A Theoretical Study of the Metal–Metal Interaction in Binuclear Complexes of Transition Groups 6 and 7

Marc Benard

Contribution from the E.R. No. 139 du CNRS, Université Louis Pasteur, 67000 Strasbourg, France. Received March 18, 1977

Abstract: Ab initio calculations at the SCF and CI levels are performed on several characterized or hypothetical binuclear complexes of transition groups 6 and 7, namely, $Cr_2(O_2CH)_4$, $Mo_2(O_2CH)_4$, $CrMo(O_2CH)_4$, $[Cr_2(CH_3)_8]^{4-}$, $[Mn_2(CH_3)_8]^{2-}$, $[Cr_2Cl_8]^{4-}$, $[Mo_2Cl_8]^{4-}$, $[Tc_2Cl_8]^{2-}$, and $[Tc_2Cl_8]^{3-}$. The ground state of all the closed-shell systems can be described by a CI wave function with the quadruply bonding configuration $(\sigma)^2(\pi)^4(\delta)^2$ as the leading term. For all the chromium systems and for $[Mn_2(CH_3)_8]^{2-}$, the SCF approximation leads to an erroneous description of the bonding. Differences in the strength of the metal-metal bond may be related to the weight of the nonbonding and antibonding configurations in the CI expansion. Calculations on anhydrous and dihydrated chromium tetraformate indicate that axial ligands have apparently not a major influence on the strength of the Cr–Cr bond. The ground state of $[Tc_2Cl_8]^{3-}$ is assigned to be $^2B_{1u}$. The analysis of the CI wave function indicates that the formal bond order 3.5, which proceeds from this assignation, is compatible with the very short experimental Tc–Tc distance of 2.117 Å. A new interpretation of the 6000–9000-cm^{-1} region of the spectrum of $[Tc_2Cl_8]^{3-}$ is proposed from CI calculations. The problem of the rotation barrier of $[Mo_2Cl_8]^{4-}$ is examined by means of calculations at the CI level on the eclipsed and staggered form of this ion.

Introduction

Among the whole set of transition metal complexes presenting metal-metal interactions, x-ray structural investigations[1] have characterized a class of such complexes for which these interactions are especially strong. For these complexes, the metal-metal distance varies from 1.98 to 2.36 Å, which is significantly shorter than the usual metal-metal single bond length. Such complexes are known with metals of transition group 6 (Cr, Mo, and very recently W[2]) and 7 (Re, Tc, but apparently not Mn). Since, in most of these complexes, the metal presents the d^4 electronic configuration, the bonding was described in terms of a quadruple bond based on the sequence $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$ of metal d orbitals[3] (σ, π, δ denote the bonding nd–nd metal orbital of a_{1g}, e_u, or b_{2g} symmetry and σ^*, π^*, δ^* the corresponding antibonding orbitals). However, in proportion as x-ray measurements and theoretical investigations became more numerous and precise, new problems arose which, without questioning the general model of the quadruple bond, demanded further refinements. For instance:

(1) The numerous binuclear complexes of rhenium and molybdenum, the bonding of which was explained in terms of a quadruple bond, present a remarkable unity. The metal-metal bond length varies in a rather narrow range, from 2.198 to 2.251 Å for complexes of rhenium and from 2.090 to 2.183 Å for complexes of molybdenum. In contrast, important structural disparities have been noted for binuclear complexes of chromium, in such a way that these complexes may be divided into two classes. Some, like $Cr_2(CH_3)_8^{4-}$ or $Cr_2(allyl)_4$, have a Cr–Cr bond length of about 1.98 Å. These complexes, as the corresponding complexes of rhenium and molybdenum, have been described in terms of a "strong" quadruple bond. However, other complexes of chromium present longer metal-metal bonds, for instance, 2.22 Å in $[Cr_2(CO_3)_4]^{4-}$ and 2.362 Å in $Cr_2(O_2CCH_3)_4\cdot2H_2O$. This has been attributed to "weak" quadruple bonds. These "weak" bonds were tentatively explained by the presence of axial ligands on the system considered.[1,4,5] A shortening of the metal-metal bonds was observed when removing the axial ligands. This effect is very weak in the case of a molybdenum complex,[4] but slightly more important for $Cr_2(O_2CCH_3)_4$ since the Cr–Cr distance in the anhydrous compound is 2.29 Å.[5] However, an important gap of 0.3 Å remains with "strongly bonded" compounds. It must be remarked that this distance of 2.29 Å is still longer than the

bond length of 2.276 Å found for $\{[\eta^5-C_5(CH_3)_5]Cr(CO)_2\}_2$, a complex which has the formal bond order 3. Another anomaly is noted when comparing the bond lengths for $Cr_2(O_2CCH_3)_4$ (2.29 Å), for $Mo_2(O_2CCH_3)_4$ (2.093 Å),[6] and for the mixed complex $CrMo(O_2CCH_3)_4$ (2.050 Å).[7] The metal-metal bond length of the mixed complex is shorter than those of the two dimers. The problem concerning $Cr_2(O_2CCH_3)_4$ was made more puzzling with a recent ab initio SCF calculation performed with a minimal basis set on the model compound $Cr_2(O_2CH)_4\cdot2H_2O$.[15] This calculation yielded a ground-state configuration $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ thus leading to the conclusion that Cr–Cr bonding interactions are absent in this complex for the experimental Cr–Cr separation of 2.362 Å. This conclusion is in contradiction with the result of SCF–Xα–SW calculations performed on binuclear complexes of the second and third transition series which all corroborated the description of the ground state in terms of a quadruple bond[2,11,16,17] (namely, with the ground-state configuration $(\sigma)^2(\pi)^4(\delta)^2$).

(2) In some cases, complexes with multiple M–M bonds known with a given metal have no parallel with the corresponding element of one or both of the other transition series. Binuclear complexes of molybdenum(II) and chromium(II) were extensively studied and, though most of the molybdenum compounds do have chromium equivalents, important exceptions are noted, especially for the $[Cr_2Cl_8]^{4-}$ ion, which has not been reported so far. The situation is somewhat different with metals of the next group. If rhenium(III) presents many binuclear complexes with high bond order, only two such complexes of technetium are known: $[Tc_2Cl_8]^{3-}$ and its reduced form $[Tc_2Cl_8]^{2-}$.[1] No mention is made of the likelihood of such complexes with manganese.

(3) The complex of technetium mentioned above, $[Tc_2Cl_8]^{3-}$, presents an interesting problem. This compound is isostructural with $[Re_2Cl_8]^{2-}$, but the difference in charge implies the presence of nine d electrons, one more than required to form a quadruple bond. Because of the eclipsed structure and of a very short metal-metal distance of 2.117 Å[8] (shorter than for $[Mo_2Cl_8]^{4-}$) it was first suggested that the extra electron might occupy either a nonbonding orbital of σ character[9,10] or an orbital involving metal-ligand rather than metal-metal bonding.[11] These hypotheses appeared later to be in contradiction with the magnetic properties of the ion.[12] A detailed study of these properties suggested a δ^* assignment of the odd electron.[13] This assignment was confirmed by a

Table I. Geometrical Parameters Used for Calculations

System	Metal-metal distance, Å	Metal-ligand distance, Å	Exptl ref
$Cr_2(O_2CH)_4$	2.362	2.018	$Cr_2(O_2CCH_3)_4 \cdot 2H_2O$[20]
$Cr_2(O_2CH)_4 \cdot 2H_2O$	2.362	2.27[a]	$Cr_2(O_2CCH_3)_4 \cdot 2H_2O$[20]
$Mo_2(O_2CH)_4$	2.093	2.125	$Mo_2(O_2CCH_3)_4$[6]
$CrMo(O_2CH)_4$	2.050	2.018 2.125	$CrMo(O_2CCH_3)_4$[7]
$[Mo_2Cl_8]^{4-}$	2.139	2.45	$K_4Mo_2Cl_8 \cdot 2H_2O$[21]
$[Cr_2Cl_8]^{4-}$	2.139	2.45	$K_4Mo_2Cl_8 \cdot 2H_2O$[21]
$[Cr_2(CH_3)_8]^{4-}$	1.980	2.199	$Li_4Cr_2(CH_3)_8 \cdot 4C_4H_8O$[22]
$[Mn_2(CH_3)_8]^{2-}$	1.980	2.199	$Li_4Cr_2(CH_3)_8 \cdot 4C_4H_8O$[22]
$[Tc_2Cl_8]^{3-}$	2.117	2.364	$K_3Tc_2Cl_8 \cdot nH_2O$[8]

[a] Axial ligand.

Table II. Representative Values of the Exchange Term K_{jj*}

	$K_{\delta\delta*}$	$K_{\pi\pi*}$	$K_{\sigma\sigma*}$
$[Cr_2Cl_8]^{4-}$	0.219	0.178	0.192
$[Mo_2Cl_8]^{4-}$	0.130	0.098	0.108
$[Tc_2Cl_8]^{3-}$		0.065	0.070

SCF-Xα-SW calculation.[2] However, if the $(\sigma)^2(\pi)^4(\delta)^2(\delta*)^1$ configuration is assigned as the ground state the question of the Tc-Tc distance, very short in spite of the decrease of the formal bond order from 4 to 3.5, remains unresolved.

We report here the result of ab initio calculations including limited CI, performed either on binuclear complexes with confirmed structures ($[Mo_2Cl_8]^{4-}$, $Mo_2(O_2CH)_4$, $[Tc_2Cl_8]^{3-}$, $[Cr_2(CH_3)_8]^{4-}$) or on model compounds which are thought to be very similar to existing ones ($Cr_2(O_2CH)_4$, anhydrous and dihydrated, and the mixed formate $MoCr(O_2CH)_4$). The recent determination of the crystal structure of $Mo_2(O_2CH)_4$ confirmed that there is no significant change between formates and acetates.[19] Two calculations were performed on still hypothetical complexes: $[Cr_2Cl_8]^{4-}$ and $[Mn_2(CH_3)_8]^{2-}$. From these calculations, an attempt is made to give a general description of the metal-metal interaction for this type of complex, including the apparently special cases, namely, $Cr_2(O_2CCH_3)_4$ and $[Tc_2Cl_8]^{3-}$. The assignment of the first band of the optical spectrum of $[Tc_2Cl_8]^{3-}$ is discussed. An attempt is made to compute the rotation barrier of $[Mo_2Cl_8]^{4-}$ which emphasizes the drastic importance of CI. The calculation on $[Mn_2(CH_3)_8]^{2-}$ does not exclude the possibility for a quadruply bonded complex of manganese to exist. Part of this work was the subject of a preliminary account.[18]

Calculation Section

The LCAO-MO-SCF calculations were carried out with the Asterix system of programs[23] using Gaussian basis sets (13, 9, 7) for Mo and Tc, (11, 7, 5) for Cr and Mn, (10, 6) for Cl, (8, 4) for first-row atoms, and (4) for hydrogen, contracted to basis sets minimal for the inner shells and the $(n + 1)$s and $(n + 1)$p shells of the metal atoms, but split for the valence shells. The geometries used are displayed in Table I.

For $Cr_2(O_2CH)_4$ and $[Cr_2(CH_3)_8]^{4-}$, the Cr-Cr bond length has been optimized through a series of calculations with various metal-metal distances. A similar optimization, at the SCF level only, has been performed for $Mo_2(O_2CH)_4$. Results are displayed in Table VII. The experimental geometries for $[Mo_2Cl_8]^{4-}$ and $[Cr_2(CH_3)_8]^{4-}$ were used respectively for the hypothetical ions $[Cr_2Cl_8]^{4-}$ and $[Mn_2(CH_3)_8]^{2-}$. All the

calculations were performed with a UNIVAC 1110 computer.

Representative Timings. The calculation on $[Mo_2Cl_8]^{4-}$ was performed with a basis set of 388 Gaussian orbitals. The computation of one- and two-electron integrals required 92 min of computer time. The total energy of the ground state converged to ±0.0001 au in ten iterations, which required 330 s of computer time each. All the calculations were performed with a UNIVAC 1110 computer.

Limited Configuration Interaction (CI). CI and MCSCF calculations of potential energy curves have emphasized the importance of configurations of the closed-shell type corresponding to double excitations from a bonding level j to the corresponding antibonding level j*. In such a case, the nondiagonal term of the CI matrix can be identified with the exchange term K_{jj*}. In order to emphasize the importance of CI in binuclear complexes, some of these exchange terms are reported in Table II. The expansion mentioned as "limited CI" includes all the configurations (from di- to octaexcited) corresponding to the excitations $a^2 \rightarrow a*^2$ where a denotes one of the σ, π, δ orbitals and a* the corresponding antibonding orbital. The configurations resulting from the excitation of more than two electrons have no direct effect on the ground state but their indirect influence is determinant for the systems which are treated. The order of the limited CI matrix is 16 when the 4 bonding levels are doubly occupied and the corresponding antibonding levels are empty. It is less for the ground and some excited states of $[Tc_2Cl_8]^{3-}$ for which at least one antibonding level is partially filled. No CI is performed on the configuration $(\sigma)^2(\delta)^2(\delta*)^2(\sigma*)^2$ which does not generate any configuration of the type $a^2 \rightarrow a*^2$.[38]

Results

Ab initio calculations at the SCF level performed on the systems mentioned above are reported for both electronic configurations $(\sigma)^2(\pi)^4(\delta)^2$ and $(\sigma)^2(\delta)^2(\delta*)^2(\sigma*)^2$. Except for $[Mo_2Cl_8]^{4-}$ and $MoCr(O_2CH)_4$, a limited CI has been performed as indicated for the bound state $(\sigma)^2(\pi)^4(\delta)^2$. Orbital energies are listed in Table III for the $(\sigma)^2(\pi)^4(\delta)^2$ configuration of the four octachloride systems and in Table IV for the $(\sigma)^2(\delta)^2(\delta*)^2(\sigma*)^2$ configuration of $[Cr_2Cl_8]^{4-}$ and $[Mo_2Cl_8]^{4-}$. Tables V and VI display orbital energies respectively for the three tetraformate and the two $[M_2(CH_3)_8]^{4-}$ systems in their bonding configuration. Energies and metal charge distribution at the SCF level and energies at the CI level with the weight of the $(\sigma)^2(\pi)^4(\delta)^2$ configuration in the CI development are presented in Table VII, except for $[Tc_2Cl_8]^{3-}$. The energies of the ground state and several excited states of $[Tc_2Cl_8]^{3-}$, both at the SCF and CI levels, are displayed in Table VIII. The problem of the rotation barrier of $[Mo_2Cl_8]^{4-}$ was examined by means of a calculation on the staggered form of this ion. Potential energy curves at both SCF and CI levels for $Cr_2(O_2CH)_4$ and $[Cr_2(CH_3)_8]^{4-}$ (stabilized with four positive charges) are displayed respectively in Figures 3 and 4. The results obtained at the SCF level for chromium and molybdenum dimers are rationalized on the basis of the interaction diagrams of Figure 1, based on the electronic ground states of the fragments $[CrCl_4]^{2-}$ and $[MoCl_4]^{2-}$ assumed to be low spin and planar. An interaction diagram drawn on the same basis accounts for the SCF ground state of $MoCr(O_2CH)_4$ (Figure 2).

Discussion

An examination of the nature of the ground state and, in the case of $[Tc_2Cl_8]^{3-}$, of the first excited states of the systems that are treated (Tables VII and VIII) confirms and extends the conclusion already noticed concerning $Cr_2(O_2CH)_4$ and $[Cr_2Cl_8]^{4-}$:[18] the relative order of some low-lying configura-

Table III. Orbital Energies for $[Cr_2Cl_8]^{4-}$, $[Mo_2Cl_8]^{4-}$, and $[Tc_2Cl_8]^{2-}$ in the $(\sigma)^2(\pi)^4(\delta)^2$ Configuration and $[Tc_2Cl_8]^{3-}$ in the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ Configuration (Symmetry D_{4h})[a]

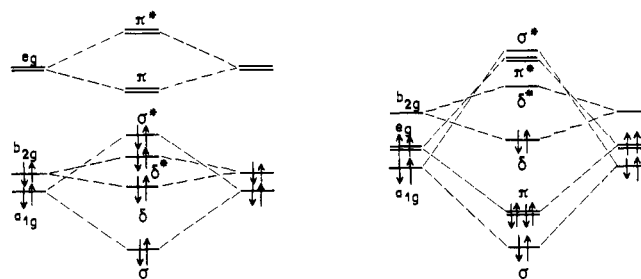| \[Cr₂Cl₈\]⁴⁻			\[Mo₂Cl₈\]⁴⁻			\[Tc₂Cl₈\]²⁻			\[Tc₂Cl₈\]³⁻		
Level	Energy	% Cr	Level	Energy	% Mo	Level	Energy	% Tc	Level	Energy	% Tc
$5a_{1g}$	0.512		$5a_{1g}$	0.541		$5a_{1g}$	0.485		$5a_{1g}$	0.514	
$4b_{2u}$	0.386		$4b_{2u}$	0.422		$4b_{2u}$	0.308		$4b_{2u}$	0.357	
$4b_{1g}$	0.366		$4b_{1g}$	0.377		$4b_{1g}$	0.278		$4b_{1g}$	0.323	
$4a_{2u}$	0.253		$4a_{2u}$	0.353		$4a_{2u}$	0.234		$4a_{2u}$	0.267	
$5e_g$	0.228		$5e_g$	0.352		$5e_g$	0.212		$5e_g$	0.254	
$2b_{1u}$	0.145		$2b_{1u}$	0.248		$2b_{1u}$	0.112				
									$2b_{1u}$	0.001	44
$2b_{2g}$	−0.089	82	$2b_{2g}$	−0.006	83	$2b_{2g}$	−0.105	56	$2b_{2g}$	−0.120	57
$5e_u$	−0.114	73	$5e_u$	−0.084	71	$5e_u$	−0.141	24	$5e_u$	−0.129	39
$1a_{1u}$	−0.145	0	$4a_{1g}$	−0.110	85	$1a_{1u}$	−0.145	0	$1a_{1u}$	−0.145	0
$3b_{2u}$	−0.149	0	$1a_{1u}$	−0.145	0	$3b_{2u}$	−0.149	0	$3b_{2u}$	−0.147	0
$1a_{2g}$	−0.152	0	$3b_{2u}$	−0.148	0	$1a_{2g}$	−0.153	0	$1a_{2g}$	−0.153	0
$4e_g$	−0.160	2	$1a_{2g}$	−0.151	0	$4e_g$	−0.161	2	$4e_g$	−0.163	1
$3e_g$	−0.163	1	$4e_g$	−0.160	2	$3e_g$	−0.169	4	$3e_g$	−0.166	4
$4a_{1g}$	−0.167	93	$3e_g$	−0.162	1	$4e_u$	−0.182	9	$4e_u$	−0.180	7
$4e_u$	−0.172	4	$4e_u$	−0.171	3	$3a_{2u}$	−0.192	8	$3a_{2u}$	−0.187	8
$3a_{2u}$	−0.175	3	$3a_{2u}$	−0.175	4	$3b_{1g}$	−0.195	1	$3b_{1g}$	−0.193	1
$3b_{1g}$	−0.185	2	$3b_{1g}$	−0.187	1	$4a_{1g}$	−0.213	36	$4a_{1g}$	−0.193	54
$2b_{2u}$	−0.196	11	$3e_u$	−0.216	6	$3e_u$	−0.229	8	$3e_u$	−0.227	7
$2b_{1g}$	−0.217	10	$2e_g$	−0.217	8	$2e_g$	−0.237	17	$2e_g$	−0.233	14
$1b_{1u}$	−0.221	7	$2b_{2u}$	−0.218	17	$3a_{1g}$	−0.244	12	$3a_{1g}$	−0.241	9
$2e_g$	−0.222	7	$3a_{1g}$	−0.224	6	$2a_{2u}$	−0.256	17	$2b_{2u}$	−0.244	26
$3e_u$	−0.223	11	$1b_{1u}$	−0.224	7	$2b_{2u}$	−0.262	33	$2a_{2u}$	−0.252	14
$3a_{1g}$	−0.223	6	$2a_{2u}$	−0.237	10	$1b_{1u}$	−0.263	23	$1b_{1u}$	−0.257	14
$2e_u$	−0.233	17	$2b_{1g}$	−0.240	18	$2b_{1g}$	−0.291	35	$2b_{1g}$	−0.271	28
$1b_{2g}$	−0.240	19	$2e_u$	−0.241	27	$1b_{2g}$	−0.302	44	$2e_u$	−0.291	56
$2a_{2u}$	−0.244	7	$1b_{2g}$	−0.245	17	$2e_u$	−0.319	69	$1b_{2g}$	−0.296	44
$2a_{1g}$	−0.260	10	$2a_{1g}$	−0.261	18	$2a_{1g}$	−0.325	66	$2a_{1g}$	−0.302	49

[a] Orbital energies of $[Cr_2Cl_8]^{4-}$, $[Mo_2Cl_8]^{4-}$, and $[Tc_2Cl_8]^{3-}$ were shifted so that the highest occupied ligand orbital of the four systems ($1a_{1u}$) has the same energy.

Table IV. Orbital Energies for $[Cr_2Cl_8]^{4-}$ and $[Mo_2Cl_8]^{4-}$ in the $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ Configuration

\[Cr₂Cl₈\]⁴⁻		% Cr	\[Mo₂Cl₈\]⁴⁻		% Mo
$5a_{1g}$	0.463		$5a_{1g}$	0.521	
$5e_g$	0.453		$5e_g$	0.454	
$4b_{2u}$	0.442		$4b_{2u}$	0.445	
$4b_{1g}$	0.415		$4b_{1g}$	0.393	
$5e_u$	0.290		$5e_u$	0.213	
$1a_{1u}$	−0.145	0	$4a_{2u}$	0.036	86
$3b_{2u}$	−0.147	0	$2b_{1u}$	−0.058	78
$4a_{2u}$	−0.147	22	$2b_{2g}$	−0.097	67
$1a_{2g}$	−0.151	0	$3b_{2u}$	−0.142	0
$4e_g$	−0.157	1	$1a_{1u}$	−0.145	0
$3e_g$	−0.165	0	$1a_{2g}$	−0.152	0
$4e_u$	−0.169	1	$4e_g$	−0.155	2
$3b_{1g}$	−0.181	2	$3e_g$	−0.162	1
$2b_{1u}$	−0.187	18	$4e_u$	−0.169	2
$2b_{2g}$	−0.194	18	$3a_{2u}$	−0.176	8
$2b_{2u}$	−0.194	10	$3b_{1g}$	−0.176	1
$3a_{2u}$	−0.209	30	$4a_{1g}$	−0.188	40
$3e_u$	−0.211	3	$2e_g$	−0.211	6
$2e_g$	−0.218	4	$2b_{2u}$	−0.214	15
$2b_{1g}$	−0.218	9	$3e_u$	−0.216	8
$4a_{1g}$	−0.219	2	$2e_u$	−0.219	7
$2e_u$	−0.228	4	$3a_{1g}$	−0.220	12
$3a_{1g}$	−0.256	10	$1b_{1u}$	−0.238	22
$2a_{2u}$	−0.280	54	$2b_{1g}$	−0.239	16
$1b_{2g}$	−0.287	83	$2a_{2u}$	−0.240	14
$1b_{1u}$	−0.296	82	$1b_{2g}$	−0.261	34
$2a_{1g}$	−0.386	97	$2a_{1g}$	−0.295	57

Figure 1. Simplified metal–metal interaction diagram for $[Cr_2Cl_8]^{4-}$ (left) and $[Mo_2Cl_8]^{4-}$ (right) *based on SCF calculations.*

SCF Level. As a general result, for all complexes of the first transition series which have been studied, i.e., chromium systems and $[Mn_2(CH_3)_8]^{2-}$, the SCF ground state is found to be the nonbonding configuration $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ which corresponds to the conclusion of Garner et al. regarding the absence of bonding interactions in $Cr_2(O_2CH)_4 \cdot 2H_2O$.[15] The potential energy curve for $Cr_2(O_2CH)_4$ appears repulsive (Figure 3) with no minimum detected up to 3.0 Å in spite of the presence of the four formate bridges. However, the bonding configuration shows a minimum, but at the very short distance of 1.65 Å and at a much higher energy. The influence of axial ligands was examined through a calculation on the bonding configuration of $Cr_2(O_2CH)_4 \cdot 2H_2O$. In a study on an axially bonded dimolybdenum complex, Collins et al.[4] suggested that the axial ligand would tend to populate the σ^* orbital, thus weakening the M–M σ bond. This effect appears very weak in the chromium formate since the $6b_{1u}$ orbital is populated 91% by electrons of water ligands and 3% only by σ^* metal electrons. The interaction between the oxygen of water and the occupied d_{z^2} orbital of chromium (σ) is of the same order of

tions can be reversed when going from SCF to CI level. In some cases, such an inversion may involve the ground state, thus leading to a completely different description of the bonding at the SCF and CI level.

Table V. Orbital Energies for $Cr_2(O_2CH)_4$ (d = 2.362 Å), $Mo_2(O_2CH)_4$ (d = 2.093 Å), and $CrMo(O_2CH)_4$ (d = 2.05 Å) in the $(\sigma)^2$-$(\pi)^4(\delta)^2$ Configuration

$Cr_2(O_2CH)_4$ (symmetry D_{4h})			$Mo_2(O_2CH)_4$ (symmetry D_{4h})			$CrMo(O_2CH)_4$ (symmetry C_{4v})			
Level	Energy	% Cr	Level	Energy	% Mo	Level	Energy	% Cr	% Mo
$3b_{2g}$	0.158	L^a	$2a_{2g}$	0.162	L	$12e$	0.174	80	15
$7e_u$	0.152	L	$7e_u$	0.146	L	$3a_2$	0.161		
$4a_{2u}$	0.038	M	$4a_{2u}$	0.134	M	$11e$	0.146	1	0
$5e_g$	−0.028	M	$5e_g$	0.091	M	$9a_1$	0.128	15	81
$2b_{1u}$	−0.059	M	$2b_{1u}$	0.030	M	$4b_2$	0.061	2	70
$2b_{2g}$	−0.303	91	$2b_{2g}$	−0.274	87	$10e$	−0.372	10	81
$6e_u$	−0.310	94	$5a_{1g}$	−0.363	91	$3b_2$	−0.428	64	3
$5a_{1g}$	−0.359	98	$6e_u$	−0.365	90	$8a_1$	−0.445	71	13
$1a_{1u}$	−0.444	0	$1a_{1u}$	−0.450	0	$2a_2$	−0.452	0	0
$4e_g$	−0.465	0	$4e_g$	−0.466	0	$9e$	−0.471	0	0
$3b_{2u}$	−0.501	2	$3e_g$	−0.493	1	$8e$	−0.495	0	0
$3e_g$	−0.502	2	$3b_{2u}$	−0.504	2	$7b_1$	−0.500	2	0
$5e_u$	−0.503	7	$3a_{2u}$	−0.504	2	$7e$	−0.507	2	7
$3a_{2u}$	−0.511	2	$5e_u$	−0.508	10	$7a_1$	−0.510	3	1
$4b_{1g}$	−0.513	9	$1b_{1u}$	−0.512	12	$2b_2$	−0.533	29	2
$1b_{1u}$	−0.519	11	$4b_{1g}$	−0.543	11	$6b_1$	−0.535	3	7
$4a_{1g}$	−0.539	6	$4a_{1g}$	−0.551	12	$6a_1$	−0.553	12	6

^{a} L: virtual orbital with predominant ligand character.

Table VI. Orbital Energies for $[Cr_2(CH_3)_8]^{4-}$ and $[Mn_2-(CH_3)_8]^{2-}$ (d = 1.98 Å) in the $(\sigma)^2(\pi)^4(\delta)^2$ Configuration (Symmetry D_{4h})^a

$[Cr_2(CH_3)_8]^{4-}$			$[Mn_2(CH_3)_8]^{2-}$		
Level	Energy	% Cr	Level	Energy	% Mo
$5e_g$	0.134	M	$6e_u$	0.142	L
$5a_{2u}$	0.132	M	$4b_{2u}$	0.106	ML
$6a_{1g}$	0.131	L	$5a_{1g}$	0.101	L
$6e_u$	0.108	L	$4b_{1g}$	0.092	ML
$4a_{2u}$	0.092	L	$4a_{2u}$	0.023	M
$5a_{1g}$	0.065	L	$5e_g$	0.006	M
$2b_{1u}$	0.042	M	$2b_{1u}$	−0.048	M
$2b_{2g}$	−0.230	96	$5e_u$	−0.349	24
$5e_u$	−0.289	87	$2b_{2g}$	−0.357	97
$4a_{1g}$	−0.320	97	$4e_g$	−0.378	22
$3b_{2u}$	−0.346	18	$3b_{2u}$	−0.401	46
$4e_g$	−0.363	8	$4a_{1g}$	−0.429	81
$3b_{1g}$	−0.374	19	$3a_{2u}$	−0.434	11
$4e_u$	−0.383	12	$3b_{1g}$	−0.434	47
$3a_{2u}$	−0.425	4	$4e_u$	−0.435	77
$3a_{1g}$	−0.458	5	$3a_{1g}$	−0.476	27
$1a_{1u}$	−0.540	0	$1a_{1u}$	−0.540	0
$2b_{2u}$	−0.555	0	$2b_{2u}$	−0.553	0
$1a_{2g}$	−0.556	0	$1a_{2g}$	−0.555	0
$3e_g$	−0.568	0	$3e_g$	−0.566	0
$2e_g$	−0.571	0	$2e_g$	−0.571	0
$2b_{1g}$	−0.581	0	$2b_{1g}$	−0.579	1
$2a_{2u}$	−0.583	0	$2a_{2u}$	−0.580	0
$3e_u$	−0.588	0	$3e_u$	−0.587	1
$2e_u$	−0.599	0	$2e_u$	−0.598	3
$1b_{1u}$	−0.600	1	$1b_{1u}$	−0.600	1
$2a_{1g}$	−0.612	1	$2a_{1g}$	−0.609	1
$1b_{2g}$	−0.622	2	$1b_{2g}$	−0.622	3

^{a} Orbital energies of $[Mn_2(CH_3)_8]^{2-}$ are shifted in order to put into coincidence pure ligand levels.

Figure 2. Simplified metal–metal interaction diagram for $CrMo(O_2CH)_4$ based on SCF calculations.

Figure 3. Potential energy curves for $Cr_2(O_2CH)_4$: (a) SCF energy of the $(\sigma)^2(\pi)^4(\delta)^2$ configuration; (b) SCF energy of the $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ configuration; (c) limited CI for the bound state.

magnitude: the population of the $8a_g$ orbital comes 92% from water and 4.5% from chromium. As expected the metal population in the other water orbitals is less than 1%. For each of the H_2O ligands, the net charge is +0.04 electron. In conclusion, the effect of axial ligands appears at this level of very little importance and even its qualitative influence on the metal-metal bond length at the SCF level cannot be determined unambiguously. Indeed the overlap population between the metal
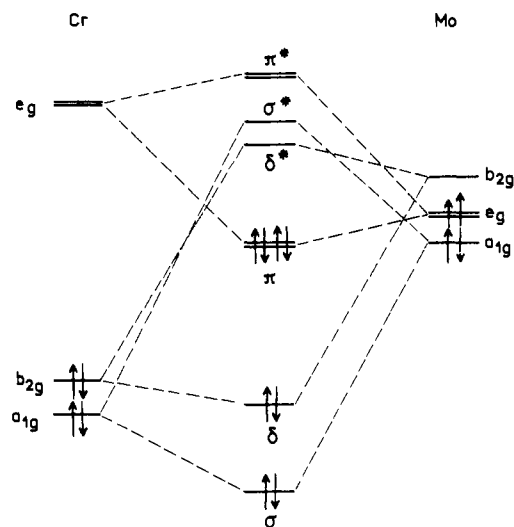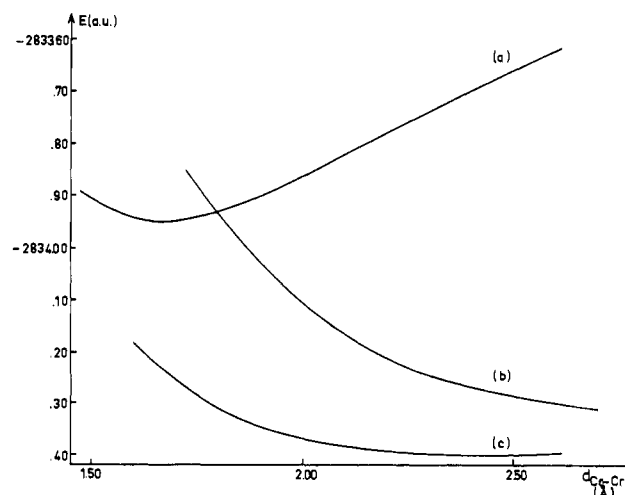
Table VII. SCF and CI Energies (au), Net Metal Charge, and Weight of the $(\sigma)^2(\pi)^4(\delta)^2$ Configuration in the CI Expansion (%)

| | Metal-metal bond length, Å | Total energy | | | | | |
| | | Electronic configuration $(\sigma)^2(\delta)^2(\delta*)^2(\sigma*)^2$ | | Electronic configuration $(\sigma)^2(\pi)^4(\delta)^2$ | | Bound state limited CI | % $(\sigma)^2(\pi)^4(\delta)^2$ |
		SCF energy	Net metal charge	SCF energy	Net metal charge		
Cr₂(O₂CH)₄	1.476			−2833.894			
	1.602			−2833.944		−2834.178	63
	1.728	−2833.851		−2833.941			
	1.980	−2834.093		−2833.868		−2834.366	32
	2.234	−2834.222		−2833.769		−2834.395	22
	2.362	−2834.258	+1.46	−2833.717	+1.34	−2834.401	18
	2.489	−2834.286		−2833.668		−2834.402	16
	2.617	−2834.301		−2833.622		−2834.397	14
	2.744	−2834.311					
	2.996	−2834.334					
Mo₂(O₂CH)₄	1.950			−8685.180			
	2.093	−8684.688	+1.39	−8685.188	+1.21	−8685.341	66
	2.236	−8684.833		−8685.181			
	2.380	−8684.921		−8685.149			
MoCr(O₂CH)₄	2.050	−5759.425		−5759.705	Cr +1.39 Mo +1.20		
[Cr₂(CH₃)₈]⁴⁻	1.980	−2399.275		−2399.163	+1.36	−2399.513	42
(stabilized	2.180	−2399.328		−2399.056		−2399.550	28
with four positive charges)	2.380	−2399.340		−2398.939		−2399.496	23
[Mn₂(CH₃)₈]²⁻	1.980	−2610.533		−2610.214	+1.27	−2610.628	38
[Tc₂Cl₈]²⁻	2.117	−12 060.294		−12 060.509	+0.72		
[Cr₂Cl₈]⁴⁻	2.139	−5751.988	+1.28	−5751.555	+1.14	−5752.015	30
[Mo₂Cl₈]⁴⁻ (eclipsed)	2.139	−11 602.639	+0.87	−11 602.958	+0.85	−11 603.110	61
[Mo₂Cl₈]⁴⁻ (staggered)	2.139			$(a_1)^2(e_1)^4(e_2)^2$ −11 603.052		−11 603.116	
[CrCl₄]²⁻		$(a_{1g})^2(b_{2g})^2$ −2876.264		$(a_{1g})^2(e_g)^2$ −2876.275			
[MoCl₄]²⁻		−5801.694		−5801.679			

Table VIII. SCF and CI Energies for Some Configurations of [Tc₂Cl₈]³⁻

Configuration	SCF energy	Limited CI energy	% leading term
B₁ᵤ	−12 060.460	−12 060.491	94
Eg	−12 060.370	−12 060.464	66
A₂ᵤ	−12 060.348	−12 060.451	70
B₁g	−12 060.265	−12 060.376	64
B₂g	−12 060.419	−12 060.451	94

atoms increases from 0.61 to 0.64 when axial ligands are introduced, which seems in contradiction with the slight mixing between the water p_z and the metal $\sigma*$ orbital. As the weight of H_2O orbitals is not higher than 10% in the metal $\sigma*$ orbital and negligible in other antibonding metal orbitals, the CI treatment is not expected to modify significantly these conclusions.

In opposition to complexes of the first transition series, the ground state of molybdenum systems, [Tc₂Cl₈]²⁻, and CrMo(O₂CH)₄ corresponds to the configuration $(\sigma)^2(\pi)^4(\delta)^2$, in agreement with the usual description of the metal–metal interaction in terms of a quadruple bond. The potential curve obtained for the ground state of Mo₂(O₂CH)₄ presents a minimum for a bond length of 2.10 Å, in excellent agreement with the experimental bond length of 2.091 Å. In order to give an interpretation of the difference found at the SCF level between compounds of the first and second transition series by means of interaction diagrams (Figure 1) calculations were performed on fragments [CrCl₄]²⁻ and [MoCl₄]²⁻. The latter

is purely hypothetical, but the former is known to be high spin. However, the high-spin configuration $(a_1)^1(b_2)^1(e)^2$ was not of great interest for our purpose since it leads to a description of the complex which is almost purely ionic and which leaves the occupied metal d levels practically degenerate. The low-spin configurations, though higher in energy, are more convenient for building the interaction diagrams since they take into account the metal–ligand interaction which appears, more or less strongly, in binuclear complexes (Tables III–VI). Thus, assuming the fragments to be low spin, the lowest electronic states of [CrCl₄]²⁻ and [MoCl₄]²⁻ were found to be different, with the respective configurations $(a_{1g})^2(b_{2g})^2$ and $(a_{1g})^2(e_g)^2$ (Table VII), which leads to a different ordering of orbital levels (Figure 1). Another feature of these interaction diagrams is the splitting between bonding and corresponding antibonding levels, which is larger for Mo than for Cr. This is the result of the increase in the overlap between metal orbitals from chromium to molybdenum (Table IX) resulting in increased metal–metal interaction terms.[26]

An examination of orbital energies and percentage of metal character in the $(\sigma)^2(\pi)^4(\delta)^2$ configuration (Tables III, V, and VI) shows a striking difference between binuclear complexes according as one considers their metal atoms as belonging to group 6 or 7. All systems containing Cr or Mo have rather ionic character. The metal d bonding orbitals, which are the highest occupied, are well specified with more than 70% metal character in all cases, and often more than 85%. The other occupied orbitals, including the b₁g and b₂ᵤ orbitals, responsible for the metal–ligand σ bonding have, with one exception, less than 20% metal character. On the contrary, [Tc₂Cl₈]ⁿ⁻ and [Mn₂(CH₃)₈]²⁻ have rather covalent character. The metal d orbitals are generally split and the main π level is the lower eᵤ

orbital. For the three compounds, the metal–ligand bonding levels b_{1g} and b_{2u} have important metal character, especially in the case of $[Mn_2(CH_3)_8]^{2-}$.

Cotton and Kalbacher[2] discussing four SCF-Xα-SW calculations on $[W_2Cl_8]^{4-}$, $[Mo_2Cl_8]^{4-}$, $[Re_2Cl_8]^{2-}$, and $[Tc_2Cl_8]^{3-}$ already noted that the covalent character of the complex increases with the formal oxidation number of the metal. We agree with this conclusion since the metal d orbitals are higher in energy than the ligand ones for all systems containing Cr and Mo (Tables III and V). Increasing the oxidation number lowers the d-orbital energies[27] which can reach the range of ligands levels and mix with them. The ionic or covalent character of the metal–ligand bond may also depend on the nature of the ligand. This assumption is supported by the SCF-Xα-SW calculation of Norman and Kolari on $Mo_2(O_2CH)_4$,[17,28] since it gives a description of the bonding for this molybdenum compound "resembling $[Re_2Cl_8]^{2-}$ more than $[Mo_2Cl_8]^{4-}$". Effectively, the d orbitals are split and the σ and π levels are the lower ones. However, our calculations do not agree with this result, since we obtain a description of $Mo_2(O_2CH)_4$ very similar to the one of $[Mo_2Cl_8]^{4-}$ (Table V).

The case of $CrMo(O_2CH)_4$ is interesting because of the dissymetry of the metal–metal bonding. The SCF ground state, which corresponds to the configuration $(\sigma)^2(\pi)^4(\delta)^2$, presents, as the symmetric formates, three doubly occupied levels of highly metallic character (Table V). Their sequence is not the classic one $\delta > \pi > \sigma$ since δ and π are inverted. The π bonds have largely predominant molybdenum character (81% Mo, 10% Cr) whereas the δ and σ bonds take their major contribution from chromium (64% Cr and 3% Mo for δ; 71% Cr and 13% Mo for σ). This "ionic quadruple bond" is rationalized in terms of the interaction diagram of Figure 2 based, as were the diagrams of Figure 1, on the different sequence of levels in Cr and Mo. Occupied orbital levels of Mo(II) are shifted to higher energies with respect to Cr(II) in agreement with atomic calculations and experimental ionization energies. The virtual antibonding orbitals which appear, with the sequence $\delta^* < \sigma^* < \pi^*$, have, as expected, major contribution from chromium for π^* and from molybdenum for δ^* and σ^*.

CI Level. Performing the CI introduces important changes in the bound state wave function which may in some cases modify the interpretation of the SCF results. The bound state corresponds now to a CI function with the bonding configuration as the leading term. As a consequence of the considerable energy lowering of the CI bound state with respect to the pure $(\sigma)^2(\pi)^4(\delta)^2$ configuration, *at the CI level, the bound state is the ground state of all considered systems* (as mentioned above, the nonbonding configuration is not affected by the CI). This result rules out the possibility suggested by Garner et al.,[15] for the nonbonding ground state computed at the SCF level to give a consistent interpretation of the metal–metal interaction in $Cr_2(O_2CH)_4 \cdot 2H_2O$.[18,39] However, an analysis of the CI expansion will give us the possibility to refine, according to the considered system, the standard scheme of the quadruple bond.

For $Cr_2(O_2CH)_4$, the potential curve shows a minimum at 2.45 Å (Figure 3) whereas the experimental Cr–Cr bond length, for the crystalline anhydrous acetate, is 2.29 Å.[5] Figure 3 shows that the potential curve is extremely flat around the minimum. The relatively important effect of the addition of axial ligands deduced from experiment can be understood in relation with this feature of the potential curve since in such a case a small perturbation of the wave function can induce a rather large shift of the minimum. However, our calculations do not support the suggestion made by Cotton et al. that the Cr–Cr distance in a truly isolated $Cr_2(O_2CR)_4$ molecule—that means not in crystalline form—might be very short.[5] The computed potential curve suggests that other factors which are

Table IX. Selected Overlap Integral Values for Valence-Shell d_1 and d_2 Orbitals of Cr and Mo at a Distance of 2.14 Å

	Cr	Mo
$\langle xy_1 \vert xy_1 \rangle$	0.0004	0.0040
$\langle xy_1 \vert xy_2 \rangle$	0.0149	0.0417
$\langle xy_2 \vert xy_2 \rangle$	0.1230	0.2035
$\langle xz_1 \vert xz_1 \rangle$	−0.0054	−0.0362
$\langle xz_1 \vert xz_2 \rangle$	−0.0817	−0.1624
$\langle xz_2 \vert xz_2 \rangle$	−0.3925	−0.4445
$\langle zz_1 \vert zz_1 \rangle$	0.0228	0.1154
$\langle zz_1 \vert zz_2 \rangle$	0.2392	0.3751
$\langle zz_2 \vert zz_2 \rangle$	0.4955	0.4593

currently of minor importance, such as the nature of R or the crystal packing, might also have an important and unforeseeable effect on the Cr–Cr bond length of $Cr_2(O_2CR)_4$.

For $[Cr_2(CH_3)_8]^{4-}$ stabilized with four positive charges, the minimum is found at a Cr–Cr distance of 2.16 Å, whereas the experimental bond length is 1.98 Å. As for $Cr_2(O_2CH)_4$, the calculated minimum is larger than the experimental bond length. However, the gap between the "weak" bond of $Cr_2(O_2CH)_4$ and the "strong" bond of $Cr_2(CH_3)_8^{4-}$ is correctly reproduced. It may be noticed that this gap is obtained without introducing axial ligands on $Cr_2(O_2CH)_4$. The relative weakness of the Cr–Cr bond in the chromium carboxylates may be understood on the basis of the CI expansion of the wave function for $Cr_2(O_2CH)_4$. The weight of the quadruply bonding configuration $(\sigma)^2(\pi)^4(\delta)^2$ in the CI wave function is only 18% at $d = 2.362$ Å and 32% at $d = 1.98$ Å. The other terms of the expansion (none of which is negligible), being either doubly bonding, nonbonding, or antibonding, weaken the quadruple bond. This is consistent with the shift of the minimum in the potential energy curve to larger distances upon the introduction of CI (Figure 3). The weight of the quadruply bonding configuration is significantly higher for $[Cr_2(CH_3)_8]^{4-}$: 42% at $d = 1.98$ Å instead of 32% for $Cr_2(O_2CH)_4$. Keeping in mind that the computed equilibrium distance for a "pure" Cr–Cr quadruple bond is about 1.65 Å (Table VII), a correlation between the relative and empirical notion of "strength" of the quadruple bond, the metal–metal bond length at equilibrium, and the weight of the $(\sigma)^2(\pi)^4(\delta)^2$ configuration of the CI expansion (at a given distance) appears consistent.

Insofar as the single $(\sigma)^2(\pi)^4(\delta)^2$ configuration computed at the SCF level can be considered as a model for a "pure quadruple bond" the binuclear complexes of chromium, even those currently classified as "strongly bonded", like $[Cr_2(CH_3)_8]^{4-}$,[1,30] are all rather far from this model. The very large shift of the minimum from 1.65 to 2.16 Å for $[Cr_2(CH_3)_8]^{4-}$ and to 2.45 Å for $Cr_2(O_2CH)_4$ is consistent with the low values obtained for the weight of the leading term in the CI expansion and indicates that the "strong Cr–Cr quadruple bond" apparently does not exist, except from a purely relative point of view. The scheme is different with molybdenum compounds. The "pure quadruple bond" model as computed from SCF calculations on $Mo_2(O_2CH)_4$ corresponds to an equilibrium position of 2.10 Å, instead of 1.65 Å for chromium. This is a considerable increase, but the weight of the $(\sigma)^2(\pi)^4(\delta)^2$ configuration becomes much larger than for chromium systems: 66% for $Mo_2(O_2CH)_4$ at 2.093 Å, 61% for $[Mo_2Cl_8]^{4-}$ at 2.139 Å.[34] From these relatively high values, the minimum of the potential curves at the CI level is expected to be not very far from the equilibrium distance obtained at the SCF level. In that sense, the Mo–Mo bond can be said to be "stronger" than the Cr–Cr bond in corresponding complexes, and its description resembles more the standard scheme of the quadruple bond.[37]

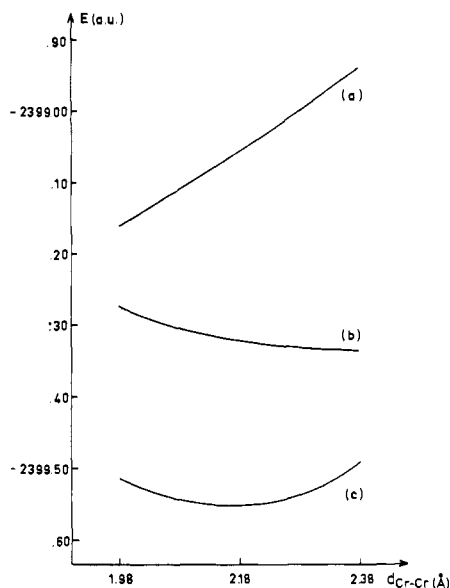The energy splitting between two electronic states corre-

Figure 4. Potential energy curves for $[Cr_2(CH_3)_8]^{4-}$: (a) SCF energy of the $(\sigma)^2(\delta)^4(\delta)^2$ configuration; (b) SCF energy of the $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ configuration; (c) limited CI for the bound state.

Figure 5. Simplified diagram of metal–metal orbital levels for $[Mo_2Cl_8]^{4-}$ in the eclipsed form (left) and in the staggered form (right).

sponding to the bonding and nonbonding configurations can also give some information about the different behavior of the chromium and molybdenum compounds. For $[Mo_2Cl_8]^{4-}$, for instance, the bonding configuration is lower in energy than the nonbonding one by more than 200 kcal/mol at the SCF level and CI is expected to increase this splitting. For $[Cr_2Cl_8]^-$, the energy gap between these two states after CI is only 17 kcal/mol at the assumed distance of 2.139 Å. If the potential curve corresponding to the nonbonding state is repulsive as for $Cr_2(O_2CH)_4$, a crossing of the two curves is not excluded at a greater distance.[35] In such a way, the fact that $[Cr_2Cl_8]^{4-}$ has not been reported so far may be tentatively explained by a fast thermal depopulation of the bonding state to the benefit of the repulsive nonbonding state.

$[Tc_2Cl_8]^{3-}$. A correlation between the "strength" of the bond and the percentage of the leading term in the CI expansion can also be applied successfully to the $[Tc_2Cl_8]^{3-}$ problem. The energy of several low-lying states was computed, both at SCF and CI levels (Table VIII). The B_{1u} configuration in which the excess electron occupies the δ^* orbital corresponds to the SCF ground state in accordance with the results of Cotton and Kalbacher.[2] The A_{1g} configuration, which was tentatively suggested to be the ground state,[9,10] or other configurations such B_{1g} or B_{2u} keeping the formal bond order equal to 4[11] seem to be definitely ruled out. The B_{1u} configuration is still the leading term of the CI wave function with a high weight of 94% due to the vanishing, because of Brillouin's theorem, of configurations involving δ^*. Comparing now the CI expansions in $[Mo_2Cl_8]^{4-}$ and $[Tc_2Cl_8]^{3-}$, the wave function of the molybdenum compound is 61% the $(\sigma)^2(\pi)^4(\delta)^2$ configuration (bond order 4) and 39% a mixture of configurations of bond order less than or equal to 2 whereas $[Tc_2Cl_8]^{3-}$ is represented by the almost pure $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ configuration, of bond order 3.5. In this case, the high weight of the leading term in the $[Tc_2Cl_8]^{3-}$ CI wave function makes consistent a lowering of the formal bond order with a still very short metal–metal bond length. A similar argument can be tentatively suggested for the problem of $Re_2Cl_4(PEt_3)_4$, which contains two more valence electrons than $[Re_2Cl_8]^{2-}$, a complex with formal bond order 4. If we assume for the ground state of $Re_2Cl_4(PEt_3)_4$ a CI wave function with the leading configuration $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$, the weight of this triply bonding configuration is probably greater than 90%, as in
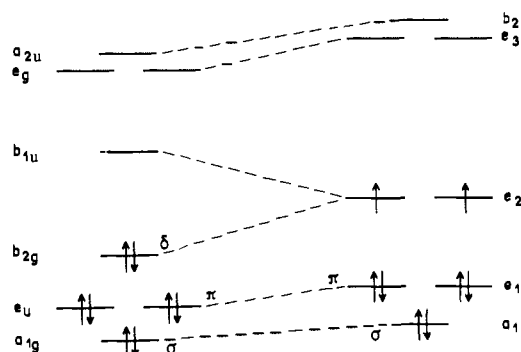
$[Tc_2Cl_8]^{3-}$. However, $[Re_2Cl_8]^{2-}$, isoelectronic to $[Mo_2Cl_8]^{4-}$, is expected to present a CI expansion the leading term of which, $(\sigma)^2(\pi)^4(\delta)^2$, has a weight of 65–75% only, which corresponds to a quadruple bond slightly but still significantly weakened. The probable vanishing of the δ bond in $Re_2Cl_4(PEt_3)_4$ would thus be reconciled with a Re–Re bond length slightly shorter than for $[Re_2Cl_8]^{2-}$.[1]

Energies obtained for the ground and first excited states of $[Tc_2Cl_8]^{3-}$ can be correlated with some of the presently known characteristics of the optical spectrum of this ion. A broad band centered at about 6800 cm^{-1} was recently found,[31] the characteristics of which are discussed by Cotton and Kalbacher.[2] On the basis of SCF-$X\alpha$-SW calculations, the experimental band was identified by these authors with the dipole-allowed, z-polarized $\delta \rightarrow \delta^*$ electronic transition ($^2B_{2g} \leftarrow {}^2B_{1u}$). The position predicted from our calculation for the $\delta \rightarrow \delta^*$ transition, ca. 8800 cm^{-1}, is in reasonable agreement with the experimental energy. The energy found for this transition at the SCF level is practically unchanged at our level of CI. Nevertheless, CI leads to a different interpretation of this region of the experimental spectrum since the transitions $\delta^* \rightarrow \pi^*$ ($^2E_g \leftarrow {}^2B_{1u}$) and $\delta^* \rightarrow \sigma^*$ ($^2A_{2u} \leftarrow {}^2B_{1u}$), rather high in energy at the SCF level, fall at the CI level in the range 6000–9000 cm^{-1}. The $\delta^* \rightarrow \sigma^*$ transition at 8800 cm^{-1} is dipole forbidden but the $\delta^* \rightarrow \pi^*$ transition, predicted to be at 5900 cm^{-1}, is dipole allowed (with a weak oscillator strength) and xy polarized. It is clear, from the experimental spectrum,[31] that there is no possibility for another allowed transition to be superimposed to the well-characterized $\delta \rightarrow \delta^*$ band. However, it can be suggested that the system corresponding to the $\delta^* \rightarrow \pi^*$ transition lies in the still unexplored infrared region *below* 5500 cm^{-1}. The band experimentally found at 15 700 cm^{-1} could be attributed to the $^2B_{1u} \rightarrow {}^1A_{2g}$ transition, the computed energy of which is 18 500 cm^{-1}.

Rotation Barrier of $[Mo_2Cl_8]^{4-}$. The staggered form of $[Mo_2Cl_8]^{4-}$, which belongs to the point group D_{4d}, is obtained from the eclipsed form (point group D_{4h}) by a 45° rotation of one $[MoCl_4]^{2-}$ monomer. The reordering of the orbital levels when going from the eclipsed to the staggered form is illustrated in Figure 5. From this diagram, it appears that the ground state of the staggered form is a triplet. In such a case, the pure SCF calculation does not lead to the same level of approximation for the two isomers, since the pair correlation effect between the two electrons associated with the HOMO is known to be more important for the closed shell systems. The energy values obtained from SCF calculations confirm that the level of approximation is different, since the staggered form is found more stable than the eclipsed form by about 60 kcal/mol. In order to obtain for both rotamers energy values with the same level of approximation, it would be necessary to compare the SCF energy of the staggered form with the energy obtained for the eclipsed form by means of a MCSCF

calculation involving the $(\sigma)^2(\pi)^4(\delta)^2$ and $(\sigma)^2(\pi)^4(\delta^*)^2$ configurations. As a first approximation a CI calculation was performed involving these two configurations. The diagonal terms of the CI matrix were obtained by optimizing the SCF energy of each of the two involved configurations. The corresponding wave functions were used to compute the nondiagonal term of the CI matrix, according to a formalism developed by Cox.[29] From this calculation, the energy of the ground state was −11 603.052 au for the eclipsed form, which is identical, to the precision of the calculations, with the SCF energy of the staggered isomer. Another approach was attempted, using, for both isomers, the limited CI as defined in the calculation section. In this case, the staggered form was found more stable by about 4 kcal/mol (Table VII). To check that this result is not an artifact due to a bad description of either metal-ligand bonds or nonbonded interactions between chlorine atoms, a new calculation was performed with a more extended basis set for chlorine atoms (10.7/4.4 instead of 10.6/4.3). The same result was obtained.

Though the rotation barriers are generally estimated with a good approximation at the SCF level, the case of $Mo_2Cl_8^{4-}$, which involves a change in the state multiplicity, is particular enough to require an extended CI or a MCSCF treatment. It is significant that the first approach, more flexible, leads to a better result.

Calculations on $Mn_2(CH_3)_8^{2-}$. Among the various classes of quadruply bonded complexes $[M_2(CH_3)_8]^{n-}$ is one of the most common. As no information is yet available about the likelihood of quadruply bonded manganese complexes, it was inviting to check the possible existence of $[Mn_2(CH_3)_8]^{2-}$, since this hypothetical complex is horizontally homologous to $[Cr_2(CH_3)_8]^{4-}$ [22] and vertically to $[Re_2(CH_3)_8]^{2-}$.[33] From the total energy value obtained at the CI level for the bound state (−2610.628 au) compared to that of the nonbonding configuration (−2610.533 au) there is apparently no reason that this ion should not exist. Though less important than for $[Cr_2(CH_3)_8]^{4-}$, the difference in energy between the two states is about 60 kcal/mol at $d_{Mn-Mn} = 1.98$ Å, which probably excludes the possibility of a crossing of the potential curves at higher distances.[35]

Conclusion

To summarize, this study has confirmed that the scheme of the quadruple bond can be applied to all the studied binuclear complexes. This scheme gives an excellent description of the bonding for complexes of the second transition series and it leads to a good approximation when metals of the first transition series are involved. This conclusion can be deduced from pure SCF calculations for complexes of molybdenum and technetium, but CI is required to obtain a correct description of the ground state for chromium compounds. In any case, CI introduces for this class of complexes a useful refinement of the wave function since a detailed analysis of the CI expansion leads to a correlation between the relative weakness of the quadruple bond (related itself to the metal-metal bond length) and the weight of the configurations other than quadruply bonding in the CI expansion.

Note Added in Proof. Two recent papers by Cotton et al. investigate the sensitivity of the metal-metal bond length in dichromium and dimolybdenum tetracarboxylates to axial coordination and changes in inductive effects.[40] For $Cr_2(O_2CR_4)L_2$, modifications holding on both L_{axial} and R lead to important variations on d_{Cr-Cr}. The authors conclude that there is no linear and independent relations between d_{Cr-Cr}, the Cr-L bond length, and the effect of R. They refer to the shallow shape of our potential curve[18] to explain the high sensitivity of d_{Cr-Cr} in $Cr_2(O_2CR_4)L_2$ to the nature of R and

L. There is consequently no more disagreement about this problem. For $Mo_2(O_2CR_4)L_2$, the insensitivity of d_{Mo-Mo} to the same factors is also in agreement with the present work since our potential curve found at the SCF level is relatively deep and, contrary to what is observed for the chromium compounds, it is not expected to be strongly modified with CI.

References and Notes

(1) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975), and references cited therein.
(2) F. A. Cotton and B. Kalbacher, *Inorg. Chem.*, **16**, 2386 (1977).
(3) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).
(4) D. M. Collins, F. A. Cotton, and C. A. Murillo, *Inorg. Chem.*, **15**, 1861 (1976).
(5) F. A. Cotton, C. E. Rice, and G. W. Rice, *J. Am. Chem. Soc.*, **99**, 4704 (1977).
(6) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).
(7) C. D. Garner, R. G. Senior, and T. J. King, *J. Am. Chem. Soc.*, **98**, 3526 (1976).
(8) F. A. Cotton and L. W. Shive, *Inorg. Chem.*, **14**, 2032 (1975).
(9) F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).
(10) W. K. Bratton and F. A. Cotton, *Inorg. Chem.*, **9**, 789 (1970).
(11) J. G. Norman, Jr., and H. J. Kolari, *J. Am. Chem. Soc.*, **97**, 33 (1975).
(12) F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 383 (1975).
(13) F. A. Cotton and E. Pedersen, *J. Am. Chem. Soc.*, **97**, 303 (1975).
(14) F. A. Cotton, D. S. Martin, P. E. Fanwick, T. J. Peters, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 4681 (1976).
(15) C. D. Garner, I. H. Hillier, M. F. Guest, J. C. Green, and A. W. Coleman, *Chem. Phys. Lett.*, **41**, 91 (1976).
(16) A. P. Mortola, J. W. Moskowitz, and N. Rösch, *Int. J. Quantum Chem.*, **8**, 161 (1974).
(17) J. G. Norman, Jr., and H. J. Kolari, *J. Chem. Soc., Chem. Commun.*, 649 (1975).
(18) M. Benard and A. Veillard, *Nouveau J. Chim.*, **1**, 97 (1977). Very recently, a Xα-SW calculation was performed on $Cr_2(O_2CH)_4$[39] which also leads to the correct ground state.
(19) F. A. Cotton, J. G. Norman, B. R. Stults, and T. R. Webb, *J. Coord. Chem.*, **5**, 217 (1976).
(20) F. A. Cotton, B. G. De Boer, M. D. La Prade, J. R. Pipal, and D. A. Ucko, *J. Am. Chem. Soc.*, **92**, 2926 (1970); *Acta Crystallogr., Sect. B*, **27**, 1664 (1971).
(21) J. V. Brencic and f. A. Cotton, *Inorg. Chem.*, **8**, 7 (1969).
(22) J. Krausse, G. Marx, and G. Schödl, *J. Organomet. Chem.*, **21**, 159 (1970).
(23) M. Benard, A. Dedieu, J. Demuynck, M.-M. Rohmer, A. Strich, and A. Veillard, "Asterix: a System of Programs for the Univac 1110", unpublished work; M. Benard, *J. Chim. Phys. Phys.-Chim. Biol.*, **73**, 413 (1976).
(24) G. Das, *J. Chem. Phys.*, **46**, 1568 (1967).
(25) H. Basch, *J. Chem. Phys.*, **55**, 1700 (1971).
(26) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).
(27) See, for instance, experimental values for ionization potentials in C. E. Moore, *Nat. Bur. Stand. (U.S.)*, *Circ.*, **2**, 467 (1952).
(28) J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
(29) P. A. Cox, private communication.
(30) D. J. Brauer and C. Krüger, *Inorg. Chem.*, **15**, 2511 (1976).
(31) F. A. Cotton, P. E. Fanwick, L. W. Gage, B. Kalbacher, and D. S. Martin, in press.
(32) F. A. Cotton, D. S. Martin, T. R. Webb, and T. J. Peters, *Inorg. Chem.*, **15**, 1199 (1976).
(33) F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shive, and G. Wilkinson, *J. Am. Chem. Soc.*, **98**, 6922 (1976).
(34) The difference observed between molybdenum and chromium systems in the weight of the leading term in the CI expansion is due to the increased energy separation between the bonding and antibonding levels of the Mo complexes and to the different order of magnitude of the exchange terms K_{ij}. (Table II).
(35) From a theoretical point of view, an "avoided crossing" between the potential curves which correspond to the bound and nonbonding states is impossible at our level of CI, since none of the configurations represented in the CI expansion of the bound state has direct interaction with the $(\sigma)^2(\delta)^2(\delta^*)^2(\sigma^*)^2$ configuration.
(36) F. A. Cotton, S. Koch, and M. Millar, *J. Am. Chem. Soc.*, **99**, 7372 (1977).
(37) A very recent experimental work[36] corroborates this analysis. Two new compounds, $M_2(2,6-dimethoxyphenyl)_4$ with M = Cr, Mo, were synthesized and their structure characterized. The Cr-Cr bond length is the shortest M-M bond known, 1.847 Å, 0.14 Å less than in $Cr_2(CH_3)_8^{4-}$. That gives consistency to the distance of 1.65 Å proposed here for an hypothetical "pure Cr-Cr quadruple bond", and to the suggestion, based on CI analysis, that other known Cr-Cr quadruple bonds are relatively weak. In the corresponding Mo compound, the bond length is 2.067 Å, that is, only 0.02 Å less than the formerly known shortest Mo-Mo bond. This result also confirms the CI development analysis, leading to the conclusion that Mo-Mo

bonds are rather close to the pure quadruple bond model.
(38) It can be thought that this CI development is extremely limited. In fact—and a close examination of the exchange terms K_{ij}, confirms it—this CI simply corrects the lack of flexibility of closed-shell restricted HF calculations for

these systems, similarly to what occurs in dissociation processes.
(39) F. A. Cotton and G. G. Stanley, *Inorg. Chem.*, **16**, 2668 (1977).
(40) F. A. Cotton, M. W. Extine, and L. D. Gage, *Inorg. Chem.*, **17**, 172 (1978); F. A. Cotton, M. W. Extine, and G. W. Rice, *Ibid.*, **17**, 176 (1978).

Electronic Structures of Azolium Ions and Their Ylides. The Imidazolium, Oxazolium, and Thiazolium Ions

Haven S. Aldrich,[*1a] William L. Alworth,[1b] and Nancy R. Clement[1a,c]

Contribution from the Department of Chemistry, St. Mary's Dominican College, and the Laboratory of Chemical Biology, Department of Chemistry, Tulane University, New Orleans, Louisiana 70118. Received October 18, 1976

Abstract: Semiempirical molecular orbital calculations of the imidazolium, oxazolium, and thiazolium ions and their conjugate bases are reported. The calculations predict that the carbon-2 proton is more acidic in the thiazolium ion than in the imidazolium ion, in good agreement with experimental evidence. Calculations were performed with and without extravalent 3d atomic orbitals on sulfur in order to establish the extent of their participation in resonance delocalization for the ground electronic state of the thiazolium ion and of the corresponding thiazolium ylide. These calculations indicate that the sulfur 3d orbitals are not necessary to describe either ground state. Polarization of the σ bonds is principally responsible for stabilizing the thiazolium ylide.

Introduction

The behavior of the thiazolium ion in thiamin (vitamin B_1) and its significance to the mechanism of action of thiamin pyrophosphate requiring enzymes[2a] has been discussed by many investigators.[2b,3-8] Deprotonation of carbon 2 of the five-membered ring with the resulting formation of an ylide is essential to the function of the thiazolium ion in enzymatic catalysis.

Rates of hydroxide-catalyzed proton exchange for hydrogens on carbon 2 of the imidazolium, oxazolium, and thiazolium ions have been determined and an unusually high exchange rate for the carbon-2 hydrogen of the thiazolium ring system has been noted.[4,7] Deuterioxide abstracts the carbon-2 hydrogen of the thiazolium ion 3000 times faster than the carbon-2 hydrogen of the imidazolium ion.[4] These relative rates are the reverse of that expected on the basis of the relative electronegativities of nitrogen and sulfur. Nitrogen, with the higher electronegativity, would be expected to stabilize the conjugate base of the imidazolium ion to a greater extent than sulfur would be expected to stabilize the conjugate base of the thiazolium ion.

Semiempirical molecular orbital calculations reported in this paper have been used to determine σ and π electronic structures and principal resonance forms for the imidazolium, oxazolium, and thiazolium ions and for the conjugate bases formed by deprotonation of the carbon 2 of these ions. One objective is to determine those factors that stabilize the conjugate base form of the thiazolium ion and thereby to gain insights into the function of thiamin pyrophosphate in enzymatic mechanism. The special ability of a sulfur atom to stabilize an adjacent negative charge has been noted;[7,8] a comparison of the semiempirical molecular-orbital calculations performed on these three azolium ions should be able to define the electronic factors which are responsible for this special feature of sulfur.

Those structural features which stabilize the conjugate base form of these ions will also stabilize the transition state for removal of the carbon-2 hydrogen as a proton.[4] A second objective of our calculations is to explain the order of the carbon-2 exchange rates: oxazolium > thiazolium > imidazolium.

Factors responsible for the relative stabilities of the transition states, and thus the relative exchange rates, may include both the σ and π electronic frameworks of the azolium ions and solvation energies. This study indicates that each of these factors may play a role in determining the relative exchange rates of these three azolium ions.

Theoretical Approach

The ARCANA semiempirical molecular orbital method, which was used for all calculations, has been described elsewhere.[9,10] ARCANA is an iterative, charge self-consistent molecular orbital method which requires the following data for each valence atomic orbital: a Slater type orbital (STO) exponent for each n, l set, where n is an effective principal quantum number; an energy parameter, $1/R_i = \langle i | 1/r | i \rangle$, which characterizes how the STO is affected by isotropic and anisotropic charge distributions in a molecular environment; a neutral atom ionization potential for a doubly occupied atomic orbital.[10,11,12]

The diagonal elements of the Hamiltonian matrix are computed according to the Cusachs approximation.[9] The unique feature of the Cusachs approximation is the neighbor atom potential[10,15] which contains all computed electron repulsion and nuclear attraction integrals. The off-diagonal elements of the Hamiltonian matrix are also calculated according to the Cusach approximation.[16,17]

In this report, a comparison is presented between ground state one-electron properties of polar, heteronuclear ions and ylides. Iterative, semiempirical methods that contain two center terms in the Hamiltonian operator provide one-electron properties that are consistent with ab initio calculations. Thus, while an ab initio configuration interaction is preferable for potential energy surfaces involving chemical reactions, a semiempirical method, as noted above, gives a good accounting of ground state properties.

The ARCANA method has been applied to the calculation of ionization potentials,[9] hydrogen bonding,[18] and transition metals complexes.[19] Calculations of bonding involving sulfur[20] and selenium[21] have also been performed with this method.