related example[46] is the reaction between the methyl radical and $CH_3Ni(cyclam)^{2+}$ to yield ethane ($k = 4.7 \times 10^7\ M^{-1}\ s^{-1}$) and the reaction of $Co(nta)R^{2+}$ complexes.[9d]

Reaction of Alkylcobalt Complexes with Cr^{2+}. The kinetic studies (Table VII) clearly show that there is a bimolecular reaction between these species (eq 6). The rate constants are dependent on the size of the coordinated alkyl group; the remarkable decrease of the rate constant from methyl to ethyl to *n*-propyl indicates the severe steric hindrance in the transition state. The mechanism appears to consist of an S_H2 displacement at the saturated carbon atom[16] and has been discussed in the literature.

Acknowledgment. This work was supported by the U.S. Department of Energy, Chemical Sciences Division, under Contract W-7405-Eng-82. We are grateful to Dr. Lee M. Daniels of the Iowa State Molecular Structure Laboratory for the crystallographic data and refinement.

Supplementary Material Available: Tables of atomic coordinates, crystallographic data, least-squares planes, positional parameters, and general displacement parameters for $[(H_2O)L^1CoCH_2Cl](ClO_4)_2$ and a stereoview of *N-rac*-$(H_2O)L^1CoCH_2Cl^{2+}$ (12 pages); a table of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Contribution from the Inorganic and Structural Chemistry and Radiochemical Diagnostics Groups (INC-4 and INC-11),
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Spectroscopy and Structure of Quadruply Bonded Complexes under Extreme Pressure ($Re_2X_8^{2-}$, $Mo_2Cl_4(PMe_3)_4$)

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Application of pressure (up to 150 kbar, where 1 kbar = 986.9 atm = 0.1 GPa) to solutions of $Re_2X_8^{2-}$ (X = F, Cl, Br) and $Mo_2Cl_4(PMe_3)_4$ results in smooth, continuous changes in experimental observables related to metal–metal bond length and, for the Re complexes, torsional angle (X–Re–Re–X dihedral angle). Resonance Raman studies show that increasing pressure engenders an increase in the frequency of the metal–metal stretching mode for all of the species studied, and this change is empirically correlated with a decrease in metal–metal bond length. Large red shifts in the energy of the $^1(\delta \rightarrow \delta^*)$ transitions with increased pressure for $Re_2Br_8^{2-}$ and $Re_2Cl_8^{2-}$, in contrast to the relative insensitivity of $Re_2F_8^{2-}$ absorption and $Mo_2Cl_4(PMe_3)_4$ fluorescence transitions, imply a tendency for the former complexes to distort torsionally from an eclipsed configuration toward a staggered configuration due to pressure-induced steric repulsion of the chloride and bromide ligands. Integrated absorption intensities further show that, at higher pressures, even $Re_2F_8^{2-}$ undergoes some torsional distortion, whereas the steric repulsion of adjacent phosphines located at a 90° dihedral angle on opposite Mo atoms prevents $Mo_2Cl_4(PMe_3)_4$ from distorting along the torsional coordinate.

Introduction

The nature and properties of the δ-component of the metal–metal quadruple bond have been the subjects of numerous experimental investigations in the 25 years following the discovery of this class of dinuclear complexes.[1] While most studies along these lines have been directed at those dimers that possess the eclipsed geometry (limiting D_{4h} symmetry), which is the structural signature of the $\sigma^2\pi^4\delta^2$ ground-state electronic configuration, significant insight into the δ-bond has recently been gleaned from comparisons of the structural and electronic properties of these species with those of compounds possessing noneclipsed (limiting D_{4d} symmetry) geometries. Such comparisons are informative because the $\sigma^2\pi^4$ triple-bond core is cylindrically symmetric and remains intact upon rotation about the metal–metal bond; differences among the properties of these two sets of complexes are thus due to variations in δ-overlap. Structural,[2] magnetic,[3] and spectroscopic[3-5] studies of compounds of the β-$Mo_2X_4[R_2P(CH_2)_nPR_2]_2$ type, where ligand-backbone strain of the bridging diphosphines induces torsional distortion about the metal–metal bond, have been particularly important in this regard and have yielded estimates of the δ-bond contribution to the metal–metal bond length, the energy of the singlet–triplet $\delta\delta^*$ excited-state splitting, and the relative energy contributions of the one- and two-electron terms to the $^1(\delta \rightarrow \delta^*)$ transition energy.

An alternate approach to using binucleating ligands to induce metal–metal torsional distortions, and one that in principle allows for the production of a continuum of rotational geometries for a single complex, involves the application of high external pressure to quadruply bonded dimers. Three investigations along these lines, all of which focus on the $Re_2X_8^{2-}$ class of quadruply bonded dimers, have recently been reported.[6-8] Unfortunately, a concensus on the interpretation of the effect of pressure on the molecular and electronic structures of these ions has failed to emerge. In the first study of this type,[6] Carroll, Shapley, and Drickamer (CSD) reported that the $^1(\delta \rightarrow \delta^*)$ transition of crystals of $[n\text{-}Bu_4N]_2[Re_2I_8]$ in poly(methyl methacrylate) lost intensity and slightly red-shifted with increasing pressure and that a new band, attributed to the $^1(\delta \rightarrow \delta^*)$ transition of a new isomer, appeared and concomitantly increased in intensity ~1100 cm^{-1} to lower energy. This observation, coupled with an analogous one of smaller

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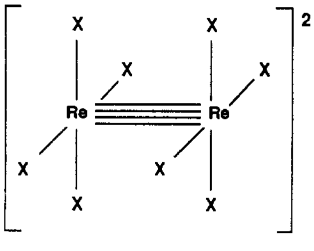
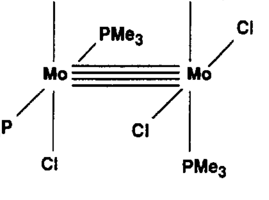
magnitude for $[n\text{-Bu}_4N]_2[Re_2Br_8]$, led the authors to postulate the existence of a pressure-dependent equilibrium between eclipsed (X–Re–Re–X torsion angle $\chi = 0°$; D_{4h}) and staggered ($\chi = 45°$; D_{4d}) isomers. The results of a subsequent study from this laboratory on the pressure dependence of the electronic and Raman spectra of $Re_2Cl_8^{2-}$ in dichloromethane solution contrasted sharply with these findings.[7] We observed the ${}^1(\delta \rightarrow \delta^*)$ transition to continuously red-shift with increasing pressure at nearly double the rate reported for the iodo derivative, with the intensity of the band *increasing* slightly between 0 and 20 kbar and steadily decreasing thereafter; no new transitions were observed. In addition, the Re–Re stretching frequency was found to increase monotonically from 275 to 357 cm^{-1} between ambient pressure and 142 kbar. We proposed that these spectral shifts were a manifestation of a continuous decrease in the Re–Re distance of $Re_2Cl_8^{2-}$ as a function of pressure combined with a pressure-dependent, steric-repulsion-induced torsional distortion. Because of the differences in both the complexes studied and the pressure-transfer media employed, the reasons for the different behaviors reported in these two studies could not be evaluated.

A second high-pressure study of quadruply bonded dimers by CSD[8] reports the changes in ${}^1(\delta \rightarrow \delta^*)$ transition energy of $Re_2X_8^{2-}$ (X = Cl, Br, I) for both crystals suspended in poly(methyl methacrylate) and as dichloromethane and acetonitrile solutions, as well as the spectral shifts of $Re_2X_4(O_2CBu^t)_2$ (X = Cl, Br) in acetonitrile solution and of crystalline $M'_4Mo_2X_8$ (M′ = K, X = Cl; M′ = NH_4, X = Br); ${}^1(\delta \rightarrow \delta^*)$ intensities were not included in this publication nor were vibrational data reported. On the basis of the observation that, except in high-dielectric media, the ${}^1(\delta \rightarrow \delta^*)$ transition is observed to red-shift with pressure, in contrast to the strong blue shift observed for the ${}^1(\sigma \rightarrow \sigma^*)$ transitions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$,[9] CSD[8] concluded that van der Waals interactions between the δ^* orbital and the surrounding medium were the dominant factor in determining the pressure dependence of the ${}^1(\delta \rightarrow \delta^*)$ transition energies, with pressure-induced changes in the splitting of the one-electron δ and δ^* levels being of lesser importance. The opposite ordering of effects had previously been proposed for the $M_2(CO)_{10}$ systems.[9] The pressure-dependent two-isomer equilibrium reported for $[n\text{-Bu}_4N][Re_2Br_8]$ and $[n\text{-Bu}_4N][Re_2I_8]$ in CSD's original paper[6] was not mentioned as being observed for any of the new complexes examined.

Our interest in resolving the differences in the interpretations set out above led us to extend our earlier study. Our specific aims were to determine the generality of our original observations of the pressure dependence of the spectroscopic properties of $Re_2X_8^{2-}$ and, in addition, to test our hypothesis of pressure-induced metal–metal bond rotation. To this end we have examined, and now report, the pressure dependence of the electronic and resonance Raman spectra of the $Re_2X_8^{2-}$ (A; X = F, Cl, Br) ions as well as that of the complex $Mo_2Cl_4(PMe_3)_4$ (B), whose D_{2d} interlocked phosphine-ligand geometry[10] contributes considerable torsional rigidity.[11,12]



A



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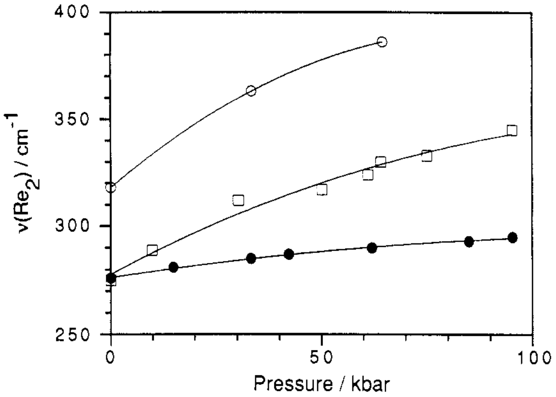

Figure 1. Pressure dependence of $\nu(Re_2)$ for $Re_2X_8^{2-}$ in dichloromethane [X = F (○), Cl (□), Br (●)].

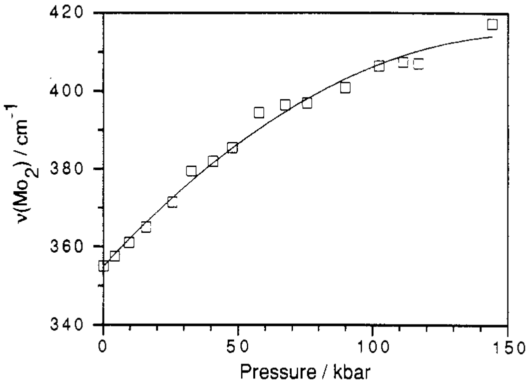

Figure 2. Pressure dependence of $\nu(Mo_2)$ for $Mo_2Cl_4(PMe_3)_4$ in cyclohexane.

Experimental Section

The complexes $[(C_4H_9)_4N]_2[Re_2X_8]$ (X = F,[13a] Cl,[13b,c] Br[13d]) and $Mo_2Cl_4(PMe_3)_4$[10] were prepared and purified by standard procedures. High-pressure measurements were carried out on dilute solutions of $Re_2X_8^{2-}$ and $Mo_2Cl_4(PMe_3)_4$ in dry[14] dichloromethane (~5 mM) and cyclohexene (~3 mM), respectively. Solutions of $Mo_2Cl_4(PMe_3)_4$ were prepared and sealed in the diamond cell under an inert atmosphere in a Vacuum Atmospheres glovebox.

Pressures from 0 to 150 kbar (1 kbar = 986.9 atm = 0.1 GPa) were achieved in a Merrill-Bassett diamond anvil cell (diamond culet ca. 0.6 mm from side to side) with Inconel gaskets (0.10 mm thick, 0.3-mm inside diameter) and determined by using the pressure-sensitive luminescence of ruby $\{P\ (\text{kbar}) = 1.33[14402.2 - (\text{emission maximum in } cm^{-1})]\}$[15] as an internal standard. Because of strong interference from the fluorescence of $Mo_2Cl_4(PMe_3)_4$, the pressure measurement for this compound employed the 801.3-cm^{-1} Raman-active breathing mode of cyclohexane. The pressure dependence of the frequency of this mode, which was determined separately by using ruby as a standard, was found to obey a linear ($R = 0.99$) relationship valid to at least 80 kbar: $P\ (\text{kbar}) = 1.72[\nu\ (cm^{-1}) - 801.3]$.

The reversibility of the Raman spectra and absorption maxima upon diamond cell compression and relaxation indicates that the solutions do not decompose during the experiments when prepared as indicated. Because material can escape from the cell upon *release* of pressure, the data presented are only from points obtained for *increasing* pressure. Although the freezing points of cyclohexane (~4 kbar) and dichloromethane (~22 kbar) were crossed in the experiments, no significant

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Table I. Effects of Pressure on the Spectroscopic and Structural Parameters of $Re_2X_8^{2-}$ (X = F, Cl, Br) and $Mo_2Cl_4(PMe_3)_4$

	$Re_2F_8^{2-}$	$Re_2Cl_8^{2-}$	$Re_2Br_8^{2-}$	Mo_2Cl_4-$(PMe_3)_4$
ν(M–M), cm^{-1} (1 atm)	318	275	276	355
r(M–M), Å (1 atm)	2.20[a]	2.22[b]	2.23[c]	2.13[d]
k(M–M), mdyn/Å	4.56[e]	4.32[e]	4.21[e]	4.01[e]
	5.55[f]	4.12[f]	4.18[f]	3.57[f]
$\Delta\nu$(M–M), cm^{-1} (64 kbar)	+68	+54	+15	+38
Δr(M–M), Å (64 kbar)	−0.13	−0.12	−0.05	−0.09

[a] Reference 22. [b] Reference 20. [c] Reference 21. [d] Reference 10. [e] Estimated; empirical force constant–bond length relationships.[19] [f] Estimated; diatomic approximation.

discontinuities in the spectral data, as judged relative to the trends observed over an extended pressure range, were noted in association with these phase changes.

Raman and fluorescence spectra were obtained on the same instrument, which has been described previously.[16] The $Re_2X_8^{2-}$ complexes were excited with the 647.1- or 413.1-nm line of a Kr^+ laser, while $Mo_2Cl_4(PMe_3)_4$ was excited with the 530.8-nm line; excitation power was maintained ≤20 mW at the sample. Because the Raman peaks broadened as the pressure was increased, the slits were gradually opened from 3- to 5-cm^{-1} resolution to allow more light into the monochromator. Electronic absorption spectra were measured on a Perkin-Elmer 1F330 spectrophotometer fitted with condenser optics in the sample beam in order to allow sufficient light through the 0.3-mm sample diameter. The reference beam contained a variable-neutral-density filter, which was used to null the absorbance in an appropriate spectral region.

Results and Discussion

Raman Spectroscopy. The application of pressure to all of the complexes studied here causes the Raman peak assigned as the metal–metal stretch, ν(M–M),[1,16,17] to broaden and, as shown in Figures 1 and 2, to shift to higher frequency. At elevated pressures overtones of ν(M–M), although weak, are also detectable for $Re_2Br_8^{2-}$ and $Mo_2Cl_4(PMe_3)_4$.[18] A comparison of the frequency shifts of the Re dimers $\Delta\nu$(M–M) (Table I) reveals a marked dependence of the magnitude of increase in metal–metal frequency on the identity of the halide ligands, with $\Delta\nu$(M–M) at 64 kbar (the highest pressure at which data for all complexes were obtained) decreasing in the order F > Cl > Br.

The bond length changes corresponding to these frequency shifts can be estimated from the application of empirical bond distance–force constant relationships.[19] We estimated the ambient-pressure force constant from the empirical relationships, using the bond lengths from X-ray crystallography[10,20,21] or EXAFS,[22] and from the diatomic approximation k (mdyn/Å) = $(3.55 \times 10^{17})\mu\nu^2$, where μ is the reduced mass in grams of the two metal atoms and ν is the vibrational frequency in cm^{-1}.[23] Subsequently, a self-consistent set of force constants as a function of pressure was estimated from the pressure-dependent frequencies by the expression $k_{hp} = k(\nu_{hp}/\nu)^2$, where the force constants at high pressure and ambient pressure are denoted by k_{hp} and k and the frequencies at high and ambient pressure are denoted by ν_{hp} and ν, respectively. Differences in bond distance were then back-calculated by using the same empirical relationships to estimate the high-pressure bond length. These differences are summarized in Table I. The metal–metal bond is shortened significantly by high pressure in all of the rhenium complexes. This effect is especially pronounced in $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$, consistent with minimum steric opposition to M–M bond compression by the small F and Cl ligands.

For $Mo_2Cl_4(PMe_3)_4$ we estimate a 0.09-Å decrease in the Mo–Mo bond length at 64 kbar, intermediate between the metal–metal bond length changes of the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ complexes. Although $Mo_2Cl_4(PMe_3)_4$ has, on average, the largest ligands and hence potentially the greatest ligand–ligand repulsion of the four species studied, the D_{2d}-interlocked phosphine geometry mitigates this effect. Additionally, the M–M force constant opposing compression is the smallest in the molybdenum complex, of the systems studied.

It is worth noting that the *limiting* high-pressure metal–metal distances estimated[24] for these complexes are comparable to the shortest found crystallographically for dimers of the "supershort" class.[1] Specifically, the *limiting* high-pressure metal–metal distances for $Re_2Cl_8^{2-}$ and $Mo_2Cl_4(PMe_3)_4$ are 2.08 and 2.00 Å, respectively, which are shorter than those of $Re_2(O_2CMe)_2Me_2(\eta^1\text{-}O_2CMe)_2$ (2.177 (1) Å)[25] and $Mo_2[pyNC(O)CH_3]_4$ (2.037 (3) Å).[26] For $Re_2Br_8^{2-}$, the Re–Re distance appears to approach a minimum (2.17 Å) within the range of pressures examined in these experiments.

A second symmetric vibration previously observed in the resonance Raman (RR) spectra of the rhenium complexes is the a_{1g} Re–X stretch, which receives considerable RR enhancement from excitation into the lowest lying ligand-to-metal charge-transfer (LMCT) absorption bands.[17] Because the LMCT absorption bands for the $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$ complexes were experimentally inaccessible ($\lambda_{max} \leq 330$ nm), diamond anvil cell RR measurements probing this mode were possible only for $Re_2Br_8^{2-}$ [$\lambda_{max} = 414$ nm; $\lambda_{exc} = 413.1$ nm (Kr^+)]. In contrast to the moderate change in the Re–Re stretching frequency seen for this complex, the Re–Br stretching frequency changes only slightly with pressure. Application of 70 kbar results in a 5-cm^{-1} shift to higher frequency (from 208 to 213 cm^{-1}), compared to a 17-cm^{-1} shift in ν(M–M).

Electronic Spectroscopy. While the pressure dependence of the metal–metal stretching frequency provides unequivocal evidence that the metal–metal distance decreases with increasing pressure, it does not yield insight into the finer details of the molecular structures of these species under these conditions. The specific question that arises is whether compression along the metal–metal axis is accomplished with retention of the eclipsed (D_{4h} for $Re_2X_8^{2-}$, D_{2d} for $Mo_2Cl_4(PMe_3)_4$) geometry found at ambient pressure or whether the molecule undergoes a torsional distortion to accommodate close contacts between adjacent ReX_4 or $MoCl_2P_2$ sub-

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(18) For $Re_2Br_8^{2-}$, the fundamental and first overtone were observed at 291 and 579 cm^{-1} at 64 kbar and at 295 and 585 cm^{-1} at 95 kbar. At 41 kbar, the fundamental for $Mo_2Cl_4(PMe_3)_4$ is observed at 382 cm^{-1} and the overtone at 768 cm^{-1}. These frequencies indicate nearly harmonic behavior at elevated pressures, as is also the case at ambient pressure.[16,17] No overtones of $\nu(M_2)$ were observed in the case of $Re_2F_8^{2-}$ or $Re_2Cl_8^{2-}$.

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(23) As noted elsewhere,[16,19a] the diatomic approximation is subject to errors in these systems because of contributions to the "diatomic" reduced mass from the ligands and G matrix mixing of M–M and M–X coordinates. In the sets of force constants so obtained, mixing of ligand coordinates should be similar for a given complex, and therefore *differences* in metal–metal distances with pressures, as opposed to the absolute distances themselves, should be reliably estimated.

(24) The pressure (P) dependence of ν(M–M) in Figures 1 and 2 could be fit satisfactorily by an equation of the form $\nu(P) = a + bP + cP^2$. The calculated parameters are

complex	a	b	10^3c	corr coeff
$Re_2F_8^{2-}$	318	1.6684	−9.5220	1
$Re_2Cl_8^{2-}$	277.94	1.0221	−3.5408	0.9897
$Re_2Br_8^{2-}$	276.40	0.2913	−1.0614	0.9980
$Mo_2Cl_4(PMe_3)_4$	354.95	0.7476	−2.3381	0.9948

"Limiting" high-pressure metal–metal distances were estimated by calculation of $\nu(P)_{max}$ at $(d\nu(P)/dP) = 0$, which, when converted into a force constant, gave r(M–M) by application of the equations in ref 19. Although there is, at present, no theoretical justification for the form of these equations, their good correlation to the data suggest that the M–M distances so obtained are reliable estimates.

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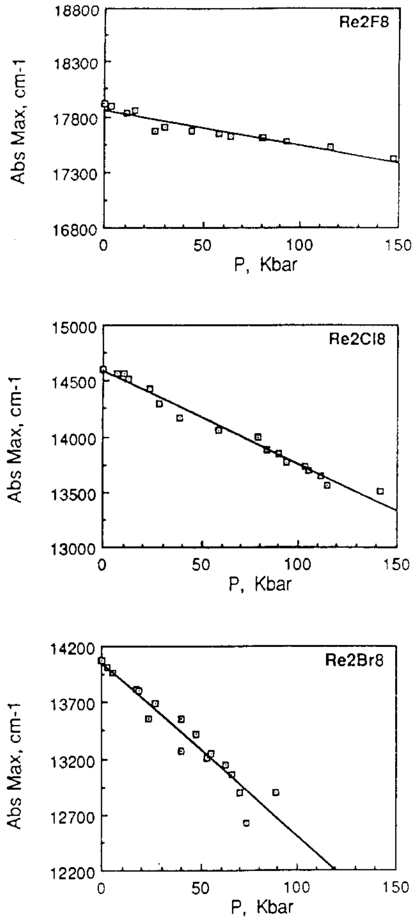

Figure 3. Pressure dependence of the $^1(\delta \rightarrow \delta^*)$ transition energies for $Re_2X_8^{2-}$ in dichloromethane (X = F, Cl, Br).

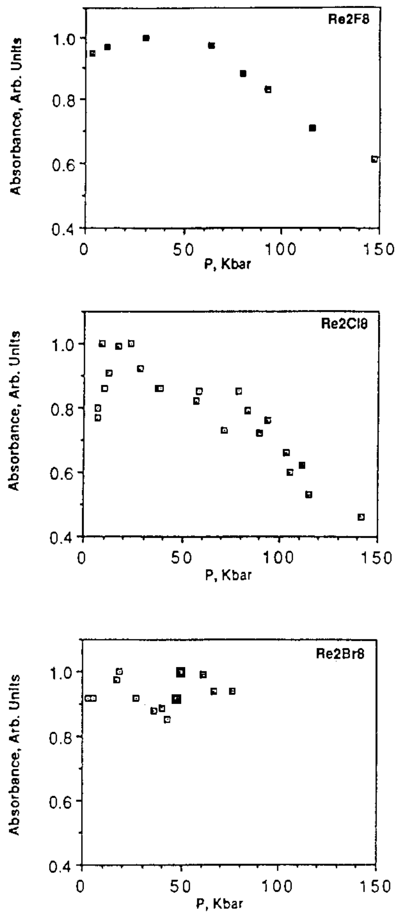

Figure 4. Pressure dependence of the integrated $^1(\delta \rightarrow \delta^*)$ absorption intensities of $Re_2F_8^{2-}$, $Re_2Cl_8^{2-}$, and $Re_2Br_8^{2-}$ in dichloromethane.

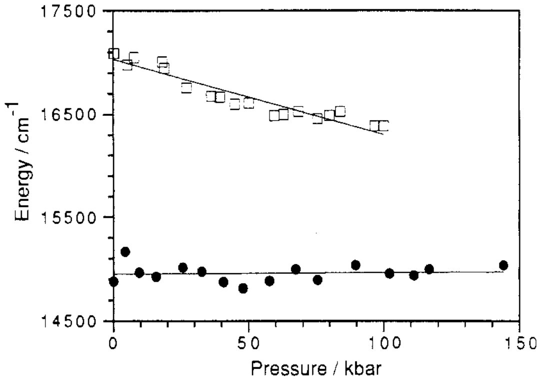

Figure 5. Pressure dependence of the energies of the $^1(\delta \rightarrow \delta^*)$ absorption (□) and $^1(\delta^* \rightarrow \delta)$ emission (●) bands of $Mo_2Cl_4(PMe_3)_4$ in cyclohexane.

units. The pressure dependence of the $^1(\delta \rightarrow \delta^*)$ transitions of these species provides insight concerning this point.

As we observed previously for $Re_2Cl_8^{2-}$,[7] dichloromethane solutions of $Re_2F_8^{2-}$ and $Re_2Br_8^{2-}$ exhibit smooth absorption spectral changes in the visible region with increasing pressure. In no instance do we observe distinct new bands in the spectra (as CSD noted for crystalline $[n\text{-}Bu_4N]_2[Re_2I_8]$ and $[n\text{-}Bu_4N]_2[Re_2Br_8]$ at high pressure[6]), nor do we see evidence at any pressure that the $^1(\delta \rightarrow \delta^*)$ absorption envelope consists of more than a single Gaussian component. The $^1(\delta \rightarrow \delta^*)$ absorption maximum of the $Re_2X_8^{2-}$ ions red-shifts nearly linearly with pressure (Figure 3), with the slope of the red shift smallest for $Re_2F_8^{2-}$ (−3.2 cm^{-1}/kbar), intermediate for $Re_2Cl_8^{2-}$ (−8.3 cm^{-1}/kbar), and largest for $Re_2Br_8^{2-}$ (−15.4 cm^{-1}/kbar). In addition to red-shifting, this absorption band also broadens with increasing pressure and, in the case of $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$, changes in intensity. The integrated absorption intensities of the $^1(\delta \rightarrow \delta^*)$ transitions of the $Re_2X_8^{2-}$ ions as a function of pressure are plotted in Figure 4. The data for $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$ show an initial rise that maximizes at ca. 45 and 15 kbar, respectively, followed by a decrease in intensity as pressure is increased further. In contrast, the integrated $^1(\delta \rightarrow \delta^*)$ absorption intensity of $Re_2Br_8^{2-}$ was essentially independent of pressure.

The $^1(\delta \rightarrow \delta^*)$ transition of $Mo_2Cl_4(PMe_3)_4$, like those of the $Re_2X_8^{2-}$ ions, red-shifts linearly with increasing pressure (Figure 5). The average rate of this shift is −7.3 cm^{-1}/kbar, which is similar to that observed for $Re_2Cl_8^{2-}$. In contrast to the case of the rhenium complexes, the $^1(\delta \rightarrow \delta^*)$ band does not broaden significantly as pressure is increased, but the integrated intensity steadily increases to at least 50 kbar.[27] Unlike its absorption counterpart, the energy of the $^1(\delta^* \rightarrow \delta)$ fluorescence band of $Mo_2Cl_4(PMe_3)_4$ was essentially invariant to pressure. That the positions of the $^1(\delta \rightarrow \delta^*)$ and $^1(\delta^* \rightarrow \delta)$ band maxima should display such different pressure dependencies is not unexpected, given the marked deviation of these bands from mirror symmetry at ambient pressure.[11] The vibronic intensity profile of the absorption band is dominated by a progression in ν(Mo–Mo), while that of the emission band contains roughly equal contributions from ν(Mo–Mo), ν(Mo–Cl), and several other metal–ligand modes.[11] Luminescence from the $Re_2X_8^{2-}$ complexes is weak and shifted to the low-frequency limit of our spectrometer, precluding a comparison study of the emission spectra of these species.

In order to interpret the changes in the energy and intensity of the $^1(\delta \rightarrow \delta^*)$ transition that occur upon the application of pressure, the dependence of the δ-overlap on metal–metal bond contraction and torsion, and the subsequent influence on the electronic states involved, need to be reviewed. Our discussion follows the lines of, and invokes the same approximations as, treatments outlined previously.[3,5] With two electrons to distribute

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(27) We were unable to obtain $^1(\delta \rightarrow \delta^*)$ intensities for $Mo_2Cl_4(PMe_3)_4$ in cyclohexane at pressures greater than ca. 50 kbar because the Inconel gaskets reproducibly deformed about the solvent matrix at this pressure.

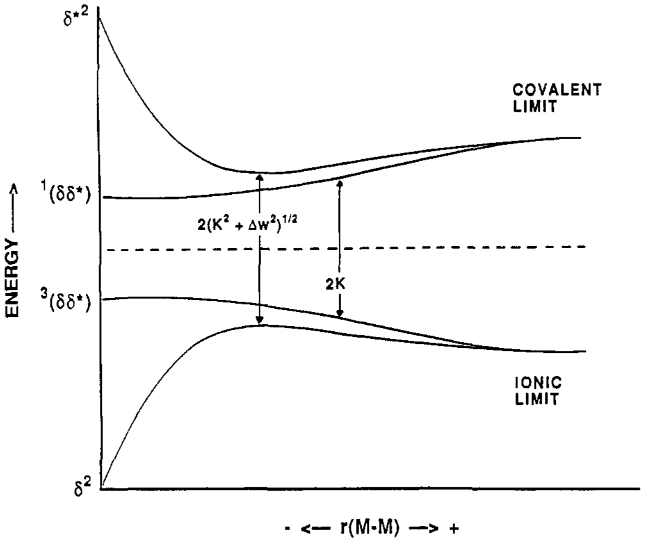

Figure 6. Dependence of the energies of the δ,δ^*-manifold of electronic states on metal–metal separation.

between the δ and δ^* frontier orbitals, four states, consistent with the Pauli principle, can be constructed: a $^1(\delta^2)$ ground state, singly excited $^3(\delta\delta^*)$ and $^1(\delta\delta^*)$ states, and a doubly excited $^1(\delta^{*2})$ state. In the regime in which pressure increasingly shortens the metal–metal distance but does not disrupt the δ-bond through torsional rotation (Figure 6), the δ-overlap steadily increases, thus increasing the splitting (Δw) of the one-electron δ and δ^* orbitals. Unlike the situation for molecules for which Δw is large at ambient pressure (e.g., $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$[9]), the energy of the $^1(\delta \rightarrow \delta^*)$ transitions of quadruply bonded dimers does not scale directly with this increase in Δw because the δ-overlap of these systems is small enough that the contribution to the transition energy from the electron correlation term (K) is comparable in magnitude to that of Δw. While the increased δ-overlap does not directly affect the correlation term, which functions to keep electron density farther apart (less electrostatic repulsion) in the triplet, the decreased distance between the centers reduces its magnitude.[5] As a result, both of the configurations involved in the $^1(\delta \rightarrow \delta^*)$ absorption, namely the $^1(\delta^2)$ ground and $^1(\delta\delta^*)$ excited configurations, are stabilized energetically from bond shortening, and any shift in the transition energy would be determined by which one is stabilized more. While the distance dependence of Δw is slightly stronger than that of K, suggesting that the $^1(\delta \rightarrow \delta^*)$ transition should blue-shift with pressure, only a small change in transition energy is expected over the range of bond distances considered here.

The pressure dependence of the *intensity* of the $^1(\delta \rightarrow \delta^*)$ transition within this regime is difficult to predict with certainty. As was pointed out some time ago,[28] these transitions are of the N → V type and hence their oscillator strengths (f) may be estimated by

$$f = 1.096 \times 10^{11} \nu S^2 r^2$$

where ν is the transition energy in cm^{-1}, S is the δ-orbital overlap, and r is the metal–metal distance in cm. It seems likely that the $^1(\delta \rightarrow \delta^*)$ transition intensity, *in the absence of torsional distortion*, would increase with pressure because the decrease in f at high pressure due to the distance term $[(r_{hp}/r)^2 \sim 0.9]$ is undoubtedly compensated for by an increase in ν, and especially S.

The pressure dependences of the $^1(\delta \rightarrow \delta^*)$ transition energy and intensity should be quite different if, in contrast to the above scenario, torsional distortion accompanies compression of the molecule along the metal–metal axis. While torsion about the metal–metal axis in the absence of metal–metal compression has no effect on the correlation energy, it decreases the δ-overlap by roughly[4a] $S(\chi) = \cos 2\chi$ and hence decreases Δw (Figure 7).

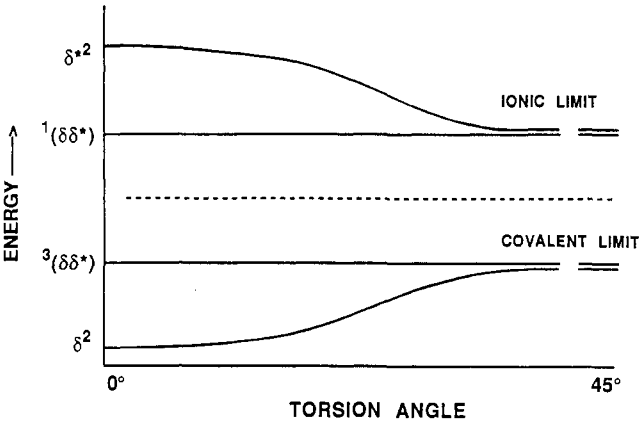

Figure 7. Dependence of the energies of the δ,δ^*-manifold of electronic states on torsion angle χ.

Since K decreases with distance, a pressure-induced decrease in metal–metal distance *and* a torsional distortion about the metal–metal axis should lead to a strongly red-shifted $^1(\delta \rightarrow \delta^*)$ transition. The intensity of this transition should also decrease dramatically because ν, S, and r all decrease.

Direct experimental evidence for this interpretation of the torsion angle dependence of the energy and intensity comes from spectroscopic measurements of ligand-bridged dimers of the type β-$Mo_2X_4(P\text{–}P)_2$ (X = Cl, Br, I; P–P = bidentate diphosphine ligand) that possess noneclipsed geometries.[3,4] As ligand-backbone strain induces torsion about the metal–metal bond in these systems, the $^1(\delta \rightarrow \delta^*)$ transition is observed to red-shift and decrease in intensity. A specific example of this behavior is given by systems with the general formula $Mo_2X_4(PR_3)_4$; in β-$Mo_2Cl_4(Me_2PCH_2CH_2PMe_2)_2$ ($\chi \sim 40°$), the $^1(\delta \rightarrow \delta^*)$ energy and intensity ($\bar{\nu}_{max}$ = 12 450 cm^{-1}, ϵ_{max} = 210 $M^{-1}\ cm^{-1}$) are considerably lower than those of its eclipsed "rotomer" $Mo_2Cl_4(PMe_3)_4$ ($\chi = 0°$, $\bar{\nu}_{max}$ = 17 090 cm^{-1}, ϵ_{max} = 3110 $M^{-1}\ cm^{-1}$).[3] Similarly, compare β-$Mo_2I_4(Ph_2PCH_2CH_2PPh_2)_2$ ($\chi \sim 27°$, $\bar{\nu}_{max}$ = 11 600 cm^{-1}, ϵ_{max} = 2000 $M^{-1}\ cm^{-1}$)[4b] with β-$Mo_2I_4(Ph_2PCH_2PPh_2)_2$ ($\chi = 0°$, $\bar{\nu}_{max}$ = 14 140 cm^{-1}, ϵ_{max} = 4108 $M^{-1}\ cm^{-1}$).[4c]

When viewed within the above framework, the pressure dependences of the $^1(\delta \rightarrow \delta^*)$ transition energies and intensities of the $Re_2X_8^{2-}$ ions do not appear to be interpretable in a straightforward manner. On the one hand, the linear red shift of this band in each case suggests that all compounds continuously torsionally distort as the pressure is raised and the metal–metal bond length decreases, with the extent of distortion dependent on the nature of the halide according to $Re_2Br_8^{2-} > Re_2Cl_8^{2-} > Re_2F_8^{2-}$. The fact that the $^1(\delta \rightarrow \delta^*)$ bands are still red-shifting at high pressure indicates that the 45° end point has not been reached. That the amount of torsional distortion parallels the size of the respective halide ligands is in line with the expectation that the steric repulsion among the halides should determine the rate of distortion along the torsional coordinates as pressure is applied. On the other hand, the pressure dependence of the $^1(\delta \rightarrow \delta^*)$ *intensity* implies that only $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$, but not $Re_2Br_8^{2-}$, torsionally distort, since these are the only compounds for which the requisite decrease in $^1(\delta \rightarrow \delta^*)$ intensity is observed. The initial increase in intensity for the fluoro and chloro compounds indicates the δ-overlap is increasing at these low pressures because the decrease in δ-overlap due to torsional distortion is more than compensated for by the increase in overlap arising from the shortened metal–metal distance.

The data for $Mo_2Cl_4(PMe_3)_4$ also appear to be at odds with simple theory, since the red shift of the $^1(\delta \rightarrow \delta^*)$ band with increasing pressure is accompanied by a steady increase in intensity. A possible explanation for the discrepancy between the observed pressure dependence of the $^1(\delta \rightarrow \delta^*)$ energy and intensity of $Mo_2Cl_4(PMe_3)_4$ and the $Re_2X_8^{2-}$ ions and that predicted by simple theory is that the theoretical treatment *assumes* that the δ and δ^* orbitals, and the states derived therefrom, are completely metal–metal localized; i.e., mixing with ligands is ignored. While

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[28] Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232.

this approach has yielded considerable insight into the factors that determine the energetic splittings of the δ,δ^*-derived manifold of electronic states of these species, there is clear experimental evidence that the nature of the ligands needs to be considered in order for the finer details of the $^1(\delta \rightarrow \delta^*)$ transition energy and intensity to be understood for specific classes of quadruply metal–metal bonded complexes. It has been proposed[5,16] that the majority of the intensity of the $^1(\delta \rightarrow \delta^*)$ transitions of halide-containing quadruply M–M bonded dimers is stolen from higher lying $\pi(X) \rightarrow \delta^*$ transitions that meet certain symmetry and polarization criteria and that the extent of intensity stealing should depend significantly upon both the energy gap between the $^1(\delta \rightarrow \delta^*)$ and $\pi(X) \rightarrow \delta^*$ transitions and the X–M–M angle. The $^1(\delta \rightarrow \delta^*)$ transition energy is also affected by such a charge-transfer mixing mechanism, albeit to a lesser extent. These phenomena are best illustrated by the $Mo_2X_4(PMe_3)_4$ series (X = Cl, Br, I), for which the metal–metal distance is essentially constant at ~2.13 Å: X = Cl, $\bar{\nu}_{max}$ = 17090 cm^{-1}, ϵ_{max} = 3110 M^{-1} cm^{-1}; X = Br, $\bar{\nu}_{max}$ = 16720 cm^{-1}, ϵ_{max} = 4060 M^{-1} cm^{-1}; X = I, $\bar{\nu}_{max}$ = 15720, ϵ_{max} = 5150 M^{-1} cm^{-1}.[16] We would expect the complexes examined in this study to be increasingly sensitive to charge-transfer mixing in the orders $Re_2F_8^{2-} < Re_2Cl_8^{2-} < Re_2Br_8^{2-}$, based on optical electronegativities, and $Re_2Cl_8^{2-} < Mo_2Cl_4(PMe_3)_4$, based on the Cl–M–M angle (∠Cl–Re–Re = 103°; ∠Cl–Mo–Mo = 112°),[10,20] with an increase in mixing with pressure being manifested as an anomalously red-shifted or intense $^1(\delta \rightarrow \delta^*)$ transition.

Taking this caveat on metal–ligand mixing into consideration, we believe the following conclusions can be drawn from the observed pressure dependence of the $^1(\delta \rightarrow \delta^*)$ transition. In the case of $Re_2F_8^{2-}$ (for which charge-transfer mixing should be negligible) and of $Re_2Cl_8^{2-}$ (for which charge-transfer mixing should be relatively small at low pressures), a decrease in Re–Re bond length is the dominant factor at low pressure, accounting for the initial increase in transition moment. At higher pressures, the torsion becomes dominant, and the turning point in the graph (Figure 4) indicates the pressure required for the onset of this distortion. That this turning point occurs at a higher pressure for $Re_2F_8^{2-}$ than for $Re_2Cl_8^{2-}$ suggests that shorter Re–Re distances are required before substantial twisting occurs in the fluoro complex, consistent with simple steric considerations.

The dramatic red shift of the $^1(\delta \rightarrow \delta^*)$ transition with pressure, evident in Figure 3, can be understood in terms of the pressure-induced torsional distortion discussed above for $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$. This effect is most extreme for the bulky Br^- ligands. However, the insensitivity of the transition moment to pressure (Figure 4) cannot be explained on the basis of simple distortion arguments. Charge-transfer mixing should be more important for $Re_2Br_8^{2-}$, and it is our view that the observation of a constant intensity for the $^1(\delta \rightarrow \delta^*)$ transition with pressure indicates that this mechanism compensates for the expected decrease in transition moment (vide supra) due to pressure-induced molecular distortions.

Finally, we need to examine the hypothesis of CSD[8] that van der Waals interactions between the δ^* orbitals and the surrounding medium are the dominant factor in determining the energies of the $^1(\delta \rightarrow \delta^*)$ transitions as a function of pressure. As we noted previously,[7] the higher energy 313-nm $\pi(Cl) \rightarrow \delta^*(Re)$ charge-transfer band of $Re_2Cl_8^{2-}$ was observed merely to broaden with pressure without changing transition energy or integrated absorption moment. CSD report a similar insensitivity to pressure of the positions of the 414- and 671-nm $\pi(X) \rightarrow \delta^*$ bands of $Re_2Br_8^{2-}$ and $Re_2I_8^{2-}$, respectively.[8] If interactions between the medium and the δ^*-orbitals of the complexes were primarily responsible for the observed behavior of the $^1(\delta \rightarrow \delta^*)$ transition, it is difficult to understand why the $^1(\pi(X) \rightarrow \delta^*)$ transitions would be insensitive to pressure. We also note that our observed pressure-induced trends are not discontinuous across the fluid/crystalline phase transitions of the solvents, which again argues that the importance of solvent–solute interactions is minor.

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Registry No. $Re_2F_8^{2-}$, 72931-84-1; $Re_2Cl_8^{2-}$, 19584-24-8; $Re_2Br_8^{2-}$, 19584-25-9; $Mo_2Cl_4(PMe_3)_4$, 67619-17-4.

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Electronic Absorption and MCD Spectra for the Triangular Platinum(0) Complex $Pt_3(\mu\text{-}CO)_3(P(t\text{-}Bu)_3)_3$

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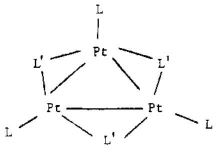
Electronic absorption and magnetic circular dichroism (MCD) spectra in the UV–vis range 1.7–5.2 μm^{-1} are reported for the triangular, trinuclear $Pt_3(\mu\text{-}CO)_3(P(t\text{-}Bu)_3)_3$ complex in CH_3CN solution at room temperature. The MCD spectrum is generally better resolved than the absorption and reveals positive A or pseudo-A terms at 2.04, 2.76, 3.85, and 4.20 μm^{-1}, a negative A term at 3.18 μm^{-1}, and a negative B term at 2.27 μm^{-1}. The spectra are interpreted in the context of some recent MO calculations in terms of transitions to E′ or A$_2$″ D_{3h} spin–orbit states of excited configurations that are primarily metal to ligand charge transfer (MLCT) in character.

Introduction

Platinum forms an interesting class of 42-electron trinuclear complexes **1** consisting of an equilateral triangle of Pt atoms and



L′ = CO; L = P(*c*-Hx)$_3$[2], P(*t*-Bu)$_3$[3], P(*n*-Bu)$_3$[4], P(CH$_2$CH$_2$CN)$_3$[4]
L′ = CNR; L = CNR, R = Me, Et, *t*-Bu[5]
L′ = SO$_2$; L = PPh$_3$[6], P(*c*-Hx)$_3$[7], P(*t*-Bu)$_3$[7]
L′ = CS$_2$; L = P(*c*-Hx)[7], P(*t*-Bu)$_3$[7]

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coplanar terminal (L) and bridging (L′) ligands.[1] The complexes have D_{3h} symmetry when the substituents on the L and L′ donor atoms are ignored, and the Pt–Pt distances are only slightly ligand

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