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Resonance Raman Spectroscopy of the One-Electron-Oxidized Analogues of the Dirhodium Complexes $\text{Rh}_2(\text{bridge})_4 \cdot 2\text{L}$: Bridge = Acetate, Acetamidate, or Trifluoroacetamidate; L = Triphenylphosphine or Triphenylarsine. Relationship between the Rhodium–Rhodium Stretching Frequency and Bond Order

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Study of the resonance Raman spectra of dichloromethane solutions of $\text{Rh}_2(\text{bridge})_4 \cdot 2\text{L}$, where bridge = acetate, acetamidate, or trifluoroacetamidate and L = PPh_3 or AsPh_3 , and of electrochemically generated solutions of the analogous one-electron-oxidized complex ions has led to the identification of the ν_{RhRh} mode in each case. The resonance Raman spectra of the neutral complexes using $\sim 350\text{-nm}$ excitation are similar for both solutions in dichloromethane and solids dispersed in KBr, with the spectra being dominated by bands attributed to ν_{RhRh} and $\nu_{\text{Rh-bridge}}$ modes and by overtone and combination bands thereof. These spectra are in turn remarkably similar to those obtained by using $\sim 450\text{-nm}$ excitation for their one-electron-oxidized analogues. These observations suggest that the electronic transitions of the neutral complexes at 300–350 nm alter the bond strengths in a way similar to that brought about by the transitions at 440–490 nm of their one-electron-oxidized analogues. Where the bridge = acetamidate and L = PPh_3 , the wavenumber of ν_{RhRh} for the cation (264 cm^{-1}) is less than that of the neutral complex (275 cm^{-1}), whereas for the other complexes studied the reverse is the case. These results, together with the evidence from available crystal structures, suggest that the HOMO is the $\delta^*(\text{RhRh})$ orbital in each case; thus for $\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{PPh}_3$, the increase in RhRh bond order from 1.0 to 1.5 on oxidation is accompanied, surprisingly, by a decrease in the wavenumber of ν_{RhRh} . This apparent anomaly is explained in terms of enhanced σ donation by the axial ligand into RhRh σ^* orbitals on oxidation rather than a different ordering of the RhRh molecular orbitals.

Studies of metal–metal-bonded complexes have shown that, while it is possible to assign bond orders for particular metal–metal bonds, the relationship between bond order and bond strength is difficult to quantify.¹ It is clear that, in cases where metal–metal bonding is weak, the metal–metal bond distance and metal–metal stretching frequency can each vary over a wide range, since metal–metal bonding may be perturbed by both σ and π interactions with the other ligands in the complex. In order to develop an understanding of metal–metal bonding and metal–ligand interactions, we have undertaken a study of dirhodium tetrabridged complexes and of their one-electron-oxidized analogues.

The complexes $\text{Rh}_2(\text{acetate})_4 \cdot 2\text{L}$ have been well characterized by both spectroscopic and structural techniques.^{2–4} There are 14 electrons to be placed in the metal–metal molecular orbitals giving, solely on the basis of metal–metal interaction, the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4$ electron configuration with a net RhRh bond order of 1. However, the ordering and composition of the metal–metal bonding orbitals may be appreciably different from one complex to another, as a result of σ and π interactions with the axial ligands. For example, unrestricted Hartree–Fock (UHF) calculations⁵ for $\text{Rh}_2(\text{formate})_4 \cdot 2\text{L}$ indicate that the highest occupied molecular orbital (HOMO) is $\text{RhRh } \delta^*$ where L is absent but is $\text{RhRh } \sigma$ where L = PH_3 or H_2O . SCF– $X\alpha$ –SW calculations give similar results,⁶ although the calculated destabilization of the $\text{RhRh } \sigma$ orbital is insufficient for it to become the HOMO. Thus for the one-electron-oxidized complexes the singly occupied (SO) MO may be either σ or δ depending on the nature of L. The ESR spectra of dirhodium tetrabridged complexes with axial ligands with phosphorus donor atoms have been interpreted to mean that the SOMO has σ symmetry,⁷ in agreement with the UHF calculations. However the crystal structure of $[\text{Rh}_2(\text{acetate})_4 \cdot 2\text{OH}_2]^+$ reveals that the Rh–Rh as well as the Rh– OH_2 bond lengths are shorter than in the analogous neutral complex,⁸ an

observation more in keeping with predominantly $\text{RhRh } \delta^*$ rather than σ character for the HOMO.

The present study is concerned with a series of dirhodium tetrabridged complexes involving axial ligands with group 15 donor atoms and also with their one-electron-oxidized analogues, the objective being to investigate the identity of the HOMO in each case. A preliminary report of this work has previously been published.⁹ In addition it has been shown that changes to the bridging groups influence both the strength of the metal–metal bond as well as the redox properties of the neutral complexes.¹⁰ For example, as a result of changing the bridge from acetate to acetamidate, the oxidation potential of the complex is reduced by ca. 0.6 V, the RhRh bond lengthens by ca. 0.04 Å, and the wavenumber of the RhRh stretch, ν_{RhRh} , decreases by ca. 15 cm^{-1} . Alternatively, if trifluoroacetamidate is the bridge, the complexes have the same redox properties as the acetates, but the same RhRh bond lengths and ν_{RhRh} values as the acetamidates.¹⁰ The influence of the bridging ligand on the RhRh bond strength, bond length, and redox properties has been interpreted in terms of the metal–bridge σ and π interactions. Since for a metal-based oxidation the metal-based orbitals will be lowered in energy relative to that of the ligand orbitals, the metal–ligand σ and π interactions will be different in the neutral and one-electron-oxidized dirhodium complexes. This will lead to differences in the RhRh bond strengths, which have to be considered in addition to those that result from the removal of an electron from the HOMO. For the dirhodium complexes under study these effects will be shown to be of similar magnitude.

Experimental Section

The neutral complexes were prepared by the dropwise addition of a concentrated methanolic solution of the axial ligand to a methanolic solution of $[\text{Rh}_2(\text{acetate})_4]$,¹¹ $[\text{Rh}_2(\text{acetamidate})_4]$,¹² or $[\text{Rh}_2(\text{trifluoroacetamidate})_4]$.¹³ Since the acetamidates were prepared from the corresponding acetates by a melt reaction, the purity of these products was

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Table I. Band Wavenumbers and Assignments of the Raman Spectra of $\text{Rh}_2(\text{bridge})_4\cdot 2\text{L}$ in CH_2Cl_2^a

		bridge, L			
acetate, PPh_3	trifluoroacetamidate, PPh_3	acetamidate, PPh_3	acetamidate, AsPh_3	acetamidate, SbPh_3	assignt
156 m	150 m				
172 m					
252 w		253 w	179 w	186 w	
		265 sh		225 w	
288 s ^b	277 s	275 sh ^b	283 s	275 m	t X-sens SbPh_3^c
	308 w			297 s	ν_{RhRh}
	327 w				
336 m	258 w	345 m	347 m	351 m	$\nu_{\text{Rh-bridge}}$
		426 m			
518 w	523 m	512 m			X-sens PPh_3^c
	559 sh	530 m			
576 m	553 m	550 m	566 m	566 w	ν_{RhRh} + t X-sens SbPh_3
625 w	570 w	619 m	630 m	584 w	$2\nu_{\text{RhRh}}$
	798 w			641 w	ν_{RhRh} + $\nu_{\text{Rh-bridge}}$
	827 w		849 w	658 w	$3\nu_{\text{RhRh}}$

^as = strong, m = medium, w = weak, and sh = shoulder. ^bObscured by a strong solvent band. ^cNomenclature as per ref 4 and: Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350.

checked by NMR spectroscopy and ac and cyclic voltammetry in order to verify that the acetamidate-for-acetate substitution had been driven to completion. Electrochemical experiments were carried out with a Metrohm E506 potentiostat and Metrohm E612VA scanner. Platinum wires were used as working and counter electrodes in conjunction with a Ag/AgCl reference electrode (Metrohm EA441/5), which was calibrated with respect to the ferrocene/ferrocenium couple. For reasons of solubility, dichloromethane (distilled under N_2 from P_2O_5) was used as solvent and tetrabutylammonium tetrafluoroborate as the supporting electrolyte.

Raman spectra were recorded on a Spex 14018/R6 spectrometer, the exciting line being provided by a Coherent Model I 70-4 or I 3000 K laser. Solutions of the one-electron-oxidized complexes were prepared in a purpose-built bulk-electrolysis cell, which is shown in Figure 1. This permits the transfer of the solution to a Raman or UV-visible cell via an all-glass path, which can be subjected to vacuum or an inert gas (N_2). The solution was cooled to 80 K and evacuated, and the Raman cell was flamed off. In each case a potential more positive than the half-wave potential (by at least 0.2 V) was applied to generate the desired product. The identity of the oxidized product was confirmed by electronic spectroscopy in the UV-visible region.

Results and Discussion

Solution Raman spectra of the neutral complexes were recorded in dichloromethane in the region $100\text{--}900\text{ cm}^{-1}$ so as to include bands attributable to ν_{RhRh} , rhodium-bridge stretching modes ($\nu_{\text{Rh-bridge}}$), and combinations thereof. The spectra of $\text{Rh}_2(\text{acetamidate})_4\cdot 2\text{AsPh}_3$ in dichloromethane are shown in Figure 2a. For this complex, the spectra are dominated by a band at 283 cm^{-1} , which is accompanied by three overtones. A band at 347 cm^{-1} is also prominent in the spectrum; this occurs in combination with the 283-cm^{-1} band. The solution spectra are similar to that of the complex in the solid state (Figure 2b), and accordingly the 283- and 347-cm^{-1} bands are assigned to the ν_{RhRh} and $\nu_{\text{Rh-bridge}}$ modes, respectively.¹⁰ The assignment of the spectra of the $\text{Rh}_2(\text{trifluoroacetamidate})_4\cdot 2\text{PPh}_3$ complex is similarly straightforward. For the acetate- and acetamidate-bridged triphenylphosphine complexes, the spectra were of poorer quality owing to the combination of lower solubility and the poorer enhancement of the spectra (the electronic band maxima are further into the UV region than is accessible with the available laser lines). In particular, a solvent band at 287 cm^{-1} obscures the ν_{RhRh} band. In these cases the observation of bands arising from $2\nu_{\text{RhRh}}$ and $\nu_{\text{RhRh}} + \nu_{\text{Rh-bridge}}$ has enabled an estimate of the wavenumber of the ν_{RhRh} mode to be made. The wavenumbers and assignments of the bands in the solution Raman spectra of the neutral complexes are given in Table I.

The properties of the complexes under study are given in Table II. Whether or not a complex is suitable for study in the oxidized

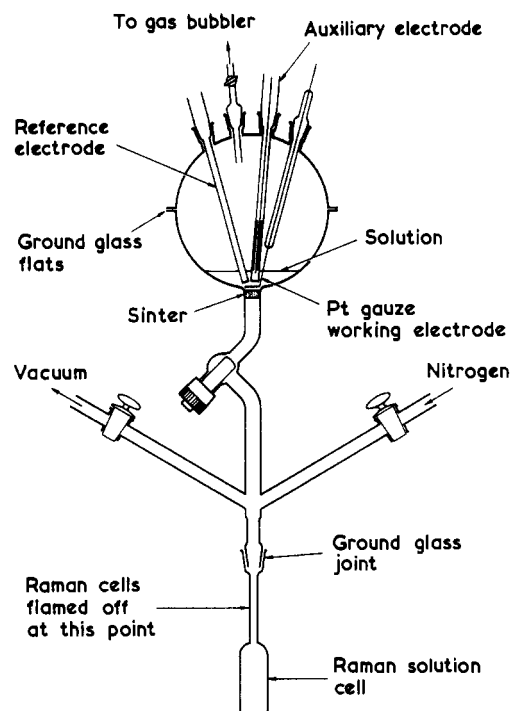


Figure 1. Bulk-electrosynthesis cell adapted for use with Raman and UV-visible cells.

form depends on its half-wave potential for oxidation compared to that of the uncoordinated axial ligand. Thus, for the acetates and trifluoroacetamidates, only the PPh_3 adducts can be studied in the oxidized form whereas, for the acetamidates, both the PPh_3 and AsPh_3 adducts are suitable. When the neutral complexes are oxidized in dichloromethane, the solution develops a deep brown color associated with a moderately intense absorption band ($\epsilon \approx 1000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) in the $400\text{--}600\text{-nm}$ region. Excitation into this absorption band gives resonance-enhanced Raman spectra that are dominated in the $250\text{--}400\text{-cm}^{-1}$ region by bands that are similar in form to those observed in the resonance Raman spectra of the parent neutral complexes obtained with near-UV excitation (Figure 3). Since the resonance Raman spectra of the neutral complexes are known to be dominated by bands due to ν_{RhRh} and $\nu_{\text{Rh-bridge}}$, the similarity of these spectra to those of the one-electron-oxidized analogues suggests that the spectra of the latter are likewise dominated by bands arising from the above skeletal modes.

Table II. Selected Properties of the Rh₂(bridge)₄·2L Complexes and Their One-Electron-Oxidized Analogues

complex	color in CH ₂ Cl ₂	$E_{1/2}/V^a$	$\nu_{\text{RhRh}}/\text{cm}^{-1}$	$\nu_{\text{Rh-bridge}}/\text{cm}^{-1}$
Rh ₂ (CH ₃ CO ₂) ₄ ·2PPh ₃	brown	+0.14	288 ^b	336
[Rh ₂ (CH ₃ CO ₂) ₄ ·2PPh ₃] ⁺	burgundy		302	346
[Rh ₂ (CD ₃ CO ₂) ₄ ·2PPh ₃] ⁺	burgundy		? ^c	334
Rh ₂ (CH ₃ CONH) ₄ ·2PPh ₃	light brown	-0.20	275 ^b	345
[Rh ₂ (CH ₃ CONH) ₄ ·2PPh ₃] ⁺	dark brown		264	318, 352
Rh ₂ (CH ₃ CONH) ₄ ·2AsPh ₃	orange	-0.09	283	347
[Rh ₂ (CH ₃ CONH) ₄ ·2AsPh ₃] ⁺	red-brown		292	366
Rh ₂ (CH ₃ CONH) ₄ ·2SbPh ₃	maroon	-0.05	297	351
[Rh ₂ (CH ₃ CONH) ₄ ·2SbPh ₃] ⁺	red-brown			
Rh ₂ (CF ₃ CONH) ₄ ·2PPh ₃	orange	+0.34	277	258
[Rh ₂ (CF ₃ CONH) ₄ ·2PPh ₃] ⁺	deep red		297	280

^a Vs Fc⁺/Fc. ^bThe ν_{RhRh} band was obscured by the 287-cm⁻¹ solvent band. The wavenumber of the ν_{RhRh} band was estimated from the wavenumbers of the bands arising from its overtones. ^cThe ν_{RhRh} band is obscured by a solvent band.

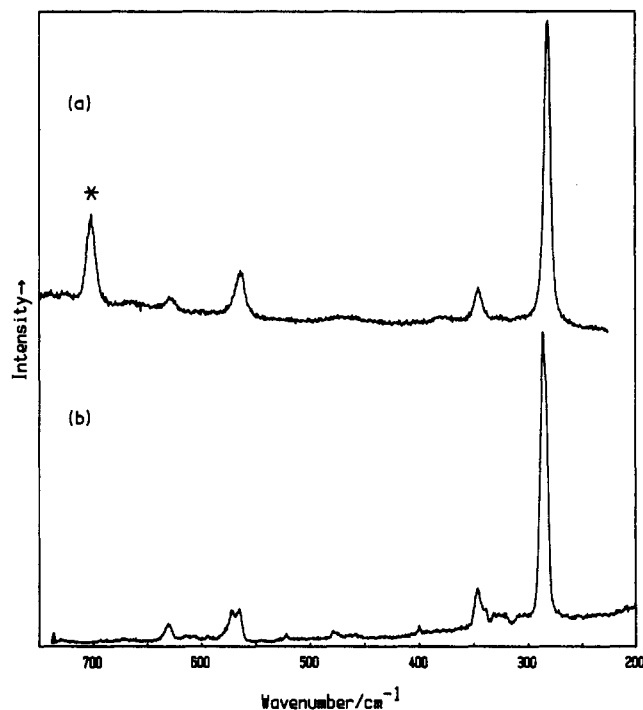


Figure 2. Raman spectra of Rh₂(acetamidate)₄·2AsPh₃ in (a) dichloromethane and (b) potassium bromide as a pressed disk at 80 K (15–25-mW, 356.4-nm radiation at the sample; spectral band-pass 3.9 cm⁻¹). Asterisk denotes a band attributable to solvent.

This suggestion is supported by arguments given below.

The resonance Raman spectra of the one-electron-oxidized adducts of Rh₂(bridge)₄·2L are given in Figure 4. For example, oxidation of a pale brown solution of Rh₂(acetate)₄·2PPh₃ in dichloromethane leads to the generation of a burgundy-colored solution. Once the solution is oxidized quantitatively, it may be transferred, under nitrogen, to a Raman solution cell and sealed in vacuo. Excitation of this solution with 488.0-nm excitation leads to rapid bleaching; however, use of 514.5-nm excitation significantly reduces the rate of decomposition, e.g. to ca. 20% in 15 min. Sufficiently good spectra to define clearly the wavenumber and relative intensities of the 287- (solvent), 302-, and 346-cm⁻¹ bands were obtained in 15-min scans. As the sample decomposes, the bands due to the oxidized complex decrease in intensity and the solvent peaks begin to dominate the spectrum; no additional bands develop in the spectra of the bleached solutions.

The assignment of $\nu_{\text{Rh-bridge}}$ is confirmed by the shift of the band at 346 cm⁻¹ in the spectrum of [Rh₂(acetate)₄·2PPh₃]⁺ to 334 cm⁻¹ on deuteration of the bridge. The corresponding shift of $\nu_{\text{Rh-bridge}}$ for the neutral complexes is 13 cm⁻¹.⁴ For the analogous acetamidate complexes, the sensitivity of the bands due to $\nu_{\text{Rh-bridge}}$ modes to oxidation of the neutral complexes is similar to that of Rh₂(acetate)₄·2PPh₃. For Rh₂(trifluoroacetamidate)₄·2PPh₃, the bands at 258 and 280 cm⁻¹ are tentatively assigned to $\nu_{\text{Rh-bridge}}$ for the neutral and one-electron-oxidized species, respectively. This

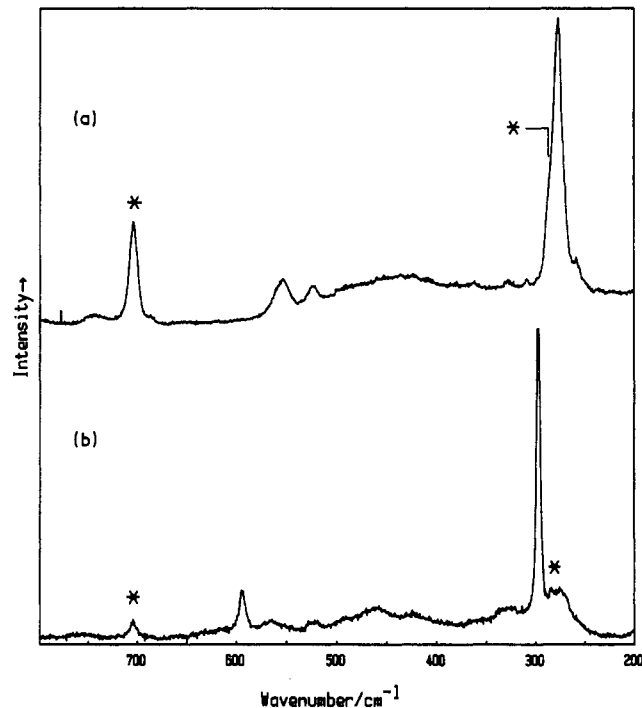


Figure 3. Raman spectra of solutions of (a) Rh₂(trifluoroacetamidate)₄·2PPh₃ and (b) its one-electron-oxidized adduct: (a) 25-mW, 356.4-nm radiation, spectral band-pass 3.9 cm⁻¹; (b) 15-mW, 457.9-nm radiation, spectral band-pass 3.2 cm⁻¹. Asterisk denotes a band attributable to solvent.

assignment is supported by the observation of a weak band at ca. 570 cm⁻¹ in the spectrum of the oxidized complex (Figure 3b), which is assigned to the combination mode $\nu_{\text{RhRh}} + \nu_{\text{Rh-bridge}}$. The assignment of the band due to ν_{RhRh} in each case follows from the comparative insensitivity of its wavenumber to the identity of the bridge. Furthermore, the enhanced intensity of bands arising from particular modes, and the appearance of overtone and combination bands involving these modes, is similar in each of the spectra, observations that strengthen the proposed assignments.

On oxidation of the neutral complexes there is an increase in $\nu_{\text{Rh-bridge}}$ and, in three cases, an increase (of 9–20 cm⁻¹) in ν_{RhRh} . For the complex Rh₂(acetamidate)₄·2PPh₃, on the other hand, there is an 11-cm⁻¹ reduction in ν_{RhRh} . This change in the direction of the band shift might be thought to be explained most simply in terms of the metal–metal bonding/antibonding character of the HOMO. Such an explanation would be made plausible by the destabilization of the RhRh σ -bonding orbital by its antibonding Rh–L character. Therefore the greatest destabilization of the RhRh σ -bonding orbital occurs for the strongest σ donors, i.e. PPh₃ > AsPh₃ > SbPh₃. In addition, the Rh–L bond lengths depend on the identity of the bridging group. When L = AsPh₃ or SbPh₃, the Rh–L bond length is shorter for the acetamidate than for the acetate-bridged complex (although the converse is true when L = H₂O).¹⁰ For the trifluoroacetamidates, pyridine

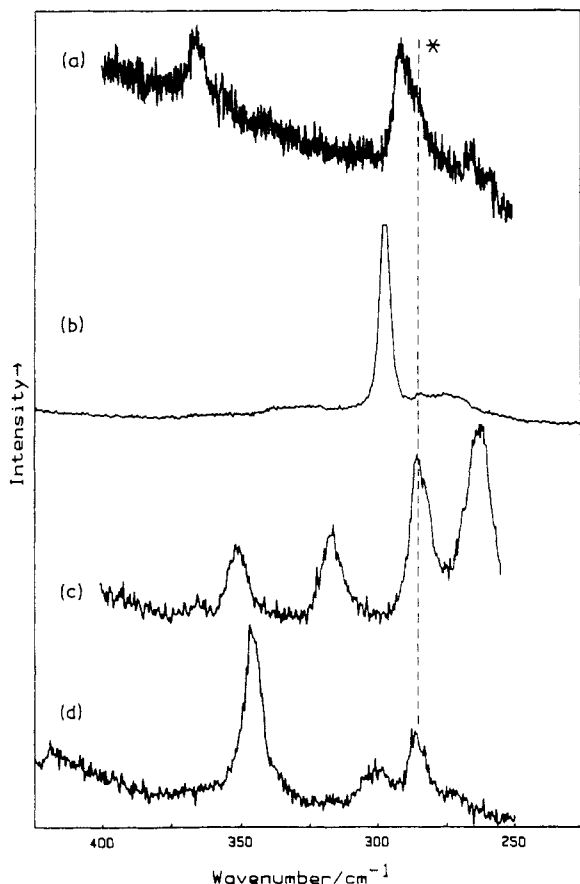


Figure 4. Raman spectra of solutions of (a) $[\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{AsPh}_3]^+$, at $\lambda_{\text{excit}} = 457.9$ nm, (b) $[\text{Rh}_2(\text{trifluoroacetamidate})_4 \cdot 2\text{PPh}_3]^+$, at $\lambda_{\text{excit}} = 457.9$ nm, (c) $[\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{PPh}_3]^+$, at $\lambda_{\text{excit}} = 457.9$ nm, and (d) $[\text{Rh}_2(\text{acetate})_4 \cdot 2\text{PPh}_3]^+$, at $\lambda_{\text{excit}} = 514.5$ nm (slits 200 μm , power at the sample ca. 15 mW, scan speed 0.5 cm s^{-1} , integration time 0.8 s). Asterisk denotes a band attributable to solvent.

is the only axial ligand having a group 15 donor atom for which there are structural data. In this case the Rh–pyridine bond length is shorter for the acetate- than for the trifluoroacetamidate-bridged complex.¹⁰ Thus the order of the Rh–L bond lengths (for group 15 donor atoms) for different bridging groups is acetamidate < acetate < trifluoroacetamidate. Since the strength of the Rh–L σ interaction will be related to the Rh–L bond length, then, for a given L, the Rh–L σ interaction will be greatest for the acetamidates and least for the trifluoroacetamidates. Thus destabilization of the RhRh σ -bonding orbital will follow the same order. Since it is the complex $[\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{PPh}_3]^+$ that is anomalous in terms of the direction of the ν_{RhRh} band shift and since, from the above arguments, this complex is expected to have the most destabilized RhRh σ -bonding orbital, the direction of the shifts argues for the RhRh σ -bonding orbital being the SOMO for $[\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{PPh}_3]^+$ and the RhRh δ^* orbital being the SOMO for the other complexes. *Despite the logic of the above arguments, the magnitude of the shift of ν_{RhRh} on oxidation is inconsistent with the foregoing explanation, since the effect of removal of an electron from a RhRh σ -bonding orbital must be substantially greater than that arising from the removal of an electron from a RhRh δ^* orbital.* Thus an alternative explanation is required. It is proposed that the SOMO is the same for all the complexes and is the RhRh δ^* orbital but that the direction of RhRh bond strength change on oxidation is not determined solely by the metal–metal bonding/antibonding nature of the SOMO.

As a result of oxidation of the complex, there is a change in the composition of the molecular orbitals. A simple LCAO–MO description of this system is as follows: for an oxidation largely localized on the dimetal entity, the metal AO's are lowered in energy relative to the ligand AO's. Thus the relative contributions of the metal and ligand AO's in the MO's of the one-electron-

oxidized complex will differ from those of the parent. When the ligand AO's lie lower in energy than the metal AO's in the neutral complex, an increase in interaction is likely to occur on oxidation of the complex, whereas the converse is expected when the ligand AO's lie higher in energy than the metal AO's. Insofar as interaction with the axial ligand is concerned, the ligand σ -donating orbital lies lower in energy than the relevant metal AO and therefore greater σ donation by the axial ligand to the dirhodium entity is expected on oxidation. The effect of this enhanced σ donation is to strengthen the Rh–L bond and weaken the Rh–Rh bond. Thus the greater propensity for σ donation by the axial ligand in the oxidized form of the complex counteracts the strengthening of the Rh–Rh bond on account of the removal of electron density from a RhRh δ^* orbital.

It is clear that both overlap and orbital energies are important in determining the magnitude of $\text{L} \rightarrow \text{Rh}$ σ donation since, for the neutral complexes $\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{L}$, ν_{RhRh} increases from 275 to 283 to 297 cm^{-1} as $\text{L} = \text{PPh}_3$, AsPh_3 , and SbPh_3 , respectively. This indicates that PPh_3 is a better σ donor than AsPh_3 , which in turn is better than SbPh_3 , i.e. in order of orbital overlap not orbital energies. For the one-electron-oxidized analogues, ν_{RhRh} shows a greater sensitivity to the σ -donating capacity of the axial ligand. For the acetamidates as L is changed from PPh_3 to AsPh_3 , ν_{RhRh} is lowered by 28 cm^{-1} ; for the neutral complexes the corresponding difference is only 8 cm^{-1} . Indeed, the increased sensitivity of ν_{RhRh} to $\text{L} \rightarrow \text{Rh}$ σ donation among the one-electron-oxidized complexes compared to the analogous neutral complexes may account for the variation of the shifts of ν_{RhRh} on oxidation. For $\text{Rh}_2(\text{bridge})_4 \cdot 2\text{PPh}_3$ the shift of ν_{RhRh} on oxidation is -11 , 14 , and 20 cm^{-1} , respectively, as the bridge is changed from acetamidate to acetate to trifluoroacetamidate. This ordering follows that found for the Rh–L bond lengths on changing the bridging group. Thus when acetamidate is the bridge and the Rh–L bond length is shortest, the Rh–Rh bond is most weakened on oxidation. In this case the increased $\text{L} \rightarrow \text{Rh}$ σ donation weakens the Rh–Rh bond more than the removal of an electron from a RhRh δ^* orbital strengthens it. This situation contrasts with that which occurs when trifluoroacetamidate is the bridge and the Rh–L bond length is expected to be longest (see above), in which case ν_{RhRh} increases by 20 cm^{-1} on oxidation.

We turn now to the crystal structures of oxidized dirhodium tetrabridged complexes. The structure of $[\text{Rh}_2(\text{acetamidate})_4 \cdot 2\text{C}_7\text{H}_8\text{N}_4\text{O}_2](\text{NO}_3) \cdot \text{H}_2\text{O}$ has been determined by X-ray techniques.¹⁴ The axial ligand, theophylline, incorporates a heterocyclic nitrogen-donor atom, which is coordinated to each rhodium atom. The Rh–Rh bond distance is 2.426 (1) Å, this being 0.011 Å shorter than the Rh–Rh distance in $\text{Rh}_2(\text{PhCONH})_4 \cdot 2\text{py}$.¹⁵ While the comparison between the neutral and oxidized complexes is complicated by there being different bridging and axial ligands, there is the strong suggestion that the Rh–Rh bond length decreases on oxidation of the complex. Stronger evidence for this trend is available from the structures of $\text{Rh}_2(\text{acetate})_4 \cdot 2\text{OH}_2$ and its one-electron-oxidized adduct. Oxidation of the neutral complex leads to a reduction of both the Rh–Rh and Rh–OH₂ bond lengths, i.e. from 2.386 and 2.310 Å to 2.316 and 2.222 Å, respectively.^{8,16} This combination of bond length changes would suggest that the HOMO is RhRh π^* or δ^* . In terms of the present interpretation, the increased $\text{L} \rightarrow \text{Rh}$ σ donation in the oxidized complex is insufficient to override the RhRh bonding character of the HOMO. This behavior is in keeping with the poor σ -donating character of water as a ligand. The interpretation of the results presented in this study is at variance with that given on the basis of ESR spectroscopy of the closely related complex $[\text{Rh}_2(\text{propionate})_4 \cdot 2\text{PPh}_3]^+$.⁷ However, it is worthwhile to note that the interpretation of the ESR spectra rules out the assignment of the RhRh π^* orbital as the SOMO but does not so clearly distinguish

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between the RhRh σ and δ^* orbitals as the SOMO. Consideration of the bond length changes that occur on oxidation, for the structures so far determined, supports the ordering of MO's outlined in this work.

Conclusion

The study of redox-related complexes that contain metal–metal

bonds provides some insight into the subtleties of the bonding. This is particularly the case when the metal–metal bonding is weak and where the other perturbations to the bonding can lead to experimentally observable changes in the system. For the dirhodium complexes the metal–metal δ bonding is weak, and its effects can be nullified by changes in the σ and π interactions between the metal and the other ligands in the complex.

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Magnetism and Electronic Structure of a Series of Encapsulated First-Row Transition Metals

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The temperature dependence of the magnetic susceptibility (4.2–300 K) is reported for a series of crystalline salts of first-row transition-metal ions encapsulated by hexamine ligands of the sar type, namely, $[M(\text{sar})]^{n+}$, where sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane, or $[M((X,Y)\text{sar})]^{n+}$, where X = Y = 1,8-NH₂ 1,8-NH₃⁺ or X = 1-CH₃, Y = 8-H. The cage complexes of Fe^{III}, Co^{III}, and Ni^{III} all exhibit low-spin ground states [of ²T_{2g} and ¹A_{1g} (*O_h*) and ²A_{1g} (*D_{4h}*) origin] whereas that of Mn^{III} is high-spin [³A_{1g} or ⁵B_{1g} (*D_{4h}*)]. The complexes of Mn^{II}, Co^{II}, and Ni^{II} are high-spin [of ⁶A_{1g}, ⁴T_{1g}, and ³A_{2g} (*O_h*) origin], but surprisingly, those of Fe^{II} exhibit either a low-spin (¹A_{1g}) or a high-spin (⁵T_{2g}) ground state depending on the nature of the apical substituent and the lattice. Clearly, the magnitude of the ligand field parameters (10Dq and B)¹ generated by these saturated macrobicycles for the 3d⁶ Fe^{II} is that required for the high-spin/low-spin crossover for six saturated amine ligands. The ground states for V^{IV} (²T_{2g}), V^{III} (³T_{1g}), Cr^{III} (⁴A_{2g}), Cu^{II} (²B_{1g} in *D_{4h}*), and Zn^{II} (¹A_{1g}) appear to be unambiguous. The magnitude of the zero-field-splitting parameter has been estimated from the low-temperature $\chi(T)$ data for the Cr^{III} and high-spin Mn^{III}, Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} cage complexes. The low-spin (²E_g origin) state for Co^{II} is stabilized by the (aza)captan ligand because of the larger nephelauxetic effect of sulfur combined with appreciable Jahn–Teller splitting of the ²E_g ground state. The magnetic properties in general reflect the reduction in symmetry observed crystallographically for the individual metal ions.

Introduction

The synthesis² of an extended series of hexadentate ligands of the macrobicyclic type based on saturated nitrogen donor atoms enables the properties of their transition-metal complexes to be studied in a common environment. The macrobicyclic cage can be synthesized by capping $[\text{Co}(\text{en})_3]^{3+}$ (en = ethane-1,2-diamine) along the C₃ axis to yield the cobalt(III) cage cation shown in Figure 1a. The free ligand can be isolated in good yield by treatment of the cobalt(II) cage with either HBr or KCN,³ thereby enabling a range of encapsulated transition-metal ions to be synthesized.⁴ Encapsulation results in transition-metal complexes that are mononuclear and kinetically inert to dissociation of the metal ion and offers the prospect of stabilizing unusual oxidation states of the metal atom.^{4,5}

Single-crystal X-ray structural studies⁶ of a number of the transition metal cages have established that all six secondary N atoms are bound to the metal ion and the molecular structure of the MN₆ core varies considerably with the electronic configuration and spin state of the central metal.⁴ Competition between the preferred metal stereochemistry and the geometrical demands of the ligand appears to determine the overall geometry, resulting in complexes that range from near-octahedral (e.g. Co^{III}) to near-trigonal-prismatic structures (e.g. V^{IV}).⁶ However, it is evident from the structural data that there are also small perturbations from the D₃ symmetry preferred by the ligand of tetragonal or rhombic origin, which may influence electronic structure and spectroscopic properties. Broadly, the metal cages fall into two groups that can be characterized crudely in terms of their trigonal twist angles, ϕ , about the C₃ axis (cf. Figure 1b): The first group (Mg^{II}, Cd^{II}, Hg^{II}, Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, Zn^{II}, Ag^{II})

has $\phi \sim 28^\circ$ with structures similar to that of the metal-free tetraprotonated ligand $[(\text{NH}_3)_2\text{sarH}_2]^{4+}$. For the second group, the trigonal twist angle, ϕ , lies between 46 and 60° and increases in the order Ni^{II} < Cr^{III} < Fe^{III} < Co^{III}.⁶ For the V^{IV} cage,^{6,7} ϕ equals 18° and the $[\text{Co}^{\text{II}}(\text{sep})]\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$ structure is a special case where the ligand cap deforms in an unusual way.

A study of the temperature dependence (4–300 K) of the magnetic susceptibility of a number of transition-metal cages has been undertaken to establish the electronic configuration of their ground states and compare their magnetic behavior with that of the closely related $[\text{M}(\text{NH}_3)_6]^{n+}$, $[\text{M}(\text{en})_3]^{n+}$, and $[\text{M}(\text{[9-aneN}_3)_2]^{n+}$ complexes ([9]aneN₃ = 1,4,7-triazacyclononane). Although structural studies indicate that distortions from ideal octahedral geometry occur for these compounds,⁶ for convenience, discussion of the magnetic data is given here in terms of ground states assumed to have their origin in octahedral MN₆ symmetry.

Experimental Section

Preparation of Complexes. All complexes were prepared either by published procedures^{2–4} or methods to be published shortly and analyzed just prior to the magnetic measurements to confirm analytical purity. The complex (ca. 20–30 mg) was finely ground with an agate mortar and pestle and packed tightly into a small gold bucket. The sample and

¹ 10Dq is used here to describe the ligand-field parameters although the symmetries are lower than octahedral; Δ is used for axial distortion. Octahedral parent (or tetragonal *D_{4h}*) symmetry notations are generally used for convenience. This is an approximation in view of the trigonal distortion preferred by the ligand⁶ and tetragonal distortions preferred by some of the metal ions.

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