Table III. Rate Constants (25°) for Reactions of V(III) with Halate Ions

Reaction	Rate const, M^{-1} sec^{-1}
$V^{3+} + IO_3^-$	189[a]
V^{3+} + Br(V)	3-6[b]
$V^{3+} + ClO_3^-$	2.0[c]

[a] This work; reaction may also be assigned to $VOH^{2+} + HIO_3$ in some part. [b] This work; [H⁺] dependence not investigated; $[H^+] = 0.83\,M$, $[V(III)] = 0.012\,M$, $[Br(V)] = 5 \times 10^{-4}\,M$. [c] Unpublished work, quoted in ref 4; temperature 20°, $[H^+] = 0.5$–$0.6\,M$, $\mu = 2.0$–$3.0\,M$.

for the complexing of NCS^- with V^{2+}.[38] It is concluded that substitution of chlorate into the V^{2+} coordination sphere does not occur prior to electron transfer. No conclusions can be drawn regarding the mechanism of the V^{2+} reduction of Br(V) based on present information.

One- and two-equivalent reactions of V^{3+} are less easily distinguished because the reaction of VO_2^+ with V^{3+} is rapid[25] and produces the 1-equiv product VO^{2+}, (13). None of the reactions of I(V), Br(V), or Cl(V), Table III, exceeds the rate of this reaction so that a distinction cannot be made on this basis. If however a 2-equiv process occurred, then extensive hydrolysis of the V(III) would have to precede formation of VO_2^+ or a less hydrolyzed (and therefore less stable) form of V(V) would be produced. In either case relatively high enthalpies of activation would be required. If the k_6 ($V^{3+} + IO_3^-$) step prevails, then there is no prior hydrolysis of the V^{3+} reactant, and it is difficult to envisage a 2-equiv change. For the $k_7K_3K_4$ ($VOH^{2+} + HIO_3$) path the enthalpy of activation for k_7 will be small (ca. 5 kcal mol^{-1}) after allowing for ΔH_3[22] and ΔH_4[23] and hardly seems consistent with a 2-equiv change. Moreover observations on the V(III) reduction of the strong oxidant Tl(III) have indicated that in this instance 1-equiv reactions are favored.[18,19]

Substitution on V^{3+} is thought to proceed by an associative mechanism with rate constants varying between 3 M^{-1} sec^{-1} for Cl^- [39] and 10^3 M^{-1} sec^{-1} for NCS^-.[40,41] The reactions of the halate ions, Table III, lie within this range, and it is therefore possible that they proceed by inner-sphere mechanisms.

Registry No. V(III), 22541-77-1; V(II), 15121-26-3; iodate, 15454-31-6; bromate, 15541-45-4.

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Comprehensive Study of Satellite Structure in the Photoelectron Spectra of Transition Metal Compounds

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A wide variety of different transition metal compounds have been studied for their satellite structure found in photoelectron spectra, with specific emphasis on the 2p shell of the first-row transition metals. In particular, data on halides and cyanide complexes are presented. Results on second- and third-row transition metal compounds are also discussed. The relative roles of electron shake-up and multiplet splitting for producing the satellite structure are evaluated. The behavior of the satellite structure is generalized as a function of metal ion and ligand and the energy spacing of the metal and ligand orbitals. It is ascertained that the large, well-defined satellite peaks are due to electron shake-up involving excitation of electrons from a ligand to a metal orbital.

Introduction

Some satellite structure is commonly observed in most photoelectron spectra. It is the result of the ejected electron created in the photoejection process undergoing some energy loss. This loss can be caused by either internal or external means. In the latter case the photoelectrons undergo inelastic collisions as they pass through the material. Such losses are characteristic of the material but not of the photoionization process. For most insulators the satellite structure due to

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electron collision is generally very broad with a long low-energy tail and a peak about 15–25 eV below the main peak. In the case of internal losses the ion with a single-hole configuration created by photoionization may be left in an excited state, and the satellite structure will appear at a kinetic energy below the normal photoelectron line, which is equal to the energy of excitation. This structure often consists of sharp peaks and is dependent on the nature of the molecular orbitals. In solids, satellite structure is observed in the presence of a large general background of secondary electrons. However, for transition metal compounds the satellite structure is often very intense and easily discernible and will be the subject of this paper.

When photoionization takes place in the 2p shell of the metal for various first-row transition metal compounds, there are two principal sources for internal excitation that are possible: electron shake-up and multiplet splitting. Electron shake-up results from monopole excitation of electrons in the valence shell as the result of a change in central potential caused by the sudden removal of an electron from a core shell. Multiplet splitting results from the coupling of a hole formed in the core shell with a valence shell that is only partially filled.

In this paper we shall first outline the basic nature of the processes leading to satellite structure and their relative importance in the photoelectron spectra of the 2p shell of the transition metal ion. Next, we shall take an overview of the experimental results on transition metal compounds using data on some 60 different systems that we have studied, mainly, halides, cyanides, and thiocyanates for the various members of the first-row transition metal compounds. Data on second- and third-row transition metal compounds are also discussed. A number of other studies on satellite structure in the 2p shell of transition metal compounds have appeared in the literature,[2-13] and we have used these data to confirm and supplement our conclusions. From the generalizations of the experimental data, an overall model of the nature of the excitation process is derived and the possible causes for the presence and extent of satellite structure as a function of chemical bonding are given. Much of the discussion is a verification and clarification of earlier results, but it is believed that this broad overview will give greater confidence to the final conclusions.

Experimental Section

Photoelectron spectra were obtained using a double-focusing electrostatic spectrometer designed and built in the Physics Division of the Oak Ridge National Laboratory. A detailed description of the instrument is given elsewhere.[14] The spectra are taken in 50-eV segments, and by the use of a sawtooth voltage in synchronization with the advance of a multichannel analyzer, the spectra are continuously swept every 100 msec. Characteristic Al $K\alpha_{1,2}$ x rays (1487 eV) produced by bombarding an Al anode with 8-keV electrons were employed as the photon source.

In addition to spectra associated with the 2p shell of the first-row transition metal ions, spectra were also taken of the 3s and 3p subshells as an aid in confirming the integrity of the sample. For the second- and third-row transition metals, the 3d and 4f subshells were chosen respectively for the study of core-shell photoionization. Spectra of the counterions were also obtained in order to analyze for characteristic energy losses. The spectra were observed as a function of time to ascertain whether any radiation damage might alter the results.

The spectra were deconvoluted with the help of a Du Pont 310 curve resolver. A smooth background was substituted, whose shape was arbitrarily chosen to include consideration of characteristic energy losses, and was patterned after detailed analysis of a few systems, which included specific contributions from characteristic energy losses as derived from photoelectrons emitted from one of the counterions.

The compounds studied were either commercially obtained analytical reagents or prepared at the University of Illinois and were used without further purification. Some materials, which were sensitive to handling in air, were loaded in a drybox and transferred under argon atmosphere to the spectrometer in a double-valve transfer chamber.

Basic Nature of Satellite Structure

Before presenting the experimental data on satellite structure, it will be necessary to discuss briefly the many sources for this structure. For the 2p shell of the first-row transition metal compounds these are (1) characteristic energy losses from electrons passing through the solid, (2) electron shake-up, and (3) multiplet splitting. Finally, we shall discuss the relative importance of multiplet splitting and electron shake-up for the 2p shell.

A. Characteristic Energy Losses. As an electron passes through a solid, it may undergo inelastic collisions due to such processes as plasmon excitation and interband excitation. In most insulators this manifests itself in the photoelectron spectrum as a broad peak at about 15–25 eV lower energy than the main peak and with a long tail stretching toward lower kinetic energy. Its shape and intensity depend essentially on the material through which the electron is passing and not on which orbital underwent photoionization. Thus, a broad satellite structure, common to all photoelectrons (and Auger electrons), can usually be attributed to characteristic energy losses.

B. Electron Shake-up. Normally, in x-ray photoelectron spectroscopy the primary electron leaving an atom or molecule has a large kinetic energy. It may be possible that this energy is "shared" with valence electrons, to promote another electron either to an excited state or to a continuum state. These processes are termed electron "shake-up" and electron "shake-off", respectively, and are discussed in several papers.[15-17] Electron shake-up and shake-off are actually special cases of configuration interaction.

The photoelectron emission process is governed by the dipole mechanism

$$\sigma \propto |\langle \psi_{\text{final}} | \vec{x} | \psi_{\text{initial}} \rangle|^2 \tag{1}$$

where the ψ's are N-electron wave functions. In the one-electron orbital limit

$$\sigma \propto |\langle U_{\mathrm{k}} | \vec{x} | \theta \rangle|^2 \tag{2}$$

where $|U_{\mathrm{k}}\rangle$ is a free-electron wave function and $|\theta\rangle$ is the orbital from which the electron came. For a two-electron process in the one-electron orbital limit

$$\sigma \propto \sum_{\mathrm{f,i}} |\langle U_{\mathrm{k}}(1) | x | \theta(1) \rangle|^2 |\langle \theta_{\mathrm{f}}'(2) | \theta_{\mathrm{f}}(2) \rangle|^2 \tag{3}$$

where $\theta_{\mathrm{i}}(2)$ is the initial orbital of the second electron and $\theta_{\mathrm{f}}'(2)$ is the final wave function of the second electron and is an eigenstate of the new Hamiltonian. Since there is no vector or tensor operator in the second matrix element, the selection rules for the second factor are of the monopole type. This has two consequences: representation of the wave functions θ_{f}' and θ_{i} must be such that $\theta_{\mathrm{f}}' \times \theta_{\mathrm{i}}$ contains the A_1 representation. If parity is a good quantum number, it must be conserved as must be angular momentum. The description of the symmetry state is, of course, contained in the Hartree–Fock approximation and may not be completely valid when applied to the real N-electron wave function. For example, Martin and Shirley[17] have suggested that calculations of electron shake-up probabilities include configuration mixing in both the initial and final states. We shall, however, put aside this added complexity for our discussion.

Using the sudden approximation, the expression for the probablity of a particular shake-up satellite occurring is

$$P = |\int \psi_{\mathrm{f}}^{*\prime} \psi_{\mathrm{i}} \mathrm{d}\tau|^2 \tag{4}$$

where $\psi_{\mathrm{f}}^{*\prime}$ is the wave function of the complex with a core hole in that particular configuration.

For atomic "shake-up" transitions one would expect s →

s, p → p, and d → d transitions. For electron shake-up in molecules one would expect $\sigma_{g,u} \rightarrow \sigma_{g,u}$ and $\pi_{g,u} \rightarrow \pi_{g,u}$ transitions with g → u transitions forbidden in both cases. For first-row transition elements, $\vec{L}$ and $\vec{S}$ are good quantum numbers; therefore, one would expect selection rules $\Delta\vec{L}$, Δm_l, $\Delta\vec{S}$, $\Delta m_s = 0$ to apply. For systems containing high-field ligands, orbital angular momentum is quenched and $\vec{S}$ is the only good angular momentum quantum number leading to selection rule $\Delta\vec{S}$, $\Delta m_s = 0$. Likewise for heavier elements with strong spin–orbit coupling, the relevant quantum number is $\vec{J} = \vec{L} + \vec{S}$ giving selection rule $\Delta\vec{J}$, $\Delta m_j = 0$.

Though the extent of overlap is tied fundamentally to the effect of creating an inner-shell vacancy, shake-up transitions are often enhanced if the transition energies are lowered and the electrons of the initial and final state orbitals tend to occupy the same space. For example, in rare gas atoms the transition rates to the various Rydberg states are largest for the first excited state and decrease rapidly as the principal quantum number increases.[18] Also calculations[19] on the probability of electron shake-off from the valence shell of rare gases show a decrease as the atomic number increases in parallel with the decrease in ionization potential. Inference between the shake-up probability and excitation energy, however, must be taken with caution.

C. Multiplet Splitting. Exchange interactions between electrons of like spin can give rise to states of different energy, as expressed by

$$V_{\mathrm{ex}} = -\iint \delta s_1 s_2 \sum_{a \neq b}\sum \psi_a{}^*(1)\psi_b(2)\frac{e^2}{\gamma_{r_{12}}}\psi_a(2)\psi_b(1)\,d\vec{r}_1\,d\vec{r}_2 \qquad (5)$$

Where there exists one or more electrons in the valence shell with unpaired spins, the act of photoionization in the core shell will lead to more than one final state, depending on the ways in which the unfilled shells couple. Because of the $1/r$ dependence, the exchange interaction will rapidly diminish with an increase in the difference between the principal quantum number of the valence shell and the location of the core vacancy. If photoionization takes place in a p shell, a large number of multiplet states can result, particularly when configuration interaction is permitted.[20] Calculations suggested that energy splitting could be as high as 11.7 eV as the result of 2p photoionization in the first-row transition metal compounds.[21]

Electron Shake-up vs. Multiplet Splitting. What are the relative roles played by electron shake-up and multiplet splitting? In the case of the first-row transition metal compounds this question has been answered by studying the satellite structure associated with photoionization in the K shell. Calculations[22] demonstrated that the relative probability and excitation energy for electron shake-up are essentially independent of whether the photoionization takes place in the K or L shell, while multiplet splitting decreases rapidly as one goes to the inner shells and for the K shell is negligible (less than 0.1 eV). Studies on 12 different iron and manganese compounds showed[22,23] that when large satellite peaks were observed in the 2p shell, similar satellites were found in the K spectrum indicating that electron shake-up and not multiplet splitting is the source of these peaks. This observation is confirmed by the study of satellites found in the Kα x-ray spectrum of transition metal compounds. In these studies x-ray satellites will occur with multiplet splitting, the spacings being the same as with photoionization in the 2p shell. However, electron shake-up from the valence shell will not be observed in the K–$L_{II,III}$ x-ray transition except as a small perturbation to the multiplet splitting. For example, in spite of the fact that substantial satellite structure was found in the photoelectron spectrum of the 2p shell of nickel compounds, very little or none was seen[24] in the satellites of the Kα x rays of the same compounds, showing that the large distinct satellite peaks were not due to multiplet splitting.

The role that multiplet splitting plays has been clarified by calculations of Gupta and Sen[25] on MnF_2. These calculations include effects of first-order configuration interaction, spin–orbit splitting, and crystal field effects. They show that although multiplet splitting results in a number of final states, some of which are widely separated in energy, the net effect to the observed spectrum is to broaden the normal $2p_{1/2}$ and $2p_{3/2}$ photo peaks and to increase the energy separation between them rather than to produce well-defined satellite peaks. The calculations have been verified by careful comparison[26] with experimental data on MnF_2.

In summary, when no satellite structure is present, we see simply two peaks in the 2p photoelectron spectrum of transition metals with an intensity ratio of approximately 2:1 corresponding to the $2p_{3/2}$ and $2p_{1/2}$ subshells. Multiplet splitting broadens these peaks and causes a slight separation of their peak positions. Electron shake-up gives rise to a well-defined satellite peak which has an intensity and energy relative to the main peak that is essentially the same for both the $2p_{3/2}$ and $2p_{1/2}$ subshells.

Results and Discussion

Results on the satellite structure seen in the photoelectron spectra of the 2p shell of transition metals are given in Table I. The satellite intensity is given as the intensity of the main satellite peak relative to that for the "normal" $2p_{3/2}$ photoelectron peak. The satellite excitation energy is taken as the separation in energy between the peaks of the satellite structure and the main $2p_{3/2}$ photoelectron line. In cases where multiple structure is clearly visible, peak positions and intensities of the secondary satellite lines are also given in parentheses. Although the results quoted are relative to the $2p_{3/2}$ subshell, similar structure is also seen in each case for the $2p_{1/2}$ subshell. Some outside data from the literature are listed to help supplement the discussion. There are only a few examples of data on vanadium compounds because the O(1s) spectrum interferes with the V(2p) spectrum, and oxygen is a common constituent or impurity.

The results on the satellite structure can be collected into eight generalizations which are given below and discussed in detail.

(1) Pure metals do not show strong satellite structure in the 2p shell other than the usual plasmon losses. However, some asymmetry in the main peaks is observed and attributed to relaxation of the Fermi sea about the core hole.[27]

(2) The photoelectron spectra of the metal oxides do not always show well-defined satellite peaks associated with the metal 2p subshells. Exceptions to this generalization are found with Sc_2O_3, TiO_2, CoO, and CuO. For the other compounds the main lines are broadened and show evidence of shoulders or asymmetry. This behavior may be due to multiplet splitting or to excitation involving transitions between insulator and conduction bands, which for some of these semiconductors is in the range of 2–3 eV.[28]

(3) Little satellite structure is found in the photoelectron spectra of the cyano complexes. There are some extra peaks found at higher excitation energy of about 12–16 eV. However, these peaks are seen in the N(1s) and K(2p) spectra as well as the metal 2p spectra. See, for example, Figure 1. The N(1s) data indicate the presence of two peaks, the second satellite of smaller intensity and about twice the energy of excitation, not unsimilar to the behavior of plasmon excitation. The first satellite peak seen in the iron spectrum is partially obscured by the main $2p_{1/2}$ peak and the second satellite peak and probably contains contributions from photoionization in both the $2p_{3/2}$ and $2p_{1/2}$ subshells. The comparative behavior of satellite structure as a function of atomic site in the molecule

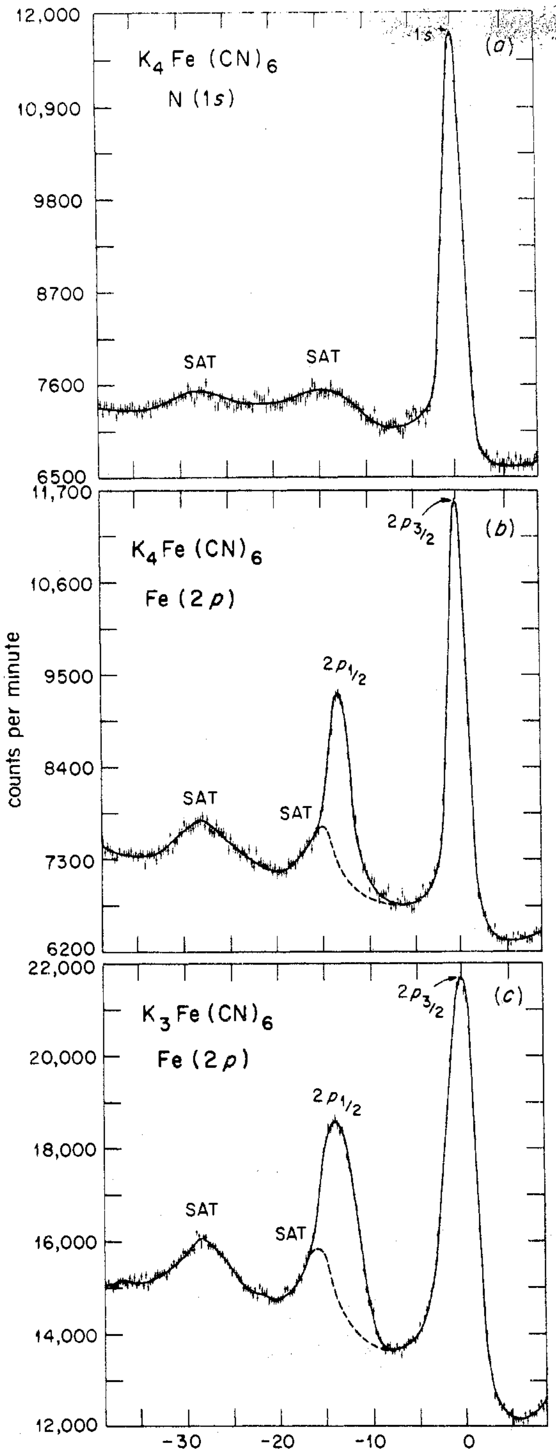

Figure 1. Photoelectron spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ using Al Kα x rays. Spectra b and c arise from photoionization in the 2p shell of iron while spectrum a comes from photoionization in the 1s shell of nitrogen. The kinetic energies of the photoelectrons are relative to that of the main peak. SAT represents satellite structure. The satellite structure in b and c at −25 to −30 eV probably contains contributions from photons in both the $2p_{1/2}$ and $2p_{3/2}$ subshells.

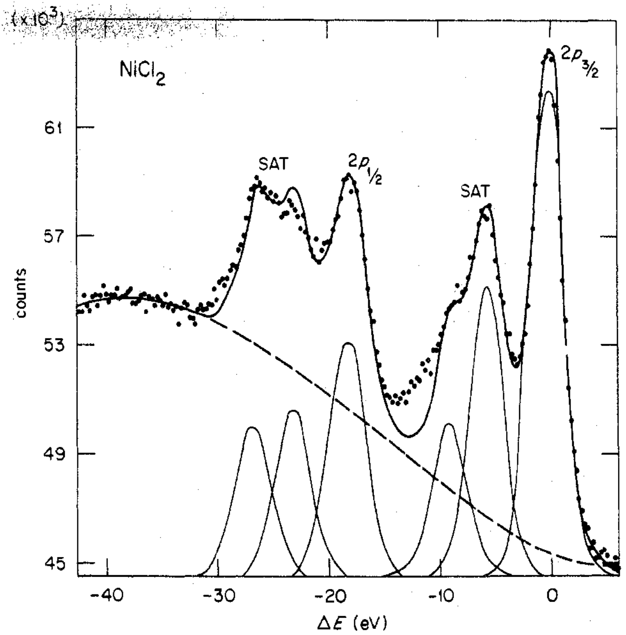

Figure 2. Photoelectron spectra of NiCl ionized in the 2p shell of Ni with Al Kα x rays. The kinetic energies of the photoelectrons are related to that of the main peak. SAT represents satellite structure. The satellite structure has been deconvoluted into two peaks. The approximate background including characteristic energy losses is given by the dotted line.

suggests that the satellite structure is independent of the photoionization process and may be partly or completely due to characteristic energy losses. The absence of high-intensity, low-energy satellite peaks in the cyano complexes may be understood by the fact that the cyanide electrons are tightly bound and localized between the carbon and nitrogen atoms. The energy differences between metal 3d levels and filled $C{\equiv}N^-$ π and σ levels are fairly large.[29]

As is also seen in Figure 1, the 2p photoelectron peaks of diamagnetic compounds (in this example, $K_4Fe(CN)_6$) have much narrower bandwidth and a slightly greater separation between the $2p_{1/2}$ and $2p_{3/2}$ peak positions, indicative of the absence of multiplet splitting.

(4) In general the transition metal halides show substantial satellite structure in the photoelectron spectra of the 2p shell for the metal ions. The behavior of the thiocyanate ion with regard to satellite structure is much like that of the chloride ion. For iron and manganese compounds the intensity of the satellite structure increases as one goes from the more electronegative element to the more covalent species: $F < Cl < Br < I$. For the configuration d^0 (Sc, Ti) the fluorides show greater intensities than the other halides. For Cr, Co, and Ni the intensities of satellites are not strongly dependent on the nature of the halide. For Cu(II) halides there is a slight decrease in intensity as one goes from CuF_2 to $CuBr_2$, accompanied by an increase in excitation energy.

(5) For transition metal compounds having a strong satellite structure in the 2p shell there is generally only one peak associated with each subshell. For some cobalt-, nickel-, and copper(II) complexes the satellite structure can be easily convoluted into more than one peak. (See Figure 2.) However, in contrast to satellite structure for gases, where one can observe a complex structure in which individual peaks rarely reach 10% of the main peak, these studies reveal that there is an unusually large transition probability to one state or a group of states, whose energies are closely spaced. Thus, one is encouraged to look for a shake-up transition that is characterized by a particular type of excitation.

(6) Satellite structure for the transition metal complex is generally most intense for paramagnetic compounds and for compounds of high-field ligands. Exceptions to this generalization are the d^0 compounds, i.e., Sc and Ti, and some of the high-field ligand–cobalt(III) complexes, although even in these cases the intensities are still lower than for the paramagnetic species. For all the diamagnetic compounds of

Table I. Satellite Structure in the Photoelectron Spectrum of the $2p_{3/2}$ Shell of Transition Metal Compounds

Compd	ΔE,[a] eV	I[b]	Compd	ΔE,[a] eV	I[b]
ScF_3	12.2^{d}	0.23	$CoBr_2$	4.9^{d}	0.69^{d}
$ScCl_3$		$Negl^{c}$	$CoBr_2$	4.7^{i}	1.20^{i}
$ScBr_3$	12.2	~ 0.1	CoI_2	$3.9\ (6.1)^{d}$	$0.50\ (0.41)^{d}$
$Sc(acac)_3$	12.7^{d}	0.16^{d}	CoI_2	$3.8\ (7.1)^{i}$	$0.59\ (0.45)^{i}$
Sc_2O_3	11.7^{l}	0.4^{l}	$Co(SCN)_2$	3.2 (6.4)	0.69 (0.55)
TiF_3	13.0^{d}	0.11^{d}	$K_3Co(CN)_6$	$12.2^{d,f}$	$0.13^{d,f}$
TiF_4	14.7^{d}	0.11^{d}	$Co(NH_3)_3(NO_2)_3$	4.9	0.28
K_2TiF_6	14.0^{d}	0.16^{d}	$[Co(NH_3)_4Cl_2]Cl$	5.1 (10.0)	0.24 (0.12)
TiO_2	13.5^{d}	0.12^{d}	$[Co(NH_3)_5Cl]Cl_2$	4.7 (9.3)	0.16 (0.09)
TiO_2	13.0^{l}	0.25^{l}	$HgCo(SCN)_4$	6.3	0.31
$Ti(acac)_4$	13.2^{d}	0.08^{d}	$Co_2(CO)_8$	4.7^{d}	0.66^{d}
VF_3	13.0	$\sim 0.1^{e}$	CoO	$4.7\ (9.2)^{i}$	$0.38\ (0.13)^{i}$
VF_4	14.4	$\sim 0.1^{e}$	$Co(en)_3Cl_3$	4.9 (6.9)(9.6)	0.29 (0.18)(0.10)
$K_2Cr_2O_7$		Negl	$(TEA)_2CoCl_4$		0.48^{h}
CrF_3	11.8^{d}	0.25^{d}	$(TMA)_2CoCl_4$		0.50^{h}
$CrCl_3$	10.3^{d}	0.16^{d}	$(TEA)_2CoBr_4$		0.55^{h}
$K_3Cr(NCS)_6$	12.5^{d}	0.17^{d}	$(TEA)_2Co(NCS)_4$		0.44^{h}
$CsCrCl_3$		Negl	$Co(acac)_2$	4.8^{d}	0.60^{d}
$CrBr_3$	11.0^{d}	0.25^{d}	$Co(SacSac)_2$	4.9^{d}	0.62^{d}
Cr_2O_3	11.3	0.16	$Co(acac)_3$	5.0^{d}	$<0.15^{d}$
$Cr(acac)_3$	12.0^{d}	0.16^{d}	NiF_2	6.1	0.52^{d}
$Cr(NH_3)_6(NO_3)_3$		Negl	NiF_2	5.9^{j}	
MnF_2	6.5^{d}	0.08^{d}	$NiCl_2$	$5.9\ (8.3)^{d}$	$0.60\ (0.37)^{d}$
$MnCl_2$	5.1^{d}	0.38^{d}	$NiCl_2$	$5.4\ (8.5)^{j}$	
$MnBr_2$	4.8^{d}	0.55^{d}	$NiBr_2$	5.4^{d}	0.60^{d}
MnI_2	4.1 (6.3)	0.53 (0.23)	$NiBr_2$	$5.2\ (9.0)^{j}$	
$K_4Mn(CN)_6$	$13.5^{d,f}$	$0.15^{d,f}$	NiI_2	6.1^{d}	0.73^{d}
MnO_2		$Negl^{g}$	NiI_2	4.2^{j}	
$(TEA)_2MnCl_4$		0.38^{h}	$NiCO_3$	5.8^{j}	
$(TEA)_2MnBr_4$		0.46^{h}	$NiSO_4$	4.3^{j}	
$Mn(acac)_3$	4.1^{d}	0.31^{d}	$K_2Ni(CN)_4$	14.2^{f}	0.07^{f}
FeF_2	$6.4\ (-2.9)^{d,m}$	0.2^{d}	$Ni(SCN)_2$	$4.2\ (8.3)^{d}$	$0.48\ (0.31)^{d}$
FeF_3		Negl	NiO	6.1^{j}	
$FeCl_3$	4.4^{d}	0.57^{d}	$(TMA)_2Ni(NCS)_4$		0.47^{h}
$FeBr_2$	4.0^{d}	0.70^{d}	$(TEA)_2NiCl_4$		0.59^{h}
$FeBr_3$	4.7^{d}	0.73^{d}	$(TEA)_2NiBr_4$		0.58^{h}
$K_4Fe(CN)_6$	$14.2^{d,f}$	$0.11^{d,f}$	$Ni(acac)_2$	4.3^{d}	0.62^{d}
$K_3Fe(CN)_6$	$16.4^{d,f}$	$0.14^{d,f}$	$Ni(SacSac)_2$	4.4^{d}	0.22^{d}
Fe_2O_3		$Negl^{g}$	$(TMA)_4Ni(NCS)_6$	6.4^{j}	0.40^{h}
$Fe(acac)_2$	4.4^{d}	0.64^{d}	CuF_2	6.7^{k}	0.61^{k}
$Fe(acac)_3$	4.5^{d}	0.66^{d}	$CuCl_2$	8.5^{k}	0.55^{k}
CoF_2	6.4	0.34	$CuBr_2$	9.7^{k}	0.41^{k}
CoF_2	4.9^{i}	0.57^{i}	CuO	$7.8\ (9.4)^{k}$	0.53^{k}
CoF_3	4.4 (7.1)	0.30 (0.41)	CuCl		$Negl^{k}$
$CoCl_2$	5.1^{d}	0.70^{d}	Cu_2O		$Negl^{k}$
$CoCl_2$	4.7^{i}	0.64^{i}			

[a] Energy separation between the $2p_{3/2}$ peak and the main peak of the satellite structure. Data on secondary satellite peak given in parentheses. [b] The intensity ratio of the peak of the main satellite and that of the $2p_{1/2}$ photopeak. Data on secondary satellite structure given in parentheses. [c] Negligible: less than 0.1 and for diamagnetic compounds less than 0.05. [d] Results originally listed in Table II of ref 7 as preliminary results. In reanalyzing the data some small corrections and additions have been made for a few compounds. [e] Data taken from $2p_{1/2}$ spectrum because of interference with O(1s) contaminant. [f] High-energy satellite structure is probably due, at least in part, to characteristic energy losses. [g] J. C. Carver (unpublished results). [h] Reference 9. [i] Reference 8. [j] Reference 3. [k] Reference 2b. [l] Reference 13. [m] Low-energy shoulder which may have arisen from radiation damage.

Co(III) the main 2p peaks were very sharp, indicative of the absence of any Co(II) impurities. The correlation of paramagnetism with intense satellite structure in the 2p shell is probably not due to the presence of unpaired spins but rather to the smaller energy difference between the ligand and metal orbitals.

(7) As one goes across the periodic table to higher Z for the first-row transition metal compounds, the intensities of the satellite structure increase. When satellites are observed, those for Sc, Ti, V, and Cr are generally low, while the intensities for Mn and Fe compounds are substantially larger, and the most intense are found with Co, Ni, and Cu compounds. In addition, for a given ligand the energy separation between the satellite and main peak will decrease with metals of higher atomic number. For example, see Figure 3. Note the drop between Cr^{3+} and Mn^{2+}. Calculations, based on the work of Larson and Connelly,[30] of the energy spectrum between the metal and ligand orbitals are also given. Although these calculations are based on only the neutral species and do not consider the effect of the core vacancy in the final state, they offer a qualitative estimate of the behavior of the transition energies, which is at least consistent with experiment.

Table II. Second- and Third-Row Transition Metal Compounds Studied for Their Satellite Structure[a]

Compd	Core shell	Compd	Core shell	Compd	Core shell
$MoCl_3$	3d	K_2TaF_7	4f	$Pt(SCN)_4$	4f
$MoCl_5$	3d	$RhCl_3$	3d	H_2PtCl_4	4f
$K_4Mo(CN)_8 \cdot 2H_2O$	3d	$AuCl_3$	4f	H_2PtCl_6	4f
MoO_3	3d	K_2OsCl_6	4f		

[a] In each case the satellite structure was observed to be less than 0.1 of the normal photoelectron peak.

(8) Unlike the first-row transition metal compounds, satellite structure due to electron shake-up rarely occurs with photoionization in the core levels of second- and third-row transition metal compounds. For example, Table II lists compounds which were examined for satellite structure but

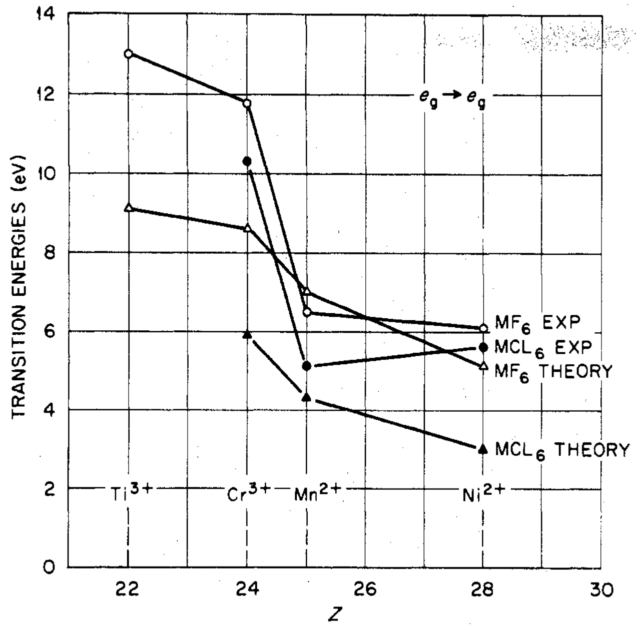

Figure 3. Transition energies for electron shake-up as a function of atomic number. Experimental values are the energy separation between the normal peak in the photoelectron spectra of the $2p_{3/2}$ subshell of the metal ion, M, and the peak of the satellite structure. The theoretical values are the energy differences between the e_g(ligand) orbital and the e_g(metal) orbital as obtained from Larson and Connelly.[30] Diagram constructed by L. J. Saethre.

showed no such structure. To the best of our knowledge no case has been reported in the literature where satellite structure has been characterized for the second- and third-row transition metals as due to electron shake-up. Second- and third-row transition metal compounds are characterized as having high crystal field splitting and high spin-orbital coupling, $\vec{J}$ being a good quantum number rather than $\vec{L}$ or $\vec{S}$. With the exception of $MoCl_3$, $MoCl_5$, and K_2OsCl_6 all of the compounds in Table II are diamagnetic.

Comparison of Monoatomic Excitation vs. Charge Transfer. When a core hole is created in the central atom, the symmetry of the valence shell can be considered invariant. Two possible types of transitions that can occur due to a sudden core vacancy in the metal ion within the framework of electron shake-up are those between two metal orbitals or between a ligand and metal orbital (charge transfer). In the former case an electron could be excited to a Rydberg state, analogous to the atomic excitation: 3d → 4d. This transition would be allowed within the framework of monopole excitation. However, one would expect the transition energy to be rather large and the transition probability to be rather small, as if it were a free atom. Intrametallic transitions such as $e_g \rightarrow a_{1g}$ for an O_h point group have been proposed[3] but are not allowed by monopole selection rules[4] unless one considers the molecular state to be approximately described by the total angular momentum, characteristic of the d electron. Even under these conditions electron shake-up is not allowed where $\vec{L} = 0$ such as when there are five unpaired spins as with Mn^{2+} and Fe^{3+} compounds, in contradiction to experiment. In addition, transitions with an initial $3d^0$ configuration would not be possible, again in contradiction to the satellite structure observed with scandium and titanium compounds.

Charge transfer or excitation between the ligand and metal orbitals [for example, in a hexahalide coupling: e_g(ligand) → e_g(metal) or t_{2g}(ligand) → t_{2g}(metal)] has been suggested by Kim[4] as the mechanism for electron shake-up in transition metal compounds. Such transitions are allowed within the monopole selection rules and are consistent with the experimental behavior of the observed satellite structure. For example, see Figure 3 and also note the general observation that the larger satellite intensities are often associated with smaller energy separations between the ligand and metal orbitals. Final proof awaits specific molecular orbital calculations on the complexes in which vacancies are created in the core shell of the transition metal ion. With these molecular wave functions one could compute both excitation energies and transition probabilities which could then be compared with experiment to clarify the exact nature of the excitation process.

Conclusion

Although final conclusions await specific molecular orbital calculations, the basic nature of satellite structure found in the photoelectron spectra of transition metal compounds is beginning to form a clear picture. Strong, well-defined satellite peaks in the photoelectron spectrum of the metal 2p orbitals are caused by electron shake-up, while multiplet splitting manifests itself by the broadening of the main peaks and the slight increase in the separation between the $2p_{3/2}$ and $2p_{1/2}$ peak positions. Electron shake-up as the result of a core vacancy in the metal ion probably involves to a large extent excitation from a ligand to a metal orbital. Factors which enhance this type of transition will increase the satellite production.

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Registry No. ScF_3, 13709-47-2; $ScBr_3$, 13465-59-3; VF_3, 10049-12-4; VF_4, 10049-16-8; Cr_2O_3, 1308-38-9; MnI_2, 7790-33-2; CoF_2, 10026-17-2; CoF_3, 10026-18-3; $Co(SCN)_2$, 3017-60-5; $Co(NH_3)_3(NO_2)_3$, 13600-88-9; $[Co(NH_3)_4Cl_2]Cl$, 24887-93-2; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $HgCo(SCN)_4$, 27685-51-4; $Co(en)_3Cl_3$, 13408-73-6; NiF_2, 10028-18-9; $K_2Ni(CN)_4$, 14220-17-8; $K_4Fe(CN)_6$, 13943-58-3; $K_3Fe(CN)_6$, 13746-66-2; $NiCl_2$, 7718-54-9; N_2, 7727-37-9; Fe, 7439-89-6.

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Carbon-13 Nuclear Magnetic Resonance Studies of Trimethylamine Adducts of the Mixed Trihalides of Boron

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Carbon-13 NMR spectra have been obtained for trimethylamine adducts of the mixed trihalides of boron, $Me_3N{\cdot}BX_nY_{3-n}$ (n = 0–3, X and Y are halogens, F, Cl, Br, and I). The $\delta(^{13}C)$ moves downfield on substitution of heavier halides, the shifts reflecting the order of Lewis acidity. Linear correlations are obtained between $\delta(^{13}C)$ and (a) the corresponding proton chemical shifts, (b) the ^{11}B complexation shifts, and (c) $J_{^{11}B-^{19}F}$ showing that the ^{13}C shifts reflect the changes in the B–N bond. From the regression line, NMR parameters of unobserved species may be calculated. No coupling of carbon to ^{11}B is noted, while fluorine-containing adducts have broadened peaks as a result of unresolved $J_{^{13}C-^{19}F}$ couplings. Both the ^{13}C and corresponding ^{1}H chemical shifts show pairwise additivity with respect to halogen substitution about boron.

Introduction

Although ^{13}C NMR has not been extensively applied to studies of adducts, recent work by Fratiello et al.[1] has shown that the ^{13}C NMR chemical shifts of the α carbons of several ethers gave downfield shifts on coordination to BF_3 or BCl_3, the stronger acceptor, BCl_3, causing the greater shift. They concluded that $\delta(^{13}C)$ for the α carbon reflected electron density shifts on complexation, essentially a diamagnetic term. They also reported the β and γ shifts to be in the opposite direction, a paramagnetic term now being predominant. Subsequently, Geanangel[2] reported the ^{13}C NMR spectra of trimethylamine–boron adducts, $Me_3N{\cdot}BH_nF_{3-n}$ (n = 1–3) and $Me_3N{\cdot}BX_3$ (X = F, Cl, Br). The shifts observed for the trihalides give the same order of Lewis acidity as is obtained from ^{1}H NMR and thermodynamic measurements.[3,4] A good correlation was also reported between $\delta(^{13}C)$ and $\Delta\delta(^{11}B)$, the boron complexation shift. Although not pointed out by Geanangel, there is not a simple downfield shift of the ^{13}C resonance on complexation, the shift being slightly upfield for BF_3 and downfield for both BCl_3 and BBr_3, only the order of shifts for the complexes and not their position relative to free trimethylamine being important.

Having previously reported ^{1}H, ^{19}F, and ^{11}B data on the trimethylamine adduct of the mixed trihalides of boron[4–7] (a total of 20 complexes) we now report the nature of their ^{13}C NMR spectra.

Experimental Section

Mixed adducts were prepared in $CDCl_3$ solution as described previously.[4] ^{13}C NMR data were obtained in $CDCl_3$ solution at 33°C in 10-mm tubes using a Bruker WP-60 FT NMR spectrometer operating at 15.08 MHz. Typical spectrometer parameters were a sweep width of 1875 Hz (to include the TMS reference) and an aquisition time of 2.18 sec for an 8K FID. FID's were obtained in the autorecur mode using 30° pulses (3.1 μsec), 1000–16000 pulses (depending on concentration) being accumulated using the PAPS sequence with 5 W of proton noise decoupling. The 4K transformed spectra had only minimal line broadening applied (0.0–0.5 Hz). The chemical shifts were not particularly susceptible to either concentration (0.1 mole % to saturated, the heavier halide adducts being less soluble), the presence of more than one adduct in solution, or the presence of an excess of free Lewis acid in solution. The average standard deviation in shifts over this wide variety of conditions was ±1.0 Hz (0.07 ppm), while for the worst cases, the sparingly soluble iodide-containing adducts, precision was still ±1.5 Hz (±0.1 ppm). Shifts were measured by interpolation on the plotted spectra, by the cursor routine available through the computer, and via the plot/list routine. Resolution was typically better than 1 Hz, often single channel for TMS and $CDCl_3$ peaks, but the adduct peaks were broadened.

No attempt was made to observe the ternary adducts such as $Me_3N{\cdot}BFClBr$ since their low concentrations would have required exceedingly long accumulation times.

Pairwise parameters were calculated as described previously.[6] Linear regressions were carried out on a Wang 2200 programmable calculator which provided the intercept A, slope B, correlation coefficient r, standard errors of estimate, and calculated points based on the regression line.

Results and Discussion

I. Carbon-13 Chemical Shift. The results of the ^{13}C chemical shift measurements are shown in Table I which lists the adducts in order of increasing methyl proton chemical shifts. These have previously been taken as a measure of the relative order of acceptor power of the boron trihalide.[3,4] Unlike the proton case, there is not an immediate downfield shift of the methyl carbons on adduct formation. The weakest adduct, $Me_3N{\cdot}BF_3$ is in fact observed at a somewhat higher field than that of free trimethylamine. Chemical shifts however decrease regularly on substitution of heavier halogens, the order essentially paralleling that observed for protons except for three pairs of adjacent adducts, $D{\cdot}BBr_2I$ and $D{\cdot}BClI_2$, $D{\cdot}BClBr_2$ and $D{\cdot}BCl_2I$, and $D{\cdot}BCl_2Br$ and $D{\cdot}BFI_2$ whose order of carbon shifts is inverted from that observed with proton spectra. All three pairs involve iodine-containing adducts, which for solubility reasons have the greatest experimental errors, and the shift differences between the adducts concerned are within the carbon and proton experimental error. Unlike hydrocarbons, there is no upfield ^{13}C shift associated with the presence of iodine atoms.

Since essentially the same order is obtained for $\delta(^{13}C)$ and $\delta(^{1}H)$, it would appear that both measurements reflect the same property of the adducts. This is further borne out by Figure 1, a plot of $\delta(^{1}H)$ vs. $\delta(^{13}C)$ which surprisingly shows a very linear relationship (correlation coefficient r = 0.991) with the greatest deviations occurring for the iodide-containing adducts. If these are omitted, an even better fit is obtained