Inorganic Chemistry, Vol. 17, No. 8, 1978 **2279**

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Chemical Shifts of the $L\alpha_{1,2}$ Lines of Niobium and Zirconium in the X-Ray Spectra of Niobium and Zirconium Chlorides

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Received December 13, 1976

The values of the chemical shifts of the $L\alpha_{1,2}$ lines of M (M = Nb, Zr) have been measured in the x-ray emission spectra of niobium and zirconium chlorides. It has been shown that the contribution to the total value of the chemical shift due to the formation of intermetallic (M–M) bonds is very important in the x-ray spectra of nominally low-valence niobium chlorides having a cluster structure, while in the x-ray spectra of lower valence zirconium chlorides which have a chain or layer structure this contribution is zero. These measured chemical shifts with reference to the respective metal have shown that in "noncluster" zirconium chlorides the M–M bonds are of the ordinary metallic nature featuring a cooperative character and delocalization of the charge density of the valence electrons of an M atom throughout the chloride lattice. Conversely, in cluster niobium chlorides, the M–M bonds are of an entirely different nature and constitute covalent homoatomic bonds localized in the chloride lattice within an insular cluster group. On the whole, analogous results were obtained from x-ray photoelectron spectroscopy for mononuclear and cluster molybdenum chlorides.

Introduction

In two previous papers[1,2] we showed that when studying the nature of the cluster compounds of heavy transition elements (primarily, when studying the electronic structure of M–M bonds arising in clusters), certain success could be achieved starting from a study of the effect of chemical shift of the emission lines of heavy d elements in the x-ray spectra of their mononuclear and polynuclear (cluster) compounds. These papers[1,2] presented the results of an x-ray spectral study of chromium, molybdenum, and tungsten chlorides, i.e., chlorides of elements of the same group of the periodic table. This concluding paper presents the results of a similar x-ray spectral study of the chlorides of Nb and Zr which belong to the same period of the table. Such an extension of the scope of these studies to transition elements of a very different nature enabled us to state conclusions in the strictest and most general possible form.

The chemical shifts of the $L\alpha_{1,2}$ lines of Nb and Zr in the x-ray emission spectra of niobium and zirconium chlorides were measured with reference to the respective metal using the IKF-3 Rigaku Denki spectrometer, the technique being described elsewhere.[3,4] Tables I and IV list the experimental results (average values of seven to ten measurements with mean-square errors).

Discussion and General Conclusions

In the Nb–Cl system, the magnitudes of the chemical shift of an x-ray spectral $L\alpha_{1,2}$(Nb) line vary linearly with the nominal valence of the M atoms for those chlorides in whose structures there are no clusters and in which M–M bonds are absent ($NbCl_5$, $KNbCl_6$, K_2NbCl_6, Rb_2NbCl_6, Cs_2NbCl_6, K_3NbCl_6, Figure 1). The absence of M–M bonds in such chlorides is unambiguously indicated by a highest nominal valence of the M atoms, a large M–M internuclear distance or, finally, effective magnetic moments approaching "spin only" values for the respective d^n electronic configurations of the M atoms. The corresponding characteristics[5-13] are listed in Table I. The linearity in the variation of the magnitudes of chemical shift may be associated with a successive variation of the effective number of valence electrons of an M atom which do not participate in bonding with ligands (Cl atoms) and are localized in the pseudoatomic 4d state on the core of the M atom. The number of these electrons, n(M), is the difference between the total number of valence electrons of the M atom and its nominal valence number in the given chloride, i.e., the number of its valence electrons in the M–Cl bonds. A fact which seems to be of importance is that the revealed *linear character*, which means proportionality in the variation of ΔE values with varying number of unbound 4d electrons of an M atom, corresponds to the physical nature of the effect of the chemical shift of x-ray spectral lines,[3] to the linear character of the dependence of ΔE values on the number of unbound 4d electrons of an M atom having negligible sensitivity to differences in the magnitudes of M–Cl internuclear distances, and to such important structural factors as differences in the environment of an M atom by a Cl atom (Table I for $NbCl_5$, $KNbCl_6$, K_2NbCl_6, K_3NbCl_6). As valence d electrons are stored in an unbound state on an M atom, the chemical shift value gradually decreases compared to the corresponding ΔE value for the highest chloride in whose molecular structure *all* valence electrons of an M atom participate in M–Cl bonds. Such a decrease is approximately −105 meV for $\Delta E_{L\alpha_{1,2}}$(Nb) in niobium chlorides. It can be concluded that a value of the same magnitude but of opposite sign (+105 meV) constitutes the chemical shift of the $L\alpha_{1,2}$(Nb) line which is due to each valence electron of an M atom in the M–Cl bonds in niobium chlorides.

In the Nb–Cl system, chemical shifts of the $L\alpha_{1,2}$(Nb) line always markedly deviate from the above-mentioned linearity for all nominally low-valence chlorides with a cluster structure ($Cs_3Nb_2Cl_9$, Nb_3Cl_8, $CsNb_4Cl_{11}$, Nb_6Cl_{14}, $K_4Nb_6Cl_{18}$: Figure 1, Table I; the nature of M–M bonds in the crystal lattice of $NbCl_4$ without pronounced clusters remains vague), such deviations always substantially exceeding the measurement errors of ΔE, thus surely expressing certain effective electronic interactions due to a considerable delocalization of the 4d electrons of the M atoms which are *not involved* in bonds with ligands (M–Cl). We believe that the deviations of ΔE values from a linear dependence are caused by the fact that in the cluster chlorides of heavy transition elements the value of the chemical shift of an L line of M is substantially influenced by delocalization of the valence 4d electrons of the M atoms of the M–M bonds, and the "anomalous" ΔE values thus directly indicate the occurrence of effective electronic interactions between metallic atoms in these chloride clusters. The arguments adduced in favor of this statement are not conclusive. However the following important fact speaks in favor of it: the deviations in question increase always *proportionally*, i.e., in full agreement with the physical nature of the effect of chemical shift of x-ray spectral lines and with increasing effective number n(M) of valence 4d electrons of an M atom which do not participate in M–Cl bonds and thus can be involved in M–M interactions (Table II). Futhermore, it has been stated[2] that in a series of chlorides of the same heavy transition element which involves M atoms with the same nominal valence, these deviations of ΔE values increase

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Table I. Characteristics of Niobium Chlorides

Compd	$\Delta E_{L\alpha_{1,2}}$(Nb), meV	Coordination pattern of Nb atoms	R_{Nb-Nb},[a] A	R_{Nb-Cl},[a] A	μ_{eff}, μ_B
$NbCl_5$	195 ± 10	$NbCl_6$ octahedron with a common edge	3.85	2.40	Diamag (4d^0)
$KNbCl_6$	180 ± 10	Isolated $NbCl_6^{3-}$	>6	Unknown	Diamag (4d^0)
K_2NbCl_6	75 ± 10	Isolated $NbCl_6^{2-}$	>7	Unknown	~1.7
Rb_2NbCl_6	85 ± 10				
Cs_2NbCl_6	85 ± 10				
$NbCl_4$	105 ± 10	$NbCl_6$ octahedron with two common edges	3.06	2.42	Diamag
K_3NbCl_6	−20 ± 10	Isolated $NbCl_6^{3-}$	>7	Unknown	Unknown
$Cs_3Nb_2Cl_9$	40 ± 10	$NbCl_6$ octahedron with a common face	2.70	2.45	~2.6
$Nb_3Cl_8(NbCl_{2.67})$	25 ± 10	$NbCl_6$ octahedron with two or three common edges	2.81	2.47	1.86
$CsNb_4Cl_{11}$	15 ± 10		2.86	2.51	~0
$Nb_6Cl_{14}(NbCl_{2.33})$	20 ± 10	$NbCl_4$ tetragonal pyramid with common vertices	2.92	2.45	Diamag
$K_4Nb_6Cl_{18}$	20 ± 10		2.92	2.45	Diamag

[a] Average values.

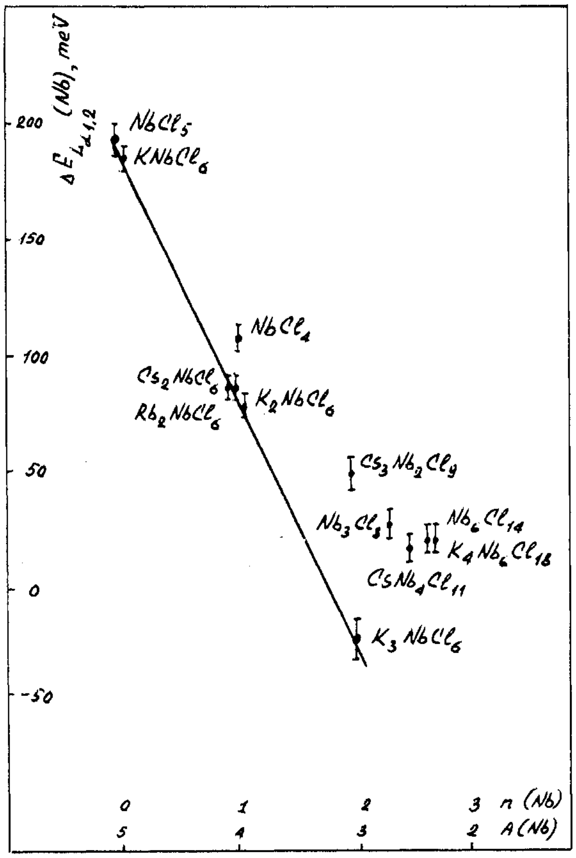

Figure 1. Values of the chemical shift of the $L\alpha_{1,2}$ line of Nb in the x-ray spectra of its chlorides: A = nominal valence of a Nb atom, n = effective number of valence 4d electrons of a Nb atom whose electrons are not involved in Nb–Cl bonding.

Table II. $\Delta E_{L\alpha_{1,2}}$(Nb) Values for Cluster Niobium Chlorides

Compd	Cluster	n(Nb)[b]	$\Delta E_{L\alpha_{1,2}}$(Nb),[a] meV	
			Σ	1/n(Nb)
$Cs_3Nb_2Cl_9$	$Nb_2Cl_9^{3-}$	1.5	64	43
Nb_3Cl_8	Nb_3Cl_8	2.33	84	36
$CsNb_4Cl_{11}$	$Nb_4Cl_{11}^{-}$	2.5	92	37
Nb_6Cl_{14}	$Nb_6Cl_{12}^{2+}$	2.67	115	43
$K_4Nb_6Cl_{18}$	$Nb_6Cl_{12}^{2+}$	2.67	115	43

[a] $\Delta E_{L\alpha_{1,2}}$(Nb) is the deviation of the chemical shift value of the $L\alpha_{1,2}$ line of Nb in the x-ray spectrum of a cluster niobium chloride calculated as the difference between the experimental value and the value expected on the basis of a linear dependence in the absence of M–M bonds. [b] n(Nb) is the effective number of the valence 4d electrons of each Nb atom which participate, in a respective chloride cluster, in the formation of M–M bonds. This number has been determined as the result of semiempirical calculations of the electronic structure of these clusters.[14-16] The value of n(Nb) for $Cs_3Nb_2Cl_9$ as well as for $A_3Mo_2Cl_9$[2] has been evaluated on the basis of a previously obtained dependence of the effective number of d electrons of each M atom in M–M internuclear distance in the chloride clusters of 4d and 5d elements.[15]

with decreasing M–M internuclear distances and simultaneously decreasing effective magnetic moments, i.e., with strengthening M–M bonds.

It follows from the data of Table II that the $\Delta E_{L\alpha_{1,2}}$(Nb) values due, in our opinion, to direct M–M bonds arising in cluster niobium chlorides are close to one another when calculated per valence 4d electron of a Nb atom in Nb–Nb bonds. The closeness of the $\Delta E_{L\alpha_{1,2}}$(Nb) values per valence 4d electron of a Nb atom in Nb–Nb bonds probably enables their mean value (approximately 40 meV) to be interpreted as the chemical shift of the $L\alpha_{1,2}$(Nb) line due to one 4d electron of a niobium atom involved in M–M bonds within the cluster chloride. Attention is drawn to the fact that in the studied cluster chlorides of niobium the value of the chemical shift of an L line of M per valence 4d electron in M–M bonds is 2–3 times less than the corresponding value due to one valence 4d electron involved in M–M bonds. This result is highly probable since the "reflow" of the charge density of the valence 4d electron of an M atom to its more electronegative partner, i.e., a Cl atom, should in fact occur to a greater extent upon formation of homoatomic M–M bonds than upon formation of M–Cl bonds. Note finally that the values of the chemical shift of the $L\alpha_{1,2}$(Nb) line in niobium chlorides which are due to one 4d electron of Nb involved in Nb–Cl or Nb–Nb (105 and 40 meV) bonds are rather close to the respective values[2] of the $L\alpha_{1,2}$(Mo) in chlorides of molybdenum (115 and 30 meV), the nearest neighbor of niobium in the periodic table. And this quite natural result supports the developed interpretation in its most general form.

Thus, the experimental values of the chemical shift of the $L\alpha_{1,2}$(Nb) line in the x-ray spectra of cluster chlorides of niobium cannot be accounted for by the existence of M–Cl bonds only. Instead, they can be naturally interpreted on the assumption of the simultaneous formation of M–M bonds. In

Table III. Absolute Energies of the Inner $3d_{5/2}$(Mo) Level for Molybdenum Chlorides and Their Chemical Shifts (±0.1 eV)

Nominal valence no. of M atoms	Compd		$E_{3d_{5/2}}$, eV	$\Delta E_{3d_{5/2}}$, eV
	Type	Formula		
5	Mononuclear	$MoCl_5$	231.0	4.0
	Cluster	Unknown		
4	Mononuclear	K_2MoCl_6	229.1	2.1
	Cluster	Unknown		
3	Mononuclear	K_3MoCl_6	228.2	1.2
		Cs_3MoCl_6	227.8	0.8
	Cluster	$MoCl_3$	229.8	2.8
		$K_3Mo_2Cl_9$	229.4	2.4
		$Cs_3Mo_2Cl_9$	229.0	2.0
2.5	Mononuclear	Unknown		
	Cluster	$Rb_3Mo_2Cl_8$	231.6	4.6
		$Cs_3Mo_2Cl_8$	231.8	4.8
2	Mononuclear	Unknown		
	Cluster	$K_4Mo_2Cl_8$	231.5	4.5

other words, the experimental values of $\Delta E_{L\alpha_{1,2}}$(Nb) are direct evidence for the occurrence of effective electronic interactions between metallic atoms in the nominally low-valence chlorides of niobium for which the presence of direct M–M bonds has been earlier assumed on the basis of the cluster nature of these chlorides (we mean the detection by x-ray diffraction analysis of M atoms directly contacting one another), of shortened M–M internuclear distances, and of largely reduced effective magnetic moments down to diamagnetism.

The same results were obtained formerly[1,2] from x-ray spectral investigations of mononuclear and cluster chlorides of Mo and W.

The experimental values of the chemical shift of the K and L lines in the x-ray spectra of all of the mononuclear and cluster chlorides of Nb, Mo, and W studied agree with the notions of their nature which follow from the results of the experimental study of their characteristics and magnetic behavior. The x-ray spectral characteristics of the cluster chlorides of niobium, molybdenum, and tungsten satisfactorily agree with the results of theoretical calculations of the electronic structure of the respective chloride clusters (the ratios and orders of two-center M–M bonds, the effective number of valence d electrons of each atom in M–M bonds in a cluster, etc.), the calculations being performed using the semiempirical methods of molecular orbital theory.[15,16]

On the whole, analogous results were obtained from x-ray photoelectron spectroscopy for mononuclear and cluster molybdenum chlorides. We have measured the absolute energies of the inner $3d_{5/2}$(Mo) level for these compounds using the 5950-A Hewlett-Packard spectrometer. The chemical shifts of the $3d_{5/2}$(Mo) level were measured with reference to the bulk molybdenum as "$3d_{5/2}$ E(compound) − $3d_{5/2}$ E(metal)", the latter value being 227.0 eV. Table III lists the experimental results. For the fixed nominal valence number of M atoms the chemical shifts of the $3d_{5/2}$(Mo) level for cluster molybdenum chlorides are always larger in comparison with mononuclear molybdenum chlorides at the expense of metal–metal bonds within insular cluster groups.

The Nature of M–M Bonds in the Chloride Clusters of Heavy Transition Elements

For the cluster compounds of the transition elements which have been studied by various experimental and theoretical methods, the principal question of what the direct bonds formed between metallic atoms are in their physical nature has not been as yet explicitly discussed. This situation is obviously due to the fact that none of the methods used so far has a sensitivity sufficient to clear up the question of whether M–M bonds in clusters are close in physical nature to the ordinary bonds between M atoms in the structure of respective metallic crystals or, to the contrary, whether they constitute an entirely different kind of M–M interaction which is dissimilar to the ordinary metallic bond. The x-ray spectral characteristics of cluster compounds as presented in this paper enable quite definite notions to be stated in this respect.

In the Nb–Cl, Mo–Cl, and W–Cl systems, with the occurrence of valence 4d or 5d electrons in M–M bonds and with the increasing number of such electrons in M–M interactions in the cluster chlorides of niobium, molybdenum, or tungsten, a successive increase in the magnitudes of the chemical shift of a K or L line of M occurs as against the ΔE values for respective mononuclear chlorides of the metal which contain no M–M bonds and comprise the metal in the same nominal valence state, i.e., with the same number of valence electrons of an M atom as in M–Cl bonds. In other words, with a fixed nominal valence of a metal, the values of the chemical shift of a K or L line of M for its cluster chlorides *always deviate* from the linear dependence which describes the charge in ΔE values with a varying number of valence electrons of an M atom in M–Cl bonds in metal chlorides without M–M bonds, this deviation being directed *toward a higher chloride* in which all of the valence electrons of an M atom are involved in M–Cl bonds and thus the maximum valence of the metal is affected (Figure 1 for the Nb–Cl system). Thus, the formation of M–M bonds in a cluster chloride always and without a single exception shifts the ΔE value, unlike in a respective mononuclear chloride, in the direction in which the ΔE value is shifted with increasing number of valence electrons of an atom which are involved in the covalent bonds with ligands. This only means that in the cluster chloride of a heavy transition metal, M–M bonds form just as M–Cl bonds do. Just as with the formation of M–M bonds the charge density of the valence electrons of an atom of M reflows from their skeleton to the bond region. The resulting additional decrease in the charge density of the valence electrons of an M atom on its skeleton (in addition to M–Cl bonds) thus reflects physically an increase of the true valence of a heavy transition element in its cluster chloride which is due to one or several valence d electrons of an M atom whose electrons are involved in M–M interactions as against the nominal valence that is provided by a certain number of valence electrons of an M atom whose electrons are involved only in the formation of metal–ligand bonds. It is in this sense that the true valence of a 4d or 5d element in its cluster chlorides considerably exceeds the nominal valence, sometimes by a factor as large as 2–3. All of this confirms the conclusions about the atomic states of 4d or 5d elements arrived at earlier[15,16] starting from the results of semiempirical calculations of the electronic structure of the chloride cluster of these elements.

Thus, the M–M interactions in the chloride clusters of heavy transition elements are close in nature to the homoatomic covalent bonds. These interactions appear to be localized bonds (despite the fact that they may often be multicentered bonds within an insular cluster grouping in the chloride lattice), quite dissimilar to the ordinary metallic bonds with their cooperative character.

Were the M–M interaction in chloride clusters and the ordinary metallic bonds not so different in nature and, just the opposite, were they close together on the character of the distribution of the charge density of those valence electrons of an M atom which are not involved in these interactions, then the value of the chemical shift of a K or L line of M in the x-ray spectrum of a cluster chloride would not have deviated from the linear dependence for mononuclear chlorides in the absence of M–M bonds. Were the M–M interactions in a chloride cluster actually close in nature to the ordinary metallic bonds, then, when measuring the ΔE values *with reference to a respective metal*, the contribution to the total value of the

Table IV. Characteristics of Zirconium Chlorides

Compd	$\Delta E_{\mathrm{L}\alpha_{1,2}}$(Zr), meV	Coordination pattern of Zr atoms	$R_{\mathrm{Zr-Zr}}$, A	$R_{\mathrm{Zr-Cl}}$, A	μ_{eff}, μ_{B}	n(Zr)
$ZrCl_4$	195 ± 10	$ZrCl_6$ octahedron with two common edges	>4	2.31 to 2.66	Diamag ($4d^0$)	0
Na_2ZrCl_6	180 ± 10	Isolated $ZrCl_6^{2-}$	>7	Unknown	Diamag ($4d^0$)	0
$ZrCl_3$	125 ± 10	$ZrCl_6$ octahedron with two common faces	3.05	2.50	Unknown	1
$ZrCl_2$	45 ± 10	$ZrCl_6$ trigonal prism with common faces	3.38	2.59	Diamag	2
ZrCl	−50 ± 10	$Zr[Zr_3Cl_3]$ trigonal antiprism	2.87	3.10	Unknown	3

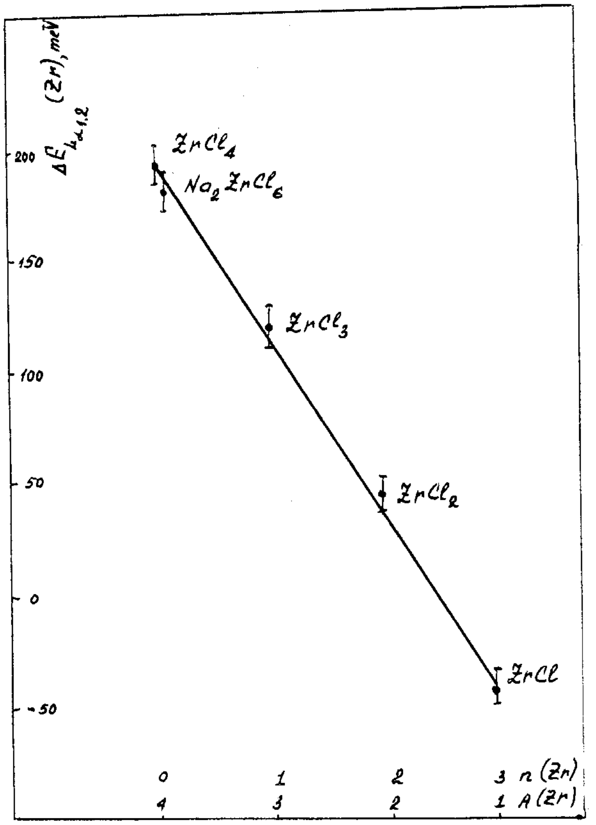

Figure 2. Values of the chemical shift of the $\mathrm{L}\alpha_{1,2}$ line of Zr in the x-ray spectra of its chlorides: A = nominal valence of a Zr atom, n = effective number of valence 4d electrons of a Zr atom whose electrons are not involved in Zr–Cl bonding.

chemical shift of a K or L line of M in the x-ray spectrum of the cluster chloride which is due to the formation of M–M bonds would have been *zero because of the additivity* inherent in the very nature of the chemical shift.[3]

To test this hypothesis, we studied the x-ray spectral characteristics of zirconium chlorides. In the crystal lattice of the nominally low-valent zirconium chlorides $ZrCl_3$, $ZrCl_2$, and ZrCl there are no clusters, and Zr atoms form either endless chains or layers.[17-19] The chain or layer structure of $ZrCl_3$, $ZrCl_2$, and ZrCl suggests rather that M–M bonds in these chlorides must be close to the ordinary metallic bonds in solid zirconium as evidenced, among other things, by a pronounced conductivity anisotropy of ZrCl reflected by a very high conductivity in the layers.[17,18]

That is why we expected a linear variation of the ΔE values in the series of all known zirconium chlorides and the absence of any deviations, i.e., anomalously high ΔE values, for zirconium nominally low-valent chlorides. The experimental values of the chemical shift of the $\mathrm{L}\alpha_{1,2}$ line of Zr, measured with respect to metallic zirconium, in the x-ray spectra of its chlorides, together with their known characteristics, are represented in Table IV as well as in Figure 2. In complete agreement with predictions, the dependence of the $\Delta E_{\mathrm{L}\alpha_{1,2}}$(Zr) values on the nominal valence of zirconium and on the effective number of valence 4d electrons of each Zr atom whose electrons are not involved in bonds with ligands is of a pronounced linear character without a single deviation. This confirms the ordinary metallic character of M–M bonds delocalized over the crystal of a lower "noncluster" zirconium chloride such as $ZrCl_3$, $ZrCl_2$, or ZrCl. This linear dependence is an indication of zero contribution to the total value $\Delta E_{\mathrm{L}\alpha_{1,2}}$(Zr) due to the formation of M–M bonds in the lowest zirconium chloride.

Thus, the study of the values of the chemical shift of the K or L line of M not only provides essential data on the characteristics of the electronic structure of these compounds and enables one to register the occurrence of direct M–M bonds in clusters and study the electronic structure of these bonds but also results in a nontrivial approach to the problem of the physical nature of direct electronic interactions between metallic atoms in clusters.

Registry No. $NbCl_5$, 10026-12-7; $KNbCl_6$, 16919-88-3; K_2NbCl_6, 19228-76-3; Rb_2NbCl_6, 19385-33-2; Cs_2NbCl_6, 16921-16-7; $NbCl_4$, 13569-70-5; K_3NbCl_6, 21324-43-6; $Cs_3Nb_2Cl_9$, 31810-68-1; Nb_3Cl_8, 12052-04-9; $CsNb_4Cl_{11}$, 65101-98-6; Nb_6Cl_{14}, 12133-87-8; $K_4Nb_6Cl_{18}$, 12371-25-4; $MoCl_5$, 10241-05-1; K_2MoCl_6, 16918-76-6; K_3MoCl_6, 13600-82-3; Cs_3MoCl_6, 33519-12-9; $MoCl_3$, 13478-18-7; $K_3Mo_2Cl_9$, 24355-00-8; $Cs_3Mo_2Cl_9$, 23667-86-9; $Rb_3Mo_2Cl_8$, 24436-24-6; $Cs_3Mo_2Cl_8$, 24436-25-7; $K_4Mo_2Cl_8$, 25448-39-9; $ZrCl_4$, 10026-11-6; Na_2ZrCl_6, 18346-98-0; $ZrCl_3$, 10241-03-9; $ZrCl_2$, 13762-26-0; ZrCl, 14989-34-5.

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