Electronic Spectra of Pseudotetrahedral Cobalt(II) and Nickel(II) Complexes of C_{3v} Symmetry

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Abstract: A simple weak crystal field treatment has been applied to the interpretation of the polarized optical spectra of pseudotetrahedral cobalt(II) and nickel(II) complexes of the type $[NLX_3]$ (L = N-ethyl-1,4-diazabicyclo[2.2.2]octonium cation). Assignments of the electronic transitions are given and the magnitude of the tetrahedral and trigonal crystal field splittings are estimated. Similar assignments of unpolarized spectra of several other cobalt(II) complexes with similar geometry indicate that the trigonal splittings behave in a regular manner, consistent with the ligand spectrochemical series.

Most of the high-spin, tetrahedral complexes of the divalent first row transition metal ions reported to date have the form $[MX_4]^{2-}$ or $[ML_2X_2]$, where X is a halide ion and L is a neutral ligand. A few examples of $[MLX_3]^-$ complexes are also known.[2,3] The species $[MX_4]^{2-}$ have spectral and magnetic properties consistent with T_d symmetry,[2a,b] although some of the finer details of the spectra are not well understood.[2c,d] The pseudotetrahedral complexes of the type $[ML_2X_2]$ and $[MLX_3]^-$ are readily characterized from the similarity of their optical spectra to those of the $[MX_4]^{2-}$ species, when the donor properties of the ligand, L, are similar to those of the halide, X.[3] If, however, the donor properties of X and L are sufficiently different, then the vibrational spectra, d–d electronic spectra, and magnetic susceptibility of the $[MLX_3]$ species may deviate considerably from those of the corresponding $[MX_4]^{2-}$ complex.

In this paper we report a study of the d–d electronic spectra of a series of pseudotetrahedral complexes of the type $[M(L^+)X_3]$, where M is Co(II) or Ni(II), L^+ is the unusual positive-ion ligand derived from monoquaternization of the ditertiary amine, 1,4-diazabicyclo[2.2.2]octane,[4] or of its mono N-oxide,[5] and X = Br and NCS. The spectra of the $[M(L^+)X_3]$ complexes present two significant features: (1) A marked high-energy shift with respect to the corresponding $[MX_4]^{2-}$ species, which is too large to be explained solely on the basis of the average ligand field expected from the spectrochemical and nephelauxetic effects of the donor atoms. (2) A very large splitting—of about 3000 cm^{-1} for the $^4T_1(F)$ term of $[Co(L_N^+)Br_3]$ and of about 1000 cm^{-1} for the $^3T_2$ term of $[Ni(L_N^+)Br_3]$ (L_N = N-ethyl-1,4-diazabicyclo[2.2.2]octonium cation)—suggested a marked effect of a low symmetry component of the crystal field. These features are indeed not surprising, as it is known that an average ligand field treatment[6] is unsuitable for large trigonal distortions in tetrahedral complexes, just as it is for large tetragonal distortions in octahedral complexes.[7–9]

Although several theoretical treatments of trigonal crystal fields are available which might have been adapted to explain the observed splittings and polarizations of the optical bands, it was felt that a crystal field perturbation treatment involving no unnecessary complexity would be instructive. In carrying out this treatment, we have confined our considerations to the first order trigonal splittings in weak crystalline fields, without including the configuration interaction of the states of maximum multiplicity.

Experimental Section

The $[M(L_N^+)X_3]$ complexes (M = Co(II), Ni(II); L_N = N-ethyl-1,4-diazabicyclo[2.2.2]octonium cation; X = Br) were prepared and characterized as described in the preceding paper[4] for their N-methyl analogs, with which they are virtually identical. The N-ethyl derivatives were chosen for this investigation because they could be more easily obtained as well-formed crystals. Single crystals, containing either $[Ni(L_N^+)Br_3]$ or $[Co(L_N^+)Br_3]$ as guest in the isomorphous $[Zn(L_N^+)Br_3]$ host lattice, were grown from hot (80°) saturated dimethylformamide solutions of $[Zn(L_N^+)Br_3]$ containing 0.1–0.01 % $[Co(L_N^+)Br_3]$ or $[Ni(L_N^+)Br_3]$, relative to Zn. The hot solutions were filtered several times to remove any suspended material which might induce nucleation, then seeded with previously obtained crystals, partially covered, and placed in a drying oven. After several days crystals of about 1 × 0.5 × 0.3 cm were isolated and cleaved into thin sections suitable for optical studies.

The $[Co(L_O^+)Br_3]$ complex, containing the oxygen-donor cation ligand N-ethyl-N′-oxo-1,4-diazabicyclo[2.2.2]octonium, was prepared and characterized as described elsewhere.[5]

Single crystal transmission spectra were recorded on a Cary 14 spectrophotometer, using light polarizers (Polaroid HR for the

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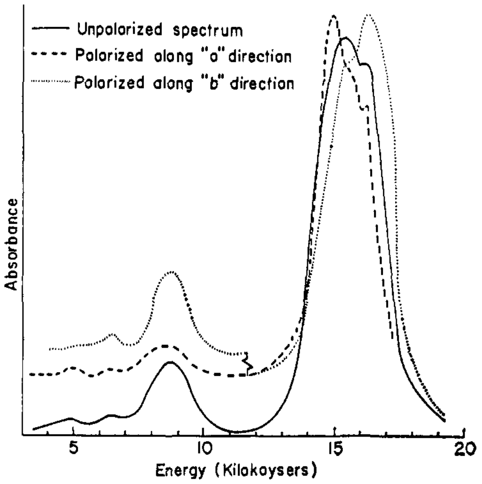

Figure 1. Single crystal spectra of dilute [Ni(L_N^+)Br_3] in the [Zn(L_N^+)Br_3] host lattice.

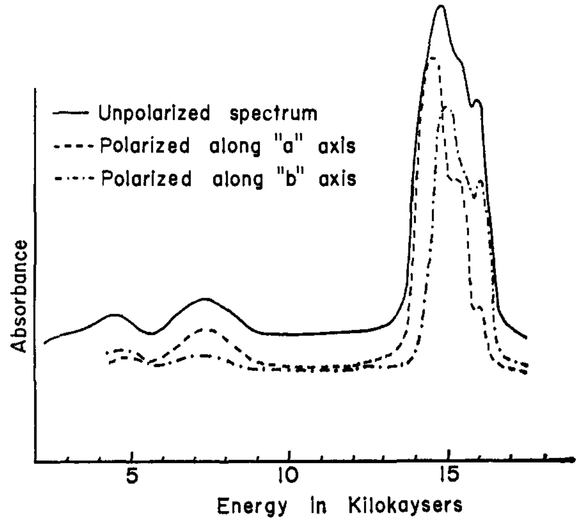

Figure 2. Single crystal spectra of dilute [Co(L_N^+)Br_3] in the [Zn(L_N^+)Br_3] host lattice.

near-infrared and polaroid HN 32 for the visible region of the spectrum). The spectra were determined with the light beam perpendicular to the main cleavage plane of the crystal. Polarized spectra were obtained by rotating the crystal until some of the absorption bands exhibited maximum intensity (*a* spectrum). After rotating the crystal by 90° from the *a* direction, the remaining absorption bands exhibited maximum intensity (*b* spectrum). Unpolarized and polarized spectra of [Ni(L_N^+)Br_3] and [Co(L_N^+)Br_3] are shown in Figures 1 and 2, respectively. Expanded spectra of the $^4A_2 \rightarrow {}^4T_1(P)$ transitions of [Co(L^+)Br_3] at 77°K are shown in Figure 3. The spectra do not exhibit complete polarization, but the relative intensities observed in different polarizations are quite adequate for the purposes of spectral assignment.

The [M(L^+)Br_3] complexes are sparingly soluble in nitromethane (in other solvents the complexes either are insoluble or dissolve with reaction). When a tenfold excess of L^+Br^- is present, the nitromethane solution contains almost exclusively the [M(L^+)Br_3] species, and the molar extinction coefficients of the observed bands are similar to those of the corresponding absorptions of the $[MBr_4]^{2-}$ ions.

Crystal Field Splittings

The d–d energy splittings in a trigonal crystal field can be described by a perturbation Hamiltonian

$$H' = \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_i V_{ci} + \sum_i V_{\tau i}$$

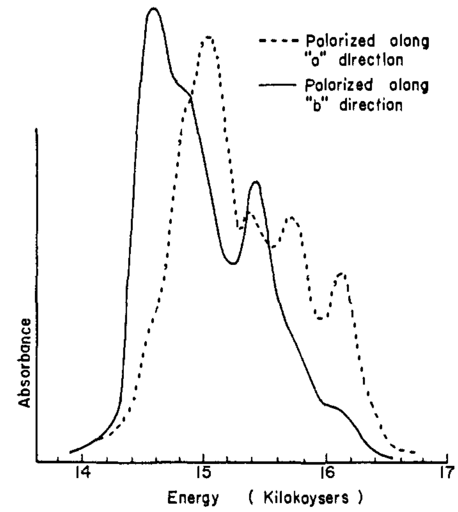

Figure 3. Polarized crystal spectra of the $^4A_2 \rightarrow {}^4T_1(P)$ transitions of dilute [Co(L_N^+)Br_3] in the [Zn(L_N^+)Br_3] host lattice at 77°K.

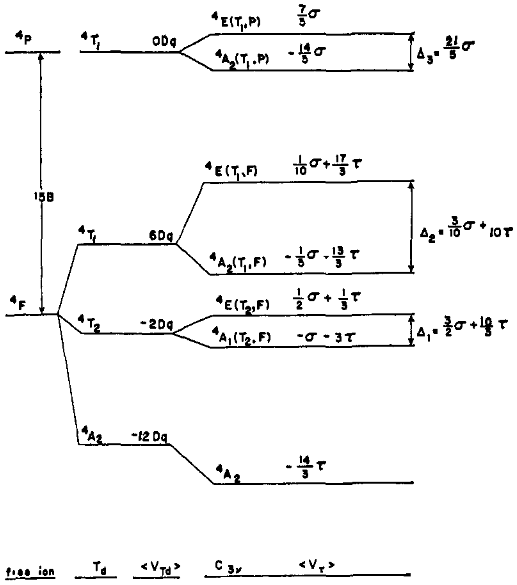

Figure 4. Trigonal field splittings of the quartet states of the d^7 configuration in pseudotetrahedral symmetry.

which includes the inter-electron repulsion, the cubic potential, and the trigonal potential, respectively. Considering only the states of maximum multiplicity for d^2, d^8, and d^3, d^7 configurations, the radial integrals can be parameterized as *B* and *Dq*, with the usual definitions. The trigonal potential,[10] $V_\tau = f_2Y_2^0 + f_4Y_4^0$, requires two parameters, $D\sigma = \langle R_{3d}(r)|^3/_2 f_2|R_{3d}(r)\rangle$ and $D\tau = \langle R_{3d}(r)|^3/_2 f_4|R_{3d}(r)\rangle$, for which the signs are chosen to stabilize the d^2_z orbital with the *z* direction along the trigonal axis.

The weak field determinantal functions, which transform according to the C_{3v} symmetry group for the d^7 configuration, allow a direct computation of the matrix elements of the trigonal potential; these are shown in Table I. A summary of the zeroth order (diagonal matrix elements) crystal field splittings and electric dipole selection rules for the d^7 quartet states is given in Figure 4. The analogous splitting diagram for the d^8

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Table I. Nonzero Matrix Elements of the Trigonal Potential for ^4F and ^4P Terms of the d^7 Configuration[a]

	$^4A_2(T_1,P)$	$^4A_2(T_2,F)$	$^4A_2(F)$
$^4A_2(T_1,P)$	$-14D\sigma/5$	$(3D\sigma - 5D\tau)8/15$	$(3D\sigma - 5D\tau)4/3\sqrt{5}$
$^4A_2(T_2,F)$		$-D\sigma/5 - 13D\tau/3$	$(3D\sigma - 5D\tau)2/3\sqrt{5}$
$^4A_2(F)$			$-14D\tau/3$

	$^4E(T_1,P)$	$^4E(T_1,F)$	$^4E(T_2,F)$
$^4E(T_1,P)$	$7D\tau/5$	$-(4D\sigma + 5D\tau)/5$	$-(4D\sigma + 5D\tau)/\sqrt{5}$
$^4E(T_1,F)$		$(D\sigma/10 + 17D\tau/3)$	$(D\sigma - 40D\tau)/6\sqrt{5}$
$^4E(T_2,F)$			$(D\sigma/2 + D\tau/3)$

[a] $^4\langle A_1|V_\tau|^4A_1\rangle = (D\sigma + 3D\tau)$.

triplet state configuration, obtained from that of the d^7 configuration by inversion about the free ion levels, is shown in Figure 5.

The splitting diagrams in Figures 4 and 5 illustrate several important features: (1) The parameter $D\sigma$ is the only contributor to the splitting of the $T_1(P)$ state, so that $D\sigma$ can be derived directly from the spectra. (2) The center of gravity of the P and F terms of the free ion are individually maintained, thus allowing an immediate assignment of the $T_1(P)$ state. (3) If $D\sigma$ is not too large, the splitting of the $T_1(F)$ state is about three times larger than the splitting of the $T_2(F)$ state, and $D\tau$ is readily obtained from the spectra. (4) The ground state ($^4A_2(F)$ for d^7, $^3E(F)$ for d^8) is lowered by about $5D\tau$ with respect to the corresponding ground state in T_d symmetry. For large values of $D\tau$, this lowering of the ground state represents a significant contribution to the stabilization of the complex of C_{3v} symmetry. (5) Estimation of Dq from the spectra requires that the split components of the T_1 and T_2 states arising from the free ion F term be properly assigned. The assignment of the observed transitions and the estimate of the crystal field parameters, Dq, $D\sigma$, and $D\tau$, can be best accomplished with polarized single crystal spectra, as discussed in the following section.

Discussion and Assignments

The spectrum of the nickel(II) complex, $[Ni(L_N^+)Br_3]$, is the most suitable for band assignments. The spectrum of this complex (Figure 3) shows a total of five absorptions, including bands at 5.10 and 15.00 kK for polarization in the *a* direction, and bands at 6.41, 8.70, and 16.2 kKfor polarization in the *b* direction. The absorptions at 15.00 and 16.2 kK are obviously transitions to the components of the $^3T_1(P)$ level. The d^8 splitting diagram shown in Figure 5 allows either an E or an A_2 ground state depending upon the sign of $D\tau$ (we expect a positive sign of $D\tau$ for complexes with a strong trigonal field). The order of the levels within the ^3F manifold is then expected to be $^3E(T_1,F)$ (ground state), $^3A_2(T_1,F)$, $^3E(T_2,F)$, $^3A_1(T_2,F)$, and $^3A_2(F)$. These assignments are in agreement with the observations that the bands at 6.41 and 8.70 kK, assigned as transitions to the $^3A_1(T_2,F)$ and $^3A_2(F)$ states, respectively, exhibit like polarizations in the *b* direction. Both of these transitions are allowed in the *xy* plane (see Table II). The absorption at 5.10 kK, which is present in both polarizations, is then assigned to the $^3E(T_2,F) \leftarrow {}^3E(T_1,F)$ transition (allowed *x*, *y*, *z*). The *a* polarization of the band at 15.00 kK identifies this absorption with the transition to the E component of the $T_1(P)$ level. It may be noted that the transition to the $^3A_2(T_1,F)$ level, which is expected to appear at about 3 kK, could not be observed with certainty because of the intense vibrational absorptions of the ligand, also occurring in this region. Without detailed calculations, these assignments give the following approximate but reasonable values of the crystal field parameters: $D\sigma = 200\ cm^{-1}$, $D\tau = 300\ cm^{-1}$, and $Dq = 400\ cm^{-1}$. Additional support for the assignment of an E ground state is to be found in the relatively large value of the room temperature magnetic moment of $[Ni(L_N^+)Br_3]$, $\mu = 3.55$ BM, which suggests a significant orbital contribution to the magnetic susceptibility.

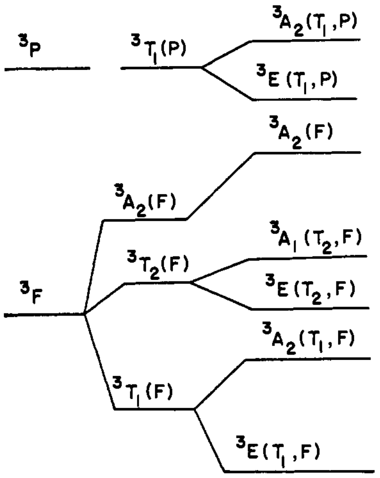

Figure 5. Trigonal field splittings of the triplet states of the d^8 configuration in pseudotetrahedral symmetry.

When the spectrum of $[Ni(L_N^+)Br_3]$ is recorded at liquid nitrogen temperature, near 77°K, the absorption corresponding to the transition to the $T_1(P)$ levels reveals considerable structure, with large intensity variations. Interpretion of these splittings, which would require a detailed analysis of spin-forbidden transitions, vibrational couplings, and spin–orbit effects, is not attempted here.

The spectra of $[Co(L^+)Br_3]$ (Figure 1) contain only four obvious absorptions. The energy level diagram of Figure 4, together with the data in Table II, suggest that the low energy bands at 4.42 and 7.27 kK, which exhibit opposite polarizations, arise from the trigonally split $T_1(F)$ state. By analogy with the order of energy levels obtained for the $[Ni(L_N^+)Br_3]$ complex, the band at 7.27 kK in the spectrum of $[Co(L_N^+)Br_3]$ is assigned to the $^4E(T_1,F) \leftarrow {}^4A_2(F)$ transition, and the 4.42-kK band is assigned to the $^4A_2(T_1,F) \leftarrow {}^4A_2(F)$ transition.

Table II. Assignments of Observed Absorption Bands

Transition	Polarization	Absorption maxima, kK	Relative direction of polarization
	$[Co(L_N^+)Br_3]$[a]		
$^4A_2(F) \rightarrow {}^4A_1(T_2,F)$	Forbidden *x*, *y*, *z*	Not observed	
$^4A_2(F) \rightarrow {}^4E(T_2,F)$	Allowed *x*, *y*	Not observed	
$^4A_2(F) \rightarrow {}^4A_2(T_1, F)$	Allowed *z*	4.42	*b*
$^4A_2(F) \rightarrow {}^4E(T_1,F)$	Allowed *x*, *y*	7.27	*a*
$^4A_2(F) \rightarrow {}^4A_2(T_1,P)$	Allowed *z*	14.99 15.70 16.10 } Av, 15.6	*a*
$^4A_2(F) \rightarrow {}^4E(T_1,P)$	Allowed *x*, *y*	14.62 14.81 15.38 } Av, 14.9	*b*
	$[Ni(L_N^+)Br_3]$[a]		
$^3E(T_1,F) \rightarrow {}^3A_2(T_1,F)$	Allowed *x*, *y*	Not observed	
$^3E(T_1,F) \rightarrow {}^3E(T_2,F)$	Allowed *x*, *y*, *z*	5.10	*a*, *b*
$^3E(T_1,F) \rightarrow {}^3A_1(T_2, F)$	Allowed *x*, *y*	6.41	*b*
$^3E(T_1,F) \rightarrow {}^3A_2(F)$	Allowed *x*, *y*	8.70	*b*
$^3E(T_1,F) \rightarrow {}^3E(T_1,P)$	Allowed *x*, *y*, *z*	15.0 15.2 16.1 } Av, 15.4	*a*
$^3E(T_1,F) \rightarrow {}^3A_2(T_1,P)$	Allowed *x*, *y*	16.2	*b*

[a] L_N^+ = N-ethyl-1,4-diazabicyclo[2.2.2]octonium cation.

The weak tail which extends below 4 kK in the unpolarized spectrum might be due to the $^4E(T_2,F) \leftarrow {}^4A_2(F)$ transition. Since the parent transition, $^4T_2(F) \leftarrow {}^4A_2(F)$, is forbidden in T_d symmetry, this band is expected to be weak. No absorption arising from the $^4A_1(T_2,F) \leftarrow {}^4A_2(F)$ transition is observed. This is not surprising, for this transition is also forbidden and therefore would likely be very weak; moreover, it would be expected to occur near 3 kK, in the region of the spectrum obscured by the vibrational bands of the L_N^+ ligand. The relative polarizations of the higher energy bands then lead to the following assignments: $^4A_2(T_1,P) \leftarrow {}^4A_2(F)$ at 15.0 kK, and $^4E(T_1,P) \leftarrow {}^4A_2(F)$ at 14.6 kK. The trigonal splitting of the $^4T_1(P)$ state is small, and indicates that the value of $D\sigma$ is about 100 cm^{-1} in this complex. The splitting of the $^4T_1(F)$ level (2.85 kK) yields $D\tau$ about 280 cm^{-1}, and one can estimate Dq to be about 320 cm^{-1}. These values of the crystal field parameters are comparable to those obtained independently for the corresponding nickel complex, $[Ni(L_N^+)Br_3]$. It may be noted that the magnetic susceptibility of $[Co(L_N^+)Br_3]$ (μ = 4.55 BM) is quite similar to that of the $[CoBr_4]^{2-}$ complex, as expected, since both species have a $^4A_2(F)$ ground state.

Both the Ni and Co complexes exhibit structure within the $T_1(P)$ bands near 15 kK. This presumably arises from vibronic and spin-orbit splittings. At low temperature (77°K) the $T_1(P)$ band of $[Co(L_N^+)Br_3]$ reveals a well-resolved structure (see Figure 3) which is not unlike that observed for $[CoCl_4]^{2-}$. In contrast, no structure develops at low temperature for the low energy absorptions of $[Co(L_N^+)Br_3]$, whereas considerable structure is revealed for $[CoCl_4]^{2-}$.

Conclusions

This work shows that the d-d electronic spectra of pseudotetrahedral d^7 and d^8 complexes of the type $[MLX_3]$ (C_{3v} symmetry) can be explained on the basis of a simple crystal field model, assuming a trigonal potential and splitting parameters of reasonable magnitude. The diagonal crystal field matrix elements, together with simple arguments based on the positions of the ligands in the spectrochemical and nephelauxetic series, then permit one to make reliable assignments of all observed absorption bands. The assignments thus obtained agree with the results of single crystal polarized spectra. It is significant that, for compounds of the type $[MLX_3]$, useful information can be obtained from polarized single crystal spectra even when the crystal structure of the compound is unknown. The results of this work can therefore be of considerable general value in the structural elucidation of complexes of similar type, for which less detailed spectral data are available.[4]

It may be logically expected that for a series of trigonally distorted pseudotetrahedral $[MLX_3]$ complexes of the same metal ion, the magnitude of the crystal field parameter $D\tau$ will be related to the difference in field strength between the unique ligand, L, and the three ligands, X. This trend is well illustrated by the splitting of the band arising from transitions to components of the $^4T_1(F)$ level, for the series of complexes listed in Table III. The largest trigonal distortion is expected, and is indeed observed, for the $[CoP(C_6H_5)_3Br_3]^-$ species, in which the odd ligand, L = triphenylphosphine, has a much greater field strength than the three bromide ligands. A smaller but still appreciable distortion is expected and found for the complex $[Co(L_O^+)Br_3]$, where

Table III. Band Splittings (cm^{-1}) in Some Trigonally Distorted Tetrahedral Cobalt(II) Complexes

	$^4T_1(F)$			$D\tau$
Complex	A_2	E	Δ[b]	(approx)
$[Co(P(C_6H_5)_3)Br_3]^-$ [a]	4,350	8,000	3,650	365
$[Co(L_N^+)Br_3]$	4,350	7,410	3,060	306
$[Co(L_O^+)Br_3]$	5,250	7,720	1,470	150
$[Co(L_N^+)(NCS)_3]$	Components unresolved		<1,000	<100

[a] Data taken from ref 4. [b] $\Delta = {}^4E(T_1,F) - {}^4A_2(T_1,F)$.

the odd ligand, the O-donor, N-ethyl-N′-oxo-1,4-diazabicyclo[2.2.2]octonium cation, has a field strength much lower than triphenylphosphine but still appreciably greater than the bromide ligands. Finally, the $[Co(L_N{}^+)(NCS)_3]$ complex is expected to have a very small value for *Dr* (that is, no appreciable trigonal distortion), because the ligand field strength of the odd ligand, the N-donor, N-ethyl-1,4-diazabicyclo[2.2.2]octonium cation, does not differ substantially from that of the three isothiocyanato ligands, NCS.

Structural Characterization of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, a Bimolecular Condensation Product of *o*-Bis(phenylethinyl)benzene: Steric Equivalence of Fe(CO)(cyclobutadiene) and $Fe(CO)_3$ Groups

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Abstract: An X-ray crystallographic investigation of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ was undertaken in order to determine the nature of one of the products, $Fe_2(CO)_4C_{44}H_{28}$, of a reaction between *o*-bis(phenylethinyl)benzene and iron pentacarbonyl. The product forms crystals with four formula units in a monoclinic cell of symmetry $P2_1/n$ and of lattice parameters $a = 13.56 \pm 0.02$ Å, $b = 24.00 \pm 0.04$ Å, $c = 11.32 \pm 0.02$ Å, $\beta = 93° 55' \pm 10'$. Refinement of the determined structure by anisotropic–isotropic least squares yielded unweighted R_1 and weighted R_2 values of 9.9% for the 1880 independent nonzero diffraction maxima collected photographically. The organoiron carbonyl complex was found to contain a Fe(CO)(cyclobutadiene) fragment which is coordinated to a ferracyclopentadiene ring system. This unusual molecular system originates from the *intermolecular* condensation of two molecules of *o*-bis(phenylethinyl)benzene with a $Fe(CO)_3$ and a Fe(CO) fragment. One pair of acetylenes forms a cyclobutadiene ring, while the other pair of acetylenes produces the five-membered ferracyclopentadiene ring by the incorporation of the $Fe(CO)_3$ fragment. Molecular stabilization is achieved through the interaction of the cyclobutadiene ring with the Fe(CO) fragment, which is also coordinated to the ferracyclopentadiene ring *via* both a (*cis*-butadiene)–iron interaction and an iron–iron electron pair bond; the resulting iron–iron single bond distance is 2.494 (5) Å. The striking stereochemical principle which emerges from a detailed comparison of the molecular parameters of $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$ with those of $Fe(CO)_3(HOC_2CH_3)_2Fe(CO)_3$ is that the cyclobutadiene ligand may sterically behave as only a bidentate ligand by the effective occupation of *two* metal coordination sites in place of two terminal carbonyl groups.

The reactions of alkynes with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$ have yielded a large number of organoiron complexes with a remarkable variety of configurations.[2,3] One such complex was isolated by Whitlock and Sandvick[4,5] in low yields from the reaction of *o*-bis(phenylethinyl)benzene with either iron pentacarbonyl or triiron dodecacarbonyl under vigorous conditions. Elemental analysis and molecular weight determination by vapor pressure osmometry[6] indicated that the compound has the molecular formula $Fe_2(CO)_4C_{44}H_{28}$. The presence of only terminal carbonyl groups was indicated from its infrared absorption spectrum in solution.[7] Attempts to characterize the structure further by chemical and physical methods were not successful.

Since *o*-bis(phenylethinyl)benzene *per se* exhibits intramolecular interaction between the triple bonds on reaction with electrophilic, nucleophilic, or radical reagents,[4,5] it was of interest to determine whether this behavior is also exhibited on reaction with iron pentacarbonyl and triiron dodecacarbonyl. In order to resolve this question and ascertain the molecular geometry of the compound, a three-dimensional X-ray analysis of *o*-bis(phenylethinyl)benzene diirontetracarbonyl, $Fe(CO)_3(C_6H_5C_2C_6H_4C_2C_6H_5)_2Fe(CO)$, was carried out. The determination of the molecular structure of this organodiiron complex instead revealed an *inter*molecular polymerization of two molecules of *o*-bis(phenylethinyl)benzene with two iron carbonyl fragments to give an unusual kind of transition metal complex.

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(1) This manuscript is based in part on a dissertation submitted by Earl F. Epstein to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1969.

(2) *Cf.* W. Hübel, "Organic Synthesis via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, pp 273–342, and references therein.

(3) *Cf.* F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968), and references therein.

(4) H. W. Whitlock, Jr., and P. E. Sandvick, *J. Amer. Chem. Soc.*, **88**, 4525 (1966).

(5) P. E. Sandvick, Ph.D. Thesis, University of Wisconsin, 1968.

(6) The empirical formula $C_{48}H_{28}O_4Fe_2$ was based on the following: *Anal.* Calcd: C, 73.87; H, 3.62; Fe, 14.31. Found: C, 74.14; H, 3.45; Fe, 14.04; mol wt: 750, 772, 790, 810 (vapor pressure osmometer).[5]

(7) The infrared spectrum in CCl_4 shows strong absorption bands at 2070, 1996, and 1894 cm^{-1}.[5]