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	d[P–C(aromatic)], Å		
Cmpd	Metalocycle	Terminal	Terminal
A	1.794	1.830	1.825
B	1.800	1.820	1.820
C	1.815	1.848	1.831
D	1.795	1.823	1.823

Further Studies of the Electronic Spectra of $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$. Assignment of the Weak Bands in the 600–350-nm Region. Estimation of the Dissociation Energies of Metal–Metal Quadruple Bonds

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Abstract: Previously published evidence bearing on the polarizations and assignments for the strong bands in $Re_2Cl_8^{2-}$ and related species is synthesized and it is shown that work from our two laboratories gives a consistent picture. New polarized spectra of thick crystals of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$, measured at 15 K, are reported and discussed. Four new regions of weak absorption between the more intense $\delta \rightarrow \delta^*$ (14 700 cm^{-1}) and $\pi(Cl) \rightarrow \delta^*$ (32 600 cm^{-1}) bands of $Re_2Cl_8^{2-}$ have been characterized. The first weak band of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ maximizes at 17 675 cm^{-1} and consists of three progressions in a 225-cm^{-1} excited state a_{1g}(ReRe) stretching vibration built on three origins. Two of the progressions are polarized parallel and one perpendicular with respect to the ReRe molecular axis. The band red shifts by only 200 cm^{-1} in $(n\text{-}Bu_4N)_2[Re_2Br_8]$. The results indicate that the band is attributable to the electric-dipole-forbidden, metal-localized transition $\delta \rightarrow \pi^*(^1A_{1g} \rightarrow {}^1E_g)$. A second absorption at 20 940 cm^{-1} exhibits only perpendicularly polarized progressions on several vibronic origins with a common vibrational spacing of ca. 400 cm^{-1} (a_{1g}(ReCl) stretch). This band also intensifies and red shifts upon warming (15 to 300 K). The 1790-cm^{-1} red shift of this band in $(n\text{-}Bu_4N)_2[Re_2Br_8]$ pinpoints it as a $\delta \rightarrow d_{x^2-y^2}(b_{2u})(^1A_{1g} \rightarrow {}^1A_{1u})$ transition. The third band, which is at 23 645 cm^{-1}, is extremely weak and only one perpendicularly polarized progression in the a_{1g}(ReReCl) skeletal bending mode was detected. A $\pi \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1E_g)$ assignment is suggested. The fourth absorption system is comprised of two sharp peaks at 27 000 and 28 100 cm^{-1}, which are parallel polarized. These peaks shift to 21 290 and 22 080 cm^{-1} in $(n\text{-}Bu_4N)_2[Re_2Br_8]$, consistent with a ligand to metal charge transfer (LMCT) assignment. As the LMCT transitions to a^1E_u and b^1E_u states are not split appreciably in $Re_2Cl_8^{2-}$, it is suggested that the fourth weak band system is derived from the corresponding $e_g\pi(Cl) \rightarrow \delta^*(^1A_{1g} \rightarrow A_{2u}(a,b^3E_u))$ excitations. Dissociation energies of Re–Re and Mo–Mo quadruple bonds have been estimated from a Birge–Sponer extrapolation, giving values of 115–130 kcal/mol for the former and 110–160 kcal/mol for the latter.

The earliest, tentative suggestions[1,2] as to how to assign the electronic spectrum of $Re_2Cl_8^{2-}$, the species in which the existence of quadruple bonds was discovered,[1,3] as well as the extension of such assignments to the spectra of closely related complexes, have not withstood recent experimental[4-10] and theoretical[6,10-12] scrutiny. Work done within the past few years[4-12] has provided new spectral assignments that seem certain to be correct in their essentials and bring us to a point of departure for delving more deeply into the details of the spectra and bonding in the entire class of compounds[13] containing quadruple M–M bonds and other multiple bonds between metal atoms. One purpose of this paper is to present some new and pertinent facts concerning the spectra of the $Re_2X_8^{2-}$ (X = Cl, Br) ions.

In the past it has appeared that there have been disagreements between publications from our two laboratories as to observations and interpretations regarding the electronic structural properties of $Re_2Cl_8^{2-}$ and related species containing quadruple bonds. In actual fact, we are in essentially complete agreement as to the observations and their interpretation. In view of the importance of establishing a clear picture of the situation regarding the prototypal[1,3] quadruple bond, i.e., that in $Re_2Cl_8^{2-}$, we also present in this report a synthesis of some isolated observations recorded in earlier publications, as well as a needed critique of our previous estimates of the bond dissociation energies (BDE's) of quadruple bonds.

Contrary to the impression created in a recent publication[5] from one of our laboratories, there was in fact a sound basis for the claim, which was advanced[4,6] first by Cowman and Gray, that the 14 000-cm^{-1} absorption band in $Re_2Cl_8^{2-}$ is polarized parallel to the Re–Re axis. The crystallographic results, showing as they do the existence of a disorder in the crystals, taken together with the earlier crystal spectra,[4,7] confirmed in the most direct way the aforementioned assignment of polarization. The misunderstanding between our laboratories was in large part attributable to the fact that the logic of the Cowman–Gray argument was not presented in full form in either of the two published documents.[4,6] To set the record straight, we shall now outline the main parts of the argument.

It should be recalled that each of the three complexes, (n-

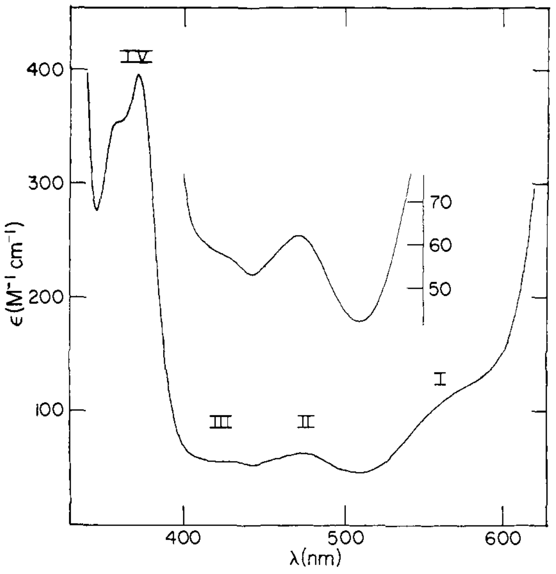

Figure 1. Electronic absorption spectrum of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ in acetonitrile solution at 298 K in the region 600–350 nm.

Bu$_4$N)$_2$[Re$_2$Cl$_8$], $(n\text{-}Bu_4N)_2[Re_2Br_8]$, and $Re_2Cl_6[P(C_2H_5)_3]_2$, exhibits a moderately intense band at about 14 000 cm^{-1}; in each case the integrated intensity of the band is independent of temperature (between 5 and 300 K) and a vibrational progression in a_{1g}(ReRe) is exhibited at 5 K. Studies on single crystals of $Re_2Cl_6[P(C_2H_5)_3]_2$ showed conclusively that the 14 000-cm^{-1} band is ReRe-axis (parallel or z) polarized.[4] Starting with this incontestable result, three important points should be emphasized: (1) There is an obvious analogy of the 14 000-cm^{-1} bands in $Re_2Cl_8{}^{2-}$ and $Re_2Br_8{}^{2-}$ with that in $Re_2Cl_6[P(C_2H_5)_3]_2$. (2) The fact that the solution MCD spectra of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$ show that the intense bands at 32 600 and 23 630 cm^{-1}, respectively, exhibit A terms.[6,7,14] These results, which show that the excited state is degenerate, establish that the intense bands are $^1A_{1g} \rightarrow {}^1E_u$, and therefore that they must be polarized perpendicular to the molecular axis. As the crystal spectra show,[4,7] the 14 000-cm^{-1} band displays polarization character opposite to that of $^1A_{1g} \rightarrow {}^1E_u$. It must therefore be parallel polarized. (3) The previously unpublished observation that a few crystals of $(n\text{-}Bu_4N)_2[Re_2Br_8]$ possess a nondichroic orange-yellow face, with the 14 000-cm^{-1} band absent.[7] No such face would be possible if the band were perpendicularly polarized.

The early reports[2,15] of the electronic absorption spectrum of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ did not concern themselves with the region of weak absorption between the 14 700 and 32 600-cm^{-1} bands. By examining concentrated solutions containing $Re_2Cl_8{}^{2-}$, we have now shown that there are four weak bands in this region. We shall first describe here the single-crystal spectra and assignments of these new band systems for $(n\text{-}Bu_4N)_2[Re_2Cl_8]$, and also report related spectroscopic results for $(n\text{-}Bu_4N)_2[Re_2Br_8]$.

Experimental Section

Crystals of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ and $(n\text{-}Bu_4N)_2[Re_2Br_8]$ were grown and oriented as previously described.[4] Low temperature polarized spectra were recorded on a Cary 17 spectrometer using a Cary liquid helium Dewar and tandem Glan–Taylor air-spaced calcite polarizers. The 0.2 and 0.5 absorbance slide wires were used to record the weak bands. Temperature was measured with a calibrated carbon resistor. Polarizations are denoted $\parallel$ and $\perp$ along the extinction directions of the (100) crystal face, corresponding to projections predominantly $\parallel$ and $\perp$ to the ReRe molecular axis.[4,7]

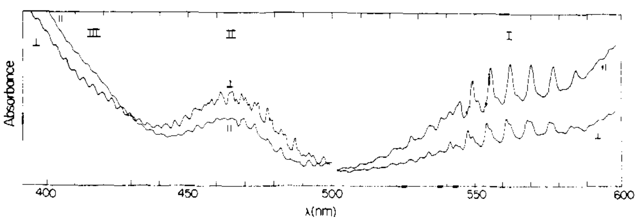

Figure 2. Single crystal polarized spectra of bands I–III in $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ at 15 K. Bands II and III were recorded at a vertical scale expansion 2.5 times that used for band I. The measurements were made at a spectral bandwidth <0.75 nm.

Results and Discussion

The electronic spectrum of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ in acetonitrile solution at 298 K (Figure 1) shows four absorption bands (I–IV) between the electric-dipole-allowed $\delta \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1A_{2u})$ and $\pi(Cl) \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1E_u)$ systems at 682 and 314 nm, respectively. In a crystal at 15 K, band I, which is centered at 17 675 cm^{-1}, consists of three vibrational progressions (Figure 2 and Table I). Owing to overlap with the $\delta \rightarrow \delta^*$ band at lower energy, it is not possible to locate the true progressional origins with certainty. A strong parallel polarized progression in a 225-cm^{-1} vibration originates at 17 062 cm^{-1}, and a less intense one begins at 17 452 cm^{-1}. The weaker progression could either represent a new vibronic origin or a single quantum of a_{1g}(ReCl) built on the one at 17 062 cm^{-1}. A perpendicularly polarized progression of the same frequency is built on a vibronic origin at 17 117 cm^{-1}. The 225-cm^{-1} progression is assigned to the excited state a_{1g} metal–metal stretching mode. For comparison, the ground and $\delta \rightarrow \delta^*$ state values are 274[16] and 248[4,6,7] cm^{-1}, respectively. A maximum in the progression is reached at the fourth band, or third vibration, in contrast to the $\delta \rightarrow \delta^*$ system, which peaks at the first vibration.[4,7] This indicates a greater distortion of the Re$_2$ bond in the excited state associated with band I than that accompanying $\delta \rightarrow \delta^*$ excitation. The reduced value of a_{1g}(ReRe) for band I is also consistent with a transition to an orbital that possesses a large amount of metal–metal antibonding character. The mixed polarization, the presence of at least two vibronic origins, and the weakness of band I suggest an electric-dipole-forbidden, vibronically-enabled transition. A similar band, with unresolved, overlapping vibronic structure, is observed at 17 475 cm^{-1} for $(n\text{-}Bu_4N)_2[Re_2Br_8]$. Such insensitivity to halide substitution confirms the metal-localized nature of the excitation. The transition $\delta \rightarrow \pi^*(^1A_{1g} \rightarrow {}^1E_g)$ is consistent with the experimental data, and would be expected to lie lower than $\pi \rightarrow \pi^*$, which is at 39 215 cm^{-1} in a crystal of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ at 5 K.[6] We prefer $\delta \rightarrow \pi^*$ to $\pi \rightarrow \delta^*$ for the 17 675-cm^{-1} band, as the π orbital possesses substantial halogen character.[6]

Band II, which is centered at 20 940 cm^{-1} (Figure 2 and Table I), exhibits *only* perpendicularly polarized components with several vibronic origins, complex overlapping progressions, and a common vibrational spacing of ca. 400 cm^{-1}. This high frequency progression clearly is not attributable to a_{1g}(ReRe), and is assigned to an excited state a_{1g}(ReCl) stretch (ground state[16] 359 cm^{-1}), which suggests a transition to an unoccupied, metal–chlorine orbital. The vibronic nature of the transition is supported by the low band intensity, the presence of several vibronic origins, and the red shift and approximately twofold increase in intensity upon increasing the temperature from 15 to 298 K. (It was not possible to assess the temperature dependence of bands I or III, owing to concomitant thermal broadening of the more intense systems with which they overlap.) A corresponding band was observed at 19 150 cm^{-1} in $(n\text{-}Bu_4N)_2[Re_2Br_8]$. This modest (1790 cm^{-1}) red shift upon halide substitution parallels the 1400–1500-cm^{-1} red

Table I. Polarized Electronic Absorption Spectra of a Single Crystal of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ at 15 K in the Region 600–350 nm

Band	nm (± 0.3)	cm^{-1} (±8)	spacing (cm^{-1})			polarization	$^1A_{1g}$ →
I	586.1	17062				∥	^1E_g
	584.2	17117				⊥	
	578.2	17295	233		226	∥	
	576.6	17343				⊥	
	573.0	17452			235	∥	
	570.1	17541	246			∥	
	568.9	17578		222		⊥	
	565.8	17674			231	∥	
	562.7	17771	230			∥	
	561.5	17809		234		⊥	
	558.4	17908	215		201	∥	
	556.0	17986				∥	
	555.3	18010		231		⊥	
	551.3	18139	216		248	∥	
	549.4	18202				∥	
	547.7	18258		213		⊥	
	544.9	18352			199		
	543.6	18396	194			∥	
	541.8	18457				⊥	
II	497.3	20109				⊥	$^1A_{1u}$
	493.8	20251				⊥	
	492.3	20313	408			⊥	
	490.4	20391				⊥	
	488.7	20462			414	⊥	
	487.4	20517				⊥	
	483.9	20665		419		⊥	
	482.5	20725	421			⊥	
	480.6	20807			414	⊥	
	478.9	20881				⊥	
	477.6	20938				⊥	
	474.4	21079		400		⊥	
	473.1	21137	402			⊥	
	471.2	21222				⊥	
	469.9	21281			408	⊥	
	468.6	21340				⊥	
	466.7	21427		406		⊥	
	465.4	21487				⊥	
	464.4	21533	394			⊥	
	462.2	21636			397	⊥	
	461.1	21687				⊥	
	460.1	21734				⊥	
	458.2	21824				⊥	
	456.9	21887				⊥	
	455.6	21949			438	⊥	
	454.2	22017				⊥	
	452.6	22095				⊥	
	449.2	22262				⊥	
	445.1	22467				⊥	
	442.2	22614				⊥	
III	439.2	22769				⊥	^1E_g
	435.5	22962	193			⊥	
	432.7	23111	150			⊥	
	429.4	23288	177			⊥	
	426.4	23452	164			⊥	
	422.9	23646	194			⊥	
	419.9	23815	169			⊥	
	416.4	24015	200			⊥	
	413.1	24207	192			⊥	
	410.0	24390	183			⊥	
	406.7	24588	198			⊥	
IV	370.	27000				∥	$A_{2u}(a^3E_u)$
	356.	28100				∥	$A_{2u}(b^3E_u)$

shift of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in $(n\text{-}Bu_4N)[OsNX_4]$ (X = Cl, Br).[18] The above data support a $\delta \rightarrow d_{x^2-y^2}$ assignment for band II. In a D_{4h} complex such as $Re_2Cl_8^{2-}$, there are b_{1g} and b_{2u} linear combinations of the $d_{x^2-y^2}$ orbitals, yielding $^1A_{2g}$ and $^1A_{1u}$ excited states, respectively, for promotion of a δ electron. A transition to either of these states is orbitally forbidden. In the Herzberg-Teller coupling scheme,[19] $^1A_{1g} \rightarrow {}^1A_{2g}$ can gain vibronic intensity both parallel and perpendicular, but $^1A_{1g} \rightarrow {}^1A_{1u}$ can *only* be allowed in perpendicular polarization, as a $D_{4h}M_2X_8$ unit does not possess an a_{2g} vibrational mode. As band II exhibits only perpendicular polarization, the assignment $\delta \rightarrow d_{x^2-y^2}(b_{2u})(^1A_{1g} \rightarrow {}^1A_{1u})$ is adopted.

Band III, which is centered at 23 645 cm^{-1}, is barely detectable on the low energy tail of band IV (Figure 2 and Table I). There is only one clear progression in a 185-cm^{-1} vibration, and it is perpendicularly polarized; however, the presence of parallel components cannot be ruled out, as the intensities are very low. The 185-cm^{-1} vibration is attributed to the symmetrical bending mode, a_{1g}(ReReCl). One striking aspect is the length of the progression, which, despite its weakness, is detectable for 12–13 vibrations. Band III is not observable in $(n\text{-}Bu_4N)_2[Re_2Br_8]$, owing to the presence of interfering charge transfer absorption. We tentatively assign band III to the electric-dipole-forbidden transition $\pi \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1E_g)$. The fact that an X$\alpha$ calculation has shown[6] that the π orbital of $Re_2Cl_8^{2-}$ possesses considerable halogen character is consistent with the assignment, as excitation of a_{1g} (ReReCl) is reasonable for a transition to $^1B_{1u}$.

Band system IV, which consists of two sharp, parallel polarized peaks at 27 000 and 28 100 cm^{-1}, shifts to 21 290 and 22 080 cm^{-1}, respectively, in $(n\text{-}Bu_4N)_2[Re_2Br_8]$. This constitutes conclusive evidence for a ligand to metal charge transfer (LMCT) assignment. Two closely spaced, allowed $e_g\pi(Cl) \rightarrow \delta^*(^1A_{1g} \rightarrow {}^1E_u)$ transitions have been predicted[6,10] for $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ by Xα calculations, and the intense band observed in a crystal of $(n\text{-}Bu_4N)_2[Re_2Cl_8]$ at 30 870 cm^{-1} is split into two components.[6] We suggest that band IV comprises the transitions to the two A_{2u} spin-orbit components derived from the LMCT states a^3E_u and b^3E_u.

Previous estimates made by us of the BDE for the quadruple Re–Re bond in $Re_2Cl_8^{2-}$ now seem likely either to be too low[20] (ca. 80 kcal/mol), because solvation contributions to excited state reactivity could be substantial,[20,21] or too high[2] (ca. 360 kcal/mol), because of accumulated errors in the MO calculation.[22] It is interesting to note that for the Re–Re double bonds in Re_2Cl_9 and Re_3Br_9 the BDE's have been estimated from thermochemical data to be 85 and 103 kcal/mol, respectively.[23] This suggests that for the quadruple bond a value somewhat over 100 kcal/mol might be sensible.

As another approach to this problem, we have utilized available vibrational data for $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$, and $Mo_2Cl_8^{4-}$. Data first reported for these species[16,17a,24,25] have recently been improved and extended by Clark and Franks for $Re_2X_8^{2-}$ [26a] (X = Cl, Br) and for $Mo_2Cl_8^{4-}$.[26b] In each case the Raman band that is due principally to totally symmetric metal–metal stretching was observed not only as the fundamental, but through several overtones. For the $Re_2X_8^{2-}$ ions, the first three overtones and for $Mo_2Cl_8^{4-}$ the first ten overtones were observed. From these overtone progressions Clark and Franks were able to evaluate ω_e and χ_e, the harmonic frequency and anharmonicity constant, respectively, for each of the $M_2X_8^{n-}$ species. It is well known in the vibrational spectroscopy of diatomic molecules[27,28] that such information may be used to estimate BDE's by a method known as the Birge-Sponer extrapolation. Specifically, the BDE is estimated as $(\omega_e^2/4\chi_e) - \omega_e/2$. This is only an approximation, even for diatomics; it can give results either too high or too low, but usually too high.[27] Its reliability in a polyatomic system is uncertain; the main difficulty arises because the "bond stretching mode", so-called, for a given bond will in general be coupled to other modes of the same symmetry and it is not clear whether the degree of coupling will vary with the state

Table II. Birge-Sponer Extrapolated Re_2 and Mo_2 Bond Dissociation Energies in $M_2X_8{}^{n-}$ Complexes

Compd[a]	ω_e, cm^{-1}	χ_e, cm^{-1}	BDE, kcal/mol
$K_4[Mo_2Cl_8]$	347	0.50 ± 0.05	172 ± 20
$Rb_4[Mo_2Cl_8]$	339	0.43 ± 0.05	190 ± 25
$Cs_4[Mo_2Cl_8]$	342	0.66 ± 0.07	127 ± 15
$(n\text{-}Bu_4N)_2[Re_2Cl_8]$	273	0.35 ± 0.05	152 ± 20
$(n\text{-}Bu_4N)_2[Re_2Br_8]$	276	0.39 ± 0.06	139 ± 25

[a] Data from ref 26.

of excitation of the vibration. In the $M_2X_8{}^{n-}$ ions, with D_{4h} symmetry, there are two other totally symmetric (a_{1g}) vibrations besides "ν_{MM}", namely, "ν_{MX}" and "ν_{MMX}". Thus we apply the Birge-Sponer extrapolation in these cases with considerable circumspection.

Table II gives the input data, from Clark and Franks,[26] and the BDE's estimated. The uncertainty intervals on the latter derive solely from those listed for the χ_e values. It can be seen that all of the BDE's obtained are in a range we consider reasonable. If we assume that the values obtained are more likely to be too high than too low, we might say, allowing for an error in this direction of 15-20%, that the BDE for Re-Re quadruple bonds may be 115-130 kcal/mol, whereas that for Mo-Mo quadruple bonds is probably in the range 110-160 kcal/mol. It should be noted that these are very substantial bond energies. The only homonuclear units with BDE's that are clearly higher are C≡C (196) and N≡N (226), and beyond the first short period only P≡P (125 kcal/mol) has a BDE in the same range.[29]

Conclusions

(1) There exists excellent experimental evidence of several kinds for the entire assignment of band polarizations for $Re_2Cl_8{}^{2-}$ given previously.[4,6] This leads, in turn, to reliable transition assignments for these bands, including four weak features, as has been detailed above. No significant disagreements exist between our two laboratories in these respects.

(2) Earlier estimates of the Re-Re quadruple bond energy based on photochemical observations[20] and a crude MO calculation[2] are recognized to be, respectively, too low and too high. We suggest, very tentatively and with full awareness of the dangers inherent in the method, that by a Birge-Sponer extrapolation using Clark's Raman data on overtones of the $M_2X_8{}^{n-}$ species, the quadruple Mo-Mo and Re-Re bond dissociation energies most likely lie in the ranges 110-160 and 115-130 kcal/mol, respectively.

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