Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

X-Ray Photoelectron Spectra of Inorganic Molecules. 12.[1,2] Chlorine 2p Binding Energies of Dinuclear Chloro Anions and Mononuclear Chloro Cations of the Transition Metals

J. R. EBNER, D. L. McFADDEN, D. R. TYLER, and R. A. WALTON*

Received April 16, 1976 AIC602902

The chlorine 2p binding energies of 25 metal complexes belonging to three different structural types have been recorded. Data for several transition metal nonachlorodimetalate anions $M_2Cl_9^{n-}$ show that the bridging chorines (Cl_b) possess higher binding energies than do those chlorine atoms in terminal metal–chlorine bonds (Cl_t). The binding energy differences $\Delta E(Cl_b–Cl_t)$ span the range 0.5–1.2 eV and vary upon changing the anion charge and the cation. For the salt $(Et_4N)_3Rh_2Cl_9$, in which a Rh–Rh bond is not present, $\Delta E(Cl_b–Cl_t)$ equals 0.8 eV, showing that metal–metal bonding is not necessary for $E(Cl_b)$ to be substantially greater than $E(Cl_t)$. The investigation of the chlorine 2p binding energies of a variety of complex salts of the types $[ML_6]Cl_3$, $[ML_5Cl]Cl_2$, and $[ML_4Cl_2]Cl$, where M = Cr, Co, or Rh, shows that for complexes containing both inner- and outer-sphere chlorines the energy difference $\Delta E(Cl_t–Cl^-)$ only has a value in excess of ~0.5 eV when L is a ligand which cannot hydrogen bond to Cl^-. Related measurements on a few double salts (e.g., $[Co(en)_3]_2[CdCl_6]Cl_2 \cdot 2H_2O$ and Cs_3CoCl_5) show that different chlorine environments have very similar chlorine 2p energies.

Introduction

Although most studies of the x-ray photoelectron spectra (XPS) of inorganic molecules have been directed toward the measurement and interpretation of the core electron binding energies of metal atoms, an area of considerable promise involves related measurements on nonmetal atoms bound to a metal. To date, such investigations have included the measurement of nitrogen 1s binding energies of dinitrogen complexes of transition metals,[3] for which the bound and unbound nitrogen atoms have quite different binding energies, and the sulfur 2p energies of plastocyanin derivatives, where it has been claimed[4] that when the cysteine sulfur atom of bean plastocyanin is coordinated to cobalt(II) and copper(II) sites, its 2p binding energies are more than 4 eV higher than those of the apoplastocyanin.

Our interest in such spectroscopic studies has centered largely on using this technique to distinguish different halogen environments in both metal halides and their complexes. While measurements of the fluorine 1s and bromine 3p binding energies of selected crystalline metal fluorides and bromides have not been particularly encouraging from this point of view,[1,5] related studies on metal chlorides show that different chlorine environments often exhibit markedly different chlorine 2p energies.

Much of our previous work has been directed toward establishing how readily bridging and terminal metal–chlorine bonds may be distinguished in metal chloride clusters of molybdenum(II)[6] and rhenium(III).[6-8] In the present investigation we have directed our attention to three additional groups of compounds, namely, (1) the nonachlorodimetalates $M_2Cl_9^{n-}$, in which a metal–metal bond may or may not be present, (2) chloro cations of the types $[ML_4Cl_2]Cl$, $[ML_5Cl]Cl_2$, and $[ML_6]Cl_3$, and (3) double salts containing a chloro anion and "free" chloride ion. These results are now reported and their significance is discussed in terms of the feasibility of using the XPS technique to characterize phases of these particular types.

Experimental Section

Spectral Measurements. The x-ray photoelectron spectra were recorded using a Hewlett-Packard 5950A ESCA spectrometer. The aluminum $K\alpha_{1,2}$ line (1486.6 eV) was used as the excitation source. Sample preparation and full details of the experimental procedure are described fully elsewhere.[6,9] Deconvolutions were carried out using the procedure we have described previously.[6]

Preparation of Metal Complexes. (a) Nonachlorodimetalates. Samples of the complexes $(Bu_4N)_3M_2Cl_9$, where M = Cr, Mo, or W, were kindly provided by Professor R. A. D. Wentworth of Indiana University and a sample of $(Bu_4N)Re_2Cl_9$ was available from an earlier investigation.[10] The salts $Rb_3Mo_2Cl_8H$, $K_3W_2Cl_9$, and $(Et_4N)_3Rh_2Cl_9$ were prepared by standard literature methods.[11-15] Their identity was confirmed by microanalyses and a comparison of their low-frequency infrared spectra with the appropriate literature data.[12,13] Anal. Calcd for $HCl_8Rb_3Mo_2$: Cl, 38.75. Found: Cl, 38.5. Calcd for $Cl_9K_3W_2$: Cl, 39.7. Found: Cl, 39.5. Calcd for $C_{24}H_{60}Cl_9N_3Rh_2$: C, 31.5; H, 6.6. Found: C, 31.3; H, 6.55.

The antimony salt $Cs_3Sb_2Cl_9$[16] was also prepared and studied for comparative purposes since it also contains bridging and terminal metal–chlorine bonds. Anal. Calcd for $Cl_9Cs_3Sb_2$: Cl, 33.2. Found: Cl, 33.4.

(b) Complex Chloro Cations. A variety of chloro cations, mainly of cobalt(III) and rhodium(III), were prepared. These complexes, together with the appropriate literature references to their synthesis, are as follows: $Co(NH_3)_6Cl_3$,[17] $Co(en)_3Cl_3$,[18] $[Co(NH_3)_5Cl]Cl_2$,[19] $[Co(NH_3)_5(ONO)]Cl_2$,[19] $[Co(en)_2Cl_2]Cl$,[20] $[Co(en)_2Cl_2]Br$,[21] $[Co(en)_2Cl_2]NO_3$,[21] $[Rh(NH_3)_5Cl]Cl_2$,[22] $[Rh(NH_3)_4Cl_2]Cl$,[23] $[Rh(py)_4Cl_2]Cl \cdot 5H_2O$,[24] $[Cr(bpy)_2Cl_2]Cl \cdot 2H_2O$,[25] and $[Ni_2(en)_4Cl_2]Cl_2$.[26] The identity of most of these complexes was checked by infrared spectroscopy although in a few instances microanalytical data were also obtained. Anal. Calcd for $H_{18}Cl_3N_6Co$: Cl, 39.8. Found: Cl, 40.0. Calcd for $C_{20}H_{20}Cl_3CrN_4O_2$: C, 47.4; H, 4.0. Found: C, 47.2; H, 4.1. Calcd for $C_4H_{16}Cl_2N_4Ni$: Cl, 22.4. Found: Cl, 23.0.

(c) Double Salts. The synthesis of the complexes Cs_3CoCl_5, $[Co(en)_3]_2[CdCl_6]Cl_2 \cdot 2H_2O$, $[dienH_3][CuCl_4]Cl$, where $dienH_3$ = diethylenetriammonium, and $[Co(NH_3)_6][ZnCl_4]Cl$ was accomplished by standard procedures.[27-30] Anal. Calcd for Cl_5CoCs_3: Cl, 27.9. Found: Cl, 27.8. Calcd for $C_{12}H_{52}CdCl_8Co_2N_{12}O_2$: Cl, 31.15. Found: Cl, 31.3. Calcd for $C_4H_{16}Cl_5CuN_3$: C, 13.8; H, 4.7; Cl, 51.1. Found: C, 14.6; H, 5.1; Cl, 49.9.

Results and Discussion

The transition metal chloride complexes studied in the present investigation constitute three separate structural classes and consequently these results are discussed separately. The appropriate binding energy data are presented in Tables I–III. In sections a–c of the discussion, correlations are made between observed chlorine 2p binding energies and differences in the relative charge densities which are expected at the different chlorine sites. While this interpretation is certainly convenient, it is also an obvious oversimplification, a point which is discussed further in section d.

(a) The Nonachlorodimetalate Anions. The transition metal complexes **1–7** in Table I possess the well-known confacial bioctahedral structure.[11,31-33] In the case of the $Mo_2Cl_8H^{3-}$ anion, one of the bridging chloride ligand positions is occupied by hydride.[11,14] The binding energies of the salt $(Bu_4N)_2Re_2Cl_8$ were recorded to check the instrumental

Table I. X-Ray Photoelectron Spectra of Nonachlorodimetalate Complexes[a]

	Cl_b		Cl_t			
Complex	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	C 1s	Other BE's
1, $[Bu_4N]_3Cr_2Cl_9$	200.1	198.5	199.5	197.9 (1.2)	284.7 (1.5)	Cr $2p_{1/2,3/2}$: 586.3, 576.8
2, $[Bu_4N]_3Mo_2Cl_9$	200.2	198.7	199.2	197.7 (1.3)	284.8 (1.6)	Mo $3d_{3/2,5/2}$: 232.6, 229.5
3, $Rb_3Mo_2Cl_8H$	200.8	199.2	199.9	198.4 (1.1)		Rb $3d_{3/2,5/2}$: 111.1, 109.6 Mo $3d_{3/2,5/2}$: 233.1, 229.8
4, $K_3W_2Cl_9$	200.2	198.7	199.6	198.2 (1.1)		K $2p_{1/2,3/2}$: 295.7, 292.9 W $4f_{5/2,7/2}$: 34.7, 32.5
5, $[Bu_4N]_3W_2Cl_9$	200.3	198.9	199.5	197.9 (1.2)	285.2 (1.6)	W $4f_{5/2,7/2}$: 34.4, 32.3
6, $[Et_4N]_3Rh_2Cl_9$	199.5	198.0	198.8	197.2 (1.3)	284.6 (2.0)	Rh $3d_{3/2,5/2}$: 313.4, 308.8
7, $[Bu_4N]Re_2Cl_9$	201.0	199.4	199.6	198.2 (1.2)	284.0 (1.2)	Re $4f_{5/2,7/2}$: 45.9, 43.4
8, $[Bu_4N]_2Re_2Cl_8$			199.8	198.3 (1.5)	284.9 (1.6)	Re $4f_{5/2,7/2}$: 45.1, 42.7
9, $Cs_3Sb_2Cl_9$			199.2	197.8 (1.4)		Cs $3d_{3/2,5/2}$: 737.9, 724.0 Sb $3d_{3/2,5/2}$: 539.6, 530.3

[a] All spectra are referenced to the C 1s binding energy of graphite taken as 284.0 eV; fwhm values are given in parentheses.

Table II. X-Ray Photoelectron Spectra of Chloro Cations[a]

Complex[b]	Cl $2p_{1/2,3/2}$			Amine N 1s	Other BE's
10, $[Co(NH_3)_6]Cl_3$	199.5		198.0 (1.3)	400.0 (1.1)	Co $2p_{1/2,3/2}$: 797.0, 782.1
11, $[Co(en)_3]Cl_3$	199.0		197.5 (1.1)	400.0 (1.1)	
12, $[Co(NH_3)_5Cl]Cl_2$	199.5		198.0 (1.4)	399.8 (1.5)	
13, $[Rh(NH_3)_5Cl]Cl_2$	199.2		197.8 (1.4)	399.8 (1.6)	
14, $[Co(NH_3)_5(ONO)]Cl_2$	199.3		197.9 (1.3)	400.0 (1.3)	N 1s (NO_3^-): 403.9
15, $[Rh(NH_3)_4Cl_2]Cl$	199.2		197.8 (1.4)	399.6 (1.4)	
16, *trans*-$[Co(en)_2Cl_2]Cl$	199.5		198.1 (1.7)	399.9 (1.4)	
17, $[Co(en)_2Cl_2]Br$	199.3		197.9 (1.3)	399.5 (1.4)	
18, $[Co(en)_2Cl_2]NO_3$	199.4		198.0 (1.3)	399.7 (1.4)	
19, $[Rh(py)_4Cl_2]Cl\cdot5H_2O$	200.3	198.8	197.0	400.9 (1.1)	
20, $[Cr(bpy)_2Cl_2]Cl\cdot2H_2O$	199.7	198.2	196.7	400.3 (1.0)	
21, $[Ni_2(en)_4Cl_2]Cl_2$	199.5		198.0 (1.3)	399.8 (1.3)	
22, $[Rh(dth)_2Cl_2]Cl$[c]	199.5	197.9	196.5		
23, $[Rh(dth)_2Cl_2]PF_6$[c]	199.6		197.9		

[a] All spectra are referenced to the C 1s binding energy of graphite taken as 284.0 eV; fwhm values are given in parentheses. [b] Ligand abbreviations are as follows: en, ethylenediamine; py, pyridine; bpy, 2,2′-bipyridyl; dth, 2,5-dithiahexane. [c] Data taken from ref 40.

Table III. X-Ray Photoelectron Spectra of Double Salts[a]

Complex	Cl $2p_{1/2,3/2}$	Amine N 1s
24, $[Co(NH_3)_6][ZnCl_4]Cl$	198.8 197.4 (1.7)	399.5 (1.5)
25, $[Co(en)_3]_2[CdCl_6]Cl_2\cdot2H_2O$	198.9 197.4 (1.5)	399.6 (1.5)
26, $[dienH_3][CuCl_4]Cl$[b]	199.6 198.1 (1.1)	401.7 (1.4) 399.8 (1.3)
27, $Cs_3[CoCl_4]Cl$	199.2 197.8 (1.3)	

[a] All spectra are referenced to the C 1s binding energy of graphite taken as 284.0 eV; fwhm values are given in parentheses. [b] $dienH_3$ = diethylenetriammonium.

performance and to demonstrate the chlorine 2p peak profile for a complex possessing a single type of chlorine environment (see Figure 1 and Table I). The related data for the complex anions $M_2Cl_9^{n-}$ and $Mo_2Cl_8H^{3-}$ are also presented in Table I and some representative spectra are shown in Figure 1. The most noticeable difference between the chlorine 2p spectra of complexes **1**–**6** and $(Bu_4N)_2Re_2Cl_8$ (Figure 1) is that the former do not exhibit well-resolved chlorine $2p_{1/2,3/2}$ doublets but rather show broad asymmetric band envelopes characteristic of the presence of different types of chlorine environments. Deconvolution of these spectra, using the procedure described by us previously,[6] gave the two sets of chlorine binding energies listed in Table I. In keeping with the arguments we have used in interpreting differences in chlorine 2p binding energies for chloride clusters of molybdenum(II) and rhenium(III),[6–8] we would expect the bridging chlorines (Cl_b) in the nonachlorodimetalate anions to exhibit higher binding energies than those in terminal metal–chlorine bonds (Cl_t). This prediction is confirmed for the present series of complexes, since the relative intensities of the two sets of chlorine binding energies are in accord with the relative numbers of Cl_b and Cl_t environments which are known to be present. For complexes **1**, **2**, **4**, **5**, and **6**, the deconvoluted spectra give Cl_b:Cl_t peak intensities of almost exactly 1.0:2.0 while for $Rb_3Mo_2Cl_8H$, the ratio increases to 1.0:3.0 in keeping with loss of one of the bridging chlorines.[34]

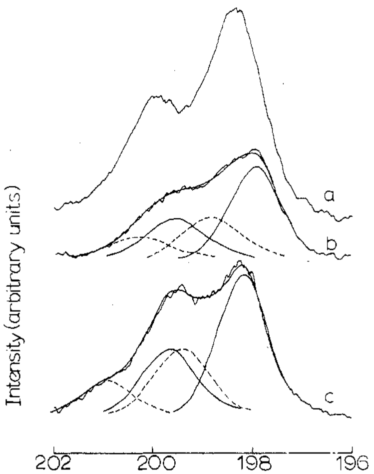

Figure 1. Chlorine 2p binding energy spectra of (a) $(Bu_4N)_2Re_2Cl_8$, (b) $(Bu_4N)_3W_2Cl_9$, and (c) $(Bu_4N)Re_2Cl_9$. Spectra b and c have been deconvoluted into two sets of Cl $2p_{1/2,3/2}$ doublets using the procedure described in ref 6.

One of the interesting features of these data is that the differences in binding energies of Cl_b and Cl_t, $\Delta E(Cl_b–Cl_t)$, occur in the range 1.0–0.5 eV and reveal no obvious correlation with the absence (i.e., $Rh_2Cl_9^{3-}$) or presence of a metal–metal bond in these anions. For the series $(Bu_4N)_3M_2Cl_9$, where M = Cr, Mo, or W, $\Delta E(Cl_b–Cl_t)$ 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. This structural feature results in shorter, stronger M–Cl_b bonds and presumably leads 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 $(Bu_4N)_3W_2Cl_9$ and $K_3W_2Cl_9$ (Table I), where $\Delta E(Cl_b–Cl_t)$ decreases from 1.0 to 0.5 eV. In these chloro anions, the variations in structure produced upon changing the cations are known to be quite dramatic,[32] 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. Although the binding energy order is clearly established to be $Cl_b > Cl_t$, differences in intra- and intermolecular solid-state interactions make further interpretations much more tenuous.

Two further complexes which we studied (**7** and **9** in Table I) produced chlorine 2p binding energy spectra whose characteristics place them at the two extremes of the systems already discussed. The spectrum of $(Bu_4N)Re_2Cl_9$ clearly shows three components (Figure 1) and its deconvolution reveals that the energy difference $\Delta E(Cl_b–Cl_t)$ is significantly greater than that observed with any of the complexes **1–6**. This difference (1.2 eV) approaches that observed between the corresponding energies of Cl_b and Cl_t in complexes of the type $Re_3Cl_9L_3$.[6–8] 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 $M_2Cl_9{}^{n-}$ anions, if we take the differences between the M–Cl_t and M–Cl_b bond lengths[31–33,35] as a measure of the difference in the strengths of these interactions. In other words, the smaller $r(M–Cl_b) - r(M–Cl_t)$ the greater the binding energy difference $\Delta E(Cl_b–Cl_t)$ should become. There is nothing apparent in the structural parameters for $(Bu_4N)Re_2Cl_9$[31,36] 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 $K_3W_2Cl_9$, for which r(W–W) is 2.41 Å,[37] the Re–Re bond length in $(Bu_4N)Re_2Cl_9$ is significantly longer (2.70 Å).[36] One possible explanation is that Re(IV) may be a sufficiently more polarizing center than any of the M(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 $\Delta E(Cl_b–Cl_t)$.

The XPS spectrum of the non transition metal salt $Cs_3Sb_2Cl_9$ (Table I) makes for an interesting comparison with the other chloro anions. Since the antimony 3d and chlorine 2p binding energies of this salt have recently been reported elsewhere,[38] it also enables us to assess the quality of our spectral data. Birchall et al.[38] reported the antimony 3d binding energies of a wide range of antimony compounds and reported that the fwhm values for these peaks occurred in the range 1.8–2.3 eV. In our measurements on $Cs_3Sb_2Cl_9$, we obtained very similar energies to those reported[38] but the peaks were much narrower (fwhm = 1.4 eV). The chlorine 2p spectrum reveals a well-resolved spin–orbit doublet with no evidence for two different sets of chlorine 2p 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 $Sb_2Cl_9{}^{3-}$ anions, related data for the $Sb_2Br_9{}^{3-}$ anion[39] suggest that the Sb–Sb distance in $Sb_2Cl_9{}^{3-}$ will be rather long (~4.0 Å). In this situation, it is likely that with the longer, weaker M–Cl_b bonds which must now be present, the charges at Cl_b and Cl_t are very similar and these different environments can no longer be easily distinguished in the XPS experiment.

(b) Chloro Cations. In a previous study involving the measurement of the rhodium 3d binding energies of a variety of rhodium complexes,[40] we also reported the chlorine 2p binding energy spectra of three complexes of the type $[RhL_4Cl_2]Cl$, where L = pyridine, $^1/_2$ 2,2′-bipyridyl, or $^1/_2$ 2,5-dithiahexane. In each instance, we observed a three-peak spectrum arising from overlap of the $2p_{3/2}$ component of chlorine bound to rhodium (Cl_t) with the $2p_{1/2}$ component of chloride in the outer coordination sphere. Such a result seemed perfectly reasonable and was consistent with the binding energy difference $\Delta E(Cl_t–Cl^-)$ between 1.7 and 1.0 eV. At the time, we anticipated that this result would be quite general for chloride complexes of these types, but upon extending these measurements to a variety of ammine and ethylenediamine complexes we find this not to be the case (Table II and Figure 2). For complexes **10–18** a two-peak spectrum is observed, 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 now rather small. A similar result is obtained for the dinuclear nickel(II) complex **21**,[41] which most likely contains weak Ni–Cl_b–Ni bridges. In this instance, the binding energies for Cl_b and chloride are very similar.

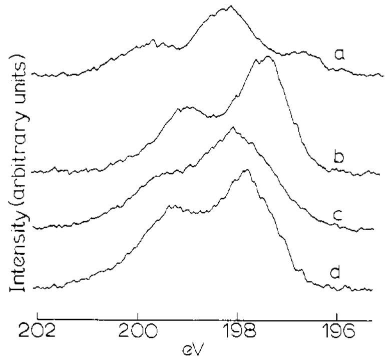

Figure 2. Chlorine 2p binding energy spectra of (a) $[Cr(bpy)_2Cl_2]Cl\cdot 2H_2O$, (b) $[Co(en)_3]Cl_3$, (c) $[Co(en)_2Cl_2]Cl$, and (d) $[Co(en)_2Cl_2]Br$.

We have remeasured the spectrum of the hydrate $[Rh(py)_4Cl_2]Cl\cdot 5H_2O$ (**19**) using a sample prepared by a route different from that employed previously.[40] The three-peak spectrum which is characteristic of the two different chlorine environments was again obtained and a similar spectrum was also displayed by the chromium(III) complex $[Cr(bpy)_2Cl_2]Cl\cdot 2H_2O$ (**20**).

It seems to us that the most obvious explanation for these spectral differences is that in the ammine and ethylenediamine complexes (**10–18**) the cooperative effect of several hydrogen-bonding interactions of the type N–H···Cl^- involving each outer-sphere chloride ion is sufficient to decrease the negative charge at Cl^- to a point where it is not very different from that residing at Cl_t. Crystallographic data for complexes such as $[Co(NH_3)_5Cl]Cl_2$[42] and $[Rh(NH_3)_4Cl_2]Cl$[43] provide convincing support for this interpretation since they indeed show that the chloride ions are hydrogen bonded in this manner. We also note that irrespective of whether the complexes **10–18** contain outer-sphere chloride, inner-sphere chloride or a mixture of both, the chlorine binding energies are very similar. This is particularly true in the case of the ammine complexes (Table II) and it is only with $[Co(en)_3]Cl_3$ that the chlorine 2p binding energies are noticeably different from those of the other complexes. This is apparent upon internally referencing the chlorine $2p_{3/2}$ energies to a nitrogen 1s energy of 400.0 eV for coordinated NH_3 or en. $[Co(en)_3]Cl_3$ is then the only complex whose $2p_{3/2}$ energy falls outside the range 198.4–197.9 eV. The implication is that the outer-sphere chlorides in $[Co(en)_3]Cl_3$ are less perturbed by hydrogen bonding than is the case with other complexes of this type.

As we change to non-hydrogen-bonding ligands such as pyridine, 2,2′-bipyridyl, and 2,5-dithiahexane, this effect should disappear and result in the two chlorine environments being readily distinguishable. This is indeed what we observe.

Our results and their interpretation can now be discussed in the light of some related XPS studies which have recently been reported in the literature. Burger et al.[44] have discussed the effects of hydrogen bonding in $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$ upon the cobalt 2p binding energies. However, their results are presented in the form of *differences* in binding energies of the $2p_{3/2}$ level of cobalt and the $2p_{1/2,3/2}$ levels of chlorine and it is accordingly very difficult to make direct comparisons with our data. While they commented that "the resolution of the measurements was not sufficient to distinguish between the two types of halides in the complexes containing them both in the inner and outer coordination sphere", it is apparent that they did not recognize that in these complexes the chlorine 2p binding energies are almost coincident, since they further stated that "only the greater line width indicated the presence of the two different bound anions". From our results, the fwhm values for the chlorine $2p_{1/2,3/2}$ doublets were observed to vary between 2.3 and 2.8 eV, but this relatively small variation does not correlate with whether one or two chlorine environments are present.

Our work also explains some earlier results of Nefedov et al.[45] on the core electron binding energies of a variety of rhodium complexes. The small variations in chlorine $2p_{3/2}$ binding energies which they observed for the series of complexes $Rh(NH_3)_3Cl_3$, $Rh(py)_3Cl_3$, $Rh(SC(NH_2)_2)_3Cl_3$, $[Rh(NH_3)_5Cl]Cl_2$, $[Rh(NH_3)_6]Cl_3$, and $[Rh(SC(NH_2)_2)_5Cl]Cl_2$ can now be rationalized in terms of the same type of hydrogen-bonding effects which we suggest influence the outer-sphere chloride ion binding energies for many of the complexes listed in Table II.[46] Also, the observation of Grim et al.[47] that different peaks for the two types of chlorine in $[Pt(NH_3)_3Cl]Cl$ are not detectable is in accord with our interpretation.

Finally, some conclusions of Nefedov et al.[48] concerning the structure of certain glycine complexes of rhodium(III), ruthenium(III), and iridium(III) should now be viewed in a different light. While their belief that the structures of these species can be represented as $[M(NH_2CH_2COO)_2(^+NH_3CH_2COO)Cl]$ may be correct, the observed values of the chlorine 2p binding energies (198.8 or 198.7 eV)[48] are not necessarily characteristic of inner-sphere chloride. They commented[48] that an outer-sphere chlorine atom has a chlorine 2p binding energy of 198.3 eV, while for an inner-sphere chlorine atom it is in the range 198.4–199.2 eV. This distinction may be no longer meaningful in the presence of hydrogen-bonding interactions involving the chlorine atoms.

(c) Double Salts. Complexes **24–26** in Table III are double salts of known structure.[28,30,49] In each, the outer-sphere chloride ions are hydrogen bonded to amine groups. As a result, we would expect them to exhibit similar chlorine 2p spectra to the complex cations **10–18** in Table II. This is in fact the case. The spectrum of $[dienH_3][CuCl_4]Cl$ shows a particularly well-resolved chlorine $2p_{1/2,3/2}$ doublet, so that the two sets of chlorine binding energies must be fortuitously coincident. In the case of complexes **24** and **25**, the spectra are more characteristic of species such as $[Co(NH_3)_5Cl]Cl_2$ (Table II) since this resolution is lost as a result of a small mismatch in these two sets of binding energies.

The remaining complex listed in Table III is the classic double salt Cs_3CoCl_5, containing both the $CoCl_4^{2-}$ anion and Cl^-.[27,50] Its chlorine 2p binding energy spectrum also failed to yield two well-separated sets of peaks. While the chloride ions are not of course perturbed by hydrogen bonds, their environment is such that they occupy sites surrounded by six nearest-neighbor cesium ions (two at 3.67 Å and four at 3.42 Å).[27] Whether this leads to an initial-state charge which is similar to that residing at the chlorine atoms in the $CoCl_4^{2-}$ anions and/or whether differences in crystal field potentials and final-state relaxation effects[51] contribute to the similarity in the binding energies is not clear at present (for a further discussion of this point see section d). Whatever the reason, it is apparent that the use of XPS as a structural tool to detect the formation of double salts of this particular type does not appear to be particularly promising and, accordingly, we did not pursue this type of complex further.

(d) Some Comments on the Factors Affecting the Chlorine 2p Binding Energies. At this point it is important to emphasize that factors other than differences in initial-state charges at the chlorine sites may contribute to the observed binding energies. Differences in valence-electron density, crystal field potential, and relaxation energy can all influence the binding energy shift.[52] In sections a–c we have discussed the binding energy differences between bridging and terminally bound chlorine and chloride ion in terms of the charge densities expected at these sites, but it is clear that the crystal field potential and relaxation energy terms cannot be neglected. Unfortunately, there is no good way of reliably estimating both of these latter contributions for the molecules discussed in the present report. Only by resorting to "implantation" techniques etc.[52] on relatively simple systems can such a separation be satisfactorily achieved. While there might well be a significant difference in the crystal potential felt by Cl_b, Cl_t, and Cl^-, it is also clear that the observed binding energy order $Cl_b > Cl_t \gtrsim Cl^-$ is the same as that expected from a consideration of initial-state charges alone. Whatever the detailed interpretation, it is apparent that the XPS technique can readily differentiate Cl_b, Cl_t, and Cl^- environments in many metal chloride complexes.

(e) Comparisons with Other Systems. Since considerable data are now available on the chlorine 2p binding energies of a variety of metal chlorides and their complexes, it is appropriate if we briefly summarize the strengths and weaknesses of the XPS technique as they apply to the structural characterization of phases of this type. Chlorine 2p binding energy measurements are of course most effective when applied to systems in which more than one type of chlorine environment is present, and this technique is particularly powerful for compounds in which strong metal–metal bonds are present since chlorine atoms bridging these bonds are characterized by rather high binding energies.[6–8] Accordingly, metal chloride clusters such as Re_3Cl_9, Mo_6Cl_{12}, and their derivatives[6–8,53] and presumably phases such as Nb_6Cl_{14}, W_6Cl_{12}, etc. are particularly suitable for this reason. Application of these studies to materials of unknown structure has also proved to be very useful as revealed by binding energy measurements on β-$MoCl_2$,[6] γ-$ReCl_4$,[54] and $OsCl_4$.[54] β-$MoCl_2$ has been shown[6,53] to be structurally quite different from the α form $[Mo_6Cl_{12}]$ and, in spite of the isoelectronic nature of $ReCl_3$ (i.e., Re_3Cl_9) and $OsCl_4$, it is clear from XPS studies[54] that $OsCl_4$ does not have the Os_3Cl_{12} structure with both bridging and terminal chlorine atoms.

The present investigation shows that the binding energy order $Cl_b > Cl_t$ is maintained in chloro anions of the type $M_2Cl_9^{n-}$, where M is a transition metal. Rather interestingly, the spectrum of the rhodium(III) complex $(Et_4N)_3Rh_2Cl_9$ proves that the presence of a metal–metal bond is not necessary for this binding energy order to be maintained.

It is also apparent that this technique can be usefully applied to the characterization of complexes of the types $[ML_5Cl]Cl_2$, $[ML_4Cl_2]Cl$, etc. provided L is a ligand which is unable to hydrogen bond to the outer-sphere chloride ions.

Acknowledgment. We thank the National Science Foundation (Grant GP-43021X) for the support of this work. R.A.W. is the recipient of a Camille and Henry Dreyfus

Foundation Teacher-Scholar Grant (1970–1975). We also thank Mr. John Sexauer for the synthesis of the complexes $K_3W_2Cl_9$, $(Et_4N)_3Rh_2Cl_9$, and $Rb_3Mo_2Cl_8H$ and Professor R. A. D. Wentworth, who kindly provided us with samples of $(Bu_4N)_3M_2Cl_9$, where M = Cr, Mo, or W.

Registry No. 1, 38845-35-1; **2**, 60260-34-6; **3**, 60260-33-5; **4**, 16843-37-1; **5**, 60260-32-4; **6**, 28681-19-8; **7**, 60260-28-8; **8**, 14023-10-0; **9**, 12016-49-8; **10**, 10534-89-1; **11**, 13408-73-6; **12**, 13859-51-3; **13**, 13820-95-6; **14**, 13782-02-0; **15**, 21288-85-7; **16**, 14040-33-6; **17**, 60260-26-6; **18**, 60260-43-7; **19**, 14077-30-6; **20**, 14406-85-0; **21**, 20647-35-2; **24**, 60260-42-6; **25**, 49732-12-9; **26**, 19121-74-5; **27**, 13774-14-6.

References and Notes

(1) Part 11: J. R. Ebner, D. L. McFadden, and R. A. Walton, *J. Solid-State Chem.*, **17**, 447 (1976).
(2) Part 10: J. R. Ebner and R. A. Walton, *Inorg. Chem.*, **14**, 2289 (1975).
(3) B. Folkesson, *Acta Chem. Scand.*, **27**, 287, 1441 (1973).
(4) E. I. Solomon, P. J. Clendening, H. B. Gray, and F. J. Grunthaner, *J. Am. Chem. Soc.*, **97**, 3878 (1975).
(5) H. D. Glicksman and R. A. Walton, *Inorg. Chim. Acta*, **19**, 91 (1976).
(6) A. D. Hamer and R. A. Walton, *Inorg. Chem.*, **13**, 1446 (1974).
(7) D. G. Tisley and R. A. Walton, *Inorg. Chem.*, **12**, 373 (1973).
(8) D. G. Tisley and R. A. Walton, *J. Inorg. Nucl. Chem.*, **35**, 1905 (1973).
(9) A. D. Hamer, D. G. Tisley, and R. A. Walton, *J. Inorg. Nucl. Chem.*, **36**, 1771 (1974).
(10) D. G. Tisley and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 1039 (1973).
(11) M. J. Bennett, J. V. Brencic, and F. A. Cotton, *Inorg. Chem.*, **8**, 1060 (1969).
(12) R. J. Ziegler and W. M. Risen, Jr., *Inorg. Chem.*, **11**, 2796 (1972).
(13) R. A. Work, III, and M. L. Good, *Inorg. Chem.*, **9**. 956 (1970).
(14) At the time we started this work, the molybdenum complex $Rb_3Mo_2Cl_8H$ was formulated[11] as $Rb_3Mo_2Cl_8$. It is only recently[15] that it has been identified as a hydride derivative, with the H^- ligand occupying one of the bridging positions between the molybdenum atoms.
(15) F. A. Cotton and B. J. Kalbacher, *Inorg. Chem.*, **15**, 522 (1976).
(16) H. Yamatera and K. Nakatsu, *Bull. Chem. Soc. Jpn.*, **27**, 244 (1954).
(17) J. Bjerrum and J. P. McReynolds, *Inorg. Synth.*, **2**, 217 (1946).
(18) J. B. Work, *Inorg. Synth*, **2**, 221 (1946).
(19) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, p 463.
(20) J. C. Bailar, Jr., *Inorg. Synth.*, **2**, 222 (1946).
(21) S. M. Jorgensen, *J. Prakt. Chem.*, **41**, 440 (1890).
(22) J. A. Osborn, K. Thomas, and G. Wilkinson, *Inorg. Synth.*, **13**, 213 (1972).
(23) S. N. Anderson and F. Basolo, *Inorg. Synth.*, **7**, 216 (1963).
(24) R. D. Gillard and G. Wilkinson, *Inorg. Synth.*, **10**, 64 (1967).
(25) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).
(26) H. M. State, *Inorg. Synth.*, **6**, 198 (1960).
(27) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).
(28) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 597 (1972).
(29) G. C. Allen and N. S. Hush, *Inorg. Chem.*, **6**, 4 (1967).
(30) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **9**, 465 (1970).
(31) F. A. Cotton and D. A. Ucko, *Inorg. Chim. Acta*, **6**, 161 (1972), and references therein.
(32) I. E. Grey and P. W. Smith, *Aust, J. Chem.*, **24**, 73 (1971), and references therein.
(33) R. Saillant, R. B. Jackson, W. E. Streib, K. Folting, and R. A. D. Wentworth, *Inorg. Chem.*, **10**, 1453 (1971).
(34) For a full listing of all the relative peak intensities see J. R. Ebner, Ph.D. Thesis, Purdue University, 1975, p 111.
(35) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).
(36) P. F. Stokely, Ph.D. Thesis, Massachusetts Institute of Technology, 1969.
(37) W. H. Watson, Jr., and J. Waser, *Acta Crystallogr.*, **11**, 689 (1958).
(38) T. Birchall, J. A. Connor, and I. H. Hillier, *J. Chem. Soc., Dalton Trans.*, 2003 (1975).
(39) S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, 1359 (1970).
(40) A. D. Hamer, D. G. Tisley, and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 116 (1973).
(41) A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **143**, 105 (1962).
(42) G. G. Messmer and E. L. Amma, *Acta Crystallogr., Sect. B*, **24**, 417 (1968).
(43) I. A. Baidina, N. V. Podberezskaya, and L. P. Solov'eva, *J. Struct. Chem. (USSR)*, **15**, 834 (1974).
(44) K. Burger, E. Fluck, H. Binder, and Cs. Várhelyi, *J. Inorg. Nucl. Chem.*, **37**, 55 (1975).
(45) V. I. Nefedov, E. F. Shubochkina, I. S. Kolomnikov, I. R. Baranovskii, V. P. Kukolev, M. A. Golubinchaya, L. K. Shubochkin, M. A. Porai-Koshits and M. E. Vol'pin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **18**, 444 (1973).
(46) As with much of the XPS data in the literature, those reported in ref 45 list the relevant binding energies but give no information on peak shapes or peak widths.
(47) S. O. Grim, L. J. Matienzo, and W. E. Swartz, Jr., *Inorg. Chem.*, **13**, 447 (1974).
(48) V. I. Nefedov, I. V. Prokof'eva, A. E. Bukanova, L. K. Shubochkin, Ya. V. Salyn', and V. L. Pershin, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **19**, 859 (1974).
(49) B. Zaslow and G. L. Ferguson, *Acta Crystallogr., Sect B*, **27**, 849 (1971).
(50) B. N. Figgis, M. Gerloch, and R. Mason, *Proc. R. Soc. London, Ser. A*, **279**, 210 (1964).
(51) D. A. Shirley, *Chem. Phys. Lett.*, **16**, 220 (1972).
(52) K. S. Kim and N. Winograd, *Chem. Phys. Lett.*, **30**, 91 (1975), and references therein.
(53) R. A. Walton, "Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Oxford University, in press.
(54) A. D. Hamer, Ph.D. Thesis, Purdue University, 1974.

Contribution from the Department of Chemistry,
University of Maine, Orono, Maine 04473

Optical Spectra of the Tetrabromopalladate(II) Ion Doped in Cesium Hexabromozirconate(IV) at 2 K

THOMAS G. HARRISON, HOWARD H. PATTERSON,* and MARTHA T. HSU

Received March 22, 1976 AIC60217B

The optical spectra of the tetrabromopalladate(II) ion doped as a substitutional impurity in cesium hexabromozirconate(IV) has been measured at 2 K. An electronic band has been observed between 19 185 and 21 836 cm^{-1} with sharp vibrational detail and is assigned as the d–d transition, $\Gamma_1({}^1A_{1g}) \rightarrow \Gamma_2({}^1A_{2g})$. The mixed crystal vibrational data for this band has been compared with recent single crystal absorption results at 15 K by Martin and co-workers. The possible presence of a Jahn-Teller effect for the $\Gamma_1({}^1A_{1g}) \rightarrow \Gamma_5({}^1E_g)$ transition for $PdBr_4^{2-}$ in Cs_2ZrBr_6 has been examined. A Cotton–Harris molecular orbital calculation has been carried out for $PdCl_4^{2-}$ and $PdBr_4^{2-}$ ions. The MO results have been used in conjunction with a crystal field calculation to correlate the available experimental data for these two ions.

I. Introduction

Polarized crystal spectra for the tetrachloropalladate(II) ion at liquid helium temperature have been reported by Francke and Moncuit.[1] Also, Rush, Martin, and LeGrand[2] have reported liquid helium polarized crystal spectra for the tetrachloropalladate(II) ion and the tetrabromopalladate(II) ion. Similar measurements have been carried out for the corresponding platinum(II) salts.[3,4]

We have reported experiments[5-7] where we have doped both the $PtCl_4^{2-}$ and the $PdCl_4^{2-}$ ions as substitutional impurities in cubic antifluorite hosts of the Cs_2ZrCl_6 type and observed the optical spectra at 4.2 and 2 K, respectively. In this type