Metal–Metal Bond Length Variations and the Electronic Structure of Dichromium(II) and Dimolybdenum(II) Complexes

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The gas-phase core-electron ionization energies of the complexes $[M_2L_4]$ [M = Cr, L = O_2CMe or mhp (6-methylpyridin-2-olate); M = Mo, L = O_2CH, O_2CMe, or mhp] are reported. These data, together with the valence *d* ionization energies of these molecules, show a correlation between metal electron ionization energies and the large variations in the metal–metal separations found for the dichromium(II) species. A model in which these separations are mainly determined by the electrostatic potential at the metal centre is suggested by the experimental observations and supported by *ab initio* calculations on $[M_2L_4]$ [M = Cr or Mo; L = $(CH_2)_2PH_2$] reported here. This electrostatic potential is a function of the ligand; the lower the potential the shorter is the metal–metal separation, primarily because of the shallowness of the Cr–Cr potential well. The description of the metal–metal interaction, for a given Cr–Cr separation, is found to be insensitive to the nature of the ligand.

The electronic structures of complexes of the type $[M_2L_4]$ (where M = Cr or Mo, and L may be any of a variety of ligands), in which there exists a formal metal–metal quadruple bond, have been extensively studied both theoretically[1–6] and experimentally.[7–9] It has been found that, in the case of the dimolybdenum(II) complexes, the metal–metal bond length is relatively insensitive to the nature of the ligand L, being in the range 2.1 ± 0.1 Å for a wide range of ligands.[10–15] For the dichromium(II) complexes, on the other hand, large variations in the M–M bond length are found, from 2.54 Å {in $[Cr_2(O_2CCF_3)_4]\cdot 2Et_2O$}[16] to 1.89 Å {in $[Cr_2(mhp)_4]$;[12] Hmhp = 2-hydroxy-6-methylpyridine}.

In this paper we present an experimental and theoretical study of the electronic structure of both the dimolybdenum(II) and the dichromium(II) complexes. The valence and core electron photoelectron spectra of these complexes are discussed in terms of their molecular orbital (m.o.) structure and overall charge distributions. Also, *ab initio* m.o. calculations are presented for $[M_2(O_2CH)_4]$ and $[M_2\{(CH_2)_2PH_2\}_4]$ (M = Cr or Mo); for chromium, these systems are representative of molecules having long and short metal–metal bonds, respectively. It is now well established[1–4] that the one-electron picture is not an adequate description of the bonding in the dichromium(II) complexes. Therefore, we have investigated the role of correlation effects in the molecules $[Cr_2(O_2CH)_4]$ and $[Cr_2\{(CH_2)_2PH_2\}_4]$, with the aid of configuration interaction (CI) calculations.

The experimental and theoretical studies described herein are concerned with a clarification, particularly for dichromium(II) complexes, of the role of the ligand in determining the metal–metal separation and the nature of this metal–metal interaction for different metal–metal bond lengths.

Experimental

The complexes studied experimentally, $[Mo_2(O_2CH)_4]$, $[Mo_2(O_2CMe)_4]$, $[Cr_2(O_2CMe)_4]$, $[Mo_2(mhp)_4]$, and $[Cr_2(mhp)_4]$, were prepared as described elsewhere.[12,17] We have previously described measurements of the He^{I} and He^{II} photoelectron spectra of these molecules.[7–9] The ionization energies associated with the metal *d* electrons are listed in Table 1. Gas-phase *X*-ray photoelectron spectra of these molecules[18] have been measured using Al-K_α radiation. The spectrometer described earlier[19] was fitted with an *X*-ray gun having a heatable gas cell attached at its end. Non-inductively wound resistance heaters allowed temperatures up to 400 °C to be attained. Gaseous samples and calibrant gases were introduced into the gas cell *via* a small side tube. The spectra were calibrated using gases having ionization energies close to those being measured.[20] Count rates of *ca.* 3 000 s^{-1} were typical for the neon 1*s* line when irradiated by Al-K_α radiation (10 kV, 40 mA). Repeated scanning and data accumulation was carried out using an Ino Tech 5300 multichannel analyser. The results are summarized in Table 1.

Computational Details

All-electron *ab initio* calculations were carried out on representative molecules having a range of metal–metal separations. The tetra-μ-carboxylates have the longer separations, and we choose the simplest of these, $[Mo_2(O_2CH)_4]$ and $[Cr_2(O_2CH)_4]$. This dimolybdenum(II) complex has a Mo–Mo bond length of 2.091 Å, and the calculation was carried out using this and the other dimensions obtained for the crystallographic molecular structure.[14] For $[Cr_2(O_2CH)_4]$, we chose a Cr–Cr separation of 2.288 Å, together with other structural parameters determined for crystalline $[Cr_2(O_2CMe)_4]$.[21] It would have been desirable to carry out calculations on $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$, these being the species actually studied experimentally; however, this was precluded by computational considerations. We decided, therefore, to study theoretically the simplest complex having an extremely short Cr^{II}–Cr^{II} separation, this being tetrakis{μ-[dimethylphosphoniumdiylbis(methylene)]}dichromium, $[Cr_2\{(CH_2)_2PMe_2\}_4]$, with a Cr–Cr bond distance of 1.895 Å. Also, we studied the corresponding dimolybdenum(II) complex, which has a Mo–Mo separation of 2.082 Å.[15] To reduce further the size of the computations, the methyl groups of these $[M_2\{(CH_2)_2PMe_2\}_4]$ complexes were replaced by hydrogen atoms and the complexes were taken to have D_{4h} symmetry, with the M_2C_2P framework planar, although experimentally the phosphorus atom is slightly out of this plane. All calculations were carried out in a near minimal basis of contracted gaussian functions. For Mo, we used the primitive set of Huzinaga,[22] in which the two diffuse *s* functions representing the 5*s* atomic orbital have been replaced by one with exponent 0.2, more properly to represent the bonding situation. This basis was then contracted to [6*s*3*p*2*d*]. Slater type orbitals, with best atom exponents[23] (except for hydrogen) expanded in terms of three gaussian functions, were used to represent the following orbitals: Cr, 1*s*, 2*s*, 3*s*, 2*p*, 3*p*; C,O, 1*s*, 2*s*; P, 1*s*, 2*s*, 3*s*, 2*p*; H, 1*s* (ζ = 1.2). For Cr, the 4*s* and 4*p* orbitals were represented by single gaussian functions having exponent 0.32, and the 3*d*

Table 1. Experimental core and valence[a] ionization energies (eV)[b]

Orbital	$[Cr_2(mhp)_4]$	$[Cr_2(O_2CMe)_4]$	
Cr $2p_{1/2}$	590.2	591.1	
Cr $2p_{3/2}$	580.6	581.5	
M–M (δ)	6.70	8.6—9.1	
M–M (π)	8.15		
O 1*s*	536.4	537.8	
N 1*s*	404.2		
C 1*s*	291.2 (sh)	294.3	
	290.2	291.1	
	$[Mo_2(mhp)_4]$	$[Mo_2(O_2CMe)_4]$	$[Mo_2(O_2CH)_4]$
Mo $3d_{3/2}$	236.9	237.7	238.4
Mo $3d_{5/2}$	233.8	234.7	235.3
M–M (δ)	5.84	6.92	7.60
M–M (π)	8.02	8.77	9.37
O 1*s*	536.5	537.9	538.5
N 1*s*	404.2		
C 1*s*	290.0	295.7[c]	296.1[c]
		293.4	293.8
		291.1	

[a] The valence ionization energies are taken from refs. 7—9. [b] Estimated uncertainty ±0.1 eV (relative to calibrant) for *X*-ray photoelectron spectra. [c] Satellite peak observed for C 1*s*.

basis of Roos *et al.*,[24] contracted into two functions, was taken in order to have a somewhat more flexible representation of the atomic 3*d* function. The carbon 2*p* [25] and phosphorus 3*p* [26] function were represented by Hartree–Fock orbitals expanded in four gaussian functions. Calculations were thus carried out using a total of 110, 114, 146, and 150 gaussian functions for $[Cr_2(O_2CH)_4]$, $[Mo_2(O_2CH)_4]$, $[Cr_2\{(CH_2)_2PH_2\}_4]$, and $[Mo_2\{(CH_2)_2PH_2\}_4]$, respectively.

To reduce both integral evaluation and SCF time, we employed a m.o. method which we have developed,[27] in which atomic integrals are systematically approximated. In this core-valence approximation molecular orbital (CVAMO) method, atomic integrals involving core-valence overlap charge densities are approximated without any significant loss of accuracy. In the calculations described herein, we use this method at the level of approximation denoted B1 in ref. 27, which was found nearly to halve the integral evaluation time; for $[Mo_2(O_2CH)_4]$ this led to errors of only 0.006 a.u. in the molecular energy of −8697.864 a.u., the maximum error in the valence eigenvalues being 0.05 eV.

In these molecules, a m.o. treatment leads to a description of the metal–metal interaction in terms of m.o.s localized within the M_2^{4+} entity, constructed from the metal *d* valence orbitals. In D_{4h} symmetry, the bonding m.o.s are $b_{2g}(d_{xy})$, $e_u(d_{xz,yz})$ and $a_{1g}(d_{z^2})$, which we denote δ, π, and σ, respectively. The corresponding antibonding orbitals, b_{1u}, e_g, and a_{2u}, are labelled δ^*, π^*, and σ^*, respectively. Calculations have been carried out at the single determinant level for the $\delta^2\pi^4\sigma^2$ ' quadruple-bond ' configuration, and also with allowance for correlation effects within this bond, by the use of CI calculations involving the four bonding and corresponding antibonding metal m.o.s. In a further investigation of the electronic structure of the metal–metal bond as a function of the metal–metal bond length variations for dichromium(II) complexes, we have carried out calculations on $[Cr_2(O_2CH)_4]$, both for the Cr–Cr separation of 2.288 Å, and at 1.895 Å, the separation found experimentally in $[Cr_2\{(CH_2)_2PMe_2\}_4]$.[15] For both Cr–Cr separations, apart from the Cr–Cr–O bond angles, the ligand geometry and Cr–O distances were kept constant, thus allowing comparisons of the electronic structure of two dichromium(II) complexes having the same metal–metal separations but containing different ligands, and the same ligands but a different metal–metal separation.

Discussion

Experimental Ionization Energies.—Core ionization energies are commonly interpreted in terms of the total electrostatic potential at the atom from which ionization occurs. This has led to the point-charge potential (PCP) model,[28] in which the potential is approximated in terms of formal atomic charges. Thus, the core ionization energy from atom *i*, E_i, is given as in equation (i), where q_j is

$$E_i = Aq_i + \sum_{j \neq i} q_j/R_{ij} \qquad \text{(i)}$$

the formal charge on atom *j*, R_{ij} is the distance between atoms *i* and *j*, and *A* is a constant. It is thus difficult (and probably not meaningful, bearing in mind that all definitions of atom charge are arbitrary) from measurements of core level shifts to obtain information on changes in the atomic charges of *both* the atom from which ionization has occurred and that of the surrounding atoms. However, with this reservation, the core and valence ionization energies shown in Table 1 do provide information on the effect of the different ligands on the electronic structures of the complexes.

First, we will consider the core ionization energies. The data for $[Mo_2(O_2CR)_4]$ (R = Me or H) show that *both* the molybdenum and oxygen core levels of $[Mo_2(O_2CMe)_4]$ are 0.6—0.7 eV to lower binding energy than in $[Mo_2(O_2CH)_4]$. This shift is the same as that observed for *both* (*a*) the metal δ and π bonding orbitals (Table 1) and (*b*) the oxygen valence ionization energies.[8] Thus, variation in the nature of the carboxylate R group affects the *total* electronic charge of the Mo_2O_8 central portion of these $[Mo_2(O_2CR)_4]$ complexes in the expected sense (*i.e.* Me groups are electron-donating to the Mo_2O_8 moiety, as compared with H atoms). In $[Mo_2(mhp)_4]$, the molybdenum core level is shifted 0.9 eV to lower ionization energy, as compared with that of $[Mo_2(O_2CMe)_4]$, indicating a considerably reduced electrostatic potential at the metal centre. That this reduction is not totally due to changes in the formal metal charges is shown by the variation in the oxygen core ionization energies between $[Mo_2(O_2CMe)_4]$ and $[Mo_2(mhp)_4]$. The large reduction (1.4 eV) in this value, on going from $[Mo_2(O_2CMe)_4]$ to $[Mo_2(mhp)_4]$, suggests that an increase in the oxygen electron density in $[Mo_2(mhp)_4]$ is a major contributor to the reduced molybdenum core ionization energy.

In $[Mo_2(O_2CMe)_4]$ and $[Mo_2(mhp)_4]$, the ionization energy of the Mo–Mo δ m.o. is shifted by the same amount as that of the molybdenum 3*d* orbital, reflecting the localized nature of this metal–metal bonding orbital. The corresponding shift of the Mo–Mo π m.o. is smaller, leading to an increase in the δ–π separation from 1.9 eV in $[Mo_2(O_2CMe)_4]$ to 2.2 eV in $[Mo_2(mhp)_4]$. We consider that this increase in the δ–π separation is due to an increase in the direct overlap of the metal–metal orbitals, $\pi > \delta$, resulting partially from a decrease in the metal–metal separation (2.093 to 2.065 Å) but, more importantly, from an increase in the size of the 4*d* orbitals arising from a decrease in the potential at the metal centre, in $[Mo_2(mhp)_4]$ as compared with $[Mo_2(O_2CH)_4]$.

For the dichromium(II) complexes, the shift in the chromium core ionization energy between $[Cr_2(O_2CMe)_4]$ and $[Cr_2(mhp)_4]$ (0.9 eV) is the same as that for the molybdenum core ionization energy in the analogous molybdenum complexes. The corresponding shift in the chromium valence ionization energies is more difficult to quantify since, in $[Cr_2(O_2CMe)_4]$, no experimental resolution has been achieved for the individual metal ionizations, which are all contained within the

Table 2. Metal orbital ionization energies (eV) calculated using Koopmans' theorem

	$[Mo_2(O_2CH)_4]$	$[Mo_2\{(CH_2)_2PH_2\}_4]$	$[Cr_2(O_2CH)_4]$ $[R(Cr-Cr) =$ 2.288 Å$]$	$[Cr_2\{(CH_2)_2PH_2\}_4]$
σ	12.0	7.7	10.1	7.2
π	12.2	8.9	9.1	6.5
δ	10.3	5.8	8.8	4.8
δ–π splitting	1.9	3.1	0.3	1.7

Table 3. Calculated atomic charges

Atom [a]	HCO_2^-	$[Mo_2(O_2CH)_4]$	$[Cr_2(O_2CH)_4]$ [b]		$(CH_2)_2PH_2^-$	$[Mo_2\{(CH_2)_2PH_2\}_4]$	$[Cr_2\{(CH_2)_2PH_2\}_4]$
			(2.288)	(1.895)			
M		+1.07	+1.27	+1.23		+0.94	+1.32
O	−0.60	−0.50	−0.54	−0.53			
C	+0.08	+0.21	+0.22	+0.21	−0.91	−0.88	−0.93
P					+0.47	+0.51	+0.45

[a] M = Mo or Cr. [b] Cr–Cr separation in parentheses.

first broad band of the photoelectron spectrum.[7,8] However, the width of this band is *ca.* 1 eV and from this a δ–π separation of approximately 0.5 eV may be estimated. In $[Cr_2(mhp)_4]$, on the other hand, the δ–π separation is increased to 1.5 eV, so that a resolution of the individual ionizations is obtained. As in the case of the corresponding dimolybdenum(II) complexes, this increase in the δ–π splitting is taken to be a consequence of both the decrease in the Cr–Cr separation (2.288 to 1.889 Å) and the change in size of the chromium 3*d* orbitals. The increase in the δ–π splitting in the dichromium(II) (*ca.* 1 eV) is larger than that for the dimolybdenum(II) complexes (0.3 eV), in line with the larger bond length variation for the former as compared with the latter complexes.

The data of Table 1 provide additional information as to the origin of these metal–metal bond length variations. Thus, the oxygen core ionization energies of $[Cr_2(O_2CMe)_4]$ and $[Mo_2(O_2CMe)_4]$ are the same within experimental error, as are the oxygen and nitrogen core ionization energies of $[Cr_2(mhp)_4]$ and $[Mo_2(mhp)_4]$. Furthermore, the decrease (0.8—0.9 eV) in the binding energy of the chromium 2*p* levels from $[Cr_2(O_2CMe)_4]$ to $[Cr_2(mhp)_4]$ matches that (0.8—1.0 eV) of the molybdenum 3*d* levels from $[Mo_2(O_2CMe)_4]$ to $[Mo_2(mhp)_4]$. Therefore, we consider it reasonable to conclude that the charge distribution is probably similar within $[Cr_2(O_2CMe)_4]$ *and* $[Mo_2(O_2CMe)_4]$, and within $[Cr_2(mhp)_4]$ *and* $[Mo_2(mhp)_4]$. This result leads to the important conclusion that the significant lengthening (by 0.40 Å) of the Cr–Cr separation from $[Cr_2(mhp)_4]$ to $[Cr_2(O_2CMe)_4]$, as compared with the much smaller (0.03 Å) lengthening of the Mo–Mo separation from $[Mo_2(mhp)_4]$ to $[Mo_2(O_2CMe)_4]$ is *not* due to differences in the bonding of the ligands to the dichromium(II), as compared with the dimolybdenum(II) centre.

As a further, and more detailed, contribution to the electronic structure of these molecules, we now present the results of the *ab initio* calculations on the four molecules, $[Mo_2(O_2CH)_4]$, $[Cr_2(O_2CH)_4]$, $[Mo_2\{(CH_2)_2PH_2\}_4]$, and $[Cr_2\{(CH_2)_2PH_2\}_4]$, and discuss the measured ionization energies in the light of these results.

Computational Results.—In view of the near minimal basis sets used in these calculations we must first say that the calculated ionization energies are of only semiquantitative value, but that trends between related molecules are probably accurately reproduced. The electronic structures of $[Mo_2(O_2CH)_4]$ and $[Cr_2(O_2CH)_4]$ have been described in detail both at the single determinant level and including correlation effects,[4] using a double zeta valence basis, and calculations on these molecules are only included here for purposes of comparison. Briefly, a clear division of the M.O.s into metal–metal bonding and ligand M.O.s is possible, with the σ, π, and δ orbitals having greater than 80% metal character. For $[Mo_2(O_2CH)_4]$, the use of Koopmans' theorem allows an assignment of the valence photoelectron spectrum, whilst in $[Cr_2(O_2CH)_4]$ there is a breakdown of the orbital picture, due to the small contribution of the $\sigma^2\pi^4\delta^2$ configuration at the large Cr–Cr separation. The calculations described herein also show these features. In both $[Mo_2\{(CH_2)_2PH_2\}_4]$ and $[Cr_2\{(CH_2)_2PH_2\}_4]$ a clear division of the m.o.s into those having metal and ligand character also occurs. In Table 2 we show the metal ionization energies from the $\sigma^2\pi^4\delta^2$ SCF configuration obtained using Koopmans' theorem. For the complexes involving the $(CH_2)_2PH_2^-$ ligand, the ionization energies are considerably smaller than those for the tetraformates, in line with the experimental data obtained for the mhp complexes. For the dimolybdenum(II) complexes, no clear trend in the splittings between δ, π, and σ m.o.s is found. Thus, although the δ–π splitting increases from 1.9 eV in $[Mo_2(O_2CH)_4]$ to 3.1 eV in $[Mo_2\{(CH_2)_2PH_2\}_4]$, the corresponding values for the δ–σ splitting, expected to show a similar trend, are 1.7 and 1.9 eV, respectively. Such inconsistencies are not unexpected, in view of the minimal 4*d* basis which does not allow for optimization of the 4*d* orbital size. For the dichromium(II) complexes, where a double zeta 3*d* basis was used, and where there are larger changes in the metal–metal separation, a more consistent trend in the δ–π–σ separations is observed. The origin of the shifts in the valence ionization energies may be sought by an examination of the formal charges, given in Table 3, obtained as a result of a Mulliken population analysis. There are only small variations in the metal charges with the different ligands. There are, however, larger changes in the charges on the ligand atoms to which the metal atoms are bonded. Thus, in the carboxylates, the oxygen charge is −0.5e, whilst in the complexes of $(CH_2)_2PH_2^-$, the carbon charges are near −0.9e. These variations reflect the different charge distributions within the corresponding ligands. A point charge calculation of the potential at the chromium atom, taking into account only the other atoms in the molecule, gives values of −0.38 a.u. for $[Cr_2\{(CH_2)_2PH_2\}_4]$ and −0.35 a.u. for $[Cr_2(O_2CH)_4]$, showing

Table 4. Summary of CI calculations for $[Cr_2(O_2CH)_4]$ and $[Cr_2\{(CH_2)_2PH_2\}_4]$

Molecule	R(Cr–Cr)/Å	Expansion	No. of bonded functions	Molecular energy (E_h) *
$[Cr_2\{(CH_2)_2PH_2\}_4]$	1.895	$\sigma^2\pi^4\delta^2$	1	−3 728.5059
		$(\sigma)^2(\pi)^4(\delta)^2$	98	−3 729.0322
		$(\sigma)^2(\pi)^4(\delta)^2$ + excitations to ligand m.o.s	256	−3 729.0362
		$(\sigma\pi\delta)^8$	264	−3 729.0335
		$(\sigma\pi\delta)^8$ + excitations to ligand m.o.s	422	−3 729.0375
$[Cr_2(O_2CH)_4]$	1.895	$\sigma^2\pi^4\delta^2$	1	−2 812.0782
		$(\sigma\pi\delta)^8$	264	−2 812.6274
$[Cr_2(O_2CH)_4]$	2.288	$\sigma^2\pi^4\delta^2$	1	−2 811.9167
		$(\sigma\pi\delta)^8$	264	−2 812.7275
		$(\sigma\pi\delta)^8$ + excitations to ligand m.o.s	2 200	−2 812.7324

* Hartree = 4.36 × 10^{-18} J.

that significant changes in the metal ionization energies can result from the differing charge distributions within the ligands. An examination of the individual orbital populations reveals that the major difference between the bonding of the two ligands studied here is an increase in the population of the $d_{x^2-y^2}$ orbital in the $(CH_2)_2PH_2^-$ complexes. Thus, the $d_{x^2-y^2}$ populations are 0.47e and 0.71e for $[Mo_2(O_2CH)_4]$ and $[Mo_2\{(CH_2)_2PH_2\}_4]$, respectively, whilst for the chromium complexes the corresponding values are 0.29e and 0.35e. There is, however, a reduction in the population of the d_{xy} orbital due to reduced ligand → metal charge transfer *via* the ligand a_2 m.o. This m.o. is the highest occupied orbital in HCO_2^-, but is more strongly bound in $(CH_2)_2PH_2^-$.

Correlation Effects and the Metal–Metal Interaction.—Previous calculations have shown the importance of correlation effects for a correct description of the metal–metal interaction in $[Cr_2(O_2CH)_4]$.[1–4] For a Cr–Cr separation of 2.36 Å, the quadruple bond configuration contributes only *ca.* 6% to the total wavefunction. A CI calculation of the Cr–Cr potential energy curve [2] for $[Cr_2(O_2CH)_4]$ yielded an extremely shallow potential well, the energy changing by only 0.05 a.u. over a bond length variation of 1.98—2.489 Å. For $[Mo_2(O_2CH)_4]$, where the quadruple bond configuration is dominant (67%), the potential well is considerably steeper. From the previous discussion, we suggest that it is the shallowness of the Cr–Cr potential well, coupled with the increase in the attractive potential at the metal centre caused to a large extent by an increase in the electron density on the ligand atoms directly bonded to the metal atoms, which allows for a decrease in the Cr–Cr separation, and is reflected in a decrease in the metal ionization energies as the separation decreases. To investigate whether the ligands have any direct effect on the description of the metal–metal correlation effects, we carried out a number of CI calculations, summarized in Table 4. The CI expansion is denoted $(\sigma)^2(\pi)^4(\delta)^2$, where, for example $(\sigma)^2$ signifies a total occupancy of 2 electrons for the σ and σ* orbitals. A larger expansion, $(\sigma\pi\delta)^8$, included all possible ways of distributing the eight valence *d* electrons amongst the eight metal valence m.o.s. These expansions include the important configurations describing the left–right correlation within the metal–metal interaction. Additional CI calculations were carried out that included double excitations from the metal to low lying ligand orbitals. The importance of correlation effects, previously noted,[1–4] can be seen from the calculations on $[Cr_2(O_2CH)_4]$ at the two Cr–Cr separations, where at the single determinant level the shorter bond length structure is more stable, whilst when correlation effects are included, the longer bond length structure becomes more stable. We have previously found [29] that for Cr_2, where correlation effects are again of prime importance, quantitative details of the calculated potential energy curve are sensitive to optimization of the basis m.o.s used in the CI calculation. Furthermore, for other metal complexes [30] there are problems associated with the calculation of accurate bond lengths. For these reasons, the variations of molecular energy with Cr–Cr bond length changes shown in Table 4 have only semiquantitative significance. The important point is that the metal–metal potential curve is shallower for the dichromium(II) than for the dimolybdenum(II) complexes, a result which parallels that found for Cr_2 and Mo_2.[29] However, an important result from the CI calculations is that, for a Cr–Cr separation of 1.895 Å, the calculated correlation energy is essentially the same for both $[Cr_2(O_2CH)_4]$ and $[Cr_2\{(CH_2)_2PH_2\}_4]$, being 0.55 a.u. and 0.53 a.u. respectively for the $(\sigma\pi\delta)^8$ expansion. In addition, there is very little gain (<0.01 a.u.) in correlation energy when excitations to the ligand orbitals are included in the expansion. Thus, for a particular Cr–Cr separation, the description of the metal–metal interaction is not dependent upon the nature of the ligand present, and metal–ligand correlation effects are of little importance.

Conclusions

The measured ionization energies described herein lead to important conclusions regarding the electronic structure of the dichromium(II) and dimolybdenum(II) molecules, which are substantiated by the *ab initio* calculations we have accomplished. The most important observation is the correlation between the metal–metal separation and both the core and valence metal ionization energies. This leads to the conclusion that it is the variation in the electrostatic potential at the metal centre, due to the different ligands, together with the shallow Cr–Cr potential well, which leads to large variations in the Cr–Cr separation. Such changes in potential arise mainly from variations in the charges on the ligand atoms directly bonded to the metal centre, and account for the short Cr–Cr bond lengths found for a variety of different ligands in molecules having different molecular symmetries {*e.g.* $[Cr_2(mhp)_4]$, $[Cr_2Me_8]^{4-}$, $[Cr_2\{(CH_2)_2PMe_2\}_4]$}. Indeed, the calculations described here show that the description of the $Cr^{II}-Cr^{II}$ interaction depends on the Cr–Cr separation, and not upon the nature of the ligand, the role of the latter being to determine the Cr–Cr separation by the variation of the electrostatic potential experienced at the dimetal centre.

The experimental measurements further suggest that, for a given ligand, the metal–ligand bonding is the same in both the dichromium(II) and dimolybdenum(II) complexes, and that the large variation in the Cr–Cr separation and the small variation in the Mo–Mo separation arise from different descriptions of the $Cr^{II}-Cr^{II}$ and $Mo^{II}-Mo^{II}$ interactions. This conclusion is consistent with the previous calculations reported for $[Cr_2(O_2CH)_4]$ and $[Mo_2(O_2CH)_4]$, and with recent calculations on Cr_2 and Mo_2.[29]

Acknowledgements

We thank the S.E.R.C. and the Royal Society for support.

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Received 8th October 1982; Paper 2/1739