

(trifluoroacetato)dimolybdenum (0.27 g, 0.00034 mol) in diethyl ether (30 mL). The solution was stirred for 30 min and cooled to -70°C . The purple solid was collected and dried under vacuum. The yield was 0.17 g (58%).

Bis[bis(dimethylphosphino)methane]tetrakis(trifluoroacetato)dimolybdenum(II). Addition of bis(dimethylphosphino)methane (1.0 mL, 0.0074 mol) to tetrakis(trifluoroacetato)dimolybdenum (0.92 g, 0.0014 mol) in diethyl ether (30 mL) resulted in formation of a pink precipitate. The solid was collected, dissolved in chloroform (50 mL), and filtered. The filtrate was concentrated to ca. 30 mL and cooled (-10°C). The pink-red prisms were collected and dried under vacuum. The yield was 87% (1.1 g).

[Bis(diphenylphosphino)methane]tetrakis(trifluoroacetato)dimolybdenum(II). Tetrakis(trifluoroacetato)dimolybdenum (0.50 g, 0.00078 mol) and bis(diphenylphosphino)methane (0.60 g, 0.0015 mol) were intimately mixed, and the mixture was heated until a homogeneous solution formed. After the solution was cooled to room temperature, the solid was pulverized and washed with cold benzene (40 mL). The residue was dissolved in hot benzene, and the solution was filtered and slowly cooled to room temperature. The microcrystalline solid was collected and dried under vacuum. The yield was 0.42 g (52%).

Reaction of 1,2-Bis(dimethylphosphino)ethane with Tetrakis(trifluoroacetato)dimolybdenum(II). Addition of 1,2-bis(dimethylphosphino)ethane (1.0 mL, 0.0067 mol) to tetrakis(trifluoroacetato)dimolybdenum (0.76 g, 0.0012 mol) in diethyl ether (50 mL) resulted in a blue-purple solid and a pink solution. The volatile material was removed under vacuum. Chloroform (40 mL) was added to the residue, and the pink solution was separated from the blue residue by filtration. The blue residue was washed with chloroform (40 mL), and the extracts were combined, concentrated to ca. 20 mL, and cooled (-10°C). The 1:3 complex tris[1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum was isolated as pink-purple needles in 20% (0.26 g) yield. Dichloromethane (40 mL) was added to the blue residue, resulting in a blue solution and an orange solid which were separated by filtration. The orange residue was washed with dichloromethane (10 mL), and the blue filtrate and

washings were combined, concentrated to ca. 10 mL, and cooled (-10°C). The 1:2 complex bis[1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum was isolated as blue prisms. The yield was 45% (0.50 g). The orange residue was dissolved in absolute ethanol (15 mL), filtered, concentrated to ca. 5 mL, and cooled (-10°C), yielding the 1:1 complex [1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum(II) as orange crystals. The yield was 20% (0.19 g).

Acknowledgment. We thank the Regents of the University of California for a fellowship (G.S.G. and V.V.M.) and the National Science Foundation for a departmental grant for purchase of the nuclear magnetic resonance spectrometer used in this work.

Note Added in Proof. We have been informed that a crystal structure analysis of $(\text{CF}_3\text{CO}_2)_4\text{Mo}_2(\text{PET}_2\text{Ph})_2$ shows that this diadduct has structure C ($\text{L} = \text{PET}_2\text{Ph}$, Chart I) in the solid state: Lay, D. G.; Cotton, F. A., personal communication, Nov 26, 1979. The cone angle (136°)³⁷ and $\nu(\text{CO})$ of $\text{Ni}(\text{CO})_3\text{PET}_2\text{Ph}$, 2064 cm^{-1} , clearly show that PET_2Ph is a Class II phosphine in agreement with the X-ray analysis.

Registry No. $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PMe}_3)_2$, 72509-74-1; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PMe}_2\text{Ph})_2$, 72509-70-7; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PMePh}_2)_2$, 72453-45-3; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4[\text{P}(t\text{-Bu})_3]_2$, 72453-46-4; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4[\text{P}(\text{SiMe}_3)_3]_2$, 72453-47-5; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PEt}_3)_2$, 72509-73-0; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PPh}_3)_2$, 41772-59-2; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4[\text{P}(c\text{-Hx})_3]_2$, 72453-48-6; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{OPMe}_3)_2$, 72453-49-7; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{quin})_2$, 72453-50-0; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{PMe}_3)_3$, 72509-72-9; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Me}_2\text{PCH}_2\text{PMe}_2)_2$, 72467-43-7; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$, 72509-69-4; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_3$, 72509-68-3; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$, 72453-51-1; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$, 72509-71-8; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{py})_2$, 39176-71-1; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 35489-62-4.

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Photoelectron and Electronic Spectra of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$. Assignments from SCF-X α -SW Calculations

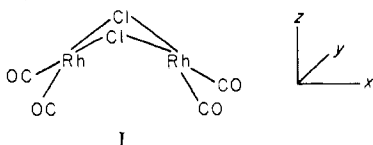
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Received June 25, 1979

Transition-state SCF-X α -SW calculations of ionization energies for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ are found to be in good agreement with the UV photoelectron spectrum. A detailed assignment of the spectrum and that of $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ is given, based on the calculations and He I/He II intensity variations. The X α -SW results also appear to agree closely with the recently reported electronic spectrum of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. This consistency with experiment lends credence to the simple orbital explanation, based on the calculations, which was previously given for the folded structure of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. Comparison of the X α -SW electronic structure with that since obtained for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ by an HF LCAO method reveals a number of similarities.

Introduction

J.G.N. and D.J.G. have previously² reported calculations of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ (I). Our chief goal at that time was to



present the simple orbital explanation revealed by the calculations for the observed folding of this type of molecule along

the bridging ligand axis. No spectroscopic data were then available with which to compare the calculations. J.F.N., R.J.S., and M.J.T. have now obtained the UV photoelectron spectra of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$, as part of a systematic comparison of such spectra for analogous CO and PF_3 complexes.³⁻⁵ In this paper we report these spectra and use the X α -SW predictions of ionization energies to assign them. We also comment on two recent papers which deal with the electronic structure of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, the first reporting the

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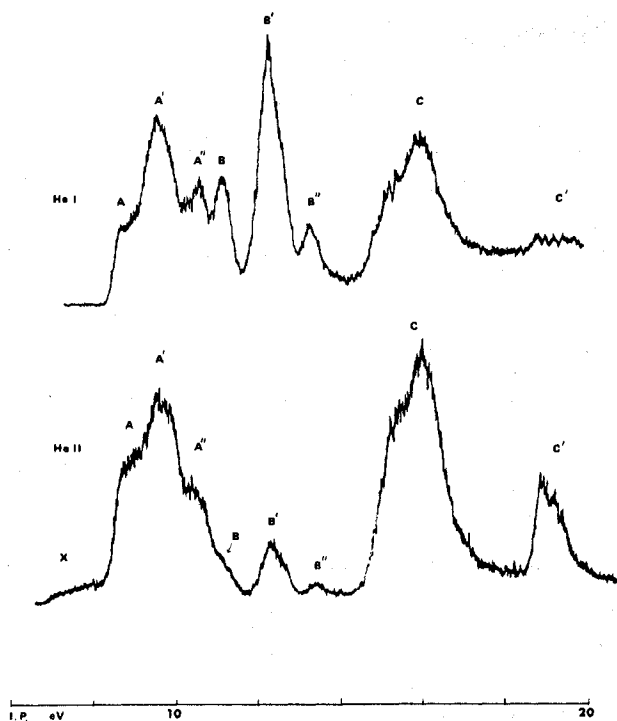


Figure 1. He I and He II photoelectron spectra of $[\text{RhCl}(\text{CO})_2]_2$.

electronic spectrum⁶ and the second HF LCAO calculations.⁷

Results and Discussion

Photoelectron Spectra—Empirical Assignments. Comparison of the intensity variations of bands in the photoelectron spectrum upon changing the ionizing radiation from He I (584 Å, 21.2 eV) to He II (304 Å, 40.8 eV) is fast becoming a powerful tool in the assignment of orbital ionizations. In general it is observed that ionizations from metal d orbitals show an enhanced relative intensity in the He II spectrum compared with that of the He I. In contrast, ionizations from halogen orbitals, particularly localized orbitals, drop in intensity relative to the He I spectrum. This technique has proved to be a very useful aid in assigning the photoelectron spectra of many systems, a few representative examples being MX_2 ($M = \text{Zn}, \text{Cd}, \text{Hg}; X = \text{Cl}, \text{Br}, \text{I}$)⁸ and $\text{MX}(\text{CO})_5$ [$M = \text{Mn}, \text{Re}; X = \text{Cl}, \text{Br}, \text{I}, \text{M}(\text{CO})_5$]⁹ and more recently $\text{M}'(\text{PX}_3)(\text{CO})_5$ ($M' = \text{Cr}, \text{Mo}, \text{W}; X = \text{F}, \text{Cl}, \text{Br}$)¹⁰ and $\text{M}''_3(\text{CO})_{12}$ ($M'' = \text{Os}, \text{Ru}$).¹¹

The He I and He II spectra of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ are shown in Figure 1, and the He I spectrum of $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ with that of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ for comparison is shown in Figure 2. The experimental orbital ionization energies are given in Table I. The three bands A, A', and A'' in the spectrum of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ show a relative gain in intensity upon changing from He I to He II ionizing radiation. From this and the position of these bands at lowest IP, A, A', and A'' are assigned as arising from orbitals of predominantly rhodium 4d character. The first band, A, shows the greatest intensity enhancement and is therefore most probably derived from an orbital or orbitals of highest rhodium character. Detailed assignments

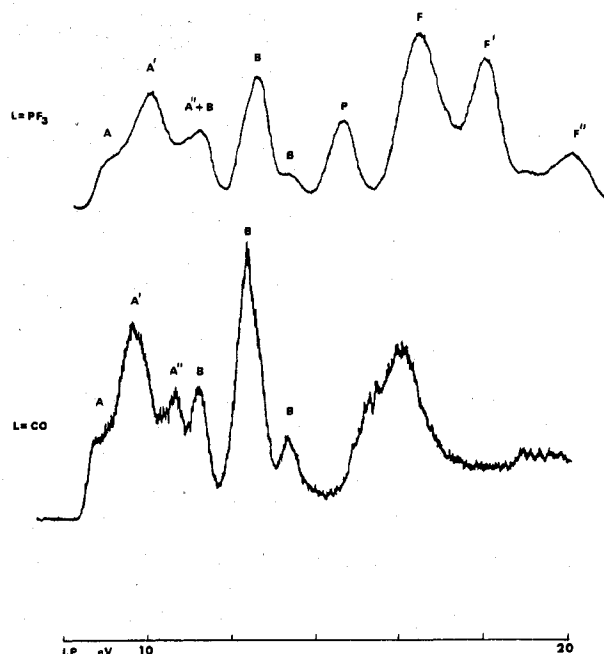


Figure 2. He I photoelectron spectra of $[\text{RhCl}_2\text{L}_2]_2$ ($L = \text{CO}, \text{PF}_3$).

Table I. Experimental Ionization Potential Data (eV) for $\text{Rh}_2\text{Cl}_2\text{L}_4$ Compounds ($L = \text{CO}, \text{PF}_3$)

label	assignt	L = CO	L = PF ₃
A	metal d	9.01	9.0
A'		9.7	10.0
A''		10.6	
B	chlorine 3p	11.29	} composite at 11.2
B'		12.39	
B''		13.41	
P	Rh-P σ	16.08	12.4
C	carbonyl orbitals	18.93	13.3
F	fluorine lone-pair		16.1
F'			17.7
F''		P-F σ	19.8

of this and the other bands are given in the next section.

The bands labeled B, B', and B'' are assigned as arising from orbitals of considerable chlorine character on the basis of their marked decrease in intensity in the He II spectrum. By analogy with the photoelectron spectra of other carbonyl complexes, the bands C and C' are unambiguously assigned to ionizations from the carbonyl orbitals. The band at highest IP, 18.9 eV, is only just detectable by He I radiation and is greatly enhanced in the He II spectrum. This behavior has been observed in other systems¹² and had been attributed to analyzer falloff in this region of the He I spectrum.

In all of the He II PE spectra, a He II β spectrum having a small fraction of the intensity of the He II α spectrum is superimposed at 7.6 eV to lower energy from the α spectrum. This arises from electrons ejected by He II β radiation of 48.4 eV present as a small fraction of the total He II radiation. The very broad band at lowest IP (ca. 8.3 eV) labeled "X" in the He II spectrum of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, which is not present in the He I spectrum, is assigned as being derived from the same orbital at 16.1 eV in the He II α spectrum but ionized by the He II β radiation, requiring an apparent IP of 8.5 eV (16.1–7.6 eV).

The above assignments are further confirmed by comparison of the He I PE spectra of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and the analogous trifluorophosphine complex $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$. The bands F, F',

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 (11) J. C. Green, E. A. Seddon, and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, **94** (1979).

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and F'' at 16.2, 17.7, and 19.8 eV, respectively, in $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ are a general feature of the photoelectron spectra of transition-metal PF_3 complexes and can be unambiguously assigned as being derived from the fluorine lone-pair and P-F σ orbitals.^{3,13} The band "P" in the spectrum of $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ has no counterpart in the spectrum of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and is readily assigned to the Rh-P σ -bond ionizations. It has an IP of 14.5 eV, which may be compared with the value of the phosphorus lone pair of free PF_3 of 12.3 eV. This stabilization of the phosphorus lone pair upon coordination has also been found to be a general feature of transition-metal trifluorophosphine complexes.^{3,13}

In all of the PF_3 complexes studied to date a net stabilization of the metal d orbitals is observed compared with their carbonyl analogues,³ and this has been attributed to the overall greater electron-withdrawing power of PF_3 compared with CO. Comparison of the ionization energies of the two $\text{Rh}_2\text{Cl}_2\text{L}_4$ systems shows that the bands assigned to the metal d orbitals, A, A', and A'' in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ all move to higher IP by 0.2 eV or more in $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$. If the bands B, B', and B'' are orbitals of high halogen content, they should be less sensitive to the nature of the ligand attached to rhodium. Comparison of the IP's B' and B'' of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ shows that there is only a difference of ca. 0.05 eV between the two. The first band, B, in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ is assumed to have remained at roughly the same IP in $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ and to have merged with the band A'' which moves to higher IP in $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$.

Preliminary results for the photoelectron spectra of related complexes of $\text{Rh}_2\text{X}_2\text{L}_4$ (L = Br, I; L = CO, PF_3) and $\text{Ir}_2\text{Cl}_2(\text{PF}_3)_4$ ¹⁴ are in full agreement with the above assignments and general trends in metal d or halogen ionization energies are observed to decrease in the order X = Cl > Br > I and L = PF_3 > CO.

Photoelectron Spectra—Detailed Assignments from Calculations. $X\alpha$ -SW valence-orbital ionization energies for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ were calculated by using Slater's transition-state procedure, which incorporates the effects of orbital relaxation. The resulting predictions are compared with the experimental spectrum in Table II. The agreement is good throughout the experimental range. This lends some confidence to the conclusions about bonding, which we presented previously,² and allows a more detailed assignment of the experimental peaks to particular orbitals.

Closely spaced ionizations which are expected to give rise to a single observed band are grouped together in Table II. The calculations predict that the first three bands in the PE spectrum should be of mainly Rh 4d character and of relative intensity 2:3:3 if all ionizations are equally probable. The $9b_1$ and $11a_1$ orbitals assigned to band A in Figure 2 are of "tilted d_{z^2} type" and are much more localized on the Rh atoms (average 91%) than the others (average 76%). This is in complete agreement with the larger observed enhancement of the A peak in the He II spectrum. The d-like orbitals ascribed to the A' and A'' peaks are at 45° to, or in, the $\text{RhCl}_2(\text{CO})_2$ planes.

The calculation predicts that there should be three bands arising from orbitals of mainly Cl 3p character, with approximate relative intensity 1:4:1, at higher IP than the three Rh 4d bands. The first of these orbitals ($8b_2$) is essentially localized on chlorine (86%) and may be assigned to B in Figure 1, since this band is almost undetected in the He II spectrum. The four orbitals assigned to B' have similar localizations (average 75% Cl) to the single $7a_1$ orbital assigned to B'' (71% Cl), and, consistently, B' is observed to be four to five times as intense as B''.

It is more difficult definitively to assign the CO region of the spectrum. The experimental resolution is poorer, and the

Table II. Detailed Assignments for $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ from $X\alpha$ -SW Calculations

exptl label	C_{2v} level	% Rh	main character	calcd ionization energy, ^a eV	exptl ionization energy, eV	calcd density	approx. obsd intens		
A	$9b_1$	92	Rh 4d	10.1	9.01	2	1		
	$11a_1$	90		10.2					
	$10a_1$	67		10.7					
A'	$8b_1$	74	Rh 4d	10.7	9.77	3	3		
	$9b_2$	70		(10.8)					
	$7a_2$	86		(11.1)					
A''	$9a_1$	72	Rh 4d	11.2	10.66	3	2		
	$7b_1$	86		(11.2)					
B	$8b_2$	7	Cl 3p	12.1	11.29	1	2		
	$6b_1$	14		(12.4)					
B'	$7b_2$	18	Cl 3p	(12.6)	12.39	4	5		
	$8a_1$	23		12.8					
	$6a_2$	9		(12.8)					
B''	$7a_1$	16	Cl 3p	13.3	13.41	1	1		
	$6b_2$	0		(14.0)					
	$5a_2$	1		(14.0)					
	$4a_2$	7		(14.2)					
	$5b_2$	8		(14.2)					
	$5b_1$	7		CO 1π				14.3	15.0 sh
	$6a_1$	8		(14.3)					
C	$5a_1$	15	CO 5σ	(14.6)	16.08				
	$4b_1$	13		(14.6)					
	$4a_1$	33		(16.6)					
	$3b_1$	33		16.7					
	$3a_2$	43		(17.3)					
	$4b_2$	45		(17.3)					
C'	$2a_2$	2	CO 4σ	(19.5)	18.93				
	$3b_2$	3		(19.5)					
	$3a_1$	1		19.6					
	$2b_1$	1		(19.6)					
	$2b_2$	3		(24.3)					
	$2a_1$	2		(24.5)				b	

^a Energies in parentheses are estimated from the ground-state eigenvalues and the explicitly calculated relaxation of levels of similar type. The accuracy of this procedure is estimated to be ca. 0.1 eV. ^b Outside range.

relative intensities are less reliable in this energy range. Moreover, the wide variation in CO character and symmetry of the calculated orbitals makes it difficult intuitively to predict their relative ionization probabilities. Nevertheless we see no obvious alternative to the assignment of C in Figure 1 to $1\pi/5\sigma$ orbitals, and C' to 4σ orbitals. The 5σ set is perhaps better designated as Rh-CO σ -bonding orbitals, in view of their substantial calculated rhodium character.

Electronic Spectrum of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. Recently the optical and MCD spectra of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ in the region 3.1–5.5 eV have been discussed in detail.⁶ There are two strong absorptions in this region, maximizing at 3.9 and 4.8 eV in CH_2Cl_2 with ϵ 8300 and ϵ 13 400, respectively. These are assigned by the authors on reasonable grounds to Rh $4d_{z^2} \rightarrow \text{CO } 2\pi$ and Rh $4d_{xz,yz} \rightarrow \text{CO } 2\pi$ transitions. They assume an energy level diagram with an orbital ordering like our own but with the small splittings due to dimerization averaged. The important feature of this diagram (both theirs and ours) for consideration of the spectrum is that the lowest unoccupied orbital is not mainly Rh $4d_{xy}$ but rather CO $2\pi/\text{Rh } 5p$.

We have not done transition-state calculations of the spectrum, but we can comment on the experimental results by using our ground-state energy diagram. Averaging out splittings due to dimerization, the ground-state energy differences for the $d_{x^2} \rightarrow 2\pi$ and $d_{xz,yz} \rightarrow 2\pi$ transitions (in our notation, $11a_1/9b_1 \rightarrow 12a_1/10b_1$ and $7b_1/7a_2/9b_2/10a_1 \rightarrow 12a_1/10b_1$) are 4.4 and 5.3 eV, respectively. Their calculated separation, 0.9 eV, is the same as that measured experimentally. Our experience with metal-to-ligand charge-transfer

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transitions is that allowing for orbital relaxation lowers the predicted excitation energies, generally by 0.3–0.5 eV. Thus transition-state excitation energies would probably be very close in absolute value to those observed experimentally. This additional evidence that the calculations are consistent with experiment further increases our confidence in our previously presented² conclusions about bonding in $\text{Rh}_2\text{Cl}_2(\text{CO})_4$.

HF LCAO Calculations of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ has recently been treated theoretically by a nonempirical Hartree-Fock LCAO method, using a pseudopotential to represent the core orbitals.⁷ Insofar as the discussion in this paper parallels our own work, there appears to be good agreement between the two calculations. In the folded conformation, a Mulliken population analysis of the LCAO orbitals yields charges of Rh^{-0.11}, Cl^{-0.13}, C^{+0.38}, and O^{-0.26}. We can obtain atomic charges from the $X\alpha$ -SW orbitals by normalizing the total number of valence electrons found within the atomic spheres to the total number possessed by the molecule;¹⁵ this gives Rh^{-0.09}, Cl^{-0.15}, C^{+0.46}, and O^{-0.34}. It is encouraging to see such close agreement between two very different methods of estimating charge.

The HF LCAO ordering for the mainly Rh 4d orbitals is identical with ours; there are minor differences in the ordering of the mainly Cl 3p orbitals. The other authors do not discuss the possibility of a weak Rh-Rh bonding interaction in the mainly Cl 3p orbitals, which we found to be the reason for the folding of the molecule. They do report a result which we did not, namely, that the folded form is calculated to be 4.1 kcal/mol more stable than the planar form. Given the close agreement between the two calculations in other respects, we

would not be surprised if an analysis of the HF LCAO mainly Cl orbitals also revealed an enhanced Rh-Rh interaction upon folding.

Experimental Section

$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ was prepared by the method of Wilkinson¹⁶ by reaction of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ with CO at ca. 90 °C. The sample was purified by vacuum sublimation at 80 °C (10^{-3} mmHg) and the IR spectrum checked prior to recording the He I and He II PE spectra. $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ was prepared from $\text{Rh}_2\text{Cl}_2(\text{C}_2\text{H}_4)_4$ ¹⁷ by treatment with PF_3 ¹⁸ and purified by sublimation at 20 °C (10^{-3} mmHg), and the ¹⁹F NMR and IR spectra were checked prior to recording the PE spectrum.

He I photoelectron spectra were recorded on a PS16 Perkin-Elmer spectrometer. The $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$ was vaporized into the instrument via an external inlet held at room temperature. $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ was vaporized internally at 60 ± 1 °C.

The spectra were recorded several times over a 6-h period and in all cases the reproducibility was excellent. No traces of free PF_3 or CO were observed under our conditions.

Acknowledgment. J.G.N., D.E.H., and D.J.G. thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support. J.G.N. is a Fellow of the Alfred P. Sloan Foundation for 1978–1980. J.F.N. thanks NATO for partial support of the work, and M.J.T. acknowledges the award of an SRC studentship. We thank Drs. J. C. Green and E. A. Seddon (Oxford University) for recording the He II spectrum and Professor M. F. Lappert for the use of the Sussex spectrometer.

Registry No. $\text{Rh}_2\text{Cl}_2(\text{CO})_4$, 14523-22-9; $\text{Rh}_2\text{Cl}_2(\text{PF}_3)_4$, 14876-98-3.

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Experimental Observation of the Effect of Crystal Field Splitting on the Electron Density Distribution of Iron Pyrite

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Received June 5, 1979

The electron density distribution of iron pyrite, FeS_2 , has been determined from high-resolution single-crystal X-ray diffraction measurements. Data collected with Ag $K\alpha$ radiation to a resolution of $(\sin \theta)/\lambda = 1.46 \text{ \AA}^{-1}$ were refined by conventional least-squares techniques to $R = 1.8\%$ and $R_w = 1.5\%$. Pyrite contains low-spin Fe^{2+} ions at 3 sites surrounded by a trigonally distorted octahedron of sulfur atoms. The crystal field splitting of the iron d orbitals is clearly revealed in the electron density maps by eight peaks of $1.2\text{--}1.6 \text{ e/\AA}^{-3}$ at 0.6 \AA from the iron directed into the faces of the octahedron as expected for a $(t_{2g})^6(e_g)^0$ electronic configuration. The slight trigonal distortion further splits the t_{2g} orbitals into a_g and e_g orbitals. Refinement of the X-ray data including multipole parameters that describe the deformations from a spherical charge distribution yields occupancies of 2.0 (1) and 3.2 (2) e in the a_g and lower e_g orbitals and 0.8 (2) e in the upper e_g orbitals. The electric field gradient at the iron nucleus calculated from the multipole parameters due to the trigonal distortion explains the observed magnitude of the quadrupole splitting in the Mössbauer spectra. The results are discussed in view of the observed diamagnetism of pyrite.

Introduction

In the presence of strong crystal fields, electrons in the partially filled d shell of a transition metal will preferentially occupy the lower energy orbitals, resulting in an aspherical distribution of the electron density about the metal atom. In recent years, techniques for the experimental determination of electron density distributions in crystals have been developed by using accurate X-ray (and neutron) diffraction measure-

ments.¹ While the number of experimental electron density studies on systems containing transition metals is still rather limited, several investigations have found aspherical features clearly related to partial occupancy of the d orbitals.² More

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