Singlet-Triplet Separations Measured by $^{31}P\{^1H\}$ NMR: Applications to Quadruply Bonded Dimolybdenum and Ditungsten Complexes

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A series of quadruply bonded dimolybdenum and ditungsten compounds $M_2X_4(PP)_2$ (M = Mo, W; PP = bidentate phosphine ligands; X = Cl, Br, I) with internal rotational angles χ varying from 0.0 to 69.4° have been studied. Their $^{31}P\{^1H\}$ NMR spectra are characterized by their temperature-dependent shifts and line widths that broaden with increasing temperature. A nonlinear, least-squares fit of this temperature dependence of the paramagnetic shifts for their NMR signals allows the evaluation of the singlet-triplet energy separation ($-2J$), the diamagnetic shift (H_{dia}), and the electron-nucleus hyperfine coupling constant (A). The singlet-triplet energy separations for all the compounds investigated are found to be in the range 1200-3000 cm^{-1}. It is now clearly established that the ground state remains $^1A_{1g}$ (δ^2) even at $\chi = 45°$, where $^3A_{2u}$ ($\delta\delta^*$) lies 1230 cm^{-1} above it. The δ-bond energy and electronic δ-barrier can also be experimentally estimated as 13.8 ± 0.5 kcal mol^{-1} and 10.3 ± 0.5 kcal mol^{-1}, respectively.

Introduction

The discovery of quadruple bonds between pairs of transition metal atoms in 1964[1] initiated a wave of research into metal-metal multiple bonds generally.[2] However, the quadruple bond has retained a position of special importance because of the fact that it contains one component, the δ bond, that has very unusual properties. The very weakness of the δ bond in these compounds is a great advantage, in that it opens to study the entire manifold of states to which a two-electron, two-orbital bond gives rise.

In a recent paper[3] the results of a theoretical treatment of $Mo_2Cl_4(PH_3)_4$ as a function of the angle of internal rotation (χ) away from the eclipsed conformation were reported. Quantitative results were presented for the behavior of the entire δ manifold, namely the $^1A_{1g}$ ground state and the three excited states, $^3A_{2u}$, $^1A_{2u}$, and $^1A_{1g}$ (δ^{*2}). One of the most interesting features of these results was the predicted variation of the energy separation of the ground singlet state and the $^3A_{2u}$ state.

At the same time, we have been engaged in an effort to obtain direct experimental values of the $^1A_{1g}$-$^3A_{2u}$ energy separation as a function of χ by employing the $Mo_2X_4(PP)_2$ compounds (where PP represents a bridging bidentate phosphine). A direct spectroscopic measurement appears to be impossible (and has not, in any case, been accomplished) because of the extreme weakness of the electronic transition. However, as we have already shown in a preliminary report,[4] $^{31}P\{^1H\}$ NMR measurements can, in many cases, be employed to determine the position of a low-lying triplet state, conveniently and accurately, for compounds of this type as well as others. We present here a detailed report of our measurements and compare them with the values previously calculated.[3]

Experimental Section

All syntheses, manipulations, and NMR studies were carried out under an inert atmosphere using standard Schlenk techniques or a glovebox. THF and toluene were dried over and freshly distilled from potassium/sodium benzophenone ketyl prior to use. CH_2Cl_2 was dried over phosphorus pentoxide.

Synthesis. The compounds $Mo_2Cl_4(PP)_2$ (PP = depe,[5] dmpe,[6] dmpm,[7] dppe,[8] dppee,[9] dppp,[10] *S,S*-dppb[11]), $Mo_2X_4(PP)_2$ (X = Br,[12] I;[13] PP = dppe) and $W_2Cl_4(PP)_2$ (PP = dppm,[14] dppe[15]) were prepared according to the published procedures.

Spectroscopic Studies. $^{31}P\{^1H\}$ NMR studies were carried out on approximately 5-25 mg of powder or crystalline samples dissolved in a suitable solvent system, which was a THF/CH_2Cl_2 mixture (proportions depending on temperature) for all but one compound. All variable-temperature $^{31}P\{^1H\}$ NMR spectra, except that for the complex $W_2Cl_4(dppm)_2$, were obtained at 80.96 MHz on a Varian XL-200E spectrometer with 5 or 10° intervals over the widest possible temperature range and a pre-aquisition delay of 10 min. A total of 400 transients were recorded at each temperature. $^{31}P\{^1H\}$ NMR spectra for $W_2Cl_4(dppm)_2$ dissolved in a CH_2Cl_2/toluene mixture were obtained at 161.92 MHz on a Varian 400 MHz spectrometer with all other conditions the same. Chemical shifts are referenced to external 85% H_3PO_4 as usual.

The electronic absorption spectra for these compounds were recorded in the same solvent as the ^{31}P NMR spectra on a Cary 17 spectrophotometer. The energy of the 0 → 0 vibronic component is estimated as about $3\nu_{Mo-Mo}$ below the band maximum. From tabulated values[2] (which vary from 330 to 400 cm^{-1}) we thus use a correction of 1000 ± 100 cm^{-1}. Note that even the complete loss of the δ bond has only a small (ca. 50 cm^{-1}) effect on ν_{Mo-Mo}.

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Results and Discussion

Variable-temperature $^{31}P\{^1H\}$ NMR spectra of quadruply bonded $M_2X_4(PP)_2$ (M = Mo, X = Cl, PP = depe, dmpe, dppe, dppee, dppp, *S,S*-dppb; M = Mo, X = Br, I, PP = dppe; M = W, X = Cl, PP = dppm, dppe) are characterized by their temperature-dependent upfield chemical shifts and line widths that broaden with increasing temperature. By assuming a contact shift model, neglecting the influence of excited states of higher energy than the lowest triplet state, and ascribing this temperature dependence of the paramagnetic shift of the NMR signals to the singlet-triplet spin equilibrium, one can use the NMR data to calculate the hyperfine coupling constant (A) between the electron and the nucleus in question, the diamagnetic resonance position (H_{dia}) for the phosphorus site, and the singlet state–triplet state energy level separation ($-2J$) from eq 1.[16-20]

$$H_{obs} = H_{dia} + \frac{2g\beta H_0 A}{(\gamma_P/2\pi)kT}(3 + e^{2J/kT})^{-1} \qquad (1)$$

H_{obs} is the observed position of the ^{31}P resonance, H_{dia} is the position that the same nucleus would have in an equivalent diamagnetic environment, T is the absolute temperature, g and β are the Landé splitting factor and Bohr magneton for an electron, and the remainder of the terms have their usual meaning. The metal-centered dipolar contributions (ΔH^M) to the paramagnetic shifts in this system may be estimated by utilizing eq 2,[18-21,31]

$$\frac{\Delta H^M}{H_0} = \frac{2\beta^2}{3kTR^3}(g_\parallel{}^2 - g_\perp{}^2)(1 - 3\cos^2\omega)(3 + e^{2J/kT})^{-1} \qquad (2)$$

where ω is the angle between the electron–nucleus vector and the metal–metal bond axis of the compound and R is the electron–nucleus distance. The metal-centered dipolar shifts, estimated using eq 2, the crystallographic data, and the estimated values for $g_\parallel$ and $g_\perp$, are too small to contribute significantly to the observed paramagnetic shifts and were subsequently ignored.

The values of $-2J$, H_{dia}, and A are calculated using a multiple parameter, nonlinear least-squares procedure to fit eq 1 to the variable-temperature NMR data. Figure 1 displays a typical plot of resonance frequency versus temperature, namely, that of $Mo_2Cl_4(dppe)_2$. Calculated parameters, including A, H_{dia}, and $-2J$, for all compounds investigated are listed in Table I, along with the corresponding average torsional angle χ calculated by averaging the two P–Mo–Mo–P and two X–Mo–Mo–X angles obtained from the structural determination[5-15] and the estimated 0 → 0 vibronic component of the $^1\delta^2$–$^1\delta\delta^*$ transition determined from the electronic spectral data tabulated elsewhere. A negative "A" value, ranging from 50 to 220 MHz in magnitude, is characteristic of the upfield shift of the signal with increasing temperature for Mo_2^{4+} and W_2^{4+} compounds. The singlet–triplet separations for all the compounds investigated are found to be in the range 1200–3000 cm⁻¹. Measurements for systems outside this range could not be made because of shifts being too small (> 3000 cm⁻¹) or lines becoming too broad (< 1200 cm⁻¹).

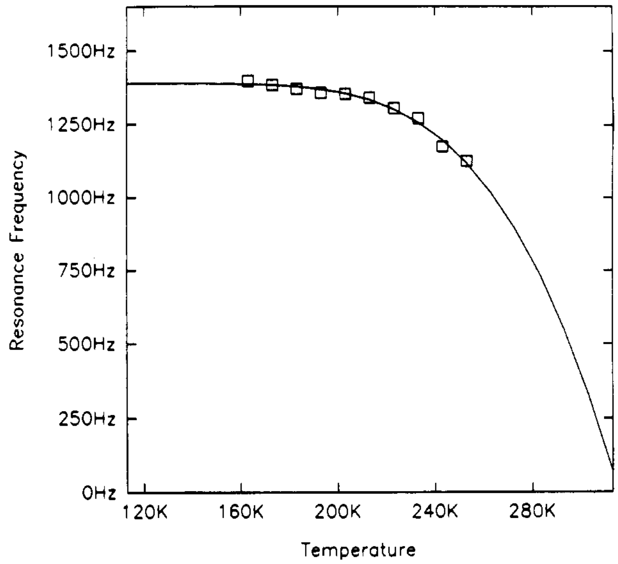

Figure 1. Representation of a typical set of data obtained for $Mo_2Cl_4(dppe)_2$ showing the temperature-dependent chemical shift of the phosphorus atoms bonded to the Mo atoms as well as the line fitted to these data with eq 1.

Table I. Summary of Experimental Data for $M_2X_4(PP)_2$ Compounds

compounds	A (MHz)	H_{dia} (Hz)	$-2J$ (cm⁻¹)[a]	χ angle (deg)	$^1\delta^2 \rightarrow {}^1\delta\delta^*$ (cm⁻¹)
$Mo_2Cl_4(dmpm)_2$				0.0	15 556
Mo_2Cl_4(*S,S*-dppb)$_2$	−83.63	2641	−2240 (90)	24.7	12 513
$Mo_2I_4(dppe)_2$	−210.1	1055	−2050 (10)	26.8	10 628
$Mo_2Cl_4(depe)_2$	−53.8	1218	−1320 (20)	41.4	11 690
$Mo_2Cl_4(dmpe)_2$	−71.6	−136	−1290 (50)[b]	50.0	11 484
$Mo_2Br_4(dppe)_2$	−79.3	1391	−1670 (40)	58.9	11 658
$Mo_2Cl_4(dppe)_2$	−65.0	1390	−1650 (40)	59.5	12 123
$Mo_2Cl_4(dppee)_2$	−114.6	1482	−2250 (20)	64.5	12 812
$Mo_2Cl_4(dppp)_2$	−193.4	2328	−2980 (20)	69.4	13 706
$W_2Cl_4(dppm)_2$	−110.4	2997	−2650 (20)	17.3	12 568
$W_2Cl_4(dppe)_2$	−61.6	1311	−1400 (60)	58.7	10 765

[a] Numbers in parentheses are esd's in the least significant figure. [b] A value of ~500 cm⁻¹ was obtained from magnetic susceptibility data.[28]

It has been known[22-25] that as the torsional angle χ increases from 0 to 45°, the overlap of the dδ orbitals goes, linearly with cos 2χ, to zero, and the separation of the $^1\delta^2$ ground state from the $^3\delta\delta^*$ state should decrease. The experimental data given here establish the behavior of the $^1\delta^2$–$^3\delta\delta^*$ separation for a series of $M_2X_4(PP)_2$ compounds. As the torsional angle χ changes from 24.7 to 41.4° and then to 69.4°, the $-2J$ value decreases from 2240 cm⁻¹ to 1320 cm⁻¹ then increases to 2980 cm⁻¹. The extrapolated values obtained from a nonlinear least-squares curve fitting are 4840, 1230, and 4840 cm⁻¹ for χ = 0, 45, and 90°, respectively (Figure 2). This result is better than our preliminary result[4] since more data have been used in the nonlinear least-squares curve fitting over a wider range of χ values. Previously, the energy separation of a low-lying triplet state from a diamagnetic ground state has been estimated by measurements of magnetic susceptibility over a broad temperature range (typical 5–300 K).[26-29] However, these measurements require large quantities of pure samples and sophisticated susceptometers (e.g. SQUIDS), in order to produce accurate results. There has been only one application of this method to a quadruply bonded compound,[28] and only a crude result was obtained. The variable-

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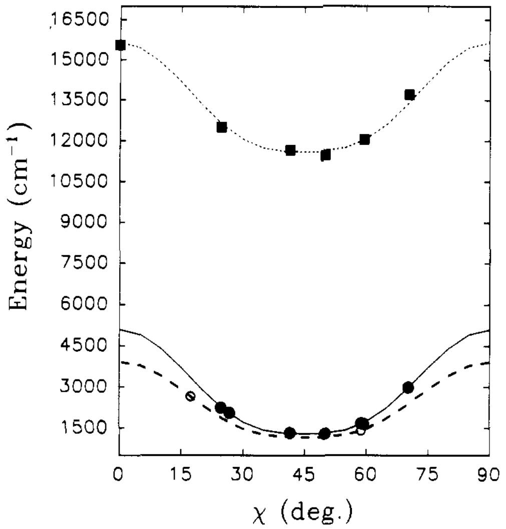

Figure 2. Plot of the $^1(\delta^2)$–$^3(\delta\delta^*)$ energy difference for $Mo_2X_4(PP)_2$ (solid cirles) and $W_2X_4(PP)_2$ (hollow circles) and $^1(\delta^2)$–$^1(\delta\delta^*)$ energy transition for $Mo_2X_4(PP)_2$ (solid squares) versus torsional angle (χ) as well as corresponding nonlinear least-squares fitting lines.

temperature $^{31}P\{^1H\}$ NMR method we use here is a convenient, sensitive, widely applicable alternative method for measuring this type of energy separation in cases where the energy separations are comparable to kT.[30,31]

The energy separation of $^1\delta^2$–$^1\delta\delta^*$ has also been measured for this series of compounds using the 0 → 0 vibronic component in electronic spectra (Table I). It also decreases from 15 556 to 11 690 cm^{-1} as χ changes from 0 to 41.4° and then increases to 13 706 cm^{-1} when χ increases to 69.4°. The extrapolated values for χ = 45 and 90° are 11 540 and 15 594 cm^{-1}, respectively (Figure 2).

The magnitude of the singlet-triplet gaps of ditungsten compounds, as expected, falls below those of the dimolybdenum compounds with the same torsional angles (Figure 2). This is due to the spin–orbital coupling that exists in ditungsten compounds. Further investigation of $W_2Cl_4(PP)_2$ type compounds with ligands other than dppm and dppe were not feasible because of a lack of satisfactory syntheses for compounds other than the two studied.

Several interesting and important points can be established from the above results. First, the two energy separations, $^1\delta^2$–$^3\delta\delta^*$ and $^1\delta^2$–$^1\delta\delta^*$, maintain an essentially constant difference, ca. 10 500 cm^{-1}. This should be twice the exchange integral K, which is the energy required, for two atoms, X, infinitely far apart, to convert $X^\bullet + X^\bullet$ to $X^+ + X^-$, and one would expect this to be essentially constant. Second, the persistence of configuration interaction, mainly, but not limited to that between the $^1\delta^2$ and $^1\delta^{*2}$ states, assures that the ground state remains $^1\delta^2$ even at χ = 45°, where $^3\delta\delta^*$ lies 1230 cm^{-1} higher. Third, the δ-bond energy and δ-barrier (i.e., the pure electronic contribution of the δ bonding to the rotational barrier about the Mo–Mo quadruple bond) can be experimentally estimated as 4840 cm^{-1} or 13.8 kcal mol^{-1} (theoretical result: 16.8 kcal) and 3610 cm^{-1} or 10.3 kcal mol^{-1} (theoretical result: 12.1 kcal), respectively, with an approximate uncertainty in each one of 0.5 kcal mol^{-1}. As shown in Figure 3, the δ-bond energy is defined as the least costly way to annul the δ-bond within the fixed molecular geometry, and the δ-barrier corresponds to the lowest rise in energy entirely due to the loss of δ bonding from an eclipsed conformation to the staggered conformation.[3,32] Previous attempts[28,29] to estimate the δ-barrier in a somewhat similar manner gave about 15 kcal mol^{-1}. In one case the result was flawed by "a crude fit of the data" and in both cases by the unjustified assumption that the energy of the ground state at χ = 45° would be that of the $^3\delta\delta^*$ state. We have taken the extrapolated $^1\delta^2$–$^3\delta\delta^*$ energies at χ = 0° (4840 cm^{-1}) and 45° (1230 cm^{-1}) and use the difference (3610 cm^{-1}) to obtain 10.3 kcal mol^{-1}. For the δ-bond energy, the $^1A_{1g}$–$^3A_{2u}$ energy difference at χ = 0° is used.

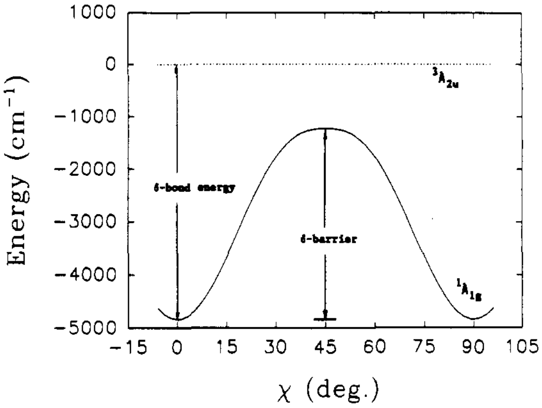

Figure 3. Definitions for δ-barrier and δ-bond energy.

Concluding Remarks

Previously, the only method used to estimate the energy separation of a low-lying triplet state from a diamagnetic ground state in M–M quadruple bonds has been by measurements of magnetic susceptibility over a broad temperature range. This is laborious and time-consuming, and the results are sensitive to even small amounts of impurities. We report here a convenient, accurate, widely applicable alternative method to determine the singlet–triplet separations by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy. A series of quadruply bonded dimolybdenum and ditungsten compounds $M_2X_4(PP)_2$ (M = Mo, W; PP = bidentate phosphine ligands; X = Cl, Br, I) with internal rotational angle χ varying from 0.0 to 69.4° have been studied. It has been shown that the ground state remains $^1A_{1g}$ (δ^2) even at χ = 45°, where $^3A_{2u}$ ($\delta\delta^*$) lies 1230 cm^{-1} above it. The δ-bond energy and electronic δ-barrier can also be experimentally estimated as 13.8 ± 0.5 kcal mol^{-1} and 10.3 ± 0.5 kcal mol^{-1}, respectively. These results are in very good agreement with theoretical results recently obtained in this laboratory.[3]

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