The Charge Distribution in Complexes having Mo–Mo or Cr–Cr 'Quadruple' Bonds, Studied by Gas-phase *X*-Ray Photoelectron Spectroscopy

By PAUL M. ATHA, MADELEINE BERRY, C. DAVID GARNER, IAN H. HILLIER,* and ALASTAIR A. MACDOWELL
(*Chemistry Department, University of Manchester, Manchester* M13 9PL)

Summary The gas-phase core-electron ionization energies of M_2L_4 (M = Cr, L = O_2CMe or mhp; M = Mo, L = O_2CH, O_2CMe, or mhp) (Hmhp = 2-hydroxy-6-methylpyridine) are reported and lead to the important conclusion that the charge distribution is the same within $[Cr_2(O_2CMe)_4]$ *and* $[Mo_2(O_2CMe)_4]$ and within $[Cr_2(mhp)_4]$ *and* $[Mo_2(mhp)_4]$ despite the large variations in the metal–metal bond lengths for these pairs of molecules.

THERE is a continuing interest concerning the description of the electronic structure of complexes involving direct metal–metal interactions, especially when these correspond to a high formal bond order such as the 'quadruple' metal–metal bonds in Cr_2^{4+} and Mo_2^{4+} complexes.[1–4] Of particular interest for the Cr_2^{4+} systems is the relationship between the electronic structure and the intramolecular metal–metal separation which varies over a remarkably wide range (currently, 1·83—2·54 Å[5,6]). Measurements of the low-energy photoelectron spectra (P.E.S.) of representative Cr_2^{4+} and Mo_2^{4+} complexes have provided a unique insight into the electronic structure of these systems.[1–4] Furthermore, the sense of the correlation between the ionization energies (I.E.s) of the metal's valence electrons and the length of the Cr^{II}–Cr^{II} bond is consistent with the suggestion[4] that the coulombic repulsion between the metal atoms has an important influence on the metal–metal separation in Cr_2^{4+} complexes. This effect is less apparent for the Mo_2^{4+} complexes, partly because the intramolecular metal–metal separation varies over a much narrower range, currently 2·04—2·18 Å,[7,8] than that for the corresponding Cr_2^{4+} complexes.

Herein we report the first measurements of the core level P.E.S. of two Cr_2^{4+} and three Mo_2^{4+} molecules as a further aid to the elucidation of the electronic structure of these systems. Gas-phase *X*-ray P.E.S. (X.P.E.S.) of $[Cr_2(O_2CMe)_4]$, $[Cr_2(mhp)_4]$ (Hmhp = 2-hydroxy-6-methylpyridine), $[Mo_2(O_2CH)_4]$, $[Mo_2(O_2CMe)_4]$, $[Mo_2(mhp)_4]$, and of the free ligand Hmhp, have been measured using AlK_α-radiation. The spectra were calibrated using gases (CO_2, N_2, Ar) having core I.E.s[9] close to those being measured. The results obtained are summarised in the Table, together with those previously reported[10] for HCO_2H and $MeCO_2H$.

We have sought to obtain an estimate of the charge distribution within $[Mo_2(O_2CH)_4]$ by interpreting the core I.E.s by means of an *ab initio* S.C.F.–M.O. calculation. A gaussian basis of double zeta quality was used to describe the valence orbitals, the total basis size being 176 contracted gaussian functions. Calculations were accomplished on the CARY-1S computer at the S.R.C. Daresbury Laboratory and resulted in an S.C.F. molecular energy of −8700·3694 a.u. ($-3{\cdot}793187 \times 10^{-14}$ J). To aid the interpretation of the X.P.E.S. data, an equivalent calculation was accomplished for HCO_2H. The interpretation of the carbon 1s I.E.s for $[Mo_2(O_2CH)_4]$ and HCO_2H is complicated by the observation of two peaks for the former compound, whereas all four carbon atoms in the molecule are equivalent. The appearance of such an intense satellite structure will be considered subsequently, with respect to more detailed theoretical studies. However, calculations of the oxygen 1*s* I.E.s by the ΔS.C.F. method,[11] which allowed for the electron reorganization occurring upon ionization, predicted the shift between the 1*s* I.E.s of the carbonyl oxygen of HCO_2H and of $[Mo_2(O_2CH)_4]$ to be

0·3 eV compared with the experimental value of 0·4 eV (see Table). Therefore, the ground-state charge distribution within $[Mo_2(O_2CH)_4]$, predicted by the *ab initio* calculation, is taken to be substantially correct. This calculation predicts that each molybdenum atom has a formal charge of $+1·26$ and each ligand a net formal charge of $-0·63$, the carbon and oxygen charges being $+0·08$ and $-0·59$ respectively.

Table. Experimental core ionisation energies (eV)[a]

	$[Cr_2(mhp)_4]$	$[Cr_2(O_2CMe)_4]$	
Cr $2p_{1/2}$	590·2	591·1	
Cr $2p_{3/2}$	580·6	581·5	
O 1*s*	536·4	537·8	
N 1*s*	404·2		
C 1*s*	291·9 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
O 1*s*	536·5	537·9	538·5
N 1*s*	404·2		
		295·7[b]	296·1[b]
C 1*s*	290·0	293·4	293·8
		291·1	
	Hmhp	$MeCO_2H$[c]	HCO_2H[c]
O 1*s*	539·5	539·9	540·6
	536·7[e]	538·1[d]	538·9[d]
N 1*s*	404·5	295·6	296·0
	405·9[e] sh	291·6	

[a] Estimated uncertainty ±0·1 eV (relative to calibrant). [b] Satellite peak observed for C 1*s*. [c] Ref. 10. [d] Carbonyl oxygen. [e] Keto-tautomer.

The core I.E.s listed in the Table provide clear indications of the charge distributions within these $[M_2L_4]$ ($M = Cr$, $L = O_2CMe$ or mhp; $M = Mo$, $L = O_2CH$, O_2CMe, or mhp) molecules. Inspection of the data for $[Mo_2(O_2CR)_4]$ and RCO_2H (R = Me or H) shows that *both* the molybdenum and oxygen core levels of $[Mo_2(O_2CMe)_4]$ are some 0·6—0·7 eV to lower binding energy than in $[Mo_2(O_2CH)_4]$. This shift is the same as that observed[2] for the molybdenum and oxygen valence I.E.s of $[Mo_2(O_2CMe)_4]$ as compared to those of $[Mo_2(O_2CH)_4]$ and the oxygen 1*s* levels of $MeCO_2H$ as compared to HCO_2H. Therefore, 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 being electron donating to the Mo_2O_8 portion, as compared to H atoms).

The oxygen core I.E.s 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 I.E.s 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, in going from $[Cr_2(O_2CMe)_4]$ to $[Cr_2(mhp)_4]$, matches that (0·8—1·0 eV) of the molybdenum 3*d* level, in going from $[Mo_2(O_2CMe)_4]$ to $[Mo_2(mhp)_4]$. Therefore, it is reasonable to conclude that the charge distribution is probably the same 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^{II}–Cr^{II} separation in going from $[Cr_2(mhp)_4]$ to $[Cr_2(O_2CMe)_4]$, as compared to the much smaller (0·03 Å) lengthening of the Mo^{II}–Mo^{II} separation in going 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 to the dimolybdenum(II), centre. Rather, it must be due to the different descriptions of the Cr^{II}–Cr^{II} and Mo^{II}–Mo^{II} interactions, in agreement with the results of multiconfigurational S.C.F. calculations,[12,13] which indicate a much shallower potential well for the former, as compared to the latter, interaction. Therefore, the Cr^{II}–Cr^{II} separation will be much more sensitive than the Mo^{II}–Mo^{II} separation to changes in the charge distribution within an M_2L_4 complex.

We thank the S.R.C. and the Royal Society for supporting this research.

(*Received*, 16*th June* 1981: *Com.* 707.)

[1] C. D. Garner, I. H. Hillier, A. A. MacDowell, I. B. Walton, and M. F. Guest, *J. Chem. Soc., Faraday Trans.* 2, 1979, **75**, 485 and references therein.
[2] A. W. Coleman, J. C. Green, A. J. Hayes, E. A. Seddon, D. R. Lloyd, and Y. Niwa, *J. Chem. Soc., Dalton Trans.*, 1979, 1057 and references therein.
[3] B. E. Bursten, F. A. Cotton, A. H. Cowley, B. E. Hanson, M. Lattman, and G. G. Stanley, *J. Am. Chem. Soc.*, 1979, **101**, 6244.
[4] M. Berry, C. D. Garner, I. H. Hillier, A. A. MacDowell, and I. B. Walton, *Chem. Phys. Lett.*, 1980, **70**, 350.
[5] F. A. Cotton and S. Koch, *Inorg. Chem.*, 1978, **17**, 2021.
[6] F. A. Cotton, M. W. Extine, and G. W. Rice, *Inorg. Chem.*, 1978, **17**, 176.
[7] F. A. Cotton, W. H. Ilsley, and W. Kaim, *Inorg. Chem.*, 1979, **18**, 2717.
[8] F. A. Cotton and J. R. Pipal, *J. Am. Chem. Soc.*, 1971, **93**, 5441.
[9] T. D. Thomas and R. W. Shaw, Jr., *J. Electron Spectrosc. Relat. Phenom.*, 1974, **5**, 1081.
[10] A. A. Bakke, H.-W. Chen, and W. L. Jolly, *J. Electron Spectrosc. Relat. Phenom.*, 1980, **20**, 333.
[11] M. E. Schwartz, J. D. Switalski, and R. E. Stronski, in 'Electron Spectroscopy,' ed. D. A. Shirley, North Holland, Amsterdam, 1972, p. 605.
[12] M. F. Guest, I. H. Hillier, and C. D. Garner, *Chem. Phys. Lett.*, 1977, **48**, 587.
[13] M. Benard and A. Veillard, *Nouv. J. Chim.*, 1977, **1**, 97.