Complex Halides of the Transition Metals. Part XIV.[1,2] The *X*-Ray Photoelectron Spectra of Mononuclear and Dinuclear Complex Halides of Rhenium(III) and Rhenium(IV), and of the $Re(NCS)_6^{2-}$ and $Re_2(NCS)_8^{2-}$ Complex Anions

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Rhenium 4*f* and chlorine 2*p* electron binding energies have been recorded for a series of complex halides of rhenium in the formal oxidation states +4 and +3. Referencing the rhenium $4f_{\frac{7}{2}}$ level to a standard chlorine $2p_{\frac{3}{2}}$ value provides a guide to the metal oxidation state and allows a ' correction ' to be made for small variations in Madelung potential within a series of salts of a particular complex halide (*e.g.*, $Re_2Cl_8^{2-}$). Both bridging and terminal rhenium-chlorine atoms have been distinguished in the $[Re_2Cl_9]^-$ and $[Re_2Cl_9]^{2-}$ anions. Little variation in rhenium 4*f* binding energies was observed for a series of anions of the type $[ReCl_5,L]^-$. The rhenium 4*f* binding energies of the $Re(NCS)_6^{2-}$ and $Re_2(NCS)_8^{2-}$ anions are also reported together with the nitrogen 1*s* and sulphur 2*p* levels of the pseudohalide ligand molecules.

As part of our studies on the synthesis, reactivity, and structures of complex halides of the heavier transition metals,[1,2] we have investigated the *X*-ray photoelectron spectra[3] of a series of complex halides of rhenium of the types ReX_6^{2-}, $[ReX_5,L]^-$, $Re_2X_8^{2-}$, and $Re_2Cl_9^{n-}$. The purpose of this study was as follows: (1) to determine the binding energies of the metal core electrons in a series of complexes of relatively simple structure containing only *one* type of ligand atom, namely chlorine; (2) to study the effect of changing the halogen within the series ReX_6^{2-}, and changing the nature of the ligand molecule L in $[ReCl_5,L]^-$, on these same binding energies; and (3) to determine the influence of the cation within the series of $ReCl_6^{2-}$ and $Re_2Cl_8^{2-}$ salts upon the metal core binding energies, and establish whether ' cation effects ' can be compensated for. Our results on these rhenium systems are now reported and complement our earlier study of the *X*-ray photoelectron spectra of co-ordination complexes of rhodium.[4]

TABLE 1

Binding energies/eV for complex halides and pseudohalides of rhenium

	Rhenium		Chlorine		Carbon	Nitrogen	
Complex	$4f_{\frac{5}{2}}$	$4f_{\frac{7}{2}}$	$2p_{\frac{1}{2}}$	$2p_{\frac{3}{2}}$	1*s*	1*s*	Other B.E.'s
K_2ReCl_6	45·9	43·5	200·1	198·5	—	—	K $2p_{\frac{1}{2},\frac{3}{2}}$, 295·8, 293·2
K_2ReBr_6	45·3	42·9	—	—	—	—	K $2p_{\frac{1}{2},\frac{3}{2}}$ 295·8, 293·1; Br $3p_{\frac{1}{2},\frac{3}{2}}$, 188·8, 182·2
K_2ReI_6	44·0	41·5	—	—	—	—	K $2p_{\frac{1}{2},\frac{3}{2}}$, 295·2, 292·5; I $3d_{\frac{3}{2},\frac{5}{2}}$, 630·8, 619·4
$[pyH]_2ReCl_6$	45·3	43·0	199·3	197·8	—	401·6	—
$\{[Et_4N]ReCl_5\}_n$	46·1	43·8	~199·8	198·7	—	—	—
$[Et_4N]ReCl_5$,MeCN	45·8	43·4	199·5	198·2	285·0	401·1	—
$[Et_4N]ReCl_5$,Me_2N·CHO	45·9	43·5	199·7	198·2	285·0	401·8	—
$[Et_4N]ReCl_5$,pyz	45·8	43·3	199·6	198·1	—	401·1	—
$\{[Et_4N]ReCl_5\}_2$pyz	45·7	43·3	199·7	198·1	285·7, 284·6	401·7	—
$[Pr^n_4N]ReCl_5$,tu	45·4	43·0	199·2	197·8	284·4	401·7, 399·8	—
$[Pr^n_4N]ReCl_5$,PPh_3	45·3	42·9	199·4	198·0	—	—	—
$[Bu^n_4N]_2[Re_2Cl_8]$	45·2	42·8	199·8	198·4	—	—	—
$[Bu^n_4N]_2[Re_2Br_8]$	44·9	42·4	—	—	285·9, 284·7	—	Br $3p_{\frac{1}{2},\frac{3}{2}}$, 188·4, 181·8
$[pyH]_2[Re_2Cl_8]$	45·2	42·8	199·7	198·3	—	—	—
$[bipyH]_2[Re_2Cl_8]$	44·9	42·5	199·3	198·0	284·7	—	—
$[Ph_4As]_2[Re_2Cl_8]$	45·1	42·8	199·6	198·2	—	—	—
$[Bu^n_4N]Re_2Cl_9$	46·0	43·6	200·7, 199·4,	198·4	285·2, 283·9	—	—
$[Bu^n_4N]_2Re_2Cl_9$	45·5	43·3	200·4, 199·3,	198·1	285·3, 284·1	—	—
$[Bu^n_4N]_2Re(NCS)_6$	45·7	43·3	—	—	285·7, 284·6	402·6, 399·0	S $2p_{\frac{1}{2},\frac{3}{2}}$, 163·3, 162·3
$[Ph_4As]_2Re(NCS)_6$	—[a]	—[a]	—[a]	—[a]	284·3	398·9	—
$[Bu^n_4N]_2Re_2(NCS)_8$	44·7	42·4	—	—	285·4, 284·3	401·9, 398·5	S $2p_{\frac{1}{2},\frac{3}{2}}$, 163·0, 162·0
$[Ph_4As]_2Re_2(NCS)_8$	44·9	42·6	—	—	284·4	398·9	S $2p_{\frac{1}{2},\frac{3}{2}}$, 162·9, 162·0
$[Et_4N]Cl$ [b]	—	—	—	—	285·7, 285·1	—	—
$[Bu^n_4N]Br$ [b]	—	—	—	—	~286·3, 285·0	402·7	Br $3p_{\frac{1}{2},\frac{3}{2}}$, 187·5, 180·7

[a] Rhenium and chlorine binding energies were poorly defined and accordingly are not reported. [b] Not diluted with graphite.

Measured binding energies for 18 complex halides of rhenium are given in Table 1, together with related data for salts of the $[Re(NCS)_6]^{2-}$ and $[Re_2(NCS)_8]^{2-}$ anions. The metal 4*f* core was the preferred level for binding

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[2] Part XII, D. G. Tisley and R. A. Walton, *J. Chem. Soc. (A)*, 1971, 3409.

[3] 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 Structures Studied by Means of Electron Spectroscopy,' Almquist and Wiksells, Uppsala, 1967.

[4] A. D. Hamer, D. G. Tisley, and R. A. Walton, *J.C.S. Dalton*, 1973, 116.

energy measurements.[5] In addition to the rhenium $4f$ levels, the chlorine $2p$ binding energies were measured, together with the bromine $3p$, iodine $3d$, carbon $1s$, nitrogen $1s$, potassium $2p$, and sulphur $2p$ levels where appropriate. The experimental procedure we used to determine these binding energies is the same as that described previously.[4] As before, the energies are referenced to the carbon $1s$ peak of graphite at 284·0 eV. Only in the case of the complex $[Ph_4As]_2Re(NCS)_6$ were we not able to locate well-defined rhenium $4f$ binding energies, even when the sample was diluted with graphite, a procedure which we have found [4,6] generally eliminates, or reduces to a minimum, troublesome charging effects.

The rhenium and chlorine binding energies were usually located with the following precision: Re $4f_{\frac{5}{2}}$ $\pm 0{\cdot}1$ and $4f_{\frac{7}{2}}$ $\pm 0{\cdot}1$ eV; Cl $2p_{\frac{1}{2}}$ $\pm 0{\cdot}2$ and $2p_{\frac{3}{2}}$ $\pm 0{\cdot}1$ eV. Typical rhenium $4f_{\frac{7}{2}}$ and chlorine $2p_{\frac{3}{2}}$ binding energy half-widths (F.W.H.M.) * occurred in the ranges 1·0—1·5 and 1·1—1·7, respectively.

Rhenium and Halogen Binding Energies of the Complex Chlorides, Bromides, and Iodides.—Since the separations of the rhenium $4f$ and chlorine $2p$ spin–orbit components generally remain constant at 2·4 ± 0·1 and 1·5 ± 0·1 eV, respectively, within these series of complexes, we will usually consider chemical shifts with reference to the more intense component of each pair, *i.e.*, Re $4f_{\frac{7}{2}}$ and Cl $2p_{\frac{3}{2}}$.

Of the complex halides listed in Table 1, only K_2ReCl_6 has been the subject [7-9] of previous X-ray photoelectron spectral studies. Fortunately, this enables us to make a useful comparison of the different calibration techniques used.† Leigh and Bremser[8] measured the binding energies with respect to an internal carbon $1s$ standard in Scotch tape of 285 eV, while Jørgensen [7,9] used a value of 290 eV for the same standard. Our samples, diluted with graphite and dispersed on a gold-plated copper surface, are referenced to carbon $1s$ at 284 eV. Applying a correction of 1 eV between our data and that of Leigh and Bremser,[8] who report Re $4f_{\frac{5}{2}}$ 46·9, Re $4f_{\frac{7}{2}}$ 44·5, Cl $2p_{\frac{3}{2}}$ 199·5, and K $2p_{\frac{3}{2}}$ 293·9 eV, we find that these two sets of rhenium $4f$, chlorine $2p$, and potassium $2p$ binding energies are in excellent agreement. A correction of 6 eV applied to the rhenium $4f$ (51·5 and 49·2 eV) and potassium $2p$ (301·3 and 298·7 eV) binding energies reported by Jørgensen [7,9] for K_2ReCl_6 also indicates acceptable agreement with our measurements.

Within the series of complexes K_2ReX_6 (X = Cl, Br, and I), the rhenium $4f_{\frac{7}{2}}$ binding energies decrease in the order Cl > Br > I, as expected from a consideration of ligand electronegativities. A similar variation in metal core binding energies has previously been observed for the complexes $RhX_3(thiox)_3$ (X = Cl, Br, or I and thiox = 1,4-thioxan).[4]

For the group of 15 chloro-complexes listed in Table 1, the rhenium $4f_{\frac{7}{2}}$ energies occur over the relatively narrow range of 43·8—42·4 eV and reveal no *clear* dependence upon formal oxidation state, *i.e.* Re^{IV} in $ReCl_6^{2-}$, $[ReCl_5,L]^-$, and $[Re_2Cl_9]^-$, $Re^{IV,III}$ in $[Re_2Cl_9]^{2-}$, and Re^{III} in $[Re_2Cl_8]^{2-}$. These values are in turn not significantly different from the $4f_{\frac{7}{2}}$ binding energies of the rhenium(III) cluster anions $[Re_3Cl_{11}]^{2-}$ and $[Re_3Cl_{12}]^{3-}$, and the new rhenium(II) anion, $[Re_3Cl_8{}^{2-}]_n$.[1] However, since these comparisons of the data in Table 1 involve binding energies measured on species containing different cations, differences in Madelung potential may well render such comparisons unrewarding. On the other hand, for these relatively simple anions it is reasonable to expect that changes in metal oxidation state will cause greater changes in the rhenium $4f_{\frac{7}{2}}$ binding energies than in the related chlorine $2p_{\frac{3}{2}}$ energies. Accordingly, if we now reference the $4f_{\frac{7}{2}}$ levels to some convenient value for the chlorine $2p_{\frac{3}{2}}$ level, say 198·0 eV, this procedure should provide a more meaningful guide to the metal oxidation state. We have previously demonstrated the validity of using such a chlorine $2p_{\frac{3}{2}}$ internal reference for a series of rhodium complexes. These adjusted rhenium $4f_{\frac{7}{2}}$ binding energies are listed in Table 2, and show that the rhenium(III) derivatives do indeed have slightly smaller $4f_{\frac{7}{2}}$ binding energies than the rhenium(IV) complexes. Further, by referencing the rhenium $4f_{\frac{7}{2}}$ binding energies to a standard chlorine $2p_{\frac{3}{2}}$ value, it is apparent that within each series of anions these energies are essentially identical, so that differences between the ' uncorrected ' data, *e.g.*, K_2ReCl_6 (43·5 eV) and $[pyH]_2ReCl_6$ (43·0 eV), are almost certainly due to small variations in Madelung potential. Also, for the salts $[ReCl_5,L]^-$ it is clear that the rhenium $4f_{\frac{7}{2}}$ binding energies are not sensitive to the nature of L, a result in keeping with our studies on the rhodium(II) acetate derivatives $Rh_2(OAc)_4,2L$, in which

TABLE 2

Rhenium $4f_{\frac{7}{2}}$ binding energies/eV internally referenced to a chlorine $2p_{\frac{3}{2}}$ binding energy of 198·0 eV

Complex	$E_b(4f_{\frac{7}{2}})$	Complex	$E_b(4f_{\frac{7}{2}})$
K_2ReCl_6	43·0	$[Bu^n_4N]Re_2Cl_9$ [a]	43·2
$[pyH]_2ReCl_6$	43·2	$[Bu^n_4N]_2Re_2Cl_9$ [a]	43·2
$\{[Et_4N]ReCl_5\}_n$	43·1	$[Bu^n_4N]_2Re_2Cl_8$	42·4
$[Et_4N]ReCl_5,MeCN$	43·2	$[pyH]_2Re_2Cl_8$	42·5
$[Et_4N]ReCl_5,Me_2N{\cdot}CHO$	43·3	$[bipyH]_2Re_2Cl_8$	42·5
$[Et_4N]ReCl_5,pyz$	43·2	$[Ph_4As]_2Re_2Cl_8$	42·6
$\{[Et_4N]ReCl_5\}_2,pyz$	43·2		
$[Pr^n_4N]ReCl_5,tu$	43·2		
$[Pr^n_4N]ReCl_5,PPh_3$	42·9		

[a] For these two complexes, which are believed to contain two types of rhenium-chlorine bond (see text), the overlap of the two sets of chlorine $2p$ binding energies complicates the spectrum. For the purpose of correcting the rhenium $4f_{\frac{7}{2}}$ binding energy, the chlorine $2p_{\frac{3}{2}}$ energy was taken as the lowest of the three-component spectrum (Table 1).

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* Full width at half maximum.

† At present there is no one standard sampling procedure or calibration technique which is used. This can sometimes present difficulties in comparing data from different sources since charging problems under the different conditions can give rise to significant differences in peak width and peak shape.

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[6] D. P. Murtha and R. A. Walton, *Inorg. Chem.*, 1973, **12**, 368.

[7] C. K. Jørgensen, *Theoret. chim. Acta*, 1972, **24**, 241.

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

[9] C. K. Jørgensen, H. Berthou, and L. Balsenc, *J. Fluorine Chem.*, 1971—1972, **1**, 327.

we observed[4] an insensitivity of the rhodium $3d_{\frac{5}{2}}$ binding energies to variations in the ligand donor strengths.

With three exceptions, the chlorine $2p$ spectra exhibited the simple two-component spectra characteristic of species containing one type of chlorine atom. For the polymeric $[\mathrm{ReCl_5}^-]_n$ anion,[2] the $2p_{\frac{1}{2}}$ component was not well resolved from the more intense $2p_{\frac{3}{2}}$ binding energy, and since this species polymerizes through Re–Cl–Re bridges[2] we attribute this broadening effect and loss of resolution to the polymeric nature of this complex. However, since for each $[\mathrm{ReCl_5}^-]$ unit there are four terminal $\mathrm{Re{-}Cl_t}$ bonds and only one bridging $\mathrm{Re{-}Cl_b}$ bond, we do not see a more complex spectrum since the binding energies of the $\mathrm{Cl_t}$ atoms dominate the spectrum. The complexes $[\mathrm{Bu^n{}_4N}]\mathrm{Re_2Cl_9}$ and $[\mathrm{Bu^n{}_4N}]_2\mathrm{Re_2Cl_9}$ exhibit a three-peak chlorine $2p$ binding-energy spectrum (Table 1) which is characteristic of a system in which overlap occurs between the binding energies of two types of non-equivalent chlorine atom.[1,10] Since the main structure features of the $\mathrm{Re_2Cl_9}^-$ anion have been established[11] and it has been shown to consist of two $\mathrm{ReCl_6}$ octahedra sharing a face with a fairly short metal–metal bond, we can see that the chlorine $2p$ binding-energy spectrum is entirely consistent with this structure. With *fairly strong* M–Cl–M bridges, which occur in such strongly metal–metal bonded systems as $\mathrm{Re_3Cl_9}$ and its derivatives, we would expect chlorine binding energies to decrease in the sequence $\mathrm{Cl_b} > \mathrm{Cl_t}$,[1,10,12] since the electron drift from $\mathrm{Cl_b}$, bound to two metal centres, would be expected to exceed that of $\mathrm{Cl_t}$, so that the formal positive charge and the binding energies would be greater. For $\mathrm{Re_2Cl_9}^-$, with a $\mathrm{Cl_b} : \mathrm{Cl_t}$ ratio of 1 : 2 and overlap such that the $2p_{\frac{3}{2}}$ component of $\mathrm{Cl_b}$ and $2p_{\frac{1}{2}}$ of $\mathrm{Cl_t}$ are nearly coincident, we would expect a three-peak spectrum with a binding-energy order of $\mathrm{Cl_b}(2p_{\frac{1}{2}}) > \mathrm{Cl_b}(2p_{\frac{3}{2}}) \sim \mathrm{Cl_t}(2p_{\frac{1}{2}}) > \mathrm{Cl_t}(2p_{\frac{3}{2}})$, which is what we observe (Table 1). This result is in accord with related studies on the binding energies of the $\mathrm{Re_3Cl_9}$ cluster and its derivatives.[1,10] The close similarity of the chlorine $2p$ binding-energy pattern of $\mathrm{Re_2Cl_9}^-$ and $\mathrm{Re_2Cl_9}^{2-}$ is good evidence that these species have similar structures.

Carbon, Nitrogen, and Sulphur Binding Energies.—The carbon $1s$, nitrogen $1s$, and sulphur $2p$ binding energies were recorded for several of the complexes and these data are also in Table 1. The precision of these measurements is generally ±0·2 eV. These spectra were recorded on undiluted samples of the complexes and the measured binding energies were then ' corrected ' for charging (if any). This correction was taken to be the difference between the rhenium $4f_{\frac{7}{2}}$ energies of undiluted and graphite diluted samples of the appropriate complex. With one exception, the salts $[\mathrm{R_4N}]\mathrm{ReCl_5,L}$ where L represents a *nitrogen*-containing donor molecule, showed only a single broad nitrogen $1s$ binding energy. Since the full width at half maximum values (2·3—3·0 eV) were twice those of the nitrogen $1s$ binding energy of the pyridinium cation in $[\mathrm{pyH}]_2\mathrm{ReCl_6}$ or of the $[\mathrm{Bu^n{}_4N}]^+$ cation in $[\mathrm{Bu_4N}]\mathrm{Br}$, which were recorded for comparison, it is clear that these peaks contain contributions from both the nitrogen $1s$ binding energies of the $[\mathrm{R_4N}]^+$ cations and the nitrogen-containing ligands. In contrast, the thiourea complex $[\mathrm{Pr^n{}_4N}]\mathrm{ReCl_5,tu}$ shows two clearly resolved peaks at 401·7 and 399·8 eV, in the intensity ratio 1 : 2, which are unambiguously assigned to the nitrogen $1s$ binding energies of $[\mathrm{Pr_4N}]^+$ and thiourea, respectively. These binding energies are in the ranges expected[13,14] for $[\mathrm{R_4N}]^+$ and an uncomplexed $-\mathrm{NH_2}$ group respectively.

For the thiocyanate complexes there is a clear distinction between the nitrogen $1s$ binding energies of the $[\mathrm{Bu_4N}]^+$ cation at *ca.* 402 eV, and those at *ca.* 399 eV due to the thiocyanate groups. Further, their relative intensities are in excellent agreement with those expected, 1 : 3 or 1 : 4, from their compositions.

For those tetra-n-butylammonium salts whose carbon $1s$ spectra were also recorded, we observed a two-component spectrum (Table 1) with binding energies at *ca.* 285·5 (shoulder) and *ca.* 284·5 eV, with relative intensities *ca.* 1 : 3. Full width at half maximum values for these peaks were in the range 1·1—1·4 eV. The binding energies and intensity pattern are similar to those we observed for tetra-n-butylammonium bromide (Table 1). The most reasonable explanation is that the α-carbon atoms, adjacent to the positively charged nitrogen atom, exhibit a higher binding energy than those of the remaining $\mathrm{CH_3{-}CH_2{-}CH_2}$ fragment through an inductive effect. Likewise, tetraethylammonium chloride exhibits a two-component spectrum (Table 1) with a 1 : 1 intensity pattern. While this pattern is essentially preserved in $\{[\mathrm{Et_4N}]\mathrm{ReCl_5}\}_2\mathrm{pyz}$, with a slight intensity variation due to overlap with the carbon $1s$ binding energies of pyrazine, no clear resolution of these two components is seen in the spectra of the related acetonitrile and dimethylformamide adducts. Rather a single broad component is located at 285·0 eV with a full width at half maximum of 2·5 eV.

EXPERIMENTAL

Preparation of Complexes.—The complex salts were either prepared by standard literature procedures or were available from earlier studies.[2,15-18]

Physical Measurements.—The *X*-ray photoelectron spectra were recorded with a Hewlett–Packard Model 5950A ESCA spectrometer. Monochromatic aluminium $K_{\alpha1,2}$ radiation (1486·6 eV) was used as the *X*-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. Further details of our experimental procedures are described elsewhere.[4] When necessary, a DuPont 310

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Curve Resolver was used for peak deconvolutions by use of a Gaussian shape fit.

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