hyperfine coupling constant of $R_a$ from $(TME)_2^+$, however, is slightly lower than that of $R_a$ from the bromide within the limit of accuracy. This might be caused by delocalization of the unpaired electron of $R_a$ to the neighboring monomer cation such as by charge-transfer mechanism.

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## Low-Temperature Polarized Spectral Study of the Lowest Electronic Absorption Band in $Re_2Cl_8^{2-}$ and Related Binuclear Complexes

*Sir:*

Quadruple metal–metal bonding is well established for the ground state of the $D_{4h}$ $Re_2Cl_8^{2-}$ complex. Properties such as diamagnetism, a very short (2.24 Å) Re–Re bond length, and an eclipsed rotational configuration of attached $ReCl_4^-$ units all point to a $^1A_{1g}$ ground-state electronic structure in which the eight d valence electrons furnished by the two Re(III) units occupy metal–metal bonding molecular orbitals of $a_{1g}\sigma$, $e_u\pi$, and $b_{2g}\delta$ symmetries.[1] The molecular orbitals that are occupied in the lowest electronic excited states are much less certain. Extended Hückel MO calculations predict that the lowest spin-allowed electronic transitions in $Re_2Cl_8^{2-}$ are $^1A_{1g} \rightarrow {}^1B_{1u}$ $(b_{2g}\delta \rightarrow a_{2u}\sigma_n)$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ $(b_{2g}\delta \rightarrow b_{1u}\delta^*)$.[2] $^1A_{1g} \rightarrow {}^1B_{1u}$, which is orbitally forbidden, was calculated[2] to fall at slightly lower energy than the $z$-allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ transition.

The electronic absorption spectrum of $Re_2Cl_8^{2-}$ in methanol solution exhibits bands at 14.5 ($f$ = 0.023), 32.8 ($f$ = 0.31), and 39.2 kcm$^{-1}$ ($f$ = 0.65).[3] Arguing that an $f$ value of 0.023 is too low for an allowed transition of the $\delta \rightarrow \delta^*$ type, Cotton assigned[4] the 14.5-kcm$^{-1}$ band to a $\delta \rightarrow \sigma_n$ (specified[2] later as $^1A_{1g} \rightarrow {}^1B_{1u}$) transition. The fact that the band in question is either shifted substantially or absent in the electronic spectra[5] of binuclear complexes such as $Re_2(O_2CC_3H_7)_4Cl_2$, which have axially coordinated groups, was cited[2,4] in support of the $\delta \rightarrow \sigma_n$ assignment. However, we would expect both $\sigma_n$ and $\delta^*$ orbitals to be destabilized in axially bonded complexes in which the metal is forced to lie approximately in the plane of the equatorial donor atoms. In order to provide additional evidence on which to base electronic structural discussion, we have measured the MCD and 5°K polarized electronic spectra of several binuclear Re(III) complexes. These studies have established that the low-energy band system in $Re_2Cl_8^{2-}$ and closely related dimers arises from the $\delta \rightarrow \delta^*$ transition, as reported herein.

The 5°K polarized spectra of a thin crystal of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ between 710 and 600 nm are shown in Figure 1.[6] The observed vibrational structure is assigned in Table I. A prominent progression in the $a_{1g}(\nu_2)$ Re–Re stretching vibration (average spacing 248 cm$^{-1}$, ground state[7] 274 cm$^{-1}$) is built on an electronic origin at 14,183 cm$^{-1}$. A slightly weaker, second progression (average spacing 245 cm$^{-1}$) of $a_{1g}(\nu_2)$ begins at 14,298 cm$^{-1}$. The 115-cm$^{-1}$ separation of the two progressions corresponds to the excitation of one quantum of $a_{1g}(\nu_3)$, the totally symmetric ReReCl bending mode (ground state[7] 115 cm$^{-1}$). At 77°K a single vibrational progression is observed with an average spacing of 254

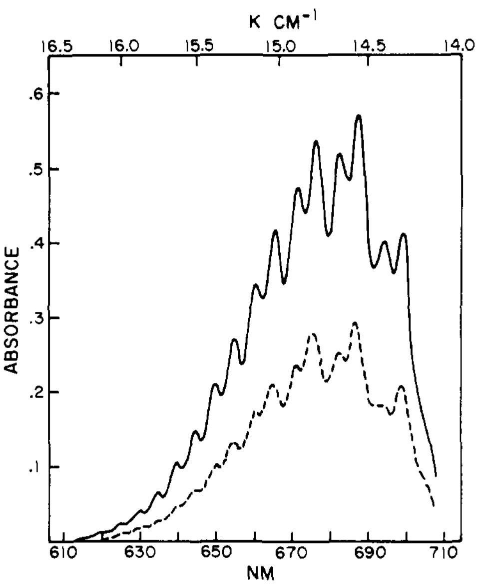

Figure 1. Parallel (—) and perpendicular (----) polarized absorption spectra on (100) of a single crystal of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.

**Table I.** Vibrational Structure of the 14,183-cm$^{-1}$ Band in $Re_2Cl_8^{2-}$ at 5°K

| nm | cm$^{-1}$ | $\Delta\bar{\nu}$(a), cm$^{-1}$ | $\Delta\bar{\nu}$(b), cm$^{-1}$ | Assignment |
|---|---|---|---|---|
| 705.06 (10) | 14,183 (2) | 0 | 0 | Origin |
| 699.41 | 14,298 | | 115 | $a_{1g}(\nu_3)$ |
| 694.12 | 14,407 | 224 | | $a_{1g}(\nu_2)$ |
| 687.65 | 14,542 | | 245 | $\nu_3 + \nu_2$ |
| 682.41 | 14,654 | 247 | | $2\nu_2$ |
| 676.24 | 14,788 | | 245 | $\nu_3 + 2\nu_2$ |
| 671.00 | 14,903 | 249 | | $3\nu_2$ |
| 665.06 | 15,036 | | 249 | $\nu_3 + 3\nu_2$ |
| 660.00 | 15,152 | 248 | | $4\nu_2$ |
| 654.35 | 15,282 | | 246 | $\nu_3 + 4\nu_2$ |
| 649.29 | 15,401 | 250 | | $5\nu_2$ |
| 644.12 | 15,525 | | 243 | $\nu_3 + 5\nu_2$ |
| 639.00 | 15,649 | 248 | | $6\nu_2$ |
| 634.29 | 15,766 | | 240 | $\nu_3 + 6\nu_2$ |

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(1) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969); and references therein.

(2) F. A. Cotton and C. G. Harris, *Inorg. Chem.*, **6**, 924 (1967).

(3) F. A. Cotton, N. F. Curtis, B. F. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965).

(4) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

(5) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(6) The $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ complex was prepared by a literature method.[3] An X-ray examination showed that the compound crystallizes in the space group $P2_1/_c$ with $a$ = 10.91, $b$ = 15.34, and $c$ = 16.43 Å, and $\beta$ = 122.66°. For two $Re_2Cl_8^{2-}$ anions per unit cell, the calculated density is 1.635 g/cm$^3$. The density determined by flotation in bromoform–carbon tetrachloride is 1.623 g/cm$^3$. For the spectral studies, thin single crystals were grown from acetonitrile on quartz substrates. Spectral data were obtained using a Cary 17 spectrophotometer equipped with an Andonian liquid helium dewar and double Glan-Taylor air-spaced calcite polarizers. Spectra were measured along the extinction directions of the (100) crystal face.

(7) W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, *J. Coord. Chem.*, **1**, 121 (1971).

cm$^{-1}$. It is important to note that the integrated intensity of the 14,183-cm$^{-1}$ band definitely does not decrease on going from 300 to 5°K, eliminating transition assignments which require vibronic intensity giving mechanisms. Furthermore, no A term is present in the MCD spectrum[8] in this region of absorption. Thus the observed temperature dependence of the absorption and the MCD results strongly suggest that an allowed transition to a nondegenerate excited state is responsible for the 14,183-cm$^{-1}$ band.

Conclusive evidence for the assignment of the low energy absorption system in quadruply bonded, binuclear Re(III) complexes to the $\delta \rightarrow \delta^*$ transition comes from 5°K polarized crystal spectral measurements on the $C_{2h}$ $Re_2Cl_6[P(C_2H_5)_3]_2$ complex.[9-11] Upon lowering the symmetry from $D_{4h}$ to $C_{2h}$, ${}^1A_{1g} \rightarrow {}^1A_{2u}$ becomes ${}^1A_g \rightarrow {}^1B_u$, which is $xz$ allowed (with $C_2 \equiv y$). For $Re_2Cl_6[P(C_2H_5)_3]_2$, in which the Re–Re vector is virtually perpendicular to the $a$ crystallographic axis, the origin of the low energy band occurs at 13,785 cm$^{-1}$. Strong $xz$ ($\perp a$) polarization is observed, exactly as predicted for a $\delta \rightarrow \delta^*$ transition. The $\delta \rightarrow \sigma_n$ assignment is eliminated as a possibility, because in $C_{2h}$ the ${}^1A_g \rightarrow {}^1A_u$ transition is allowed only in the direction ($y$) where essentially no absorption is found.

The electronic origin of the $\delta \rightarrow \delta^*$ band in $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$[12] at 5°K is found at 13,597 cm$^{-1}$, upon which is built a progression in the $a_{1g}(\nu_1)$ metal–metal stretch (average spacing 255 cm$^{-1}$, ground state[7] 277 cm$^{-1}$). Additional 255-cm$^{-1}$ progressions develop from peaks at 13,694 and 13,765 cm$^{-1}$, which allow us to assign excited-state values of 98 and 168 cm$^{-1}$ to the $a_{1g}(\nu_3)$ ReReBr bending (ground state not observed, calcd[7] 65 cm$^{-1}$) and $a_{1g}(\nu_2)$ Re–Br stretching (ground state[7] 184 cm$^{-1}$) vibrations, respectively. Undoubtedly there is substantial mixing of the three excited-state $a_{1g}$ modes for both $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, as there is in the ground state.[7]

The Raman spectra of compounds containing the quadruply bonded $Mo_2Cl_8^{4-}$ [13] exhibit[14,15] a band at *ca.* 350 cm$^{-1}$ which is resonance enhanced upon irradiation at 4800 Å.[15] Our 5°K electronic absorption spectrum of $K_4MoCl_8$[16] reveals that a richly structured system (origin 17,897 cm$^{-1}$; vibrational spacing *ca.* 351 cm$^{-1}$) attributable to $\delta \rightarrow \delta^*$ falls in that region. The fact that the ground- and excited-state vibrational frequencies are approximately equal is intriguing, but an interpretation in terms of bonding changes is not possible in the absence of quantitative information concerning the extent of mixing of Mo–Mo and Mo–Cl stretching modes. Low-temperature electronic absorption spectral studies of several binuclear Mo(II) complexes are now being investigated in an attempt to clarify this point.

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(8) The MCD spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ was measured in acetonitrile solution. We thank Professor P. J. Stephens of the University of Southern California for allowing us access to his equipment and for assistance with the measurements.

(9) The compound $Re_2Cl_6[P(C_2H_5)_2]_2$ was prepared by addition of $P(C_2H_5)_3$ to a slightly acidified methanol solution of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, as described in more detail for the analogous $P(C_6H_5)_3$ derivative.[10] Crystals of the compound are monoclinic, space group $P2_1/n$, with lattice constants $a$ = 7.644, $b$ = 10.985, and $c$ = 14.206 Å, $\beta$ = 96.5° (two molecules per unit cell).[11] The crystals grow as prisms elongated on $a$. The normal to the well-developed face makes an angle of 52.1° with the $c^*$ axis, confirming assignment as (011). The crystals are strongly dichroic (blue $\perp a$, yellow $\parallel a$). Thin single crystals for spectral measurements were grown from chloroform solution.

(10) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

(11) F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, **7**, 2135 (1968).

(12) Thin crystals of $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$[10] for spectral work were grown from acetonitrile solution.

(13) J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).

(14) A. Ketteringham and C. Oldham, *J. Chem. Soc., Dalton Trans.*, 1067 (1973).

(15) C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Chem. Soc., Chem. Commun.*, 399 (1973).

(16) $K_4MoCl_8$ was prepared as described by J. V. Brencic and F. A. Cotton, *Inorg. Chem.*, **9**, 351 (1970).

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## A Breakdown of the Hammett Acidity Function Concept

*Sir:*

The Hammett acidity function concept[1-3] requires that $pK_{HA}$, for all the acids correlated, in any one of the solvent mixtures involved, be a linear function of $pK_{HA}^0$, the corresponding quantity in a reference solvent (usually water) *with unit slope.* For the acid, HA (which is usually an indicator acid in the present context) $pK_{HA}^S$ is given by eq 1. Parker's notation[4] is

$$pK_{HA}^{S} = \log \frac{(HA)}{(H^+)(A^-)} + \log \frac{{}^{S}\gamma^{S'}_{HA}}{{}^{S}\gamma^{S'}_{A^-}\,{}^{S}\gamma^{S'}_{H^+}} \qquad (1)$$

used for activity coefficients. S′ is the solution in which the concentrations are actually determined. S is a convenient reference solution. Quantities in parentheses are concentrations. If S is an ideal aqueous solution it is denoted by 0. Then $pK_{HA}^S$ is $pK_{HA}^0$ and is given by an equation analogous to eq 1. Similar equations can also be written for a standard indicator acid, $HA_0$. By an appropriate combination of these equations, eq 2 is obtained.

$$pK_{HA}^{S} - pK_{HA_0}^{S} = pK_{HA}^{0} - pK_{HA_0}^{0} + \log \frac{{}^{0}\gamma^{S}_{A^-}\,{}^{0}\gamma^{S}_{HA_0}}{{}^{0}\gamma^{S}_{A_0^-}\,{}^{0}\gamma^{S}_{HA}} \qquad (2)$$

The basic hypothesis of Hammett acidity functions[1,2] holds that activity coefficient ratios such as ${}^{0}\gamma^{S}_{A^-}/{}^{0}\gamma^{S}_{HA}$ are independent of $pK_{HA}^0$; that is that ${}^{0}\gamma^{S}_{A^-}\,{}^{0}\gamma^{S}_{HA_0}/{}^{0}\gamma^{S}_{A_0^-}\,{}^{0}\gamma^{S}_{HA}$ should be unity if the acids are of the same structural type. Thus $pK_{HA}^S$ should be a linear function of $pK_{HA}^0$ with unit slope. This has always been recognized as an approximation.[1-3] It is the purpose of the present communication to point out a systematic failure of this approximation.

It has been known for some time that, for acids of related structural type, $pK_{HA}^S$ is a linear function of

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(1) A. J. Deyrup and L. P. Hammett, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

(2) J. F. Coetzee and C. D. Ritchie, "Solute Solvent Interactions," Marcel Dekker, New York, N. Y., Chapter 3.

(3) (a) R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1681 (1964); (b) A. Albagli, A. Buckley, A. M. Last, and R. Stewart, *J. Amer. Chem. Soc.*, **95**, 4711 (1973).

(4) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).