for chlorobenzene apparently aids in the promotion of a pathway generating the greater number of charged species in solution, whereas in heptane solvent, the initiating species is neutral, and fewer ionic intermediates are involved.

This research provides direct evidence that the olefin metathesis reaction is initiated by coordinated carbene species. In addition, the evidence indicates that in chlorobenzene solvent, the initial coordinated carbene formed on Mo(CO)$_5$py occurs in a manner analogous to that of the tungsten-based catalysts. Where heptane functions as the solvent, a modified approach to that of Re(CO)$_5$Cl occurs in the formation of the initial coordinated carbene.

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Registry No. 1-Hexene, 592-41-6; 1,7-octadiene, 3710-30-3; 1-pentene, 109-67-1; Mo(CO)$_5$py, 14324-76-6; Mo(CO)$_5$P(C$_6$H$_5$)$_3$, 14971-42-7; Mo(CO)$_4$(py)$_2$, 33570-29-5; Mo(CO)$_4$bpy, 15668-64-1; CH$_3$AlCl$_2$, 917-65-7; C$_2$H$_5$AlCl$_2$, 563-43-9; (C$_4$H$_9$)$_4$NCl, 1112-67-0.

References and Notes

(1) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 7808 (1975).
(2) R. H. Grubbs, P. L. Buck, and D. D. Carr, *J. Am. Chem. Soc.*, **97**, 3265 (1975).
(3) W. S. Greenlee and M. F. Farona, *Inorg. Chem.*, **15**, 2129 (1976).
(4) T. J. Katz, J. McGinnis, and C. Altus, *J. Am. Chem. Soc.*, **98**, 606 (1976).
(5) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).
(6) H. W. Ruble, German Patent 2062448; *Chem. Abstr.*, **75**, 151341 (1971).
(7) M. F. Farona and V. W. Motz, *J, Chem. Soc., Chem. Commun.*, 930 (1976).
(8) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).
(9) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).
(10) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).
(11) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).
(12) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976).
(13) C. P. Casey, H. G. Tuinstra, and M. C. Saeman, *J. Am. Chem. Soc.*, **98**, 608 (1976).
(14) P. G. Gassman and T. H. Johnson, private communication; preprint of manuscript submitted to *J. Am. Chem. Soc.*
(15) J. Chatt, R. H. Crabtree, E. A. Jeffrey, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1167 (1973).

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X-Ray Photoelectron Spectroscopic Study of Iron(II) Spin Equilibrium Complexes and Their Cobalt(II) and Nickel(II) Analogues

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The 2p x-ray photoelectron spectra (XPS) of a series of iron(II) spin equilibrium complexes exhibit broad satellite structure. It is generally assumed that transition metal satellites are the result of either multiplet splitting or shake-up. From a comparison of the XPS spectra of the iron(II) complexes with the analogous cobalt(II) and nickel(II) systems and from temperature-dependence studies on the iron(II) spin equilibrium complexes we have been able to conclude that the satellites in these cases are associated with a decomposition product which appears upon irradiation in the spectrometer. Decomposition of the iron(II) complexes follows a pattern based on the spin state of the metal center. For the two complexes which are mostly high spin at 40 °C, decomposition appears to be complete before statistically significant spectra can be collected. The low-spin complex and the spin equilibrium complex which is mostly low spin at 40 °C did not exhibit any signs of the broad satellite associated with decomposition. At elevated temperatures (150 °C) where the latter complex approaches a 50/50 mixture of high spin and low spin decomposition is again complete before a minimal spectrum can be completed. Preliminary evidence for a correlation between the crystal field stabilization energy or the spin multiplicity of the metal center and the decomposition process is discussed.

Introduction

In recent years x-ray photoelectron spectroscopy (XPS) has been extensively applied to the study of the electronic structure of transition metal complexes. In these studies three types of spectral features have been considered. The first, and most widely studied, involves the chemical shift of the core binding energy. In addition, smaller satellite peaks at higher binding energy often accompany the main ionization peak. Two mechanisms are invoked in order to explain these additional peaks. These are known as multiplet splitting and shake-up.

Analysis of the chemical shift, multiplet splitting, and shake-up transitions in insulating solids containing transition metals has been attempted. The insulating property of these materials tends to make the chemical shifts, referenced against a given standard, somewhat unreliable.[2] Multiplet splitting of the metal ion 3s lines for paramagnetic first-row transition metal complexes is generally considered to be related to the magnetic moment localized at the metal center, i.e., to the number of unpaired electrons on the metal.[3] The effect of multiplet splitting on the metal 2p lines generally results in line broadening of the main peak accompanied by weak features in the background.[4-6] Shake-up peaks in octahedral transition metal complexes have generally been assigned to ligand-to-metal charge-transfer transitions.[7,8] The creation of a core hole can lead to a number of final states. In one, the electrons attain a configuration characteristic of the core-hole ground state. This configuration generally produces the main ionization peak. Alternatively, an electron may be promoted, subject to the monopole selection rules, to a higher electronic level producing shake-up satellites.[8]

It was believed that some metal 2p satellite peaks in photoelectron spectra of first-row transition metal complexes were associated with paramagnetism.[4] Presently, these satellites are viewed as arising from a shake-up process in which initially unoccupied molecular orbitals with the appropriate symmetry and energy provide a large enough transition probability for the lines to be observed.[8] This provides an explanation for the observations of satellite peaks in the 2p x-ray photoelectron spectra of such diamagnetic compounds as ScF$_3$, TiO$_2$, and TiF$_4$.[9] In this view a change in metal ion electronic configuration from paramagnetic to diamagnetic (e.g., iron(II), d^6; nickel(II), d^8) must result in a significant raising in energy of the unoccupied states if the shake-up satellites observed in the paramagnetic complexes are to be

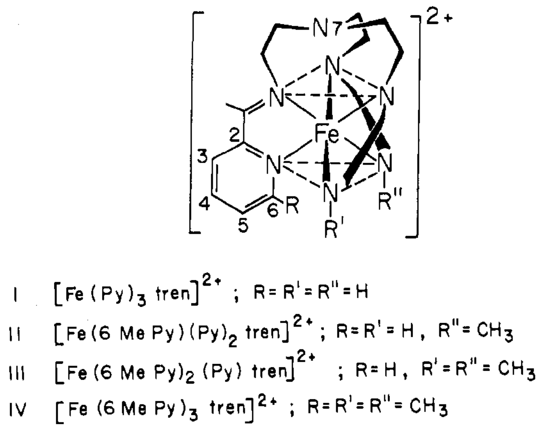

Figure 1. Outline of the overall structural arrangement of the iron(II) spin equilibrium complexes $[Fe(6MePy)_n(Py)_{3-n}tren](PF_6)_2$, n = 0, 1, 2, 3, i.e., Fe-I, Fe-II, Fe-III, and Fe-IV, respectively. See ref 11.

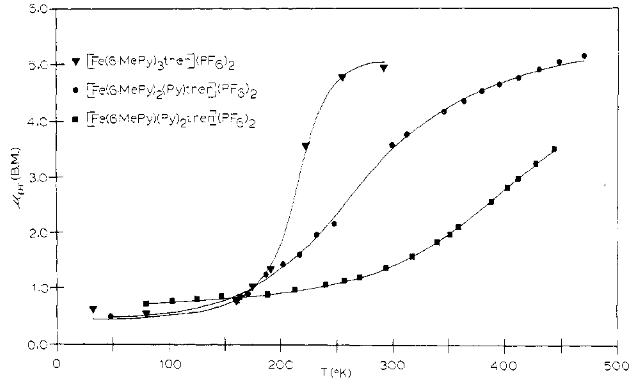

Figure 2. Temperature dependence of the bulk magnetic moment of the iron(II) spin equilibrium complexes $[Fe(6MePy)_n(Py)_{3-n}tren](PF_6)_2$, n = 1, 2, 3, i.e., Fe-II, Fe-III, and Fe-IV, respectively. See ref 11.

absent in the diamagnetic complexes. For nickel(II) complexes large geometric changes (octahedral vs. square planar) accompany these magnetic and energetic changes ($10Dq_{oct} < 10Dq_{sp}$), and the satellites observed in paramagnetic octahedral nickel(II) complexes do not appear in diamagnetic square-planar nickel(II) complexes.[10] This observation conforms to the current view and is taken as confirmatory evidence that increasing the energy separation between the electronic states decreases the probability of shake-up transitions.

The symmetry changes accompanying the magnetic changes in nickel(II) complexes make the interpretation somewhat suspect. A better test of the theory may be available by studying the recently reported iron(II) spin equilibrium complexes shown in Figure 1.[11,12] These compounds provide an excellent probe for the significant features of both multiplet splitting and shake-up transitions. All four complexes in the series are based on the same hexadentate ligand system, having pseudooctahedral geometry and differing only in the number of 6-methylated pyridine groups. At room temperature this series spans a magnetic range in which for solid samples Fe-I is low spin and Fe-IV is high spin, while Fe-II and Fe-III have intermediate magnetic moments (Figure 2).[11,12] The intermediate moments arise from an equilibrium population distribution of both high-spin and low-spin magnetic isomers. Though less extensively studied, both cobalt(II) and nickel(II) analogues have also been synthesized. The complexes of both these metals are paramagnetic and the cobalt(II) complexes are exclusively high spin.[13] All the iron complexes have $10Dq$ values within the small range 12 200 ± 800 cm^{-1}.[12] At the same time the bulk room temperature magnetic moments span a range from 0.5 to 5.2 μ_B (Bohr magnetons).[11] This means that major changes in the magnetic moment on the iron(II) center are associated with only small changes in the energies of ^5A state relative to the ^1A state (~400 cm^{-1}). Thus, it is possible to investigate the effects of changes in the magnetic properties of these complexes independent of significant changes in the energies of the excited states. In addition, a significant alteration in the bulk magnetic moments of Fe-II, Fe-III, and Fe-IV can be obtained by varying the temperature.[11] By this procedure the effect of large magnetic moment changes on the 2p spectrum of an individual complex can also be investigated.

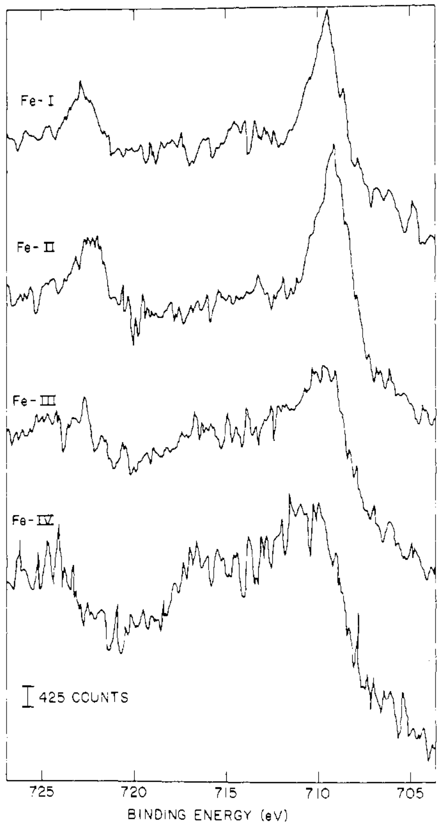

Figure 3. Iron 2p XPS spectra at 40 °C of the series of iron(II) complexes $[Fe(6MePy)_n(Py)_{3-n}tren](PF_6)_2$, n = 0, 1, 2, 3, i.e., Fe-I, Fe-II, Fe-III, and Fe-IV, respectively.

Experimental Section

Synthesis of the iron(II) complexes has been previously reported.[11] Nickel(II)[12] and cobalt(II) complexes were prepared by the identical procedure, with substitution of the appropriate metal chloride for $FeCl_2$. Satisfactory elemental analyses were obtained for all of the complexes studied.

All x-ray photoelectron spectra were obtained on a Varian IEE-15 spectrometer using the Mg ($K\alpha_{1,2}$) 1254-eV source. The spectrometer was calibrated using the 4f lines of gold foil.

Unless specifically indicated all samples which were run only at normal probe temperature (~40 °C) were introduced into the spectrometer after brushing the powdered material onto a double-backed adhesive tape which was mounted on an aluminum cylinder. These samples were each run for 4 h. Counting rates during this period vary somewhat from sample to sample; however, 4 h was considered to be an acceptable compromise for obtaining reasonable counting statistics and minimal sample decomposition. For variable-temperature studies good thermal contact was achieved by using a titanium foil, which provides a flat background in the region of the iron 2p spectrum, welded concentrically onto an aluminum cylinder. Evaporation of a concentrated solution of the complex salt in acetone on the titanium foil produced a deposit of finely crystalline material which adhered to the foil. A Varian variable-temperature controller was used to thermostat the sample holder in these experiments.

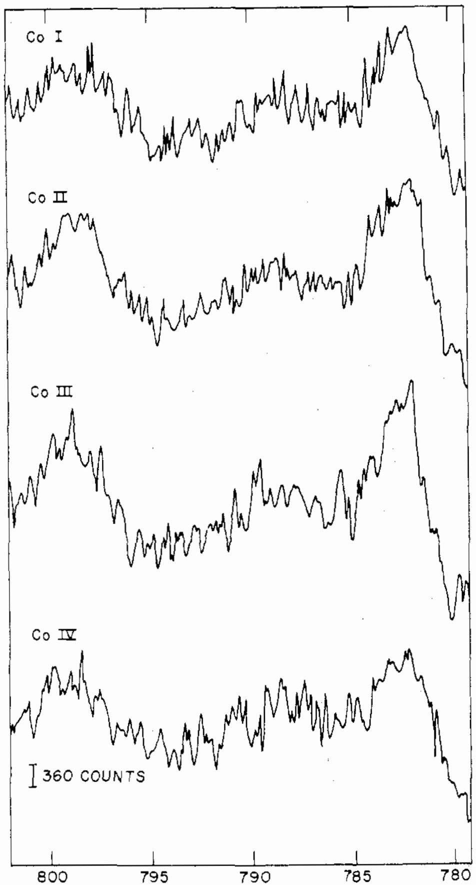

Figure 4. Cobalt 2p XPS spectra at 40 °C of the series of cobalt(II) complexes $[Co(6MePy)_n(Py)_{3-n}tren](PF_6)_2$, $n = 0, 1, 2, 3$, i.e., Co-I, Co-II, Co-III, and Co-IV, respectively.

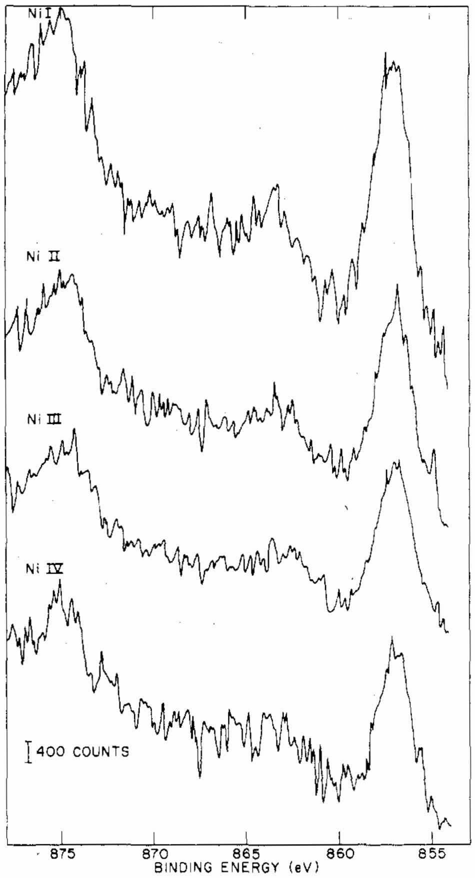

Figure 5. Nickel 2p XPS spectra at 40 °C of the series of nickel(II) complexes $[Ni(6MePy)_n(Py)_{3-n}tren](PF_6)_2$, $n = 0, 1, 2, 3$, i.e., Ni-I, Ni-II, Ni-III, and Ni-IV, respectively.

Results

Room temperature 2p x-ray photoelectron spectra of all 12 complexes—Fe-I → Fe-IV, Co-I → Co-IV, and Ni-I → Ni-IV—were obtained. These appear in Figures 3, 4, and 5, respectively. All samples used in obtaining these spectra were freshly prepared on adhesive backing and had not previously been exposed to the x-ray source of the spectrometer. In addition, 2p spectra of the complexes Fe-II and Fe-III were obtained at several temperatures, using freshly prepared samples deposited on titanium foil. Two fresh samples of the complex Fe-II were examined at 100 and 150 °C, respectively. The sample run at 150 °C was subsequently reexamined at room temperature. These three spectra and a fresh room-temperature comparison spectrum are shown in Figure 6. A sample of Fe-III was examined consecutively at normal probe temperature and at −80 °C (Figure 7).

Discussion

Changes in the iron 2p spectra shown in Figure 3 appear to follow a trend based on the bulk magnetic moment of the samples. Thus Fe-I (low spin) and Fe-II (~90% low spin) exhibit spectra at 40 °C without any obvious satellites. Spectra of both Fe-III (~50% high spin) and Fe-IV (high spin) show broad satellites at 40 °C on the high binding energy side of the $2p_{1/2}$ peak. The main peaks themselves are also somewhat broadened and less intense in the two latter complexes.

While $10Dq$ is not the sole factor determining the energies of all the excited states in these complexes, the differences can reasonably be expected to be small in such a closely related series. Thus, with only an ~15% excursion in the value of $10Dq$ over the whole series of iron complexes it does not seem reasonable based on the current model to assign the 2p satellites to shake-up transitions.[12] One other factor which may affect the satellite structure involves the differences among the ligands associated with the changing number of methyl groups attached to the pyridine rings on the lower polyhedral faces of the Fe^{2+} complexes. This might be important if the satellites are produced by a shake-up mechanism involving a charge-transfer transition. As an experimental check on this possibility the cobalt(II) and nickel(II) complexes of the same series of ligands were examined. The spectra of these complexes in Figures 4 and 5 show only minor variations within a given series, certainly nothing as dramatic as in the series of iron(II) complexes.

Examination of the spectra in Figures 3, 4, and 5 cannot provide, in our view, a clear assignment for the satellite appearing in the 2p photoelectron spectra of the iron(II) complexes. It should perhaps be pointed out here that the definitive experiments, discussed below, are usually not reported in making assignments of satellite peaks in photoelectron spectra of transition metal complexes, neither, usually, is the information about the complexes so detailed nor the complexes so closely related.

A temperature-dependence study of the 2p spectrum of Fe-II (Figure 6) shows that fresh samples run at different temperatures do indeed exhibit spectral differences, just as would be expected if these features were sensitive to the magnetic moment. A crucial point, however, is that the spectral changes are not reversible (Figure 6b, c) as they should be if they were arising only from the change in the magnetic moment of this spin equilibrium complex with temperature. Such a result provides strong evidence that sample decomposition is occurring. This set of spectra is unusual because the decomposition can be documented quite clearly. The effect of increasing the temperature is to increase the magnetic moment

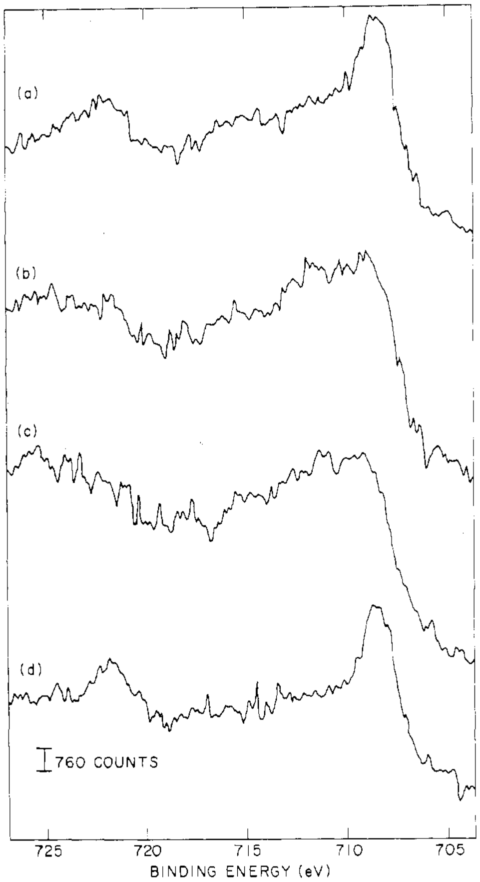

Figure 6. Temperature dependence of the XPS spectrum of [Fe(6MePy)(Py)$_2$tren](PF$_6$)$_2$, Fe-II: (a) fresh sample run at 100 °C; (b) fresh sample run at 150 °C; (c) same sample as in (b) after cooling down to 40 °C; (d) comparison spectrum of a fresh sample run at 40 °C.

and, therefore, the fraction of high-spin iron(II) in this spin equilibrium sample. It appears likely, therefore, that decomposition proceeds only from the high-spin iron(II) in the sample, since at 150 °C Fe-II is ~50% high spin. Spectra of Fe-III and Fe-IV at the temperature studied appear to be identical with the spectrum of the decomposed Fe-II sample. In these samples the decomposition process cannot be as clearly documented as in the Fe-II case; however, the similarities among the spectra strongly indicate that the samples of Fe-III and Fe-IV have also decomposed. The fact that essentially complete decomposition occurs even in the short times used to collect these spectra points out the potential hazard of using repetitive scans as a check of sample stability. When the sample completely decomposes during the time it takes to collect statistically meaningful data, as Fe-III and Fe-IV appear to have done here, the decomposition will likely go undetected.

The results from the temperature-dependence studies show clearly that the assignment of XPS satellites is by no means limited only to a choice between multiplet splitting and shake-up. Spurious peaks may arise due to decomposition in the x-ray beam of otherwise stable complexes. As the spectra in Figure 7 show, the actual process of decomposition is not necessarily easy to observe. Three consecutive runs on the same sample at 40, −80, and 100 °C are nearly identical. The spectra in this figure could be interpreted as an indication that Fe-III is stable if it were not for the data on complex Fe-II. The rapid decomposition of Fe-III and Fe-IV at ~40 °C is inconsistent with the stability of these complexes observed in solid-state magnetic susceptibility measurements at temperatures up to 200 °C.[11] This strongly implicates the x-ray beam as the primary source of the decomposition.

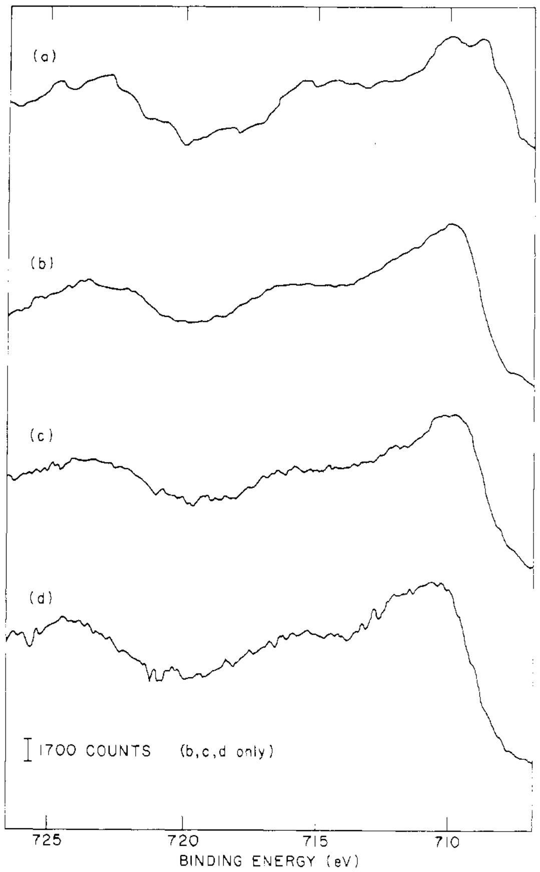

Figure 7. Temperature dependence of the XPS spectrum of [Fe(6MePy)$_2$(Py)tren](PF$_6$)$_2$, Fe-III: (a) comparison spectrum of Fe-IV showing the relative positions and intensities of the main ionization peak (2p$_{3/2}$) at ~711 eV and the broad satellite at ~713–718 eV; (b), (c), (d) consecutive runs on a single sample of Fe-III at 40, −80, and 100 °C, respectively.

The observation of sample decomposition in this series of iron(II) complexes places some severe restrictions on our ability to study and characterize the satellite peaks in solid samples of transition metal complexes generally. From the data available here it is clear that XPS spectra of the high-spin forms of Fe-II, Fe-III, and Fe-IV have not yet been obtained. It is possible that decomposition of paramagnetic complexes is more common than is generally realized. From examination of the spectra for the cobalt(II) and nickel(II) complexes (Figures 4 and 5) it is clear that these complexes also produce satellite peaks having binding energies 2–8 eV higher than the main ionization peak. In an investigation of a number of cobalt complexes[14] satellites similar to those observed here were also observed in the 2p spectra of paramagnetic species that were absent in the diamagnetic cases. The authors were unable to identify these satellites with shake-up and offered an explanation based on magnetic exchange between the photoelectron and the unpaired 3d spins. Because of the demonstrated decomposition of the paramagnetic iron(II) complexes reported here, the best first approach to take in the assignment of all the cobalt and nickel satellites must be a demonstration that some form of decomposition is not involved in these systems as well.

In the event that sample decomposition in the x-ray beam will account for the paramagnetic cobalt(II) and nickel(II) satellites the following correlation is suggested. Qualitatively, the satellite intensities appear to be less pronounced in the cobalt(II) than in the corresponding high-spin iron(II) systems. In the nickel(II) complexes these effects are even less extensive.

Since the 10*Dq* values for all three metal systems are expected to be comparable (±20%), the only major differences between them appear to be their spin multiplicities and crystal field stabilization energies (CFSE). The CFSE of the octahedral complexes increase in the order high-spin iron(II) < cobalt(II) < nickel(II) < low-spin iron(II). Spin multiplicities increase in the reverse order. Thus, the satellite intensities are observed to follow the same order as the CFSE with high-spin iron(II) having the most intense satellite lines and low-spin iron(II) the least intense lines. The satellites in the cobalt(II) and nickel(II) spectra show a behavior consistent with a decomposition sensitivity analogous to that observed in the iron(II) systems, and these trends may provide a consistent qualitative explanation for the features of the 2p XPS spectra of all three sets of complexes. There is clearly reason to exercise considerable caution both in the assignment of satellites observed in the XPS of insulating solids and in the extension of theoretical models of satellite structure[14] until satisfactory experimental criteria for identifying decomposition can be established.

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Registry No. Fe-I,, 55222-32-7; Fe-II, 55190-32-4; Fe-III, 55190-34-6; Fe-IV, 55190-36-8; Co-I, 63526-13-6; Co-II, 63449-04-7; Co-III, 63449-02-5; Co-IV, 63449-00-3; Ni-I, 56348-41-5; Ni-II, 56348-43-7; Ni-III, 56348-45-9; Ni-IV, 56348-47-1.

References and Notes

(1) (a) Herbert H. Lehman College; Research Collaborator, Brookhaven National Laboratory. (b) Brookhaven National Laboratory; current address is the Department of Chemistry Southern Methodist University, Dallas, Tex. 75275. (c) Brookhaven National Laboratory.
(2) C. K. Jorgenson, *Struct. Bonding (Berlin)*, **24**, 1 (1975).
(3) M. S. Lazarus and T. S. Chou, *J. Chem. Phys.*, **64**, 3544 (1976).
(4) T. A. Carlson, J. C. Carver, and G. A. Vernon, *J. Chem. Phys.*, **62**, 932 (1975).
(5) R. P. Gupta and S. K. Sen, *Phys. Rev. B*, **10**, 71 (1974).
(6) S. P. Kowalczyk, L. Ley, F. R. McFeely, and D. A. Shirley, *Phys. Rev. B*, **11**, 1721 (1975).
(7) K. S. Kim, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 217 (1974).
(8) G. A. Vernon, G. Stucky, and T. A. Carlson, *Inorg. Chem.*, **15**, 278 (1976).
(9) D. C. Frost, C. A. McDowell, and B. Wallbank, *Chem. Phys. Lett.*, **40**, 189 (1976).
(10) L. J. Matienzo, L. I. Yin, S. O. Grim, and W. E. Swartz, Jr., *Inorg. Chem.*, **12**, 2672 (1973).
(11) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).
(12) L. J. Wilson, D. Georges, and M. A. Hoselton, *Inorg. Chem.*, **14**, 2968 (1975).
(13) M. A. Hoselton, unreported experimental data.
(14) Yu. G. Borod'ko, S. I. Vetchinkin, S. L. Zimat, I. N. Ivleva, and Yu. M. Shul'ga, *Chem. Phys. Lett.*, **42**, 264 (1976).

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Kinetics of the Formation and Bond Cleavage Reactions of an Alkyl-Bridged Dicobalt Organocobaloxime[1]

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The reaction of the tributylphosphine–cobaloxime(I) complex with 1,4-dibromobutane forms, in succession, 4-bromobutylcobaloxime and a 1,4-butenyldicobaloxime, $BCo(dmgH)_2(CH_2)_4Co(dmgH)_2B$. The latter complex with $B = H_2O$ undergoes successive dealkylation reactions with Hg_{aq}^{2+}, forming first $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ and then $Hg(CH_2)_4Hg^{2+}$. The organocobaloximes also undergo protonation equilibria at oxime oxygen positions. Quantitative studies of the rates and equilibria of these reactions are reported, along with data for the comparison complex *n*-butylcobaloxime.

Introduction

Several examples are known of dimetallic complexes in which an alkyl (or aralkyl) bridges two cobalt chelates,[2] including $pyCo(dmgH)_2(CH_2)_nCo(dmgH)_2py$ (n = 2–5),[3] $pyCo(bae)(CH_2)_nCo(bae)py$ (n = 3, 4),[4] and $pyCo(dmgH)_2CH_2C_6H_4CH_2Co(dmgH)_2py$ (meta and para isomers).[5] Also, stable rhodium analogues, $BrRh(N_4chel)(CH_2)_nRh(N_4chel)Br$, are known,[6] and claims have been made for transient dichromium intermediates, $[(H_2O)_5Cr]_2(CHX)^{4+}$ ($X = Cl$,[7] Br[8]).

A key question for which the literature contains scant but discrepant data, for these difunctional compounds, is whether the two centers function independently. If they are indeed independent, one would expect the same chemistry at each site. One would also expect the chemical reactivity to be about the same at each center and comparable to monofunctional analogues, after making allowance for statistical factors. On the other hand the possibility of an interaction between the two centers cannot be excluded. In extreme instances this could result in new reactions such as alkyl coupling or cyclization or metallocycle formation, although it would perhaps more likely be manifest as altered reactivity and expressed in terms of neighboring group effects.

To explore these possibilities we first carried out work, which is the subject of the present paper, in which it seemed that such interaction might be relatively *unimportant*. The complex used in these studies is the well characterized,[3] bridged 1,4-butenyldicobaloxime $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2py$ (I). In this connection we have obtained data for three reactions which, at least for the monofunctional analogues, are relatively well characterized: (a) the nucleophilic displacement[9,10] of Br^- from alkyl bromide by $Co(dmgH)_2^-$ (eq 1), (b) the protonation equilibrium[11-13] of coordinated dimethylglyoxime (eq 2), and (c) cleavage of the cobalt–carbon bond upon reaction with mercury(II)[11,12,14,15] (eq 3).

$$RBr + Co(dmgH)_2^- \xrightarrow{k_{Co}} RCo(dmgH)_2 + Br^- \qquad (1)$$

$$RCo(dmgH)_2(H_2O) + H^+ \overset{K_H}{\rightleftharpoons} RCo(dmgH)(dmgH_2)(H_2O)^+ \qquad (2)$$

$$RCo(dmgH)_2(H_2O) + Hg^{2+} \xrightarrow{k_{Hg}} (H_2O)_2Co(dmgH)_2^+ + RHg^+ \qquad (3)$$