Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

An X-ray Photoelectron Spectral Study of Iron and Cobalt Nitrosyl Complexes[1] of *o*-Phenylenebis(dimethylarsine)

PATRICK BRANT and ROBERT D. FELTHAM*[2]

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The N 1s, As 3d, and M 2p core binding energies have been obtained from the X-ray photoelectron spectra (XPS) of a series of iron and cobalt complexes of *o*-phenylenebis(dimethylarsine) (das). The As 3d binding energies of these $[MLL'(das)_2]^{m+}$ (L = L′ = Cl, Br, NCS; L = NO, L′ = Cl, Br, I, NCS; L = Cl, L′ = CO, CH_3CN) complexes are unaffected by the other ligands and are independent of *m*, indicating that the effects of the Madelung potential on the core binding energies are small. A linear relationship between ν_{NO} by the N 1s binding energies was also observed for the nitrosyl complexes.

Introduction

X-ray photoelectron spectroscopy (XPS) can provide direct information about the distribution of charge in complex molecules and in molecular fragments. Consequently, transition-metal complexes of a variety of small molecules including NO^+, N_2, ArN_2^+, CO, CN^-, and O_2 have been subjected to prior XPS investigations.[3-16] Complexes of NO have been of particular interest because the nitrosyl ligand exhibits diverse chemical and structural properties. Finn and Jolly[3] examined the N 1s binding energies of nitrosyl complexes and found a rough correlation between the geometry of the $\{MNO\}^n$ group[17] and ν_{NO}. Su and Faller,[11] who studied both the N 1s and O 1s binding energies of metal nitrosyls, reported finding a correlation of [O(1s)–N(1s)] with MNO geometry. Folkesson[10] has also studied the N 1s and O 1s binding energies of metal nitrosyl complexes. The agreement between the data for comparable compounds in these several reports was poor, however. Moreover, although many of the previously reported complexes were charged, the possible effects of the Madelung potential on the core binding energies were not assessed.

In undertaking the present investigation, a closely related series of complexes with variable charge *m* and well-known structural and electronic features was sought. The cobalt and iron complexes with *o*-phenylenebis(dimethylarsine) (das), $[MLL'(das)_2]^{m+}$ (L = L′ = Cl, Br, NCS; L = NO, L′ = Cl, Br, I, NCS; L = Cl, L′ = CO, CH_3CN), fit these criteria. The nitrosyl derivatives have the additional advantage that their MNO bond angles encompass nearly the full range of possible MNO geometries (180–132°). Consistent referencing of their core-binding energies to the C 1s level of the das ligand is an added experimental advantage afforded by these compounds. The N 1s, M 2p, and As 3d binding energies of these das complexes have been obtained and are the subject of this report.

Experimental Section

Materials. Except for *cis*-$[CoH_2(das)_2]ClO_4$, each of the compounds used in this study was available from other work in this laboratory. References to the preparative details, elemental analyses, and/or crystal structures of the compounds are listed in Table I.

cis-$[CoH_2(das)_2]ClO_4$ was prepared according to the method of Bosnich et al.[18] and was characterized by its color, melting point, and IR spectrum. At ambient temperature this complex decomposes within 3 or 4 h of preparation. Consequently, elemental analyses were not obtained, and the samples of $[CoH_2(das)_2]ClO_4$ were prepared and stored at 0 °C under N_2 prior to use. The XPS data for this complex were obtained within 2 days of its preparation.

XPS Spectra. The XPS data were obtained with a McPherson ESCA-36 photoelectron spectrometer calibrated as described elsewhere.[19] Both Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) radiation sources were used. Bremstrahlung was reduced with a beryllium window. Operating pressures were typically in the low 10^{-7} torr range. Many of the complexes examined were stable under ambient spectrometer conditions, but the dihydrido complex and several nitrosyl complexes were not. Consequently, data for these samples were obtained at −95 °C by using a cryogenic probe of our own design. Decomposition of nitrosyl complexes was readily detected by loss of the N 1s peak, by a shift in its binding energy, and/or by the appearance of extra or broadened M $2p_{3/2}$ peaks.

Samples were mounted on double-stick tape (3M) or were lightly pressed onto etched aluminum planchettes. The binding energies of core levels in all the das complexes were standardized by using a C 1s binding energy for das of 285.0 eV except for compounds **6**, **7**, and **8**. These complexes were isolated as tetraphenylborate salts. Consequently, the C 1s binding energy was taken as the weighted average (284.7 eV) of the C 1s binding energy of das (285.0 eV) and of BPh_4^- (284.5 eV).[20]

Each binding energy reported in Table I is the average of two to six separate measurements. Nitrosyl O 1s binding energies are not reported because of contaminant oxygen-containing compounds present on the surface of each sample. Without exception, the standard deviation of the binding energies for narrow peaks (FWHM < 2.0 eV) is ±0.2 eV. Broader peaks could be located to within ±0.3 eV. When two or more overlapping peaks were observed, the spectra were resolved with a Du Pont 310 curve resolver or the spectrum was simulated by using a curve generation subroutine in the program package provided by McPherson for the PDP 8e minicomputer. Relative peak areas were determined by the paper weighing method. The intensity of metal 2p satellites is defined as

$$I_{sat} = \frac{A_{sat}}{A_{sat} + A_{primary}} \qquad (1)$$

Results and Discussion

Arsenic 3d Binding Energies. The As 3d binding energy of compound **16** reported in Table I was obtained by using an external Au $4f_{7/2}$ standard (83.8 eV) and an internal C 1s standard (285.0 eV). This double standardization procedure

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Table I. XPS Data for *o*-Phenylenebis(dimethylarsine) Complexes

no.	compd	ν_{NO}, cm^{-1}	MNO angle, deg	$E_B(M\ 2p_{3/2})^a$	M $2p_{1/2}-2p_{3/2}$	$E_B(N\ 1s)^a$	$E_B(As\ 3d)^a$	ref
1	$Fe(NCS)_2(das)_2$			708.1 (1.4)^b	12.7	398.4 (1.7)^b	43.7 (2.1)^b	*i*
2	$Fe(NO_2)Cl(das)_2$			708.1 (1.6)	12.6	403.4 (2.0)	43.7 (2.3)	*i*
3	$FeCl_2(das)_2$			708.1 (1.5)	12.6		44.0 (2.0)	*j*
4	$CoBr_2(das)_2$			779.6 (2.0)	15.0		43.8 (2.1)	*k*
5	$[FeCl_2(das)_2][BF_4]$			709.1 (2.0)	12.7		43.9 (2.5)	*i*
6	$[FeCl(CH_3CN)(das)_2][BPh_4]$			708.1 (1.7)	12.7	400.1 (1.8)	43.7 (2.3)	*i*
7	$[FeCl(CO)(das)_2][BPh_4]$			710.0 (1.7)	12.5		43.8 (2.2)	*i*
8	$[Fe(NO)Cl(das)_2][BPh_4]$	1620	160	709.2 (1.9)	12.7	400.2 (1.6)^c	43.9 (2.3)	25, *i*
9	$[Fe(NO)I(das)_2][I]$	1620	160	708.7 (2.2)	12.7	399.7 (1.9)	43.5 (2.7)	26
10	$[CoCl_2(das)_2][ClO_4]$			781.0 (2.1)	14.9		43.5 (2.1)	*l*
11	$[Co(NO_2)Br(das)_2][Br\}$			781.0 (1.8)	15.0	404.2 (1.7)	43.9 (1.9)	*m*
12	$[CoH_2(das)_2][ClO_4]$			780.3 (2.0)	15.0		43.6 (2.3)	18
13	$[Co(NO)Cl(das)_2][ClO_4]$	1562, 1584	134	781.1 (2.2)	15.1	401.1 (1.9)^d	43.5 (2.2)	*m, n*
14	$[Co(NO)Br(das)_2][ClO_4]$	1540, 1545	130	780.8 (2.0)	14.8	401.3 (2.0)	43.6 (2.4)	*m, n*
15	$[Fe(NO)(das)_2][ClO_4]_2$	1760	168	709.9 (2.4)	12.7	402.1 (1.7)^e	44.5 (3.3)	25, *i*
16	$[Fe(NO)Cl(das)_2][BF_4]_2$	1883	180	710.3 (2.2)	12.8	403.2 (1.8)^f	43.8 (2.6)	*i*
17	$[Fe(NO)(NCS)(das)_2][ClO_4]_2$	1870	180	710.1 (2.2)	12.6	403.2 (1.5)^g 398.6 (1.8)^g	43.9 (2.4)	*i*
18	$[Fe(NO)I(das)_2][ClO_4]_2$	1835	180	709.9 (8.6)	12.6	402.5 (1.9)	44.3 (2.3)	*i*
19	$[Co(NO)(das)_2][ClO_4]_2$	1852	179	780.9 (2.3)	15.0	402.1 (1.5)^h	44.1 (2.2)	*m, n*

[a] Binding energies in eV. [b] Values in parentheses are FWHM. [c] 400.0 eV reported in ref 3. [d] 400.4 eV reported in ref 3. [e] 401.2, 399.6 eV reported in ref 3. [f] 402.9 eV reported in ref 3. [g] N 1s of NCS$^-$. [h] 402.3 eV reported in ref 3. [i] Nappier, T. E.; Feltham, R. D.; Enemark, J. H.; Kruse, A.; Cooke, M. *Inorg. Chem.* 1975, *14*, 806. [j] Lewis, J.; Nyholm, R. S.; Rodley, G. A. *J. Chem. Soc.* 1965, 1483. [k] Rodley, G. A.; Smith, P. W. *J. Chem. Soc. A* 1967, 1580. [l] Dunn, T. M.; Nyholm, R. S.; Yamada, S. *J. Chem. Soc.* 1962, 1564. [m] Feltham, R. D.; Nyholm, R. S. *Inorg. Chem.* 1965, *4*, 1334. [n] Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* 1975, *14*, 624.

gave the same value for As 3d and demonstrates that the C 1s binding energy of the das ligand is sufficiently insensitive to its crystal environment to be an acceptable internal standard. Consequently, each of the As 3d binding energies listed in Table I was standardized with C 1s of the das ligand.

The range of As 3d binding energies observed for these $[MLL'(das)_2]^{m+}$ complexes was only 0.8 eV (4σ) with an average value of 43.8 eV. The average As 3d binding energies are 43.72 (14), 43.70 (14), and 44.10 (22) eV, respectively, for $m = 0$, 1, and 2. The standard deviations of these averages are within the estimated errors for measurements of the individual binding energies (±0.2 eV). Thus, any change in As 3d binding energy of these $[MLL'(das)_2]^{m+}$ species with cationic charge, m, is of marginal significance and demonstrates that the effects of the Madelung potential are sufficiently small that they can be neglected for these complexes with $m = 0$, 1, or 2.

Nitrogen 1s Binding Energies. In contrast with the As 3d binding energies, the N 1s binding energies are sensitive to the electronic features of the $\{MNO\}^n$ group. The N 1s XPS data are summarized in Table I. Good agreement (1σ) was obtained between the values of N 1s and those reported earlier for **8** and **19**. However, the N 1s values for **13**, **15**, and **16** differ by more than 3σ from the previously reported values. Decomposition is the probable source of these discrepancies.

Finn and Jolly[3] reported an N 1s binding energy of 400.5 eV for *trans*-$[Co(NO)(das)_2Cl]Cl$, while Su and Faller[11] found *trans*-$[Co(NO)(das)_2Br]Br$ to have an N 1s binding energy of 404.9 eV. The discrepancy ($>3\sigma$) between the value reported in Table I for *trans*-$[Co(NO)(das)_2Cl]ClO_4$, **13**, and that reported by Finn and Jolly is not unusual since the data were obtained from different spectrometers. However, the discrepancy between the data for **13** (401.1 eV) and that reported by Su and Faller is outside instrumental error. The Co $2p_{3/2}$ and N 1s binding energies of *trans*-$[Co(NO)(das)_2Br]Br$ from the work of Su and Faller closely correspond to those of *trans*-$[Co(NO_2)(das)_2Br]Br$, **11**, a known product obtained from oxidation of the nitrosyl complex. Thus, sample oxidation is the probable source of this discrepancy.

The N 1s value, 402.1 eV for $[Fe(NO)(das)_2][ClO_4]_2$, **15**, also differs from the literature values (400.9 and 399.6 eV) by more than 3σ. Except for the large FWHM of the single Fe $2p_{3/2}$ peak (2.5 eV), no unusual features were observed in the spectrum of our sample. However, the presence of two peaks in the spectrum of **15** reported by Finn and Jolly strongly indicates sample decomposition, since the separation of these two peaks is too large to be attributed to multiplet splitting. Moreover, **15** decomposed under our ambient spectrometer conditions, and reasonable spectra could be obtained only at −95 °C with the cold probe. The spectra of three six-coordinate diamagnetic $\{FeNO\}^6$ complexes with the general formula, *trans*-$[Fe(NO)(das)_2X]^{2+}$ (X = Cl, **16**; NCS, **17**; I, **18**) range between 402.9 and 403.7 eV. The N 1s binding energy of *trans*-$[Fe(NO)(das)_2Cl][BF_4]_2$, **16**, is 0.8 eV higher than that reported previously, but the earlier investigators noted that their sample decomposed.

The range of N 1s binding energies found for the iron complexes makes the correlation with other physical properties possible. Finn and Jolly[3] have previously reported a very rough correlation between N 1s binding energies and ν_{NO}. The large scatter in their data is likely due to the variety of central metals and attendant ligands from which their data were drawn. The compounds comprising the present series provide a data set with fewer variables than that of Finn and Jolly. The relationship between the N 1s binding energies and ν_{NO} for the $\{FeNO\}^n$ complexes is shown in Figure 1. The data were subjected to least-squares linear fits which correspond to the equation

$$E_B(\text{N 1s}) = (0.013 \pm 0.001\ \text{eV/cm}^{-1})\langle\nu_{NO}\rangle + 379.8 \pm 2.5\ \text{eV} \quad (2)$$

with a correlation coefficient, r, of 0.98. This relationship is similar to that found by Jolly and co-workers[21] between *gas phase* O 1s binding energies and ν_{CO}.

$$E_B(\text{O 1s}) = (0.0146\ \text{eV/cm}^{-1})\langle\nu_{CO}\rangle + 510.0\ \text{eV} \quad (3)$$

Effects of the Unpaired Electron on the Spectra of $\{MNO\}^7$. Under normal circumstances, the M 2p spectra of paramagnetic first-row transition-metal complexes exhibit broad sat-

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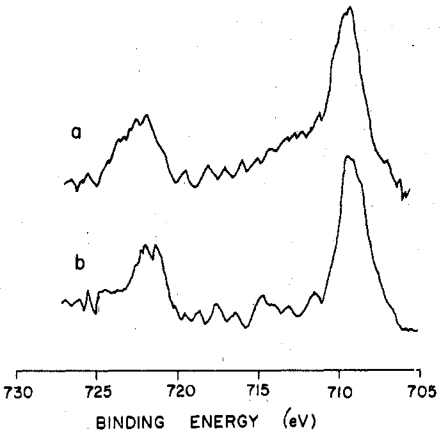

Figure 1. The Fe $2p_{3/2}$–$2p_{1/2}$ region of (a) *trans*-[$FeCl_2(das)_2$]BF_4 and (b) *trans*-[Fe(NO)Cl$(das)_2$]BPh_4.

ellites on the high binding energy side of each primary 2p peak with relative intensities of roughly 0.1–0.5.[22,23] These satellites are usually attributed to interactions with valence electrons. In addition, the M 2p peaks broaden and the separation between the spin–orbit components increases. Each of these changes is more striking the greater the unpaired spin density on the metal. In keeping with these general observations, satellites of modest intensities were found in the M 2p spectra of *trans*-[$FeCl_2(das)_2$]BF_4, **5** ($I_{sat} = 0.1$) (Figure 1), and *trans*-$CoBr_2(das)_2$, **4** ($I_{sat} = 0.1$), each of which has one unpaired electron. The M $2p_{3/2}$ peaks of **4** and **5** are broadened slightly (FWHM 2.0 eV) compared with the related diamagnetic complexes *trans*-$Fe(NCS)_2(das)_2$, **1**, *trans*-Fe$(NO_2)(das)_2$Cl, **2**, and *trans*-$FeCl_2(das)_2$, **3**. The separation of the M $2p_{1/2}$–$2p_{3/2}$ peaks of the paramagnetic complexes is the same as those of diamagnetic complexes.

Main-group compounds such as NO and NO_2 which contain unpaired electrons also exhibit strong satellites in the (1s) core-level spectra which are attributed to final-state multiplet splitting.[24] In the N 1s spectra the splitting of the two final states (singlet and triplet), to first approximation, is proportional to the valence electron spin state, *S*, and the degree of localization of the unpaired electron on the core ionized atom, as given in eq 4. For gaseous NO·, the singlet and triplet final

$$E = (2S + 1)\langle \rho_{ns}(\text{core})\rho(\text{valence})|\rho(\text{valence})\rho_{ns}(\text{core})\rangle \quad (4)$$

states which arise from N 1s ionization are separated by 1.4 eV[24] (relative intensity 1:2). Since the valence spin state, *S*, in both NO and the $\{MNO\}^7$ complexes is $^1/_2$, the splitting in the N 1s spectra of $\{MNO\}^7$ complexes may depend only on the degree of localization of the unpaired electron on the nitrogen atom. Thus, M 2p and N 1s satellites can provide additional information about the distribution of the unpaired electron in the $\{MNO\}^7$ moiety. Were the unpaired electron localized on the metal, M 2p satellites and a symmetric N 1s signal should be observed. On the other hand, localization of the electron on the nitrosyl group could produce satellites in the N 1s region. If the unpaired electron is highly delocalized, both M 2p and N 1s satellites may be weak or absent.

In the present study, three low-spin $\{FeNO\}^7$ complexes have been examined: *trans*-[Fe(NO)$(das)_2$Cl]BPh_4, **8**, *trans*-[Fe(NO)$(das)_2$I]I, **9**, and [Fe(NO)$(das)_2$]$(ClO_4)_2$, **15**. The N 1s spectra of each complex exhibit a single symmetric N 1s peak (FWHM 1.6–1.9 eV). Although no satellites were observed in the Fe 2p region for **8** (Figure 2), additional peaks of modest intensity (I_{sat} of ~0.2) were found in the Fe 2p spectrum of **9**. The general spectral features of **9** are similar to that of *trans*-[$FeCl_2(das)_2$]BF_4 (Figure 2) which also has $S = {}^1/_2$. The additional peaks in the Fe 2p spectrum of *trans*-[Fe(NO)$(das)_2$I]I are believed to be the result of partial sample decomposition, consistent with its increased reactivity compared with **8**. The spectrum of [Fe(NO)$(das)_2$]$(ClO_4)_2$, **15**, also exhibits extra peaks (I ~0.15) very near the $2p_{1/2}$ and $2p_{3/2}$ primary peaks. The shoulder in each of the components of the Fe 2p spectrum of **15** is separated from the primary peak by no more than 2.5 eV (curve resolution). Satellite separations of less than 3.5 eV have not been observed previously. Consequently, the shoulders in the Fe 2p spectrum of **15** may be due to sample decomposition, although the possibility that the extra peaks are satellites cannot be ruled out. Although the extra peaks in **9** and **15** are suspect, the data for *trans*-[Fe(NO)$(das)_2$Cl]BPh_4, **8**, are reliable. The absence of satellites in the Fe 2p and N 1s spectra of **8** suggest that the unpaired electron is delocalized over the FeNO moiety. These results are consistent with ESR, magnetic susceptibility, and Mössbauer data[25,26] which show the unpaired electron in these six-coordinate $\{FeNO\}^7$ complexes to reside in a component of the ^2E (d_{xz}, d_{yz}, $\pi_{NO}{}^*$) orbital set.

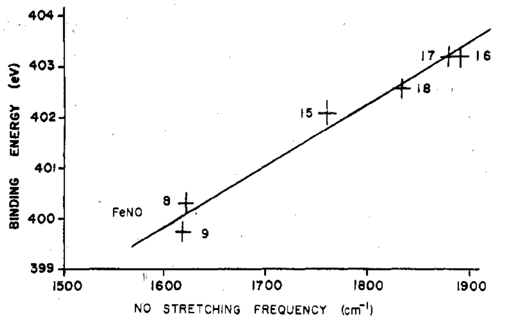

Figure 2. The relationship between ν_{NO} and N 1s for the [Fe(NO)$(das)_2$X]$^{m+}$ complexes.

Metal 2p Binding Energies. The metal $2p_{3/2}$ binding energies are listed in Table I and typical examples of the spectra are displayed in Figure 1. The M $2p_{3/2}$ binding energies are strongly dependent upon the chemical environment of the metal and consequently can be utilized for probing the electron density at the metal center.

The series of isostructural and isocharged complexes *trans*-[Fe(XY)$(das)_2$Cl]BPh_4 affords the opportunity of directly comparing the electron accepting/donating power of the XY ligands since changes in the relaxation energy and Madelung potential are minimal. The Fe $2p_{3/2}$ binding energy for XY = CH_3CN, **6**, CO, **7**, and NO^+, **16**, increases from 708.1 to 710.3 eV and spans the entire range of Fe $2p_{3/2}$ binding energies found for the compounds listed in Table I. If changes in the relaxation energy are neglected, the Fe $2p_{3/2}$ binding energies can be related by the simplified equation[27]

$$E_B(\text{Fe 2p}) = \sum_{\text{gr.}} \Delta E_{\text{gr.}} + l \quad (5)$$

where E_B (Fe 2p) is the observed binding energy, $\Delta E_{\text{gr.}}$ is the chemical shift of the attached group, and l is the binding energy of the bare central atom. The increasing Fe $2p_{3/2}$ binding energies of **6**, **7**, and **16** can then be taken as an indication of the relative electron density transfer upon the

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addition of the ligand to the parent ion, [Fe(das)$_2$Cl]$^+$. The sequence found[28] for these ligands, $CH_3CN < CO < NO^+$, corresponds to that normally accorded their π-acceptor properties.[29]

The effect of oxidation state on the Fe 2p$_{3/2}$ and Co 2p$_{3/2}$ binding energies can also be discerned. Comparison of *trans*-[FeCl$_2$(das)$_2$]$^{0,+}$ (**3** and **5**), *trans*-[Fe(NO)I(das)$_2$]$^{+,2+}$ (**9** and **18**), and *trans*-[Fe(NO)Cl(das)$_2$]$^{+,2+}$ (**8** and **16**) shows that the metal binding energies increase by 1.0, 1.2, and 1.1 eV, respectively. This increase in binding energy follows the relationship generally expected for an increase in oxidation state of the metal[30] and indicates that any effects of the Madelung potential are small. Finally, comparison of the iron binding energies of **15** with those of **9** and **8** provides the approximate values for ΔE_I and ΔE_{Cl} of −1.2 and −0.7 eV, respectively. The errors in these differences are rather large, but the general trends in the data of Table I indicate that the M 2p$_{3/2}$ binding energies of corresponding metal–halide complexes increase in the order $I^- < Br^- < Cl^-$.

Summary and Conclusions

The As 3d core binding energies of the complexes derived from the [MLL′(das)$_2$]$^{m+}$ moiety show that the effects of molecular charge on the core binding energies are small. Consequently, the shifts observed in the Fe 2p$_{3/2}$ and Co 2p$_{3/2}$ binding energies of *trans*-[Fe(XY)(das)$_2$Cl]$^{m+}$ and *trans*-[Co(XY)(das)$_2$Cl]$^{m+}$ reflect the electron-withdrawing ability of each ligand. A linear relationship was observed between ν_{NO} and the N 1s binding energy, but the core binding energies could not be directly related to the MNO geometry.

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Registry No. **1**, 53966-28-2; **2**, 53966-30-6; **3**, 14127-26-5; **4**, 60536-79-0; **5**, 37817-55-3; **6**, 53966-14-6; **7**, 53966-32-8; **8**, 53966-12-4; **9**, 47558-44-1; **10**, 17083-97-5; **11**, 73891-35-7; **12**, 54548-84-4; **13**, 67684-46-2; **14**, 66777-80-8; **15**, 54002-69-6; **16**, 73891-36-8; **17**, 73891-38-0; **18**, 64070-46-8; **19**, 53495-87-7.

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[28] Of course, the assignment of formal charges and oxidation states is arbitrary, but the total charge on the complex is not. Thus, since we wish to compare the properties of compounds **6**, **7**, and **16**, the XY ligands are assigned the formal charges 0, 0, and 1+, respectively. Had we chosen to compare compounds **6** and **7** with **8**, then the ligands would each have had formal charges of 0 leading to the most reasonable conclusion that NO$^+$ is a better π acceptor than NO!

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Contribution from the Chemistry Department,
Northeastern University, Boston, Massachusetts 02115

A Mössbauer Spectroscopy Study of Bis(acetylacetonato)iron(II): A Novel Example of Slow Paramagnetic Relaxation of High-Spin Iron(II) in Five- and Six-Coordination in Zero Field

CLAUDIO NICOLINI and WILLIAM MICHAEL REIFF*

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The temperature dependence of the zero-field ^{57}Fe Mössbauer spectrum of a powder sample of bis(acetylacetonato)iron(II), Fe(acac)$_2$, has been studied over the range 1.67–295 K. At 295 and 95 K, the Mössbauer spectrum consists of two highly overlapped quadrupole doublets reflecting the two iron sites present in this material. Between 16.0 and 1.67 K, the spectra display a hyperfine splitting gradually increasing with decreasing temperature. At 1.67 K, two fully resolved hyperfine patterns are observed. The ratio of the area of the hyperfine pattern is 1.0, and the calculated value for the hyperfine field, H_{hf}, at each ferrous site is ≃220 kG. *The large temperature interval over which hyperfine splitting occurs, low-temperature susceptibility data, and the isolated tetrameric structure of the compound clearly indicate that slow paramagnetic relaxation, rather than cooperative magnetic order, is responsible for the hyperfine splitting.*

Introduction

The phenomenon of intermolecular association leading to oligomer formation in complexes of divalent transition metals with the 2,4-pentanedionato ion[1] has stimulated much interest in these complexes, both in the solid state and in solution. Several X-ray diffraction studies have shown that bis(acetylacetonato) complexes of divalent transition metals, M(acac)$_2$ (M = Co,[2] Ni,[3] Zn[4]), are polymeric in the solid state with bridging oxygen atoms, resulting in higher coordination numbers of the metal ions. The analogous Cu and Cr complexes are monomeric and isomorphous.[5,6] In the latter compounds, the metal has a square-planar coordination. In addition, the C(3) atoms of the ligands of adjacent metal atoms interact weakly in the axial position. Recently, and almost simultaneously, the structure of Fe(acac)$_2$ has been reported by two different laboratories.[7,8] In one structural study,[7] Fe(acac)$_2$ was found to crystallize in the monoclinic form, space group $P2_1/c$, with *four dimeric* molecules in the unit cell. The cell dimensions are $a = 14.95$ (2) Å, $b = 8.51$ (1) Å, $c = 19.03$ (2) Å, and $\beta = 105.1$ (1)°. In the dimer the iron atoms are linked through three shared oxygen atoms (Figure 1). One iron atom (Fe(1)O$_6$ chromophore) is in a distorted, octahedral

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[1] Usually designated the acetylacetonato ion and abbreviated acac.

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