addition of the ligand to the parent ion, $[Fe(das)_2Cl]^+$. 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*-$[Fe(XY)(das)_2Cl]^{m+}$ and *trans*-$[Co(XY)(das)_2Cl]^{m+}$ 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!

[29] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; Chapter 22.

[30] Bakke, A. A.; Jolly, W. L.; Pinsky, B. L.; Smart, J. C. *Inorg. Chem.* **1979**, *18*, 1343.

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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

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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 $\simeq$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.

[2] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 4, 1145 (1965).

[3] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 4, 456 (1965).

[4] M. J. Bennett, F. A. Cotton, and R. Eiss, *Acta. Crystallogr., Sect. B*, **B24**, 904 (1968).

[5] Z. A. Starikova and E. A. Shugam, *Zh. Strukt. Khim.*, **10**, 290 (1969).

[6] F. A. Cotton, C. E. Rice, and G. W. Rice, *Inorg. Chim. Acta*, **24**, 231 (1977).

[7] S. Shibata, S. Onuma, A. Iwase, and H. Inoue, *Inorg. Chim. Acta*, **25**, 33 (1977).

[8] F. A. Cotton and G. W. Rice, *Nouv. J. Chim.*, **1**, 301 (1977).

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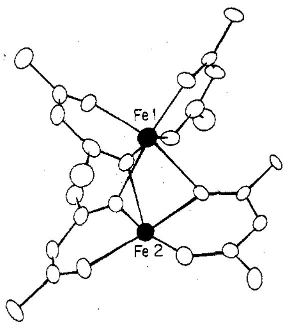

Figure 1. Schematic drawing of the dimeric representation of Fe(acac)$_2$ (based on ref 7).

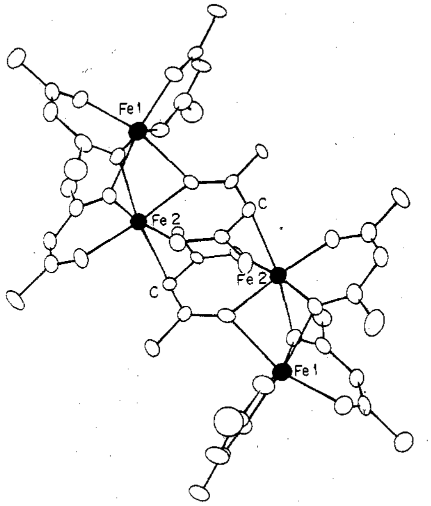

Figure 2. Schematic drawing of the tetrameric representation of Fe(acac)$_2$ (based on ref 8).

environment, and the second iron atom (Fe(2)O$_5$ chromophore) has a distorted square-pyramidal coordination. In a more refined structural study[8] ($R = 0.056$), similar cell constants, local bond distances, and angles were reported; however, the unit cell assumed ($P2_1/c$) consisted of two equivalent, *centrosymmetric* [*Fe*(*acac*)$_2$]$_4$ *tetramers.* Each tetramer chain is formed by two dimers linked through two rather long Fe(2)–C bonds (2.785 (9) Å). The sixth coordination sites of the Fe(2)O$_5$ chromophores are filled by C atoms of adjacent ligands which formally increases the coordination number of Fe(2) to 6, i.e., Fe(2)O$_5$C (Figure 2). The observed iron–carbon distance (2.785 Å) is shorter than the distances found for the Cr and Cu complexes (3.01 and 3.05 Å, respectively[5,6]). This appears to be the most strongly bonding interaction yet observed between a first-row transition metal and C(3) of 2,4-pentanedionate.[8] To see whether this Fe–C bond is electronically significant in the coordination environment of Fe(2), we have studied the temperature dependence of the Mössbauer spectrum of a powder sample of Fe(acac)$_2$ from 300 to 1.6 K. Moreover, in this study we have found that this material exhibits a novel slow paramagnetic relaxation between 16 and 1.67 K. The slow relaxation found in this compound and the presence of a relatively short metal–C(3) ligation are the subject of this study.

Experimental Section

Bis(acetylacetonato)iron(II) was prepared as described in the literature.[9] The synthesis and all manipulations of the product were carried out in oxygen-free atmospheres.

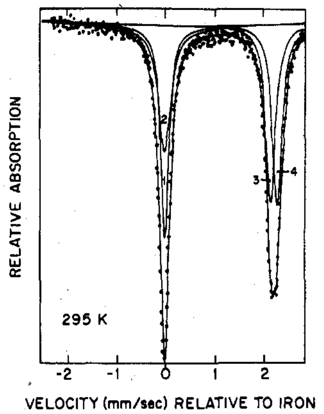

Figure 3. Mössbauer spectrum of Fe(acac)$_2$ at 295 K.

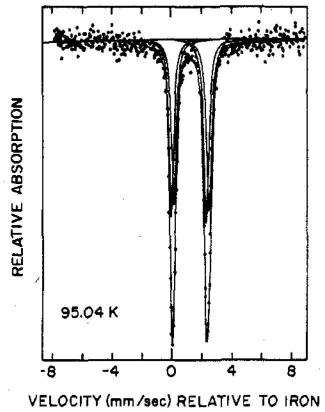

Figure 4. Mössbauer spectrum of Fe(acac)$_2$ at 95 K.

Table I. Mössbauer Spectral Parameters[a] of Bis(acetylacetonato)iron(II)

T, K	$\delta(1,4)^b$	$\delta(2,3)^b$	$\Delta E_{1,4}$	$\Delta E_{2,3}$
295	1.115	1.044	2.288	2.160
95	1.215	1.196	2.470	2.170

[a] In mm s^{-1}. [b] Relative to Fe metal.

The details of the techniques and apparatus used for zero-field Mössbauer spectroscopy and temperature control have been described previously.[10] Lorentzian fits to Mössbauer spectra were accomplished by using the program of Stone.[11] The thickness of the absorber used in the Mössbauer spectroscopy experiments was 10.0 mg/cm^2 of natural iron.

Results and Discussion

Figures 3 and 4 show the Mössbauer spectra of Fe(acac)$_2$ at 295 (7% absorption) and 95 K (12% absorption), respectively. At these two temperatures, the Mössbauer spectrum consists of two highly overlapped quadrupole doublets, reflecting the two iron sites present in this material. The ratio of the area of Fe(1) to the area of Fe(2) (A(Fe(1))/A(Fe(2))) is ~1.0 for both temperatures. Mössbauer parameters are given in Table I. It is well established that the magnitude of the high-spin iron(II) isomer shift, δ, increases with coordination number.[12] The δ values at room temperature ($\delta(1) = 1.115$ mm s^{-1} and $\delta(2) = 1.044$ mm s^{-1}) are consistent with six- and five-coordinate Fe(II).

At 295 K, it is observed that the intensity of line 2 (corresponding to the spectrum of the Fe(2) site) is asymmetric. This asymmetry is not present in the spectrum at 95 K, indicating that this intensity difference may be due in part to

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(9) D. A. Buckingham, R. C. Gorges, and J. T. Henry, *Aust. J. Chem.*, **20**, 281 (1967).

(10) W. M. Reiff and C. Cheng, *Inorg. Chem.*, **16**, 2097 (1977).

(11) G. M. Bancroft, A. G. Maddock, W. K. Ong, R. H. Prince, and A. J. Stone, *J. Chem. Soc. A*, 1966 (1967).

(12) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971.

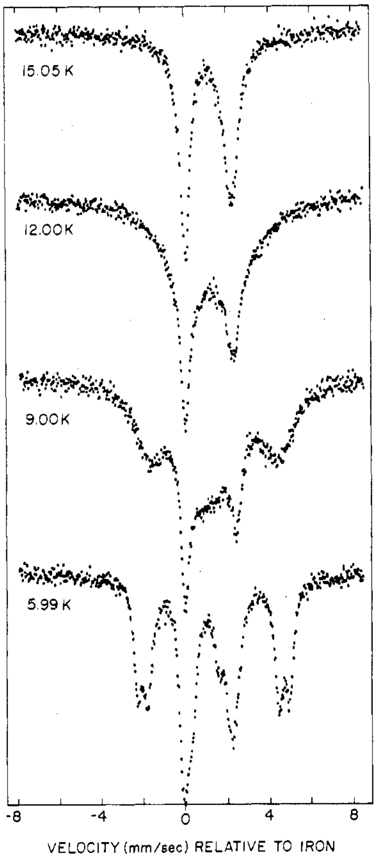

Figure 5. Temperature dependence of the Mössbauer spectrum of Fe(acac)$_2$ at 15.05, 12.00, 9.00, and 5.99 K.

a real anisotropy of the recoil-free fraction (Goldanski–Karyagin effect). It has been observed that the lattice dynamic anisotropy is especially prominent for strong intermolecularly bonded chain polymers and increases at higher temperatures.[13] The magnitude and temperature behavior depends upon the detailed geometry and intermolecular bonding in the solid. In the particular case of the Fe(acac)$_2$ oligomer, the Fe(2) local coordination consists of five oxygen–iron bonds and one Fe–C "bond". This interaction may very well be responsible for the asymmetry of the line intensity observed in the Mössbauer spectra at 295 K. Attempts to fit the 295 K spectrum with four lines, in which the areas are constrained equally, resulted in a divergent fit.

During the study of the temperature dependence of the Mössbauer spectrum of Fe(acac)$_2$, we found a hyperfine splitting gradually increasing with decreasing temperature between 16.0 and 1.67 K (Figure 5). At 1.67 K (13% absorption), one observes two fully split hyperfine patterns (Figure 6a). As can be seen, the hyperfine spectra are highly overlapped. However, the inequivalence of the iron sites in terms of slightly different hyperfine splitting is now clearly evident. We have obtained the "best" fit by assuming 14 Lorentzian lines (Figure 6b). This corresponds to seven γ-ray transitions per hyperfine pattern per iron atom, i.e., the observation of one of the normally forbidden pair of $\Delta m_I = \pm 2$ transitions for each ferrous ion present. This situation is not uncommon for high-spin iron(II) in an environment for which the electric field gradient tensor is nonaxial, i.e., $\eta \neq 0$. In this circumstance there is mixing of $|I, m_I\rangle$ states, specifically $|^3/_2, \pm^1/_2\rangle$ with $|^3/_2, \pm^3/_2\rangle$, and the $\Delta m_I = \pm 2$ transitions become "weakly" allowed. The crystallographic data indicate distortion and nonaxiality about each metal ion so that $\eta \neq$ 0 is likely. We point out that reasonable fits (vis-â-vis χ^2) of the low-temperature spectra were also obtained for overlapping eight transition spectra. However, the observation of both $\Delta m_I = \pm 2$ transitions is somewhat less common. In any event, these observations serve to point out that Lorentzian fits are by no means unique. From this point of view and because of the high degree of overlap of the spectra, i.e., difficulty in distinguishing which transitions correspond to Fe(1) and which to Fe(2), we make no attempt to theoretically model the spectra by using a spin Hamiltonian formalism to various relaxation times, τ. The ratio of the area of the hyperfine patterns is ~1, and the calculated value for the hyperfine field, H_{hf}, at each ferrous site is $H_{\text{hf}} \simeq 220$ kG. This H_{hf} value is reasonable for high-spin iron(II) with the Fermi contact contribution (~440 kG) reduced somewhat by an opposing orbital contribution (H_{L}) and to a lesser extent by an additional dipolar factor (H_{D}). *The large temperature interval over which hyperfine splitting occurs and the isolated tetrameric structure of the compound lead us to believe that slow paramagnetic relaxation, rather than cooperative (long-range) magnetic order, is responsible for the Zeeman splitting of the Mössbauer spectra below 16 K. Moreover, we have been informed*[14] *that the magnetic moment of Fe(acac)$_2$ approaches the expected spin-only value at 4.2 K and there is no evidence of cooperative three-dimensional magnetic ordering phenomena for temperatures as low as 4.2 K. Since we observe the hyperfine splitting well above 4.2 K, it seems clear that we are, in fact, observing slow paramagnetic relaxation.* However, weak *intra* dimer (tetramer) magnetic exchange is not ruled out. While slow paramagnetic relaxation for high-spin Fe^{2+} is not common,

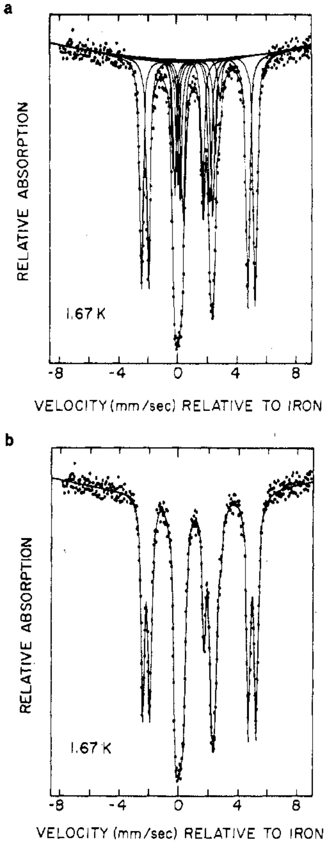

Figure 6. (a) Mössbauer spectrum of polycrystalline Fe(acac)$_2$ at 1.67 K (solid line through the data points represents a best fit to the sum of the 14 Lorentzian peaks indicated in Figure 6b). (b) Best fit of the Mössbauer spectrum of Fe(acac)$_2$ at 1.67 K, composite spectral fit only.

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[13] H. A. Stockler and H. Sano, *Chem. Phys. Lett.*, **2**, 448 (1968).

[14] A. K. Gregson and N. T. Moxon, private communication.

cases of slow relaxation in the presence of applied magnetic fields have been demonstrated for a number of distorted octahedral Fe(II) compounds.[15,16] More unusual is the observation of slow relaxation in zero magnetic field. In addition to this study that extends the examples of slow relaxation in zero magnetic field, we have recently reported a study of slow paramagnetic relaxation in the monomeric, pseudotetrahedral complexes Fe(2,9-(CH$_3$)$_2$-1,10-phen)(NCS)$_2$ and Fe(2,9-(CH$_3$)$_2$-4,7-Ph$_2$-1,10-phen)(NCS)$_2$.[17] It is hoped that further studies of the latter coordination systems will give a better understanding of the nature of slow paramagnetic relaxation for high-spin Fe^{2+}.

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Registry No. Fe(acac)$_2$, 14024-17-0.

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[15] D. C. Price, C. E. Johnson, and I. Maartense, *J. Phys. C*, **10**, 4843 (1977).
[16] C. Nicolini, J. Chappert, and J. P. Mathieu, *Inorg. Chem.*, **16**, 3112 (1977), and references therein.
[17] W. M. Reiff, C. Nicolini, and B. Dockum, *J. Phys. (Orsay, Fr.)*, **40**, C2–230 (1978).

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Single-Crystal EPR Studies on Nickel(III), Palladium(III), and Platinum(III) Dithiolene Chelates Containing the Ligands Isotrithionedithiolate, *o*-Xylenedithiolate, and Maleonitriledithiolate

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Single-crystal EPR studies of the tetra-*n*-butylammonium salts of bis(isotrithionedithiolato)nickelate(III), -palladate(III), and -platinate(III), bis(maleonitriledithiolato)nickelate(III), and bis(*o*-xylenedithiolato)nickelate(III) and -palladate(III), diamagnetically diluted in the corresponding Cu(III) or Au(III) complexes, are reported. Enrichment of the magnetic isotope of nickel (^{61}Ni) has been used in order to determine the nickel hyperfine tensor. Satellite lines due to hyperfine coupling of the electron spin with naturally abundant ^{33}S were observed in the spectra of most of the chelates studied. The ^{33}S hyperfine structure data support a b_{2g} ground state in which the half-filled out-of-plane π molecular orbital is extensively delocalized over the ligands. The spin-Hamiltonian parameters of the bis(maleonitriledithiolato)nickelate(III) monoanion have been calculated from the results of extended Hückel molecular orbital calculations. These calculations confirm the b_{2g} ground state but difficulties arise in the explanation of the full set of the experimentally obtained EPR parameters. Several general conclusions concerning the EPR parameters and the metal–ligand bonds of the d^7 low-spin chelates studied have been derived from the experimental data. The electron spin–lattice relaxation was studied for the bis(maleonitriledithiolato)nickelate(III) monoanion in the temperature range $1.5 \leq T \leq 20$ K. Spin–lattice interactions were found to be mainly responsible for the small line widths observed in the spectra. The synthesis of the tetra-*n*-butylammonium salts of the new chelates bis(isotrithionedithiolato)nickelate(III), -palladate(III), -platinate(III), and -aurate(III) is reported.

Introduction

Dithiolene ligands are known to form transition-metal complexes in which unusual oxidation states of the metal ions are stabilized.[1–5] During the last years single-crystal EPR studies were made on the dithiolene chelates $[Ni(mnt)_2]^-$,[6,7] $[Rh(mnt)_2]^{2-}$,[6] and $[Au(mnt)_2]^{2-}$[8–10] (mnt = maleonitriledithiolate) which contain the metals in the oxidation states Ni(III), Rh(II), and Au(II), respectively. Recently we reported the single-crystal EPR spectra for $[Pd(mnt)_2]^-$[11] and $[Pt(mnt)_2]^-$.[12] Some other dithiolene chelates containing three-valent nickel, palladium, or platinum were studied by means of EPR in liquid or frozen solutions only.[13–18] The unusually small line widths observed in the single-crystal EPR

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[1] J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
[2] (a) G. N. Schrauzer, *Transition Met. Chem.*, **4**, 299 (1968); (b) G. N. Schrauzer, *Acc. Chem. Res.*, **2**, 72 (1969).
[3] E. Hoyer, W. Dietzsch, and W. Schroth, *Z. Chem.*, **11**, 41 (1971).
[4] W. E. Geiger, Jr., C. S. Allen, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **16**, 2003 (1977).
[5] R. Kirmse, J. Stach, and W. Dietzsch, *Inorg. Chim. Acta*, **29**, L 181 (1978).
[6] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
[7] R. D. Schmitt and A. H. Maki, *J. Am. Chem. Soc.*, **90**, 2288 (1968).
[8] J. G. M. van Rens and E. de Boer, *Mol. Phys.*, **19**, 745 (1970).
[9] R. L. Schlupp and A. H. Maki, *Inorg. Chem.*, **13**, 44 (1974).
[10] J. G. M. van Rens, M. P. A. Viegers, and E. de Boer, *Chem. Phys. Lett.*, **28**, 104 (1974).
[11] R. Kirmse and W. Dietzsch, *J. Inorg. Nucl. Chem.*, **38**, 255 (1976).
[12] R. Kirmse, W. Dietzsch, and B. V. Solovev, *J. Inorg. Nucl. Chem.*, **39**, 1157 (1977).
[13] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).
[14] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).
[15] E. Billig, S. I. Shupack, J. H. Waters, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 926 (1964).
[16] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).
[17] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).
[18] A. V. Ryshmanova and N. S. Garif'yanov, *Zh. Neorg. Khim.*, **15**, 3095 (1970).

0020-1669/80/1319-2679$01.00/0