T_{1e} in the low-spin complex but the broadening near room temperature cannot be explained in this way. The latter broadening begins at about $T = T_c$ and increases so that lines are no longer observable at $T = T_c + 30 (\pm 10)$°K.

These observations are consistent with the formation of a high-spin complex as the temperature increases, with the rate of exchange between the two spin states being very much greater than the frequency shift difference of the protons in the two environments so that a single resonance is observed for each set of protons. As expected, the greater the basicity of the pyridine ligand, the more the low-spin form is favored. Recent investigations[21] of the temperature dependence of the magnetic susceptibilities and absorption spectra of the complexes in solution support these conclusions and suggest that the high-spin form is possibly the intermediate $S = {}^3/_2$ state and not the expected $S = {}^5/_2$ state. A detailed analysis of the temperature dependence of all three properties will be published shortly.

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(21) H. A. O. Hill, C. M. Wernham, and R. J. P. Williams, unpublished observations.

Organometallic Electrochemistry. XVII.[1] Electric Charge Distribution in Organometallic Compounds, Tetrahedral Derivatives of $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$

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Abstract: The investigation of electric charge distribution in transition metal carbonyl and nitrosyl molecules has been extended to a remarkable series of cobalt and iron compounds of the general formulas $CoL_2(CO)(NO)$ and $FeL_2(NO)_2$, where L_2 = 2,2′-bipyridyl, *o*-phenanthroline, and di-2-pyridyl ketone. Coupling electrochemical and spectroscopic tools four distinct charge states of the tetrahedral geometry were examined: dianion (2−), radical anion (1−), neutral (0), and radical cation (1+). Mössbauer magnetic resonance and infrared studies on these systems have led to considerable insight as to the nature and mechanism of molecular charge distribution. Spin density and charge density are not directly related in this series, in comparison to polycyclic aromatic systems.

The preceding papers[1,3,4] in this series dealt with the nature of electron charge and spin distribution in trigonal-bipyramidal, octahedral, and linear organometallic species. The present study probes the mechanism and nature of electron distribution in a tetrahedral series of cobalt and iron molecules of the general formulas $CoL_2(CO)(NO)$ and $FeL_2(NO)_2$ where L_2 = 2,2′-bipyridyl, *o*-phenanthroline, and di-2-pyridyl ketone. Aside from the obvious interest in the extension of these studies to the tetrahedral geometry, there were a number of attractive aspects leading to the initiation of the present investigation. The first of these involves the unusual span of charged species that may be derived from a single neutral precursor molecule. In several cases four distinct charge states may be generated in stable bulk quantities. The (di-2-pyridyl ketone)iron dinitrosyl molecule, for example, has served as the neutral precursor to stable radical anions, dianions, and radical cations. With the subsequent application of Mössbauer, infrared, electron spin resonance, nuclear magnetic resonance and uv-vis[5] techniques to all the species generated, by chemical or electrochemical action, a considerable degree of information as to the electronic structure of these molecules may be derived. As was emphasized in the preceding investigations, this general method of attack offers one the ability of keeping the ligand, metal atom, and to a first approximation, the geometry fixed, while varying the electric charge density. Thus one may avoid the serious risks encountered in chemical alteration of the molecules being considered.

Another important aspect prompting the present inquiry relates to the presence of the nitrosyl moieties in these molecules. The presence of the NO group offers one the opportunity to probe the spin density residing on the nitrosyl groups in these systems. This is in contrast to the octahedral and trigonal-bipyramidal cases where, except for the bidentate organic ligand, only carbonyl ligands having low abundances of magnetic nuclei were present.

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(1) For the previous paper in this series, see R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *J. Amer. Chem. Soc.*, **92**, 3947 (1970).

(2) American Chemical Society–Petroleum Research Fund Fellow, 1969–1970.

(3) R. E. Dessy and L. Wieczorek, *J. Amer. Chem. Soc.*, **91**, 4963 (1969).

(4) R. E. Dessy, M. Kleiner, and S. C. Cohen, *ibid.*, **91**, 6800 (1969).

(5) Uv-vis experiments on these systems and, in fact, the other systems investigated by Dessy and coworkers have been performed, and a quantitative treatment of these molecules based on those results is forthcoming.

Finally, the implementation of the di-2-pyridyl ketone ligand seemed particularly well suited with respect to these studies for the following reasons. The coordination of this ligand leads to a six-membered ring system which seemed to yield molecules of overall greater stability when compared to the five-membered rings formed on coordination of the bipyridyl type ligands most often employed in previous investigations. Also, the keto carbonyl group should increase the electron-withdrawing ability and the delocalization potential of the ligand, once again yielding systems of considerable stability. In addition to these promising characteristics, the di-2-pyridyl ketone ligand provides one the opportunity of employing a "charge label" to track electric charge density in the iron-containing molecules. The infrared spectrum of these molecules in the 2000- to 1500-cm^{-1} region should display three distinct absorption bands, two resulting from nitrosyl (nitrogen–oxygen) stretching modes and one resulting from the carbon–oxygen stretch of the ligand keto carbonyl group. Carefully following the shifts in these frequencies as one spans the various charge states (2−, 1−, 0, 1+) should yield definitive information concerning electric charge distribution in these molecules. Thus, the use of the "charge label" di-2-pyridyl ketone ligand was deemed particularly attractive as a probe for infrared studies.

Experimental Section

Electrochemical. The electrochemical work and preparation of infrared, nmr, and esr samples were performed in a Vacuum Atmospheres Dry Lab-Dry Train employing an argon atmosphere controlled to not more than 1 ppm water vapor and oxygen.

With the exception of the oxidative exhaustive controlled-potential electrolyses employed to generate bulk radical cation species, the electrochemical methods and instrumentation were identical with those described in the previous publications by Dessy and coworkers.[6-8] $E_{1/2}$ values were taken relative to a Ag|Ag$^+$ ($10^{-3}M$) reference solution with 1,2-dimethoxyethane as solvent and with tetrabutylammonium perchlorate as supporting electrolyte. Electrochemical reversibility was established by rapid triangular voltammetric sweeps; chemical reversibility was determined by cyclic controlled-potential electrolyses as previously described. All steps involved one-electron processes as determined by exhaustive controlled-potential electrolysis (cpe).

The ligands employed in the tetrahedral case (bipyridyl, *o*-phenanthroline, and di-2-pyridyl ketone) displayed rather interesting electrochemistry, and in all cases it was possible to generate bulk concentrations of radical anion whose esr spectrum was subsequently interpreted. Table I lists the $E_{1/2}$ values for the reductive steps observed. Unlike the complexed species, no oxidative steps could be detected at voltages more negative than 0.0 V relative to the Ag|Ag$^+$ reference couple. In each case, the reductive steps were electrochemically and chemically reversible, although dianion generation did require care to avoid decomposition.

Table I. Electrochemical Data for Uncoordinated Ligands

Ligand	$E_{1/2}$[red.(1)]	$E_{1/2}$[red.(2)]
2,2′-Bipyridyl	−2.80	−3.11
o-Phenanthroline	−2.72	−3.24
Di-2-pyridyl ketone	−2.31	−2.92

It should be noted that in the cases of the di-2-pyridyl ketone ligands the polarogram of the reduced species (radical anion) displayed an oxidative potential not in line with the corresponding reductive potential of the neutral material. This result was also clearly observed in the iron–dinitrosyl and (cobalt carbonyl)–nitrosyl complexes. Considering the chemical and electrochemical reversibility of these systems, it is apparent that in the complexes we are dealing with some sort of slow structural reorganization upon reduction.

The electrochemistry of the transition metal complexes was characterized by polarograms exhibiting one oxidative wave and two reductive waves, which were both electrochemically and chemically reversible in the Fe system. Thus oxidation of the iron system[9] at the first wave gave radical cation, while reduction at the first wave and second wave resulted in radical anion and dianion, respectively. These half-wave potentials are given in Table II. The colors of the various species (radical cation, neutral, radical anion, and dianion) in dimethoxyethane are listed in Table III. All the cobalt systems were electrochemically reversible (triangular voltammetry), but only reductions were chemically reversible (cyclic cpe). The nickel systems were electrochemically reversible but all chemically irreversible.

Table II. Electrochemical Data for Iron and Cobalt Complexes

Complex	$E_{1/2}$[ox.(1)]	$E_{1/2}$ [red.(1)]	$E_{1/2}$ [red.(2)]
Bipyridyl–Fe(NO)$_2$	−0.56	−2.14	−2.78
o-Phenanthroline–Fe(NO)$_2$	−0.60	−2.16	−2.80
(Di-2-pyridyl ketone)–Fe(NO)$_2$	−0.30	−1.68	−2.40
Bipyridyl–Co(CO)(NO)	−0.50	−2.26	−2.81
o-Phenanthroline–Co(CO)(NO)	−0.36	−2.19	−2.82
o-Phenanthroline–Ni(CO)$_2$	−0.74	−2.42	−2.76

Table III. Colors of the Various Cobalt and Iron Charged Species

Complex	Dianion	Radical anion	Neutral	Radical cation
(Di-2-pyridyl ketone)–Fe(NO)$_2$	Deep purple	Purple	Green	Light brown
o-Phenanthroline–Fe(NO)$_2$		Gray-green	Orange-brown	Orange
Bipyridyl–Fe(NO)$_2$		Orange-brown	Brown	Orange-pink
Bipyridyl–Co(CO)(NO)		Red-violet	Violet	
o-Phenanthroline–Co(CO)(NO)		Gray-green	Dark maroon	

Electron Spin Resonance. Two methods were employed to investigate the esr spectra of the tetrahedral Co and Fe derivatives. The first was electrochemical generation of the radical anion, this species being placed in a standard esr quartz tube fitted with a Delmar Teflon needle valve. The esr spectrometer used throughout this study was the Varian E-3 unit with a variable-temperature accessory.

The second method employed vacuum-line technique. The solvent, 1,2-dimethoxyethane, was predried over calcium hydride and distilled from lithium aluminum hydride, after which it was thoroughly degassed with argon. Using the Vacuum Atmospheres Dry Lab unit, 500-ml bulbs were charged with Na/K eutectic alloy. These flasks, one of which contained the solvent prepared as described above, were then transferred to a vacuum line. After bulb-to-bulb distillation and thorough degassing, the solvent displayed the familiar blue color of the solvated electron at room temperature.

The esr samples were then prepared as follows. A specially constructed tube, having a side arm and quartz esr tube attached, was transferred to the drybox. For low-temperature esr work,

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(6) R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 5112 (1966).

(7) R. E. Dessy, W. Kitching, and T. Chivers, *ibid.*, **88**, 453 (1966).

(8) R. E. Dessy, P. M. Weissman, and R. L. Pohl, *ibid.*, **88**, 5117 (1966).

(9) It should be noted that the neutral complex air oxidized to the radical cation, as evidenced by the appearance of an intense radical-cation, esr signal. After several minutes the intensity of this signal subsided, apparently the result of further reactions leading to cation-radical decomposition.

the quartz esr tube was fitted with a quartz plate to minimize power losses. Graded seals were employed for all Pyrex glass to quartz connections. Clean potassium metal was then placed in a side arm and the tube was charged with 2 mg of neutral sample. After transferring the tube to the vacuum line, a potassium mirror was deposited and solvent was bulb-to-bulb distilled over the sample. The tube containing frozen solvent, sample, potassium mirror, and esr tube was then sealed from the upper portion. Dissolution of the sample and subsequent contact of this solution with the potassium mirror generated the radical-anion species whose esr properties were then investigated.

The spectra obtained were simulated by use of two programs. The first was the SESR program described by Stone and Maki[10] with suitable modifications to permit use on the Virginia Polytechnic Institute Computing Center IBM 360/50-65 with associated Calcomp plotter. The second program was supplied by the Digital Equipment Corp. and employed the PDP 8/I computer.

Infrared. The infrared spectra of all species in these series were taken in 1,2-dimethoxyethane at a concentration of 2.0×10^{-2} *M* in the presence of supporting electrolyte. Infrared spectra throughout this study were recorded on a Perkin-Elmer Model 621 double-beam instrument. The cell in the reference beam contained only solvent and supporting electrolyte, thus removing these components from the observed spectra. The cells (Barnes Engineering) employed Teflon spacers (0.1 mm), gaskets, and "O" rings to achieve a well-sealed unit. A needle plate, tightly fitted with suitable serum caps, was employed to facilitate the syringing of samples within the drybox. The windows employed were of the Irtan-2 type.

The infrared data were analyzed using a nonlinear least-squares method described by Wentworth[11] as applied to the Cotton–Kraihanzel force-field matrices.[12] After expansion of the secular equations in a Taylor series, successive iterations were performed until the process had gone to convergence. The entire least-squares analysis was coded in Fortran IV for the IBM 360/50-65 for use at the Virginia Polytechnic Institute Computing Center.

Mössbauer. Only electrochemical methods were used to generate Mössbauer samples. Large-scale oxidations and reductions were performed by the use of two Kepco CK 60-0.5 power supplies wired in a master–slave configuration and boot strapped for high-input impedence. A Heath voltage reference source was used to offset the summing point of the master unit, thus setting the controlled $E_{\text{ref}} - E_{\text{test}}$ for electrolysis at the large mercury pool in the cathode compartment. Current passed during the electrolysis was monitored by a small dropping resistor in series with the working electrodes, the *IR* drop being fed into a Yellowsprings Instrument recorder. After the current had fallen to the residual level, the exhaustively reduced or oxidized material was syringed into a suitable round-bottom flask fitted with a vacuum stopcock. Upon removal of the solvent, the solid charged species remained and was subsequently encapsulated by heat sealing between two 1.5-in. square trilaminated sheets (polyethylene–Mylar–aluminum). The resultant packet was removed from the drybox and transferred immediately to a tail dewar filled with liquid nitrogen.

The Mössbauer spectra were obtained at liquid nitrogen temperature by use of the tail dewar. A constant acceleration drive system was employed and the data were collected on a Nuclear Data 512 channel analyzer. The system was calibrated before and after each run using either iron foil or sodium nitroprusside as a standard. The drift was found to be less than 2×10^{-3} mm/sec over the course of a run. The source was ^{57}Co diffused in platinum as prepared by the Nuclear Science and Engineering Division of the International Chemical and Nuclear Corp. and was found to have an activity of approximately 1 mCi.

Data from the multichannel analyzer were read out on punched tapes and the spectra were analyzed by fitting the peaks to Lorentztian curves using a least-squares routine. Two computer programs were utilized. One was the general least-squares program referred to in the infrared section and was processed on the IBM 360/50-65 system. The second program was a curve-simulating program which was written for the PDP 8/I "in-house" computer. This latter program permitted the rapid analysis of complex spectra and a quick comparison of simulated and actual data.

Chemicals. Solvent (dimethoxyethane), supporting electrolyte (tetrabutylammonium perchlorate), and mercury were prepared as thoroughly described in the previous publication. Cobalt tricarbonyl nitrosyl, which served as the starting material for the tetrahedral cobalt derivatives, was purchased and employed without further purification from Strem Chemicals. The iron dinitrosyl derivatives were synthesized from iron dicarbonyl dinitrosyl and the respective ligand, the former being prepared according to the procedure fully outlined by King.[13] Nickel tetracarbonyl was purchased in lecture bottles from Matheson.

The syntheses of the bipyridyl and *o*-phenanthroline complexes have been described in an early paper by Hieber and Anderson.[14] These authors performed the synthesis of the iron and cobalt derivatives in pyridine, thus converting the parent nitrosyl and/or carbonyl molecule to a bispyridine stage before the formation of the desired complex. Another and, in fact, simpler method was employed to synthesize the molecules in this study. The following general procedure yields highly pure crystals of each iron and cobalt complex in good yield.

General Procedure for the Preparation of Fe and Co Derivatives. All manipulations were performed in a highly pure argon atmosphere. A solution of 25 ml of thoroughly dried and degassed benzene and approximately 1 g of ligand was prepared in a 50-ml round-bottomed flask. This flask was subsequently charged *via* a syringe with a slight excess of the parent $Fe(NO)_2(CO)_2$ or $Co(CO)_3(NO)$. The reactants were allowed to stand under inert atmosphere for 2 days during which time large, well-formed crystals of the complex developed. These crystals were then filtered and washed with either dimethoxyethane or light petroleum ether. After thorough drying, the crystals were stored under argon. The complexes thus synthesized were stable to heat and could be stored indefinitely under an inert atmosphere. The various complexes under argon have the following melting points: bipyridyl-$Fe(NO)_2$ (I), 237°C dec; *o*-phenanthroline-$Fe(NO)_2$ (II), 234°C dec; (di-2-pyridyl ketone)-$Fe(NO)_2$ (III), 215°C dec; bipyridyl-Co(CO)(NO) (IV), 187°C dec;[14] *o*-phenanthroline-Co(CO)(NO) (V), 189°C dec.[14]

All complexes analyzed correctly for C, H, and N. The Co derivatives have been previously prepared. *Anal.* Calcd for $C_{10}H_8N_4O_2Fe$ (I): C, 44.12; H, 2.94; N, 20.59. Found: C, 33.91; H, 2.71; N, 20.82. Calcd for $C_{12}H_8N_4O_2Fe$ (II): C, 48.65; H, 2.70; N, 18.92. Found: C, 48.85; H, 2.95; N, 19.81; N, 19.01. Calcd for $C_{13}H_8N_4O_3Fe$ (III): C, 44.30; H, 2.01; N, 18.79. Found: C, 44.02; H, 2.20; N, 18.57.

Ultraviolet, infrared, and nmr spectra are all consistent with the proposed structures. Ultraviolet and infrared studies on the charged radical species are also consistent with the proposed structures.

Nuclear Magnetic Resonance. All spectra were measured as 0.5 *M* degassed dimethoxyethane solutions at 32–34° using a Varian A-60A spectrometer and were referenced to the solvent. The solvent chemical shifts relative to τ 10.00 TMS were calibrated by standard side-band techniques. The values used herein are τ 6.64 (CH_2) and τ 6.82 (CH_3). The dianion solutions were prepared both by potassium-mirror reduction using the same techniques employed in obtaining the esr samples and by electrochemical reduction as employed with the Mössbauer samples. Paramagnetic concentrations from residual radical anion were monitored by esr. Only after virtual exhaustive two-electron reduction to the diamagnetic dianion state had been achieved could nmr spectra of acceptable resolution be obtained. Pseudo-first-order appearances of the pyridyl ring multiplets were used to assign their identity. These identities were confirmed by the unambiguously assignable AB pattern for 4,4′-dipyridine and by comparison of this spectrum to that of 2,2′-dipyridine and di-2-pyridyl ketone.

Results and Discussion

The iron $[FeL_2(NO)_2]$ and cobalt $[CoL_2(CO)(NO)]$ complexes form a large number of stable charge states upon electrochemical treatment. All redox systems reported were *chemically reversible* as determined by cyclic cpe and ir/uv–vis spectrometry. A tetrahedral geometry is assumed for all cases in the following discussion, which focuses on the subject of electric charge distribution. Structural reorganization upon alteration

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[10] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

[11] W. E. Wentworth, *J. Chem. Educ.*, 42, 96 (1965).

[12] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[13] R. B. King, "Organometallic Synthesis," J. J. Eisch and R. B. King, Ed., Vol. I, Academic Press, New York, N. Y., 1965.

[14] (a) W. Heiber and J. S. Anderson, *Z. Anorg. Allgem. Chem.*, **211**, 132 (1933); (b) L. Bares and R. E. Dessy, unpublished observations.

of charge conditions may occur, but since no evidence on this subject is spectrometrically available in these systems in solution a standard geometry has been chosen.

Esr Results. In all the cases, the neutral complexes were diamagnetic. Upon one-electron reduction, the $CoL_2(CO)(NO)$ complexes formed stable radical anions whose esr spectra at $-50°$ in dimethoxyethane displayed well-resolved hyperfine structure arising from the interaction of the unpaired electron with the cobalt nucleus (spin $^7/_2$), two nitrogens (spin 1), and two protons (spin $^1/_2$). Figure 1 represents the experimental and simulated spectra for the *o*-phenanthroline-Co-(CO)(NO) radical anion. Pertinent couplings for both the bipyridyl and *o*-phenanthroline cases are $a_{Co} = 6.9$ G, $a_{2N} = 3.4$ G, and $a_{2H} = 6.9$ G. Further hyperfine (hf) structure from interaction with other magnetic nuclei was clearly visible for the bipyridyl case, but interaction with nitrosyl N must be 0.2 G or less. An investigation of the uncoordinated ligand radical anions was also undertaken; the probable electron-nuclear hf coupling constants for those species are given in Table IV.

Table IV. Probable Electron-Nuclear Hyperfine Coupling Constants for Ligand Radical Anions[a]

Ligand	a, G
Di-2-pyridyl ketone	$a_{H_{5,5'}}$ 4.81
	$a_{N,N'}$ 1.52
	$a_{H_{3,3'}}$ 0.49
2,2′-Bipyridyl	$a_{H_{5,5'}}$ 4.91
	$a_{N,N'}$ 2.48
	$a_{H_{3,3'}}$ 1.40
	$a_{H_{4,4'}}$ 0.70
1,10-Phenanthroline	$a_{H_{3,8}}$ 5.38
	$a_{N,N'}$ 2.72
	$a_{H_{5,6}}$ 0.20

[a] Assignments with respect to hyperfine coupling constants are based on successful computer simulation. Assignment of the group causing the hyperfine coupling, where a possible ambiguity exists, is based on known assignments in model compounds.

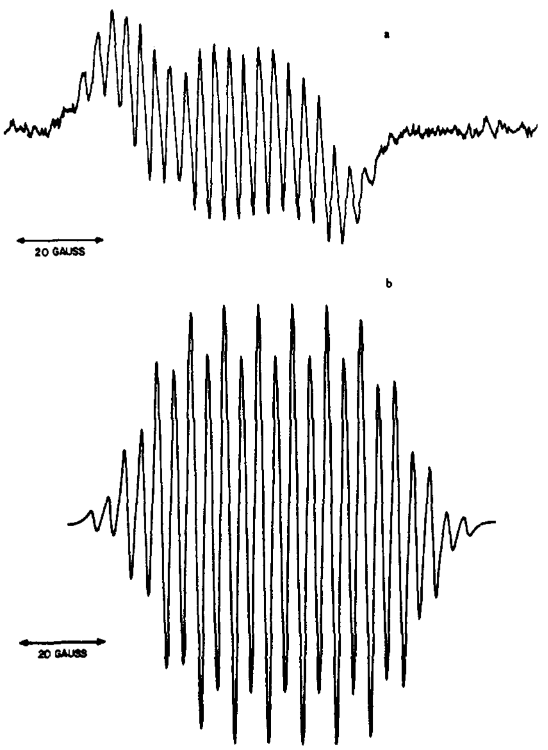

Figure 1. (a) Esr spectrum of *o*-phenanthroline-Co(CO)(NO) radical anion. (b) Simulated spectrum.

As can be seen from Figure 1, the esr spectra for the $CoL_2(CO)(NO)$ radical anions displayed an average total width of some 90 G. It is interesting to note that not only were the average g values (solution, $-50°$) close to the value of 2.00 for an unbounded electron, but also that, except for modulational effects, there was no detectable variation in line width. The nondeviation of g from the free-spin value indicates that the electron introduced by reduction experiences little spin-orbit coupling.[15] In line with this result is the fact that no variation in line width was observed, a phenomenon expected if the electric field gradient around the Co nucleus was nonsymmetric.[16]

Another interesting facet to the present study relates to the small or nonexistent hf splitting from the nitrosyl nitrogen. Previous to this investigation *unpaired spin* density on the carbonyl groups of octahedral and trigonal-bipyramidal $L_2M(CO)_4$ and $L_2M(CO)_3$ species[2] could not be observed. But natural abundances of ^{13}C make this negative data at best. That $CoL_2(CO)(NO)$ radical anions displayed little *or no* hf splitting suggests that spin density is highly localized in the L_2 portion of all the octahedral, trigonal-bipyramidal, and tetrahedral $L_2M(CO)_x(NO)_y$ radical ions.[17]

Four distinct charge states (1+, 0, 1−, 2−) were generated in the $FeL_2(NO)_2$ series. The neutral and dianion species were both diamagnetic, but the radical cations and radical anions clearly displayed strong esr signals. Since oxidation to the 1+ state corresponds to removal of an electron from the highest occupied molecular orbital, while reduction to the 1− state corresponds to addition of an electron to the lowest previously unoccupied molecular orbital, the esr spectra of these systems were of special interest. Figure 2a displays the esr signal for the radical cation for the L_2 = di-2-pyridyl ketone case which is, in general, representative of this series.

The radical-cation spectra (see Figure 2a) are characterized by several outstanding features which may be directly attributed to the nature of the molecular orbital left half occupied. Without exception, the cation spectra measured approximately 50 G in total width. The L_2 = bipyridyl and L_2 = di-2-pyridyl ketone spectra clearly displayed under 1-2-G modulation 11 and 13 lines, respectively. From the intensity pattern observed, these splittings in the latter may be assigned to four equivalent hydrogens (~3.7 G) and two equivalent nitrogens (~7.5 G) (*cf.* Figure 2b). It is also interesting to note that in each case the average g value measured deviated considerably from the spin-free value of 2.00, taking up values in the range 1.95–1.98. The low g values observed strongly indicate that the unpaired electron in these radical cations experiences a

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(15) E. König in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience Publishers, New York, N. Y., 1968.

(16) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

(17) Electron-nuclear coupling is discussed in detail by Beck and Beringer[18] for NO.

(18) (a) W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965); (b) T. Beringer and J. C. Castle, *Phys. Rev.*, **78**, 581 (1950).

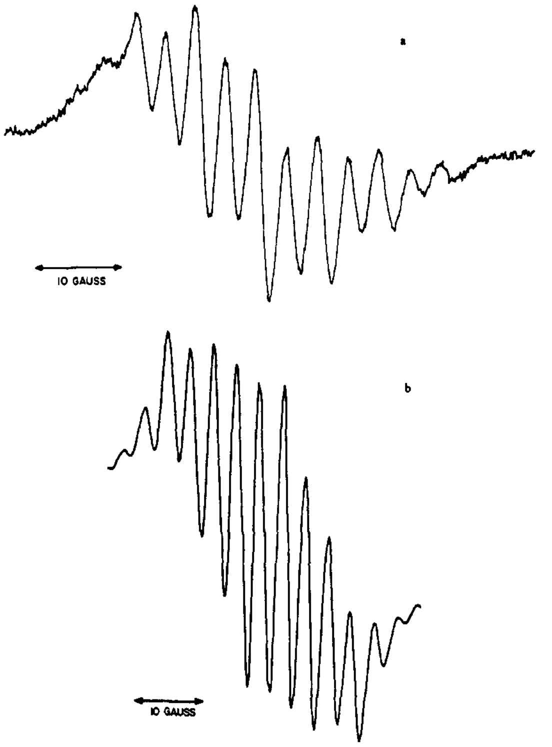

Figure 2. (a) Esr spectrum of di-2-pyridyl ketone–$Fe(NO)_2$ radical cation. (b) Simulated spectrum.

substantial degree of spin–orbit coupling, a result to be expected if the electron occupies a molecular orbital having some metal s character with contribution from L_2 ligand orbitals.[19] The latter result is supported by Mössbauer experiments which are discussed in a later section.

Reduction of the $FeL_2(NO)_2$ molecules proceeds *via* two distinct one electron steps–first to the radical anion and finally to the singlet-state dianion species. The radical anions of each L_2 derivative exhibited well-resolved esr signals, while the singlet state diamagnetic dianions display no esr signal even at −196° in methyltetrahydrofuran frozen matrices.

The esr spectra of each of the radical anions of this series were characterized by several outstanding features, some of which were in direct contrast to the spectra obtained for the 1+ charge state (radical cation) previously discussed. For example, each spectrum measured approximately 25 G in total width as compared to the 50 G total spectral width observed for the radical cations of this series. In all cases the average *g* value measured was close to the spin-free value of 2.00, once again a result unlike the result obtained for the 1+ charge state.

In each case the radical-anion spectrum closely resembled that obtained for the corresponding uncoordinated ligand radical anion, *e.g.*, di-2-pyridyl ketone radical anion $a_{H_{5,5'}} = 4.81$, $a_{N,N'} = 1.52$, $a_{H_{3,3'}} = 0.49$; di-2-pyridyl ketone iron–dinitrosyl radical anion $a_{H_{5,5'}} = 4.80$, $a_{N,N'} = 2.41$, $a_{H_{3,3'}} = 0.62$.

The preceding evidence strongly indicates that one-electron reduction in the $FeL_2(NO)_2$ series results in occupation of a molecular orbital which is, in large part, made up of ligand π^* orbitals. Use of biquinolyl, 4,4′-dimethylbipyridyl, and 5-bromo-1,10-phenanthroline as ligands gave esr spectra for the $L_2Fe(NO)_2$ radical anion species very similar to those of the ligand radical-ion alone. These results parallel the situation reported in the octahedral and trigonal-bipyramidal $L_2M(CO)_4$ and $L_2Fe(CO)_3$ cases.[1] Reduction leads to only slight changes in most coupling constants.

It should be noted that again in both the radical-cation $FeL_2(NO)_2$ species and the radical-anion $FeL_2(NO)_2$ species no strong evidence was obtained for hf interaction of the unpaired electron with the nitrosyl groups.

Nmr Results. It is well demonstrated that the proton chemical shift in homocyclic aromatic molecules reflects quantitatively the π-electron density (and therefore also the charge distribution) on the carbon atom to which the proton is attached.[20] The change in chemical shift (referred to a suitable molecule, $\Delta\delta$, can be correlated to the excess charge, q, by the linear relationship[21] $\Delta\delta = -Kq$, where the constant K is usually taken to be 10.7 ppm per unit charge.[22]

While the measurement of excess charge by nmr methods on systems more complex than simple homocyclic aromatic hydrocarbons involves factors which are difficult to assess,[22,23] our purpose will be to offer largely qualitative indications of the relative magnitudes of paired and unpaired spin distribution in the pyridyl ring systems. This can be provided by a comparison of the unpaired electron distribution obtained from the esr hf coupling constants for the complex radical anion and the results from the evaluation of the observed nmr chemical shift differences between neutral molecules and their diamagnetic dianions in the above equation.

Whereas for homocyclic systems the usual procedure is to reference all chemical shifts to that of benzene, it will be preferable for the heterocyclic aromatic systems of the ligands under present study to reference the chemical shifts of the dianions to that of their neutral precursor. This procedure will offset the imprecisely known magnitude of the deshielding magnetic anisotropic effects of heteroatoms and other-than-proton ring substituents.[22,24,25] Since the contribution to the chemical shift from anisotropic effects has a $1/r^3$ dependence,[22] only those protons bonded to carbon atoms α to the heteroatom position will be appreciably affected.

The nmr data for the ligand di-2-pyridyl ketone, its $L_2Fe(NO)_2$ complex, and the complex dianion are presented in Table V. Neglecting the effects produced by the alteration in ring currents by the addition of electron density to the π-electron systems and the effects produced by the perturbing influence of the counterion,[26] the total change in chemical shift on formation

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(20) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1965, and references contained therein.

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(24) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(25) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

(26) This is the common practice in the utilization of the above equation. Ring diameters will not be appreciably affected by an increase in electron density, and although there is undoubtedly a decrease in the

Table V. Nmr Data for the Di-2-pyridyl Ketone Ligand and $Fe(NO)_2$ Complex

System	Chemical shift (τ) for position 3	4	5	6
Ligand only	2.15	2.62	2.23	1.47
Neutral complex	1.84	2.64	2.07	1.35
Complex dianion	2.05	3.12	2.57	1.60
$\Delta\delta$, ppm	+0.21	+0.48	+0.50	+0.25

of the complex dianion of +2.88 ppm reflects a total charge density at ring positions 3, 4, 5, and 6 of 0.135. To this must be added an approximation of the charge density contained in the ligand carbonyl group, at the ring nitrogen atoms, and at the 2-position ring carbon atom.

The ir results reported in the next section strongly suggest that the molecular orbital into which the two electrons are added on forming the complex dianion produces no alteration of the electron density at the carbonyl group. The contribution to the total charge density contained in the complexed ligand from the carbonyl group is, therefore, taken to be zero. The contribution from the ring nitrogen atoms may be approximated by the charge density at the nitrogen atom in pyridine by reference to molecular orbital calculations[27] which reflect well the observed pyridine chemical shift data for the β and γ positions, where heteroatom anisotropic influences are negligible. The estimate is then made that the excess charge density at the ring nitrogens will be about 0.05. A somewhat smaller contribution from the 2-position ring carbon atoms is anticipated and for the present purposes may be set at about 0.02. The total excess charge is estimated to be about 0.21. Since two electrons have been added, roughly 10% of the charge is found in the ligand π-electron system.

Comparison then can be made of this charge density to the unpaired spin density found by esr techniques in the radical anion.[28] The spin densities, ρ, may be evaluated from the observed hf coupling constants using the modification of the McConnell equation derived by Bolton[29] to reflect the higher order effects of charge in determining bond polarizabilities

$$A_H = Q\rho - K\rho^2$$

where Q is usually taken to be −27 G and K to be −12 G. When applied to the observed coupling constants at the 3 and 5 ring positions, the spin density combined for both positions is 0.13. The spin density for the ring nitrogen atoms may be assessed by a comparison of the nitrogen coupling constant observed for the 4,4′-bipyridyl anion and the associated calculated spin density. A spin density of 0.16 was calculated from a nitrogen coupling constant of 3.6 G.[30] By proportion, the coupling constant in the present system of 4.80 G represents a combined spin density at both nitrogen atoms of 0.42. The total *observable* spin density produced by the addition of one electron to the complex radical anion is 0.55. Additional, but undoubtedly large unobservable spin density on the carbonyl group and the ring atoms to which this group is attached, when added to the observable total, makes conclusive our argument that considerably more spin than charge density can be delocalized into the ligand π-electron system. Or, conversely, the $Fe(NO)_2$ moiety is an extremely efficient sink for withdrawing charge density from the ligand, but is relatively inefficient as a spin sink.

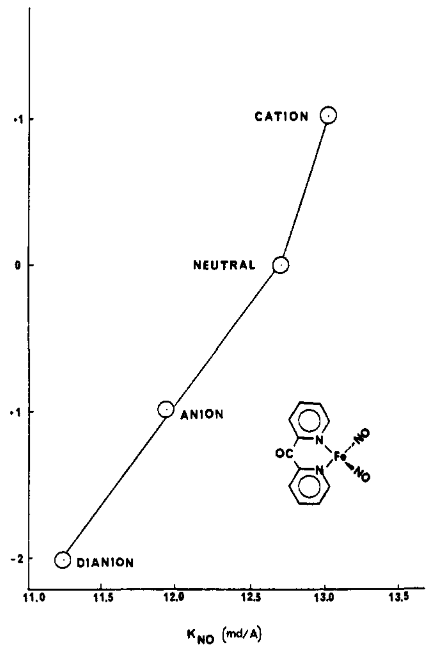

Figure 3.

Infrared Results. Being of tetrahedral geometry, the $FeL_2(NO)_2$ molecules belong to point group C_{2v} and one therefore predicts two infrared-active nitrosyl (nitrogen–oxygen) stretching frequencies, one A_1 mode and a B_1 mode. Since the nitrosyl groups in these molecules are terminal in nature (nonbridging), the two stretching absorptions should be observed in the 1600–1800-cm^{-1} region.[31] This is indeed the case, and the nitrosyl ν_{NO} frequencies for the neutral molecules in this study are given in Table VI. The secular equations necessary to calculate approximate nitrogen–oxygen force constants for tetrahedral $ML_2(XO)_2$ molecules have been given by Cotton.[32] Table VII lists the nitrosyl force constants calculated on this basis from the observed frequencies for the neutral compounds in this study. *Cf.* Figure 3.

Table VI. Nitrosyl Stretching Frequencies (±2 cm^{-1}) for Neutral $FeL_2(NO)_2$ Molecules

L_2	A_1	B_1
2CO	1847	1808
Di-2-pyridyl ketone	1704	1645
2,2′-Bipyridyl	1690	1635
1,10-Phenanthroline	1687	1630

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diamagnetic ring-current shielding, its relative effect is minor. Counter-ion effects in THF have been shown[22] to be at least an order of magnitude smaller than the shifts we report.

[27] R. McWeeny and T. E. Peacock, *Proc. Phys. Soc.* (*London*), *Sect. A*, **70**, 41 (1957).

[28] R. G. Lawler and C. V. Ristagno, *J. Amer. Chem. Soc.*, **91**, 1534 (1969).

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[31] G. R. Van Hecke and W. D. Horrocks, *Inorg. Chem.*, **5**, 1960 (1966).

[32] F. A. Cotton, *ibid.*, **3**, 702 (1964).

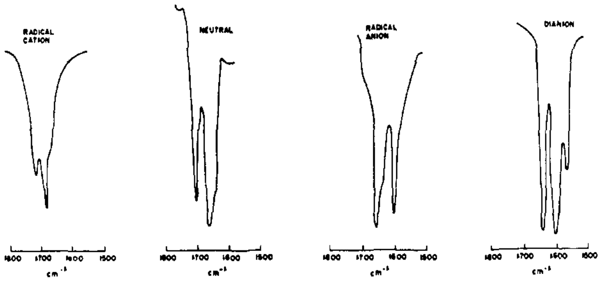

Figure 4. Infrared spectra of 2-10^{-2} M solutions of di-2-pyridyl ketone-$Fe(NO)_2$ radical cation, neutral, radical anion, and dianion species.

As in the case of the carbonyl ligand, the nitrosyl ligand should be quite sensitive to electron density in its antibonding orbitals as well as the nature of the M-NO bond. A perturbation in electron density in these regions should, then, be directly manifested in the nitrogen-oxygen force constants. Unlike the octahedral and trigonal-bipyramidal cases studied previously, the $FeL_2(NO)_2$ molecules contain but one type of XO group. This being the case, it seemed particularly attractive to employ an L_2 ligand having a functional group whose infrared properties were also sensitive to variation in electric charge density. The implementation of the di-2-pyridyl ketone ligand, having a keto carbonyl group, seemed well suited for this task. Therefore, this $FeL_2(NO)_2$ molecule was synthesized, where now the ligand serves as a "charge label" in tracking electron density in the molecule as the overall charge is varied.

Table VII. Nitrosyl Force Constants (mdyn/Å) for Neutral $FeL_2(NO)_2$ Molecules

L_2	k	k_1
2CO	13.02	0.23
Di-2-pyridyl ketone	12.69	0.45
2,2′-Bipyridyl	12.47	0.47
1,10-Phenanthroline	12.29	0.34

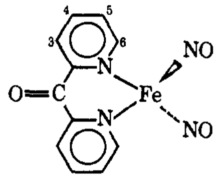

Figure 4 displays the infrared spectra observed in the 1500-1800-cm^{-1} region for the radical-cation, neutral, radical-anion, and dianion charged species. The nitrosyl stretching frequencies are given in Table VIII, while the corresponding force constants are shown in Table IX.

Table VIII. Nitrosyl Stretching Frequencies (±2 cm^{-1}) for Neutral, Radical Cation, Radical Anion, and Dianion of Di-2-pyridyl Ketone-Iron Dinitrosyl

Charge species	A_1	B_1
Radical cation	1715	1685
Neutral	1704	1645
Radical anion	1645	1605
Dianion	1605	1562

Table IX. Nitrosyl Force Constants for Neutral, Radical Cation, Radical Anion and Dianion of Di-2-pyridyl Ketone-Iron Dinitrosyl

Charge species	k, mdyn/Å	k_1, mdyn/Å
Radical cation	12.99	9.22
Neutral	12.69	0.45
Radical anion	11.91	0.31
Dianion	11.25	0.29

That the di-2-pyridyl ketone ligand serves adequately as a "charge label" is demonstrated by the marked change observed for the keto ν_{CO} frequency in going from the uncoordinated to coordinated system. Thus, while the ν_{CO} frequency for the uncoordinated ligand is 1681 cm^{-1}, removal of electron density from the iron atom into the di-2-pyridyl ketone ligand in the complex results in a lowering of this frequency to 1661 cm^{-1}.

Given the necessary condition that if either the A_1 or B_1 mode is affected by molecular charge variation the other must also be affected, the infrared data obtained may be interpreted on the following basis. Addition of either one or two electrons to the molecule results in a low frequency shift for the A_1 and B_1 ν_{NO} absorptions, while the ν_{CO} frequency remains unaltered (±4 cm^{-1}) at 1661 cm^{-1}. Thus, although the esr spectrum of the radical anion demonstrates high localization of *unpaired electron density* on the di-2-pyridyl ketone ligand, the excess charge introduced by one electron reduction is apparently distributed over the $Fe(NO)_2$ moiety.[33] Figure 3 shows the nitrosyl force constants for the charge states studied. The delocalization of excess charge results in an overall stabilized system, and, indeed, the radical anions of this series remained unchanged in sealed tubes indefinitely.

These results, in fact, corroborate those obtained through esr and nmr studies on this system and those obtained during the investigation of the charge distribution in the octahedral group VIb diacetylanil tetracarbonyls.[1] As in the present investigation, it was seen from esr and nmr studies on the neutral, radical-anion, and dianion species that excess charge (paired electron density) and unpaired electron density were quite different phenomena, and that although unpaired electron density resides in a molecular orbital of chiefly ligand character, excess charge is delocalized over the $M(CO)_4$ moiety.

Mössbauer Results. A general introduction to the ^{57}Fe Doppler-induced γ-ray resonance experiment was given in the original paper of this series.[1] The isomer shifts (IS) and quadrupole splittings (QS) for the $FeL_2(NO)_2$ neutral molecules along with several of their charged ions were measured, and the interpretation of these results is presented below.

The parent compound of this series, $Fe(CO)_2(NO)_2$, serves well as a point of departure for the discussion of the Mössbauer results. IS and QS values for the 2L = 2CO case along with the other members of this series in the neutral charge state are listed[35] in Table X.

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(33) A molecular orbital treatment of di-2-pyridyl ketone itself as a perturbed 1,1-diphenylethylene system[34] demonstrates that the lowest unoccupied molecular orbital of the neutral ligand is strongly antibonding and should lead to a strong shift to lower energy for the carbonyl stretching frequency when occupied.

(34) A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, Oxford, 1965.

(35) During the course of this work, another Mössbauer study of

Table X. IS and QS Values for Neutral $FeL_2(NO)_2$ Molecules[a]

L_2	IS, mm/sec	QS, mm/sec
2CO	0.337	0.329
Di-2-pyridyl ketone	0.482	0.542
2,2′-Biquinolyl	0.513	0.809
2,2′-Bipyridyl	0.520	0.724
1,10-Phenanthroline	0.556	0.740

[a] All values of IS and QS are relative to sodium nitroprusside. All measurements made at −196°. All values are ±0.005.

Classically, the bonding of nitric oxide to transition metals may be visualized as involving two concerted steps,[36] one the donation to metal d orbitals of the high-energy antibonding electron (IP 9.4 eV) and second the coordination to the metal *via* an sp lone pair on nitrogen. The $FeL_2(NO)_2$ molecules, therefore, approach a d^{10} electronic configuration for iron, and in line with this one would predict a relative decrease in QS and increase in IS when compared with iron systems having a lower d-electron population, all other factors being equal. The observed IS and QS values for the $Fe(CO)_2(NO)_2$ molecule confirm this prediction (see Table X). Because of its geometry and greater d-electron-withdrawing ability, the carbonyl ligand when compared to the other L_2 ligands of this study should form a molecule having, within this series, the lowest and most symmetrical iron d-electron population. That this is indeed the case is seen by comparing the values for the IS and QS in Table X. It is interesting to note that the nitrosyl force constant data given in Table IX also predict the same result (K_{NO} is highest when L_2 = 2CO).

Large-scale one-electron reductions and one-electron oxidations were performed on the L_2 = 2,2′-bipyridyl and di-2-pyridyl ketone derivatives, the resulting samples being subjected to Mössbauer analysis at −196°. Deconvolution of the spectra obtained gave the IS and QS values for the ionic species. Figure 5 displays, for example, the experimental and calculated spectra for the L_2 = 2,2′-bipyridyl radical anion. The IS and QS values for both derivatives and their ions are given in Table XI.

Table XI. IS and QS Values for Neutral, Radical-Cation, and Radical-Anion $FeL_2(NO)_2$ Molecules[a]

2L	IS, mm/sec	QS, mm/sec
2,2′-Bipyridyl		
Radical cation	0.64	0.66
Neutral	0.52	0.72
Radical anion	0.43	0.97
Di-2-pyridyl ketone		
Radical cation	0.53	0.74
Neutral	0.48	0.54
Radical anion	0.40	0.77

[a] All values of IS and QS are relative to sodium nitroprusside. All measurements made at −196°. All values are ±0.02.

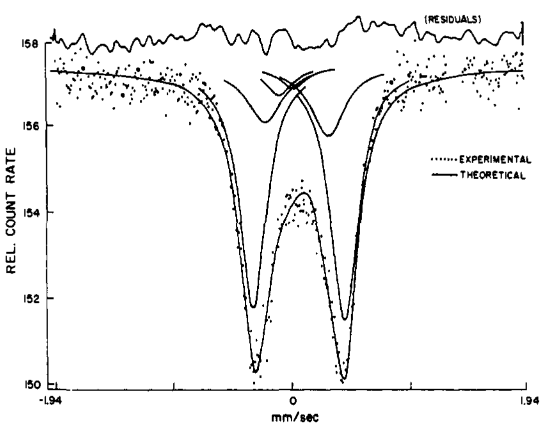

Figure 5. Mössbauer spectra of neutral and radical anions of 2,2-bipyridyl–$Fe(NO)_2$ showing experimental and calculated spectra and the differences between the two (residuals).

Oxidation to the radical cation, for both derivatives, yields a positive IS relative to the neutral molecules. As was previously mentioned, esr experiments on the radical cations of this series indicate high localization of unpaired electron density in a molecular orbital having a considerable contribution from a σ-type orbital. The positive IS observed on oxidation implies that the molecular electron removed during this process resided in a molecular orbital having a substantial contribution from an iron s-type orbital. The iron orbitals participating in σ bonding with the ligand are surely hybrid orbitals made up from iron s and p atomic orbitals (sp^3 hybrid orbitals). Removal of the electron from a largely ligand π orbital should only lead to a decrease in IS, as shielding around the iron is removed–contrary to the observations.

Table XI demonstrates the fact that one-electron reduction results in a negative IS for both derivatives. On the basis of esr experiments performed on the radical anions of $FeL_2(NO)_2$ series, it was concluded that the unpaired electron introduced by reduction resides in a molecular orbital highly ligand π* in character. Since a negative IS signals an increase in s-electron density at the iron nucleus, the Mössbauer experiments on the radical-anion species indicate a σ transmission of electric charge from the ligand to the iron atom.[1]

Upon oxidation and reduction significant changes in QS occur for both derivatives (Table XI). As was the case for the trigonal-bipyramidal geometry,[1] the changes in QS seem less well defined than those in IS. Thus, while both one-electron oxidation and one-electron reduction result in an increase in QS for the L_2 = di-2-pyridyl ketone derivative, only the latter process yields an increase in QS for the L_2 = 2,2′-bipyridyl derivative. At the present time it is not possible to explain this apparent anomaly. The experimental technique for observing QS values appears to be a decade in advance of the theory.

Acknowledgments. The authors wish to acknowledge the financial support of this research in terms of research grants from the Air Force Office of Scientific Research and the National Science Foundation.

$Fe(CO)_2(NO)_2$ was published. The values for IS and QS given in that publication were in close agreement with those obtained in these laboratories. See R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, **51**, 3220 (1969).

(36) B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 1 (1966).