Table VIII

Ultraviolet Transitions in Ni(DPM)$_2$

	Obsd		Calcd			
Band	Cm^{-1}	Oscillator strength	Cm^{-1}	Polarization	Oscillator strength	Assignment
I	42,700	~0.2	48,220	y	0.31	ψ_{32} to ψ_{21} (σ_L to $3d_{xy}$)
II	37,300	~0.4	32,230	y	0.44	ψ_{30} to ψ_{22} (π_L to π^*_L)
			32,910	y	0.35	ψ_{31} to ψ_{23} (π_L to π^*_L)
	~29,000 (sh)	...	27,370	x	0.41	ψ_{28} to ψ_{21} (σ_L to $3d_{xy}$)

and corresponds to band III in the copper complex. Calculated and observed energies and oscillator strengths compare well as shown in Table VIII.

Shoulder on Band II.—A lower energy band representing a σ_L to Ni $3d_{xy}$ transition would be expected on the basis of the MO calculations (see Table VI). A transition with a calculated oscillator strength of 0.41 and x polarization is predicted to occur near 27,000 cm^{-1}. However, as in the corresponding region of the Cu(DPM)$_2$ spectrum, the consistency between calculated and observed spectra is poor and further discussion is not warranted.

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Molecular Orbital Calculations for Complexes of Heavier Transition Elements. III. The Metal–Metal Bonding and Electronic Structure of Re$_2$Cl$_8^{2-}$ [1]

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The metal–metal and metal–chlorine bonding in (Re$_2$Cl$_8$)$^{2-}$ are treated by "extended" Hückel molecular orbital theory. The calculation suggests that the π-bonding contribution to the Re–Re bond is five times that of the δ bonding and almost three times that of the σ bonding. The Re–Re bond stabilization and the rotational barrier in (Re$_2$Cl$_8$)$^{2-}$ are calculated as 366 and 51 kcal, respectively, by comparing a hypothetical (ReCl$_4$)$^-$ anion (C_{4v}) with the (Re$_2$Cl$_8$)$^{2-}$ anion (D_{4h}). The ordering of the molecular orbitals is discussed with respect to the magnetic properties and the observed and calculated spectral properties.

Introduction

The preparation[3] and structure[4] of the [Re$_2$Cl$_8$]$^{2-}$ anion have been discussed. Its chemistry[5] appears to be consistent with the proposed[6] quadruple metal–metal bond. It therefore provides an excellent opportunity to study the effects of the various factors contributing to metal–metal bonding. This approach, however, requires a detailed knowledge of the individual orbital contributions to the metal–metal bond; therefore, an extensive molecular orbital calculation for [Re$_2$Cl$_8$]$^{2-}$ has been undertaken. All Re–Re, Re–Cl, and Cl–Cl interactions have been considered in a semiempirical approach of the type generally called an extended Hückel calculation. It is recognized that for various reasons, to be discussed in detail below, such a calculation cannot provide results which can be taken literally. It is our belief, however, that the results obtained, when interpreted properly, do provide a semiquantitative picture of the main features of the metal–metal bonding and their relative importance. For this reason, we believe that the study reported here provides a useful advance beyond the level of the simple overlap treatment which has already been given[6] for Re$_2$Cl$_8^{2-}$.

Method of Calculation

Choice of the Basis Set.—A basis set of fifty atomic orbitals, χ_i (i = 1, 2, ..., 50), was used to construct the molecular orbitals ψ^j (j = 1, 2, ..., 50), in the LCAO–MO approximation[7] (eq 1). This basis set included the 5d, 6s, and 6p orbitals of each Re atom and the 3s and 3p orbitals of each Cl atom. It was assumed that the nonvalence atomic orbitals on both Re atoms and the eight Cl atoms did not participate in bonding, but formed a core potential that was unaltered by interactions of the valence electrons. The atomic orbitals, χ_i's, were expressed as single term Slater-type orbitals[8] (STO's) as given in eq 2, where α_i is the shielding parameter, N is the normalization co-

$$\psi^j = \sum_i C_i^j \chi_i \qquad (1)$$

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[1] Work supported by the U. S. Atomic Energy Commission.

[2] Predoctoral Fellow of the National Institutes of Health, 1964–1966; AEC Postdoctoral Fellow, 1966–1967.

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

[4] F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

[5] (a) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *ibid.*, **4**, 1696 (1965); (b) F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **5**, 1798 (1966).

[6] F. A. Cotton, *ibid.*, **4**, 334 (1965).

[7] J. H. Van Vleck, *J. Chem. Phys.*, **2**, 22 (1934).

[8] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

efficient, n_i is the principle quantum number, and $Y_l^m(\theta,\varphi)$ is the usual spherical harmonic. All atomic

$$\chi_i = N_i r^{n_i-1} \exp(-\alpha_i r) Y_l^m(\theta,\varphi) \qquad (2)$$

orbitals were expressed in a right-handed coordinate system as shown in Figure 1.

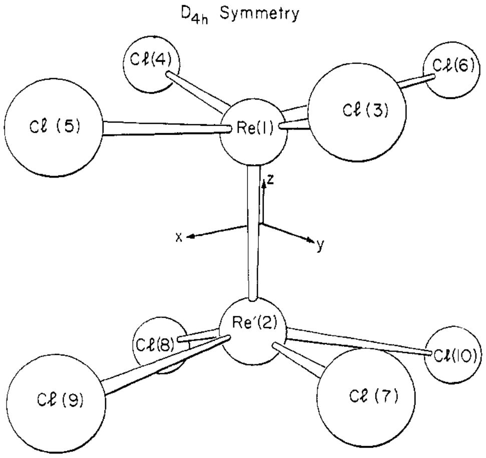

Figure 1.—$Re_2Cl_8^{2-}$ structure and coordinate system used to calculate overlap integrals. All atoms in a right-hand coordinate system. Numbers in parentheses correspond to atom numbers in Table I.

Evaluation of the Overlap Integrals.—The shielding parameters, α_i's, for the Re orbitals were determined by adjusting α_i to fit the overlap integrals between STO orbitals centered on Re and Re′ (Figure 1) to a numerical overlap integral between self-consistent field (SCF)[9] Re wave functions. This method has been discussed more fully earlier.[10] The α_i's for the Re 5d and 6s orbitals were obtained in this fashion from the overlap integrals of the type Re–Re′ 5d–5d and 6s–6s, respectively. Since the SCF Re 6p wave function was not available, the Re 6p radial wave function distribution was assumed to be slightly more diffuse than that of an Re 6s orbital.

The Cl α_i's were determined by numerically integrating the SCF Re orbital with an SCF[11,12] Cl orbital and fitting the resultant overlap with an overlap integral between STO Re and Cl wave functions. The Re α_i's had already been fixed by the Re–Re′ overlaps; thus, only the Cl α_i's needed to be varied. The Cl 3s and 3p α_i's listed with the Re α_i's in Table I were obtained by averaging the α_i's from Re–Cl 5d–3s, 6s–3s, 5d–3p, and 6s–3p overlaps. In this fashion all Re–Re and Re–Cl overlap integrals are essentially the same as overlap integrals between SCF wave functions. Only the very small Cl–Cl overlaps are in error. We assumed that the shielding parameters did not change with charge configuration changes. The fact that only a very small error is introduced by such an assumption has been discussed earlier.[10]

Evaluation of the Diagonal Matrix Elements, H_{ii}.—

TABLE I

INPUT PARAMETERS

Orbital	Atom	Orbital type	Coordinates, A			Orbital exp	H_{ii}
			X	Y	Z		
1	1	$6s$	0	0	1.12	1.56	−9.65
2	1	$6p_z$	0	0	1.12	1.50	−5.20
3	1	$6p_x$	0	0	1.12	1.50	−5.20
4	1	$6p_y$	0	0	1.12	1.50	−5.20
5	1	$5d_{z^2}$	0	0	1.12	2.11	−10.46
6	1	$5d_{xz}$	0	0	1.12	2.11	−10.46
7	1	$5d_{x^2-y^2}$	0	0	1.12	2.11	−10.46
8	1	$5d_{yz}$	0	0	1.12	2.11	−10.46
9	1	$5d_{xy}$	0	0	1.12	2.11	−10.46
10	2	$6s$	0	0	−1.12	1.56	−9.65
11	2	$6p_z$	0	0	−1.12	1.50	−5.20
12	2	$6p_x$	0	0	−1.12	1.50	−5.20
13	2	$6p_y$	0	0	−1.12	1.50	−5.20
14	2	$5d_{z^2}$	0	0	−1.12	2.11	−10.46
15	2	$5d_{xz}$	0	0	−1.12	2.11	−10.46
16	2	$5d_{x^2-y^2}$	0	0	−1.12	2.11	−10.46
17	2	$5d_{yz}$	0	0	−1.12	2.11	−10.46
18	2	$5d_{xy}$	0	0	−1.12	2.11	−10.46
19	3	$3s$	0	2.22	1.66	3.37	−23.01
20	3	$3p_z$	0	2.22	1.66	2.46	−13.85
21	3	$3p_x$	0	2.22	1.66	2.46	−13.85
22	3	$3p_y$	0	2.22	1.66	2.46	−13.85
23	4	$3s$	0	−2.22	1.66	3.37	−23.01
24	4	$3p_z$	0	−2.22	1.66	2.46	−13.85
25	4	$3p_x$	0	−2.22	1.66	2.45	−13.85
26	4	$3p_y$	0	−2.22	1.66	2.46	−13.85
27	5	$3s$	2.22	0	1.66	3.37	−23.01
28	5	$3p_z$	2.22	0	1.66	2.46	−13.85
29	5	$3p_x$	2.22	0	1.66	2.46	−13.85
30	5	$3p_y$	2.22	0	1.66	2.46	−13.85
31	6	$3s$	−2.22	0	1.66	3.37	−23.01
32	6	$3p_z$	−2.22	0	1.66	2.46	−13.85
33	6	$3p_x$	−2.22	0	1.66	2.46	−13.85
34	6	$3p_y$	−2.22	0	1.66	2.46	−13.85
35	7	$3s$	0	2.22	−1.66	3.37	−23.01
36	7	$3p_z$	0	2.22	−1.66	2.46	−13.85
37	7	$3p_x$	0	2.22	−1.66	2.46	−13.85
38	7	$3p_y$	0	2.22	−1.66	2.46	−13.85
39	8	$3s$	0	−2.22	−1.66	3.37	−23.01
40	8	$3p_z$	0	−2.22	−1.66	2.46	−13.85
41	8	$3p_x$	0	−2.22	−1.66	2.46	−13.85
42	8	$3p_y$	0	−2.22	−1.66	2.46	−13.85
43	9	$3s$	2.22	0	−1.66	3.37	−23.01
44	9	$3p_z$	2.22	0	−1.66	2.46	−13.85
45	9	$3p_x$	2.22	0	−1.66	2.46	−13.85
46	9	$3p_y$	2.22	0	−1.66	2.46	−13.85
47	10	$3s$	−2.22	0	−1.66	3.37	−23.01
48	10	$3p_z$	−2.22	0	−1.66	2.46	−13.85
49	10	$3p_x$	−2.22	0	−1.66	2.46	−13.85
50	10	$3p_y$	−2.22	0	−1.66	2.46	−13.85

As noted earlier,[10] H_{ii}, the energy of an electron of the ith atomic orbital moving in the field of the nuclei and other electrons of the molecule, can be expressed in terms of the one-center atomic energy integrals, A_{ii}, and the multicentered molecular energy integrals, M_{ii}. This is expressed in eq 3. The A_{ii}'s can be estimated

$$H_{ii} = A_{ii} + M_{ii} \qquad (3)$$

by the valence state ionization potentials (VSIP) of the ith atomic orbital.

However, since most of the spectral states and processes[13] for Re(0) and Re(I) have not been assigned,

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[9] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

[10] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

[11] R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 521 (1961).

[12] R. E. Watson and A. J. Freeman, *ibid.*, **120**, 1125 (1960).

[13] C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington D. C., 1949 and 1952.

the VSIP's for Re(0) cannot be determined with any accuracy by this method. Therefore, the VSIP's for the Re(0) 6s, 6p, and 5d orbitals utilized in this calculation were set equal to those used in the $ReCl_6^{2-}$ calculation.[14] This can be justified, to a large extent, by the *a posteriori* success in obtaining reasonable Re–Cl interactions in $ReCl_6^{2-}$ as shown by the agreement of the results with various experimental data, particularly by the satisfactory correlation of quadrupole coupling constant data[15] with the calculated charge distribution[14] using a recently published theoretical relationship.[16]

While one might expect, therefore, that the calculation of the Re–Cl interactions in $Re_2Cl_8^{2-}$ could be carried out employing these VSIP's, there remains, however, the effect of the Re–Re interactions or the metal–metal bonding on these parameters. Little can be said quantitatively about this, but qualitatively, the Re orbitals can only become more stable (more negative values for the VSIP's) because of the Re–Re interactions. This is a consequence of the increased electron-nuclear Coulombic interaction resulting from both a short Re–Re bond[2] and an effective positive charge on the Re atoms in $Re_2Cl_8^{2-}$.

Semiquantitatively, this stabilization should be proportional to the extent of penetration by the wave function on one Re atom into the core of the other Re atom; consequently the σ orbitals would be stabilized more than the π orbitals which would be stabilized more than the δ orbitals. It is not feasible to try to calculate the amount of stabilization energy for each orbital type (σ, π, δ). Therefore, rather than make arbitrary guesses at these energies the calculations were carried out making no changes in the Re VSIP's from the values[14] used in $ReCl_6^{2-}$ with the intention of making allowances for penetration effects in interpreting the results.

Basically, there should be two effects on the final MO diagram (Figure 2). First, the separations between the σ–σ^*, π–π^*, and δ–δ^* molecular orbitals ought to be greater than those calculated since the bonding states should be more stable than indicated. Second, the nonbonding $\sigma_n(1)$ molecular orbital should have lower energy than that calculated. Because of the large positive effective charge (1.25) calculated for Re, the sensitivity of penetration corrections,[17] and the diffuseness of the 6s and 6p wave function,[9] we believe that the $\sigma_n(1)$ could be stabilized by about 2 ev and the δ–δ^* separation could be increased by 1 ev.

The M_{ii}'s can be approximated by a point charge expression and an additional penetration correction. The same dependence on charge was assumed here for M_{ii} as was assumed in the $PtCl_4^{2-}$ molecular orbital calculation.[10]

The Cl 3s and 3p A_{ii}'s used were those calculated by Hinze and Jaffé[18] for $sp^2p^2p^2$ and $s^2p^2p^2p$ states, respectively. All input parameters are summarized in Table I.

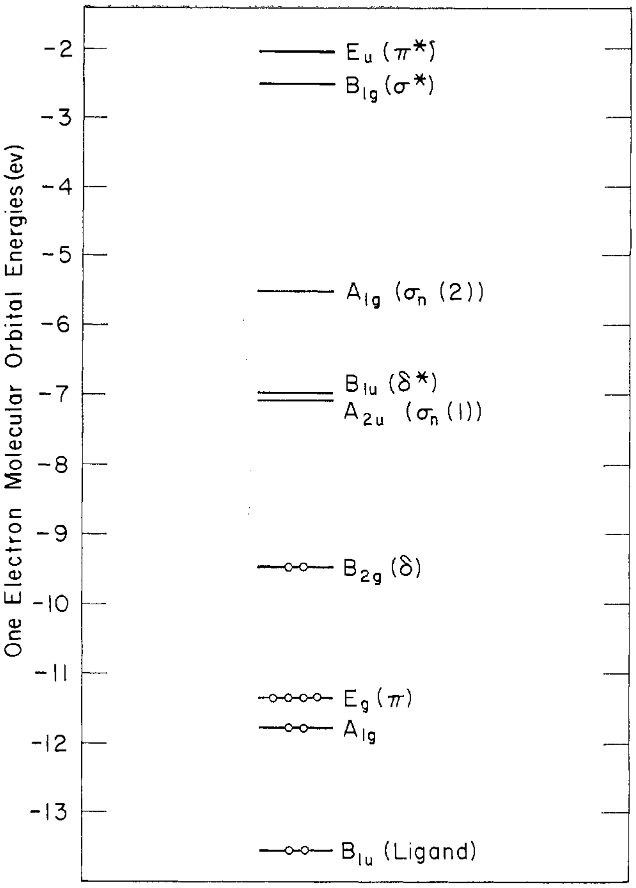

Figure 2.—A partial one-electron MO diagram for orbitals having predominant metal d character.

Evaluation of the Off-Diagonal Matrix Elements, H_{ij}.—The H_{ij}'s, the Hamiltonian matrix elements between the ith and jth atomic orbitals, were evaluated by the Mulliken–Wolfsberg–Helmholz approximation[19,20]

$$H_{ij} \approx KS_{ij}(H_{ii} + H_{jj})/2 \qquad (4)$$

K is the Wolfsberg–Helmholz factor and S_{ij} is the overlap integral between the ith and jth atomic orbitals.

A K equal to 1.80 was used for all H_{ij}'s. This value is the same as the optimum value determined from previous calculations[8] and is close to the "best fit" value for small molecules.[21,22]

Calculation Procedure.—The extended Hückel molecular orbital theory was employed, in which all overlap integrals were evaluated.[23] No assumption was made as to the extent of hybridization of either the ligand or metal wave functions. These conditions and the LCAO-MO assumption lead directly to the familiar constraint on the secular determinant

$$\det|H_{ij} - ES_{ij}| = 0 \qquad (5)$$

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(14) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 376 (1967).

(15) R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **69**, 2101 (1965).

(16) F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

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(18) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(19) R. Mulliken, *J. Chem. Phys.*, **46**, 497 (1949).

(20) M. Wolfsberg and L. Helmholz, *ibid.*, **20**, 837 (1952).

(21) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **53**, 1089 (1965).

(22) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2474 (1963).

(23) A modification of the program written by R. Hoffmann was used. All α_i's were determined by a MAD program WAVEF written by C. B. Harris.

The calculation was refined on charge to a self-consistency[10] of 0.01 electronic charge unit on Re.

Results

A table giving all overlap integrals, eigenvectors, and eigenvalues for the molecular orbitals has been filed with the American Documentation Institute.[24] A diagram giving the positions of the one-electron MO's most likely to be involved in discussing the spectrum and the bonding is given in Figure 2.

Interpretation of the Spectrum.—The calculated energies for both electric-dipole-allowed and vibronically-induced transitions together with the observed transition energies and estimates of the oscillator strengths of the observed transitions are collected in Table II.

TABLE II

CALCULATED AND OBSERVED ELECTRONIC TRANSITIONS

Electric dipole allowed	Polarization	Calcd transition energy, cm^{-1}	Experimental spectrum Energy, cm^{-1}	Experimental spectrum Oscillator strength
$^1b_{2g} \rightarrow {}^1b_{1u}$ ($\delta \rightarrow \delta^*$)	z	19,700	32,800	0.31
$^1e_g \rightarrow {}^1a_{2u}$ ($\pi \rightarrow \sigma_n(1)$)	x,y	34,800	39,200	0.65
$^1e_g \rightarrow {}^1b_{1u}$ ($\pi \rightarrow \delta^*$)	x,y	35,000		
$^1a_{1g} \rightarrow {}^1a_{2u}$ ($\sigma \rightarrow \sigma_n(1)$)	z	43,100		
$^1b_{2g} \rightarrow {}^1e_u$ ($\delta \rightarrow \pi^*$)	x,y	59,700		
Electric dipole forbidden				
$^1b_{2g} \rightarrow {}^1a_{2u}$ ($\delta \rightarrow \sigma_n(1)$)		18,700	14,500	0.023
$^1b_{2g} \rightarrow {}^1a_{1g}$ ($\delta \rightarrow \sigma_n(2)$)		30,900		
$^1e_g \rightarrow {}^1a_{1g}$ ($\pi \rightarrow \sigma_n(2)$)		46,100		
$^1a_{1g} \rightarrow {}^1a_{1g}$ ($\sigma \rightarrow \sigma_n(2)$)		49,400		

The low-energy, electric-dipole-forbidden transition at 14,500 cm^{-1} has been previously[6] assigned as the $^1b_{2g} \rightarrow {}^1a_{2u}$ ($\delta \rightarrow \sigma_n(1)$) transition. Such an assignment was based on very qualitative theoretical considerations[6] and also on the comparison of the $Re_2Cl_8^{2-}$ spectrum with the spectra of $Re_2(O_2CR)_4X_2$ systems.[5b,6] In the latter systems there are halide ions, X, coordinated at each end of the molecule, on the fourfold axis.[25] In order to bond these halide ions, the rhenium σ orbitals used to form the $\sigma_n(1)$ and $\sigma_n(2)$ MO's would have to be used, thus eliminating (or drastically shifting) the $^1b_{2g} \rightarrow {}^1a_{2u}$ transition in these molecules. Experimental results[5b] are in accord with this.

The difference between the observed and calculated transition energies, ~4000 cm^{-1}, is probably due in part to neglect of penetration effects on the Re atomic orbitals, as noted earlier, and in part to neglect of interelectronic repulsion energies (that is, to the fact that the actual transitions are between states of the system whereas the calculations pertain only to one-electron orbitals). Both of these factors would tend to make the calculated energy greater than that observed, as is the case.

The two transitions at 32,800 and 39,200 cm^{-1} have oscillator strengths approaching unity. As such, they should be electric-dipole-allowed transitions. The 32,800 cm^{-1} band was previously[6] assigned to a $^1b_{2g} \rightarrow {}^1b_{1u}$ ($\delta \rightarrow \delta^*$) transition. Although the agreement between the calculated and observed transition energy for this assignment is poor, primarily because of the neglect of the penetration correction, no other reasonable assignment is possible. Both the $^1b_{2g} \rightarrow {}^1e_u$ and the $^1e_g \rightarrow {}^1b_{1u}$ assignments can be ruled out as possibilities. Such assignments would require an inversion of the b_{2g} and e_g (δ and π) molecular orbitals. In other words, the interaction of the Re δ orbitals would be greater than that of the Re π orbitals. Clearly this is unreasonable. If, as suggested earlier, the penetration effect might lower the δ orbital by about 1 ev relative to the δ^* orbital, the calculated separation would become ~28,000 cm^{-1}, which is in reasonable agreement with the observed transition energy of ~33,000 cm^{-1}.

Assigning this transition as $^1a_{1g} \rightarrow {}^1a_{2u}$ would mean that the σ to nonbonding σ separation would be less than the $\delta \rightarrow \delta^*$ separation. This is highly unlikely in view of the very large overlap difference between σ and δ orbitals.

The only other possible assignment for this transition would be $^1e_g \rightarrow {}^1a_{2u}$. If this were, in fact, the case one would expect this transition to be absent, which it is not, in the $Re_2(O_2CR)_4X_2$ molecules, since the σ_n's (Figure 2) would be greatly shifted by the interaction with the X's in such molecules. Furthermore such an assignment would require an inversion in the order of the e_g and b_{2g} orbitals. A measurement of the polarization of the band would certainly distinguish between the $^1b_{2g} \rightarrow {}^1b_{1u}$ and $^1e_g \rightarrow {}^1a_{2u}$ assignments since the former is z polarized while the latter is x,y polarized. However, such experiments have not yet proven feasible.

The transition appearing at 39,200 cm^{-1} cannot be assigned unambiguously, although in all likelihood it is a $^1e_g \rightarrow {}^1a_{2u}$ transition.

It should again be emphasized that the MO diagram is used only as a qualitative guide in assigning the spectrum. As a quantitative tool, extended Hückel theory is far from satisfactory. This point has been discussed in earlier papers.[10,14,26]

Nature of the Re–Re Bond.—The Re 5d molecular orbitals have an occupation of $(a_{1g})^2(e_g)^4(b_{2g})^2$. This $^1A_{1g}$ ground state is in agreement with the observed diamagnetism of $[Re_2Cl_8]^{2-}$.

Within the framework of the electron pair definition of a single bond, the Re–Re bond is a quadruple bond. It is even possible to represent the Re–Re bonding in terms of an equivalent (in the Lennard-Jones sense) set of orbitals as four separate but equivalent, bent single bonds.[27] However, it seems more appropriate

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(24) Overlap integrals, eigenvectors, and eigenvalues have been deposited as Document No. 9304 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for 35-mm microfilm, payable to Chief, Photoduplication Service, Library of Congress.

(25) This statement is based upon structural results obtained by W. R. Robinson for $Re_2(O_2CC_6H_5)_4Cl_2$; the assumption that such a structure is general for $Re_2(O_2CR)_4X_2$ molecules seems reasonable.

(26) F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).

(27) F. A. Cotton, *Rev. Pure Appl. Chem.*, **16**, 175 (1966).

to describe the Re–Re bond directly in terms of the occupied molecular orbitals which contribute to it.

Bond order, as defined by Mulliken,[28] is given in eq 6. $N(k)$ is the number of electrons in the kth molecular orbital, $C^{\alpha}{}_{ik}$ and $C^{\beta}{}_{jk}$ are coefficients of the ith and jth atomic orbitals in the kth molecular orbital, $S^{\alpha\beta}{}_{ij}$ is the overlap between the ith and jth atomic orbitals, and the sum over i and j is restricted to orbitals on the α and β atoms. Thus the Re–Re bond order can be expressed as

$$BO_{\alpha\beta} = \sum_i \sum_j N(k) C^{\alpha}{}_{ik} C^{\beta}{}_{jk} S^{\alpha\beta}{}_{ij} \qquad (6)$$

$$BO_{\mathrm{Re,Re}} = \sigma + \pi + \delta \qquad (7)$$

where σ, π, and δ are the designations for σ, π, and δ contributions. Table III lists the various contributions to the Re–Re bond. In an analogous way the Re–Cl bond is also described in Table IV.

Table III

Re–Re Bond Contributions[a–d]

σ Bond[a]

	6s	6pσ	5dσ
6s	0.2243	0.0286	−0.0117
6pσ	0.0286	0.0019	−0.0094
5dσ	−0.0117	−0.0094	0.1551

π Bond[b]

	6pπ(2)	5dπ(2)
6pπ(2)	0.0318	0.0894
5dπ(2)	0.0894	0.9424

δ Bond[c]

	5d$_{xy}$ (δ)	5d$_{x^2-y^2}$ (δ')
5d$_{xy}$ (δ)	0.2213	0.0
5d$_{x^2-y^2}$ (δ')	0.0	0.0041

[a] σ bond order = 0.3923. [b] π bond order = 1.1530. [c] δ bond order = 0.2254. [d] Total Re–Re bond order = 1.7707.

Table IV

Re–Cl Bond Contributions[a]

	3s	3p$_y$ (σ)	3p$_z$ ($\pi(\|\|)$)	3p$_x$ ($\pi(\perp)$)
6s	0.0422	0.0182	0.0001	. . .
6p$_y$ (σ)	0.0522	0.0127	0.0002	. . .
6p$_z$ ($\pi(\|\|)$)	0.0028	0.0037	0.0174	. . .
6p$_x$ ($\pi(\perp)$)	. . .	. . .	. . .	0.0164
5d$_{x^2-y^2}$ (σ)	0.0292	0.0940	0.0153	. . .
5d$_{z^2}$ (σ)	0.0145	0.0244	0.0203	. . .
5d$_{yz}$ ($\pi(\|\|)$)	0.0049	0.0257	−0.0039	. . .
5d$_{xy}$ ($\pi(\perp)$)	. . .	. . .	. . .	0.0061

[a] Total Re–Cl bond order = 0.3986.

It is apparent that the major components of the Re–Re bond are the π bonds. Furthermore, the total π bonding is about five times as strong as the δ bond and three times as strong as the σ bond. The $BO_{\mathrm{Re,Re}}/BO_{\mathrm{Re,Cl}}$ ratio of 4.4 is the Re–Re electron pair bond order assuming the Re–Cl bonds to be single bonds.

Because the Re–Re π and σ bonds are symmetric about the fourfold rotation axis in $[Re_2Cl_8]^{2-}$, they should not preferentially stabilize[29] the molecule in D_{4h} (eclipsed) as opposed to D_{4d} (staggered) symmetry. Only the δ bond has the proper symmetry characteristics to stabilize the molecule in the observed eclipsed D_{4h} symmetry. However, the Cl–Cl′ repulsions would be higher for a D_{4h} (as opposed to D_{4d}) configuration. Therefore, the ultimate stabilization of the molecule in D_{4h} requires that the δ bonding stabilization energy be greater than the Cl–Cl′ repulsion energy.

In order to calculate the δ bond stabilization energy, either the energy of the δ molecular orbital in a staggered D_{4d} $[Re_2Cl_8]^{2-}$ configuration must be known or the energy of the δ molecular orbital in a hypothetical $[ReCl_4]^-$ molecule must be known. The latter approach was preferred because it not only gives the δ bond stabilization energy but, in fact, gives an approximate *total* Re–Re′ bond energy.

The one-electron molecular orbitals were calculated[30] for a hypothetical $[ReCl_4]^-$ ($^1/_2$ of $[Re_2Cl_8]^{2-}$) molecule. The correlation between the $[ReCl_4]^-$ and $[Re_2Cl_4]^{2-}$ molecular orbitals is given in Table V for the δ, π, and σ orbitals. Assuming a high-spin d^4 system for $[ReCl_4]^-$, eq 8 is the Re–Re′ bond stabilization energy for individual orbital interactions (i = σ, π, and δ).

$$\text{stabilization energy} = [2N(i)\epsilon_i(\mathrm{ReCl_4})^- - \epsilon_i N(i)(\mathrm{Re_2Cl_8})^{2-}] \qquad (8)$$

$N(i)$ is the number of electrons in the ith molecular orbital and the ϵ_i's are the molecular orbital energies of the ith orbital for the species indicated. The sum of these stabilization energies is the total Re–Re′ bond energy.[31] These results are listed in Table V.

Table V

Contributions to the Re–Re Bond Energy[a]

MO symmetry	$ReCl_4^-$ (C_{4v}), ev	$Re_2Cl_8^{2-}$ (D_{4h}), ev	Re–Re bond energies, kcal/mole
δ	−8.35	−9.45	51
π	−8.87	−11.35	114
σ	−9.87	−11.75	87

[a] Total Re–Re bond energy = 366 kcal/mole (Re–Re bond = $\sigma + 2\pi + \delta$).

If we assume that the fourfold rotation barrier arising from the Cl–Cl′ repulsions in $[Re_2Cl_8]^{2-}$ is the same order of magnitude as the threefold rotation barrier in C_2Cl_6 ($\geq$7 kcal/mole), then the δ bond stabilization is *seven times* the energy of the fourfold rotational barrier. Thus, the δ bond provides a potential well far in excess of the Cl–Cl′ barrier to rotation and the molecule is stabilized in an eclipsed D_{4h} rather than a staggered D_{4d} configuration.

Nature of the Re–Cl Bond.—It is apparent from Table IV that the σ contribution to the Re–Cl bond order is about three times that of the π. Since the Re_1 (Figure 1) is not in the plane of the 4 Cl (Cl_1, Cl_2, Cl_3,

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(28) R. W. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(29) Since the Cl–Cl′ overlap integrals would change under a C_4 rotation, there could be a very slight stabilization in one or the other symmetry. However, these effects would be energetically small compared to the energy differences between the δ bond in the two symmetries.

(30) The same parameters were used in this calculation as were used in the $[Re_2Cl_8]^{2-}$ calculation.

(31) No claim is made for the absolute accuracy of these energies. They are, in fact, only upper limits. Their significance can be only in the ratios, σ/π, π/δ, etc.

Cl_4), the σ and π contributions to the Re–Cl bonds are not rigorously separable by molecular symmetry. Thus, the values of σ and π Re–Cl bonds in Table IV are accurate only insofar as they represent an upper limit of π bonding and lower limit of σ bonding within the framework of rigorous σ–π separability. The total Re–Cl bond order, 0.40, is, of course, not subject to the separability of σ and π orbitals.

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Some Reactions of the Octahalodirhenate(III) Ions. IV. Reactions with Sodium Thiocyanate and the Preparation of Isothiocyanate Complexes of Rhenium(III) and Rhenium(IV)[1]

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The reaction of sodium thiocyanate with the $Re_2Cl_8^{2-}$ ion gives the complex anions $Re_2(NCS)_8^{2-}$ or $Re(NCS)_6^{2-}$, depending upon the reaction conditions. The use of acidified media favors the dinuclear rhenium(III) species, while the use of acetone as solvent resulted in oxidation to rhenium(IV) and the isolation of $Re(NCS)_6^{2-}$. Magnetic susceptibilities, spectral data, and electrolytic conductances for these two anions are reported and shown to be consistent with structures proposed for them. Infrared spectral measurements indicate that the thiocyanate groups are nitrogen bonded in each case. A complex of empirical formula $[(C_4H_9)_4N]_3[Re_2(NCS)_{10}(CO)_2]$ was isolated as a by-product during the preparation of $[(C_4H_9)_4N]_2Re(NCS)_6$. The carbonyl groups which appear to be present are presumably derived from the solvent (acetone). Solutions containing $Re_2(NCS)_8^{2-}$ react with triphenylphosphine to give a green complex which apparently has the formula $[(C_4H_9)_4N]_2[Re_2(NCS)_8(P(C_6H_5)_3)_2]$. Available evidence suggests that a direct Re–Re bond is not present in this compound. The magnetic moment of this complex (~4.1 BM per rhenium) is unusual and difficult to interpret.

Introduction

We have recently[2-4] investigated the reactivity of the $Re_2X_8^{2-}$ ions, where X = Cl or Br, toward a variety of donor molecules. One of the most interesting results of these studies is that in a wide variety of ligand substitution reactions (with carboxylic acids, phosphines, and sulfur ligands) the Re–Re bond is normally preserved even though it may not remain a quadruple bond, as is present in the dinuclear $Re_2Cl_8^{2-}$ ions.[5,6] Thus a crystallographic investigation[7] has revealed that a Re–Re triple bond, not a quadruple bond, is present in the dinuclear 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$) complex, $Re_2Cl_5(DTH)_2$.

Changing X from Cl to Br usually has little effect upon the reactivity of the $Re_2X_8^{2-}$ species and the formation and stability of the resulting complexes. This is of course not unexpected. Consequently, we have investigated the reaction of $[(C_4H_9)_4N]_2Re_2Cl_8$ with sodium thiocyanate in an attempt to isolate salts of octathiocyanatodirhenate(III) ions and thereby obtain more information about the effect that the nature of X has upon the stability and reactivity of the $Re_2X_8^{2-}$ species. The results of these investigations are now reported and several new complexes of rhenium described.

Experimental Section

$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ was prepared as previously described.[2] All other reagents and solvents were commercially available. Analyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparation of Compounds. $[(n\text{-}C_4H_9)_4N]_2Re_2(NCS)_8$.—This complex was prepared by two procedures, both of which are described below. The second is by far the more convenient method.

(a).—To 150 ml of tetrahydrofuran under nitrogen was added 5.0 g of $[(C_4H_9)_4N]_2[Re_2Cl_8]$ and 4.0 g of NaSCN. The brown solution was stirred for 1 hr, then refluxed for 30 min. The solvent was removed on a rotary evaporator, and the resulting thick oil was filtered to recover a brown precipitate. After this precipitate had been washed with 20 ml each of water, ethanol, and ether, it was dissolved in a minimum amount of acetonitrile, passed through an alumina column to remove some small amounts of by-products, and recovered by evaporation of the solvent. The compound was dried under vacuum at 80°; yield 77%.

Anal. Calcd for $C_{40}H_{72}N_{10}S_8Re_2$: C, 36.34; H, 5.48; N, 10.60; S, 19.41. Found: C, 36.0; H, 5.32; N, 10.7; S, 19.3.

(b).—$[(C_4H_9)_4N]_2Re_2Cl_8$ (0.15 g) and NaSCN (0.10 g) were dissolved in 15 ml of methanol. Acetic acid (1 ml) and acetic anhydride (2 ml) were added, and the reaction mixture was stirred under nitrogen for 6 hr. The dark red solution was filtered and reduced to a small volume at room temperature. The resulting red crystalline material was filtered off, washed freely with ethanol, water, and ether, and dried *in vacuo;* yield 0.17 g.

Anal. Calcd for $C_{40}H_{72}N_{10}S_8Re_2$: C, 36.34; H, 5.48; N, 10.60; S, 19.41. Found (for separate preparations): C, 36.0, 36.6; H, 5.37, 5.57; N, 10.7, 10.5; S, 19.1.

An identical product was isolated when tetrahydrofuran, acidified with a few drops of acetic acid, was used as the solvent.

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