wrong. More likely the force field chosen using only five frequencies may be incorrect.

Concerning the trends in force constant sets there is a clear distinction between subgroups Va and Vb. Data are almost constant in Vb while variations are more pronounced in Va. On account of an increase in bonding strength with atomic number, the stretching force constant *K* increases from P to Sb in Va, but its value is lower for Bi than for Sb, which may be due to a longer central atom–fluorine distance, giving a stronger ionic contribution.

The angular deformation constants *H* or *D*, again almost constant and negative in Vb, decrease from P to Bi in Va and possess a positive value. This suggests that the fluorine atom arrangement around the central atom gives a stiffer configuration in Va than in Vb and that in Va this stiffness is decreasing from P to Bi.

The value of the repulsive force constant *F* is approximately constant in Vb and decreases in Va from P to Bi in agreement with the increase in bond length and with the above remarks concerning the stiffness.

Table XI listing OVFF force constants for both the hexafluoro anions and the isoelectronic molecules shows that the trends are the same for both species, and as expected, values are of the same magnitude. The decrease in stiffness from comparison of *D* or *H* values is less pronounced for Va hexafluoro anions than for the corresponding isoelectronic molecules. To sum up, the strong basic property of $ClOF_3$ makes possible the preparation of stable one-to-one adducts with group V element pentafluorides. The new crystalline phases have been defined by their X-ray powder patterns, while their ionic structure has been characterized by vibrational spectroscopy. The investigations performed on the entire group of possible XF_6^- anions allow a discussion of the OVFF and UBFF force field trends in this group. These force fields give good agreement between observed and calculated frequencies.

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Registry No. $ClOF_3$, 30708-80-6; PF_5, 7647-19-0; AsF_5, 7784-36-3; SbF_5, 7783-70-2; BiF_5, 7787-62-4; VF_5, 7783-72-4; NbF_5, 7783-68-8; TaF_5, 7783-71-3; PF_6^-, 16919-18-9; AsF_6^-, 16973-45-8; SbF_6^-, 17111-95-4; NbF_6^-, 16918-69-7; TaF_6^-, 16918-70-0; BiF_6^-, 49772-03-4; VF_6^-, 49756-64-1; $ClOF_2^+PF_6^-$, 49756-65-2; $ClOF_2^+AsF_6^-$, 36544-27-1; $ClOF_2^+VF_6^-$, 49756-67-4; $ClOF_2^+SbF_6^-$, 38199-85-8; $ClOF_2^+TaF_6^-$, 49756-69-6; $ClOF_2^+NbF_6^-$, 49756-70-9; $ClOF_2^+BiF_6^-$, 49772-04-5.

Supplementary Material Available. Table I representative of the X-ray powder data, Tables II–VIII representative of the vibrational spectra, and Table XII (GVFF values) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-690.

Contribution from the Department de Chimie-Physique, IRCHA, Vert-Le-Petit, France,
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X-Ray Photoelectron Spectroscopy Study of Some Metal(II) Halide and Pseudohalide Complexes

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In order to examine the value of ESCA spectroscopy in the field of metal coordination complexes, we have investigated a number of compounds of general formula $C^I_2(MX_4)$, where M is a divalent metal (Co, Zn, and in some cases Mn, Ni, and Cu), X = Cl, Br, NCO, NCS, or NCSe, and C^I is a monovalent tetraalkylammonium cation (alkyl = methyl, ethyl, and in some cases *n*-butyl). For comparison, some related octahedral complexes, $C^I_4(MX_6)$, and salts containing the same cations and anions were also considered. The *fine structure* observed in *metal* $2p_{3/2}$ spectra when the metal atom has unpaired d electrons varies with the ligand X along the spectroscopic series and with the metal. This behavior qualitatively agrees with a *multiplet splitting* mechanism. In addition, changes in *binding energies* of all the elements, with changing cation, ligand, or metal, also appear to correlate with a multiplet splitting mechanism.

I. Introduction

Recent photoelectron spectroscopic studies on coordination complexes[2] using the ESCA technique of Siegbahn and coworkers[3] have shown the usefulness of this new tool. We have applied it to an investigation of a series of complexes of general formula $C^I_2(MX_4)$, where M is a metal of oxidation number 2 (Mn, Co, Ni, Cu, and Zn), X = Cl, Br, NCO, NCS, or NCSe, and C^I is a (monovalent) tetraalkylammonium cation (R = methyl, ethyl, or *n*-butyl).[4] In such complexes the coordination geometry around the metal atom in solids is generally a distorted tetrahedron. For the sake of comparison, some related octahedral complexes, $C^I_4(MX_6)$, have been considered.

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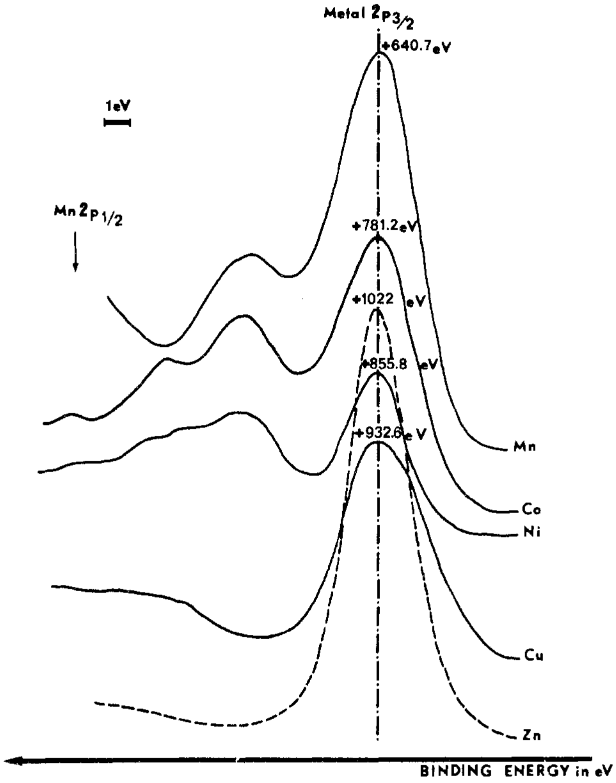

Figure 1. Fine structure in the metal $2p_{3/2}$ spectra of $[(C_2H_5)_4N]_2$-MCl_4 for various metals.

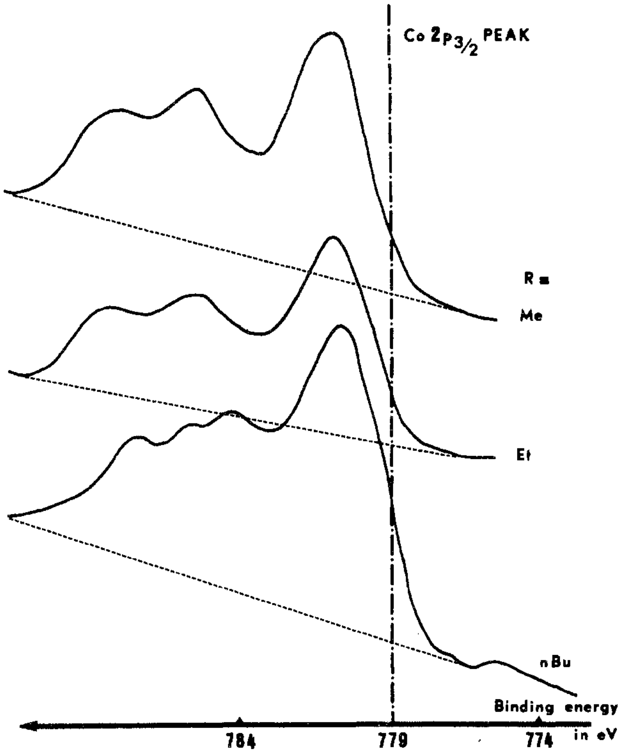

Figure 2. Fine structure in the cobalt $2p_{3/2}$ spectra of $(R_4N)_2Co$-Br_4 for various cations, R_4N^+ (R shown in the figure).

II. Experimental Section

1. The preparation of complexes followed known methods.[4-7] Compounds were studied as microcrystalline powders with a Varian spectrometer (V-IEE 15).[8] This machine uses the filtered Kα radiation of aluminum (1487 eV) to bombard the sample and expel photoelectrons. An electrostatic spherical analyzer gives the relevant energy spectrum. Elements have been characterized by the ionization of the levels in Chart I (approximate binding energy in eV). As discussed below, other metal levels were studied in specific instances.

Chart I

1s	C (284)	N (399)	O (532)
$2p_{3/2}$			S (164), Cl (200)
$3d_{5/2}$			Se (57), Br (69)
$2p_{3/2}$	Mn (641)	Co (779)	Ni (855), Cu (931), Zn (1021)

For some compounds, traces of surface decomposition were evident in the spectra; these samples are not reported in the following tables.

2. The absolute determination of binding energies requires a knowledge of the sample work function. It is generally preferred to take as a reference the *Fermi level of the spectrometer*, which is nearly constant.[9] Binding energies are thus corrected for the spectrometer work function. As this correction is the same for all spectra obtained at a time on a given sample, it is possible to use a secondary standard for binding energies by recording a "trace" element, oxygen for most cases in our study, for which we choose 532 eV as a reference level. This procedure would correct for any appreciable change in charging effect from one sample to another.

All observed peaks, including those of trace oxygen and carbon, are given *uncorrected* in Tables I and II. For metals, only the principal maximum is given (fine structure will be discussed later on). For comparison, we report data for simple salts containing the same cations or anions as studied here.

III. Results

1. **Spectral Line Shape.** For most elements observed in the samples, only one peak appears and its position will be discussed in section III.2. For complexes with isocyanate and similar ligands, two peaks appear in the *nitrogen* 1s spectrum, one for this group and one for the tetraalkylammonium cation. Their assignment is straightforward.

Fine structure appears on the metal $2p_{3/2}$ peak for the tetrahedral complexes of Mn, Co, Ni, and Cu but not with Zn. This fact is clearly related to the existence of unpaired d electrons and is reminiscent of fine structure observed in the relevant X-ray K or L absorption edges (which also involve the 2p level).[10] Similar effects in ESCA spectra have been previously observed on iron and manganese metals and on manganese oxide and fluoride[11a] and, more recently, on cobalt and nickel compounds, including complexes.[11b] In the latter case, it was particularly noticeable that low-spin nickel(II) complexes have only one peak for each of the two spin-orbit components ($2p_{1/2}$ and $2p_{3/2}$), whereas the high-spin complexes exhibit two for each.

In our case, a rather complicated fine structure has been observed for the aforementioned complexes, especially for cobalt and nickel (Figure 1). This indeed corresponds to high-spin complexes as shown by magnetic moments measured on these or closely related species.[5-7]

We shall now comment on the different aspects of this fine structure according to the metal, the ligand, or the ca-

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Table I. Binding Energies (Uncorrected) Observed on Investigated Complexes

Mn complexes	C	O	N	Cl	Br	S	Se	Mn
$[(C_2H_5)_4N]_2MnBr_4$	284.7	531.5	401.3		67.8			640.5
$[(C_2H_5)_4N]_2MnCl_4$	284.4	531.2	400.9	197.1				640.7
$[(C_2H_5)_4N]_2Mn(NCO)_4$	283.4	530.6	396.7 400.6					640.2
Co complexes	**C**	**O**	**N**	**Cl**	**Br**	**S**	**Se**	**Co**
$[(CH_3)_4N]_2CoBr_4$	286	531.7	402.8		69.1			781
$[(C_2H_5)_4N]_2CoBr_4$	285.5	531.9	402.4		69			780.8
$[(CH_3)_4N]_2CoCl_4$	285.8	531.9	402.9	198.6				781.3
$[(C_2H_5)_4N]_2CoCl_4$	285.4	531.6	401.6	198.2				781.2
$[(CH_3)_4N]_2Co(NCO)_4$	284.5	530.5	396.6 401					779.8
$[(C_2H_5)_4N]_2Co(NCO)_4$	284.2	531	398.2 401.1					780.4
$[(CH_3)_4N]_2Co(NCS)_4$	285.4	531.6	397.7 402			162.3		781
$[(C_2H_5)_4N]_2Co(NCS)_4$	284.4	531.3	397.1 401			161.6		781.6
$[(C_4H_9)_4N]_2Co(NCS)_4$	284.2	531.5	396.3 399			160.5		779.7
$[(CH_3)_4N]_2Co(NCSe)_4$	286.3	532.6	398.9 403.1				55.6	780.9
$[(CH_3)_4N]_4Co(NCSe)_6$	286.1	531.2	398 402.7				55.8	779
Ni complexes	**C**	**O**	**N**	**Cl**	**Br**	**S**	**Se**	**Ni**
$[(C_2H_5)_4N]_2NiBr_4$	285.5	532.6	402.4		69.6			855.9
$[(C_2H_5)_4N]_2NiCl_4$	285.1	532.1	402	198.2				855.8
$[(CH_3)_4N]_2Ni(NCS)_4$	285.6	531.8	398 402.6			162.4		856.9
$[(CH_3)_4N]_4Ni(NCS)_6$	285.1	531.7	397.2 401.8			161.8		856.4
$[(C_2H_5)_4N]_4Ni(NCS)_6$	284.2	531.4	396.6 400.9			161.2		855.3
$[(C_2H_5)_4N]_4Ni(NCSe)_6$	285.5	531.4	398.1 402.4				54.9	855.7
Cu complexes	**C**	**O**	**N**	**Cl**	**Br**	**S**	**Se**	**Cu**
$[(CH_3)_4N]_2CuBr_4$	286.1	532.2	403.8		69			933.7
$[(CH_3)_4N]_2CuCl_4$	285.9	531.8	402.5	198				933.8
$[(C_2H_5)_4N]_2CuCl_4$	284.9	531.5	401.3	197.4				932.6
Zn complexes	**C**	**O**	**N**	**Cl**	**Br**	**S**	**Se**	**Zn**
$[(CH_3)_4N]_2ZnBr_4$	286.6	531.9	403.2		69.6			1022.7
$[(C_2H_5)_4N]_2ZnBr_4$	285.4	531.7	402		68.9			1022.2
$[(CH_3)_4N]_2ZnCl_4$	286.5	531.9	403.1	198.9				1022.5
$[(C_2H_5)_4N]_2ZnCl_4$	285.3	531.9	402	198.3				1022
$[(CH_3)_4N]_2Zn(NCO)_4$	284.1	531.2	397 401.8					1020.7
$[(C_2H_5)_4N]_2Zn(NCO)_4$	284.7	531.7	397.8 401.8					1021.2
$[(CH_3)_4N]_2Zn(NCS)_4$	285.7	531.6	397.9 402.2			162.3		1021.6
$[(C_2H_5)_4N]_2Zn(NCS)_4$	284.5	531.5	397 401			161.8		1020.9
$[(CH_3)_4N]_2Zn(NCSe)_4$	285.1	531.6	399.1 403.3				55.8	1022.5
$[(C_2H_5)_4N]_2Zn(NCSe)_4$	285.5	531.6	398.5 402.4				55.2	1022
Ref compd	**C**	**O**	**N**	**Cl**	**Br**	**S**	**Se**	**K**
NH_4Cl	283.8	532.4	400.3	196.9				
$(CH_3)_4NBr$	285.4	531.9	402		67.5			
$(CH_3)_4NCl$	284.7	531.1	401.4	196.1				
$(C_2H_5)_4NCl$	284.3	531.6	400.9	195.9				
KNCO	285	531.8	398.5					292.9
KNCS	284.4	531.6	397.8			162.4		292.6
NH_4NCS	283.8	531.7	397.1 400.3			161.8		
$(CH_3)_4N(NCS)$	284.6	531.5	396.6 401.3			161.3		

tion involved. This comment may rely on the line shape itself (in a qualitative manner as the resolution of peaks presented by some metals, especially cobalt and nickel, is not straightforward) and on the relative importance of the satellite peaks. This importance may be quantitatively characterized by the area of satellites relative to the area of the complete pattern of peaks for a given sublevel ($2p_{1/2}$ or $2p_{3/2}$); ρ = satellites area/total area. The ρ's have been determined by planimetry for a number of complexes and are reported in Table II. In that determination, we assumed a sym-

Table II. Relative Importance of the Satellite Peaks Observed in Metal 2p Spectra

Complex	ρ for $2p_{3/2}$ structure[a,b]	
Mn Complexes		
$[(Et)_4N]_2MnBr_4$	0.46	[0.51]
$[(Et)_4N]_2MnCl_4$	0.38	[$\geqslant$0.35]
$[(Et)_4N]_2Mn(NCO)_4$	0.22	
Co Complexes		
$[(Me)_4N]_2CoBr_4$	0.55	
$[(Me)_4N]_2CoCl_4$	0.50	
$[(Me)_4N]_2Co(NCO)_4$	0.49	
$[(Me)_4N]_2Co(NCS)_4$	0.53	
$[(Et)_4N]_2CoBr_4$	0.55	
$[(Et)_4N]_2CoCl_4$	0.48	
$[(Et)_4N]_2Co(NCO)_4$	0.49	[0.59]
$[(Et)_4N]_2Co(NCS)_4$	0.44	
$[(Bu)_4N]_2Co(NCS)_4$	0.41	
Ni Complexes		
$[(Me)_4N]_2Ni(NCS)_4$[c]	0.47	
$[(Me)_4N]_4Ni(NCS)_6$	0.40	
$[(Et)_4N]_2NiBr_4$	0.58	[$\geqslant$0.68]
$[(Et)_4N]_2NiCl_4$	0.59	[$\geqslant$0.68]
$[(Et)_4N]_4Ni(NCS)_6$	0.53	[0.81]
Cu Complexes		
$[(Me)_4N]_2CuBr_4$	0.35	[0.35]
$[(Me)_4N]_2CuCl_4$	0.34	[0.37]
$[(Et)_4N]_2CuBr_4$	0.32	[0.36]
$[(Et)_4N]_2CuCl_4$	0.22	[0.37]

[a] ρ for $2p_{1/2}$ between brackets when pertinent. [b] See text for the definition of ρ. [c] This complex is actually pseudooctahedral (see ref 12).

metrical line shape for the normal line without satellite (after properly substracting background), taking the high binding energy side as a mirror image of the observed low binding energy profile.

(a) The *cation* seems not too important in determining the fine structure, at least from Me_4N^+ to Et_4N^+ (Figure 2). The only discernible trend may be a "compression" of the structure toward the main peak.

(b) The *ligand* is of prime importance in determining the fine structure (Figure 3). Some change appears in the line shape (except for Mn for which just one satellite is observed) all along the spectroscopic series with a decreasing separation between satellites and main peaks, but the main trend is a reduction of ρ (Figure 4).[12] We note that for cobalt and nickel complexes the metal main peak is rather sharp for halogen ligands but broader for NCO, NCS, and NCSe ligands.[14]

(c) The nature of the *metal* governs the general aspect of the satellites, as depicted in Figure 1. From a relatively sharp peak for Mn, we pass to a much more intricate structure for Co and Ni and to a relatively broad and small band for Cu. On the other hand, ρ appears to change rather regularly (Figure 5).

For some of the complexes investigated, we have recorded other metal peaks. 2s and 3s peaks have been found quite difficult to observe properly (probably due to the Coster-Kronig effect).[10a] $2p_{1/2}$ peaks are easily obtained. Satellite structures in $2p_{1/2}$ and $2p_{3/2}$ patterns present roughly the same complexity (for Mn, we observe one satellite in both cases). The principal change is for ρ to be greater for $2p_{1/2}$ (Table II).[15]

2. Peak Position. We restrict ourselves in the following to the presentation of data obtained on tetrahedral species, as no clear distinction can be made from *peak position* (for all the investigated elements) between related tetrahedral and octahedral complexes.

When considering chemical shifts relative to the neutral element[17] and corrected for the oxygen standard at 532 eV (except for -NCO compounds), one finds a number of regular trends when the following substitutions are made.

(a) We substitute one *tetraalkylammonium* cation for another. From $C^I = Me_4N^+$ to Et_4N^+ (and n-Bu_4N^+, when possible), we note a trend to *decreasing binding energies*, either in the cation (N 1s of the R_4N^+) or in the anion (metal, halogen, or pseudohalogen), with the only possible exception of isocyanate complexes (for which no convenient standard exists). The decrease is the greatest for the ammonium type nitrogen atom in the cation (2.0 to 2.5 eV from Me_4N^+) to n-Bu_4N^+); it is sizable for the elements of the anion (0.3 to 0.6 eV for Zn; 1.1 for Cu; 0.3 to 0.8 eV for the halogen or pseudohalogen, always from Me_4N^+ to Et_4N^+). Despite difficulties encountered in referencing (carbon and oxygen peaks of the compounds overlapping "trace" peaks), the difference in behavior of isocyanate complexes compared to complexes containing halogens or isothio- and selenocyanates seems significant.

It is to be noted that "classical" spectroscopic properties of such complexes (ir frequencies and uv parameters) are not so much affected by a change in cation as are binding energies reported here.[5,6,13]

(b) We substitute one *ligand* for another. When we consider ligands in the order of the spectroscopic series Br, Cl, NCO, NCS, and NCSe, a regular trend exists in the binding energies for all elements in cobalt and zinc compounds (we note that these compounds are generally not isomorphous). For cobalt complexes, the N 1s binding energy of R_4N^+ decreases and the Co binding energy increases along the spectrochemical series. On the other hand, for zinc complexes, both N 1s and Zn binding energies decrease along the same series.

(c) We substitute a *metal* for another. The change only appears for the metal, all other binding energies being roughly the same. For the metal itself, the comparison of binding energies needs a common standard; we have chosen the neutral element position, as given in ref 3.[18,19] In this way, we find that the change in metal binding energy roughly

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[12] $(Me_4N)_2Ni(NCS)_4$, which contains bridging thiocyanates in a *pseudooctahedral* environment,[13] or $(Me_4N)_4Ni(NCS)_6$ can be used to demonstrate the role played by ligands in *octahedral* systems. In this case, the change in neighbors is accompanied by a change in line shape but not a significant change in ρ. Unfortunately, among the complexes considered here, no pair of related tetrahedral-octahedral complexes can be usefully compared in terms of the relevant metal fine structure.

[13] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 4, 823 (1965).

[14] The classification of ligands according to the (experimental) spectroscopic series is probably not the best as it mixes contributions of σ and π bonding, when these are possible. From this point of view, it is interesting to observe that J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, 57, 973 (1972), found in their study of first-row transition metal salts that the splitting in the 3s shell varies inversely to the position in the *nephelauxetic* series for halogen ligands when splitting and ρ in the 2p shell seems to vary inversely to the ligand position in the *spectrochemical* series, in our case.

[15] When investigating lamellar clay compounds with inserted cobalt, nickel, copper, or zinc derivatives,[16] we have observed similar and quite significant changes in ρ. For example, extreme values for nickel are $\rho = 0.12$ in $Ni(en_2)Cl_2$ inserted in Na montmorillonite (en = ethylenediamine) and $\rho = 0.57$ for nickel hydroxide in Na montmorillonite.

[16] J. Escard, I. Mantin, and G. Mavel, "Surface Structure and Properties of Clay Minerals," Louvain, June 2–4, 1971; *Bull. Groupe Fr. Argiles*, 25, 181 (1973)

[17] For metal elements, we discuss the position of the $2p_{3/2}$ peak only. We have checked in a number of cases that the interval $2p_{1/2}$-$2p_{3/2}$ is nearly constant for a given metal.

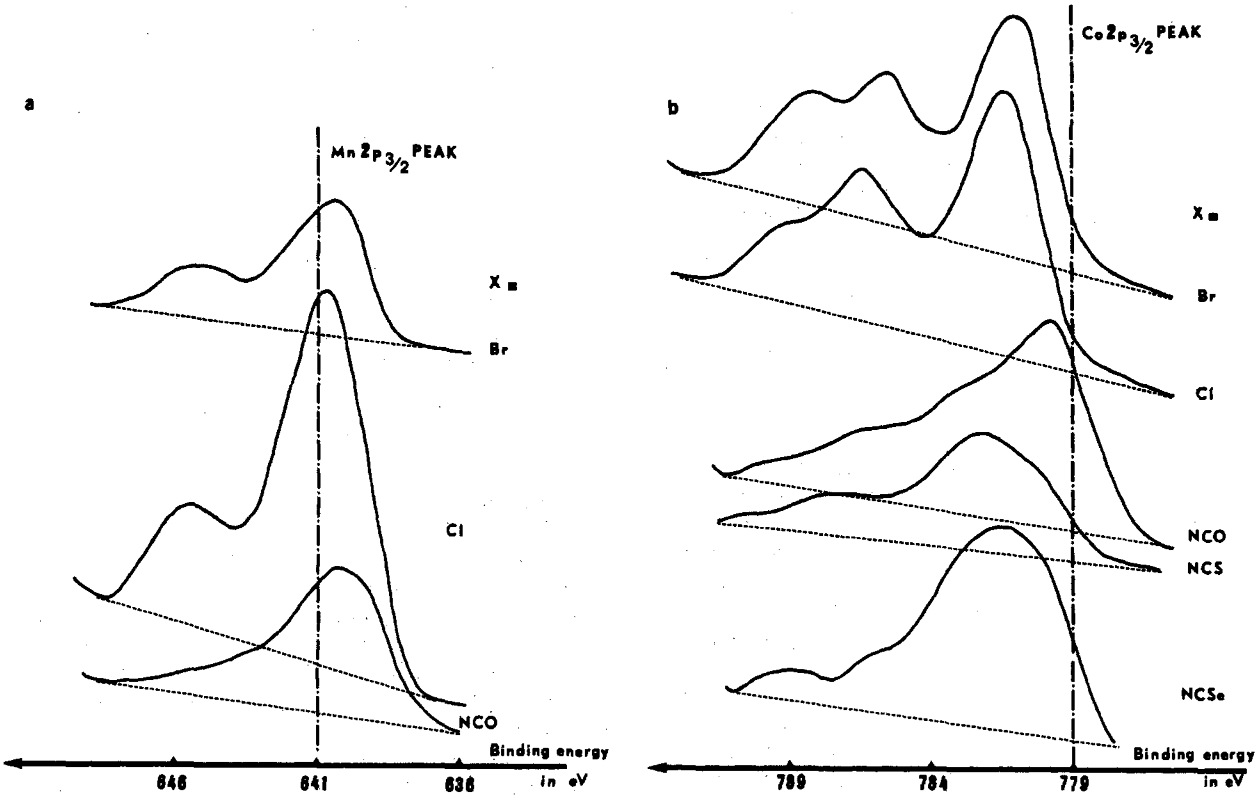

Figure 3. Fine structure in the manganese $2p_{3/2}$ spectra of (a) $[(C_2H_5)_4N]_2MnX_4$ and (b) $[(CH_3)_4N]_2CoX_4$ for various ligands, X, shown in the figure.

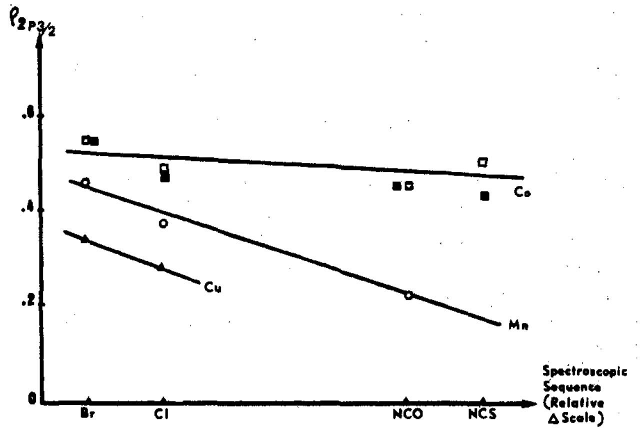

Figure 4. Change in relative importance of satellite peaks in metal $2p_{3/2}$ spectra of $(R_4N)_2MX_4$ complexes for various metals, according to the ligand, X: (○) $(Et_4N)_2MnX_4$; (□) $(Me_4N)_2CoX_4$; (■) $(Et_4N)_2CoX_4$; (▲) $(Me_4N)_2CuX_4$.

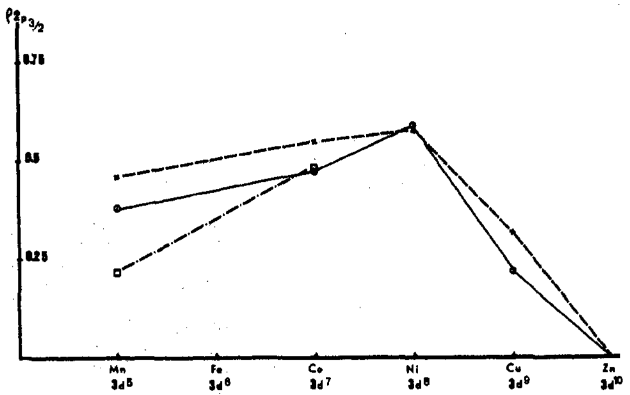

Figure 5. Change in relative importance of satellite peaks in metal $2p_{3/2}$ spectra for various ligands, according to the metal: (X) $(Et_4N)_2MBr_4$; (⊙) $(Et_4N)_2MCl_4$; (□) $(Et_4N)_2M(NCO)_4$.

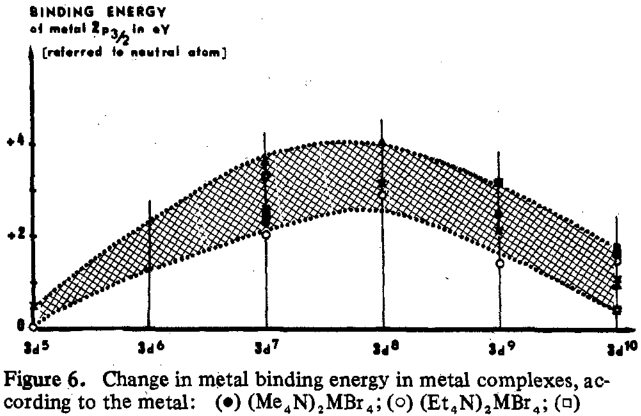

Figure 6. Change in metal binding energy in metal complexes, according to the metal: (●) $(Me_4N)_2MBr_4$; (○) $(Et_4N)_2MBr_4$; (□) $(Me_4N)_2MCl_4$; (X) $(Et_4N)_2MCl_4$; (▲) $(Me_4N)_2M(NCS)_4$; (■) $(Et_4N)_2M(NCS)_4$.

parallels the well-known crystal field stabilization (Figure 6); this relationship is illustrated for a series of complexes in Figure 7.

IV. Discussion

1. Metal Line Shape. As mentioned earlier, fine structure has been observed in ESCA spectra of manganese compounds[11a] and of other salts and complexes.[11b,20] It was

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[18] With only one exception for Ni, it seems that the value accepted by Siegbahn[3] for Ni $2p_{3/2}$ actually refers to the broader component present in the metal peak, which is actually a satellite peak.

[19] Jorgensen has measured a value of 857.8 eV with a work function (for carbon) of 5.3 eV. The corresponding BE 852.5 (857.8−5.3) has been used hereafter.

[20] G. K. Wertheim, A. Rosencwaig, R. L. Cohen, and H. J. Guggenheim, *Phys. Rev. Lett.*, 27, 505 (1971).

attributed in both cases to *multiplet splitting.*[21,22] But, later on, other explanations have been advocated for similar fine structures (shake-up processes,[11c,25] multielectron ionization,[10a] and plasmon structure[26]). In addition, one must not forget the possibility of Auger peaks (ruled out from our observations) and of overlapping chemical shifts due to metal contamination. The latter explanation can be partly valid for Ni with NCS or NCSe ligands and for Co with NCO, NCS, or NCSe ligands, as previously indicated.

As no conclusive argument can be use to decide on the mechanism responsible for fine structure (except for excluding plasmon effects), this point will not be discussed further.

2. **Peak Position.** (a) As our samples are ionic solids, the first requisite is to account for relevant *polarization* effects.[3a,27] Fadley, *et al.*,[9,28] proposed to describe these by considering the potential exerted on the photoelectron by the ions surrounding it but, as discussed by others,[29] this "Madelung effect" cannot explain all observed features. For instance, in our experiments on complexes and related salts, the change in cation size (section III.2.a) would reduce the Madelung effect, thus *decreasing* binding energies for anion elements and *increasing* that for cation elements. In fact, we actually observe a trend to *decreasing* binding energies for all elements in the complexes,[30] especially noticeable for the *ammonium type* cation nitrogens. A similar decrease (but less regular and of smaller size) has been observed in the reference compounds we investigated; for instance, the change is only by *ca.* 0.4-0.6 eV from NMe_4NCS to NBu_4-NCS. Whatever change in bonding is expected during this replacement of Me_4N^+ by Et_4N^+ or Bu_4N^+,[32] Madelung terms cannot be the only ones to operate. It has been suggested[11b,29] that, besides some covalence contribution, *polarizability* would play a part in ionic crystals.

(b) As our observations show that *anion* chemical shifts in our complexes are much more sensitive to cation size effects than in the reference salts, it is fair to assume that the main factors governing relevant binding energies are linked to the anion structure itself.

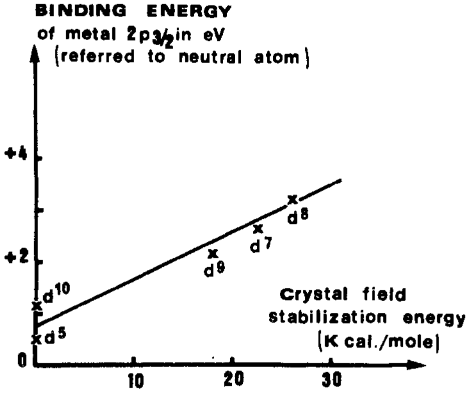

Figure 7. Relationship between metal binding energy and crystal field stabilization energy (after ref 36) for $(Et_4N)_2MCl_4$ compounds.

Two conflicting factors are likely to be important in connection with the nephelauxetic influence of ligands. On one hand, the participation of 3d metal electrons in antibonding MO's is accompanied by a radial expansion, *i.e.*, a decrease in all metal binding energies.[34] On the other hand, the 3d-2p interaction advocated in section IV.1. gives (according to free atom calculations[35]) a decrease in binding energies which is less and less pronounced as 3d metal electrons participate in the MO's. For zinc, which has its 3d levels completely filled, only the first factor is important and 2p energy goes down along the spectroscopic series; for cobalt, which has its 3d levels incompletely filled, the second factor dominates and 2p energy goes up along the spectroscopic series.

If we turn now to *cation* chemical shifts in the same sequence, we note a larger sensitivity to cation size in complexes than in reference salts (ammonium N 1s spectra). The decrease observed in binding energies along the spectroscopic series is the same whatever the number of unpaired electrons. This is consistent with the correlated trend to lower ionicity in the metal anion, thus to lower local electric field at the nitrogen; it is known that such fields cause orbital contraction (for bonding or closed shell orbitals).

(c) Trends observed when substituting one metal for another in a given complex are not too easy to interpret except for the metal itself (Figure 6) for which binding energy (referred to neutral atom) roughly behaves as solvation energies, a function of hyperfine splitting.[36] This may be consistent with a 3d-2p interaction for unpaired electrons in addition to progressive metal charge reduction and metal-ligand valence contribution[37] when Z increases.

Acknowledgments. We are pleased to thank Drs. D. M. L. Goodgame, C. K. Jorgensen, and S. Pignataro for stimulating

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(22) A similar type of fine structure was observed in the L_{II}, L_{III} *X-ray absorption spectra* (which involve $2p_{1/2}$,$2p_{3/2}$ levels) of nickel oxide[23a] and other transition metal oxides.[23b] The consideration of the electron repulsion between 3d and 2p levels in transition metals[24] permitted a qualitative explanation of these observations using a free atom model. It was especially noticeable that the *$2p_{3/2}$ level presented a more complex splitting and spread over a broader range than the $2p_{1/2}$ level.*[23a] This model (or a more elaborate one) can be used to account for the ESCA fine structure on the basis of *electronic exchange interaction* between 3d metal levels (perturbed by ligands and local symmetry) and the observed 2p levels.

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discussions on several parts of this study as well as Mlle. C. Chappuis and Mme. C. Mimouni for their technical assistence.

Registry No. $[(Et)_4N]_2MnBr_4$, 2536-14-3; $[(Et)_4N]_2MnCl_4$, 6667-73-8; $[(Et)_4N]_2Mn(NCO)_4$, 14127-43-6; $[(Me)_4N]_2CoBr_4$, 22033-49-4; $[(Et)_4N]_2CoBr_4$, 2041-04-5; $[(Me)_4N]_2CoCl_4$, 16594-85-7; $[(Et)_4N]_2CoCl_4$, 6667-75-0; $[(Me)_4N]_2Co(NCO)_4$, 29950-55-8; $[(Et)_4N]_2Co(NCO)_4$, 14283-72-8; $[(Me)_4N]_2Co(NCS)_4$, 14052-14-3; $[(Et)_4N]_2Co(NCS)_4$, 14518-17-3; $[(Bu)_4N]_2Co(NCS)_4$, 23467-62-1; $[(Me)_4N]_2Co(NCSe)_4$, 29950-53-6; $[(Me)_4N]_4Co(NCSe)_6$, 10171-20-7; $[(Et)_4N]_2NiBr_4$, 35063-90-2; $[(Et)_4N]_2NiCl_4$, 5964-71-6; $[(Me)_4N]_2Ni(NCS)_4$, 42615-06-5; $[(Me)_4N]_4Ni(NCS)_6$, 14054-70-7; $[(Et)_4N]_4Ni(NCS)_6$, 14096-03-8; $[(Et)_4N]_4Ni(NCSe)_6$, 10478-60-1; $[(Me)_4N]_2CuBr_4$, 15692-22-5; $[(Me)_4N]_2CuCl_4$, 15692-26-9; $[(Et)_4N]_2CuCl_4$, 13927-32-7; $[(Me)_4N]_2ZnBr_4$, 2041-07-8; $[(Et)_4N]_2ZnBr_4$, 2041-06-7; $[(Me)_4N]_2ZnCl_4$, 14240-97-2; $[(Et)_4N]_2ZnCl_4$, 5964-74-9; $[(Me)_4N]_2Zn(NCO)_4$, 29950-56-9; $[(Et)_4N]_2Zn(NCO)_4$, 14283-74-0; $[(Me)_4N]_2Zn(NCS)_4$, 14187-47-4; $[(Et)_4N]_2Zn(NCS)_4$, 34287-49-5; $[(Me)_4N]_2Zn(NCSe)_4$, 29950-54-7; $[(Et)_4N]_2Zn(NCSe)_4$, 29950-54-7; $[(Et)_4N]_2CuBr_4$, 13927-35-0.

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Microwave, Infrared and Raman Spectra, Structure, Dipole Moment and Barrier to Internal Rotation of Vinyldifluoroborane[1]

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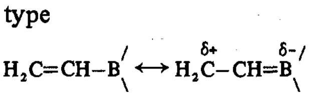
The microwave spectra of $CH_2CH^{10}BF_2$ and $CH_2CH^{11}BF_2$ have been recorded from 12.4 to 40.0 GHz. Both A- and B-type transitions were observed and Q- and R-branch assignments have been made for the ground state. Satellite lines resulting from the excited states of the BF_2 torsion and two skeletal deformation modes were also identified and assigned. From the near-zero value of the inertial defect, $\Delta = I_C - (I_A + I_B) = 0.032$ amu Å^2, it is concluded that the molecule is planar. The total dipole moment was determined to be 1.74 ± 0.04 D, with components $\mu_a = 1.69 \pm 0.04$ D and $\mu_b = 0.37 \pm 0.02$ D. The infrared (200–4000 cm^{-1}) and Raman spectra (0–3500 cm^{-1}) have been recorded for both the gas and the solid. A complete vibrational assignment is proposed. The internal torsional mode was observed at 103 cm^{-1} in the Raman spectrum of the gas and a twofold periodic barrier of 4.17 kcal/mol was calculated. These data were consistent with the relative intensity measurements in the microwave spectrum. The B–C bond distance appears reasonable relative to the values reported for this distance in other organoboranes.

Introduction

The compound vinyldifluoroborane was first prepared and characterized by Brinckman and Stone[2] in 1960. Since that time, this particular compound has received very little attention although vinylboranes in general have been widely investigated. Interest in this general class of compounds has centered on the question of boron–carbon π bonding since the boron atom has a low-lying vacant p_π orbital which could accept electron density from delocalization of the π system of the vinyl group. Mesomeric interactions of the type



$$H_2C{=}CH{-}B\!\left\langle \; \longleftrightarrow \; H_2\overset{\delta+}{C}{-}CH{=}\overset{\delta-}{B}\!\right\langle$$

could make a substantial contribution to the bonding in vinylboranes. Studies of the acceptor ability of vinylboranes,[3] ^{19}F nmr studies of vinylfluoroboranes,[3] a study of the absorption frequencies of the C=C stretching band in α,β-unsaturated organoboron compounds,[4] as well as a consideration of the position and intensities of the C=C stretching absorption in the infrared spectra[4] of $H_2C{=}CHBCl_2$ and $Me_3N{\cdot}BCl_2(CH{=}CH_2)$ have been used as chemical and spectroscopic evidence for the occurrence of π character in the boron–carbon bonds of these compounds. In addition, B–C π bonding has been invoked as a possible explanation for the relative stability towards disproportionation of vinylalkylboron compounds,[5] as well as the absence of reaction between trivinylboron and oxygen at room temperature.[5]

Theoretical studies have also addressed themselves to the question of π bonding. An approximate linear combination of atomic orbitals-molecular orbitals computation,[6] as well as self-consistent field calculations,[7] has been performed to investigate delocalization in these systems. These calculations predicted a considerable π-electron density contribution by the halogen atoms to the boron atom in halovinylboranes. By contrast the vinyl group was found to supply little π-electron density to the boron atom. More recently, the photoelectron spectrum of trivinylborane has been obtained[8] and the conclusion reached that there is only limited conjugation in the molecule.

Thus, the question of boron–carbon π bonding in vinylboranes is still in doubt. We have embarked on a program to investigate various vinylboranes from a vibrational, rotational, and nmr point of view in order to elucidate more fully appropriate parameters of these molecules. The determination of boron–carbon bond lengths, the barrier to internal rotation about the boron-carbon bond, and boron–carbon coupling constants should all present a clearer picture of the bonding in vinylboranes. In this paper we

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