

THE X-RAY PHOTOELECTRON SPECTRA OF METAL HALIDES AND THEIR COMPLEXES: HALOGEN BINDING ENERGIES AND THEIR CORRELATION WITH STRUCTURE *

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A. INTRODUCTION

Since the publication by Siegbahn et al. [1,2] of their classic texts on the X-ray photoelectron spectra (XPS, also called ESCA) of organic and inorganic compounds, this technique has found wide application in the characterization of many inorganic molecules. Certain aspects of more recent advances have been reviewed in considerable detail, a particularly good general account being that by Jolly [3] in which the application of XPS to inorganic chemistry is discussed.

Much of the interest in inorganic molecules has centered on the measurement of metal core electron binding energies and a study of the associated multiplet splitting [4,5] and shake-up phenomena [6,7]. In contrast to this,

* This article is considered as Part XIII of a series entitled X-Ray Photoelectron Spectra of Inorganic Molecules; for Part XII see ref. 37.

related studies on the binding energies of ligand atoms and the ways in which this information may be used to determine the molecular structure of metal complexes have not generally attracted as much attention. One major exception has been the measurement of the nitrogen 1s binding energies of a variety of nitrogen-containing ligands, including nitrosyls [8,9], azides [10] and dinitrogen [10–13].

It is now becoming increasingly apparent that the measurement of the binding energies of ligand atoms can provide valuable structural information for a variety of metal complexes. This is particularly true when different chemical environments for the same element occur within a molecule. In these instances, both chemical shift differences and the relative intensities of the binding energy peaks can be used to probe the nature of the metal–ligand bonds. It is this particular aspect of the application of XPS to inorganic chemistry which will be the subject of the present review.

Much of the available data which relates to the distinction between different ligand environments concerns transition metal halides and their complexes. These systems are particularly ideal since we do not have to consider the complicating effect of organic substituents on the ligand atoms, a situation which can occur with other donor atoms; compare for example, the isoelectronic series $M-Cl$, $M-SR$ and $M-PR_2$.

While we will be concerned in this article with halogen core electron binding energies, some interesting results are beginning to emerge for other systems. For instance, it has been shown [10–13] that for dinitrogen complexes of the transition metals which contain terminal $M-N\equiv N$ units, the bound and unbound nitrogen atoms have N 1s binding energies which differ by 1–2 eV. Accordingly, it can be anticipated that increasing use will be made of this technique in studying the electronic structures of coordinated ligands.

Since details of instrument design, sampling procedures, the types of experimental problems which can arise with XPS, and the correlation of chemical shifts with calculated atomic charge have all been reviewed adequately elsewhere [3,14–16], these aspects will not be covered here.

B. CHEMICAL SHIFTS IN HALOGEN OXY-ANIONS

Prior to the detailed investigation of the binding energies of halogen atoms in metal halides and their complexes, data were already available on the halogen binding energies of alkali metal halides and their oxy-anions. For instance, within the series KCl , $KClO_3$, $KClO_4$ and KI , KIO_3 , KIO_4 , the chlorine 2p and iodine 3d binding energies were found to increase by 10.7 and 6.1 eV, respectively [17,18]. Since these data are consistent with average increases of ~ 1.3 and ~ 0.8 eV per unit increase in oxidation number, it is apparent that XPS is capable of distinguishing the halogen-containing species of this type which may be present in metal complexes. However, as far as inorganic chemists are concerned, a much more important question concerns whether XPS can distinguish different halogen environments in a molecule

when they are all in the same 'formal' oxidation state. Such a situation will exist when comparisons are made between halide ion and halogen in terminal and/or bridging metal-halogen bonds, and between halogen in terminal metal-halogen bonds which differ in bond strength. Systems of these types will be discussed in the following section.

C. CHEMICAL SHIFTS IN METAL HALIDES AND THEIR COMPLEXES

Before reviewing the pertinent literature data, it is appropriate if we introduce some suitable abbreviations for the different types of metal-halogen bonds which will be discussed.

- (1) Terminal metal-halogen bonds, $M-X_t$.
- (2) Bridging metal-halogen bonds, $M-X_b$.
- (3) In the case, where there is a need to distinguish halogen atoms bridging two or more metal centers, the abbreviation $X_{b(n)}$ will be used, where n is the number of metal centers bridged by the halogen atom.
- (4) In discussing metal halide clusters, we will need occasionally to refer to intercluster metal-halogen bridges. In such cases, X_b' will be used as the symbol for the intercluster bridging halogen atom.

Since a variety of calibration techniques [1,19-22] and sampling procedures have been used by different research groups, account must be taken of this in comparing data taken from different sources. However, since we will be more concerned with measured differences in binding energies within the same compound, absolute binding energies will not normally be of particular concern to us. When dealing with such binding energy differences, uncertainties due to work function and charging effects * normally vanish [3].

(i) Fluorides

In a recent study of the fluorine 1s binding energies of gaseous trigonal bipyramidal PF_5 and 'pseudo' trigonal bipyramidal SF_4 and ClF_3 [23], it was observed that the binding energies due to the equatorial fluorine atoms were between 1.2 and 2.5 eV higher than those assigned to the axial fluorines (Table 1 and Fig. 1). This result was considered to be consistent with the axial fluorines being bonded to the central atom with partially ionic, three center bonds [23]. Since these binding energy shifts reflect much more subtle structural differences in the nature of the $X-F$ bonds than might be expected in the case of metal fluorides containing both $M-F_t$ and $M-F_b$ bonds, it is reasonable to anticipate that differences in fluorine 1s binding energies may be detectable in crystalline metal fluoride phases.

A few studies have been devoted to the measurement of fluorine 1s binding energies of metal fluorides [24,25,27,28]. Some of these results [24,25] have

* Provided of course that the charging effects are uniform. Non-uniform charging can lead at best to peak asymmetry and at worst to multiple peaks.

TABLE 1

Fluorine 1s binding energies (eV) of gaseous non-metal fluorides ^a

Compound	F_{eq}	FWHM	F_{ax}	FWHM	$\Delta E(F_{eq}-F_{ax})$
ClF ₃	694.76(4)	1.74(8)	692.22(3)	2.00(5)	2.54
SF ₄	695.26(2)	1.87(3)	692.88(2)	2.15(4)	2.38
PF ₅	695.3(1)	—	694.1(1)	—	1.2
SF ₆	695.04(2)	—	—	—	—

^a All data are taken from ref. 23.

a direct bearing on the question of whether F_t and F_b can be distinguished and the relevant data are presented in Table 2. In one of these studies [24], involving fluorides which possessed a variety of different structures, the relatively wide range of measured fluorine 1s binding energies was attributable in part to differences in surface charging effects. However, since these peaks were both relatively narrow and symmetric in shape it is clear that the surface charging was quite uniform. Since we will not be particularly concerned with

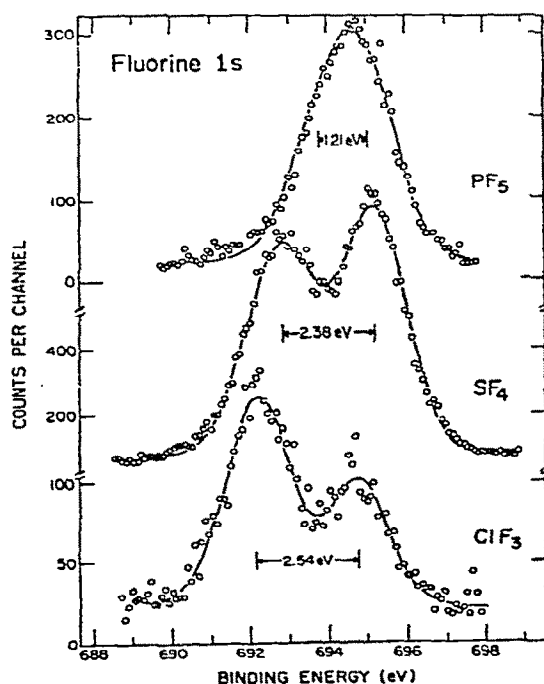


Fig. 1. Fluorine 1s binding energy spectra of PF₅, SF₄ and ClF₃. (Reproduced with permission from ref. 23).

TABLE 2

Fluorine 1s binding energies (eV) of crystalline metal fluorides and their complexes

Compound	F 1s	FWHM ^a	Ref.	Compound	F 1s	FWHM ^a	Ref.
Na ₂ TiF ₆	684.9	1.7	24	BeF ₂	686.0	—	25
K ₂ VOF ₅ · H ₂ O	684.6	1.6	24	NaBeF ₃	685.9	—	25
K ₂ MnF ₆	683.9	1.5	24	Na ₂ BeF ₄	685.4	—	25
ZrF ₄	685.2	1.6	24	AlF ₃ · 3 H ₂ O	686.5	—	25
	685.3	—	25	GaF ₃ · 3 H ₂ O	685.5	—	25
KZrF ₅ · H ₂ O	685.0	—	25	InF ₃ · 3 H ₂ O	685.5	—	25
K ₂ ZrF ₆	684.0	1.7	24	K ₂ SiF ₆	685.1	1.5	24
	684.8	—	25	SnF ₄	684.0	2.0	24
K ₃ ZrF ₇	684.5	—	25	K ₂ SnF ₆	685.6	1.5	24
NaTaF ₆	685.8	—	25	K ₂ [(CH ₃) ₂ SnF ₄]	685.4	1.4	24
Na ₂ TaF ₇	685.8	—	25	NaSbF ₄	684.1	1.9	24
Na ₃ TaF ₈	685.7	—	25	Na ₂ SbF ₅	683.6	2.2	26
K ₂ MoO ₂ F ₄ · H ₂ O	684.2	1.9	24	K ₂ SbF ₅	684.1	2.0	26
Cs ₂ MoO ₂ F ₄	684.9	—	25	NaSb ₂ F ₇	684.3	1.8	24
K ₂ WO ₂ F ₄ · H ₂ O	685.3	2.1	24	KSb ₂ F ₇	684.5	2.2	26
Cs ₂ WO ₂ F ₄	684.9	—	25	[Co(NH ₃) ₆]Sb ₂ F ₉	684.2	1.7	24

^a Full width at half maximum values given when available.

absolute binding energies, uniform charging of the sample surface will not usually affect any structural conclusions. Many of the complex fluoro-anions listed in Table 2 were studied as their potassium salts [24,25], and it is useful to internally reference the fluorine 1s energies to some standard value of the potassium $2p_{3/2}$ energy, say 293.0 eV. When this is done, the fluorine 1s energies of these fluoro-anions are seen to fall in the much narrower range of 686.0–694.5 eV, consistent with the suggestion that charging may be partly responsible for this wide spread of fluorine 1s energies. Clearly, structure changes can also dramatically influence the measured fluorine 1s binding energies. With the sodium fluorotantates(V), the invariance of the fluorine 1s, tantalum 4d and sodium 1s binding energies throughout the series NaTaF₆, Na₂TaF₇ and Na₃TaF₈ has been attributed to a compensation of the charge differences, which must occur as the coordination number changes, by variations in the Madelung potential [25]. On the other hand, within the series ZrF₄—KZrF₅ · H₂O—K₂ZrF₆—K₃ZrF₇, there is a change in charge without a corresponding increase in coordination number. While the potassium 2p energies do not vary significantly, both the fluorine 1s and zirconium 3d values decrease with increase in formal anion charge [25].

Turning now to the question of whether bridging and terminal fluorine atoms can in fact be distinguished, leads to some differences of opinion, at least on the basis of published data. In one study [24], the complexes studied were chosen from a variety of structural classes as indicated below.

(1) Compounds containing terminal M—F bonds, e.g., K₂MnF₆ [29].

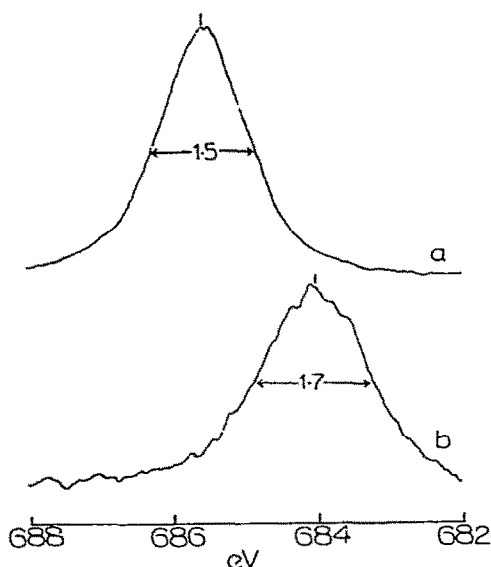


Fig. 2. Fluorine 1s binding energy spectra of (a) K_2SnF_6 , and (b) K_2ZrF_6 .

(2) Compounds containing two types of terminal M—F bonds, those which are either *trans*- to M=O or M—F, e.g., $K_2MoO_2F_4 \cdot H_2O$ [30].

(3) Compounds containing only bridging M—F bonds, e.g., ZrF_4 [31].

(4) Compounds containing both bridging and terminal M—F bonds, e.g., K_2ZrF_6 [32], SnF_4 [33], and salts of the fluoroantimonates [34–36].

Although the broadest of the fluorine 1s peaks were usually found [24] to be associated with compounds which possess two different fluorine environments, it is apparent from the data in Table 2 that the associated binding energy differences are sufficiently small to preclude their separation within the present limits of instrumental resolution. This is clearly seen in Fig. 2 where the fluorine 1s peak of K_2ZrF_6 is similar to that of K_2SnF_6 . These results can be contrasted with the claim of Nefedov et al. [25] that for the zirconium(IV) fluoride complex K_2ZrF_6 “the overall profile of the fluorine 1s line breaks down into two components with intensity ratio 2 : 1, the distance between them amounting to approximately 0.6 eV”. Similarly the fluorine 1s spectra of the *cis*- $[MO_2F_4]^{2-}$ anions [M = Mo or W] were purported to show a difference in the fluorine 1s energies of the fluorine atoms in the *trans*- and *cis*-positions of 0.9–1.0 eV [25], but no such chemical shifts were detected in a more recent study [24]. One possible explanation for the observed differences between these two sets of results is that the spectra obtained by Nefedov et al. [25] are complicated by the occurrence of differential surface charging thereby leading to asymmetric broadening of the fluorine 1s peaks.

Several other compounds studied by Nefedov et al. [25] were also reported

to exhibit fluorine 1s spectra which "revealed a difference in the effective charges of the bridging and terminal fluorine atoms". These were the hydrates $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$, $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$ and $\text{InF}_3 \cdot 3\text{H}_2\text{O}$, which give broad asymmetric fluorine 1s peaks which could be deconvoluted to give an apparent energy difference $\Delta E(F_t - F_b)$ of ~ 1.5 eV (note that the bridging fluorines were reported [25] to have the lower binding energies). In addition to differential charging effects, two other phenomena could be complicating the spectra of these hydrates. First there is the possibility that partial dehydration is occurring in the spectrometer, thereby leading to a variety of different surface sites and hence to asymmetric fluorine 1s peaks. Second, hydrogen bonding interactions of the type $\text{O}-\text{H} \cdots \text{F}-\text{M}$ may lead to variations in charge at the different fluorine atoms. Hydrogen bonding effects are known to influence chlorine binding energies in metal chloride complexes [37], and there is no reason to believe that the same will not be true with metal fluorides. Until these alternative explanations for the observed fluorine 1s spectra of $\text{MF}_3 \cdot 3\text{H}_2\text{O}$, where $\text{M} = \text{Al}, \text{Ga}$ or In , can be ruled out, the interpretations of Nefedov et al. [25] should be treated with caution.

Others [26,38] have also noted that sharp narrow fluorine 1s spectra are often characteristic of metal fluorides in which crystallographically distinct fluoride sites are present. It is apparent that with metal fluorides, the differences in charge at the various fluorine atoms are significantly less than is the case with chlorine in the much less ionic metal chloride phases (see Sect. C(ii)). This tendency towards an equalization of charge at the different fluorine sites ensures that, for the time being, XPS measurements on metal fluorides are unlikely to be of routine use in distinguishing different fluorine environments.

(ii) Chlorides

In contrast to the situation found for metal fluorides, the measurement of chlorine 2p binding energies has proved to be extremely useful in the structural characterization of several classes of metal chlorides and their complexes. Once again it should be emphasized that in comparing literature data from different sources account must be taken of differences in instrumental resolution, since small but significant chemical shifts between Cl_b and Cl_t may not be detected with instruments of lower resolution. In fact, since the separation between the chlorine $2p_{1/2}$ and $2p_{3/2}$ spin-orbit components is only about 1.5 eV, this doublet may not be resolved by certain instruments. In Fig. 3 we show the chlorine 2p spectra of two complexes in which the $2p_{1/2}$ and $2p_{3/2}$ components are well resolved. These spectra, which are typical for complexes containing a single type of chlorine environment, were recorded in the author's laboratory using an H-P 5950A ESCA instrument.

One of the earliest studies which raised the question of whether bridging and terminal chlorine environments could be differentiated, involved the measurements by Moddeman et al. [39] of the chlorine 2p binding energies

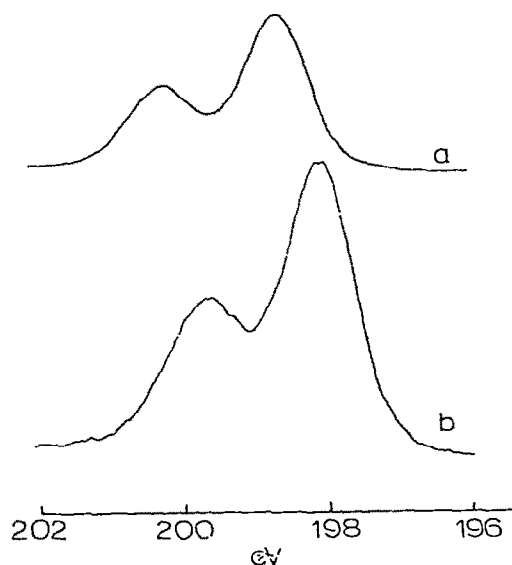


Fig. 3. Chlorine 2p binding energy spectra of (a) $\text{Re}_2\text{Cl}_6(\text{PPr}_3^+)_2$ and (b) $\text{trans-ReCl}_4\cdot(\text{CH}_3\text{CN})_2$.

of K_2PtCl_6 , K_2PtCl_4 , PtCl_2 and KCl . The appropriate binding energies are listed in Table 3. A comparison of the raw data for K_2PtCl_6 , K_2PtCl_4 and PtCl_2 can be interpreted to mean that the bridging chlorines in polymeric PtCl_2 do indeed have higher binding energies than the terminally bound chlorines in K_2PtCl_6 and K_2PtCl_4 . This result is intuitively reasonable, since from the simple charged shell model a bridging chloride attached to two Pt(II) ions would be more positively charged than chloride bound to only one Pt(II) ion. However, the fact that the chlorine 2p energies of KCl and PtCl_2 are the same (Table 3)

TABLE 3

Chlorine 2p binding energies (eV) of platinum chlorides ^a

Compound	'Cl 2p' ^b	K 2p
K_2PtCl_6	201.0	295.1
K_2PtCl_4	200.7	294.8
PtCl_2	201.1	—
KCl	201.2	295.7

^a All data are taken from ref. 39.

^b It is apparent that the chlorine $2p_{1/2,3/2}$ spin-orbit components were not resolved in this study. A further indication of this lack of resolution is the rather large FWHM values which were reported for these peaks (3.2 eV). In contrast to this situation, the chlorine 2p spectra given in Fig. 3 have FWHM values for the spin-orbit doublets of only 2.3 eV.

immediately raises the difficult question of how differences in Madelung potential can be accounted for. This is an inevitable complication when comparing data for compounds of quite different structure. An attempt to overcome this problem was originally made [39] by "normalizing" the potassium 2*p* and chlorine 2*p* data to a value of 294.8 eV for the former. When this is done, there is a net difference of only 0.4 eV between the coordinated and uncoordinated chloride. As a final indication that it is unreasonable to interpret such a small difference as being consistent with any one structural feature in so varied a series of molecules, it is instructive to include in our comparison the data of Moddeman et al. [39] for the salts $K_2Pt(CN)_4Cl_2$ and $K_2Pt(NO_2)_4Cl_2$. When this is done, and the chlorine 2*p* energies referenced to a potassium 2*p* value of 294.8 eV, then these values are identical (within experimental error) to the chlorine 2*p* energy of $PtCl_2$.

Having illustrated the complexities of making a meaningful comparison of binding energies associated with different molecules, it is now appropriate to turn our attention to systems in which different chlorine environments occur within the same molecule. These conveniently fall into four categories.

- (a) Chlorine-bridged dimers in which no metal-metal bond is present.
- (b) Metal chlorides containing a pair or cluster of metal atoms.
- (c) Salts containing both 'inner' and 'outer' sphere chloride.
- (d) Mononuclear complexes containing different types of metal-chlorine terminal bonds.

(a) Chlorine-bridged dimers not containing a metal-metal bond

The types of molecules of interest are transition metals in either very high (low *d* orbital populations) or very low oxidation states (filled or almost filled *d* orbitals) and non-transition metals (*d*¹⁰ configurations), since these are the systems which will not normally assume structures containing metal-metal bonds. Generally speaking, data on chlorides of these types are rather scarce at present, although some interesting binding energy correlations are now just beginning to emerge. Clearly, the possibilities which arise for the relative ordering of the Cl_b and Cl_t binding energies are as follows: $Cl_b \sim Cl_t$, $Cl_b < Cl_t$ or $Cl_b > Cl_t$. At the present time examples of all three situations are known.

The XPS spectrum of the non-transition metal salt $Cs_3Sb_2Cl_9$ has been reported by three groups [26,37,40]. Its chlorine 2*p* spectrum reveals [40] a well resolved spin-orbit doublet with no evidence for two distinct sets of energies. Although full structural details are not available for $Cs_3Sb_2Cl_9$, and there is no reason to assume that it necessarily contains discrete $Sb_2Cl_3^{3-}$ anions [26], data for a salt of the $Sb_2Br_3^{3-}$ anion [41] suggest that the Sb-Sb distance in $Sb_2Cl_3^{3-}$ will be rather long (ca 4.0 Å). In this situation, the long, weak Sb- Cl_b bonds which must be present ensure that Cl_b and Cl_t will possess comparable charges, and hence almost identical binding energies.

As part of a more extensive study of the XPS of square planar platinum(II) complexes, Clark et al. [42,43] reported the chlorine 2*p* spectra of the com-

plexes $\text{trans}-(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pt}_2\text{Cl}_4$, $\text{trans}-(\text{Bu}_3^{\text{n}}\text{P})_2\text{Pd}_2\text{Cl}_4$ and $\beta-(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pt}_2(\text{SCN})_2\text{Cl}_2$. A comparison of these data with those resulting from ^{35}Cl NQR studies [44,45] (Table 4) led to the conclusion [42,43] that in these complexes the binding energy order was $\text{Cl}_b < \text{Cl}_t$. The chlorine $2p$ spectra of $\text{trans}-(\text{R}_3\text{P})_2\text{M}_2\text{Cl}_4$ ($\text{M} = \text{Pd}$ or Pt) would not on their own have permitted this assignment since equal numbers of Cl_b and Cl_t are present in this molecule [46]. However, since the complex $\beta-(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pt}_2(\text{SCN})_2\text{Cl}_2$ contains thiocyanate bridges and terminal $\text{Pt}-\text{Cl}$ bonds, its chlorine $2p$ energies (Table 4) must be characteristic of Cl_t . Also, there is a very satisfactory correlation of these binding energies with the ^{35}Cl NQR frequencies ($^{35}\nu$) of the chloride ligands. Assuming that chlorine hybridization changes for a closely related series of platinum(II) complexes could be neglected and that participation by chlorine in π -bonding is negligible, Clark et al. [43] modified the Townes-Dailey 'approximation' to $^{35}\nu = c\sigma$, where c is a constant and σ is the covalent character of a σ bond involving the $3p_z$ orbital of chlorine. As population of the $3p_z$ orbital of chlorine is decreased (i.e. increasing σ character) $^{35}\nu$ should increase. This should be paralleled by an increase in the chlorine $2p$ energies (assuming the electrostatic potential model), and indeed such a correlation has been shown [42,43] to hold. This general tendency for $^{35}\nu$ to decrease as the $\text{Pt}-\text{Cl}$ bond lengths increase suggests [45] that the principal factor determining $^{35}\nu$ for chlorine bound to $\text{Pt}(\text{II})$ is the $\text{Pt}-\text{Cl}$ σ bond order. Since the bridging chlorines have lower binding energies, this implies [43] that attachment to two $\text{Pt}(\text{II})$ centers increases the electron drift towards chlorine.

In contrast to the ^{35}Cl NQR results on the platinum(II) and palladium(II) dimers $(\text{R}_3\text{P})_2\text{M}_2\text{Cl}_4$, related studies [47] on heavy transition metal penta-chloride dimers M_2Cl_{10} , where $\text{M} = \text{Nb}$, Ta , Mo , W and Re , indicate that bridging halogen resonances occur consistently at higher frequencies than the terminal halogen resonances. However, for as yet unexplained reasons, the resonances which are expected for the terminal chlorines are not observed in the NQR spectra of $\text{Nb}_2\text{Cl}_{10}$ [47] and $\text{Mo}_2\text{Cl}_{10}$ [48]. Nonetheless, if this frequency order $^{35}\nu_{\text{bridge}} > ^{35}\nu_{\text{terminal}}$ is quite general, we might expect the

TABLE 4

Comparison of chlorine $2p$ binding energies (eV) and ^{35}Cl NQR frequencies (MHz) for complexes of platinum(II) and palladium(II) ^a

Compound	Cl $2p_{3/2}$	$^{35}\nu$	Assignment
$\text{trans}-(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pt}_2\text{Cl}_4$	198.2	22.36	Cl_t
	197.0	15.46	Cl_b
$\text{trans}-(\text{Bu}_3^{\text{n}}\text{P})_2\text{Pd}_2\text{Cl}_4$	198.7	19.5	Cl_t
	197.7	~12.8	Cl_b
$\beta-(\text{Pr}_3^{\text{n}}\text{P})_2\text{Pt}_2(\text{SCN})_2\text{Cl}_2$	198.0	21.50	Cl_t

^a Data taken from refs. 42-45.

binding energy order to now become $\text{Cl}_b > \text{Cl}_t$. Recent measurements in our laboratory [49] indicate that this may indeed be the case. As shown in Fig. 4, the chlorine $2p$ spectrum of $\text{Mo}_2\text{Cl}_{10}$ can be deconvoluted into two sets of chlorine $2p_{1/2,3/2}$ doublets, with a separation of 0.9 eV and relative intensity of $\text{Cl}_b : \text{Cl}_t = 1 : 4$, consistent with the known structure of this phase [50].

The above examples serve to illustrate the sensitivity of the relative ordering of the binding energies of Cl_b and Cl_t to the structure of a phase. Only after more data on chlorine-bridged dimers become available will it be possible to more fully understand the factors which determine the relative energies of Cl_b and Cl_t in such systems.

(b) Metal chlorides containing pairs or clusters of metal atoms

The tendency for many low oxidation state transition metal halides to assume structures containing clusters of metal atoms [51] in turn influences the types of metal-halogen bonds which are present. In particular, these phases invariably contain halogen atoms bridging strong metal-metal bonds as well as those present in metal-halogen terminal bonds. As will be seen, these differences result in Cl_b possessing significantly higher binding energies than Cl_t , a result which is of considerable use in the structural characterization of such phases. Since certain metal chlorides containing pairs of metal atoms exhibit similar spectral properties to these metal halide clusters, they are also considered in this section.

The metal chloride clusters which have received most attention are rhenium(III) chloride, molybdenum(II) chloride and their derivatives [52–56]. Rhenium(III) chloride possesses a trimeric structure [57] in which three chlorine atoms bridge the edges of the triangular Re_3 cluster. An additional three chlorines are bound to the rhenium atoms in conventional two-electron terminal bonds (one per rhenium) while the three remaining chlorines are

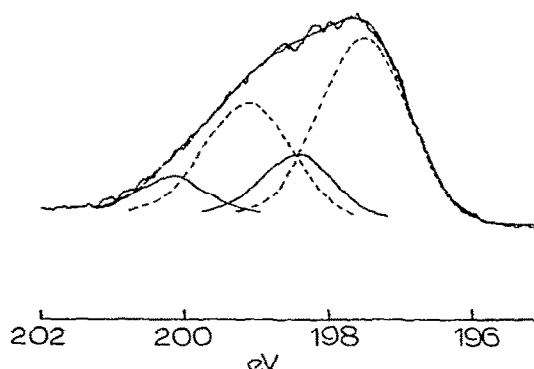


Fig. 4. Chlorine $2p$ binding energy spectrum of $\text{Mo}_2\text{Cl}_{10}$ showing deconvolution into two sets of chlorine $2p_{1/2,3/2}$ doublets.

present in weak intercluster $\text{Re}-\text{Cl} \cdots \text{Re}$ bridges. The presence of these three different chlorine environments results in a broad unresolved chlorine $2p$ band envelope, centered at ~ 199.0 eV (FWHM = 2.4 eV) [54]. This band contains six overlapping chlorine $2p$ spin-orbit components but no effort has yet been made to deconvolute the spectrum. The reaction of this chloride with two-electron donor molecules such as triphenylphosphine, pyrazine, dimethylformamide or chloride ion, results in the disruption of the intercluster bridges and the formation of complex species of the types $\text{Re}_3\text{Cl}_9\text{L}_3$, where $\text{L} = \text{Ph}_3\text{P}$, pyz or DMF, and $\text{Re}_3\text{Cl}_{12}^{3-}$ or $\text{Re}_3\text{Cl}_{11}^{2-}$ [51,58]. This is accompanied by a marked change in the chlorine $2p$ spectra of these species [52–55]. The spectra display a three peak pattern that is due to the overlap of two sets of chlorine $2p_{1/2,3/2}$ binding energies (see Table 5 and Figs. 5 and 6). Deconvolution of the spectrum of $\text{Re}_3\text{Cl}_9(\text{pyz})_3$ showed [54] that the two sets of binding energies differ by ~ 1.5 eV and that the spin-orbit doublet at lower energy is twice as intense as the higher energy doublet. This latter observation is clearly in accord with the binding energy order $\text{Cl}_b > \text{Cl}_t$ since from the crystal structure of Re_3Cl_9 and its derivatives [57,59], the $\text{Cl}_b : \text{Cl}_t$ ratio is known to be 1 : 2. The observed binding energy order is also the one which is anticipated from a simple charged shell model, but nonetheless, confirmation that this assignment is indeed correct is of course desirable. This was

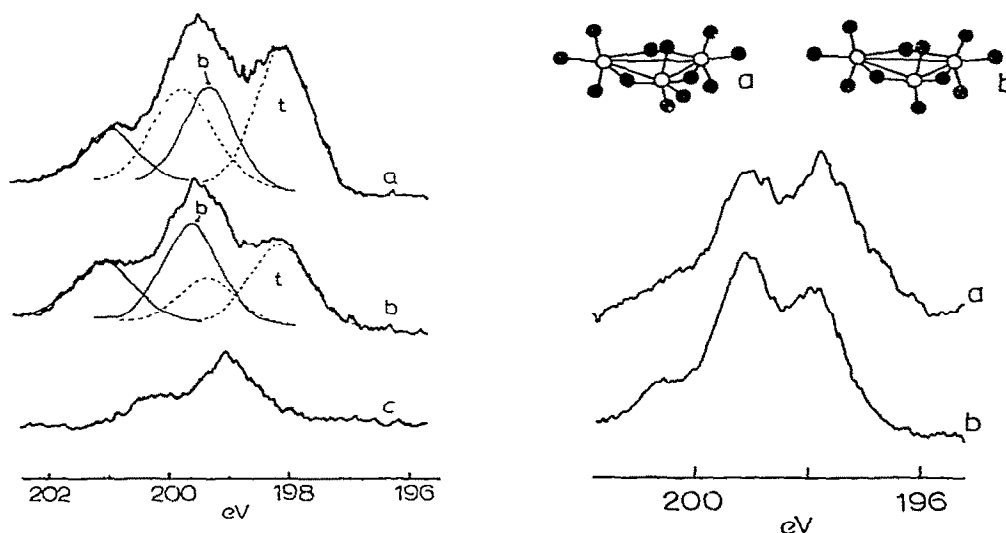


Fig. 5. Chlorine $2p$ binding energy spectra of (a) $\text{Re}_3\text{Cl}_9(\text{pyz})_3$, (b) $\text{Re}_3\text{Cl}_6(\text{acac})_3$ and (c) $\text{Re}_3\text{Cl}_3(\text{SCN})_3[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_3$. Deconvolutions into chlorine $2p_{1/2,3/2}$ doublets due to Cl_b and Cl_t are denoted by labels b and t.

Fig. 6. Chlorine $2p$ binding energy spectra of (a) $[\text{AcrH}]_3\text{Re}_3\text{Cl}_{12}$ and (b) $[\text{pyH}]_2\text{Re}_3\text{Cl}_{11}$.

TABLE 5

Chlorine 2*p* binding energies (eV) of derivatives of rhenium(III) chloride and molybdenum(II) chloride ^a

Compound ^b	Cl 2 <i>p</i> _{1/2,3/2} ^c		
Re ₃ Cl ₉ (pyz) ₃	201.0	199.5	198.0
Re ₃ Cl ₉ (PPh ₃) ₃	200.6	199.3	198.0
Re ₃ Cl ₉ (DMF) ₃	200.3	199.1	197.7
Re ₃ Cl ₆ (acac) ₃	200.5	199.0	197.7
Re ₃ Cl ₆ (S ₂ CNEt ₂) ₃	200.5	199.2	197.8
Re ₃ Cl ₃ (SCN) ₃ (S ₂ CNEt ₂) ₃	200.2	198.9	
Cs ₃ Re ₃ Cl ₁₂	200.5	199.4	197.9
[AcrH] ₃ Re ₃ Cl ₁₂	200.2	199.0	197.8
[pyH] ₂ Re ₃ Cl ₁₁	200.7	199.2	197.9
[bipyH] ₂ Re ₃ Cl ₁₁	200.5	199.1	198.0
[Re ₃ Cl ₆ (py) ₃] _n	200.8	199.2	197.8
[Re ₃ Cl ₆ (γ-pic) ₃] _n	200.7	198.8	197.7
[{AcrH} ₂ Re ₃ Cl ₈] _n	200.4	198.7	197.6
[H ₃ O] ₂ [(Mo ₆ Cl ₈)Cl ₆] · 6 H ₂ O	201.2	199.6	197.4
[Et ₄ N] ₂ [(Mo ₆ Cl ₈)Cl ₆]	201.7	200.1	197.8
[Bu ₄ N] ₂ [(Mo ₆ Cl ₈)Br ₆]	201.7	200.1	
[Bu ₄ N] ₂ [(Mo ₆ Cl ₈)I ₆]	201.4	199.9	
Mo ₆ Cl ₁₂ (py) ₂	201.2	199.6	197.4
Mo ₆ Cl ₁₂ (PEt ₃) ₂ ^d	202.0	200.4	197.9
Mo ₆ Cl ₁₂ (PPh ₃) ₂	201.3	199.8	197.4
Mo ₆ Cl ₁₂ (DMF) ₂	201.2	199.6	197.4
Mo ₆ Cl ₁₂ (DMSO) ₂	201.0	199.4	197.2
Mo ₆ Cl ₁₂ (NEt ₃) ₂	201.3	199.7	197.4
Mo ₆ Cl ₁₂ (dppe) ₂	201.3	199.8	197.6
Mo ₆ Cl ₁₂ (bipy) ₂	201.3	199.7	197.4
Mo ₆ Cl ₁₂ (phen) ₂	201.4	199.9	197.8

^a Data are taken from refs. 52–55; binding energies are referenced to a values of 284.0 eV for the carbon 1*s* binding energy of graphite unless otherwise stated.

^b Ligand abbreviations are as follows: AcrH = acridinium; py = pyridine; pyz = pyrazine; γ-pic = γ-picoline; DMF = dimethylformamide; DMSO = dimethylsulfoxide; dppe = 1,2-bis-(diphenylphosphino)ethane; phen = 1 : 10-phenanthroline; bipy = 2,2'-bipyridyl; acac = acetylacetonato.

^c FWHM values for the individual chlorine 2*p* peaks were 1.3 ± 0.3 eV.

^d Binding energies for Mo₆Cl₁₂(PEt₃)₂ are referenced to a carbon 1*s* binding energy of 284.0 eV for the carbon atoms of the PEt₃ ligands (ref. 55).

accomplished [54] by utilizing the observations of Robinson and Fergusson [60] that the Re—Cl_l bonds are much more readily substituted than Re—Cl_b, in order to study the chlorine 2*p* binding energy spectra as a function of changes in the relative numbers of Cl_b and Cl_l. The rhenium(III) complexes of diethyldithiocarbamate and acetylacetone, Re₃Cl₆(S₂CNEt₂)₃ and Re₃Cl₆(acac)₃ [60], were ideal for this purpose and afforded chlorine 2*p* spectra (Table 5 and Fig. 5) in which the Cl_b : Cl_l ratio was now 1.0 : 1.0 [54].

In the complex $\text{Re}_3\text{Cl}_3(\text{SCN})_3(\text{S}_2\text{CNEt}_2)_3$ [60], all the terminal chlorine atoms have been replaced. XPS measurements have confirmed [54] this conclusion since the chlorine 2*p* binding energies associated with Cl_t were observed to be absent (Table 5 and Fig. 5).

Although Cl_b and Cl_t environments can be readily distinguished in the XPS of salts of the $\text{Re}_3\text{Cl}_{11}^{2-}$ and $\text{Re}_3\text{Cl}_{12}^{3-}$ anions [53], it has not yet proved possible to establish the non-equivalence of the apical and equatorial $\text{Re}-\text{Cl}_t$ bonds.

The results of the measurement of the chlorine 2*p* binding energy spectra of Re_3Cl_9 and its derivatives have enabled complexes of unknown structure to be characterized as the following example serves to illustrate. The reduction of Re_3Cl_9 by pyridine, γ -picoline and acridine results in the formation of the polymeric rhenium(II) complexes $[\text{Re}_3\text{Cl}_6(\text{py})_3]_n$, $[\text{Re}_3\text{Cl}_6(\gamma\text{-pic})_3]_n$ and $\{[\text{AcrH}]_2\text{Re}_3\text{Cl}_8\}_n$ [52,53]. Their chlorine 2*p* binding energy spectra [52–54] are consistent with the retention of the $[\text{Re}_3\text{Cl}_3]$ core, containing the three bridging chlorine atoms, and the reduction in the number of terminal $\text{Re}-\text{Cl}_t$ bonds. As a result, the spectrum of $[\text{Re}_3\text{Cl}_6(\text{py})_3]_n$ resembles closely that of $\text{Re}_3\text{Cl}_6(\text{acac})_3$ in possessing two types of chlorine environments in a 1 : 1 stoichiometric ratio.

The surprisingly large magnitude of the binding energy separation between the different chlorine environments in $\text{Re}_3\text{Cl}_9\text{L}_3$, raises the important question of whether similar shifts will be observed in other metal chloride clusters. Measurements on α -molybdenum(II) chloride ($\text{Mo}_6\text{Cl}_{12}$) and its derivatives show this to be the case (see Table 5 and Fig. 7). The dichloride contains the

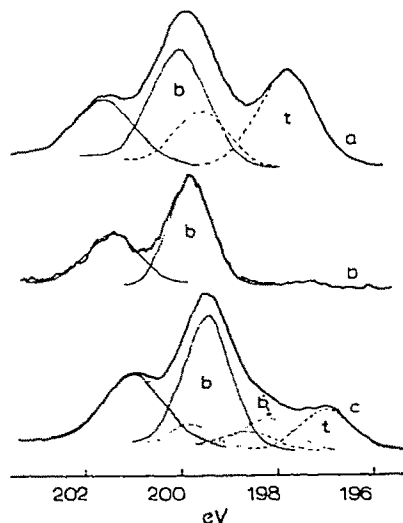
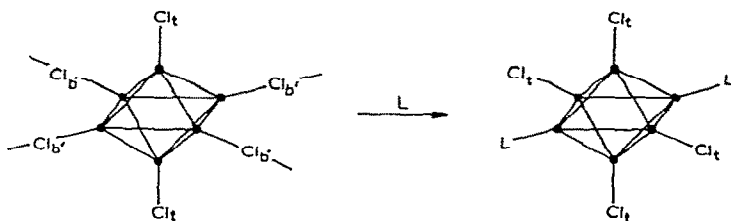


Fig. 7. Chlorine 2*p* binding energy spectra of (a) $[\text{Et}_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$, (b) $[\text{Bu}_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{I}_6]$ and (c) $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_{4/2}\text{Cl}_2]$. Deconvolutions into Cl_b , $\text{Cl}_{b'}$ and Cl_t are distinguished by the labels b, b' and t.

$[\text{Mo}_6\text{Cl}_8]^{4+}$ cluster (see ref. 51) in which a chlorine atom (Cl_b) lies above each face of the Mo_6 octahedron and is bonded to three molybdenum atoms, together with six "external" chlorine atoms, four of which ($\text{Cl}_{b'}$) occupy intercluster bridging positions between the molybdenum atoms of adjacent clusters and the remaining two (Cl_t) are each bound to one molybdenum atom [61]. As a consequence of this structure, α -molybdenum chloride is best represented as $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_{4/2}\text{Cl}_2]$. In reactions of this halide with monodentate donor molecules, the intercluster bridges ($\text{Cl}_{b'}$) are disrupted and products of stoichiometry $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4\text{L}_2$, where L presents a neutral donor molecule such as py or PEt_3 , and $[(\text{Mo}_6\text{Cl}_8)\text{X}_6]^{2-}$, where $\text{X} = \text{Cl}, \text{Br}$ or I , can be isolated [62]. This process is represented in the following reaction scheme.



The replacement of chlorine atoms in terminal $\text{Mo}-\text{Cl}_t$ bonds by bromine or iodine removes the lower energy chlorine $2p$ doublet (Fig. 7). This confirms, as for the rhenium chloride clusters, the binding energy order $\text{Cl}_b > \text{Cl}_t$. Furthermore, for the molybdenum(II) complexes listed in Table 5, the binding energy difference between Cl_b and Cl_t was found to be 2.3 ± 0.2 eV [54], significantly greater than corresponding value of ~ 1.5 eV for the rhenium(III) chloride cluster. This result implies that chlorine atoms bridging three or two metal centers in metal-metal bonded clusters may be distinguished by the binding energy order $\text{Cl}_{b(3)} > \text{Cl}_{b(2)}$ [54].

From a comparison of the XPS of α -molybdenum(II) chloride and its complexes (Table 5 and Fig. 7), the lowest energy component of the three peak spectrum of molybdenum(II) chloride was observed [54] to be much less intense than for any of the complexes containing only Cl_b and Cl_t environments. The explanation for this lies in the presence of a third type of chlorine atom ($\text{Cl}_{b'}$), as present in the intercluster bridges. This spectrum may be readily deconvoluted using three chlorine $2p$ doublets and a binding energy order $\text{Cl}_{b(3)} > \text{Cl}_{b'} > \text{Cl}_t$ [54].

Some measure of the sensitivity of this technique to changes in the relative numbers of Cl_b and Cl_t , can be judged from a comparison of the chlorine $2p$ spectra of the complexes $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4\text{L}_2$, where $\text{L} = \text{py}, \text{PEt}_3, \text{PPh}_3, \text{DMF}, \text{DMSO}$ or NEt_3 , $[\text{Et}_4\text{N}]_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]$ and $[(\text{Mo}_6\text{Cl}_8)(\text{PR}_3)_6]^{2+}[(\text{Mo}_6\text{Cl}_8\text{Cl}_6)]^{2-}$, where $\text{PR}_3 = \text{PEt}_3$ or PPr_3 [54,55]. Deconvolution of these spectra gave $\text{Cl}_b : \text{Cl}_t$ ratios of $2.0 (\pm 0.2) : 1.0$, $1.33 : 1.0$ and $2.4 : 1.0$, respectively, very close to the expected values of $2.0 : 1.0$, $1.33 : 1.0$ and $2.67 : 1.0$.

One of the advantages of the XPS technique is that it may be used to help characterize metal chlorides which are either amorphous to X-rays or, if crys-

talline, do not yield crystals of sufficient quality to enable a single crystal X-ray diffraction study to be pursued. We have already considered one group of complexes which fall in this category, namely the rhenium(II) clusters $[\text{Re}_3\text{Cl}_6\text{L}_3]_n$, where $\text{L} = \text{py}$ or $\gamma\text{-pic}$, and $\{[\text{AcrH}]_2\text{Re}_3\text{Cl}_8\}_n$ (see Table 5). In addition, recent XPS measurements on the phases $\beta\text{-MoCl}_2$ [54], $\gamma\text{-ReCl}_4$ [63] and OsCl_4 [63] merit consideration.

The phase known as $\beta\text{-MoCl}_2$ may be prepared by the reaction of dry hydrogen chloride gas with molybdenum(II) acetate ($\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$) at elevated temperatures [64–66]. On the basis of reactivity differences between $\beta\text{-MoCl}_2$ and $\alpha\text{-MoCl}_2$ (i.e. $[(\text{Mo}_6\text{Cl}_8)\text{Cl}_{4/2}\text{Cl}_2]$) it is clear [66] that they are not structurally related. Measurement of the chlorine $2p$ binding energies of $\beta\text{-MoCl}_2$ (199.9 and 198.4 eV) [54] confirms this contention. The single chlorine $2p_{1/2,3/2}$ spin-orbit doublet rules out the presence of a cluster structure involving different types of chlorine environment. It has also been noted [65] that the X-ray powder pattern for $\beta\text{-MoCl}_2$ shows a distinct resemblance to the stronger lines of the CdCl_2 pattern. Indeed, the chlorine $2p$ binding energy peaks of $\beta\text{-MoCl}_2$ and CdCl_2 , which for the latter chloride are at 199.5 and 198.0 eV [54], have a very similar profile, so that $\beta\text{-MoCl}_2$ may adopt a close-packed layer structure related to that of CdCl_2 .

A comparison has been made [63] between the chlorine $2p$ binding energy spectra of β - and $\gamma\text{-ReCl}_4$. The structure of crystalline $\beta\text{-ReCl}_4$ [67,68] is known [69] to be based on zig-zag chains of $[\text{Re}_2\text{Cl}_9]$ confacial bioctahedra, in which one terminal chlorine at each end of this dimeric unit bridges between the bioctahedra. Structurally this phase is very similar to salts of the $\text{M}_2\text{Cl}_9^{2-}$ anions, where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ or Re [70]. The phase $\gamma\text{-ReCl}_4$ has recently been prepared [71,72] and although its structure is unknown, X-ray powder photographs show it is different from $\beta\text{-ReCl}_4$ [69]. The chlorine $2p$ spectral profiles of both polymorphs indicate [63] the presence of more than one type of chlorine environment. The $\beta\text{-ReCl}_4$ chlorine $2p$ spectrum could be deconvoluted to give a $\text{Cl}_b : \text{Cl}_t$ ratio of 1.0 : 1.7, close to that expected if it is assumed that the chlorines (Cl_b) which link the confacial bioctahedra have very similar chlorine $2p$ binding energies to the terminally bonded chlorines (Cl_t). Although this was the most reasonable deconvolution obtained [63], it was not unique.

The chlorine $2p$ binding energy spectrum of $\gamma\text{-ReCl}_4$ (Fig. 8) similarly had no unique deconvolution but the best fit to the experimental data was obtained for a $\text{Cl}_b : \text{Cl}_t$ ratio of approximately 1.0 : 2.5. Because Cl_b is at a higher binding energy than Cl_t by only ~ 0.8 eV, it is difficult to arrive at a definitive structure for this phase. In spite of this, it is clear that more than one type of chlorine environment exists. It is likely, by comparison with the analogous data for $\beta\text{-ReCl}_4$, that both terminal $\text{Re}-\text{Cl}_t$ and $\text{Re}-\text{Cl}_b-\text{Re}$ units bridging relatively weak $\text{Re}-\text{Re}$ bonds are present. The relatively small magnitude of the binding energy separation $\Delta E(\text{Cl}_b-\text{Cl}_t)$ for both β - and $\gamma\text{-ReCl}_4$ is reminiscent of the chlorine $2p$ spectral characteristics of dinuclear transition metal chloro-anions of the type $\text{M}_2\text{Cl}_9^{2-}$ (see later in this section).

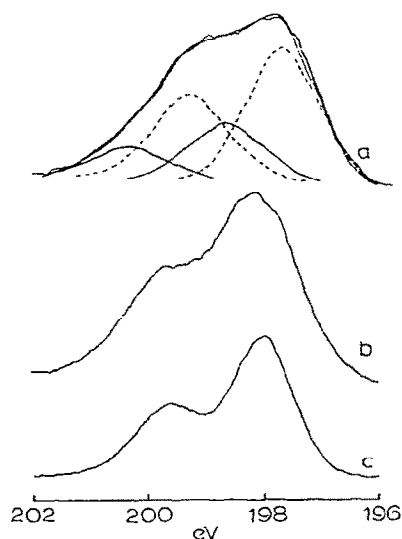


Fig. 8. Chlorine 2p binding energy spectra of (a) γ -ReCl₄, (b) OsCl₄ and (c) (NH₄)₂OsCl₆.

Apparently, single crystals of OsCl₄ are difficult to obtain so its chlorine 2p spectrum has been recorded [63] to aid in a structural investigation. The spectral profile (Fig. 8) is not too different from that expected for either a single type of chlorine environment (e.g. (NH₄)₂OsCl₆) or two chlorines in very similar environments. In spite of the isoelectronic relationship between Re₃Cl₁₂³⁻ and OsCl₄, it is clear that the latter phase does not have the related structure Os₃Cl₁₂, containing both Cl_b and Cl_t. The spectrum implies that Os—Cl_b—Os units bridging strong Os—Os bonds and Os—Cl_t are not both present in this phase. However, the presence of Os—Cl_t and weak Os—Cl_b—Os bridges cannot be ruled out at present, since Cl_t and Cl_b may then have almost identical binding energies.

The final group of compounds which will be considered in this section are metal—metal bonded dimers which contain both Cl_b and Cl_t environments. As we have already seen, the presence of a metal—metal bond is not required for differences in the binding energies of Cl_b and Cl_t to be detected (i.e. Cl_b < Cl_t for *trans*-(R₃P)₂M₂Cl₄, where M = Pd or Pt, and Cl_b > Cl_t for Mo₂Cl₁₀) [43,49]. However, for nonachlorodimetallate anions of the type M₂Cl₉³⁻ which contain a metal—metal bond, the binding energy order Cl_b > Cl_t is expected by analogy with results for chloride clusters of molybdenum(II) and rhenium(III) [52–55]. These anions possess the well known confacial bioctahedral structure for M = Cr, Mo, W or Re [70,73,74]. A related structure is also shown by the Mo₂Cl₈H³⁻ anion, with the exception that one of the bridging chloride ligand positions is occupied by hydride [75,76], and by the Rh₂Cl₉³⁻ anion, although the latter species contains no Rh—Rh bond [70]. With the exception of Re₃Cl₉³⁻, the chlorine 2p spectra of salts of these anions

TABLE 6

Chlorine 2*p* binding energies (eV) of nonachlorodimetallate anions ^a

Compound	Cl _b		Cl _t ^b	
	2 <i>p</i> _{1/2}	2 <i>p</i> _{3/2}	2 <i>p</i> _{1/2}	2 <i>p</i> _{3/2}
[Bu ₄ N] ₃ Cr ₂ Cl ₉	200.1	198.5	199.5	197.9(1.2)
[Bu ₄ N] ₃ Mo ₂ Cl ₉	200.2	198.7	199.2	197.7(1.3)
Rb ₃ Mo ₂ Cl ₈ H	200.8	199.2	199.9	198.4(1.1)
K ₃ W ₂ Cl ₉	200.2	198.7	199.6	198.2(1.1)
[Bu ₄ N] ₃ W ₂ Cl ₉	200.3	198.9	199.5	197.9(1.2)
[Et ₄ N] ₃ Rh ₂ Cl ₉	199.5	198.0	198.8	197.2(1.3)
[Bu ₄ N]Re ₂ Cl ₉	201.0	199.4	199.6	198.2(1.2)

^a These binding energies were obtained by deconvolution of the chlorine 2*p* spectra (see ref. 37) and are referenced to a value of 284.0 eV for the carbon 1*s* binding energy of graphite.

^b FWHM values given in parentheses.

exhibit [37] broad asymmetric band envelopes characteristic of the presence of different types of chlorine environments. Deconvolution of these spectra [37] gave the two sets of chlorine binding energies listed in Table 6 and Cl_b : Cl_t peak intensities of almost exactly 1.0 : 2.0 for M₂Cl₉³⁻, where M = Cr, Mo, W or Rh, and 1.0 : 3.0 for Rb₃Mo₂Cl₈H, in keeping with loss of one of the bridging chlorines.

One of the interesting features of these data is that the differences in binding energy between Cl_b and Cl_t, Δ*E*(Cl_b—Cl_t), occur in the range 1.0—0.5 eV, and reveal no obvious correlation with the absence (i.e. Rh₂Cl₉³⁻) or presence of a metal—metal bond in these anions. This conclusion is expected in the light of our previous discussion of the chlorine 2*p* spectra of *trans*-(R₃P)₂M₂Cl₄, where M = Pd or Pt, and Mo₂Cl₁₀ [43,49].

For the series [Bu₄N]₃M₂Cl₉, where M = Cr, Mo or W, Δ*E*(Cl_b—Cl_t) is much smaller for Cr than for the Mo or W salts, in keeping with the existence of a metal—metal bond in the latter anions [37]. This structural feature results in shorter, stronger M—Cl_b bonds and presumably to an increase in the positive charge at Cl_b relative to Cl_t. However, changing the cation can have an equally dramatic but opposite effect, as illustrated by the pair of salts (Bu₄N)₃W₂Cl₉ and K₃W₂Cl₉ (Table 6), where Δ*E*(Cl_b—Cl_t) decreases from 1.0 to 0.5 eV. [37]. In these chloro-anions, the variations in structure produced upon changing the cations are known to be quite dramatic [73], particularly as they affect the strength of the metal—metal interaction which in turn influences the M—Cl_b bond lengths and M—Cl_b—M angles. It appears that with the present instrumental resolution, 0.5 eV is close to the limit where differences in chlorine binding energies can be both easily detected and readily interpreted.

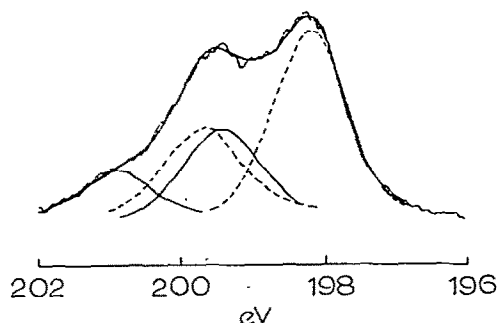


Fig. 9. Chlorine 2p binding energy spectrum of $[\text{Bu}_4\text{N}]\text{Re}_2\text{Cl}_9$.

The spectrum of $[\text{Bu}_4\text{N}]\text{Re}_2\text{Cl}_9$ clearly shows [37,77] three components (Table 6 and Fig. 9) and its deconvolution [37] reveals a significantly greater energy difference for $\Delta E(\text{Cl}_b - \text{Cl}_t)$ than that observed with any of the other M_2Cl_9^- anions. This difference (1.2 eV) approaches that observed between the corresponding energies of Cl_b and Cl_t in complexes of the type $\text{Re}_3\text{Cl}_9\text{L}_3$ [52–54]. In the latter systems, the bridging chlorines are more strongly bound to two metal centers than is the case with any of the salts of the M_2Cl_9^- anions [59,70,73,74]. There is nothing apparent in the structural parameters for $(\text{Bu}_4\text{N})\text{Re}_2\text{Cl}_9$ [70,78] which would indicate that it contains more strongly bound bridging chlorines than do other anions of this type. Indeed, compared to the isoelectronic tungsten(III) dimer $\text{K}_3\text{W}_2\text{Cl}_9$, for which $r(\text{W}-\text{W})$ is 2.41 Å [79], the $\text{Re}-\text{Re}$ bond length in $(\text{Bu}_4\text{N})\text{Re}_2\text{Cl}_9$ is significantly longer (2.70 Å) [78]. One possible explanation is that $\text{Re}(\text{IV})$ may be a much more polarizing center than any of the $\text{M}(\text{III})$ oxidation states present in the other chloro-anions. This could lead to an increase in the charge difference between Cl_b and Cl_t and hence to a larger value for $\Delta E(\text{Cl}_b - \text{Cl}_t)$.

As with metal chloride clusters, it is possible to use XPS in the routine characterization of new metal chloride complexes which contain pairs of metal atoms. This is clearly seen in the spectral characterization of several low oxidation state rhenium complexes which have recently been prepared from reactions of metal–metal bonded rhenium dimers [80,81]. Thus the chlorine 2p spectra of the product resulting from the carbon tetrachloride oxidation of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ confirms its formation as the salt $[\text{Et}_3\text{PCl}]_2\text{Re}_2\text{Cl}_8$ [80]. The three peak spectrum can be deconvoluted into two sets of chlorine $2p_{1/2,3/2}$ doublets in the ratio 1 : 4. Since there is independent evidence for the presence of the $\text{Re}_2\text{Cl}_8^{2-}$ anion in this product, it is clear that the higher energy doublet is due to chlorine in the phosphonium cation and the lower energy doublet to the chlorine atoms in the $\text{Re}-\text{Cl}_t$ bonds of the anion. In other words, in spite of the two sets of chlorine $2p_{1/2,3/2}$ binding energies, neither is due to bridging chlorines. The XPS spectrum of the complex $\text{Re}_2\text{Cl}_6(\text{dppm})_2$, which is prepared by the reaction of $[\text{Bu}_4\text{N}]_2\text{Re}_2\text{Cl}_8$ with

bis(diphenylphosphino)methane (dppm) [81], is consistent with a chlorine-bridged dimer which contains two bridging $\text{Re}-\text{Cl}_b-\text{Re}$ units and four terminal $\text{Re}-\text{Cl}_t$ bonds.

(c) *Salts containing both inner and outer sphere chloride*

The binding energy order $\text{Cl}_b > \text{Cl}_t$ which is characteristic of many transition metal chlorides can be extended to include chloride ion. In this case $\text{Cl}_b > \text{Cl}_t > \text{Cl}^-$ becomes the expected sequence of binding energies. Careful measurements of the chlorine $2p$ binding energy spectra of complexes of the type $[\text{RhL}_4\text{Cl}_2]\text{Cl}$, where $\text{L} = \text{pyridine}$, $1/2(2,2'\text{-bipyridyl})$ or $1/2(2,5\text{-dithiahexane})$ [37,83], and of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ [83], have shown this to be the case (see Table 7). In each instance, a three peak spectrum is observed which arises from overlap of the $2p_{3/2}$ component of chlorine bound to rhodium or chromium (Cl_t) with the $2p_{1/2}$ component of chloride in the outer coordination sphere. The data are consistent with a binding energy difference $\Delta E(\text{Cl}_t-\text{Cl}^-)$ of between 1.7 and 1.0 eV, and the spectra may be

TABLE 7

Chlorine $2p$ binding energies (eV) of transition metal chloro-cations and some related species

Compound ^a	Cl $2p_{1/2,3/2}$ ^b		Ref.
$\text{Rh}(\text{NH}_3)_3\text{Cl}_3$	—	198.8 ^c	82
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	199.5	198.0(1.3)	37
$[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$	—	198.3 ^c	82
$[\text{Co}(\text{en})_3]\text{Cl}_3$	199.0	197.5(1.1)	37
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	199.5	198.0(1.4)	37
$[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	199.2	197.8(1.4)	37
$[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$	—	198.9 ^c	82
$[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$	199.3	197.9(1.3)	37
$[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	199.2	197.8(1.4)	37
$\text{trans-}[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	199.5	198.1(1.7)	37
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$	199.3	197.9(1.3)	37
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{NO}_3$	199.4	198.0(1.3)	37
$[\text{Ni}(\text{en})_4\text{Cl}_2]\text{Cl}_2$	198.8	197.3(1.3)	37
$\text{Rh}(\text{py})_3\text{Cl}_3$	—	198.7 ^c	82
$[\text{Fe}(\text{tu})_6]\text{Cl}(\text{NO}_3)_2$	—	198.3 ^c	82
$[\text{Fe}(\text{tu})_5\text{Cl}]\text{Cl}_2$	—	198.3 ^c	82
$\text{Rh}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 5 \text{H}_2\text{O}$	200.3	198.8 197.0	37
$\text{Rh}(\text{bipy})_2\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$	199.6	197.9 196.9	83
$\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$	199.7	198.2 196.7	37
$\text{Rh}(\text{dth})_2\text{Cl}_2]\text{Cl}$	199.5	197.9 196.5	83
$\text{Rh}(\text{dth})_2\text{Cl}_2]\text{PF}_6$	199.6	197.9	83
$\text{Rh}(\text{dth})_2\text{Cl}_2]\text{ClO}_4$	199.1	197.7	83

^a Ligand abbreviations are as follows: en = ethylenediamine; tu = thiourea; py = pyridine; bipy = 2,2'-bipyridyl; dth = 2,5-dithiahexane.

^b FWHM values for the chlorine $2p_{3/2}$ components are given when available.

^c Only the binding energy of the chlorine $2p_{3/2}$ component is quoted in ref. 82.

deconvoluted to give a $\text{Cl}_t : \text{Cl}^-$ ratio of close to 2 : 1. It might be anticipated that this result would be quite general for six-coordinate chloride complexes of the types $[\text{ML}_5\text{Cl}]\text{Cl}_2$ and $[\text{ML}_4\text{Cl}_2]\text{Cl}$. However, upon extending these measurements to a variety of ammine and ethylenediamine complexes this was found [37] not to be the case (Table 7). For all the ionic cobalt(III) and rhodium(III) complexes of NH_3 and en listed in Table 7, a two peak spectrum is observed [37] and although there is generally a loss in the resolution of the $2p_{1/2}$ and $2p_{3/2}$ spin-orbit components, it is clear that any difference between outer-sphere and inner-sphere chlorine environments is very small. A similar result has been obtained [37] for the dinuclear nickel(II) complex which most likely [84] contains weak $\text{Ni}-\text{Cl}_b-\text{Ni}$ bridges. In this case, the binding energies for Cl_b and Cl^- are also very similar.

A reasonable explanation for these spectral differences is that in the ammine and ethylenediamine complexes the cooperative effect of several hydrogen bonding interactions of the type $\text{N}-\text{H}\cdots\text{Cl}^-$, involving each outer sphere chloride ion, is sufficient to decrease the negative charge at Cl^- to a point where it is comparable to that residing at Cl_t . Crystallographic data for complexes such as $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [85] and $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ [86] provide convincing support for this interpretation since they indeed show that the chloride ions are hydrogen bonded in this manner. The similarity of the chlorine binding energies of the ammine and ethylenediamine complexes is illustrated upon comparing the spectra of the complexes $[\text{Co}(\text{en})_3]\text{Cl}_3$, $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$ and $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ (Fig. 10). These complexes contain outer-sphere chloride, inner-sphere chloride and a mixture of both, respectively, yet they exhibit remarkably similar spectra.

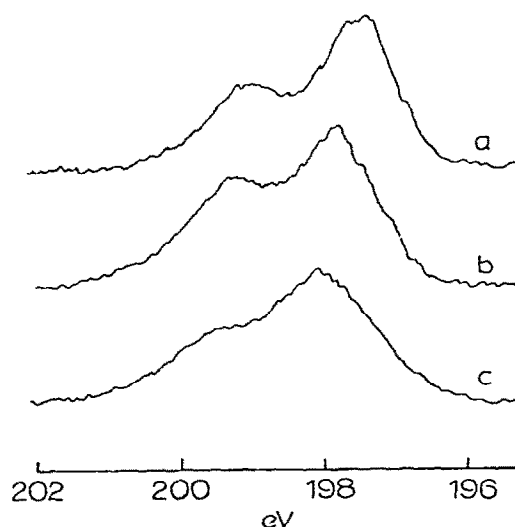


Fig. 10. Chlorine $2p$ binding energy spectra of (a) $[\text{Co}(\text{en})_3]\text{Cl}_3$, (b) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Br}$ and (c) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.

Most of the data presented in Table 7 are from the author's own laboratory [37,83] but some results of Nefedov et al. [82] are also included. The binding energies reported by these two groups were measured using different reference standards but nonetheless some interesting comparisons are possible. The data of Nefedov et al. [82] for $\text{Rh}(\text{NH}_3)_3\text{Cl}_3$, $[\text{Rh}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$ and $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ (chlorine $2p_{3/2}$ binding energies of 198.8, 198.9 and 198.3 eV, respectively) could be taken to imply that inner- and outer-sphere chloride differ in binding energy by ~ 0.5 eV. However, other complexes containing only inner-sphere chloride (i.e., RhCl_3py_3 , $\text{RhCl}_3(\text{SMe}_2)_3$ and $\text{RhCl}_3(\text{SEt}_2)_3$) have binding energies (198.2–198.6 eV) which resemble the values expected for outer-sphere chloride. Clearly a variation of 0.5 eV for a set of complexes which contain different ligands and are of different structural types is too small a value to be useful for diagnostic purposes. Of the three rhodium complexes whose X-ray photoelectron spectra were recorded by Nefedov et al. [82] and which contained both inner-sphere and outer-sphere chloride — $[\text{Rh}(\text{EtNH}_2)_4\text{Cl}_2]\text{Cl}$, $[\text{Rh}(\text{SMe}_2)_4\text{Cl}_2]\text{Cl}$ and $[\text{Rh}(\text{tu})_5\text{Cl}]\text{Cl}_2$ — only one had its chlorine $2p$ binding energies reported. The value of the chlorine $2p_{3/2}$ energy for $[\text{Rh}(\text{tu})_5\text{Cl}]\text{Cl}_2$ was identical [82] to $[\text{Rh}(\text{tu})_6]\text{Cl}(\text{NO}_3)_2$ and $\text{Rh}(\text{tu})_3\text{Cl}_3$ (Table 7), consistent with the idea that hydrogen bonding can have a leveling effect on chlorine $2p$ binding energies.

On the basis of the above information, it is now clear that the earlier arguments of Nefedov et al. [87] that an outer-sphere chlorine atom has a chlorine $2p$ binding energy of less than 198.3 eV, while for an inner-sphere chlorine atom it is in the range 198.4–199.2 eV, may no longer be meaningful in the presence of hydrogen bonding interactions involving the chlorine atoms. As a result, some conclusions [87] concerning the structure of certain glycine complexes of rhodium(III), ruthenium(III) and iridium(III) should now be viewed in a different light. While it may indeed be true that the structures of these species can be represented as $[\text{M}(\text{NH}_2\text{CH}_2\text{COO})_2(\text{NH}_3\text{CH}_2\text{COO})\text{Cl}]$, the observed values of the chlorine $2p$ binding energies (198.8 or 198.7 eV) [87] are not necessarily characteristic of inner-sphere chloride. There is also evidence that hydrogen bonding may also influence the measured chlorine $2p$ binding energies of several hydrated complexes of zirconium(IV) and hafnium(IV) with glycine [88] and alanine [89].

A recent example where the binding energy difference between Cl_0 and Cl^- was used to characterize a novel complex, involved a comparison of the chlorine $2p$ binding energies of $\text{Si}(\text{quinol})_2\text{Cl}_2$, where quinol = 8-quinolino-lato, and Ph_3SiCl [90]. In these non-hydrogen bonded systems, binding energies of 197.4 and 199.9 eV for $\text{Si}(\text{quinol})_2\text{Cl}_2$ and Ph_3SiCl , respectively, were interpreted [90] in support of the former complex having the ionic structure $[\text{Si}(\text{quinol})_2]^{2+}2\text{Cl}^-$.

(d) Mononuclear complexes containing different types of metal—chlorine terminal bonds

There are many octahedral metal chloride complexes which contain non-

equivalent M—Cl_t bonds but in no instance is there clear evidence that the associated chlorine 2*p* binding energies are separated by more than a few tenths of an electron volt. Included among the systems which have been studied are *mer*-MCl₃(PMe₂Ph)₃, where M = Mo, Re, Ru, Os or Ir [91], *cis*-ReCl₄L₂, where L = CH₃CN or 1/2(dppe) [92,93], RhCl₃L₃, where L = py, γ-pic, CH₃CN, Me₂S, Et₂S and 1,4-thioxan [82,83], and Cs₂MoOCl₅ [95]. Only by carrying out a very careful line shape analysis is it possible to find evidence for a measureable difference in the binding energies of different Cl_t environments. Such a study has been carried out by Clark et al. [43] for the square planar platinum(II) complexes K[LPtCl₃], where L = C₂H₄ or C₃H₆, and [Pr₄N][LPtCl₃], where L = Me₃P or Me₃As. In these cases, differences between the binding energies of Cl_t *trans* to L and *trans* to Cl_t were reported [43] to be in the range 0.3–0.8 eV. These results correlate with ³⁵Cl NQR data on Zeise's salt [94].

(iii) Bromides and iodides

Up to the present time, there is no information in the literature on whether I_b, I_t and I[−] can be distinguished by XPS. However, recent measurements on metal bromides indicate that the binding energy shifts which are likely to be observed in bromides and iodides will be of much smaller magnitude than has been found in structurally related chlorides. As with much of the published XPS data on metal complexes, those reported for metal bromides and their complexes include the relevant binding energies but often give no information on peak shapes or peak widths. Accordingly, the bromine 3*p* binding energies (together with the appropriate FWHM values) for a selection of bromides which have been studied over the past few years in the author's laboratory are presented in Table 8. The group of complexes listed in the top half of this Table provide FWHM data for the bromine 3*p* peaks of systems which contain only M—Br_t bonds. In contrast to the situation for the cluster complexes Re₃Cl₉L₃ and [Re₃Cl₆L₃]_n (Table 5), the halogen *np* binding energy spectra of Re₃Br₉(pyz)₃ and [Re₃Br₆L₃]_n (see Table 8) [97] do not show two sets of well resolved binding energies associated with Br_t and Br_b. While the bromine 3*p* peaks are slightly broader than those exhibited by complexes which contain only a single type of bromine environment, the instrumental resolution was insufficient to allow a separation of the two sets of peaks in the spectra of Re₃Br₉(pyz)₃ and [Re₃Br₆L₃]_n [97]. The smaller magnitude of Δ*E*(Br_b—Br_t) compared to Δ*E*(Cl_b—Cl_t) [52–54] reflects the fact that charge differences at Br_b and Br_t are occurring at much larger atoms than is the case with Cl_b and Cl_t, and so the effect on the core level binding energies is proportionally smaller.

The only other study which has a direct bearing on the preceding discussion, is that reported by Kumar et al. [98] on certain palladium(II) bromides. The bromine 3*p*_{3/2} binding energies of K₂PdBr₄, PdBr₂(PPh₃)₂ and PdBr₂ were 182.1, 182.1 and 182.6 eV, respectively, implying that bridging bromine atoms

TABLE 8

Bromine 3p binding energies (eV) of a selection of molybdenum and rhenium bromide complexes ^a

Compound ^b	Br 3p _{1/2} , 3/2 ^d		Ref.
<i>Compounds Containing M—Br_t bonds</i>			
Cs ₂ MoOBr ₅	188.3	181.6(2.3)	95
[Ph ₄ As]MoOBr ₄	188.2	181.6(2.3)	95
[(Mo ₆ Cl ₈)(PEt ₃) ₆][(Mo ₆ Cl ₈)Br ₆] ^c	187.7	181.2(2.3)	63
K ₂ ReBr ₆	188.8	182.2(1.8)	77
ReOBr ₃ (PPh ₃) ₂	188.3	181.4(2.1)	96
[Bu ₄ N] ₂ Re ₂ Br ₈	188.4	181.8(1.9)	77
Re ₂ (O ₂ CCH ₃) ₄ Br ₂	188.4	181.7(2.2)	96
Re ₂ Br ₆ (PEtPh ₂) ₂	188.7	182.0(2.2)	80
Re ₂ Br ₅ (PEtPh ₂) ₃	188.6	182.0(2.3)	80
Re ₂ Br ₄ (arphos) ₂	188.3	181.6(2.0)	81
<i>Compounds containing M—Br_t and M—Br_b bonds</i>			
Re ₃ Br ₉ (pyz) ₃	188.9	182.3(2.5)	97
[Re ₃ Br ₆ (py) ₃] _n	188.7	182.0(2.9)	97
[Re ₃ Br ₆ (3-Clpy) ₃] _n	188.6	181.9(2.5)	97
[Re ₃ Br ₆ (γ-pic) ₃] _n	188.5	181.7(2.6)	97
[Re ₃ Br ₆ (benz) ₃] _n	188.9	182.0(2.8)	97

^a Binding energies are referenced to a value of 284.0 eV for the carbon 1s binding energy of graphite unless otherwise state.

^b Ligand abbreviations are as follows: arphos = 1-diphenylphosphino-2-diphenylarsino-ethane; pyz = pyrazine; py = pyridine; 3-Clpy = 3-chloropyridine; γ-pic = γ-picoline; benz = benzimidazole.

^c Binding energies referenced to a carbon 1s energy of 284.0 eV for the carbon atoms of the PEt₃ ligand.

^d FWHM values given in parentheses.

(as in PdBr₂) have the higher binding energies. This result is therefore analogous to that obtained for the related chloride systems by this same group [39]. Since these comparisons were made between molecules of different structure types, the conclusion that Br_b > Br_t is a rather tenuous one. As we have seen from the results of the XPS studies on Re₃Br₉(pyz)₃ and [Re₃Br₆L₃]_n (Table 8) [97], when Br_b and Br_t are present in the same molecule any binding energy differences are very small.

D. COMPARISONS WITHIN THE ISOELECTRONIC SERIES M—Cl, M—SR AND M—PR₂

In view of the variety of chlorine environments that can be differentiated in metal chloride phases and the wide binding energy range over which these can occur (up to 4.0 eV in ideal circumstances), it is logical to question whether related behavior may be observed in M—SR and M—PR₂ systems in which the donor atom is formally isoelectronic with Cl in M—Cl.

Dialkylphosphido derivatives invariably contain bridges between two metal

atoms and there is no information presently available on whether phosphorus 2*p* energies are likely to be different for terminal and bridging PR₂ units. Indeed, the rarity of terminal M—PR₂ bonds [99] will most likely ensure that the XPS technique will not generally be useful in the characterization of di-alkylphosphido complexes.

However, it would be interesting to compare the phosphorus 2*p* spectra of the monomer (η^5 -C₅H₅)Fe(CO)₂P(CF₃)₂ and the phosphido bridged dimer [(η^5 -C₅H₅)Fe(CO)P(CF₃)₂]₂ into which it may be converted [100], since this should give some insight into the sensitivity of XPS in differentiating terminal and bridging —PR₂ groups.

Even with tertiary alkyl or aryl phosphine derivatives of the transition metals, there is little variation between the phosphorus 2*p* binding energies of different complexes [101–103], and, at least in the case of triphenylphosphine, only a small increase in the 2*p* energy upon coordination. It is suggested [3] that metal → ligand π -back bonding effectively cancels the increase in formal charge of the phosphorus. In contrast to this situation, the formation of phosphine oxides or phosphonium salts, e.g. [Ph₄P]Br [104] or [Et₃PCl]₂Re₂Cl₈ [80], is readily detected by an increase in the phosphorus 2*p* binding energies.

The situation with thiol-derivatives is rather more intriguing because there are some close structural similarities between metal complexes of Cl[−] and SR[−] (or S^{2−}) i.e. M—(SR)₄, M—(SR)₆ and M—S₆. Unlike PR₂[−], both Cl[−] and SR[−] can bridge either two or three metal atoms. Although a considerable amount of data is now available on sulfur 2*p* binding energy shifts of organic molecules [1,105,106] and simple inorganic species such as H₂S, SO₄^{2−} and SF₆ [2,107], it is only recently that information on sulfur containing metal complexes has become available. Included in this work is the claim [108] that the sulfur spectra of the ferredoxins contain two lines separated by ~1.2 eV. Unfortunately, no information was made available in this paper to make it possible to judge the quality of the spectra that were obtained. Since Holm and co-workers [109] found little difference in the sulfur 2*p* energies of the synthetic iron protein analog (Et₄N)₂[Fe₄S₄(SCH₂Ph)₄], there is still doubt whether such binding energy differences exist [108]. In contrast to this situation, it has been found [110] that when the cysteine sulfur atom of bean plastocyanin is coordinated to cobalt(II) and copper(II) sites, its binding energies are approximately 4 eV higher than those of the apo plastocyanin. The magnitude of this shift is surprisingly large, being comparable to that

observed when R—S—R is oxidized to R— $\overset{\text{O}}{\underset{\text{O}}{\text{S}}}$ —R. Also, it is more than twice

as large a shift as that found on going from Cl[−] to M—Cl [37,83]. However, related sulfur binding energy shifts have now been observed for sulfur bound to iron in cytochrome c [111], so the study of metal—sulfur bonding by XPS may prove to be as useful as that experienced with many transition metal chlorides.

E. CONCLUDING REMARKS

It is hoped that this review indicates some of the areas where the XPS technique may be used to advantage in probing the nature of the metal-ligand bond. Much insight can be gained by monitoring binding energy changes which occur at the ligand donor atom. Nonetheless, the application of XPS to the measurement of binding energy shifts of the non-metal atoms in metal complexes is still very much in its infancy and many more systems need to be investigated before its full utility can be judged. For instance, from the data already available on fluorides, bromides and iodides it is clear that measurements will need to be carried out on the halogen binding energies of cluster species such as Nb_6F_{15} , $\text{Mo}_6\text{Br}_{12}$, $\text{Ta}_6\text{Br}_{15}$, Mo_6I_{12} and Ta_6I_{14} [112] before it is clear whether bridging and terminally bound fluorine, bromine and iodine atoms can be usefully differentiated by this technique. Up to the present time, measurements of nitrogen 1s, sulfur 2p and chlorine 2p binding energies in coordination complexes have yielded important structural information.

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REFERENCES

- 1 K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.E. Karlsson, I. Lindgren and B. Lindberg, ESCA; Atomic, Molecular and Solid State Structure by Means of Electron Spectroscopy, Almqvist and Wiksell, Uppsala, 1967.
- 2 K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. Hedan, K. Hamrin, U. Gelius, T. Bergmark, L. Werme, R. Manne and Y. Baer, ESCA Applied to Free Molecules, North-Holland, Amsterdam, 1969.
- 3 W.L. Jolly, Coord. Chem. Rev., 13 (1974) 47.
- 4 R.L. Cohen, G.K. Wertheim, A. Rosencwaig and H.J. Guggenheim, Phys. Rev. B, 5 (1972) 1037.
- 5 C.S. Fadley and D.A. Shirley, Phys. Rev. A, 2 (1970) 1109.
- 6 K.S. Kim, J. Electron Spectrosc. Relat. Phenom., 3 (1974) 217.
- 7 M.A. Brisk and A.D. Baker, J. Electron Spectrosc. Relat. Phenom., 7 (1975) 197.
- 8 P. Finn and W.L. Jolly, Inorg. Chem., 11 (1972) 893.
- 9 B. Folkesson, Acta Chem. Scand., Ser. A, 28 (1974) 491.
- 10 P. Finn and W.L. Jolly, Inorg. Chem., 11 (1972) 1434.
- 11 G.J. Leigh, J.N. Murrell, W. Bremser and W.G. Proctor, Chem. Commun., (1970) 1661.
- 12 B. Folkesson, Acta Chem. Scand., 27 (1973) 287.

- 13 B. Folkesson, *Acta Chem. Scand.*, 27 (1973) 1441.
- 14 R.S. Swingle, II and W.M. Riggs, *CRC Critical Revs. Anal. Chem.*, (1975) 267.
- 15 C. Nordling, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 83.
- 16 K. Siegbahn, K. Hammond, H. Fellner-Feldegg and E.F. Barnett, *Science*, 176 (1972) 245.
- 17 W.E. Morgan, J.R. Van Wazer and W.J. Stec, *J. Am. Chem. Soc.*, 95 (1973) 751.
- 18 C.S. Fadley, S.B.H. Hagstrom, M.P. Klein and D.A. Shirley, *J. Chem. Phys.*, 48 (1968) 3779.
- 19 W.M. Riggs, *Anal. Chem.*, 44 (1972) 830.
- 20 D.J. Hnatowich, J. Hudis, M.L. Perlman and R.C. Ragaini, *J. Appl. Phys.*, 42 (1971) 4883.
- 21 D. Betteridge, J.C. Carver and D.M. Hercules, *J. Electron Spectrosc. Relat. Phenom.*, 2 (1973) 327.
- 22 W.P. Dianis and J.E. Lester, *Anal. Chem.*, 45 (1973) 1416.
- 23 R.W. Shaw, Jr., T.X. Carroll and T.D. Thomas, *J. Am. Chem. Soc.*, 95 (1973) 5870.
- 24 J.R. Ebner, D.L. McFadden and R.A. Walton, *J. Solid State Chem.*, 17 (1976) 447.
- 25 V.I. Nefedov, Yu.V. Kokunov, Yu.A. Buslaev, M.A. Porai-Koshits, M.P. Gustyakova and E.G. Il'in, *Russ. J. Inorg. Chem.*, 18 (1973) 490.
- 26 M.J. Tricker, *Inorg. Chem.*, 13 (1974) 742.
- 27 C.K. Jørgensen, H. Berthou and L. Balsenc, *J. Fluorine Chem.*, 1 (1971/72) 327.
- 28 V.I. Nefedov, Yu.A. Buslaev and Yu.V. Kokunov, *Russ. J. Inorg. Chem.*, 19 (1974), 637.
- 29 H. Bode and W. Wendt, *Z. Anorg. Chem.*, 269 (1952) 165.
- 30 D. Grandjean and R. Weiss, *Compt. Rend.*, 262 (1966) 1864.
- 31 M. Goldstein, R.J. Hughes and W.D. Unsworth, *Spectrochim. Acta, Part A*, 31 (1975) 621.
- 32 H. Bode and G. Teufer, *Acta Crystallogr.*, 9 (1956) 929.
- 33 R. Hoppe and W. Dähne, *Naturwissenschaften*, 49 (1962) 254.
- 34 A. Byström, S. Bäcklund and K.A. Wilhelmi, *Ark. Kemi*, 6 (1953) 77.
- 35 S.H. Mastin and R.R. Ryan, *Inorg. Chem.*, 10 (1971) 1757.
- 36 D.R. Schroder and R.A. Jacobson, *Inorg. Chem.*, 12 (1973) 515.
- 37 J.R. Ebner, D.L. McFadden, D.R. Tyler and R.A. Walton, *Inorg. Chem.*, 15 (1976) to be published.
- 38 R.G. Hayes and N. Edelstein, in D.A. Shirley (Ed.), *Electron Spectroscopy*, North-Holland, Amsterdam, 1972, pp. 771-779.
- 39 W.E. Moddeman, J.R. Blackburn, G. Kumar, K.A. Morgan, R.G. Albridge and M.M. Jones, *Inorg. Chem.*, 11 (1972) 1715.
- 40 T. Birchall, J.A. Connor and I.H. Hillier, *J. Chem. Soc., Dalton Trans.*, (1975) 2003.
- 41 S.K. Porter and R.A. Jacobson, *J. Chem. Soc., A* (1970) 1359.
- 42 D.T. Clark, D.B. Adams and D. Briggs, *Chem. Commun.*, (1971) 602.
- 43 D.T. Clark, D. Briggs and D.B. Adams, *J. Chem. Soc., Dalton Trans.*, (1973) 169. ;
- 44 C.W. Fryer and J.A.S. Smith, *J. Chem. Soc. A*, (1970) 1029.
- 45 C.W. Fryer, *Chem. Commun.*, (1970) 907.
- 46 See for example, M. Black, R.H.B. Mais and P.G. Owston, *Acta Crystallogr., Sect. B*, 25 (1969) 1760.
- 47 P.A. Edwards and R.E. McCarley, *Inorg. Chem.*, 12 (1973) 900.
- 48 T.L. Brown and L.G. Kent, *J. Phys. Chem.*, 74 (1970) 3572.
- 49 A.D. Hamer, Ph.D. Thesis, Purdue University, 1974.
- 50 D.E. Sands and A. Zalkin, *Acta Crystallogr.*, 12 (1959) 723.
- 51 R.A. Walton, *Prog. Inorg. Chem.*, 16 (1972) 1.
- 52 D.G. Tisley and R.A. Walton, *Inorg. Chem.*, 12 (1973) 373.
- 53 D.G. Tisley and R.A. Walton, *J. Inorg. Nucl. Chem.*, 35 (1973) 1905.
- 54 A.D. Hamer and R.A. Walton, *Inorg. Chem.*, 13 (1974) 1446.
- 55 A.D. Hamer, T.J. Smith and R.A. Walton, *Inorg. Chem.*, 15 (1976) 1014.
- 56 R.A. Walton, *Prog. Inorg. Chem.*, 21 (1976) 105.

- 57 F.A. Cotton and J.T. Mague, *Inorg. Chem.*, 3 (1964) 1402.
58 F.A. Cotton, S.J. Lippard and J.T. Mague, *Inorg. Chem.*, 4 (1965) 508.
59 F.A. Cotton and J.T. Mague, *Inorg. Chem.*, 3 (1964) 1094.
60 B.H. Robinson and J.E. Fergusson, *J. Chem. Soc.*, (1964) 5683.
61 H. Schäfer, H.G. von Schnering, J. Tillack, F. Kuhn, H. Wohrle and H. Baumann, *Z. Anorg. Allg. Chem.*, 353 (1967) 281.
62 D.L. Kepert, *The Early Transition Metals*, Academic Press, New York, 1972.
63 A.D. Hamer and R.A. Walton, unpublished observations, 1974.
64 T.A. Stephenson, E. Bannister and G. Wilkinson, *J. Chem. Soc.*, (1964) 2538.
65 G.B. Allison, I.R. Anderson and J.C. Sheldon, *Aust. J. Chem.*, 22 (1969) 1091.
66 H.D. Glicksman, A.D. Hamer, T.J. Smith and R.A. Walton, *Inorg. Chem.*, 15 (1976) to be published.
67 F.A. Cotton, W.R. Robinson and R.A. Walton, *Inorg. Chem.*, 6 (1967) 223.
68 P.W. Fraiss, A. Guest and C.J.L. Lock, *Can. J. Chem.*, 47 (1969) 1069.
69 F.A. Cotton, B.G. DeBoer and Z. Mester, *J. Am. Chem. Soc.*, 95 (1973) 1159.
70 F.A. Cotton and D.A. Ucko, *Inorg. Chim. Acta*, 6 (1972), 161 and refs. therein.
71 A. Brignole and F.A. Cotton, *Chem. Commun.*, (1971) 706.
72 H. Muller and R. Waschinski, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 413.
73 I.E. Grey and P.W. Smith, *Aust. J. Chem.*, 24 (1971) 73 and refs. therein.
74 R. Saillant, R.B. Jackson, W.E. Streib, K. Folting and R.A.D. Wentworth, *Inorg. Chem.*, 10 (1971) 1453.
75 M.J. Bennett, J.V. Brencic and F.A. Cotton, *Inorg. Chem.*, 8 (1969) 1060.
76 F.A. Cotton, *First Chemical Congress of the North American Continent*, Mexico City, Mexico, 1975 (Abstract No. INOR 002).
77 D.G. Tisley and R.A. Walton, *J. Chem. Soc., Dalton Trans.*, (1973) 1039.
78 P.F. Stokely, Ph.D. Thesis, M.I.T., 1969.
79 W.H. Watson, Jr., and J. Waser, *Acta Crystallogr.*, 11 (1958) 689.
80 J.R. Ebner and R.A. Walton, *Inorg. Chem.*, 14 (1975) 2289.
81 J.R. Ebner, D.R. Tyler and R.A. Walton, *Inorg. Chem.*, 15 (1976), 833.
82 V.I. Nefedov, E.F. Shubochkina, I.S. Kolomnikov, I.R. Baranovskii, V.P. Kukolev, M.A. Golubnichaya, L.K. Shubochkin, M.A. Porai-Koshits and M.E. Vol'pin, *Russ. J. Inorg. Chem.*, 18 (1973) 444.
83 A.D. Hamer, D.G. Tisley and R.A. Walton, *J. Chem. Soc., Dalton Trans.*, (1973) 116.
84 A.S. Antsyshkina and M.A. Porai-Koshits, *Dokl. Akad. Nauk S.S.S.R.*, 143 (1962) 105.
85 G.G. Messmer and E.L. Amma, *Acta Crystallogr., Sect. B*, 24, (1968) 417.
86 I.A. Baidina, N.V. Podberezskaya and L.P. Solov'eva, *J. Struct. Chem.*, 15 (1974) 834.
87 V.I. Nefedov, I.V. Prokof'eva, A.E. Bukanova, L.K. Shubochkin, Ya.V. Salyn' and V.L. Pershin, *Russ. J. Inorg. Chem.*, 19 (1974) 859.
88 G.S. Kharitonova, V.I. Nefedov and L.N. Pankratova, *Russ. J. Inorg. Chem.*, 17 (1972) 1649.
89 G.S. Kharitonova, V.I. Nefedov, L.N. Pankratova and V.L. Pershin, *Russ. J. Inorg. Chem.*, 19 (1974) 469.
90 M.M. Millard and G. Urry, *Inorg. Chem.*, 14 (1975) 1982.
91 G.J. Leigh and W. Bremser, *J. Chem. Soc., Dalton Trans.*, (1972) 1216.
92 A.D. Hamer and R.A. Walton, *Synth. React. Inorg. Met-Org. Chem.*, 4 (1974) 573.
93 J.A. Jaecker, D.P. Murtha and R.A. Walton, *Inorg. Chim. Acta*, 13 (1975) 21.
94 T.L. Brown and T.P. Yesinowski, *Inorg. Chem.*, 10 (1971) 1097.
95 J.R. Ebner and R.A. Walton, unpublished observations, (1974).
96 D.G. Tisley and R.A. Walton, *J. Mol. Struct.*, 17 (1973) 401.
97 H.D. Glicksman and R.A. Walton, *Inorg. Chim. Acta*, 19 (1976) 91.
98 G. Kumar, J. Blackburn, R.G. Albridge, W.E. Moddeman and M.M. Jones, *Inorg. Chem.*, 11 (1972) 296.
99 R.C. Dobbie, M.J. Hopkinson and D. Whittaker, *J. Chem. Soc., Dalton Trans.*, (1972) 1030.

- 100 R.C. Dobbie and P.R. Mason, *J. Chem. Soc., Dalton Trans.*, (1973) 1124.
- 101 C.A. Tolman, W.M. Riggs, W.J. Linn, C.M. King and R.C. Wendt, *Inorg. Chem.*, **12** (1973) 2770.
- 102 M. Pelavin, D.N. Hendrickson, J.M. Hollander and W.L. Jolly, *J. Phys. Chem.*, **74** (1970) 1116.
- 103 S.O. Grim and L.J. Matienzo, *Inorg. Chem.*, **14** (1975) 1014.
- 104 W.E. Swartz, Jr., J.K. Ruff and D.M. Hercules, *J. Am. Chem. Soc.*, **94** (1972) 5227.
- 105 M. Patsch and P. Thieme, *Angew. Chem., Int. Ed. Engl.*, **10** (1971) 569.
- 106 B.J. Lindberg, *Acta Chem. Scand.*, **24** (1970) 2242.
- 107 W.E. Swartz, Jr., K.J. Wynne and D.M. Hercules, *Anal. Chem.*, **43** (1971) 1884.
- 108 D. Leibfritz, *Angew. Chem., Int. Ed. Engl.*, **11** (1972) 232.
- 109 T. Herskovitz, B.A. Averill, R.H. Holm, J.A. Ibers, W.D. Phillips and J.F. Weiher, *Proc. Nat. Acad. Sci. U.S.A.*, **69** (1972) 2437.
- 110 E.I. Solomon, P.J. Clendening, H.B. Gray and F.J. Grunthaner, *J. Am. Chem. Soc.*, **97** (1975) 3878.
- 111 Y.A. Isaacson Z. Majuk, M.A. Brisk, M.E. Gellender and A.D. Baker, *J. Am. Chem. Soc.*, **97** (1975) 6603.
- 112 For a survey of the available cluster species of these types, see refs. 51 and 62.