Electronic Structures of Tetrachlorobis(phosphine)niobium(IV) Complexes

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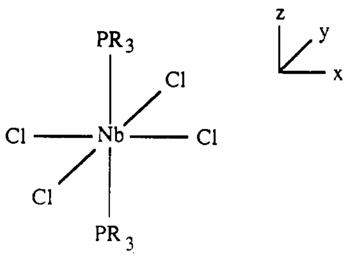
Previous interpretation of the EPR spectra of the d^1 pseudo-D_{4h} $NbCl_4(PR_3)_2$ complexes assumed that the unpaired electron resides in the $b_{2g}(d_{xy})$ orbital. In contrast, simple molecular orbital considerations suggest that the unpaired electron resides in the Jahn–Teller unstable $e_g(d_{xz},d_{yz})$ orbital. Ab initio self-consistent field calculations, which should be reasonably accurate for the relative energies of these various d^1 states, predict the ground state to be a Jahn–Teller-distorted ^2E_g. Although the predicted geometry of this state is in agreement with the X-ray structure, the calculated g values for this and other possible states are incompatible with the experimental g values. We conclude that the observed spectra are due to some other species.

Introduction

The group 5 tetrahalobis(phosphines) were first reported by Manzer[1] and Samuel et al.[2,3] In these pseudo-D_{4h} $MX_4(PR_3)_2$ (M = V, Nb, Ta) complexes, **1**, the single d electron could occupy either a $b_{2g}(d_{xy})$ or an $e_g(d_{xz},d_{yz})$ orbital, both of which arise from the splitting of the octahedral t_{2g} set. (The octahedral e_g set is split into $a_{1g}(d_{z^2})$ and $b_{1g}(d_{x^2-y^2})$ in D_{4h} symmetry.) The EPR spectra of these complexes have been interpreted on the assumption that the single electron is in the b_{2g} orbital, as in **2a**.[3] However, when the symmetry is reduced from O_h to D_{4h} in a complex such as this, where two weak π-acceptor ligands are axial and four π-donor ligands are equatorial, one expects the t_{2g} set to be split with the $e_g(d_{xz},d_{yz})$ lower in energy than the $b_{2g}(d_{xy})$ as shown in **2b**. This conclusion is supported by theory at all levels, from the least (e.g., simple crystal field, or EH) to the most (e.g., SCF–Xα, Hartree–Fock) sophisticated. Although a single electron in an e_g orbital would result in an EPR silent state, this ^2E_g would be subject to a Jahn–Teller distortion. In fact, the structure of more than one of these systems shows a distortion from pseudo-D_{4h} to pseudo-D_{2h} through a differentiation in the M–X bond lengths which occur as short and long trans pairs.[4] When the long trans pair is the y axis, the expected orbital structure for this lower symmetry is shown in **2c**.



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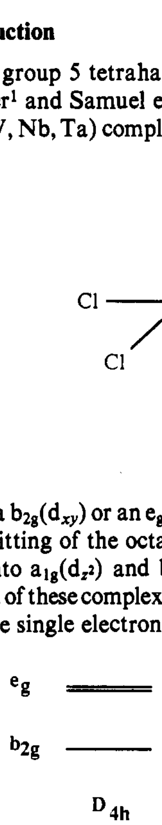
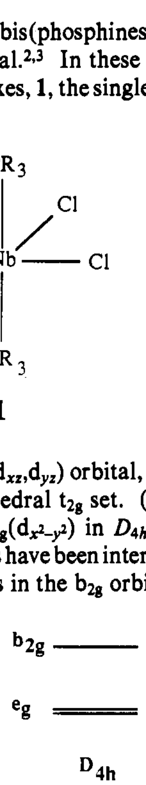
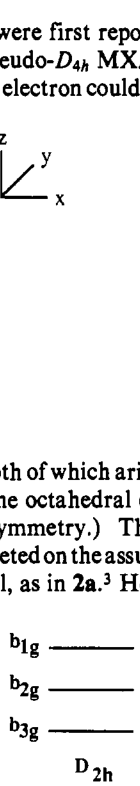


2a



2b



2c

In this work we sought the answers to several questions. What ground state is predicted by accurate ab initio calculations? Is the Jahn–Teller distortion of the ^2E_g state large enough to make the ground state appear nondegenerate? Can we predict the observed g values?

Theoretical Details

Models. The model compounds were $NbCl_4(PR_3)_2$ (PR_3 = PH_3, PMe_3). Except for those of the PR_3 group, all bond lengths and angles were optimized or fixed at previously optimized values. For PR_3 = PH_3, the P–H bond length was taken as 1.415 Å, and the H–P–H bond angle was taken as 98.7°. For PR_3 = PMe_3, the C–H bond length was 1.09 Å, the P–C bond length was 1.87 Å, and the H–C–H bond angle was 108.9°.

Basis Sets. Four basis set combinations were used. For the first basis set, basis set A, pseudopotentials[5] were used on all atoms (ECP2[5] for Nb) except for H. H was represented by a (21) basis set. Basis set B for Nb, (4322/4221/331), was derived from Huzinaga's basis set (43222/422/33)[6] by adding diffuse p and d functions.[7] The basis sets for Cl, P, and H were (3321/321), (3321/321), and (21), respectively. The Cl and P basis sets were developed from Huzinaga's (333/33) by splitting the 3s and 3p. Basis set C for Nb was Huzinaga's (43333/433/43) split into a (4332111/43211/4111), in which the 5s was removed, the 4s was split 2–1, and two s functions were added with exponents one-third of the previous exponent. Similarly, the 4p was split 2–1 and an additional function was added which was one-third of the previous exponent. The 4d was split completely. The basis set for Cl, P, and H was the same as that of basis set B. Basis set D was basis set B with polarization functions added to Cl and P with exponents of 0.514 and 0.340, respectively.[6]

Calculations. Ab initio calculations were performed using restricted Hartree–Fock (RHF) self-consistent field (SCF) open-shell techniques.[8] Since the possible ground states of these complexes are effectively one-electron problems, CI calculations should not be necessary to determine the order of the states, and SCF calculations should give correct energy splittings.[9] Configuration interaction with single excitations (CIS) was used to obtain higher Franck–Condon transition energies and charge-transfer states. Although SCF calculations are more accurate, CIS calculations are needed to obtain higher energy states with the same symmetry as lower energy ones. All calculations were performed on the Chemistry Department's Cray S-MP, on Texas A&M University's IBM 3090-200E computer, and at the Supercomputer Center of Cray Research,

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(1) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525.

(2) Samuel, E.; Labauze, G.; Livage, J. *Nouv. J. Chim.* **1977**, *1*, 93.

(3) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* **1980**, *19*, 1384.

(4) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592.

(5) (a) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026. (b) Wadt, W. R.; Hay, J. H. *J. Chem. Phys.* **1985**, *82*, 299.

(6) Huzinaga, S.; Andzelm, J.; Klobukowski, M.; Radzio-Andzelm, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

(7) Sargent, A. L.; Hall, M. B. *Inorg. Chem.* **1991**, *12*, 923.

(8) Roothaan, C. C. *Rev. Mod. Phys.* **1960**, *32*, 179.

(9) Simpson, C. Q., II; Hall, M. B.; Guest, M. F. *J. Am. Chem. Soc.* **1991**, *113*, 2898.

0020-1669/94/1333-1473$04.50/0

Table 1. Relative Energies for Low-Lying States of $NbCl_4(PR_3)_2$ in Basis Sets A–D (cm^{-1})

	A(H,opt)[a]	A(H,fix)[b]	A(Me)[c]	A(H,CIS)[b]	B(H)[b]	C(H)[b]	D(H)[b]
$^2A_{1g}$				29719			
$^2A_{1g}$	8706	19475	22062	20384	18496	18950	18741
$^2B_{1g}$	3881	4161	3112	5035	4580	4405	5349
$^2B_{2g}$		874	839	1783	804	839	874
$^2B_{3g}$	0	0	0	0	0	0	0

[a] Each state's geometry was optimized. [b] The Franck–Condon transition energies for the $^2B_{3g}$ optimized structure.

Inc., on a Cray Y-MP8I/8128-2,[10] with the GAMESS[11] and Gaussian92[12] sets of programs.

Results and Discussion

Geometry. The states of $NbCl_4(PH_3)_2$ were optimized with pseudo-D_{2h} symmetry using basis set A (ECP) with the P–H bond length and the H–P–H bond angle fixed. For the $^2B_{3g}$ state, the geometry relaxed to a structure with Nb–Cl bond lengths (2.458 Å) along the y axis being longer than those (2.386 Å) along the x axis. Thus, the ab initio calculations predict a 0.072-Å difference in Nb–Cl bond length as a result of the Jahn–Teller distortion. Experimentally, the difference in bond lengths was 0.017(5) Å for $PR_3 = PEt_3$[4] and 0.068(1) Å for $PR_3 = PEtPh_2$.[4] No geometry optimization is reported for the $^2B_{2g}$ state since its geometry and energy would relax to those of a structure equivalent to that of the $^2B_{3g}$ state in which the x axis and y axis are exchanged. As expected, the Jahn–Teller distortion is removed for the $^2B_{1g}$ and $^2A_{1g}$ states. The $^2A_{1g}$ state optimized with the Nb–P bond length (3.251 Å) being greater than the $^2B_{3g}$ and $^2B_{1g}$ Nb–P bond lengths (2.736 and 2.750 Å, respectively). This Nb–P bond elongation for the $^2A_{1g}$ state is expected since the unpaired electron occupies the σ-antibonding orbital. Thus, our calculations confirm a Jahn–Teller distortion that lowers the symmetry from D_{4h} to D_{2h} in agreement with the X-ray structure.

Models. Using the optimized geometry of the ground states ($^2B_{3g}$) for $NbCl_4(PH_3)_2$ and $NbCl_4(PMe_3)_2$, we performed open-shell SCF calculations with basis set A, an ECP basis set, for the Franck–Condon transitions to the $^2B_{2g}$, $^2B_{1g}$, and $^2A_{1g}$ states of each molecule. Both models gave the same splitting pattern as shown in **2c** (Table 1). The $^2B_{3g}$–$^2B_{2g}$ splitting is small and essentially identical for $NbCl_4(PH_3)_2$ and $NbCl_4(PMe_3)_2$. However, the $^2B_{3g}$–$^2B_{1g}$ splitting for $NbCl_4(PMe_3)_2$ is about 1049 cm^{-1} smaller than that for $NbCl_4(PH_3)_2$. The $^2B_{3g}$–$^2A_{1g}$ splitting is 2587 cm^{-1} greater for $NbCl_4(PMe_3)_2$ than for $NbCl_4(PH_3)_2$. Since PH_3 is a better π-acceptor than PMe_3,[13] both $^2B_{3g}$ and $^2B_{2g}$ are stabilized more effectively for $NbCl_4(PH_3)_2$ than they are for $NbCl_4(PMe_3)_2$.

CIS Energies. Configuration interaction with single excitations (CIS) was performed on the optimized geometry of $NbCl_4(PH_3)_2$ with basis set A. The $^2B_{3g}$–$^2B_{2g}$ splitting increased to 1783 cm^{-1} (see Table 1). The $^2B_{3g}$–$^2B_{1g}$ and $^2B_{3g}$–$^2A_{1g}$ splittings also increased slightly. Although CIS energies are probably not as accurate for the lower lying states, they give energies for higher energy states of the same symmetry as lower energy states. Standard SCF techniques are not able to calculate these higher transitions. For example, only a single $^2A_{1g}$ state could be calculated by promoting the unpaired electron to a higher lying a_{1g} orbital and completing a SCF calculation. With CIS, additional states with the same symmetry, i.e. both $^2A_{1g}$ states, can be found. For this second $^2A_{1g}$ state's energy the CIS results will be utilized for all calculations since the second $^2A_{1g}$ state cannot be found with the more accurate method of promoting an electron to a higher lying orbital and completing an SCF calculation.

Basis Set. To determine how sensitive these splittings are to changes in the basis set, several all-electron fixed-geometry calculations with $PR_3 = PH_3$ were completed. Since the all-electron calculation treats all electrons, it removes the effects of freezing the core electrons. With basis set B, the $^2B_{3g}$–$^2B_{2g}$ splitting was virtually unaffected and the $^2B_{3g}$–$^2B_{1g}$ splitting increased by only 489 cm^{-1} (Table 1).

Basis set C, which has a much more flexible Nb valence space, did not affect the $^2B_{3g}$–$^2B_{2g}$ splitting, nor did it greatly influence the $^2B_{3g}$–$^2B_{1g}$ splitting. In fact, the splittings fell between those for basis set A and basis set B.

Polarization functions for Cl and P were added to basis set B, giving basis set D (Table 1). Again, the $^2B_{3g}$–$^2B_{2g}$ splitting was essentially the same. When phosphorus d orbitals are added, the PH_3 group becomes a better π-acceptor. Thus, the $^2B_{3g}$ and $^2B_{2g}$ states are stabilized relative to $^2B_{1g}$, causing a larger $^2B_{3g}$–$^2B_{1g}$ splitting.

Method of Calculating *g* Values. Having determined that the Jahn–Teller $^2B_{3g}$ is the lowest energy state, we next addressed the question of whether our wave functions and energies can be used to reproduce the empirical g values. Usually g values are expressed quantum mechanically by perturbation theory[14] with the well-known formula

$$g_a = 2 - 2\sum_n \frac{|\langle \Phi_n | l_a | \Phi_0 \rangle|^2 \xi}{E_n - E_0} \qquad (1)$$

where E_n and E_0 are the energies at the nth state and the ground state, respectively, Φ_n and Φ_0 are the total wave functions of these states, l_a is the angular momentum operator along vector a, and ξ is the spin–orbit coupling parameter. Although this formula is often used to give an upper bound to g values, it is inadequate when energy differences are very small. Hence, for $NbCl_4(PR_3)_2$ we must diagonalize the full 10 × 10 (five d orbitals plus spin) crystal-field–spin–orbit coupling matrix with elements $\langle \Phi_a | \xi l \cdot s | \Phi_b \rangle$. Once completed, two degenerate vectors, one for each spin, will represent each state. Each pair of vectors is known as a Kramers doublet, $\Psi_\pm$.

To calculate the g_z value, one must evaluate all four combinations of

$$E = B\langle \Psi_\pm | l_z + 2s_z | \Psi_\pm \rangle H \qquad (2)$$

where $\Psi_\pm$ are Kramers doublets, B is the Bohr magneton, and H is the external magnetic field. For the four possible combinations, two of the elements will be zero while the other two will have equal but opposite energies. For example, by representing the Kramers doublet as $\langle +|$ and $\langle -|$, we find that

$$B\langle + | l_z + 2s_z | - \rangle H = B\langle - | l_z + 2s_z | + \rangle H = 0 \qquad (3)$$

$$B\langle - | l_z + 2s_z | - \rangle H = -B\langle + | l_z + 2s_z | + \rangle H \qquad (4)$$

Since by definition $\Delta E = g_z BH$, $g_z = 2\langle + | l_z + 2s_z | + \rangle$. Likewise,

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(11) Guest, M. H. *GAMESS*; SERC Daresbury Laboratory: Warrington WA4 4AD, U.K., 1992.

(12) Frisch, M. J.; Trunks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision B; Gaussian Inc.: Pittsburgh, PA, 1992.

(13) Sargent, A. L.; Hall, M. B. *Inorg. Chem.* **1992**, *31*, 317.

Table 2. Comparison of g Values for Different States for Basis Set A and R = H with Niobium Spin–orbit Coupling Parameters 750 cm^{-1} (750), 500 cm^{-1} (500), and Inclusion of Contributions from Phosphine and Chlorine (P+Cl)

	$^2B_{3g}$			$^2B_{2g}$			$^2B_{1g}$			
	750	500	P+Cl	750	500	P+Cl	750	500	P+Cl	exptl
g_z	0.743	1.033	0.912	3.136	2.916	3.026	1.504	1.694	1.690	1.959
g_x	1.244	1.544	1.468	1.027	1.392	1.261	2.432	2.298	2.343	1.912
g_y	1.394	1.603	1.517	1.486	1.674	1.635	2.313	2.223	2.259	1.912

the g_x value can be derived from the equations

$$B\langle -|l_x + 2s_x|+\rangle H = -B\langle +|l_x + 2s_x|-\rangle H \qquad (5)$$

$$B\langle +|l_x + 2s_x|+\rangle H = B\langle -|l_x + 2s_x|-\rangle H = 0 \qquad (6)$$

and the g_y value can be derived from corresponding equations.[14,15]

Although g values do not differ much from 2.00 for nondegenerate states, their deviation depends on the degree to which states interact with one another. Thus, a large deviation from 2.00 for a particular ground state means that the ground state interacts strongly with other states.[16] For a system like **2b** with a completely degenerate ground state, the g_z value is zero and the transitions corresponding to g_x and g_y values are forbidden.[16] However, if a Jahn–Teller distortion lifts this degeneracy, then g_z becomes greater than zero, and transitions corresponding to g_x and g_y would be allowed.

Calculated *g* Values. Calculated g values for all three states with several approximations for the spin–orbit coupling parameters and the experimental values[3] are shown in Table 2. The g values for the $^2B_{3g}$ ground state obtained were close to those expected for compounds with a single electron in a Jahn–Teller-distorted ^2E_g ground state.[16] Reducing the spin–orbit coupling parameter from its free-ion value (750 cm^{-1}) to account for the ligand interactions does not bring the g values into agreement with experiment.

When the percent character of each atom's contribution to the model is calculated and the contributions from chlorine spin–orbit coupling (588 cm^{-1}) and phosphorus spin–orbit coupling (269 cm^{-1}) are included, the g values are intermediate between those for Nb-only values of 750 and 500 cm^{-1}. It is clear that no reasonable spin–orbit coupling will bring the theoretical g values into agreement with the experimental ones. The Jahn–Teller distortion (0.072 Å) does not provide sufficiently large energy splittings to reproduce the experimental g values.

The g values of the other states (Table 2) are also in poor agreement with experimental g values. Thus, neither thermal averaging of the $^2B_{3g}$ and $^2B_{2g}$ nor thermal population of the $^2B_{1g}$ state could account for the experimental EPR spectra.

Charge-Transfer Contributions. From the CIS calculations, the first three charge-transfer state energies are 31 551, 32 307, and 32 691 cm^{-1}. These lowest charge-transfer states are primarily excitations from chlorine 3p_x and 3p_y orbitals at the shorter Nb–Cl distance to the niobium $b_{2g}(d_{xz})$ orbital. If we set each chlorine coefficient to its maximum value of 50% or $1/\sqrt{2}$ (normalized), the maximum contribution to the g value from the lowest lying charge transfer is merely 0.037. Since only 11% of the ground state is of chlorine character, this maximum contribution to the g value will decrease proportionately. Thus, none of the charge-transfer states are predicted to be low enough in energy to make "major" contributions to the g values. If the calculated g values were very close to the experimental one (i.e. differences of a few hundredths), inclusion of all the charge-transfer states would be important in producing agreement. However, this small perturbation is not large enough to bring the calculated g values into agreement with the experimental ones. These results confirm expectations that the mixing of charge-transfer states can change the g values, but their inclusion usually causes only a very small perturbation.[17]

Hyperfine Splitting Constants. With 88% of the molecular orbital being niobium d character, 11% being chlorine p character, and less than 1% being phosphorus character, it follows from our results that the spectra should show niobium hyperfine splittings with weak phosphorus hyperfine splittings. However, the hyperfine splittings are not very structure sensitive and are less sensitive to orbital splittings than to orbital character. Thus, interpretation of the hyperfine splittings is inconclusive evidence. The hyperfine splitting proves that the electron resides mostly on the niobium center and mixes slightly with two equivalent phosphorus centers, a result which would be true for a wide variety of compounds and structures.

Additional Structures. Since experimental methods used to make $MCl_4(PR_3)_2$ do not preclude the existence of other isomers in solution, two of these isomers were studied by using the same theoretical methods.

The cis isomer (two phosphine ligands cis to each other) was optimized with C_{2v} symmetry to give a $^2A_1$ ground state with an energy 4.22 kcal/mol lower than the ground-state energy of the trans isomer. The system had $^2A_2$ and $^2B_1$ excited states that were 2182 and 5098 cm^{-1} higher in energy than the ground state. For the $^2A_1$ ground state, the calculated g values are $g_z = 0.683$, $g_x = 1.82$, and $g_y = 1.23$. Although this isomer is energetically possible, it, too, fails to explain the observed g values. Replacement of PH_3 ligands with realistic PR_3 ligands would raise the energy of this isomer relative to that of the trans isomer.

Since a trigonal prism would have the d-orbital splitting "one below two", as needed to explain the EPR data, we optimized a trigonal prismatic structure with C_{2v} symmetry. The $^2A_1$ ground-state energy was 29.98 kcal/mol above that for the octahedral trans isomer, thus making it an unrealistic possibility.

Conclusion

Since our calculations correctly predict the geometry of the molecule, including the Jahn–Teller distortion, but not the observed EPR spectra, we are forced to conclude that the reported EPR spectra are not those of trans-octahedral $MX_4(PR_3)_2$. Two other isomers of $MX_4(PR_3)_2$ also fail to account for the observations. F.A.C. is investigating the experimental aspect of this dilemma.

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(14) Golding, R. M. *Applied Wave Mechanics*; D. Van Nostrand Co. Ltd.: New York, 1969.

(15) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.

(16) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill International Book Co.: New York, 1979.

(17) Garner, C. D.; Hillier, I. H.; Mabbs, F. E.; Taylor, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2258.