

pling, the direct spin-orbit coupling grants an intensity to the spin-forbidden transition ${}^3A_2 \rightarrow {}^1A_1$ only from the spin-allowed planar oscillator ${}^1E \rightarrow {}^1A_1$. The transition ${}^3A_2 \rightarrow {}^1A_1$ is actually a planar oscillator. However, the transition ${}^3E \rightarrow {}^1A_1$ is a three-dimensional oscillator consisting of an intense component of polarization in a plane and only a weak component perpendicular to it. In the region of $21,000\text{ cm}^{-1}$, a weak linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$ is superposing on an intense plane-polarized transition ${}^1E \leftarrow {}^1A_1$. The polarization ratio must be $+1/7$ when the planar component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the plane-polarized transition ${}^1E \leftarrow {}^1A_1$, while it is $-1/3$ when the planar component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$ or the linear component of the transition ${}^3E \rightarrow {}^1A_1$ emits upon excitation of the plane-polarized transition ${}^1E \leftarrow {}^1A_1$. Only in the case of the emission of the linear component of the transition ${}^3E \rightarrow {}^1A_1$ upon excitation of the linearly polarized transition ${}^1A_2 \leftarrow {}^1A_1$, the

polarization ratio is a higher positive value $+1/2$. Thus, a weighed mean value of the polarization of the luminescence arising from the transition ${}^3E \rightarrow {}^1A_1$ upon excitation at $21,000\text{ cm}^{-1}$ can exceed $+1/7$, although the value depends upon the contribution of the components. The corresponding value expected for the transition ${}^3A_2 \rightarrow {}^1A_1$ upon the same excitation is $+1/7$ or less than $+1/7$. Therefore, it is concluded that the lowest emitting triplet state is 3E rather than 3A_2 .

The polarization was also measured by monitoring at $16,100\text{ cm}^{-1}$ (620 nm) in the second emission maximum. The results were in good agreement with that measured by monitoring at $17,400\text{ cm}^{-1}$ (575 nm).

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X-Ray Photoelectron Spectroscopy of Nickel Compounds

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X-Ray photoelectron spectra (XPS) of the Ni($2p_{3/2,1/2}$) levels for about 70 compounds containing nickel in all of its known oxidation states have been studied. The binding energies have been correlated with ligand electronegativities, delocalization of charge on the ligands, and stereochemistry. Shake-up satellites associated with the Ni(2p) photoelectron lines have been investigated in detail, and a definitive relationship between the shake-up transition and paramagnetism has been established. In the case of octahedral compounds of nickel(II), the separation between the shake-up satellite and main line is found to correlate with the nephelauxetic series of the ligands attached to the metal. The investigation of several carefully chosen isomeric pairs has proven that XPS can be used to differentiate the magnetic behavior between them. The Ni(2p) binding energies are observed to increase in the order square planar < tetrahedral < octahedral, as expected on the basis of known metal-ligand bond lengths.

Introduction

The transition metals as a group show such interesting properties as variable valence, paramagnetism, and a highly diverse stereochemistry. Hence, they are ideally suited for study by X-ray photoelectron spectroscopy (XPS), with which one probes directly the electronic environment of the transition metal atom or ion. Recent studies of this kind have uncovered such phenomena as shake-up satellites in the XPS of 2p orbitals²⁻⁴ and multiplet splitting in the 3s spectra arising from the exchange interaction between the partially filled 3s and 3d orbitals.⁵⁻⁷ The latter phenomenon has been investigated in depth by Carver, *et al.*,^{6,7} from

the spectra of some 40 Cr, Mn, Fe, and Co compounds. Most recently Frost, *et al.*,⁸ reported the first systematic XPS measurements on the copper ion in 46 copper compounds and attempted to correlate the characteristics of the shake-up satellites and the binding energies of the copper core levels with its electronegativity and oxidation states, as well as the kind and the number of ligand atoms surrounding the copper.

The diversity of structures possible for nickel offers yet another possibility for the detailed XPS study of the variation of binding energies and shake-up satellites as a function of stereochemistry, magnetic properties, and ligand surroundings. Hitherto, such information concerning nickel compounds has been scant and desultory.⁹ In general, the results of our XPS investigations on 70 nickel compounds tend to confirm the trends and interpretations reported by Frost, *et al.*,⁸ for copper compounds. In addition, we have studied in detail and established the definitive relationship between shake-up satellites and paramagnetism. In some instances, existing ambiguities in electronic structure have also been clarified by XPS through the examination of both

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the binding energies and shake-up satellites of the nickel ion.

In the present investigation, binding energy is defined according to the conservation of energy relationship

$$E_b = E_{X\text{-ray}} - E_{\text{kin}} - \phi$$

where E_b is the electron binding energy of a specific level; $E_{X\text{-ray}}$, the energy of the X-ray radiation; E_{kin} , the kinetic energy of the ejected electron; and ϕ , the work function of the spectrometer. Hence, binding energy in the discussion is not used in the thermodynamic sense of metal-ligand interaction.

Experimental Section

The compounds used in this study were prepared, purified, and characterized according to published methods.¹⁰⁻⁴¹ Air-sensitive compounds were handled under nitrogen and stored in Schlenk tubes. The compounds for which no preparative methods are given were reagent grade chemicals, used without further purification. The spectra were obtained from powdered samples mounted on cellophane tape using a Varian Associates IEE-15 electron spectrometer. The Mg K α X-ray line (1253.6 eV) was used of photoelectron excitation. In order to compensate for the charging of insulating samples during the photoelectron ejection process. All the spectra were referenced to the photoelectron line of Au(4f_{7/2}), $E_b = 83.0$ eV,⁴² by vacuum deposition of gold onto the samples. Such charging

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corrections ranged from -0.4 to -4.0 eV. The region of interest was scanned before and after depositing gold to make sure that no extraneous peaks had originated by this method of standardization. A decrease in intensity of the nickel signals and a broadening of the 4f doublet of gold were observed in only two cases. The photoelectron spectra of paramagnetic compounds known to be unstable at room temperature in high vacuum were taken at 78°K using a cryogenic probe. All spectra were recorded in triplicate in the regions of interest and in most cases gave binding energies reproducible to ± 0.1 eV. The reported binding energies were taken at a position corresponding to the midway point of the full peak at half-height. Peak widths are characteristically larger for the paramagnetic compounds as mentioned previously.⁹

An attempt was also made to reference the spectra to the C(1s) photoelectron line. However, since this line originates not only from the carbon in the sample but also from any hydrocarbon contaminants present in the vacuum system, the resulting signals were found to be too broad to serve as a reliable reference in the determination of binding energies.

Since the Mg K α X-rays are not monochromatized, for every primary photoelectron line that is excited by the K $\alpha_{1,2}$ radiation, there is also a satellite line excited by the K $\alpha_{3,4}$ radiation. These $\alpha_{3,4}$ satellites are, however, easy to distinguish because they appear at 8.9 eV on the low binding energy side of the primary line with a constant relative intensity.

Results

In the present investigation, the majority of the spectra covered the energy region containing the Ni(2p_{3/2,1/2}) levels. The binding energies of these levels, as well as the positions of their associated shake-up satellites, when present, were determined. In some cases, binding energies of some of the atoms of the coordinating ligands were also measured. For ligands containing nitrogen, the binding energies reported correspond to the N(1s) level; for those containing arsenic, to the As(3p_{3/2}) level.

The results are presented in tables which also contain references to the method of synthesis. Similarity between the binding energies of the I(3p_{3/2}) level (~875 eV) and the Ni(2p_{1/2}) level satellite (~872 eV) make it impossible to record all of the Ni(2p) signals of compounds containing iodide ions.

The shake-up satellites, as shown in Figure 1, have been classified following the convention of Frost:⁸ a type A compound, which has two satellites in both 2p levels; a type B, which has only one satellite for the Ni(2p_{3/2}) signal and two well-defined or sometimes overlapping satellites for the Ni(2p_{1/2}) signal; and a type C, which has one satellite to each Ni(2p) signal.

It is known that nickel can form a variety of complexes in different stereogeometries containing the metal ion in different oxidation states.^{18,43,44} For the sake of clarity and convenience, the data will be grouped according to the structure of the compounds.

(1) Octahedral complexes which produce electronic configurations d⁶, d⁷, and d⁸ are listed in Table I.

(2) Nickel adopts tetrahedral stereochemistry in compounds containing the metal in oxidation states of 0 and 2, which show different magnetic properties—the former diamagnetic and the latter paramagnetic. For reasons which will be discussed later, nickel(0) compounds do not produce shake-up satellites, whereas tetrahedral nickel(II) compounds do. Table II summarizes the data obtained for the tetrahedral compounds.

(3) All known square-planar complexes of nickel(II) are diamagnetic, and their Ni(2p) photoelectron spectra are without satellites. The binding energies of the planar compounds used in this study are given in Table III.

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Table I. Binding Energies (eV) of Octahedral Compounds of Nickel

| No. | Compd ^f | E | | | E | | | E | | | Method of syn.ref |
|-----|---|-------------------------|--------------------------|-------------------|-------------------------|--------------------------|-------------------|--------------------------|-------------------|---------------------------------|-------------------|
| | | Ni (2p _{3/2}) | SAT (2p _{3/2}) | ΔE _{3/2} | Ni (2p _{1/2}) | SAT (2p _{1/2}) | ΔE _{1/2} | SAT (2p _{1/2}) | ΔE _{1/2} | N(1s) or As(3p _{3/2}) | |
| 1 | K ₂ [Ni(NO ₂) ₆] ^c | 855.9 | 860.7 | 4.8 | 873.4 | 877.9 | 4.5 | | | | 10 |
| 2 | BaK ₂ [Ni(NO ₂) ₆] ^c | 855.0 | 860.0 | 5.0 | 872.9 | 877.5 | 4.6 | | | 403.2 | 11 |
| 3 | NiSO ₄ ·6H ₂ O ^b | 856.5 | 861.7 | 5.2 | 874.2 | 879.2 | 5.0 | | | | |
| 4 | NiSO ₄ ^b | 856.3 | 860.6 | 4.3 | 874.1 | 879.6 | 5.5 | | | | |
| 5 | NiO ^c | 854.0 | 860.1 | 6.1 | 872.0 | 878.8 | 6.8 | | | | |
| 6 | NiF ₂ ^c | 857.2 | 863.1 | 5.9 | 874.7 | 880.7 | 6.0 | | | | |
| 7 | NiCl ₂ ^a | 855.3 | 860.7 | 5.4 | 873.0 | 878.3 | 5.3 | | | 881.6 | |
| 8 | NiBr ₂ ^a | 854.3 | 859.5 | 5.2 | 871.5 | 876.6 | 5.1 | | | 880.6 | |
| 9 | NiI ₂ ^d | 852.9 | 857.1 | 4.2 | | | | | | | |
| 10 | [(CH ₃) ₄ N][NiCl ₃] ^a | 854.8 | 859.9 | 5.1 | 872.5 | 877.0 | 4.5 | | | 880.5 | |
| 11 | [NH ₄] ₂ [NiF ₄] ^c | 856.7 | 862.1 | 5.4 | 874.6 | 880.3 | 5.7 | | | | 12 |
| 12 | [Ni(bzbx) ₂] ₃ ^b | 854.7 | 858.2 | 3.5 | 872.2 | 879.9 | 7.7 | | | | 13 |
| 13 | [Ni(N-Me(sal)) ₂] ₁₇ ^b | 854.7 | 860.2 | 5.5 | 872.1 | 878.5 | 6.4 | | | | 14 |
| 14 | Ni(tfac) ₃ ^b | 854.3 | 858.3 | 4.0 | 871.8 | 880.6 | 8.8 | | | | 15 |
| 15 | [(CH ₃) ₄ N][Ni(NCS) ₆] ^c | 855.4 | 861.8 | 6.4 | 873.3 | 879.5 | 6.2 | | | 401.9, 397.1 | 16 |
| 16 | [Ni(diars) ₂ Cl ₂][ClO ₄] ₂ | 854.7 | | | 872.6 | | | | | | 17 |
| 17 | Ni(OAc) ₂ ·4H ₂ O ^b | 855.5 | 860.0 | 4.5 | 872.9 | 878.8 | 5.9 | | | | |
| 18 | [Ni(diars) ₂ Cl ₂ Cl] ^b | 853.9 | 860.9 | 7.0 | 871.6 | 878.8 | 7.2 | | | 141.0 | 18 |
| 19 | NiCO ₃ ^c | 854.7 | 860.5 | 5.8 | 872.9 | 878.7 | 5.8 | | | | |
| 20 | [Ni(dipy) ₃ Cl ₂ ·6H ₂ O] ^b | 854.7 | 861.4 | 6.7 | 872.7 | 879.6 | 6.9 | | | 398.9 | 19 |
| 21 | Ni(dipy) ₂ Cl ₂ ^b | 854.9 | 861.2 | 6.3 | 872.7 | 878.9 | 6.2 | | | 399.1 | 19 |
| 22 | Ni(N-Me(sal)) ₂ (phen) ^b | 854.2 | 860.7 | 6.5 | 872.1 | 877.6 | 5.5 | | | 879.6 | 20 |
| 23 | [Ni(DMSO) ₆][ClO ₄] ₂ ^{b,e} | | | 5.8 | | | 3.8 | | | 6.5 | 21 |
| 24 | [Ni(phen) ₃ Cl ₂ ·10H ₂ O] ^b | 855.0 | 862.0 | 7.0 | 872.8 | 879.8 | 7.0 | | | 398.1 | 19 |
| 25 | [Ni(en) ₃ Cl ₂ ·2H ₂ O] ^b | 854.6 | 860.9 | 6.3 | 872.4 | 878.1 | 5.7 | | | 398.7 | 22 |
| 26 | Ni(en) ₂ Cl ₂ ·2H ₂ O ^b | 854.2 | 860.2 | 6.0 | 871.9 | 877.4 | 5.5 | | | 398.8 | 22 |
| 27 | Ni(en) ₂ Br ₂ ·2H ₂ O ^b | 854.2 | 860.2 | 6.0 | 871.9 | 877.4 | 5.5 | | | 398.4 | 22 |
| 28 | Ni(en) ₂ I ₂ ·2H ₂ O ^a | 854.2 | | | | | | | | | 22 |
| 29 | [Ni(Quin) ₂ (NO ₂) ₂] ^b | 854.5 | 859.7 | 5.2 | 872.4 | 877.2 | 4.8 | | | 402.1, 398.3 | 38 |
| 30 | Ni(phen) ₂ Cl ₂ ·4H ₂ O ^b | 854.1 | 859.8 | 5.7 | 871.6 | 877.9 | 6.3 | | | 398.3 | 19 |
| 31 | Ni[(C ₂ H ₅) ₃ NH ₂] ₂ (ClO ₄) ₂ ^{b,e} | | | 5.8 | | | 5.0 | | | | 39 |
| 32 | Ni(Gly) ₂ (H ₂ O) ₂ ^b | 854.4 | 859.8 | 5.4 | 872.4 | 878.2 | 5.8 | | | | 40 |
| 33 | [Ni(dien) ₂](NO ₃) ₂ ^b | 854.5 | 860.5 | 6.0 | 872.3 | 877.7 | 5.4 | | | 406.0, 398.8 | 41 |

^a Type of satellite A. ^b Type of satellite B. ^c Type of satellite C. ^d Unable to measure due to I(3p_{3/2}) signal. ^e Sample measured at 77°K. ^f Ligand abbreviations: bzbx, dibenzoylimethanato ion; tfac, trifluoroacetylacetonate ion; dipy, α,α'-dipyridyl; phen, o-phenanthroline; Ni-Me(sal), N-methylsalicylaldimine; diars, o-phenylenebis(dimethylarsine); DMSO, dimethyl sulfoxide; en, ethylenediamine; Quin, quinoline; Gly, glycine; dien, diethylenetriamine.

Table II. Binding Energies (eV) of Tetrahedral Compounds of Nickel

| Compd | No. | E | | $\Delta E_{3/2}$ | SAT ($2p_{3/2}$)' | $\Delta E_{3/2}$ | E | | $\Delta E_{1/2}$ | SAT ($2p_{1/2}$)' | $\Delta E_{1/2}$ | Method of syn ref |
|---|-----|----------------------|-----------------------|------------------|------------------------|------------------|----------------------|-----------------------|------------------|------------------------|------------------|----------------------|
| | | Ni ($2p_{3/2}$) | SAT ($2p_{3/2}$) | | | | Ni ($2p_{1/2}$) | SAT ($2p_{1/2}$) | | | | |
| Ni(Br)(NO)[(C ₆ H ₅) ₃ P] ₂ | 34 | 853.1 | | | | | | 871.1 | | | | 23 |
| [(C ₆ H ₅) ₃ P] ₂ NiCl ₂ ^b | 35 | 853.6 | 860.1 | 6.5 | | | | 871.6 | 873.6 | 2.0 | 879.1 | 24 |
| [(C ₆ H ₅) ₃ P] ₂ NiBr ₂ ^b | 36 | 853.7 | 857.7 | 4.0 | | | | 870.5 | 874.2 | 3.7 | 879.7 | 24 |
| [<i>n</i> -C ₃ H ₇ P(C ₆ H ₅) ₂] ₂ NiBr ₂ ^b | 37 | 853.7 | 860.0 | 6.3 | | | | 871.5 | 873.5 | 2.0 | 880.0 | 25 |
| [(C ₆ H ₅) ₃ P] ₂ Ni(NO ₃) ₂ ^a | 38 | 854.4 | 860.1 | 5.7 | 862.5 | 8.1 | | 872.1 | 877.1 | 3.6 | 879.4 | 24 |
| [CH ₃ P(C ₆ H ₅) ₃] ₂ [NiCl ₄] ^a | 39 | 854.4 | 859.6 | 5.2 | 862.3 | 7.8 | | 873.5 | 880.1 | 3.5 | 880.1 | 26 |
| [CH ₃ P(C ₆ H ₅) ₃] ₂ [NiBr ₄] ^a | 40 | 854.1 | 858.7 | 4.6 | 862.4 | 8.3 | | 871.9 | 875.4 | 3.5 | 880.1 | 26 |
| [(C ₂ H ₅) ₂ N] ₂ [Ni] ^c | 41 | 853.0 | 856.5 | 3.5 | | | | | | | | 16 |
| [(CH ₃) ₄ N][Ni(NCS) ₄] ^b | 42 | 854.0 | 857.7 | 3.7 | | | | 871.7 | 874.7 | 3.0 | 880.7 | 12 |
| [(C ₂ H ₅) ₂ N][Ni(C ₆ H ₅) ₂ P]NiBr ₃ ^a | 43 | 853.6 | 858.9 | 5.3 | | | | 871.7 | 874.9 | 3.2 | 880.2 | 12 |
| Ni(CO) ₂ [(C ₆ H ₅) ₂ PCH ₂ CH ₂ P- (C ₃ H ₅)(C ₆ H ₅)] | 43a | 852.9 | | | 862.6 | 9.0 | | | | | | d |

^a Type of satellite A. ^b Type of satellite B. ^c Unable to measure due to I(3p_{3/2}) signal. ^d Compound donated by J. DeIcaudio, University of Maryland.

Table III. Binding Energies (eV) of Square-Planar Compounds of Nickel

| Compd ^a | No. | E | | Method of syn ref |
|---|-----|----------------------------|----------------------------|-------------------------|
| | | Ni (2p _{3/2}) | Ni (2p _{1/2}) | |
| Ni(diars) ₂ Cl ₂ | 44 | 853.7 | 870.8 | 18 |
| Ni(DMG) ₂ | 45 | 854.3 | 871.6 | 27 |
| [(C ₂ H ₅) ₂ N][Ni[S ₂ C ₂ (C ₆ H ₅) ₂] ₂] | 46 | 852.5 | 869.7 | 28 |
| [Ni(diphos)] ₂ [ClO ₄] ₂ | 47 | 853.6 | 870.8 | 29 |
| [(C ₆ H ₅) ₂ PH] ₂ NiI ₂ ^b | 48 | 851.9 | | 30 |
| Ni[S ₂ C ₂ (C ₆ H ₅) ₂] ₂ | 49 | 852.9 | 870.3 | 31 |
| [N ₂ H ₅] ₂ [Ni[S ₂ C ₂ (C ₆ H ₅) ₂] ₂] | 50 | 852.8 | | 31 |
| Ni(diphos)Br ₂ | 51 | 853.3 | 870.6 | 29 |
| [(<i>n</i> -C ₄ H ₉) ₃ P] ₂ NiCl ₂ | 52 | 853.7 | 870.9 | 32 |
| Ni(CN) ₂ | 53 | 853.9 | 871.4 | |
| [(C ₆ H ₅) ₃ P] ₂ Ni(NCS) ₂ | 54 | 853.6 | 871.3 | 24 |
| Ni(<i>N</i> -Me(sal)) ₂ | 55 | 854.1 | 871.3 | 33 |
| Ni(bz bz) ₂ | 56 | 853.5 | 870.9 | 14 |
| K ₂ [Ni(CN) ₄] | 57 | 855.0 | 872.5 | |
| [(C ₂ H ₅) ₄ N] ₂ [Ni[S ₂ C ₂ (CN) ₂] ₂] | 58 | 853.1 | 870.5 | 34 |
| [(C ₂ H ₅) ₄ N][Ni[S ₂ C ₂ (CN) ₂] ₂] | 59 | 853.1 | 870.8 | 28 |
| [<i>n</i> -C ₃ H ₇ P(C ₆ H ₅) ₂] ₂ NiBr ₂ | 60 | 853.3 | 870.5 | 25 |
| {K ₂ [Ni(CN) ₃] ₂ } | 61 | 854.7 | 871.9 | 35 |

^a Ligand abbreviations: diars, *o*-phenylenebis(dimethylarsine); DMG, dimethylglyoxime; diphos, *P,P,P',P'*-tetraethylethylenediphosphine; *N*-Me(sal) = *N*-methylsalicylaldimine; bz bz, dibenzoylmethane. ^b Unable to measure due to strong I(3p_{3/2}) signal.

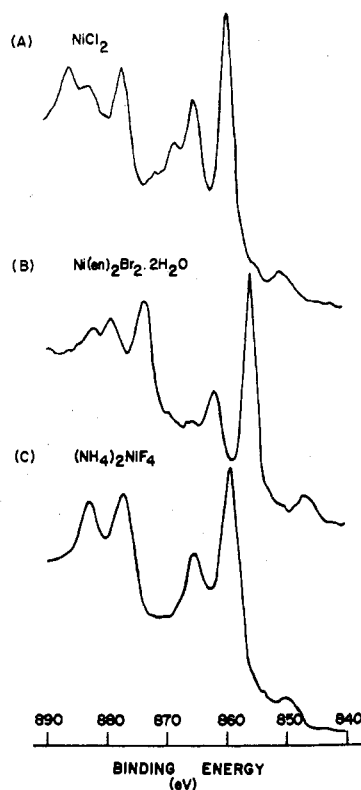


Figure 1. Types of satellites observed in the Ni(2p) photoelectron spectra of (A) NiCl₂, (B) Ni(en)₂Br₂·2H₂O, (C) (NH₄)₂NiF₄.

(4) Five-coordinate complexes of nickel(II) are of two types: they have either two unpaired electrons or none. In the diamagnetic complexes the donor atoms of the ligands are carbon, phosphorus, arsenic, or sulfur. All known paramagnetic complexes contain nitrogen or oxygen as ligand atoms. Table IV summarizes the data collected for some low-spin complexes.

(5) There are, however, a number of nickel(II) complexes whose behavior is not consistent within any one of the structural types described above, and, therefore, they were

Table IV. Binding Energies (eV) of Pentacoordinated Compounds of Nickel

| Compd ^a | No. | E | | Method of syn ref |
|---|-----|-------------------------|-------------------------|-------------------|
| | | Ni (2p _{3/2}) | Ni (2p _{1/2}) | |
| [(C ₆ H ₅) ₂ PH] ₃ NiBr ₂ | 62 | 851.9 | 868.5 | 30 |
| [Ni(QP)Cl][ClO ₄] | 63 | 853.2 | 870.6 | 36 |
| [Cr(en) ₃][Ni(CN) ₅]·2H ₂ O | 64 | 854.1 | 871.9 | 37 |
| [Ni(QAS)Cl][ClO ₄] | 65 | 853.3 | 871.0 | 36 |

^a Ligand abbreviations: QP, tris(*o*-diphenylphosphinophenyl)-phosphine; QAS, tris(*o*-diphenylarsinophenyl)arsine.

once described as anomalous. In recent years, however, with the advent of ligand field theory and the widespread use of new physical methods, some of these anomalies have been satisfactorily explained. In the present investigation, we have studied three isomeric pairs of nickel(II) complexes with different magnetic properties. Such isomers are useful also because they give some information on the relation of binding energy of the central ion to stereochemistry.

Discussion

Binding Energies. Binding energies vary considerably throughout the series of octahedral compounds studied. It can be seen from Table I that if one considers only compounds containing the nickel(II) ion, binding energy reaches its maximum value in nickel(II) fluoride (857.2 eV) and its minimum in nickel(II) iodide (852.9 eV). Among the halides (compounds 6–9), a correlation between binding energy and ligand electronegativity is expected—*i.e.*, binding energy increases in the following order: I < Br < Cl < F. The method pursued is as follows. Some simple binary nickel(II) compounds were chosen to estimate the charge on the metal ion and to correlate this with their Ni(2p_{3/2}) binding energies. The charge on nickel was estimated by Pauling's method,⁴⁵ combined with Huheey's group electronegativities⁴⁶ in the cases of polyatomic groups. Table V gives the shifts of Ni(2p_{3/2}) binding energies relative to nickel(II) fluoride and the charges on nickel estimated for those compounds.

As shown in Figure 2, the experimental binding energy correlates fairly well with the estimated charge using Pauling's method, although no corrections for Madelung potentials have been incorporated. These results show once more that oxidation states cannot be determined from measured binding energies alone. Although all of the compounds in Table V contain nickel(II) ions, the range of 4.3 eV in the binding energies indicates that the binding energies also depend on how well the ligands are able to remove charge from the metal ion.

As the ligand becomes more structurally elaborate, the calculation of charge is more complicated, though a qualitative trend can be applied to account for the variations observed in binding energy. For instance, the binding energies of the hydrated (3) and anhydrous (4) forms of nickel(II) sulfate can be compared. In this case, there is an increase in binding energy for the hydrated form attributable to the change in lattice energy and also to the increase of ionic character between nickel and sulfate due to substitution.

Another way to illustrate these trends is by comparing nickel(II) chloride with some other coordination compounds in which chlorine atoms are systematically replaced by other ligands such as *o*-phenanthroline, ethylenediamine, or α, α' -

(45) K. Siegbahn, et al., "ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, Sweden, 1967.

(46) J. E. Huheey, *J. Phys. Chem.*, **70**, 2086 (1966).

Table V. Binding Energies and Estimated Charges for Some Nickel(II) Compounds

| Compd | Binding energy shift, ^a eV | Charge on Ni | Compd | Binding energy shift, ^a eV | Charge on Ni |
|---|---------------------------------------|--------------|---------------------------------|---------------------------------------|--------------|
| | | | | | |
| NiBr ₂ | -2.9 | 0.488 | NiSO ₄ | -0.9 | 0.838 |
| NiO | -3.2 | 0.440 | [NH ₄] ₂ | -0.5 | 1.16 |
| [(CH ₃) ₄] ₂ NiCl ₃ | -2.4 | 0.656 | NiF ₄ | | |
| NiCl ₂ | -1.9 | 0.646 | NiF ₂ | 0.0 | 1.31 |

^a Relative to NiF₂.

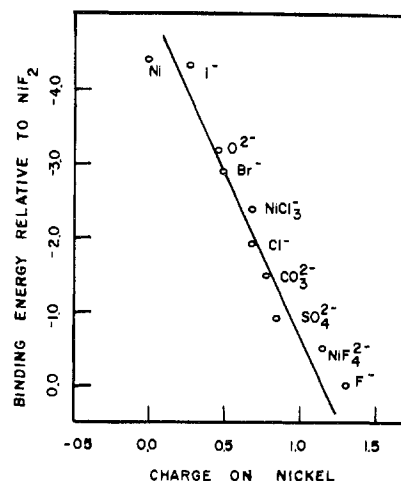


Figure 2. Correlation between the Ni(2p_{3/2}) binding energy (relative to NiF₂) and the estimated charge on nickel for some simple nickel(II) compounds.

dipyridyl. Table I gives the N(1s) or As(3p_{3/2}) binding energies of ligands in some of the octahedral compounds studied. The Ni(2p) binding energies of compounds of the formula NiL₂Cl₂·xH₂O, where L = dipyridyl, ethylenediamine, or phenanthroline, are lower than those of nickel(II) chloride, because these complexes contain ligands with more effective donor atoms. In the comparison of the N(1s) binding energy of free *o*-phenanthroline (397.5 eV) with that of a nickel complex of *o*-phenanthroline, Ni(phen)₂·Cl₂·4H₂O, compound 30, a net increase of 0.8 eV is observed. This effect is expected since the lone pair of nitrogen electrons will be donated to nickel, thus increasing nitrogen's positive charge.

Tetrahedral compounds of the type MX₄²⁻ (compounds 39–41), where X = I, Br, or Cl, show the same increase in binding energy observed for octahedral compounds—*i.e.*, binding energy increases in the following order: I < Br < Cl. When tetrahedral anionic species such as NiX₄²⁻ (X = Cl, Br) are compared with compounds of the formula L₂NiX₂ (L = triphenylphosphine), the binding energies of nickel are lower in the latter case in which phosphorus donates to the metal (compare compounds 35 and 36, and 39 and 40). If a bromide ion of the tetrabromonickelate(II) ion is replaced by triphenylphosphine (compound 43), the binding energy of nickel also decreases.

According to Nyholm,^{17,18} diarsine forms complexes with nickel ions in oxidation states of 2+, 3+, and 4+. Here also the binding energies are lowered according to the same effects discussed above. For example, [Ni(diars)₂]Cl₂, compound 44, is a planar complex which has a Ni(2p_{3/2}) binding energy of 853.7 eV. Generally speaking, a high binding energy is expected for a compound with a high oxi-

dation state (such as 4+), but $[\text{Ni}(\text{diars})_2\text{Cl}_2][\text{ClO}_4]_2$, compound 19, is an exception since the arsenic atoms donate efficiently to the metal and decrease its binding energy.

It has been mentioned previously that octahedral and tetrahedral shake-up satellites can be grouped into three types. Octahedral compounds containing chlorine, bromine, and presumably iodine belong to type A (with two satellites for each photoelectron line), those containing fluorine, nitrite, oxide, carbonate, or isothiocyanate ions belong to type C (with one satellite each); the rest of the octahedral compounds studied show satellites of type B (with one satellite for $2p_{3/2}$ and two for $2p_{1/2}$). Different compounds of nickel containing the same ligand show similar types of shake-up satellites. For example, in spite of tetragonal distortions, NiCl_2 (7) and $[(\text{CH}_3)_4\text{N}][\text{NiCl}_3]$ (10) both have type A satellites, while NiF_2 (6) and $[\text{NH}_4]_2[\text{NiF}_4]$ (11) both have type C satellites. This indicates that shake-up satellites depend on the coordinated ligand rather than on stereochemistry and that a similar spectrum should be expected whenever the same ligands appear in any paramagnetic compounds.

Because square-planar compounds of nickel are diamagnetic, the photoelectron spectrum of the $\text{Ni}(2p)$ region becomes fairly simple, as will be discussed in the next section. Several planar complexes containing phosphorus ligands have been investigated. The $\text{Ni}(2p_{3/2})$ binding energies for these compounds are grouped, on the average, at 853.5 ± 0.2 eV, with the exception or $[(\text{C}_6\text{H}_5)_2\text{PH}]_2\text{NiI}_2$, compound 48, which shows a $\text{Ni}(2p_{3/2})$ signal at 851.9 eV. The reason for this discrepancy seems to be that this compound is fairly sensitive to decomposition when gold is vaporized onto the sample as evidenced by the considerable broadening of the $\text{Au}(4f_{5/2,7/2})$ doublet. Perhaps the phosphine forms a more stable compound with gold and this causes broadening of the doublet.

The dithiolate compounds 46, 49, 50, 58, and 59 are best described as planar compounds containing nickel(II) ions. While the metal binding energies remain more or less constant for compounds containing the same dithiolate ligand, the $S(2p)$ binding energies decrease with increasing negative charge on the anionic species.⁴⁷ This suggests that the ligand, not the metal ion, accommodates the excess of negative charge in these complexes.

Both $[\text{Ni}(\text{QP})\text{Cl}][\text{ClO}_4]$ and $[\text{Ni}(\text{QAS})\text{Cl}][\text{ClO}_4]$, compounds 63 and 65, are known to exist in a trigonal-bipyramidal structure; and on the basis of their electronic spectra, it has been pointed out that the electron delocalization of the arsenic and phosphorus ligands (QP and QAS) is comparable.⁴⁸ Thus, a similar binding energy of the nickel(II) ion is expected in both complexes. The pentacyanonickelate(II) ion is the only five-coordinate complex containing just monodentate ligands. Recently Basolo and Raymond³⁷ isolated $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 2\text{H}_2\text{O}$, compound 64, which has two of these anions per unit cell with different geometries: one a tetragonal pyramid and the other a distorted trigonal bipyramid. In this compound the binding energy of nickel increases perhaps through coordination with the strongly withdrawing cyanide group. The unusually low binding energy of $[(\text{C}_6\text{H}_5)_2\text{PH}]_3\text{NiBr}_2$, compound 62, may be due to decomposition in the probe similar to that of $[(\text{C}_6\text{H}_5)_2\text{PH}]_2\text{NiI}_2$, compound 48.

Shake-Up Satellites. The satellites associated with the $2p$

photoelectron lines of transition metal compounds are interpreted to be due to the excitation of a metal 3d electron into an unoccupied metal orbital (predominantly 4s)⁴ concurrently with the emitted photoelectron.²⁻⁴ Photoemission being a very fast process ($<10^{-15}$ sec), the instantaneous creation of the 2p vacancy abruptly changes the potential of the remaining electrons. In the sudden approximation⁴⁹⁻⁵³ the subsequent relaxation energy of the remaining electron orbitals as they shrink toward the positive hole can be used either for ejecting another electron (shake-off) or promoting it into an unoccupied bound level (shake-up).⁴⁹⁻⁵³ Consequently one observes a photoelectron satellite line representing electrons of lower kinetic energy (an apparently higher binding energy), whose separation from the main line corresponds to the shake-up transition. It is clear from this description that shake-up or shake-off transitions occur prior to the normal deexcitation of the photohole by either Auger electron emission or fluorescence ray emission.

The selection rules for the shake-up transitions (monopole) are $\Delta J = \Delta L = \Delta S = 0$, where J , L , and S represent the total, orbital, and spin angular momenta of the ion after photoemission.⁵³ These are essentially the consequences of momentum conservation laws. In the central-field approximation the additional selection rule $\Delta l = 0$ (and $\Delta m_l = \Delta m_s = 0$)^{49,51,52} also applies where l denotes the orbital momentum of the electron making the shake-up transition. This model has been successfully applied to the shake-up spectra of Ne and Ar.^{49,53} In this single-particle model, the outer electrons are assumed to move in an effective spherically symmetric potential and are independent of each other. In solids, however, there is rather strong interaction among the valence electrons. In this latter case, since the shake-up transition still depends mainly on the wave function overlap of the valence orbitals (assuming negligible interaction with the core), these orbitals must possess the same symmetry. In other words, one expects the additional selection rules to be $\Delta L_v = 0$ and $\Delta S_v = 0$ in Russell-Saunders coupling, where L_v and S_v now denote the combined orbital and spin momenta of the valence configurations involved in the shake-up transition.

Applying these selection rules to the transition metal ions with initial state $(2p)^5(3d)^n$ (the filled shells are omitted in the notation) and final state $(2p)^5(3d)^{n-1}(4s)$, we find that shake-up transitions of the 3d-4s type can occur for either n odd or n even but L_v not zero. Because paramagnetic ions belong to this class shake-up transitions of the 3d-4s type are possible for them. On the other hand, for diamagnetic ions, all electrons are paired to give an initial state $L_v = 0$; but the final state would always have the equivalent configuration $(3d)(4s)$, which cannot couple to give a final-state L_v of zero. Thus shake-up transitions in such cases are forbidden by the selection rules. Indeed, shake-up satellites have not been observed in diamagnetic compounds by either Frost, *et al.*,⁸ or us.⁹ It should be emphasized at this point that we have so far discussed only the selection rules governing shake-up transitions. These transitions also depend on the energetics and other favorable competing modes of excitation, such as intraband transitions. As

(49) M. O. Krause, T. A. Carlson, and R. D. Dismukes, *Phys. Rev.*, **170**, 37 (1968), and citations therein.

(50) T. A. Carlson and M. O. Krause, *Phys. Rev. A*, **140**, 1057 (1965).

(51) J. S. Levinger, *Phys. Rev.*, **90**, 11 (1953).

(52) T. Aberg, *Phys. Rev.*, **156**, 35 (1966).

(53) K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969, Chapter IV.

(47) S. O. Grim, L. J. Matienzo, and W. E. Swartz, Jr., *Inorg. Chem.*, in press.

(48) G. Dyer and D. W. Meek, *Inorg. Chem.*, **6**, 149 (1957).

shown in Figure 1, the shake-up satellites in solids have a much higher intensity, relative to the main line, than those observed in Ne and Ar.^{49,53} This is partially due to the lower energy involved in the allowed solid shake-up satellites and partially due to the highly broadened valence orbitals in solids which result in much enhanced overlaps. Shake-off transitions have higher energies and lower probabilities. With the present signal-to-background ratio in solid photoelectron spectra, such transitions would be quite difficult to observe.

Now we must turn specifically to our data on the nickel compounds. Since all known square-planar complexes of nickel(II) are diamagnetic, no shake-up satellites are observed in their 2p photoelectron spectra. The compound $[\text{Ni}(\text{diars})_2\text{Cl}_2][\text{ClO}_4]_2$ (**16**) is octahedral structurally. However, since its nickel ions has a spin-paired (diamagnetic) $3d^6$ configuration, there are no shake-up satellites. Similarly, among the tetrahedral compounds listed in Table II, $\text{NiBr}(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ (**34**) is diamagnetic with the oxidation state of nickel being zero. As expected, its 2p photoelectron lines are narrow and show no satellites. In the five-coordinated complexes of nickel(II), again only those diamagnetic with donor atoms of C, P, S, or As show no shake-up satellites. These observations are further supported by those of Frost, *et al.*,⁸ on copper compounds where shake-up satellites are seen in cupric ($3d^9$) compounds, but not in cuprous ($3d^{10}$) compounds.

Having established the correlation between the presence or absence of shake-up satellites with the magnetic and, to a certain extent, the structural properties of transition metal complexes, such a correlation can, in turn, be advantageously utilized to clarify existing ambiguities in these properties. Some examples of such applications will be given in the next section.

Frost, *et al.*,⁸ suggested that the second satellite with smaller separation from the main line in copper compounds may be due to a shake-up transition of the type metal $3d \rightarrow$ ligand-antibonding orbital. Detailed examination of our data on nickel compounds reveals the following features. (1) Double satellites are observed only in the more covalent complexes where one expects considerable delocalization of the metal electrons and consequently more overlap between metal and ligand orbitals. (2) As mentioned earlier, the general characteristics and relative intensities of the double satellites are found to be only a function of the coordinated ligand, although their separations may be affected by stereochemistry. For example, NiCl_2 (**7**), NiCl_3^- (**10**), and NiCl_4^{2-} (**39**) all show similar satellite characteristics and relative intensities although the structures of NiCl_2 and NiCl_3^- are octahedral, whereas NiCl_4^{2-} is tetrahedral. These general features seem to support the metal-ligand transition hypothesis of the second shake-up satellite.

We have also found a strong correlation between the satellite separation from the main line and the degree of covalency in the bonding. The data indicate that the more covalent the bonding, the larger the satellite separation. The order essentially follows the nephelauxetic series. Similar trends in copper compounds can likewise be established from the data of Frost, *et al.*⁸ It seems possible that shake-up satellites separation may be used in conjunction with binding energy to yield qualitative information about the relative degree of covalency between the ligand and the central ion.

The origin of the type B satellites—single satellite for one 2p photoelectron line, double for the other—remains unclear. For a given compound, photoelectrons from $2p_{1/2}$ and $2p_{3/2}$

levels experience identical ligand fields. The fact that their satellites exhibit different characteristics seems to imply that the origin of the difference is atomic in nature and is perhaps related to their difference in angular momentum. It is also puzzling that while in nickel compounds the $2p_{1/2}$ photoelectron line possesses double satellites, in copper compounds it is the $2p_{3/2}$ line that shows double satellites in type B spectra. The resolution of this problem is currently under study.

Applications. As mentioned earlier, XPS is a powerful tool in clarifying a considerable number of ambiguities in oxidation state assignments and magnetic properties. Furthermore, investigation of nickel compounds has enabled us to establish a relationship between binding energy and stereochemistry. In the following paragraphs, we cite some specific examples of such applications.

For example, $[\text{K}_2\text{Ni}(\text{CN})_3]_2$, compound **61**, which is known to contain nickel(I), should correspond to a d^9 paramagnetic configuration. However, this compound shows only two single-lines in its Ni(2p) spectrum, without any shake-up satellite. X-Ray diffraction studies have shown that this compound is dimeric with a short metal to metal distance,⁵⁴ thus suggesting a metal-metal bond. The absence of shake-up satellites certainly bears out this latter interpretation.

The magnetic data of dithiolate compounds **46** and **59**, known to be planar and paramagnetic both in the solid state and in solution, indicate that they possess an unpaired electron. On the basis of these data, it was erroneously concluded that these compounds contained nickel(III) ions.³⁴ Later, Gray, *et al.*,⁵⁵ suggested, by means of molecular orbital calculations carried out on compound **59**, that the unpaired electron occupies a molecular orbital mainly ligand in character. But the photoelectron spectra of compounds **46** and **59** do not show any shake-up satellites supporting Gray's interpretation;⁴⁷ *i.e.*, although the compound is paramagnetic, the nickel behaves as if it were diamagnetic in the XPS sense, *viz.*, no shake-up satellites. Consequently the unpaired electron must reside mainly on the ligand.

As mentioned earlier, diarsine forms complexes with nickel in different oxidation states. If a direct relationship of binding energy and oxidation state were possible, the oxidation state of nickel in $[\text{Ni}(\text{diars})_2\text{Cl}_2][\text{ClO}_4]_2$ could have erroneously been postulated as II rather than IV, judging from its unusually low binding energy. However, such a low binding energy can be easily explainable on the basis of the donor properties of the ligand.

To illustrate more dramatically the usefulness of shake-up phenomena to distinguish between isomeric pairs with different magnetic properties, three pairs of examples in which a particular ligand forms planar and tetrahedral or octahedral isomeric compounds with nickel(II) were chosen.

Nickel halides react with tertiary phosphines to form complexes of the type NiL_2X_2 . Venanzi, *et al.*,^{25,56} have shown that as the aryl groups of the tertiary phosphines are replaced by alkyl groups, there is a change of structure from tetrahedral to square planar. Hayter and Humiec²⁵ have reported a rather unusual group of compounds which can be isolated in tetrahedral and planar forms as rather stable, solid compounds, among which is $[\eta\text{-C}_3\text{H}_7\text{P}(\text{C}_6\text{H}_5)_2]_2\text{NiBr}_2$.

(54) R. Nast and W. Pfab, *Naturwissenschaften*, **39**, 300 (1952).

(55) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 4594 (1964).

(56) M. C. Browing, J. R. Mellor, L. E. Sutton, D. J. Morgan, S. A. J. Pratt, and L. M. Venanzi, *J. Chem. Soc.*, 693 (1962).

Bis(dibenzoylmethanato)nickel(II) has been isolated in isomers of two different colors:⁵⁷ one diamagnetic and monomeric with a square-planar distribution of the oxygen atoms about nickel (compound **56**) and the other paramagnetic and trimeric with an octahedral distribution of the oxygen atoms about nickel (compound **12**).¹⁴ Similarly bis(*N*-methylsalicylaldimine)nickel(II) also occurs in diamagnetic and paramagnetic isomeric forms (compounds **55** and **13**, planar and octahedral, respectively).¹⁵ Figure 3 (not corrected for sample charging) shows the XPS spectra of the latter pair of compounds (**55** and **13**). We see that the planar isomer (**55**) does not show any shake-up satellites, whereas for the octahedral isomer, compound **13**, shake-up satellites appear at 860.2 and 878.5 eV. In addition, the binding energy of the Ni(2p_{3/2}) signal is found to be 0.6 eV higher in the octahedral form when compared to the planar isomer. Analogous results are obtained with the other isomeric pair, compounds **12** and **56**. Likewise, an increase in coordination number produces an increase of 1.2 eV in the binding energy of the Ni(2p_{3/2}) signal.

Structurally, the isomers of $[n\text{-C}_3\text{H}_7\text{P}(\text{C}_6\text{H}_5)_2]_2\text{NiBr}_2$ (compounds **37** and **60**) are slightly different from those discussed in the previous paragraph. In this case, while compound **60** is planar, compound **37** is tetrahedral rather than octahedral. Nevertheless, the Ni(2p_{3/2}) binding energy is again found to be 0.4 eV higher in the tetrahedral form. These results seem to indicate that the positive charge on the metal ion is greater in octahedral coordination than tetrahedral or square-planar coordination. In a recent report⁵⁸ the authors reported the usefulness of this technique as a means for providing information on the stereochemistry of silver(II) complexes. Furthermore, the authors found that a higher coordination number in these silver compounds results in a decrease in the metal electron binding energy. In light of our results presented above it seems that in order to establish uniquely the trend of binding energy with stereochemistry one should, strictly speaking, limit oneself to comparing those compounds containing the same ligands. This method of comparison has also been suggested by Walton.⁵⁹ Recently a report on XPS studies on some magnesium and aluminum compounds showed that the change from four- to six-fold coordination increases the binding energies of the metal ions. This suggests that the bonds in the latter case are more ionic.⁶⁰ Yet in another case, isothiocyanate ions react with nickel to give $[(\text{CH}_3)_4\text{N}]_2[\text{Ni}(\text{NCS})_4]$ and $[(\text{CH}_3)_4\text{N}]_4[\text{Ni}(\text{NCS})_6]$, as reported by Forster and Goodgame.¹⁶ The Ni(2p_{3/2}) binding energy of the latter (compound **15**) is 855.4 eV, and that of the former (compound **42**) is 854.0 eV. These results indicate that when nickel is bonded to the same ligand under different geometries, the binding energy of the nickel ion increases in the order planar < tetrahedral < octahedral. For a given type of ligand, the nickel to donor distances increase from square planar to tetrahedral to octahedral, as shown in the complexes containing salicylaldiminato groups.⁴³

Summary

The XPS results presented in this paper on nickel compounds generally confirm the trends observed by Frost,

(57) L. Wolf, E. Butter, and H. Weinhelt, *Naturwissenschaften*, **48**, 378 (1961).

(58) D. P. Murtha and R. A. Walton, *Inorg. Chem.*, **12**, 368 (1973).

(59) A. D. Hamer, D. G. Tisley, and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 116 (1973).

(60) C. J. Nichols, D. S. Urch, and A. N. L. Kay, *J. Chem. Soc., Chem. Commun.*, 1198 (1972).

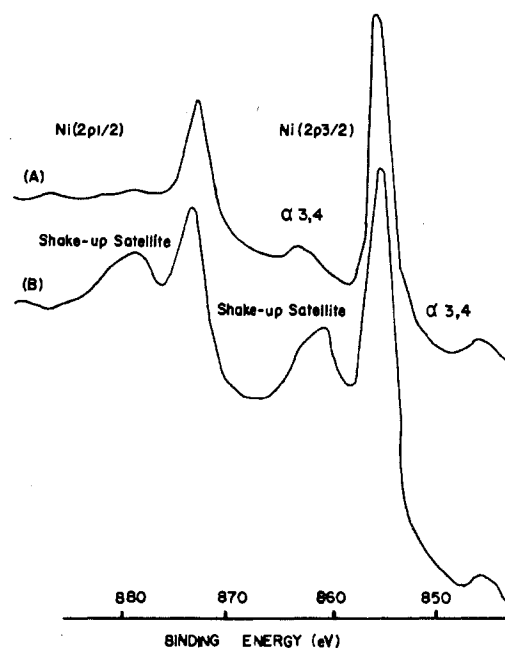


Figure 3. Photoelectron spectra of the Ni(2p) region of the isomeric forms of bis(*N*-methylsalicylaldimine)nickel(II): (A) square-planar isomer; (B) octahedral polymer.

et al.,⁸ on copper compounds. These trends can be summarized as follows.

1. Binding energy alone is insufficient to determine the oxidation state of a metal ion. At a given oxidation state the metal ion binding energy is proportional to its positive charge and inversely proportional to covalency.
2. For the same ligand under different stereochemical geometries, the 2p binding energies of the nickel ion increase in the order planar < tetrahedral < octahedral.
3. Shake-up satellites are found only in paramagnetic compounds; they are absent in diamagnetic compounds.
4. The separation of shake-up satellites from the main line is proportional to the degree of covalency, essentially following the nephelauxetic series.

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Registry No. 1, 15278-50-9; 2, 13782-21-3; 3, 10101-97-0; 4, 7786-81-4; 5, 1313-99-1; 6, 10028-18-9; 7, 7718-54-9; 8, 13462-88-9; 9, 13462-90-3; 10, 1111-85-9; 11, 35278-25-2; 12, 37369-45-2; 13, 41828-47-1; 14, 41828-70-0; 15, 14054-70-7; 16, 41828-71-1; 17, 6018-89-9; 18, 30138-27-3; 19, 3333-67-3; 20, 15554-91-3; 21, 15554-97-9; 22, 41828-51-7; 23, 16742-94-2; 24, 14434-48-1; 25, 33908-61-1; 26, 41828-53-9; 27, 41828-54-0; 28, 41828-55-1; 29, 14318-82-2; 30, 41901-60-4; 31, 41828-57-3; 32, 14215-54-4; 33, 15129-99-4; 34, 14586-72-2; 35, 14264-16-5; 36, 14126-37-5; 37, 15632-23-2; 38, 41765-71-3; 39, 41765-72-4; 40, 41765-73-5; 41, 13927-28-1; 42, 13978-36-4; 43, 41828-60-8; 43a, 29955-02-0; 44, 41828-61-9; 45, 13478-93-8; 46, 41828-62-0; 47, 41901-58-0; 48, 41828-63-1; 49, 38961-86-3; 50, 41828-64-2; 51, 37504-46-4; 52, 15274-43-8; 53, 557-19-7; 54, 15709-62-3; 55, 14322-02-2; 56, 14405-47-1; 57, 14220-17-8; 58, 38930-11-9; 59, 39008-57-6; 60, 15632-24-3; 61, 40810-33-1; 62, 38199-79-0; 63, 41875-87-0; 64, 42080-46-6; 65, 41765-69-9.