X-Ray Photoelectron Emission Studies of some Complexes of Molybdenum in Formal Oxidation States of III, IV, V, and VI

By **Joseph Chatt, Clive M. Elson, G. Jeffery Leigh,*** A.R.C. Unit of Nitrogen Fixation, The University of Sussex, Brighton BN1 9QJ
Joseph A. Connor, Department of Chemistry, The University of Manchester, Manchester M13 9PL

The binding energies of some inner-shell electrons in atoms of complexes $[MoCl_2O_2L_2]$, $[MoCl_3OL_2]$, $[MoCl_4L_2]$, and $[MoCl_3L_3]$ are reported [L = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, MeCN, EtCN, tetrahydrofuran (thf), pyridine (py), $\frac{1}{2}$ 2,2′-bipyridine (bipy), $\frac{1}{2}$ 1,10-phenanthroline (phen), or $\frac{1}{2}$ 1,2-bis(diphenylphosphino)ethane (dppe)]. Over this limited range of complexes, the metal binding energies are a function of the proportions of the anionic to neutral ligands, rather than of the metal oxidation state. The binding energies of the nitrogen atom in complexes of the donor py do not appear to correlate with simple inferences concerning atomic charges.

OUR studies of the value of *X*-ray photoelectron emission (*X*-p.e.) spectroscopic measurements to determine the way in which metal ions and ligands interact have been mainly confined to complexes containing metal ions in low formal oxidation states. All the complexes have contained tertiary phosphines.[1] We have demonstrated that, as ligands in such complexes, tertiary phosphine molecules and chloride ions are overall strong electron donors, and that chlorine and nitrogen atoms, and dinitrogen, carbon monoxide, and nitrogen oxide molecules are electron acceptors.[1] In this paper, we discuss attempts to extend this work to complexes containing molybdenum in oxidation states III—VI and with other ligands.

There have been at least two studies of molybdenum complexes related to ours. Hughes and Baldwin[2] reported the *X*-p.e. spectra of $[MoCl_4(PPh_3)_2]$ and $[MoCl_3O(PPh_3)_2]$ as well as of some nitrosyls and carbonyls. Their results (see Table) are comparable to ours, although we do not accept their inferences from them, since they are based on too many unlikely assumptions. For example, the Pauling ionic-character relation only works well for compounds such as hydrogen chloride, and certainly not well for transition-metal complexes. The data in ref. 1 show that CO is electron withdrawing, not neutral, and that tertiary phosphines are electron donating and not neutral. Grim and Matienzo[3] studied an extensive series of molybdenum carbonyl derivatives. Their inferences are generally in agreement with our inferences from rhenium complexes, but there is no overlap with the studies reported here.

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[1] J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1975, 2392.

[2] W. B. Hughes and B. A. Baldwin, *Inorg. Chem.*, 1973, **13**, 1531.

[3] S. O. Grim and L. J. Matienzo, *Inorg. Chem.*, 1975, **14**, 1014.

We have hitherto adopted the policy of selecting a set of arbitrary standard complexes and using these as a basis for the comparison of the other complexes.[1] Here we have adopted an alternative approach, which is less reliable because of the problem of correction for Madelung effects, but is forced upon us because of the narrow range of comparable complexes [$MoCl_xL_y$] ($x + y = 6$; L = neutral ligand) of the required kinds which are available. We have prepared, and measured by *X*-p.e. spectroscopy the binding energies for, a range of complexes [$MoCl_2O_2L_2$], [$MoCl_3OL_2$], [$MoCl_2L_3$], [$MoCl_4L_2$], and [$MoCl_3L_3$]. The results are shown in the Table, and are discussed below.

Electron binding energies of some molybdenum complexes

Formal oxidation state and complex	Binding energies/eV				
	Mo(3*d*)		P(2*p*)	Cl(2*p*)	N(1*s*)
	$\frac{5}{2}$	$\frac{3}{2}$			
	Stoicheiometric type [Mo(anion)$_4$L$_2$]				
(VI)					
[$MoCl_2O_2$(bipy)]	235.6	232.5		198.6	339.1
(V)					
[$MoCl_3$(bipy)O]	235.0	232.0		198.9	399.3
[$MoCl_3(py)_2O$]	235.0	232.1		198.6	399.3
[$MoCl_3O$(dppe)]	234.9	232.0	131.4	198.9	
[$MoCl_3O(PPh_3)_2$] [a]	235.5	232.5	132.9	198.3	
(IV)					
[$MoCl_4(thf)_2$]	235.3	232.0		199.4	
[$MoCl_4(NCEt)_2$]	235.3	232.3		199.2	399.4
[$MoCl_4(PEtPh_2)_2$] [b]	235.2	232.2	132.8	199.6	
[$MoCl_4$(bipy)]	235.1	232.2		198.2	398.8
[$MoCl_4(py)_2$]	235.0	232.0		198.5	398.3
[$MoCl_4(PPh_3)_2$] [a]	235.2	232.1	131.6	198.9	
	Stoicheiometric type [Mo(anion)$_3$L$_3$)				
(IV)					
[$MoCl_2$(phen)O(PMe_2Ph)] [c]	233.2	230.2	131.3	197.9	399.3
[$MoCl_2$(bipy)O(PMe_2Ph)]	233.6	230.8	131.3	198.2	399.2
[$MoCl_2$(py)O(dppe)]	233.1	230.1	131.2	198.0	399.5
[$MoCl_2O(PMe_2Ph)_3$] [b]	233.2	230.4	132.3	198.9	
(III)					
[$MoCl_3(py)_3$]	232.7	229.7		197.7	399.2
[$MoCl_3(py)_2$(thf)]	232.9	229.8		198.3	399.4
[$MoCl_3(py)(thf)_2$]	233.2	230.4		198.7	399.6
[$MoCl_3(thf)_3$]	233.8	230.8		199.5	
[$MoCl_3(thf)_2(PEtPh_2)$]	233.0	229.9	131.4	198.3	
[$MoCl_3(thf)(PMePh_2)_2$] [b]	232.9	229.8	131.4	198.7	
[$MoCl_3(PMe_2Ph)_3$]	232.6	229.4	131.5	198.2	
[$MoCl_3$(bipy)(thf)]	233.0	230.0		198.0	399.0
[$MoCl_3(NCMe)_3$]	233.5	230.5		198.7	399.7

[a] Data taken from ref. 2. [b] Suffered some radiation damage, but the values are considered to be reliable. [c] phen = 1,10-Phenanthroline.

RESULTS AND DISCUSSION

Metal Binding Energies.—The Table shows the metal 3*d*-electron binding energies of the complexes, which are arranged according to stoicheiometric type, and within each type are grouped according to oxidation state. The energies are sensibly constant to within ±0.5 eV * for the individual groups. They show that it is not possible to use *X*-p.e. spectroscopic data to determine the oxidation state of a metal ion in a complex, because, even where there is a linear correlation between binding energy and oxidation state for a series of complexes {as exemplified by [$ReCl_x(PMe_2Ph)_y$] ($x = 2$—4; $x + y = 6$) [1,4]}, this no longer holds when the kinds of ligands change. Thus all the complexes of the stoicheiometric type [Mo(anion)$_3$(neutral ligand)$_3$] have similar metal 3*d* binding energies (see Table), independent of oxidation state, and the same applies to the type [Mo(anion)$_4$-(neutral ligand)$_2$]. This can be interpreted as showing that, regardless of the neutral ligands, L, the oxygen atom as a ligand has about the same electron-withdrawing effect on the metal as a ligating chlorine atom.

This finding accords with the fact that the rhenium 4*f* binding energies in [$ReCl_4(PPh_3)_2$] and [$ReCl_3O$-$(PPh_3)_2$] are 45.6 and 43.0 and 45.5 and 43.2 eV respectively.[5] Dipole-moment data also support the view that chloride and oxide ions as ligands have similar charges; *e.g.* *trans*-[$ReCl_4(PEt_2Ph)_2$] and *trans*-[$ReCl_3O$-$(PPr^n_3)_2$] have dipole movements of 0.87 [6] and 1.3 D,[7] respectively.

Over the limited range of ligands considered above, it would appear, therefore, that the 3*d*-electron binding energy of molybdenum is a function of the relative numbers of neutral and anionic ligands, and not of their kind, nor of the formal oxidation state of the metal. This generalisation probably applies where strongly electron-donating neutral ligands [*e.g.* tetrahydrofuran

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* 1 eV ≈ 1.60×10^{-19} J; 1 D ≈ 3.33×10^{-30} C m; 1 mmHg ≈ 13.6×9.8 Pa.

[4] G. J. Leigh, *Inorg. Chim. Acta*, 1975, **14**, L35.

[5] D. G. Tisley and R. A. Walton, *J. Mol. Structure*, 1973, **17**, 401.

[6] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 601.

[7] J. Chatt and G. A. Rowe, *Chem. and Ind.*, 1962, 92.

(thf)] and strongly electronegative anionic ligands (*e.g.* Cl^-) are concerned, but would be expected to fail with strongly back-bonding ligands (*e.g.* CO, NO, N_2, or olefins) which carry very little, if any, positive charge, or electropositive anionic ligands (*e.g.* H^- or CH_3^-) which carry little negative charge in their complexes.[1,4]

We have established [4] for a series of complexes of the third-row transition metals, $[MCl_x(PMe_2Ph)_y]$ (M = W, Re, Os, Ir, or Pt; $x + y = 6$), that there is a change in 4*f* binding energies of 1.5 eV per unit change in oxidation state. Our data in the Table are more limited, but are not restricted to tertiary phosphine complexes. The difference in Mo(3*d*) binding energies for the thf complexes $[MoCl_3(thf)_3]$ and $[MoCl_4(thf)_2]$ is *ca.* 1.4 eV. For pyridine (py) and tertiary phosphine complexes the corresponding changes are *ca.* 2.5 eV. This presumably reflects the greater electron-donor character of py and tertiary phosphines relative to thf.

We also wished to establish whether there is any empirical relation between Mo(3*p*) and Mo(3*d*) binding energies. In the stoicheiometric type $[Mo(anion)_3L_3]$, a difference in Mo(3*d*) binding energies between two complexes of Δ eV is paralleled by a similar difference Δ for the Mo(3*p*) binding energies. However, for the type $[Mo(anion)_4L_2]$ a difference Δ between the 3*d* binding energies is apparently reflected by a difference of *ca.* 3Δ in the 3*p*. The data of Hughes and Baldwin are consistent with this. However, we are not altogether satisfied with our measurements of Mo(3*p*) binding energies because the Mo(3*p*) ionisation has a low cross-section, the peak is often partly obscured by the N(1*s*) ionisation, for which the cross-section is high, and because the higher-oxidation-state complexes, especially those with phosphine ligands, have a tendency to photoreduce. This interesting observation should thus be treated with reserve.

There is a significant change in 3*d*-electron binding energies in the series $[MoCl_3(thf)_3]$, $[MoCl_3(py)(thf)_2]$, $[MoCl_3(py)_2(thf)]$, and $[MoCl_3(py)_3]$, from 233.8 eV at one extreme to 232.7 eV at the other. This is paralleled in the series $[MoCl_3(thf)_3]$ to $[MoCl_3(PR_3)_3]$ (PR_3 = tertiary phosphine). This presumably again reflects the greater σ-electron-donor strength of py and tertiary phosphines towards molybdenum relative to thf. There is an even greater variation in the thf series in the Cl($2p_{\frac{3}{2}}$) binding energies (199.5—197.7 eV), the more strongly σ-donating the other ligands the more apparently negative is the Cl. This contrasts with the general invariance of Cl($2p_{\frac{3}{2}}$) which we observed [8] in complexes of the third transition series. We infer that in the second transition series the metal is relatively less polarisable than in the third, especially in higher oxidation states, and thus the halido-ligands are more sensitive to changes in binding energy arising from changes in the constitution of the complex. This will require wider testing.

Ligand-atom Binding Energies.—The variation of Cl($2p_{\frac{3}{2}}$) binding energy in each of the series $[MoCl_4L_2]$, $[MoCl_3L_3]$, and $[MoCl_2OL_3]$ implies that the donor power of L towards both Mo^{III} and Mo^{IV} decreases in the order py > PR_3 ⩾ thf, in broad agreement with the interpretation of variations of the Mo(3*d*) binding energy in these complexes.

These inferences concerning donor ability are probably less reliable than those based on Mo(3*d*) binding energies. Phosphines other than PMe_2Ph could conceivably be stronger donors than py and, contrary to our findings [8] for heavier elements, nickel, for example, shows considerable variation in binding energy with the composition of the phosphine.[9] Thus care should always be taken in extrapolating results, particularly from one transition series to another.

The N(1*s*) electron binding energies of $[MoCl_2OL_3]$ and $[MoCl_3L_3]$ are sensibly constant in cases where at least one of the ligands L is pyridine (py) or ½ 2,2′-bipyridyl (bipy). However, in $[MoCl_4L_2]$, the N(1*s*) binding energies appear to be less than in the py or bipy complexes for the two groups $[MoCl_2OL_3]$ and $[MoCl_3L_3]$, whereas, on the basis of the molybdenum data, one would expect them to be greater. Apparently the thf O(1*s*) binding energies follow the same pattern, although, due to surface-contamination problems, O(1*s*) binding energies are often unreliable and we choose not to quote them. Nevertheless, our results emphasise that simple charge–binding energy–oxidation state correlations are often misleading.

We find it difficult to rationalise these results. Comparing both py and thf complexes, a similar pattern emerges:

	Binding energy/eV	
	Mo(3*d*)	Cl ($2p_{\frac{3}{2}}$)
$[MoCl_3(thf)_3]$	233.8	199.5
$[MoCl_4(thf)_2]$	235.3	199.4
$[MoCl_3(py)_3]$	232.7	197.7
$[MoCl_4(py)_2]$	235.0	198.5

The molybdenum and chlorine binding energies are consistent with an electron-donor power of py > thf. However, whereas three py ligands push more negative charge on to the chlorine ligands than do two, three thf ligands apparently push about the same amount as two. A possible explanation is that each of the two *trans* ligands L in $[MoCl_4L_2]$, because they are in opposition, release, *on average*, less charge than each of three ligands in a *mer* or *fac* configuration. Certainly, compared to N(1*s*) in py (398.0 eV),[10] the nitrogen atoms are nearly neutral in $[MoCl_4(py)_2]$, but it seems unlikely that geometrical factors could give rise to differences of the order of 1 eV.

Tentative Conclusions.—The distribution of electrons in an isolated neutral atom reaches an equilibrium arrangement which is a function of the nuclear charge

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[8] G. J. Leigh and W. Bremser, *J.C.S. Dalton*, 1972, 1216.

[9] C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, 1973, **12**, 2770.

[10] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlssen, I. Lindgren, and B. Lindberg, ' ESCA, Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy,' Almquist and Wiksells AB., Uppsala, 1967.

and the number of electrons. When the atom combines with other atoms this preferred equilibrium distribution is modified. Our earlier X-p.e. results mainly on complexes of rhenium in oxidation states I—IV were rationalised using a model which assumed that the ligands (generally chlorine or tertiary phosphine) were not significantly distorted (polarised) on binding to the metal, and thus reached an equilibrium electron distribution which was not very different from that in the unbound state.[1,8] Only ligands containing polarisable units, such as N_2, NO, or CO, released charge to varying extents depending on the circumstances of co-ordination.[1] However, the metal ion, being the most polarisable unit in the complex, would be most easily perturbed from its equilibrium electron distribution in the free state, and thus would show the most significant changes in electron binding energies with changes in co-ordination.

This model is reasonably valid when applied to complexes of third-row transition metals. In this paper we have discussed complexes with metal ions of the second transition series having no more than three d electrons. The metal ion in these molybdenum complexes, although still showing significant changes in binding energy with changes in structure, is less polarisable, and thus harder ligands (*e.g.* Cl^-) also show significant variations in binding energies according to the nature of their co-ligands. It is therefore no longer justifiable to regard the electron-withdrawing properties of chlorine and tertiary phosphines as properties so completely characteristic of the ligand that they can be extrapolated from one complex to another. We expect that this should be even less valid for metals of the first transition series. The data of Tolman *et al.*[9] and of Matienzo *et al.*[11] are consistent with this.

From our data, there is no simple correlation between binding energy and charge for donor ligand atoms such as nitrogen. It may be that changes in hybridisation of the donor atom are equally important in determining binding energies in our compounds, but testing this hypothesis will be difficult. However, it seems valid to define a metal binding energy as characteristic of a given constitutional type, within broad limits (±0.5 eV) and provided the metal has a high (>III) oxidation state. The metal in these higher oxidation states is less polarisable than in the lower oxidation states, and metal ions of the second transition series are less polarisable than those of the third.

It is expected that any set of internal-energy levels should give the same general information regarding the condition of a bound metal ion. However, it may be that the ' chemical shifts ' vary with the quantum level investigated, although this requires confirmation.

A final caveat is that we have found radiation damage to be a problem. In particular, it seems to be relatively more severe the lighter the metal atom, and is very significant in the first transition series and with complexes containing tertiary phosphines which are potential reducing agents. Thus, for the complex $[CoCl_2(NO)_2(PPh_3)_2]$ we have been able to obtain a variety of spectra depending on the residual pressure in the spectrometer, the X-ray flux, and the irradiation time. This may explain the anomalies in the interpretation of data obtained by i.r., X-ray, and X-p.e. methods.[12,13] We were unable to obtain meaningful data from $[MoCl_4(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] despite three attempts on three different samples.

EXPERIMENTAL

Complexes were prepared according to literature methods. X-Ray photoelectron spectra were determined on an ES-200 spectrometer at the University of Manchester for solid samples using internal carbon (= 285 eV) as standard. The complexes were handled in a special inert-atmosphere preparation chamber and inlet system which minimised the problems of surface oxidation and hydrolysis. The solid samples were loaded on to adhesive tape on a plate shaft. Residual pressures were always less than 10^{-8} mmHg. Measurements were made in duplicate for at least one sample of each complex, and generally for more. The errors in the quoted binding energies are ±0.3 eV.

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[12] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. Reed, *Inorg. Chem.*, 1973, **12**, 1304.

[13] C. C. Su and J. W. Faller, *J. Organometallic Chem.*, 1975, **84**, 53.