

between the g_{av} and g_{zz} values in the present Ni(III) complexes. In particular, the g_{zz} value is sensitive to the number of axial nitrogen donor atoms. The g_{zz} values of the Ni(III) complexes with two, one, and no axial nitrogen donors are approximately 2.025, 2.020, and 2.016, respectively. On the other hand, the g_{av} values are approximately 2.12, 2.14, and 2.17, respectively. As the binding in the axial direction increases, the energy of the d_{z^2} orbital increases relative to d_{xy} , d_{yz} and vibronic mixing of the d_{z^2} and $d_{x^2-y^2}$ ground states increases. Therefore, the g_{xx} , g_{yy} values decrease and the g_{zz} value increases as the complex approaches octahedral geometry.

In conclusion, the 1:1 Ni(II) complexes of various histidine-containing tripeptides are easily oxidized by Ir^{IV} ion to form the corresponding Ni(III) complexes. These Ni(III) complexes show ESR spectra which are typical of tetragonal geometry. The large g_{xx} value of the sulfur-nickel(III) complexes suggests the trend of $S^- > NH_2$ in the equatorial donor strength for Ni(III). The 1:1 Ni(III) complex of BLM, a histidine-containing glycopeptide antibiotic, has five-line hyperfine splittings in the g_{zz} region, indicating the presence of two axial nitrogen donor atoms. In the present Ni(III) complexes, the g_{zz} value is sensitive to axial nitrogen donors and a good correlation between the g_{av} and g_{zz} values is observed for axial nitrogen coordination.

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Organobis(dioximato)cobalt(IV) Complexes: Electron Paramagnetic Resonance Spectra and Electronic Structures

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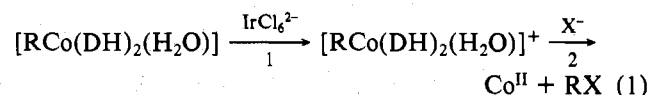
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Organobis(dioximato)cobalt(III) complexes can be oxidized either chemically (Br₂, PbO₂, or cerium(IV) nitrate) or electrochemically to generate radical cations, [RCo(DH)₂L]⁺. One-electron oxidations have been confirmed by spectral titrations and cyclic voltammetry. While such radical cations are short-lived at 25 °C, they are quite stable at low temperatures (<-50 °C). [RCo(DH)₂L]⁺ is paramagnetic exhibiting unusual EPR parameters ($g_{iso} = 2.0197$ to 2.0326 , $g_{\parallel} = 2.016$ to 2.037 , $g_{\perp} = 2.022$ to 2.031 ; $A_{iso}^{Co} = 11.5 \times 10^{-4}$ to $14.5 \times 10^{-4} \text{ cm}^{-1}$, $A_{\parallel}^{Co} = 25.0 \times 10^{-4}$ to $35.0 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp}^{Co} = 4.0 \times 10^{-4}$ to $5.5 \times 10^{-4} \text{ cm}^{-1}$). Ligand superhyperfine parameters indicate that electron delocalization is small. Hyperfine equations are derived for a low-spin 3d⁵ electronic configuration with a 3d_{x²-y²} ground state. To account for the unusually small magnitude of A_{\parallel}^{Co} , A_{\perp}^{Co} 3d/4p orbital mixing is incorporated into the hyperfine equation derivation. The experimentally observed A_{\parallel}^{Co} and A_{\perp}^{Co} values can be accommodated by this description by assuming that the orbital of the unpaired electron is approximately 70% 3d and 30% 4p in character. The EPR results support the formulation of these radical cations as organocobalt(IV) complexes.

Introduction

Considerable interest has recently been focused on the cleavage of transition-metal-carbon bonds. The formation and subsequent breaking of metal to carbon bonds is involved both in catalytic reactions¹ and in the biochemical reactions associated with vitamin B₁₂ coenzymes.² Several modes for such cleavage reactions have already been described, including homolysis,³ photolysis,⁴ and reductive dealkylation.⁵ However, the mechanism of oxidative dealkylation has only recently been investigated.⁶ The chemistry of organomercurials⁷ suggests that halogens attack the metal-carbon bond by electrophilic displacement with retention of configuration at the α carbon. The mechanistic aspects of cleavage of transition-metal alkyls are less clear and, at least in certain cases (e.g., RCo(DMH)₂L where DMH₂ is dimethylglyoxime), inversion occurs at the

α -carbon atom.⁸⁻¹⁰ Anderson et al.⁸ have suggested that in such cases the electrophile does not directly attack the α carbon but instead oxidizes the metal complex to a radical-cation, with metal-carbon bond cleavage resulting from subsequent nucleophilic attack at the α carbon thus explaining the observed inversion of configuration. Halpern et al.¹¹ have shown that IrCl₆²⁻, a one-electron outer-sphere oxidant, oxidizes RCo(DH)₂L¹² according to the following scheme:



A detailed examination of step 2 of the above sequence⁶ has confirmed that Cl⁻ does induce the nucleophilic decomposition of [RCo(DH)₂(H₂O)]⁺ and that cleavage of the cobalt-carbon

Table I. EPR Parameters for $[\text{RCo}(\text{dioxime})_2\text{L}]^+$ Complexes

R	dioxime ^c	g_{iso} (± 0.0003)	$10^4 A_{\text{iso}}^{\text{Co}}$ cm^{-1} (± 0.5)	g_{\parallel} (± 0.002)	$10^4 A_{\parallel}^{\text{Co}}$ cm^{-1} (± 0.5)	g_{\perp} (± 0.002)	$10^4 A_{\perp}^{\text{Co}}$ cm^{-1} (± 0.5)
CH ₃	DMH ₂	2.0256 ^a	12.9 ^a	2.025	29.1	2.026	4.8
CH ₃	DPH ₂	2.026	11.7	2.028	27.2	2.025	4.0
CH ₃	DMPH ₂	2.026	12.0	2.027	27.1	2.026	4.5
CH ₃	DNPH ₂	^b					
CH ₃ CH ₂	DMH ₂	2.0292	13.6	2.031	31.3	2.028	4.8
CH ₃ CH ₂ CH ₂	DMH ₂	2.0291	13.8	2.031	32.0	2.028	4.7
(CH ₃) ₂ CH	DMH ₂	2.0326	14.3	2.037	34.9	2.030	4.0
<i>p</i> -NO ₂ -C ₆ H ₄ CH ₂	DMH ₂	2.0264	13.2	2.024	28.8	2.028	5.4
<i>p</i> -Cl-C ₆ H ₄ CH ₂	DMH ₂	2.0294	13.5	2.030	30.4	2.029	5.1
<i>p</i> -F-C ₆ H ₄ CH ₂	DMH ₂	2.0304	13.6	2.031	30.9	2.030	5.0
C ₆ H ₅ CH ₂	DMH ₂	2.0311	13.5	2.034	31.7	2.030	4.4
<i>p</i> -CH ₃ -C ₆ H ₄ CH ₂	DMH ₂	2.0326	13.8	2.036	32.1	2.031	4.7
C ₆ H ₅	DMH ₂	2.0197	11.8	2.016	24.8	2.022	5.3

^a Identical isotropic parameters were measured for R = ¹³CH₃ and R = CD₃. ^b No oxidation occurred. ^c Key: DMH₂ = dimethylglyoxime, DPH₂ = diphenylglyoxime, DMPH₂ = α -4,4'-dimethoxydiphenylglyoxime, DNPH₂ = α -4,4'-dinitrodiphenylglyoxime.

bond occurs with inversion of configuration at the α carbon.

Subsequent to these earlier studies using IrCl₆²⁻, we examined^{13,14} the chemical and electrochemical oxidations of an extensive series of organobis(dioximato)cobalt(III) complexes in an effort to gain a clearer understanding of the oxidative cleavage of the metal-carbon bond. Oxidations of RCo(DH)₂L complexes in aqueous methanol at low temperatures (-10 to -78 °C) yield stable solutions of the corresponding [RCo(DH)₂L]⁺ radical cations. Spectral titrations at -78 °C of various RCo(DH)₂L complexes with cerium(IV) nitrate demonstrated the occurrence of a stoichiometric 1:1 reaction similar to eq 1. Cyclic voltammetry also confirmed a reversible one-electron oxidation of RCo(DH)₂L in aqueous solution to form the radical cation. It is the purpose of this paper to elaborate the characterization of these radical cations and to examine the possible role of such species in oxidative dealkylation. The EPR spectra of the radical cations have been obtained and from these spectra a detailed description of the electronic structure of these unusual organometallic compounds is deduced.

Experimental Section

Materials. α -4,4'-Dimethoxydiphenylglyoxime (DMPH₂) and α -4,4'-dinitrodiphenylglyoxime (DNPH₂) were prepared as previously described.¹⁵ Dimethylglyoxime (DMH₂) (Aldrich) and diphenylglyoxime (DPH₂) (Eastman) were used without further purification. The common alkyl, aryl, and benzyl halides were obtained from commercial sources. CD₃I (99.5% D) and ¹³CH₃I (90 atom % ¹³C, lot no. E-1042) were obtained from Stohler Isotope Chemicals and Merck, Sharp and Dohme, respectively.

Preparation of Cobalt(III) Complexes. Complexes of the type H[X₂Co(DH)₂] (X = Cl, Br; DH₂ = general dioxime) were synthesized according to Nakahara.¹⁶ XCo(DH)₂Y complexes (Y = pyridine or triphenylphosphine) were prepared by dissolving H-[X₂Co(DH)₂] in hot aqueous methanol followed by addition of a stoichiometric amount of base. A crystalline product separated upon cooling and partial evaporation of the solution. Organobis(dioximato)cobalt(III) complexes were prepared according to the method of Schrauzer¹⁷ or from XCo(DH)₂Y by the procedure of Hill and Morallee.¹⁸

Generation of [RCo(DH)₂L]⁺ and Physical Measurements. Solutions were prepared by dissolving either [RCo(DH)₂(py)] or [RCo(DH)₂(H₂O)] in CH₂Cl₂ or in CD₃OD-D₂O solutions containing 0.1 M HClO₄ and oxidizing to [RCo(DH)₂L]⁺ with Br₂, PbO₂, or with a stoichiometric amount of cerium(IV) nitrate. The EPR spectra of the resulting solutions, in both the liquid (-20 to -50 °C) and frozen states, were recorded with a Varian E-9 spectrometer equipped with a Varian E4540 variable-temperature unit. All EPR spectra were calibrated with DPPH. Deuteration of the solvent decreased the dipole-dipole interaction of solvent nuclei with the unpaired electron and improved substantially the resolution of the spectra. It was established, at least for the case of R = CH₃, that solvent variation, the presence or absence of O₂ and the alternative procedures for generation of [RCo(DH)₂L]⁺ described above yielded identical spectra.

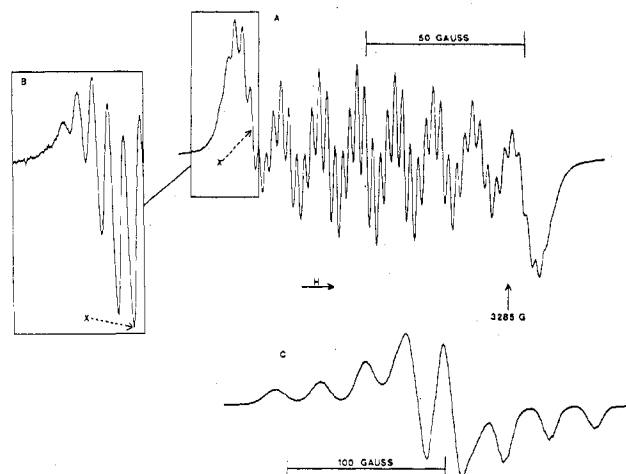


Figure 1. (A) First-derivative EPR spectrum of $[\text{C}_6\text{H}_5\text{Co}(\text{DMH})_2\text{L}]^+$ in CH_2Cl_2 at -30 °C. Microwave frequency is 9.172 GHz. (B) Second-derivative EPR spectrum of the low-field HF component of $[\text{C}_6\text{H}_5\text{Co}(\text{DMH})_2\text{L}]^+$. X indicates central nitrogen SHF line of this HF component. (C) First-derivative EPR spectrum of $[\text{CH}_3\text{Co}(\text{DMH})_2\text{L}]^+$ in frozen $\text{CD}_3\text{OD}-\text{D}_2\text{O}$ (9:1) at -110 °C. Microwave frequency is 9.170 GHz.

The concentration of $[\text{RCo}(\text{DH})_2\text{L}]^+$ was measured by double integration of its frozen solution EPR spectrum by using a frozen toluene solution of DPPH as a reference and was found to correspond to about 80% of the initial $[\text{RCo}(\text{DH})_2\text{L}]$ concentration.

Results and Discussion

EPR Characterization. The complexes $[\text{RCo}(\text{DH})_2\text{L}]^+$ are paramagnetic and exhibit rather unusual isotropic and frozen glass EPR spectra. A principal objective of this study was to characterize the distribution of the unpaired electron in these radical cations, particularly with a view to distinguishing between the cobalt atom and the ligands as possible sites of electron removal, i.e., between the limiting configurations $[\text{Co}^{\text{III}}\text{R}\cdot]$ and $[\text{Co}^{\text{IV}}\text{R}]$.

The isotropic EPR spectra consist of eight lines due to the interaction of the unpaired electron with the cobalt nuclear spin ($I = 7/2$). Isotropic g values are listed in Table I. In addition, superhyperfine (SHF) coupling is observed in several cases from the dioxime nitrogens and in one instance from the ¹³C of $[\text{CH}_3\text{Co}(\text{DMH})_2\text{L}]^+$. For the interaction of the unpaired electron with the four in-plane nitrogen donors one would expect a nine-line SHF pattern. In CH_2Cl_2 , the isotropic EPR spectra for $[\text{RCo}(\text{DMH})_2\text{L}]^+$ (R = CH₃ and C₆H₅) gave well-resolved spectra showing at least seven of the expected nine SHF components. For R = C₆H₅ (Figure 1) all nine SHF lines were observed. There was no indication of a SHF interaction from the N or P of axially coordinated

pyridine or triphenylphosphine, respectively. No change in the EPR spectrum was observed when $R = CD_3$ was substituted for $R = CH_3$. However, a SHF interaction of ~ 1 G was observed in the isotropic spectrum for $[^{13}CH_3Co(DMH)_2L]^+$ ($I_{13C} = 1/2$). The nitrogen SHF constants are insensitive to the nature of R and have the values $A_{iso}^N = (2.28 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$. Computer simulation¹⁹ of the isotropic spectra was used to confirm the SHF assignments.

Anisotropic EPR spectra (Figure 1) were obtained in frozen glass solution. The anisotropic spectra showed the presence of two g components. The hyperfine (HF) structure observed in the frozen glass spectra is attributed to the parallel orientation of the radical cation in the magnetic field. The experimental and calculated anisotropic g and A parameters for $[CH_3Co(DMH)_2L]^+$ were used as input data for computer simulation¹⁹ of the frozen glass spectrum. The experimental and simulated spectra were virtually superimposable. The experimentally determined EPR parameters, g_{\parallel} and A_{\parallel}^{Co} , are listed in Table I along with the calculated g_{\perp} and A_{\perp}^{Co} ($g_{\perp} = 3/2[g_{iso} - g_{\parallel}/3]$) and $A_{\perp}^{Co} = 3/2[A_{iso}^{Co} - (A_{\parallel}^{Co}/3)]$. The absolute values for A_{\parallel}^{Co} and A_{\perp}^{Co} establish that A_{iso}^{Co} , A_{\parallel}^{Co} , and A_{\perp}^{Co} must all have the same sign; however, the sign is undetermined. The frozen glass EPR spectra were not well resolved with respect to SHF components which were detected only in a few cases (i.e., $R = CH_3$ and C_6H_5). The A^N SHF coupling observed is assigned to the perpendicular SHF direction. This is in analogy with complexes of the porphyrin type²⁰ where the principal SHF component is assumed to be along the metal-nitrogen bond. The frozen glass EPR spectrum for $R = C_6H_5CH_2$ was observed at 6 K. No improvement in resolution was observed at this temperature.

Analysis of HF and SHF Parameters. Attention is directed to the following features of the experimental HF and SHF data: (i) For all the compounds the cobalt HF parameters are in the range $A_{iso}^{Co} = 11.5 \times 10^{-4}$ to $14.5 \times 10^{-4} \text{ cm}^{-1}$, $A_{\parallel}^{Co} = 25.0 \times 10^{-4}$ to $35.0 \times 10^{-4} \text{ cm}^{-1}$, and $A_{\perp}^{Co} = 4.0 \times 10^{-4}$ to $5.5 \times 10^{-4} \text{ cm}^{-1}$. (ii) The unpaired electron exhibits equivalent interaction with the four nitrogen atoms of the planar bis(dioxime) ligand. (iii) Substitution of $R = ^{12}CH_3$ by $R = ^{13}CH_3$ resulted in only a slight broadening of the SHF lines in the isotropic spectrum, corresponding to a ^{13}C SHF constant $A_{iso}^{13C} \sim 1$ G.

Result (iii) demonstrates conclusively that the unpaired electron in $[CH_3Co(DMH)_2L]^+$ is not significantly localized on the axial ligand, R , since the value for A_{iso}^{13C} is negligible compared with that expected for the tetrahedral ^{13}C methyl radical ($A_{iso}^{13C} \sim 300$ G). Since the EPR parameters for all the complexes are similar, this inference can also be extended to the other $[RCo]^+$ compounds studied. Result (ii) further suggests that the unpaired electron is not extensively localized on the equatorial dioxime ligand. The values of A^N are considerably smaller than those observed for the free dimethylglyoxime radical ($A_{iso}^N = 31.7$ G).²¹ Thus it must be concluded that the unpaired electron is localized on the cobalt atom. The SHF results favor the location of the molecular orbital of the unpaired electron in the equatorial plane. The small values of A^N (cf. $A_{iso}^N \sim 16$ G for $Cu(DMH)_2$) suggest the π -type $d_{x^2-y^2}$ rather than the σ -type d_{xy} metal orbital. (The coordinate system adopted for $[RCo(DH)_2L]$ has the z axis along $R-Co-L$ with the x and y axes in the molecular plane bisecting the $N-Co-N$ angles.)

At the same time, the isotropic and anisotropic cobalt HF parameters are seen to be consistently smaller than the values ($0.01-0.02 \text{ cm}^{-1}$)²² which are expected from theoretical calculations for a free cobalt ion. The small values of A_{iso}^{Co} can be interpreted in a manner similar to that used to explain the small A_{iso}^{Co} values for various $Co(II)$ complexes.²³ This explanation assumes some $4s$ orbital admixture to the $3d_{x^2-y^2}$

orbital of the unpaired electron, resulting from low-symmetry components in the ligand field of cobalt. Contributions to A_{iso}^{Co} from direct s -orbital admixture and through spin polarization from d orbitals have opposite signs and thus can partially cancel each other. The unpaired electron density in the $4s$ orbital (ρ_{4s}) which is necessary to account for the observed A_{iso}^{Co} values can be estimated to be $\rho_{4s} \sim 0.02-0.06$.

An understanding of the electronic structures of these radical cations must accommodate the unusually small anisotropic cobalt HF parameters. Because of the small anisotropy in the g tensor, one can, to a first approximation, ignore the spin-orbit coupling and take the pure $3d$ states as proper eigenfunctions. With this approximation:

$$A_{\parallel}^{Co} = P(-K - (4/7)) \text{ and } A_{\perp}^{Co} = P(-K + (2/7)) \quad (2)$$

for the $3d_{x^2-y^2}$ orbital being that of the unpaired electron. K is the Fermi contact term. Using the values of A_{\parallel}^{Co} and A_{\perp}^{Co} for $[CH_3Co(DMH)_2L]^+$ we obtain $P \sim 0.003 \text{ cm}^{-1}$ which is an order of magnitude smaller than $P_0 = 0.0317 \text{ cm}^{-1}$ for free $Co(IV)$. $P = 2.0023g_N B_e B_N (r^{-3})_{av}$ and $(r^{-3})_{av}$ for $Co(IV)$ is 7.4212 au .²⁴ It is not unusual for P to be reduced from its free ion value in a transition-metal complex, however, not by as much as observed here. One way in which P can be reduced is through a large covalent interaction between metal and ligand orbitals. The SHF results, however, do not support this. The mixing of $3d$ and $4p$ metal orbitals, allowed in C_{2v} symmetry, also can lead to an apparent reduction in P . The contribution to the cobalt HF components for d and p orbitals are opposite in sign and cancel.

Using the method of Abragam and Pryce,^{25,26} where

$$A_{\parallel} = A_{zz} = P[-K - (4/7) - 2\lambda\Lambda_{zz} + (2/7)\lambda u_{zz}] \quad (3)$$

$$A_{\perp} = A_{xx} = A_{yy} = P[-K + (2/7) - 2\lambda\Lambda_{xx} + (2/7)\lambda u_{xx}] \quad (4)$$

with Λ_{ij} and u_{ij} being tensors formed from the matrix elements of the orbital angular momentum, L , and the orbital energy spacings according to the definitions

$$\Lambda_{ij} = \Lambda_{ji} = \sum_{n \neq 0} \frac{\langle 0|L_i|n\rangle \langle n|L_j|0\rangle}{E_n - E_0} \quad (5)$$

$$u_{ij} = -\frac{i}{2} \sum_{k,l} \epsilon_{ikl} \sum_{n \neq 0} \frac{\langle 0|L_i|n\rangle \langle n|L_j L_k + L_k L_j|0\rangle}{E_n - E_0} \quad (6)$$

(the summation extending over all the energy levels, with $\epsilon_{ikl} = \pm 1$ according to the commutation properties of the spin angular momentum and the index 0 referring to the ground state), we derived the following HF equations for the $3d^5$ electronic configuration with a $|x^2 - y^2\rangle$ ground state:

$$A_{\perp} = P \left[-K + (2/7) - 2\lambda \left(-\frac{1}{E_{x^2-y^2} - E_{yz}} + \frac{3}{E_z^2 - E_{yz}} + \frac{1}{E_{xy} - E_{xz}} \right) + (3/7)\lambda \left(\frac{1}{E_z^2 - E_{xz}} + \frac{1}{E_{x^2-y^2} - E_{xz}} - \frac{1}{E_{xy} - E_{yz}} \right) \right] \quad (7)$$

$$A_{\parallel} = P \left[-K - (4/7) - \frac{8\lambda}{E_{xy} - E_{x^2-y^2}} + (3/7)\lambda \times \left(-\frac{1}{E_{x^2-y^2} - E_{yz}} - \frac{1}{E_z^2 - E_{yz}} + \frac{1}{E_{xy} - E_{xz}} + \frac{1}{E_{xy} - E_{yz}} - \frac{1}{E_z^2 - E_{xz}} - \frac{1}{E_{x^2-y^2} - E_{xz}} \right) \right] \quad (8)$$

These equations are not sufficient to reproduce the experi-

mental $A_{\parallel}^{\text{Co}}$ and A_{\perp}^{Co} unless P is reduced to an unreasonably low value. This type of problem has been treated by Stevens^{27a} in a study of the paramagnetic resonance of 4d and 5d transition elements. It was shown that the formation of molecular orbitals could lead to a reduced orbital contribution to the total angular momentum and also that the operation of the Zeeman term, $\mu H = BH(L + 2S)$, upon molecular orbital wave functions could be represented by the retention of pure "crystal field" metal d wave functions but with the use of a reduced orbital angular momentum operator in the Zeeman term, $\mu H = BH(kL + 2S)$, where k is the "orbital reduction factor".^{27b} k can be used to account for either MO formation or 3d/4p metal orbital mixing if it is symmetry allowed. The modified Zeeman term can be introduced into the equations used to derive the HF expressions (7) and (8). In view of the SHF results, the orbital reduction factor is used to describe 3d/4p mixing rather than the alternate possibility of metal-ligand molecular orbital formation.

The mixing of the $3d_{x^2-y^2}$ and $4p_z$ orbitals^{28,29} is consistent with the idealized C_{2v} symmetry of $[\text{RCo}(\text{DH})_2\text{L}]^+$. Wave functions of the type $|\text{3d}\rangle = N3d + n4p$, are considered. Since the deviation of the g values from the free electron value is small, we can neglect the small u_{ij} HF terms. This yields

$$A_{\parallel}^{\text{Co}}/P = -K + (4/35) - (24/35)k + (g_{\parallel} - 2.0023) \quad (9)$$

and

$$A_{\perp}^{\text{Co}}/P = -K - (2/35) + (12/35)k + (g_{\perp} - 2.0023) \quad (10)$$

It should be noted in the equations for $A_{\parallel}^{\text{Co}}$ and A_{\perp}^{Co} that the second and third terms in each are of opposite sign. They are the contributions to the HF interaction from the 3d and 4p orbital, respectively. The fact that they are of opposite sign leads to the small experimentally observed cobalt HF values. When $k = 1$, the HF equations, (9) and (10), reduce to those derived without the inclusion of the orbital reduction factor, as they should.

With terms in u_{ij} neglected, the results for both positive and negative cobalt HF values have been considered although the latter is thought to be more realistic. They show that for negative HF values, the experimental HF parameters are consistent with $K \sim 0.1$ and $k \sim 0.3$. Thus the orbital of the unpaired electron is $\sim 70\%$ 3d and 30% 4p in character. These results suggest that 3d/4p mixing is an effective mechanism for producing the unusually small HF values that are experimentally observed.

Molecular Orbital Description of $[\text{RCo}(\text{DH})_2]^+$. In the coordinate system adopted for these complexes, it is reasonable to assume the $3d_{z^2}$ and $3d_{xy}$ orbitals are involved in strong σ bonds with the surrounding ligands and that their antibonding components are quite high in energy. The ^{13}C SHF results also preclude the $3d_{z^2}$ orbital from being the MO of the unpaired electron. There is also considerable experimental evidence³⁰⁻³² for a $d\pi-\pi^*$ interaction of the filled metal orbitals with the antibonding π orbitals of the planar dioxime ligand. This interaction will stabilize the $3d_{xz}$ and $3d_{yz}$ orbital with respect to the essentially nonbonding $3d_{x^2-y^2}$ orbital. It should be noted that the $3d_{x^2-y^2}$ orbital is also of π symmetry; however, the amount of metal-ligand π bonding for this orbital is uncertain. Using these facts, we constructed the MO diagram given in Figure 2. This description places the unpaired electron in an MO consisting of mainly the $3d_{x^2-y^2}$ metal orbital, possibly ligand π^* orbitals and as has been discussed some $4p_z$ orbital.

The detailed EPR results presented in this paper convincingly support the formulation of the $[\text{RCo}(\text{DH})_2\text{L}]^+$ radical cations as cobalt(IV) complexes, i.e., formally as $[\text{Co}^{\text{IV}}\text{R}]$. At the same time, it is of interest to note that the

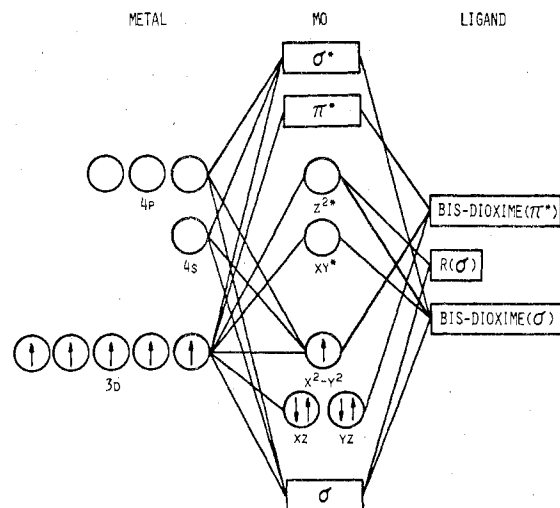


Figure 2. Proposed molecular orbital diagram for organobis(dioximate)cobalt(IV) complexes. The coordinate system adopted for $[\text{RCo}(\text{DMH})_2\text{L}]^+$ has the z axis along R-Co-L with the x and y axes in the molecular plane bisecting the N-Co-N angles.

nucleophilically induced reactivity patterns of these radical cations (i.e., step 2, eq 1) correspond to the formation of products (i.e., RX) formally derived from Co^{II} and "R⁺".⁶

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Unusual Charge Distributions in Some Bis(fulvalene)dimetal Complexes As Revealed by X-ray Photoelectron Spectroscopy

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A series of bis(fulvalene)dimetal species, $[(C_{10}H_8)_2M_2]^{n+}$, was studied by using X-ray photoelectron spectroscopy. Some of the complexes have metal binding energies which are lower than one would expect, assuming the ligands to be dianions. These data are rationalized by considering the metal atoms to be in reduced oxidation states and the fulvalene ligands to be partially oxidized. The metal 2p spectra of the mixed-valence compounds ($n = 1$) of cobalt and nickel show line broadening indicative of two inequivalent core-ionized states. Most of the paramagnetic compounds show an increase in spin-orbit splitting and line broadening attributable to multiplet splitting. Satellite structure, arising from ligand-to-metal charge-transfer transitions, appears in the spectra of some of the paramagnetic compounds.

Introduction

The electronic properties of the mixed-valence compound biferrrocene $[Fe^{II}Fe^{III}]$ picrate and the doubly bridged bis(fulvalene)diiron complex have been studied by a wide variety of techniques,¹⁻⁶ including X-ray photoelectron spectroscopy (XPS). In this paper we present the results of an XPS study of several bis(fulvalene)dimetal complexes of cobalt and nickel and the corresponding dicyclopentadienylmetal complexes.

Experimental Section

XPS. Spectra were obtained with three different spectrometers: the AEI Model E200, the DuPont Model 650, and the McPherson ESCA 36 electron spectrometer. The neutral complexes were run by subliming samples under vacuum onto a polished gold surface which, in the case of the dicyclopentadienylmetal complexes, was cooled to $-50^\circ C$ to prevent evaporation during the irradiation process. The salts were run as powders brushed onto one side of double-stick Scotch tape. The contaminant C 1s line was used as a reference. This line was arbitrarily assigned a binding energy of 285.0 eV on the AEI spectrometer. Binding energies of compounds run on more than one spectrometer were compared with one another, and reference binding energies were chosen so that binding energies were consistent. On this basis, the contaminant C 1s line was assigned a binding energy of 285.6 eV for the DuPont and McPherson spectrometers.

In all cases, Mg $K\alpha$ X-rays (1253.6 eV) were used. Binding energies were determined by fitting the data to Lorentzian curves with a least-squares computer program.⁷ The uncertainties given in Table I are twice the standard deviations obtained by the fit.

Syntheses. Ferrocene,⁸ cobaltocene,⁹ cobaltocenium hexafluorophosphate,¹⁰ nickelocene,¹¹ bis(fulvalene)diiron,¹² bis(fulvalene)dnicobalt and its salts,¹³ and bis(fulvalene)dnicol and its salts¹⁴ were prepared by previously described methods.

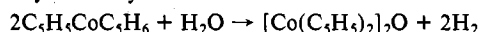
Ferrocenium hexafluorophosphate was made by dissolving 0.1 mol of ferrocene and 0.15 mol of ferric chloride hexahydrate in 100 mL of acetone and 300 mL of water. The solution was filtered and added to a concentrated aqueous solution of NH_4PF_6 . The precipitate was recrystallized from acetone/ethanol, with some ferric chloride added to keep the product oxidized. Anal. Calcd: C, 36.29; H, 3.05. Found: C, 36.38; H, 3.12.

Under nitrogen, nickelocenium hexafluorophosphate was made by dissolving 3 mmol each of nickelocene and ferrocenium hexafluorophosphate in 40 mL of degassed acetone, filtering, and then adding the solution to 100 mL of hexane. The precipitate was recrystallized from acetone/hexane and washed with diethyl ether.

The complex $(C_5H_5)_2Co(C_5H_6)$ was prepared by slowly adding, under nitrogen, 5.9 g of $NaBH_4$ to a stirred mixture of 4.1 g of

$Co(C_5H_5)_2PF_6$ in 150 mL of tetrahydrofuran. The mixture was stirred and then filtered. Solvent was removed from the filtrate, and the resulting solid was sublimed at room temperature to a $-78^\circ C$ cold finger. Red crystals were obtained, mp $101-102^\circ C$ (lit.¹⁵ $98-99^\circ C$).

Decomposition of $(C_5H_5)_2Co(C_5H_6)$ during its study in the spectrometer was indicated by the appearance of a peak at 781.7 eV which increased in relative intensity as scanning time increased. It is possible that the decomposition product is cobaltocenium ion, produced by an X-ray-induced reaction such as



Results and Discussion

Binding Energies. The experimental binding energies are given in Table I. The relative binding energies of the iron compounds are in good agreement with the values reported by LeVanda et al.⁶ In the case of the neutral and cationic dicyclopentadienyl complexes of the same metal, the metal $2p_{3/2}$ binding energies follow the expected trend; i.e., the metal $2p_{3/2}$ binding energies increase with increasing oxidation state. Close agreement is expected between the binding energies of the dicyclopentadienylmetal complexes and those of the corresponding fulvalene complexes, because the potential field at the metal atom is similar in the two types of compounds, with the metal atom sandwiched between two five-membered rings in each case. This agreement is observed within experimental error except for the neutral bis(fulvalene)dnicobalt complex and the dicationic bis(fulvalene)dnicol complex.

The fact that the bis(fulvalene)dnicol dication has a lower metal binding energy than the corresponding monocation was completely unexpected. This apparent anomaly can be explained by assuming that, in the dication, the nickel atoms are in the relatively stable $2+$ oxidation state and that one pair of electrons has been removed from the two fulvalene dianions. The ligands are presumably equivalent, and the situation can be represented by the following resonance structures, in each of which one fulvalene dianion has been oxidized to a neutral fulvalene ligand.

