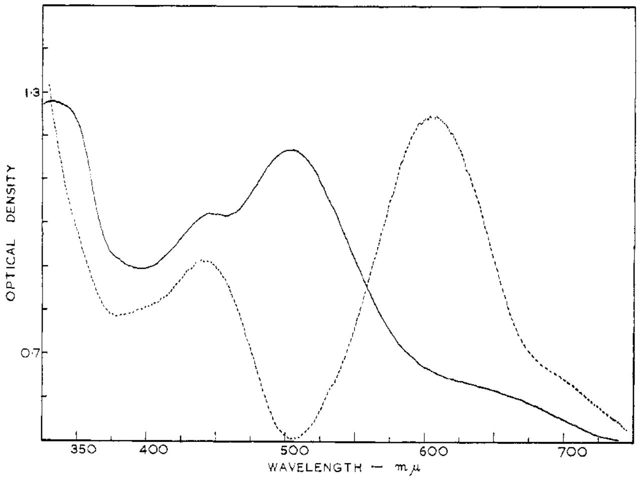

Figure 1.—Diffuse reflectance spectra of anhydrous rhodium(II) isobutyrate (dotted line) and rhodium(II) acetate pyridine (full line), both at 77°K. The spectra of rhodium(II) acetate monohydrate and anhydrous rhodium(II) isobutyrate are similar except that band I lies at ~580 mμ for the former complex.

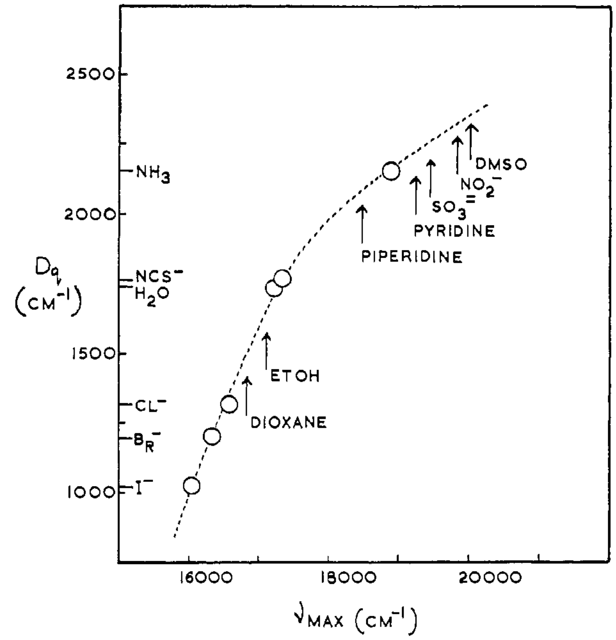

Figure 2.—Spectrochemical behavior of band I in $[Rh(CH_3CO_2)_2L]_2$. The spectra of most of these adducts have been reported in ref 3.

and its spectrochemical behavior toward I^-, Br^-, Cl^-, H_2O, NCS^-, NH_3, and NO_2^- has been noted by Johnson, *et al.*[3] This behavior appears to be more general. Thus if we use the *Dq* values of I^-, Br^-, Cl^-, H_2O, NCS^-, and NH_3 obtained from data on Cr(III) complexes,[6] a fairly smooth variation of band I energy with the *Dq* values is obtained (*cf.* Figure 2). The positions of other ligands is reasonably consistent with the spectrochemical series.[7] The soft-acid character of Rh(II) is demonstrated by the high energy of band I for NO_2^-, $(CH_3)_2SO$ (DMSO), and SO_3^{2-} adducts. In these complexes it is likely that the terminal groups bond *via* nitrogen and sulfur atoms, a view which is supported by the infrared spectrum of the DMSO adduct.[3]

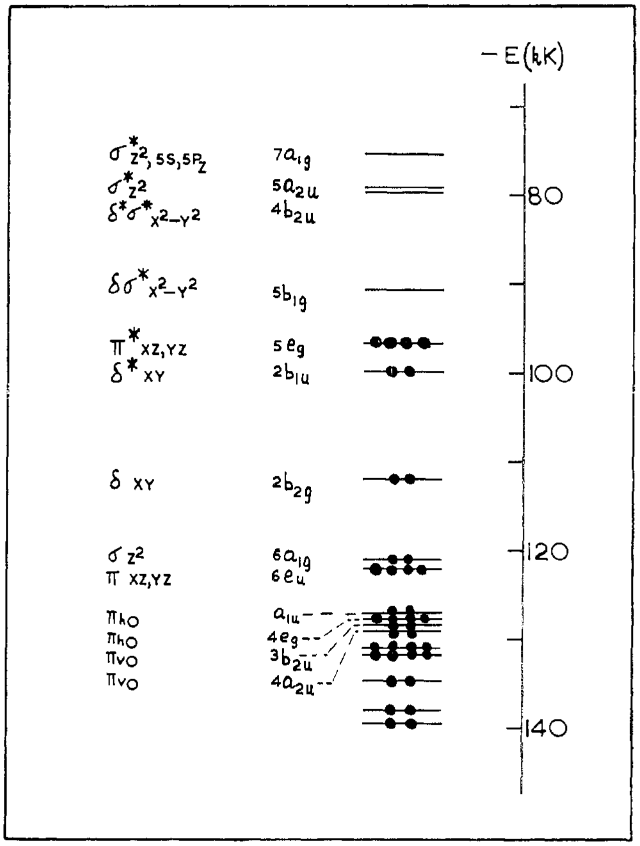

Figure 3.—Molecular orbitals for $[Rh(CH_3CO_2)_2H_2O]_2$. The ground-state configuration is $(6e_u)^4(6a_{1g})^2(2b_{2g})^2(2b_{1u})^2(5e_g)^4$. All Wolfsberg and Helmolz *F* factors are set to 2.0. For details of calculation see ref 8.

The pronounced sensitivity of the energy of band I to ligands terminally coordinated along the Rh–Rh axis suggests that the transition is between MO's, one having a large amount of $4d_{z^2}$ (and some $5p_z$) character. Furthermore, the spectrochemical behavior of band I indicates that this d_{z^2} character is associated with the MO in which the transition terminates. The fact that band I for anhydrous rhodium(II) isobutyrate (~16.6 kK) is not greatly shifted from its position in the corresponding monohydrate (~17.3 kK) does not necessarily preclude our suggested assignment since the carboxylate oxygen atoms may well lie along the Rh–Rh axis in the solid anhydrous compound.

In the absence of polarized single-crystal spectra to assist assigning these bands, an SCCC–MO (self-consistent charge and configuration–molecular orbital) calculation on $[Rh(CH_3CO_2)_2(H_2O)]_2$, similar to the one performed on $[Mo(CH_3CO_2)_2]_2$,[1,8] was undertaken. For these calculations the Rh–H_2O distance was taken to be 2.20 Å compared with 2.26 Å (private communication received later from Professor Porai-Koshits), and the pattern of orbitals shown in Figure 3 was obtained.

This diagram may be compared with the recently published qualitative MO diagram of Bennett, *et al.*[9]

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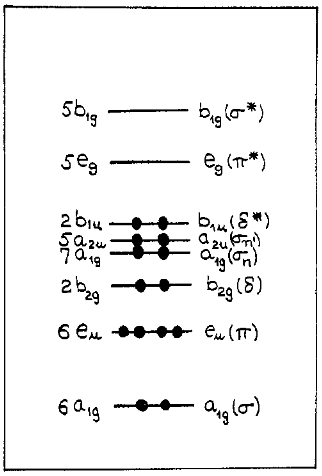

Figure 4.—A qualitative MO diagram for diamagnetic rhodium(II) carboxylates proposed by Bennett, Caulton, and Cotton.[9] The labeling on the left-hand side corresponds to that employed in the present work (see Figure 3).

(Figure 4). Both interpretations are consistent with a closed-shell configuration as required by the observed diamagnetism. However, Bennett, *et al.*,[9] described the Rh–Rh bonding as being triple ($\sigma + 2\pi$) arising from the configuration $[(\sigma)^2(\pi)^4(\delta)^2(\sigma_n)^2(\sigma_{n'})^2(\delta^*)^2]$ and account for the long Rh–Rh distance of ~2.45 Å in terms of repulsion between the filled δ and δ^* orbitals pushing the two Rh atoms apart. This is in sharp contrast with the results of our calculations which lead to the formulation of the metal–metal bonding as being single (σ) arising from the configuration $[(\pi)^4(\sigma)^2(\delta)^2(\delta^*)^2(\pi^*)^4]$. A single Rh–Rh σ bond is consistent with the reported Rh–Rh distance of ~2.45 Å which may be compared with the extremely short M–M distance of 2.11 Å in $Mo_2(CH_3COO)_4$ where a strong quadruple bond is believed to exist.[10–13]

The present description is considered to offer a more plausible interpretation of the electronic spectrum. The fundamental difference between the two schemes of energy levels is that the $7a_{1g}$ and $5a_{2u}$ orbitals in Figure 3, which correlate with the nonbonding a_{1g} (σ_n) and a_{2u} ($\sigma_{n'}$) orbitals in Figure 3 of ref 9, lie at much higher energies and are empty. These orbitals are involved in terminal bonding (*i.e.*, they are directed outward along the metal–metal axis) and a one-electron excitation like $\pi^*(5e_g) \rightarrow \sigma^*(5a_{2u})$ should display the spectrochemical behavior observed for band I. Thus increasing the terminal (*i.e.*, axial) ligand field will destabilize the $5a_{2u}$ orbital and so move band I to a higher energy. The insensitivity of band II to terminal groups may be rationalized if electrons are excited into $d_{x^2-y^2}$-type orbitals, *viz.*[14]

$$\pi(6e_u) \longrightarrow \delta\sigma^*(5b_{1g}) \text{ and } \pi^*(5e_g) \longrightarrow \delta^*\sigma^*(4b_{2u})$$

The ultraviolet spectrum of Rh(II) acetate monohydrate has two main absorptions. Band III occurs as a shoulder at ~250 mμ and band IV as a more intense peak at ~220 mμ (*cf.* Figure 5).[15] Addition of ammonia or pyridine leads to a dramatic change in this spectrum, suggesting that a large portion of the uv absorption, particularly band III, results from transitions between orbitals associated with axial L–Rh–Rh–L bonding. Our SCCC–MO calculations on the ammonia adduct show that the replacement of H_2O by NH_3 results in a large shift of the $6a_{1g}$ orbital to higher energy while energy changes in all other orbitals are comparatively much smaller.[1] It seems reasonable to assign band III as the $\sigma(6a_{1g}) \rightarrow \sigma^*(5a_{2u})$ transition which corresponds to the N → V transition[16] of the Rh–Rh σ bond. Band IV may be the $\sigma(4a_{2u}) \rightarrow \sigma^*(7a_{1g})$ transition. The $\sigma(4a_{2u})$ orbital is composed mainly of π_{vo}, the molecular orbital containing the out-of-plane oxygen 2p orbitals, and its energy should be less sensitive to terminal ligands. The $\sigma(6a_{1g})$ orbital is predominantly $4d_{z^2}$ in character.

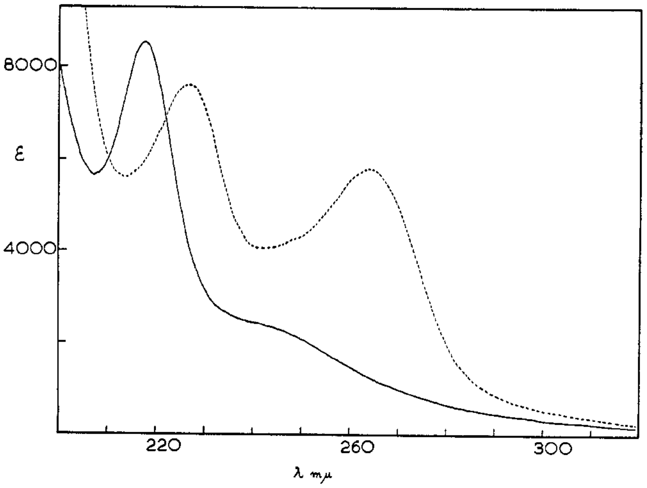

Figure 5.—The ultraviolet spectrum of Rh(II) acetate monohydrate (full line) and its ammonia adduct (dotted line), in water.[15] [The extinction coefficient ε is the "molar" extinction coefficient per monomer.]

The limitations of semiempirical MO calculations are well known and the present interpretation rests primarily on the marked sensitivity of band I to axial substitution (and the consistent pattern of spectrochemical behavior observed) rather than on any unshaken belief in the numbers which emerge from the SCCC–MO* calculation. However, the comparison between the MO diagrams of Figures 3 and 4 reveals, at least qualitatively, that if the axial interaction is large enough, then the σ orbitals ($5a_{2u}$ and $7a_{1g}$) can be sufficiently perturbed so that they can eventually lie higher in energy than the π^* and δ^* orbitals resulting from Rh–Rh bonding.

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(14) The notation $\delta\sigma^*$ means that the $5b_{1g}$ orbital is antibonding with respect to the σ interaction of the metal $d_{x^2-y^2}$ orbital with the in-plane σ oxygen orbitals and bonding with respect to the (δ) Rh–Rh bonding.

(15) The addition of a small excess of ammonia results in a rapid change of the spectrum of the hydrated complex to the spectrum shown in Figure 5. This spectrum (dotted line) then changes more slowly. The first reaction probably involves terminal substitution which is followed by a slower reaction in which the binuclear structure is destroyed. This feature has also been observed by Johnson, *et al.*[3]

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