Metal–Metal Bonding in Dirhodium Tetracarboxylates. Trans Influence and Dependence of the Rh–Rh Bond Distance upon the Nature of the Axial Ligands

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Abstract: The structures of metal–metal bonded dirhodium tetracarboxylate complexes, $Rh_2(OAc)_4X_2$, where X = py, $NHEt_2$, CO, $P(OPh)_3$, PF_3, and $P(OMe)_3$, have been determined by three-dimensional X-ray crystallography. The rhodium–rhodium distances are found to vary with the nature of X from 2.3963 (2) to 2.4555 (3) Å, the latter being the longest yet observed in such tetracarboxylate dirhodium complexes. The variation of M–M distance is rationalized on the basis of a qualitative trans-influence theory which considers σ and π interactions and their mutual dependence upon M–X bond distance. The Rh–Rh distances are much shorter than the 2.7 Å expected for a single Rh–Rh bond, a result easily explained if a triple Rh–Rh bond is assumed. The details of the spectra, inconsistent with a triple bond formulation, have been found to be easily explained by a single bond formulation originally proposed by Dubicki and Martin and more recently supported by the theoretical work of Norman and Kolari. Although a simple interpretation of our structural results appears to favor the triple bond assignment, a more careful consideration of the metal-bridging ligand interactions shows that the data are also consistent with a single Rh–Rh bond of extraordinary strength. The shortness and high strength of the Rh–Rh bond are judged to be due in part to the extensive mixing of metal and bridging ligand orbitals and in part to Rundle-type interactions that stabilize the axially stacked arrangement of formally nonbonded Ni(II), Pd(II), and Pt(II) d^8 complexes. As a consequence of the complicated orbital interactions, the comment is made that the formal bond order is not a particularly useful measure of the metal–metal interactions in these complexes.

Introduction

Strongly metal–metal bonded complexes have been the subject of much recent lively interest, particularly from the standpoint of the strength and multiplicity of the metal to metal bonds. Cotton and co-workers' elegant efforts[1] to unravel the nature of multiple M–M bonds, particularly in the d^4–d^4 (Re_2^{6+}, Tc_2^{6+}, Mo_2^{4+}, Cr_2^{4+}) and d^3–d^3 (Mo_2^{6+}, W_2^{6+}) systems, both with and without bridging ligands, have substantially extended the limits of what are considered "normal" bonds, and firmly established the δ bond as a permanent resident in the structural chemist's stable of bonding modes. At the same time, however, the results of this rapidly expanding area have raised a more fundamental, and consequently, troublesome, question of how to "best" or most properly describe the bonding in such complexes, where the usual concepts of formal bond order, bond strength, and oxidation number are no longer wholly adequate. We have chosen to attack this problem of the "proper" description of metal–metal bonds by further investigating the dirhodium tetracarboxylate system, in which the metal–metal bonding interaction has been described both as triple[2] and as single,[3] by different criteria. The basis of the former claim rested primarily upon interpretation of bond length data, while the latter assignment relied upon spectral results. Two simple molecular orbital energy level schemes that have been advanced are reproduced in Figure 1. The extra, effectively nonbonding σ_n' and σ_n'' orbitals in the triple bond scheme arise from the $5p_z$ orbitals on each metal center. The single bond scheme is what one expects if the 5p level is too high to interact with the 4d manifold (the $4d_{x^2-y^2}$ lobes are directed toward the oxygens of the bridging acetates). A solution ESR study of a 1:1 adduct of dirhodium tetra(trifluoroacetate) with a spin label has been reported[4] which is consistent with the single bond interpretation, and recent SCF-Xα-Sw calculations on dirhodium tetraformate and its dihydrate recommend the single bond formulation.[5] Although a main issue we would wish to help resolve in this study is the question of the metal–metal bond order (if that be the term we should really use to characterize the M–M bond), we also anticipate that by studying a system which consists of formally d^7 metal ions we would complement the extensive work by Cotton et al. on dimers of the d^3 and d^4 metal ions, and that integrated conclusions on the nature of metal–metal interactions might thereby have more general validity.

The dirhodium tetracarboxylate system also presents an excellent opportunity to examine the trans influence of a variety of ligands in a unique way: whereas previous studies of trans influence have relied upon examination of some property, such as M–X distance, infrared stretching frequency, or NMR coupling constant, for a specific trans ligand X in complexes XML_4Y or XML_2Y as the ligand Y is varied, with the dirhodium tetracarboxylates, which uniformly and reliably produce symmetrical axially substituted complexes of the formY–M–M–Y, it is possible to observe the *doubled* effect of the Y ligands upon the M–M linkage. Unlike the XML_4Y and XML_2Y systems, such complexes are synthetically easily accessible for a wide variety of axial ligands without the necessity of altering the nature of the equatorial ligands. Furthermore, the nature of the carboxylate bridging groups is such that they offer minimal steric hindrance to the axial ligands (ligand cone angles[6] at least as great at 180° can be accommodated), and these dimers are thus free from complications due to crowding of bulky ligands. This is a very desirable property; Steffen and Palenik have shown that even very slight changes in XML bond angles introduce significant changes in the M–X distance[7], of 10–50% of the magnitude of expected trans influence. Such effects hinder the interpretation of the trans influence parameters in even the best understood and most thoroughly investigated systems, such as square-planar Pt(II).

Cotton and co-workers[8] have very recently described their studies on a series of dichromium tetracarboxylates in which they found a general qualitative correlation of the Cr–Cr distance and the Cr–X distance to the axial ligands, all of which possessed either oxygen or nitrogen donors. Their interpretation of the results, which demonstrated the striking trans influence effects of the Cr$\equiv$Cr bond, was rendered substantially more difficult because a variety of different carboxylic acid ligands were used, and their cis effects on the Cr–Cr interaction could not be cleanly separated from those arising from the trans influence of the axial ligands. Although we are presently preparing complexes in which the nature of the bridging carbox-

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ylate ligand is systematically varied and the axial ligand X held constant, our present concern is with the trans influence effects of the axial ligands upon the metal-metal bond in the dirhodium tetraacetate system. We report here some results of our research, principally of the single-crystal X-ray structural studies of a number of symmetrical axially substituted dirhodium tetraacetates, and discuss these results in terms of qualitative trans influence theory that takes account of both σ and π interactive effects. A semiquantitative version of a unified trans influence theory is a goal of our current work.

Experimental Section

Full details of the individual syntheses, characterization, and X-ray structural analyses will be reported separately;[9] however, the similarity in procedure permits the following general description of the work. The green dirhodium tetraacetate dihydrate or dimethanolate were prepared by literature methods[10] or small variations thereof. Where necessary, the anhydrous dirhodium tetraacetate was prepared by vacuum dehydration immediately prior to direct reaction with the desired ligands. In most cases, however, it was possible to prepare the adducts simply by addition of stoichiometric amounts or slight excess of the appropriate base to toluene, dichloromethane, tetrahydrofuran, or alcohol solutions of the dirhodium tetraacetate. Yields were generally essentially quantitative. Spectra for known complexes were in good agreement with those published.[11] Chemical analyses, when performed, were of proper stoichiometry, and were confirmed by the X-ray structure analyses. The extreme lability of the axial ligands proved at once the most difficult synthetic obstacle and at the same time a good check on the syntheses of new adducts: quantitative reversible displacement reactions of the type

$$Rh_2(OAc)_4L_2 + \text{excess MeOH} \rightleftharpoons Rh_2(OAc)_4(MeOH)_2 + 2L$$

were displayed by all adducts.

Suitable crystals for X-ray diffraction analysis were obtained either by slow recrystallization from solution or in some cases directly from the reaction mixture. Preliminary cell constants and the space groups were determined by precession photography. Crystal densities were measured by flotation, and were uniformly in good agreement with those calculated using the number of formula units appropriate for the specific space group, taking into consideration that a space group symmetry element usually coincided with a molecular symmetry element. Cell constants determined from diffractometer setting angles for 12–15 accurately centered reflections are given with other pertinent crystal data in Table I. Data were collected by the ω–2θ scan method on an automated four-circle diffractometer using monochromatized Mo Kα radiation, at reduced temperature (e.g., −100 °C) for the less stable adducts, and reduced to F^2's by standard techniques. Data were collected in the range $4.0° \leq 2\theta \leq 60.0°$. Necessity of performing absorption corrections was determined by examination of ψ scans for a number of reflections for each crystal. When appropriate, the absorption coefficients were calculated using Gaussian integration with an 8 × 8 × 8 grid.[12] The heavy atom Patterson technique provided the solution to the structures, which were then refined by standard Fourier and least-squares procedures.[13] Hydrogen atom contributions were always included, and when possible, their parameters were also refined. All refinements were based upon F^2, with the function minimized

$$R_w = \sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4$$

where the weights were estimated using a standard form.[14] Final difference Fourier maps demonstrated that all significant electron density had been accounted for in each of the structures.

Results

The structures each consist of the familiar tetracarboxylate framework encapsulating octahedrally coordinated rhodium atoms (Figure 2). Table II summarizes the bonding parameters of particular interest: the rhodium-rhodium bond distance, the distance from the rhodium atom to the coordinating atom of the proximal axial ligand, Rh–X, and, for comparison, literature Rh–X distances for Rh(I) and Rh(III) complexes. The tetraacetate framework is essentially constant from structure to structure despite the differences in the constitution of the axial ligands and thus also in the molecular packing; for example, the O–C–O angles only range 125–126°, the Rh–O distances are all within the range 2.03–2.05 Å, and the internal Rh–Rh–O angles are all about 88°. The molecular packing in each structure is dominated by simple van der Waals contacts; although these sometimes introduce slight deviations from linearity of the Rh–Rh–X linkages, such deviations are by no means severe.

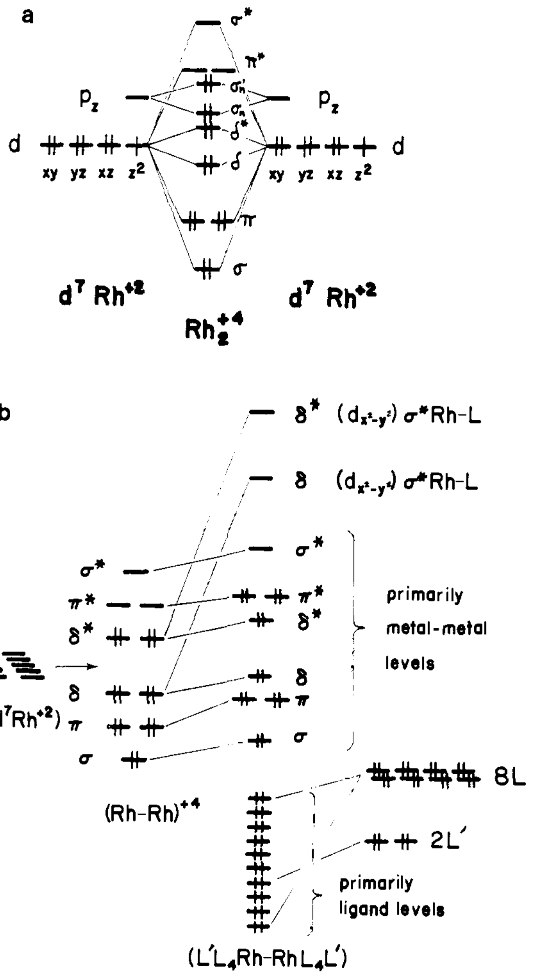


Figure 1. (a) Valence bond formulation of Rh–Rh d^7-d^7 triple bond. Each rhodium atom utilizes $d_{x^2-y^2}$, s, p_x, and p_y (dsp^2) for bonding to the equatorial oxygen donors, leaving d_{z^2}, p_z, $d_{xy}d_{yz}$, and d_{xz} for formation of the metal-metal only orbitals. The two p_z orbitals give rise to the nonbonding $p_{za} + p_{zb}$ and $p_{za} - p_{zb}$ combinations which are here occupied and embedded among the d levels. (b) Crystal field formulation of Rh–Rh d^7-d^7 single bond. The $d_{x^2-y^2}$ orbital lobes on each rhodium atom are directed toward the oxygen donors of the bridging carboxylates. These orbitals, which would otherwise form a second δ, δ^* pair degenerate with those arising from the d_{xy} orbitals, are moved to much higher energy and are identified as Rh–O σ^* antibonding orbitals.

Discussion

The rhodium-rhodium bond distances in these complexes range from 2.3855 to 2.455 Å, some 0.07 Å, but not in the usual order of increasing trans influence of the axial ligands. This is a surprisingly small effect, considering that the range of trans-influence ability from H_2O to $P(OMe)_3$ is quite substantial and that the presence of two axial ligands should yield double the trans influence. The axial ligands studied here span nearly the full range of strong σ to weak σ donor ability and from ligands of weak or no π-accepting ability (H_2O, $NHEt_2$) to what are generally considered very strong π acceptors, such as C≡O and PF_3.

Simple qualitative orbital pictures such as those given in Figures 3a–c have often[15] been used to rationalize observed

Table I. Crystal Data for Dirhodium Complexes $Rh_2(O_2CCH_3)_4X_2$

ligand X space group temp, °C	C≡O *Pbca* −104 (3)	py *C*2/*c* 20 (1)	$NHEt_2$ *Pbcn* 20 (1)	$P(OMe)_3$ *P*2$_1$/*c* 20 (1)	$P(OPh)_3$ *C*2/*c* 20 (1)	PF_3 *I*23 −109 (3)
a, Å	14.368 (8)	9.923 (3)	16.329 (4)	14.133 (3)	26.134 (9)	14.339 (2)
b, Å	12.151 (5)	17.009 (6)	8.011 (4)	15.799 (4)	9.951 (2)	14.339 (2)
c, Å	8.800 (3)	12.540 (3)	17.660 (6)	8.309 (2)	22.512 (7)	14.339 (2)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	90.0	83.40 (2)	90.0	138.65 (1)	61.45 (2)	90.0
δ, deg	90.0	90.0	90.0	90.0	90.0	90.0
V, Å^3	1536.4 (9)	2102 (1)	2310 (1)	1225.7 (5)	5143 (2)	2948.3 (7)
Z	4	4	4	2	4	6
mol wt	498.0	600.2	588.3	690.2	1062.6	617.9
ρ_{measd}	dec	1.85 (1)	1.60 (1)[b]	1.85 (1)	1.42 (1)	dec
ρ_{calcd}	2.153	1.896	i.691	1.877	1.372	2.087
μ, cm	21.4	15.8	14.3	15.1	7.5	18.8
no. of data[c]	2768	2987	3740	3557	7073	649
$R(F^2)$	0.045	0.031	0.068	0.035	0.12[a]	0.039[a]
$R_w(F^2)$	0.098	0.048	0.109	0.054		
COF	3.01	1.30	2.25	1.52		

[a] Refinement in progress. [b] Crystals partially dissolved. [c] Includes all data used in least squares.

Table II. Structural Parameters of Dirhodium and Monorhodium Complexes

X	pK_b	Rh–Rh, Å	Rh–X, Å	Rh(I)–X, Å	Rh(III)–X, Å
OH_2[a]	15.7[r]	2.3855 (5)	2.310 (3)		2.03 (1)[c]
py	8.6	2.3963 (2)	2.227 (3)	2.107 (8)[d]	2.06 (1)[e] 2.09 (2)[f] 2.12 (1)[g]
$NH(Et)_2$	2.9	2.403 (3)[b]	2.308 (3)[b]		2.07 (1)[h]
C≡O		2.4196 (4)	2.092 (4)	1.82 (2)[i]	1.89 (1)[j]
PF_3		2.430 (3)	2.42 (1)	2.155 (9)[t]	
$P(OPh)_3$		2.445 (1)[b]	2.418 (3)[b]	2.142 (3)[k]	
$P(Ph)_3$[l]	11.3[s]	2.449 (2)	2.479 (4)	2.290 (4)[m]	2.338 (4)[n] 2.378 (2)[o] 2.375 (5)[p]
$P(OMe)_3$	~10.5[s]	2.4555 (3)	2.437 (5)		2.199 (5)[q]

[a] Reference 2b. [b] Preliminary results: refinement in progress. [c] C. K. Thomas and J. A. Stanko, *J. Coord. Chem.*, **2**, 211–219 (1973); H_2O trans to H_2O. [d] R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, and G. Turner, *Inorg. Chem.*, **16**, 314–319 (1977); py trans to π-bound C≡C. [e] B. M. Gatehouse, B. E. Reichert, and B. O. West, *Acta Crystallogr., Sect. B*, **32**, 30–34 (1976); py trans to :NR_2 sp^2. [f] J. A. Evans, D. R. Russell, A. Bright, and B. L. Shaw, *Chem. Commun.*, 841–842 (1971); py trans to py. [g] R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601–1613 (1970); py trans to Cl. [h] A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969); for NH_3, average of chemically equivalent Rh–N bonds in $[Rh(NH_3)_5C_2H_5](Br)_2$. [i] R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2141–2145 (1972); C≡O trans to Cl. [j] P. B. Hitchcock, M. F. Lappert, G. M. McLaughlin, and A. J. Oliver, *J. Chem. Soc., Dalton Trans.*, 68–74 (1974); C≡O trans to sp^2 NR_2. [k] J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985–991 (1970); $P(OPh)_3$ trans to Cl. [l] J. Halpern and G. Khare, private communication. [m] M. J. Doyle, M. F. Lappert, G. M. McLaughlin, and J. McMeeking, *J. Chem. Soc., Dalton Trans.*, 1494–1501 (1974); PPh_3 trans to PPh_3. [n] K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440–447 (1970); PPh_3 trans to PPh_3. [o] M. Cowie and J. A. Ibers, *Inorg. Chem.*, **15**, 552–557 (1976); PPh_3 trans to PPh_3. [p] G. G. Christoph and E. B. Fleischer, unpublished work; PPh_3 trans to PPh_3. [q] F. H. Allen, G. Chang, K. K. Cheung, T. F. Lai, and L. M. Lee, *Chem. Commun.*, 1297–1298 (1970); $P(OMe)_3$ trans to Cl. [r] W. P. Jencks and J. Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778–1786 (1960). [s] T. Takayanagi, K. Yamamoto, and T. Kwan, *Bull. Chem. Soc. Jpn.*, **48**, 2618–2622 (1975). [t] P. B. Hitchcock, J. F. Nixon, and J. Sinclair, *Acta Crystallogr., Sect. B*, **33**, 179–181 (1977); PF_3 trans to H.

structural and spectroscopic trans influence data. These are extended to the binuclear, metal–metal bonded situation for the two cases of a metal–metal single bond interaction (filled π and π^* levels) (Figures 4a–c) and a multiple metal–metal bond involving both σ and π type overlaps (Figures 5a–d). As the trans influence depends upon both the σ and π interactions of a ligand with the metal,[16] we should expect to see, as depicted in these diagrams, somewhat different behavior of the system depending upon the order of the metal–metal bond, particularly upon the degree of π involvement of the metal d orbitals with the ligand orbitals. For example, Figure 4b suggests that a strong σ donor such as N should cause a weakening of the trans M–M σ bond by donation of electrons to the metal. In the weak σ-donor case, Figure 3a (or, for X = CO, Figure 3c), the M–M σ interaction should be enhanced and the M–M distance correspondingly shorter than in Figure 3b. Secondary effects, namely, expansion of metal d orbitals by the increased electron density on the metal (as in Figure 4b), or extraction of metal d-orbital electrons into the ligand π^* system (such as in Figure 4c) would only accentuate the respective lengthening or shortening of the metal–metal bond. Comparing the Rh–Rh distances in Table II for X = H_2O (pK_b = 15.7) and $NHEt_2$ (pK_b = 2.9) we see that this is indeed the case; the stronger σ donor does cause the trans M–M bond to weaken and lengthen. However, the Rh–Rh bond is seen to be much more sensitive to the weak σ donors X = CO and phosphine, and in the wrong direction to that predicted by this model.

If on the contrary we assume that the M–M bond is multiple, or rather, possesses π-type bonding components, then in addition to the competition between M(1) and the trans ligand X for the σ-bonding orbital density of M(2), we will also have competition for the π-bonding density, as shown in Figure 5. Differing σ-donor strengths of ligands X will, in the absence of π-accepting ability, yield the same qualitative prediction as before, that with increasing σ basicity of X the M–M bond

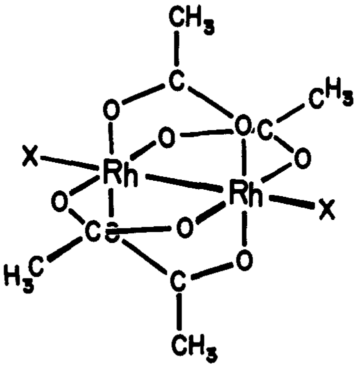


Figure 2. Geometry of dirhodium tetraacetate adducts.

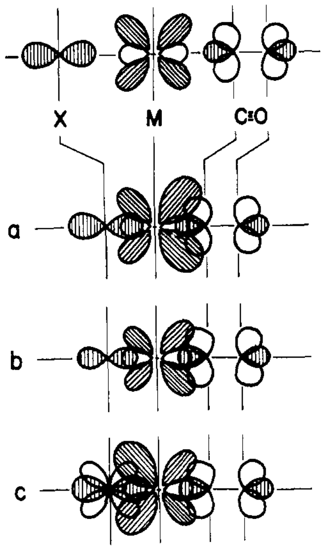


Figure 3. (Top) Representations of filled (hatched) and empty bonding orbitals of interest for a separated ligand X, a metal M, and a trans CO molecule. Donation from ligand X is assumed to be from a filled p orbital, from a filled sp orbital for CO, into an empty low-lying metal d_z orbital, while the filled metal d orbital can back-donate to empty ligand d or π^* levels. The internally bonding filled σ and π orbitals for CO have been omitted. The sizes of the orbitals are intended to qualitatively depict adjustments in the metal electron distribution due to changes in the nature of bound ligands. (a) X trans to CO: X a good σ donor, but poor π acceptor. The increased metal electron density is reflected in the expanded d-orbital lobes, which are polarized toward CO. (b) X trans to CO: X a poor σ donor, poor π acceptor. (c) X trans to CO: X a good σ donor, good π acceptor, which competes with CO for the metal d orbital density, weakening the M–CO bond relative to that in (a).

should weaken and lengthen. However, the amount of lengthening for the same X should be qualitatively smaller here than in the single M–M bond case because the M–M π interaction is here affected only by secondary, inductive effects of X and the weakening of the total M–M interaction is consequently, as a proportion, less.

If X is a strong π-accepting ligand, then it will compete with M(1) for the M(2) $d\pi$ orbital density and thereby weaken the M–M π interaction (Figure 5c). If the σ-donor ability of X is weak, however, as it is when X = CO, the M–M σ bond trans to it will be stabilized. Although this will to some degree mitigate the loss of M–M π-bonding density, the net effect will still be a longer, weakened M–M bond. For X = phosphine, the behavior is similar to that for CO. Replacement of the alkyl groups, –R, on a phosphine PR_3 by more electronegative, electron-withdrawing groups such as –OR or –F will increase the π acidity of the phosphine, but will also simultaneously decrease the σ-donating ability of the phosphorus. Infrared and structural studies of complexes with various substituted phosphines situated trans to CO[15,17] yield the following relative ordering of π acidity of some ligands:

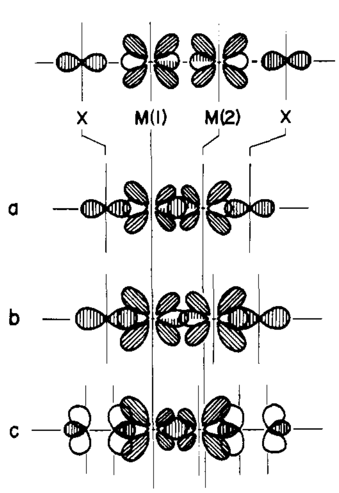


Figure 4. Orbital diagram for case of two metal atoms linked by a single bond. The filled d-orbital lobes exert some repulsive pressure on each other and are polarized outward toward the X ligands. The metal–metal bond is shown as formed from the overlap of two half-filled d_z orbitals. (a) The outer halves of each orbital are shown as empty, since they represent the σ^* antibonding combination into which the ligands donate their electrons. The more the M–M σ orbital is stabilized the more the σ^* orbital is destabilized and thus the less effective the bonding to the ligand. X a weak σ donor, weak π acceptor (e.g., H_2O); the ligands X compete poorly for the metal d_z orbital. The M–M bond is short and strong. (b) X a strong σ donor, weak π acceptor (e.g., $:NR_3$); the ligands compete well for the metal d_z orbital density, weakening the metal–metal bond and lengthening it relative to (a). Note that increased donation of ligand electrons to the metals serves to expand the filled d orbitals and further spread the M–M distance. (c) X a weak σ donor, strong π acceptor (CO); the strong π-accepting ability permits the delocalization of the metal d-orbital density into the ligand system and reduces M–M repulsion; the M–M bond is strong (weak σ donor) and shortened relative to (a) and (b).

$$PF_3 > CO > P(OR)_3 \gtrsim PPh_3 > P(alkyl)_3$$

This is, for example, the order of trans influence strength for X observed in the chromium(0) complexes, $Cr(CO)_5X$, shown in Table III. If, however, such ligands are trans to a ligand possessing only very weak π-accepting ability, such as Cl^-, in complexes $PtClL_2X$, a more familiar trans influence ranking results, namely,

$$P(alkyl)_3 > PPh_3 > P(OR)_3 > CO$$

as would be expected considering only the decreasing σ-donor abilities of these ligands.

In terms of the above bonding models, the observed variation of the Rh–Rh bond distances in Table II as a function of axial ligand is only consistent with a multiple Rh–Rh bond. Although the placement of CO in this ranking and the ordering of the phosphines is anomalous based upon the π-acidity ranking above, it is still necessary to invoke the metal–metal π bonding to explain the greater trans influence of CO and the phosphines over that of the strong σ donors. Because of the interplay of σ and π effects on the trans bond, it can be seen that circumstances may arise that will cause such a reordering within the series of π acceptors. We rationalize the observed order as follows: assuming that the metal–metal interactions are strong, i.e., M(1) competes in a superior way with the ligand X trans to it for *both* the σ and π bonding density of M(2), then M(1) is characterized as having a stronger trans influence than X. This is illustrated in Figure 6, with X assumed to be either a phosphine or CO. The MX bond is in this case expected to be much weaker, and longer, than normal. Since the π overlap in the MX bond is a much more sensitive (steeper) function of the internuclear distance than is the σ

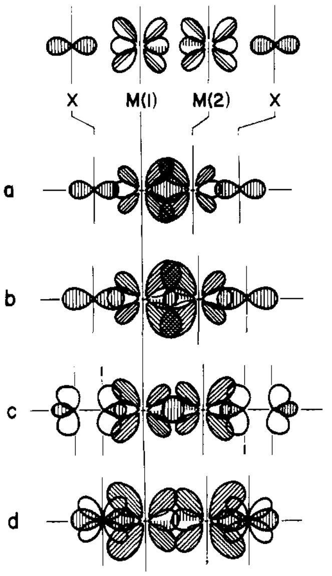


Figure 5. Orbital diagram for case of two metal atoms linked by a multiple bond consisting of σ and π components. (a) X a weak σ donor, weak π acceptor (H_2O). The M-M bond is short and very strong. (b) X a strong σ donor, weak π acceptor (:NR_3). The expansion of the metal d orbitals permits even more effective M-M orbital overlap but the M-M σ bond is weakened, and the M-M distance somewhat lengthened. (c) X a weak σ donor, strong π acceptor (CO). The M-M σ bond is strong (as in a) but the π-accepting ability of CO weakens the M-M π interaction, lengthening the M-M distance. (d) X a strong σ donor, strong π acceptor (:PR_3). Both the M-M σ and π bonds are weakened by competition from the axial phosphines and the M-M distance is lengthened relative to (a), (b), and (c).

Table III. Bond Parameters in Cr(O) Complexes, $Cr(CO)_5X$

X	Cr-X, Å	normal Cr-X, Å	Cr-C, Å trans to X	Cr-C, Å cis to X
CO^a	1.909 (3)	1.909	1.909	1.909
$P(OPh)_3{}^b$	2.309 (1)	2.252 $(1)^c$	1.861 (4)	1.896 (4)
$PPh_3{}^b$	2.422 (1)	2.381 $(5)^d$	1.844 (4)	1.880 (4)

[a] A. Whitaker and J. W. Jeffery, *Acta Crystallogr.*, **23**, 977–984 (1967). [b] Reference 16b. [c] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, **11**, 161 (1972). [d] F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **91**, 7000–7005 (1969).

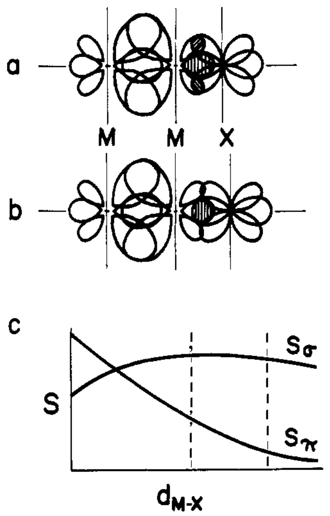


Figure 6. Dependence of magnitude of the overlap (S) of metal and ligand orbitals on the M-X distance. (a) M-X distance is normal and the M-X σ (vertical hatching) and π (diagonal hatching) are substantial. (b) As the M-X distance increases, the relative orientation of the different orbitals causes the π interaction to fall off in magnitude much faster than the σ interaction. The M-X distances for (a) and (b) are approximated by the dotted vertical lines in (c). Note that for short M-X distances the S_π overlap can dominate the S_σ in strength.

overlap, the increase in the MX distance as the bond becomes weaker causes the proportion of total bonding contribution from the π interaction to decline relative to that of the σ contribution, and the trans influence becomes proportionally more sensitive to variations in the σ basicity of the ligand. For phosphines, this is simply illustrated in Figure 7. For short internuclear distances, the trans influence order follows the π acidity; at longer internuclear distances, the order is dominated by the σ basicity of the phosphine.

The strong metal-metal bonding model, consisting of *both* σ and π metal-metal bond interactions, thus appears to well explain both the unusually short rhodium-rhodium bond distance and its observed variation as a function of axial ligand. For ligands with no π-accepting ability, the trans influence order follows the σ basicity; the stronger the base, the weaker the Rh-Rh bond. For ligands that are π acceptors, the metal-metal bond is *always* lengthened relative to the non-π-acceptors. Within the group of strong π acceptors, the trans influence ordering again follows the σ basicity. This is illustrated in Figure 8, which plots the available gas-phase proton affinities (PA's) for the axial ligands as a function of observed Rh-Rh distance. The dirhodium unit, as a Lewis acid, resembles a proton only in terms of its σ-bonding ability; the separation of the ligands into two groups clearly shows the increased trans influence effect of the π-acceptor ligands on the metal-metal bond.

The points for pyridine deserve some comment: though it *can* function as a π acceptor in some circumstances, pyridine here appears to behave strictly as a σ donor toward the dirhodium tetraacetate nucleus. This is readily understandable, however, since even in the most favorable circumstances pyridine is at best a weak π acceptor, and, as is discussed elsewhere,[9] the much longer than normal Rh-N distance effectively diminishes even that capacity so that pyridine functions here almost entirely as a σ-donor base.

It is apparent from the above arguments that the strength of a particular ligand, in both the σ and π senses, can vary considerably from situation to situation. In essence it is the interaction between the metal and ligand and not the ligand alone that determines the "strength" of the ligand in that circumstance, and the nature and extent of the interaction will depend primarily on two factors, namely, the magnitude of the metal-ligand orbital overlaps (S_{M-X}) and the energy difference (ΔE) between the orbitals of the separated moieties. These were taken into account by McWeeny, Mason, and Towl in their discussion of trans influence in Pt(II) compounds,[18] but only in terms of the σ-interacting orbitals; they related the strength of the metal-ligand bond to the quantity $S^2/|\Delta E|$ (Figure 9). Muir and co-workers[19] have shown this quantity to be reasonably well correlated with Pt-C, Pt-Cl, and Pt-P bond strengths as measured by their equilibrium metal-ligand bond distances. As our reasoning so far has been purely qualitative, we would like to put our arguments on a firmer basis by means of such quantitative measures. If we assume that this σ-only formalism applies equally well to M-X bonds in octahedral rhodium complexes (deficiencies *under this assumption* due to ignoring M-X π interactions should if anything be smaller owing to the larger than normal M-X distances, Figure 7), then we can see that changes in either S_{M-X} or $|\Delta E|$ can result in significant, but inversely related, changes in $S^2/|\Delta E|$. To demonstrate that for the X-Rh-Rh-X system the observed trans influence ordering, a function of the Rh-X bond strength, requires Rh-X π interactions which will weaken the Rh-Rh bond, it is necessary to show that the $|\Delta E|$ energy level separations and S overlaps for a σ-only bonding model are insufficient to explain the observations. This demonstration, how-

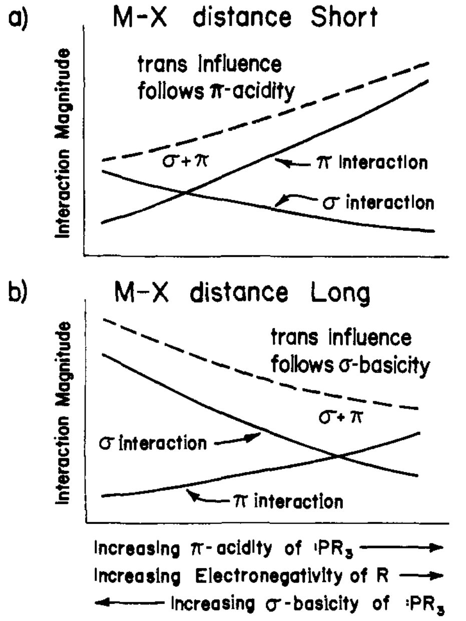


Figure 7. The S_σ and S_π overlap integrals (Figure 5) depend not only upon the M-X bond distance, but as well upon the shape and extent of the orbital lobes involved. For ligands such as trisubstituted phosphines, :PR_3, the latter are strongly perturbed by the electronegativity of the groups R and their geometrical disposition (e.g., see J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1-106 (1972). As the electronegativity of the R groups increases (say from $-CH_3$ to $-F$) the contraction of density on the phosphorus decreases the σ-donor ability but increases the π-accepting ability of the empty phosphorus d orbitals. Depending upon the M-P distance the magnitude of the σ effect will be greater, the same, or less than that of the π effect for a given R. If they are the same, changing R will yield immeasurably small changes in the trans influence (the resultant of the σ and π effects) because decreases in σ basicity are compensated for by increases in the π acidity. However, if one or the other dominates, as, for example, if the M-X distance is very short or very long, then the trans influence depends strongly upon R, and this resultant dependence can follow either the π acidity or the σ basicity as here shown in (a) and (b).

ever, is burdened with difficulties: although vertical ionization potentials for several of the ligands are available, the energy of the Rh σ-accepting orbital is unknown, and because the proportions of 5s, $5p_z$ and $4d_{z^2}$ character in the Rh σ orbital are also not known, the overlap integral S is difficult to estimate. McWeeny, Mason, and Towl have calculated S for Rh(III)-X for various atom types X assuming only p-orbital contributions from the metal and standard covalent radii.[18] Because of the longer than normal Rh-X distances we observe, we should expect the overlaps in the $Rh_2(OAc)_4X_2$ system to be systematically smaller than calculated by McWeeny et al., but their relative ordering should not be much different. The deficiencies of neglecting 5s and $4d_{z^2}$ orbital contributions are more difficult to assess; calculations now in progress bearing on this question will be reported in due course. Despite these shortcomings, it is reasonable to expect that if the M-M and M-X bonds are only single bonds, then the Rh-Rh distance should be at least a monotonic function of $S^2/|\Delta E|$. Using McWeeny's estimates of S and two values of energy for the Rh σ^* accepting level, we have derived in Table IV two sets of estimates for $S^2/|\Delta E|$. The order changes only slightly depending upon the particular value of the energy used for the Rh σ^* level. Plots of these values against Rh-Rh distance, given in Figure 10, show reasonably linear relationships for the ligands H_2O, py, and $NHEt_2$, but a scatter of points, far from the σ-donor line, for CO and the phosphines. In particular, CO and PF_3 have anomalously large observed trans-influence effects on the Rh-Rh bond based upon this σ only model. The predicted trans influence of $NHEt_2$ is seen to be comparable to that for $P(OMe)_3$. To be sure, the overlap integrals used in

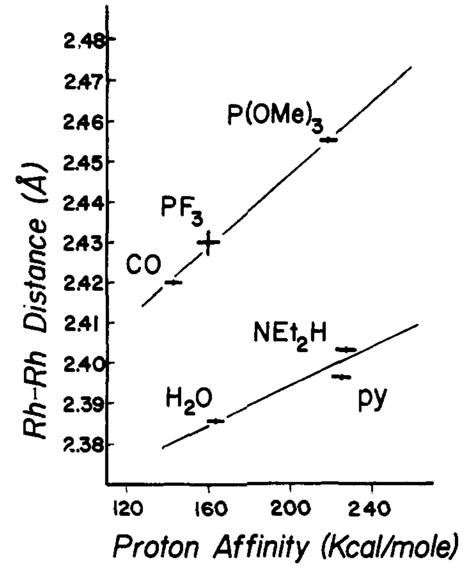


Figure 8. Correspondence of Rh-Rh distance to the σ basicity of the various ligands as measured by the gas-phase proton affinities. The latter values were obtained from R. R. Corderman and J. L. Beauchamp, *Inorg. Chem.*, **16**, 3135-3139 (1977); R. V. Hodges, T. J. McDonnell, and J. L. Beauchamp, in press; D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311-317 (1976), and references cited therein; T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectroscopy", Wiley-Interscience, New York, N.Y., 1976.

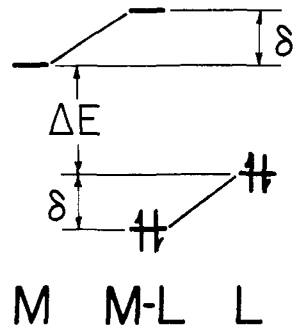


Figure 9. Interaction of a filled ligand donor level with an empty metal orbital. The stabilization δ arising from the interaction is proportional to $S^2/\Delta E$ where ΔE is the difference between the interacting levels.

these estimates are based upon normal Rh-X interatomic separations, and all the Rh-X distances under consideration here are 5-10% longer than normal. However, for the σ-only model to hold (i.e., for the calculated $S^2/|\Delta E|$ values to be a monotonic function of the Rh-Rh distance), it would be necessary for the Rh-X σ overlap to fall off nearly twice as fast with distance for py and $NHEt_2$ than for CO and the phosphines, so that the $S^2/|\Delta E|$ values of the former would be brought below those for the latter. Since the S^2 values in Table IV for the phosphines are all identical (McWeeny et al. did not consider differing hybridization of the P lone-pair orbital with different substituents R in PR_3), the S^2 for PF_3 is certainly already a serious overestimate, and this would require an even greater reduction in the relative magnitudes of S^2 for py and $NHEt_2$ in order to bring the $S^2/|\Delta E|$ values into line.

If the ordering of $S^2/|\Delta E|$ does not change with increasing Rh-X distance in the manner required above, and our reasoning is that it is highly unlikely that it does, then the one-term, σ-only $S^2/|\Delta E|$ measure of bond strength is inadequate and an additional π-interaction $S^2/|\Delta E|$ contribution is necessary to rationalize the separation of the ligands into the two distinct groups.

Unfortunately, the energies of the higher lying empty ligand

Table IV. Estimates of $S^2/\Delta E$

Ligand[a]	VIP[b]	S^{2} [c]	$\lvert\Delta E\rvert_{\mathrm{Rh}\sigma*} = -4.78$ eV	$S^2\lvert\Delta E\rvert$	$\lvert\Delta E\rvert_{\mathrm{Rh}\sigma*} = -7.18$ eV[d]	$S^2/\lvert\Delta E\rvert$
H_2O	−14.0[e]	0.1600	9.22	0.0174	6.82	0.0235
py	−9.88	0.2209	5.10	0.0410	2.70	0.0818
$NHEt_2$	−8.63	0.2025	3.85	0.0526	1.45	0.1400
CO	−13.79	0.3025	9.01	0.0336	6.61	0.0458
PF_3	−12.27	0.2500	7.49	0.0334	5.09	0.0491
PPh_3	−7.88	0.2500	3.10	0.0806	0.70	0.3571
$P(OMe)_3$	−9.25	0.2500	4.47	0.0559	2.07	0.1208

Predicted Trans Influence Order:

$\lvert\Delta E\rvert(\mathrm{Rh}\sigma^* = -4.78\ \mathrm{eV})$: $H_2O < PF_3 \lesssim CO < py < NHEt_2 \lesssim P(OMe)_3 \ll PPh_3$

$\lvert\Delta E\rvert(\mathrm{Rh}\sigma^* = -7.18\ \mathrm{eV})$: $H_2O < CO \lesssim PF_3 < py < P(OMe)_3 < NHEt_2 \ll PPh_3$

[a] In order of observed Rh–Rh lengthening. [b] Vertical ionization potential. [c] Values taken from ref 18. [d] The value for the σ^* level derived from the Xα-SW calculations of ref 5 is −4.78 eV, which should be corrected downwards by ca. 2.4 eV (thus −7.18 for the value) in order to bring the Xα-SW ground state eigenvalues (which represent orbital electronegativities, not ionization energies) onto the same scale as experimental ionization energies (ref 5 and J. Norman, private communication, 1978). [e] This is a weighted mean for the a_1 (−14.7 eV) and b_2 (−12.6 eV) lone pairs of H_2O, assuming that the rehybridization of the oxygen upon assuming a pyramidal configuration mixes ca. 30% a_1 with 70% b_2 to give the donor lone pair utilized in coordination to the metal.

d or π^* levels are, in general, not experimentally known, and this severely restricts quantitative interpretation of our observed trans influence ordering in terms of the orbital energetics. However, the strikingly different behavior apparent in Figures 8 and 10 clearly distinguishes the π-acceptor ligands from the non-π-acceptors despite the very close correspondence of the σ-donating levels and PA's of some of them to those of the purely σ donors. Deviations from an ordering of the π-acceptor ligands based strictly upon their σ-donor strength reflects an unknown variation in the phosphorus hybridization and accepting d levels with different substituents.

In spite of our lack of information of the ligand π-accepting levels, if there is back-donation to the ligand from a filled metal π^* level, a stabilization of the Rh–Rh bond must result which will drive the metal-metal σ^* level higher in energy. This will cause a reduction in $S^2/\lvert\Delta E\rvert$ for the Rh–X σ bond, rather than the increase necessary to explain the observed lengthening of the Rh–Rh bond; the σ and π Rh–X interactions are opposing each other. On the other hand, back-donation to the ligand from a filled metal-metal *π-bonding* level will destabilize the Rh–Rh bond, causing a lowering of the Rh–Rh σ^* level. The consequent enhancement of $S^2/\lvert\Delta E\rvert$ for the σ part of the Rh–X bond will complement the positive contribution to the Rh–X bond from the π interaction; the σ and π effects will be working together to lengthen the Rh–Rh bond. The observed unusual trans influence ordering of the ligands on this basis requires significant back-donation to the axial ligands from a high lying, filled, principally metal-metal bonding, π molecular orbital.

That strong metal-metal bonds do exert a very large trans influence was discovered by Cotton and co-workers in their work on the quadruply bonded metal-metal dimers,[1] and this effect is particularly exemplified in the dimolybdenum tetracarboxylate complexes.[20] When axially coordinated complexes could be prepared or isolated, the metal-ligand distances were extremely long, nearly always 0.4 Å longer than that expected for a normal Mo–X bond.[20a] That it was extremely difficult to prepare such axially substituted complexes was itself taken as evidence of the extraordinarily strong trans influence of multiply bonded metal-metal dimers.[20b]

The situation in the dirhodium complexes is different in that it *is* possible to prepare a wide variety of axially coordinated complexes—the metal-metal bond is certainly weaker than in the quadruply bonded dimolybdenum system, and the trans influence accordingly weaker—but it and its trans influence are still remarkably strong, as can be seen by comparing the Rh–X distances in Table II with those of mononuclear complexes of the same ligand. In *all* cases, the Rh–X bond in the dirhodium complexes is at least 0.1 Å greater than the corresponding Rh–X bond in either Rh(I) or Rh(III) complexes, and in many cases the difference is 0.2 Å or larger.[21]

The Question of Bond Order. The high strength and extraordinary shortness of the Rh–Rh bond seem to argue strongly for a multiple bond formulation. The trans influence arguments above appear to require it, inasmuch as the bonding schemes of Figure 1 yield the required highest filled level of π symmetry only for a triple bond formulation. We shall see that, in fact, what the preceeding trans influence arguments require is only that the highest *filled* level of π symmetry (which interacts with the axial ligands' empty π^* accepting orbitals) must be π-bonding rather than π-antibonding in character. We shall then show that it is possible, within a more elaborate perturbation MO scheme, to achieve a net single bond formulation in which the highest filled π MO is π-bonding. In this way, although our arguments above would appear to require a multiple bond formulation, the data are also seen to be consistent with a "single" Rh–Rh bond of extraordinary strength, a result which has received recent strong theoretical support.[5] In dealing with this unusual situation, we will face the larger question alluded to in the introduction: is the formal metal-metal bond order a useful, or indeed, desirable measure of the bonding in these d^7-d^7 complexes.

Certainly, the most incontrovertible evidence of strong metal-metal bonds is their persistence in solution under conditions in which a supporting structure of encapsulating bridging groups has been replaced by an assembly of monodentate ligands. This is the case with the Re^{6+},[23] $Tc_2{}^{5+}$,[24] and $Mo_2{}^{4+}$,[25] systems, the more recently discovered $Mo_2{}^{6+}$ and $W_2{}^{2+}$,[26] and to some extent with $Cr_2{}^{4+}$ [27] (the only first-row transition metal dimer of this type). Although no structural proof of dimeric complexes of Rh(II) with exclusively monodentate ligands. This is the case with the Re^{6+},[23] Tc_2,${}^{5+}$,[24] and $Mo_2{}^{4+}$,[25] systems, the more recently discovered Mo^{6+} and $W_2{}^{2+}$,[26] and to some extent with $Cr_2{}^{4+}$ [27] (the only first-row *bridged* Rh(II) dimer structure containing a rhodium-rhodium bond has been reported: it consists of Rh(II) atoms, equatorially chelated by dimethylglyoxime, with a Rh–Rh separation of 2.936 Å.[2a] The approximately planar equatorial ligand systems are quite close (~2.9 Å), less than the 3.2 Å van der Waals graphitic interplanar spacing, and this must result in more than insubstantial repulsive forces between the two halves of the molecule that are resisted by the Rh–Rh bond.

The arguments which initially led to the formulation of the Rh–Rh bond in $Rh_2(OAc)_4(H_2O)_2$ as triple[2] were based primarily upon the following evidence: (a) the very short Rh–Rh bond in comparison with the much longer distance in the $Rh_2(dmg)_4(PPh_3)_2$ complex, which had been assigned a bond order of one,[29] (b) the "normality" of the Rh–P distances in

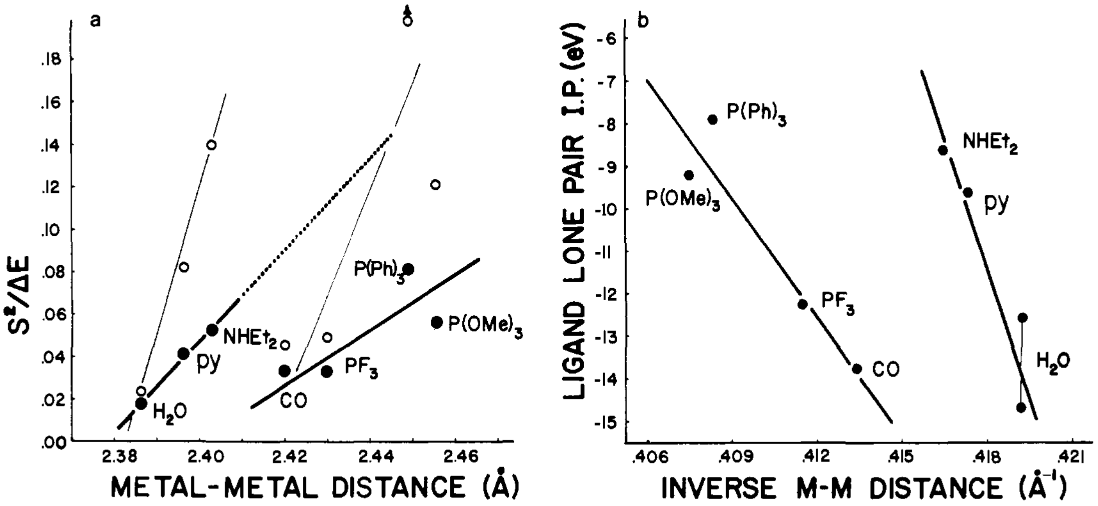
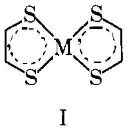


Figure 10. The trans influence of the ligands, as measured by their lengthening of the Rh-Rh bond, correlates with $S^2/\Delta E$ and with the vertical ionization potential of the ligands only if the π-acceptor ligands are considered as a separate groups; σ-donation effects alone are insufficient to account for the observed trans influence order of the ligands. (a) Plot of data from Table IV against Rh-Rh distance. Points (●) are for $E(\text{Rh } \sigma^*) = -4.78$ eV, and points (○) are for $E(\text{Rh } \sigma^*) = -7.18$ eV. Addition of ca. 0.06 to the $S^2/\Delta E$ values for the π acceptor ligands (such as might arise from an $S^2\pi/\Delta E\pi$ contribution term) would make the line for the π-acceptors continuous with that of the σ-only donors (heavy dotted line). (b) Plot of vertical ionization potential of ligand lone pair against $1/d$(Rh-Rh). Ionization potential data from tabulations in D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311-317 (1976), and O. Stelzer and E. Unger, *Chem. Ber*, **108**, 1246-1258 (1975). For H_2O, there are two lone pair orbitals, one of b_1 symmetry and the other of a_2 symmetry. These mix on forming a complex, and the resulting lone-pair energy must be intermediate between the energies of these two "isolated molecule" ionization potentials.

the latter as opposed to the "abnormality" of the long Rh-OH_2 distances in the former, and (c) the assumption that as the bridging tetracarboxylate framework appears to be capable of accommodating a wide range of metal-metal distances (viz., 2.89 Å in $Cu_2(O_2CCF_3)_4(\text{quinoline})_2$[33] to 2.09 Å in $Mo_2(OCCF_3)_4$),[34] it would not particularly influence or restrict the metal ions to adopt particular values of internuclear distance. This final assumption drew support from the near identity of the metal-metal distances, for example, in bridged and nonbridged Re^{6+} systems: 2.241 (7) Å in $K_2Re_2Cl_8 \cdot 2H_2O$,[35] 2.228 (4) Å in $Cs_2Re_2Br_8$,[36] 2.224 (5) Å in $Re_2Cl_4(O_2CCH_3)_2 \cdot 2H_2O$,[37] and 2.235 (2) Å in $Re_2(O_2CPh)_4Cl_2$.[38] Given these points, which rely entirely upon distance information, and particularly upon metal-metal separations, and ignoring any but inductive (electronegativity) effects of the equatorially disposed ligands, one is inescapably led to the conclusion that the metal-metal bond in dirhodium tetraacetate dihydrate must indeed be multiple. Simple qualitative molecular orbital arguments based on the quadruply bonded d^4-d^4 cases then dictate that the value of the multiplicity should be three[2c] (Figure 1a).

The only difficulty with this argument is the explicit assumption that the metal-metal interaction is the sole determiner of the equilibrium metal-metal bond distance, and that the ligands effect but small perturbations on the magnitude and extent of their interaction. Although electron delocalization via π overlaps in metallocycles (e.g., as in I)[39] and π back-donation in metal-CO and metal-phosphine situations are well accepted, there is an understandable reluctance to express metal ligand bonding arguments in terms of generalized molecular orbitals. The successes of crystal field theory in explaining transition metal electronic spectra have probably encouraged this, and it is consequently not too surprising that the more substantial involvement of the bridging ligands in the tetracarboxylate metal dimer systems was not fully recognized[40] until the results of SCF-Xα-SW molecular orbital calculations became available.[41] Dubicki and Martin had quite early pointed out the possibility of extensive π-type delocalization involving the carboxylate ligands[42] in the heavily studied[43] copper(II) dimer structures, and proposed that spin-spin interaction of the unpaired electron on each copper center (which could explain the magnetic properties of the copper dimers) through the π system was likely to be a significant exchange mechanism. Although the delocalized π bonding was deduced to play some role in the electronic structure of the dicopper complexes, the lack of accurate measures of the contributions of the individual atomic orbitals (metal and ligand) to the molecular orbitals precluded a more quantitative assessment of the direct metal-metal interaction.



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Such a detailed assessment is necessary in order to fully understand the bonding where the bond, say between A and B, is no longer the result of simple overlap of two or more atomic orbitals from just the two centers A and B, but consists of the net contributions of many molecular orbitals, each containing lesser or greater amounts of A and B character. In the strictly two-atom case, the filling of bonding and antibonding levels will yield a net bond order that clearly will follow the bond strength quite closely—a filled antibonding level quite neatly cancels the effect of the corresponding filled bonding level. Interaction of A-B with a set of ligands causes mild to extensive mixing of the ligand orbitals into the A-B MOs and thus substantially alters their relative stabilities and ordering. No longer pure A-B, a filled *formerly* pure π_{A-B} bonding orbital is in general *not* exactly canceled by a filled *formerly* pure π^*_{A-B} antibonding orbital and a residual π contribution to the total bond order may result.

A simple orbital energy diagram (Figure 11) illustrates how this heavy mixing of a ligand π-system with the metal orbitals can affect both the ordering and bonding nature of the ultimate molecular orbitals. The $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration on the left is that based upon calculations for the multiply bonded d^3-d^3

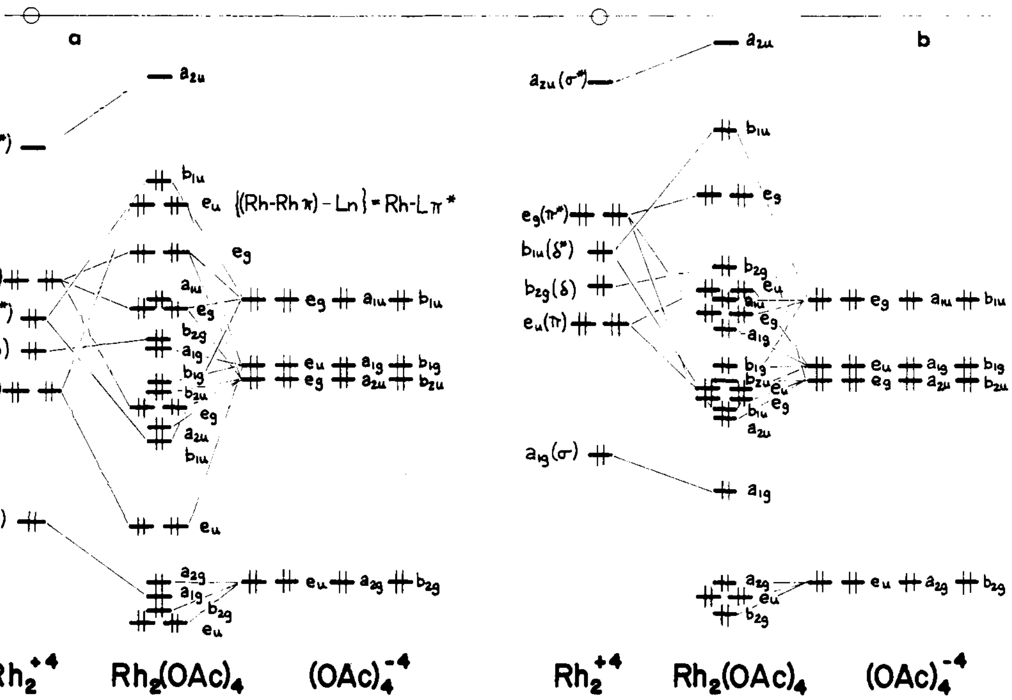


Figure 11. Qualitative MO diagram showing the extensive mixing possible of the bridging carboxylate orbitals with those of the binuclear d^4-d^7 manifold. Carboxylate levels are indicated on the right in both (a) and (b) which have only the relative positions of the dimetal levels changed with respect to those of the carboxylate. The changes in position and ordering of the resultant MO's are illustrative of the great importance of the relative positioning of the contributing metal and ligand levels. This figure does not consider the empty rhodium 5s and 5p levels, which should as well mix with both the appropriate symmetry combinations of metal d orbitals and of the ligand orbitals, and lead to further modifications of the position and ordering of the resulting MO's.

and d^4-d^4 systems and to which sufficient electrons have been added to represent a "metal atom only" d^7-d^7 system. These "metal-metal only" MO's are then allowed to interact with ligand σ and π MO's (center, of configuration (filled levels) $(1b_1)^2(4b_2)^2(ba_1)^2(1a_2)^2$ for local RCO_2^- C_{2v} symmetry) of the bridging carboxylate groups. Considering only the interactions of the metal π and δ levels with the appropriate symmetry combinations of the carboxylate orbitals yields the levels for the complex. The entire diagram is reproduced on the right, but with the relative positions of the two manifolds of interacting levels changed. It is significant that the specific ordering of the derived levels is highly sensitive to the relative separations of the constituent metal and ligand orbitals. In particular, one can see that the relative orbital coefficients will depend strongly upon the nature of the bridging ligands. Depending upon the magnitudes of the coefficients of the atomic orbitals comprising the MO's one can as one chooses give each MO different labels, all of which will be more or less correct; for example, the highest filled level of overall π symmetry in Figure 11a can be described as Rh-Rh π, as carboxylate (L)n or as Rh-L π^*. As long as the atomic orbitals are strongly mixed, all of these appellations will be appropriate. The Rh-Rh bond order can be taken as the algebraic sum of the Rh contributions to such orbitals. The net resultant metal-metal bond order may only be 1.0, but it could as well be fractional, e.g., 1.2, and may consist of σ, π, and even δ components due to inexact cancellation of the metal contributions to filled bonding and antibonding orbitals of σ, π, and δ symmetry.[41b] Such a calculation is tantamount to a Mulliken bond order analysis, which generally gives bond order values much lower than the *formal* bond order obtained by subtracting the number of filled antibonding orbitals from the number of filled bonding orbitals. The *bond energy* of the interaction will be determined by the stabilities of the filled MO's, and the strength of the bond, as measured by the bond energy, can thus be quite independent of the bond order in such complicated cases.[44]

We thus visualize the extraordinary shortness and high strength of the Rh-Rh bond in these complexes to a very large extent to be the consequence of the encapsulating carboxylic acid framework. The electron density diagrams for the filled MOs in dimolybdenum tetraformate[41] demonstrate the heavy mixing of the individual atomic orbitals and the consequent extensive delocalization of the bonding electrons, with substantial ligand density steered into the metal-metal π-bonding region. This additional π density effectively strengthens the M-M interaction without formally increasing the bond order calculated on the basis of the metal orbitals alone. In this sense as well, the bonding in the dirhodium complexes can be multiple, but is not reflected in the formal bond order of the bond *between the rhodium atoms*. Thermodynamic measures of the net bond energy would thus be a more reliable measure of the total interactions in these complexes, and we eagerly await the appearance of such experimental values.[48]

We now consider the results, recently reported by Norman and Kolari, of molecular orbital calculations at the SCF-Xα-SW level of approximation on dirhodium tetraformate and its diaquo adduct.[5] They found the rhodium-rhodium bond order to be 1.0 and the metal-metal bond to consist *wholly* of σ character, with the contributions of filled π and π^* orbitals canceling almost perfectly. Their molecular orbital energy level scheme for dirhodium tetraformate is reproduced in Figure 12.

Unlike the triple bond scheme (Figure 1a), which predicts two strong z-polarized dipole-allowed transitions ($\sigma^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$), the "single" bond scheme derived by Norman and Kolari rationalizes the observed UV-vis spectral bands quite well.[5] The ordering of the levels they found for the diaquo adduct of dirhodium tetraformate is essentially the same as that in the scheme found by Dubicki and Martin using the much less sophisticated SCCC MO method.[3] Their scheme as well predicts the proper sensitivity of the spectral bands to the nature of the axial ligands,[3,5] and these bands have very recently been found to possess the predicted polarizations, at least for the diaquo adduct.[50]

In the face of this evidence, it is very difficult to defend the multiple bond formulation for the metal-metal bond in the dirhodium tetracarboxylates. As we have seen, our structural data can be rationalized on the basis of a "single" bond scheme if one postulates that the Rh-Rh single bond is extraordinarily strong; a triple Rh-Rh bond, though attractive, is not required. Perhaps the strongest remaining argument for the multiple bond formulation is one's intuitive feeling that the Rh-Rh distance is much too short for it to only be a single bond. Even Norman and Kolari feel compelled to invoke constraints in the form of restrictive bonding requirements of the bridging carboxylate groups to explain the shortness of the Rh-Rh distance.

We have shown qualitatively how the complicated molecular orbital scheme of Norman and Kolari can arise; the ordering of the levels in our Figure 11b is very similar to theirs. Our trans influence results seem to require the somewhat different ordering of Figure 11a, with a filled π-bonding (e_u) level higher in energy than the antibonding π^* (e_g) level. For several reasons, we do not view this disagreement with the Xα-SW calculations as serious. As shown above, the level ordering should be sensitive to the position of the bridging ligand π levels, and thus to the constitution of the bridging groups. The differences between formate and acetate (a stronger base) are themselves possibly sufficient to yield the different ordering found in the calculation. Also, the calculations for the tetraformate were carried out using the geometry of the dirhodium tetraacetate nucleus found in the crystal structure of its diaquo adduct,[51] whereas we expect, in analogy to the $Cr_2(O_2CR)_4$ and $Mo_2(O_2CR)_4$ dimers, that the Rh-Rh distance in the axial-ligand-free $Rh_2(OAc)_4$ should be measurably shorter than in $Rh_2(OAc)_4(H_2O)_2$. Although these approximations are probably sufficient to perturb the relative positions of some of the levels of interest, they are not severe enough to abrogate the coherent explanations[5] of the spectral properties and of the strong trans influence of the Rh-Rh bond that the calculations yield. The Norman and Kolari analysis reveals the latter to be a consequence of the exceptionally strong σ component of the Rh-Rh bond; the only empty axial orbital available to accept the ligand lone pair is the high-lying Rh-Rh σ^* orbital. As the energy match between the donor and acceptor levels is poor (Figure 12), the Rh-X interactions are inefficient and weak, leading to the much longer than normal Rh-X bond lengths.[5] As the ligand donor levels approach that of the Rh-Rh σ^* level, the energy match and the orbital mixing improves, with consequent stabilization and shortening of the Rh-X bond and concomitant destabilization and lengthening of the Rh-Rh bond.

The Xα-SW calculation places the highest filled Rh-Rh π^* ($5e_g$) level above that of the filled π ($6e_u$) level. If this is true, then the σ and π trans influence arguments detailed above in our analysis would require both that Rh-X π-back-bonding be negligible (since it would otherwise lead to Rh-Rh bond strengthening by removal of antibonding π^* density) and that the Rh-X σ overlaps (S) for H_2O, py, and $NHEt_2$ must decrease very much more rapidly with distance than for CO and PR_3 (in order to account for the shorter Rh-Rh distances for the former compared to the latter). Although, as noted above, the longer than normal Rh-X distances are expected to reduce the Rh-X π interactions to a greater extent than the Rh-X σ interactions, we do have evidence that significant π-back-bonding does occur, in that the CO stretching frequency in $Rh_2(OAc)_4(CO)_2$ is 2105 cm^{-1}, below that of free CO, 2143 cm^{-1}.[54] Since the CO 5σ lone pair orbital is slightly antibonding with respect to the CO bond, donation of density from it should increase the CO bond strength: the decrease in the CO stretching frequency requires back-donation of electron density into the antibonding CO π^* orbital. The ramifications of this back-bonding for the σ and π components of the $S^2/|\Delta E|$ measures of the trans influence strength for the various ligands have already been discussed.

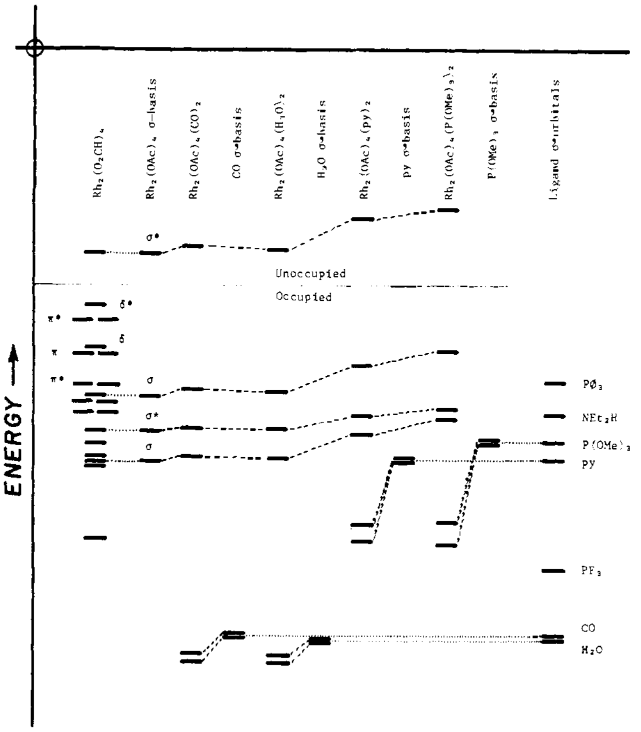


Figure 12. Predicted trans influence of ligands based upon $Rh_2(O_2CH)_4$ energy level scheme (left) derived by SCF-Xα-SW methods (ref 5), and considering only σ interactions. The upper and lower of the pairs of ligand basis σ orbitals are respectively the antisymmetric and symmetric combination of orbitals from the two ligand molecules; the separation has been exaggerated for clarity. The ligand lone pair levels at right are in correct energetic relationship based upon the experimental ionization potentials used in previous figures. Adjustment of the whole orbital structure of $Rh_2(O_2CH)_4$ by 1 or 2 eV up or down does not seriously alter the predicted interactions or the predicted incorrect trans influences of the ligands. The manifold of $Rh_2(O_2CH)_4$ levels contains all levels given in ref 5 which have at least 10% Rh contribution; the designation σ, π, δ, σ^*, etc., are thus predominantly indicative of the *symmetry* of these orbitals with respect to the metal-metal axis.

Placement of the filled π ($6e_u$) level above the filled π^* ($5e_g$) level, as we favor, does not lead to disagreement with the assignments of the UV-vis bands in these complexes made by Norman and Kolari. The same transitions ($\sigma^* \leftarrow \sigma$ and $\sigma^* \leftarrow \pi^*$) are the only dipole allowed ones, and the interposition of a filled π level generates no new bands.

Using either the Norman and Kolari scheme, Figure 12, or our scheme, Figure 11a, one obtains a *formal* Rh-Rh bond order of 1. The large trans influence effects of the Rh-Rh bond on the Rh-X bonds are self-consistent with the high strength of the Rh-Rh bond, but in essence the very strength and unusual shortness of the Rh-Rh linkage are still unexplained. Examination of the structural results for a large number (>40) of tetracarboxylate bridged transition metal dimers has convinced us that the carboxylate linkage is actually quite flexible, and itself imposes no serious constraints on the metal-metal distances.[55] However, we do feel, as we have suggested above, that the bridging ligands, with their σ and delocalized π system MO's lying in the appropriate energy range to mix well with the metal-metal orbitals, facilitate additional net bonding interactions which would otherwise not occur.

We propose that the forces which strengthen the metal-metal bond arise simply from mixing of higher lying empty orbitals into the ground-state MO's for the complex. The idea itself is certainly not new,[56] but to our knowledge has not before

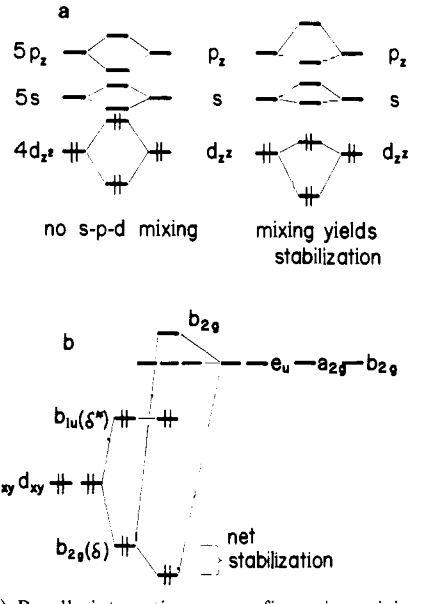
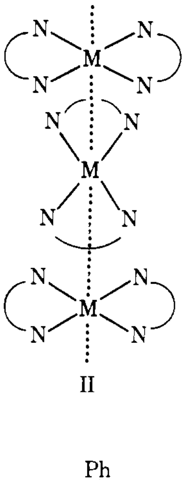


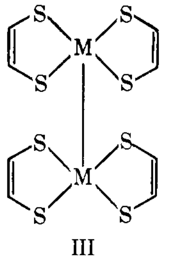
Figure 13. (a) Rundle interactions or configuration mixing of empty higher lying s and p orbitals into filled valence levels stabilizes the metal-metal bond even when no formal bond exists. (b) Similar mixing of empty ligand levels with M-M valence levels can also lead to bond stabilization in a formal no-bond situation.

been invoked in this way to yield a rational explanation for the bonding in the d^7-d^7 complexes. Cotton's original triple bond formulation[2] is in a sense a version of this, except that the 5s and 5p levels were thought to be low lying and to yield the separate σ_n and σ_n', which were seen as being embedded among the 4d levels. The Norman and Kolari analysis has clearly shown that no such new orbitals "drop into the proper range";[5] the 5s and 5p levels are simply too high in energy for such an event. However, the 5s and 5p levels are *not* too high for appropriate symmetry combinations to mix into the lower lying valence MO's (Figure 13).

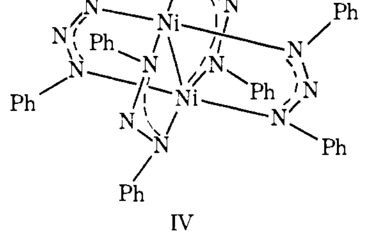
Such orbital interactions as these were proposed by Rundle[56a] to account for the stabilization of axially stacked Ni(II), Pd(II), and Pt(II) bis(dimethylglyoximato) complexes, II (M-M distances ~3.23-3.25 Å),[57] and can as well account for the very short (but weak) metal-metal bond in the Ni(II), Pd(II), and Pt(II) bis(ethylene-1,2-dithiolate) complexes, III (Pd-Pd and Pt-Pt distances, respectively, of 2.790 and 2.748 Å).[58] In the scheme of Figure 1b, all the metal-metal bonding *and* antibonding orbitals for such d^8-d^8 complexes are filled. Although the *formal* bond order is zero, the dimers exist and indeed are formed spontaneously. A large number of other such *formally* nonbonding dimers of d^8-d^8 configuration have been found, both with nonbridging[59] and with bridging ligands.[60] Of particular interest are the dimeric complexes $[M_2(S_2CCH_2Ph)_4]$ with M = Ni(II) or Pd(II), where the M-M distances are respectively 2.56 Å (vs. 2.492 Å in metallic Ni) and 2.715 Å (vs. 2.751 Å in metallic Pd).[61] Within each dimer the metals are displaced inwards toward each other from the respective planes of the square of sulfur atoms of the 1,1-dithiolate ligands, which bridge in much the same fashion as do the carboxylic acid groups in the $M_2(O_2CR)_4$ complexes. A similar example is provided by the tetrakis(1,3-diphenyltriazeno)dinickel(II) complex, IV, which possesses a Ni-Ni distance of 2.38 Å.[62] The existence of net metal-metal bonding interactions in these *formally* nonbonded dimers cannot be denied. We propose that these same stabilizing forces are also present in the d^7-d^7 dirhodium complexes, effectively strengthening the metal-metal bond without adding to the formal bond order.



II



III



IV

The nature of the stabilization is illustrated in Figure 13. The total energy of the assembly is lowered by interaction of the filled orbitals with the higher empty levels; without having a bond in the *normal* sense of electron-pair sharing, the close proximity of the interacting metal atoms is energetically more favorable than having the atoms separated. A different way of looking at this is that the mixing of higher empty levels provides a means of rehybridizing (or polarizing) the orbitals so as to make the antibonding orbitals more diffuse and the bonding orbitals more concentrated in the region between the atoms. The degree of the stabilization afforded by this "configuration interaction" depends entirely upon the proximity in energy of the virtual orbitals to the filled orbitals, and this of course depends upon the particular metals and ligands involved in the complex. For the d^8-d^8 nickel complexes II, III, and IV we see substantial shortening effects of the M-M distance with different ligands. The bridging ligands appear to be especially effective, presumably by either providing their own low-lying virtual orbitals which can dissipate antibonding density (in the limit of complete charge transfer to the ligands, the Ni ions in III and IV could be considered as Ni(IV), yielding a *formal* Ni-Ni bond order of 2) or by perturbing the metal-metal only levels (as in Figure 11) so that the filled levels can approach closer to the virtual levels and thus mix more strongly.

These arguments allow the variations in metal-metal distance in a whole variety of transition metal dimers to be qualitatively understood. For example, within a triad, for a particular set of ligands, the M-M distance generally decreases (relative to covalent radii) with increasing atomic number because of the systematic lowering of the absolute levels and the increasing diffuseness of the d orbitals. As one goes from first to second to third transition series the metal d-manifold should mix more effectively with the ligand levels and these perturbed orbitals may then more effectively mix with the virtual orbitals either on the metals or on the ligands. Similar reasoning suggests that the "extra" stabilization should increase as one proceeds from left to right along a transition series. The increasing M-M bond strengths for the isoelectronic $Ni(S_2CR)_4$ and $Pd_2(S_2CR)_4$ are thus readily rationalized, and an explanation is thus given for the decreasing Ni-Ni distances in $[Ni(dmg)_2]_n$, Ni_2(ethylene-1,2-dithiolate)$_4$, $Ni_2(S_2CCH_2Ph)_4$, and Ni_2(1,3-diphenyltriazenide)$_4$, all of which formally contain no M–M bond. The remarkable differences between the M–M distances in $Co_2(O_2CR)_4X_2$ and $Rh_2(O_2CR)_4X_2$(ca. 2.8[63] vs. 2.4 Å) are ascribed, first, to the tendency of the first-row +II transition ions, with their much more compact d orbitals, to not form M–M bonds (the dicobalt complex can be considered to contain an extremely weak single Co–Co bond), and, second, to the enhanced aspects of the formal single bond in the dirhodium complex. The presence of $5p_z$ character in the Rh–Rh σ and σ^* orbitals is hinted at in one orbital energy table in Norman and Kolari's Xα-SW paper,[5] but is unfortunately not more fully explicated. We feel that the involvement of these higher levels provides a simple rationalization for, and resolves the paradox of, the formally too short, too strong single bond between the rhodium atoms in the dirhodium tetracarboxylates. Such effects prompt us to comment that the formal bond order does not necessarily reflect the true nature of the bonding in such compounds and, at least in the dirhodium tetracarboxylates, is probably not a particularly useful index of the metal–metal interactions.

Further structural and spectroscopic studies of additional, new, axially substituted dirhodium complexes are in progress and will be reported upon shortly.

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(22) The trans influence of a particular ligand X is actually the sum of a complicated variety of factors, primarily of the metal d and ligand p orbital overlaps and of the separation of the orbital energies,[18] but also of the hybridization of the metal and of the ligand orbitals, the electronegativities of substituents and of other ligands, and so on. Thus no cohesive, quantitative theory of trans influence yet exists, and each oxidation state of each metal must be considered as a separate case; one as of yet cannot even reliably carry over the results for a metal in one coordination geometry to the same metal in a different geometry, except in very general terms. The interpretation of trans influence effects we propose in this paper (especially see Figure 7) permits a simple rationalization of how the relative trans influence strengths of a given set of different X ligands can change completely in going from one metal to another (order reversal, for example) and how some metals appear to evidence only very weak or no trans influence effects at all (e.g., when the slopes of the σ and π effects in Figure 7 just balance each other). The oxidation state of the metal and the valence orbital energy levels of the metal and ligand determine the magnitudes and the slopes of the σ and π overlap effects in Figure 7 as a function of internuclear M–X distance. Whichever individual effect dominates the sum yields the observed ordering of trans influence.

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Solid State Structure, Magnetic Susceptibility, and Single Crystal ESR Properties of *cis*-Diammineplatinum α-Pyridone Blue

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Abstract: The crystal and molecular structure and magnetic and ESR properties of *cis*-diammineplatinum α-pyridone blue are reported. The compound, a mixed valent tetramer having the formula $[(NH_3)_4Pt_2(C_5H_4NO)_2]_2(NO_3)_5{\cdot}H_2O$, crystallizes in the triclinic system, space group $P\bar{1}$. The lattice parameters are a = 10.219 (7) Å, b = 11.225 (7) Å, c = 9.538 (6) Å, α = 106.32 (2)°, β = 93.91 (2)°, and γ = 73.75 (2)°. The structure was solved using 4421 independent reflections collected on a four-circle X-ray diffractometer and refined to final values of the residuals R_1 = 0.045 and R_2 = 0.058. There is one cation per unit cell, consisting of two *cis*-diammineplatinum units bridged by two α-pyridonate ligands, and two of these are further linked across a crystallographic inversion center to form a tetranuclear chain. The platinum atoms at the ends of the chain are bonded to two ammine ligands in a cis configuration and two deprotonated nitrogen atoms of the α-pyridonate rings. The inner platinum atoms have two cis ammine groups and two exocyclic α-pyridonate ring oxygen atoms in their coordination spheres. Apart from the bridging α-pyridonate ligands, the two square planar platinum moieties are further joined by a Pt–Pt bond of 2.7745 (4) Å. The linkage of two of these binuclear units across the center of symmetry is achieved by a Pt–Pt bond, 2.8770 (5) Å in length, and by intramolecular hydrogen bonds formed between the ammines coordinated to one platinum atom and the coordinated oxygen atoms of its inversion mate. As a result of nonbonded steric interactions, the Pt_4 chain is not quite linear, with the Pt1–Pt2–Pt2′ angle being 164.60 (2)°. The Pt–O and Pt–N bond lengths range from 2.016 (8) to 2.041 (7) Å. There are, additionally, five nitrate anions and one water molecule in the unit cell. The average formal platinum oxidation state is therefore 2.25. Magnetic susceptibility measurements of the solid over the range 4.2 K < T < 300 K show *cis*-diammineplatinum α-pyridone blue to be a simple Curie paramagnet. The magnetic moment of 1.81 μ_B is consistent with the presence of one unpaired spin per tetrameric unit. Single-crystal electron spin resonance measurements revealed the principal g values to be g_{xx} = 2.307, g_{yy} = 2.455, and g_{zz} = 1.975. The magnitudes and orientations of the **g** tensor components indicate that the unpaired spin resides in a molecular orbital comprised of d_{z^2} atomic orbitals directed approximately along the platinum chain axis.

Blue platinum complexes have long been of interest to chemists.[3-6] In 1908 a blue compound was reported to form in a reaction between dichlorobis(acetonitrile)platinum(II) and silver salts.[3] This "Platinblau" was formulated as the monomeric platinum(II) complex, $[(CH_3CONH)_2Pt]{\cdot}H_2O$. Later it was proposed, by analogy to other deeply colored platinum and ruthenium compounds, that platinum complexes having anomalous blue colors were polymeric with bridging amidate linkages.[4] The tendency for square-planar platinum complexes to stack at close distances with favorable metal–metal axial interactions was realized at about the same time.[5] When blue crystals of a material, formed in the reaction of trimethylacetamide and $[(CH_3CN)_2PtCl_2]$, were obtained,[6] it appeared that the structure of a platinum blue would at last be solved by X-ray diffraction. Unfortunately, the crystals were found to be a 7:2:1 mixture of two isomorphous, yellow, crystalline components and an amorphous, blue material. Based on extensive chemical and spectroscopic analyses, the blue component was formulated as a mononuclear platinum(IV) compound, $[(t\text{-}C_4H_9CONH)_2PtCl_2]$. The original "Platinblau" was assigned the analogous formula $[(CH_3CONH)_2Pt(OH)_2]$.[6]

More recently, following the discovery[7] that *cis*-dichlorodiammineplatinum(II) (DDP) is an antitumor drug, a blue

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