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Rapid Electronic Relaxation between $S = 3/2$ and $S = 1/2$ States in (N,N' -*o*-Phenylenebis(salicylideneaminato))nitrosyliron, [Fe(salphen)NO]

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Detailed studies of the ^{57}Fe Mössbauer effect between 82.3 and 300.1 K have been employed to confirm the spin transition between the low-spin ($S = 1/2$) and intermediate-spin ($S = 3/2$) states in [Fe(salphen)NO] (salphenH₂ = N,N' -*o*-phenylenebis(salicylideneamine)). The spectra show that the transition is centered at $T_c \approx 181$ K, the electronic relaxation between the two spin states being rapid with $\tau \lesssim 1 \times 10^{-8}$ s. A linear dependence between the quadrupole splitting ΔE_Q and μ_{eff}^2 demonstrates that the V_{zz} components of the EFG tensors of the two spin states are parallel and are of equal sign. The behavior of the Mössbauer absorption area in the region of T_c indicates that marked changes of unit cell dimensions or molecular parameters or both are associated with the transition.

Spin-state transitions between $S = 3/2$ and $S = 1/2$ states in iron mononitrosyl complexes were observed for the first time by Earnshaw et al.¹ on the basis of magnetic susceptibility measurements and infrared spectra. Subsequently, the transition in [Fe(salen)NO] where salenH₂ = N,N' -ethylenebis(salicylideneamine) was studied in considerable detail.² The transition is of the discontinuous type, the transition temperature having been reported as $T_c = 175$ K. Hysteresis effects, which were observed both in magnetism¹ as well as in the absorption area of the Mössbauer effect,² indicate that the transition is thermodynamically first order. In the Mössbauer effect, individual spectra corresponding to the $S = 3/2$ and $S = 1/2$ states are observed. These spectra replace each other in the region of T_c as the transition progresses in either direction of the temperature variation. Accordingly, the transition is slow on the Mössbauer effect time scale; i.e., the relaxation time for the change between the two spin states is slower than 1×10^{-7} s. The structure of [Fe(salen)NO] was determined³ at both 296 and 98 K, i.e. in the practically pure $S = 3/2$ and $S = 1/2$ states. The space group is orthorhombic $Pna2_1$ with $Z = 4$ at both temperatures. The crystal structures are essentially similar with square-pyramidal coordination about the Fe atom, the NO group being in the axial position. At the molecular level, moderate changes of bond distances and angles are observed due to the transition. Thus the average distance between the Fe atom and the N atoms of the salen ligand decreases from 2.075 Å at 296 K to 1.974 Å at 98 K, i.e. by about 0.10 Å. The distance from the Fe atom to the mean plane of the coordinating N and O atoms of the salen ligand decreases also by ~ 0.10 Å from 0.47 to 0.36 Å, and the Fe-N-O bond angle decreases from 147° above the transition to 127° below the transition. Moreover, a closer approach to coplanarity of the salicylideneaminato moieties of the salen ligand is observed in the 98 K structure. As a consequence of these modifications, the unit cell volume changes from $V = 1576.4$ Å³ at 296 K to 1513.0 Å³ at 98 K.

The [Fe(salphen)NO] complex, where salphenH₂ = N,N' -*o*-phenylenebis(salicylideneamine) shows a similar spin-state transition between $S = 3/2$ and $S = 1/2$ states.⁴ On the basis of magnetic susceptibility measurements, the transition appeared to be of the continuous type. Mössbauer effect measurements performed at 300 and 77 K showed values of quadrupole splitting ΔE_Q and isomer shift δ^{IS} rather similar to the values observed for the salen complex.

The present investigation has been initiated in order to characterize the spin-state transition in [Fe(salphen)NO] more thoroughly. The study is a contribution within our program to define the physical nature and the mechanism of spin-state transitions in more detail.^{5,6}

Experimental Section

Compound Preparation. Samples of [Fe(salphen)NO] were prepared as described previously.⁴ Ascorbic acid has been used in the preparative procedure to prevent contamination with the oxo-bridged iron(III) complex. The purity of the samples was checked by chemical analysis as well as by magnetic and Mössbauer effect measurements. Anal. Calcd for [Fe(salphen)NO], C₂₀H₁₄N₃O₃Fe: C, 60.03; H, 3.53; N, 10.50; Fe, 13.95. Found: C, 60.04; H, 3.75; N, 10.01.

Physical Measurements. The ^{57}Fe Mössbauer spectra were measured with a spectrometer consisting of a constant-acceleration electromechanical drive and a Nuclear Data ND 2400 multichannel analyzer operating in the multiscaling mode. The source used consisted of 50-mCi ^{57}Co in rhodium at room temperature, the calibration being effected with a 25- μm iron foil absorber. All velocity scales and isomer shifts are referred to the iron standard at 298 K. For conversion to the sodium nitroprusside scale, add +0.257 mm s⁻¹. Variable-temperature measurements between 80 and 300 K were performed by using a custom-made cryostat, the temperature being monitored by means of a calibrated iron vs. constantan thermocouple and a cryogenic temperature controller (Thor Cryogenics Model E 3010-II). The Mössbauer spectra were least-squares fitted to Lorentzian line shapes, and the areas were corrected for the nonresonant background of the γ -rays.

Measurements of X-ray powder diffraction at variable temperatures were obtained with a Siemens counter diffractometer equipped with an Oxford Instruments CF 108A flow cryostat and liquid nitrogen as coolant.

Results

The ^{57}Fe Mössbauer effect for the complex [Fe(salphen)NO] has been measured between 82.3 and 300.1 K, the results being collected in Table I. In addition, Mössbauer spectra at 82.3, 180.0, 190.3, and 300.1 K are illustrated in Figure 1. The detailed temperature dependence of the quadrupole splitting ΔE_Q and the isomer shift δ^{IS} is plotted in Figure 2. The measurements have been performed for increasing as well as for decreasing temperatures, the results displayed in the figure showing that no hysteresis effects are encountered. Figure 3 presents the temperature dependence of the line width Γ and the total area A from the Mössbauer spectra of the compound.

Discussion

From Figure 1 it is seen that all the measured ^{57}Fe Mössbauer spectra for the [Fe(salphen)NO] complex show a unique doublet that collapses into a broad single line at the highest temperatures, e.g. 300.1 K. The quadrupole doublet that appears at 82.3 K is assigned to an $S = 1/2$ state of iron, evidence for this being the

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- Earnshaw, A.; King, E. A.; Larkworthy, L. F. *J. Chem. Soc. A* **1969**, 2459.
- Wells, F. V.; McCann, W.; Wickman, H. H.; Kessel, S. L.; Hendrickson, D. N.; Feltham, R. D. *Inorg. Chem.* **1982**, *21*, 2306.
- Haller, K. J.; Johnson, P. L.; Feltham, R. D.; Enemark, J. H.; Ferraro, J. R.; Basile, L. J. *Inorg. Chim. Acta* **1979**, *33*, 119.
- Fitzsimmons, B. W.; Larkworthy, L. F.; Rogers, K. A. *Inorg. Chim. Acta* **1980**, *44*, L53.
- König, E.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219.
- König, E. *Prog. Inorg. Chem.* **1987**, *35*, in press.

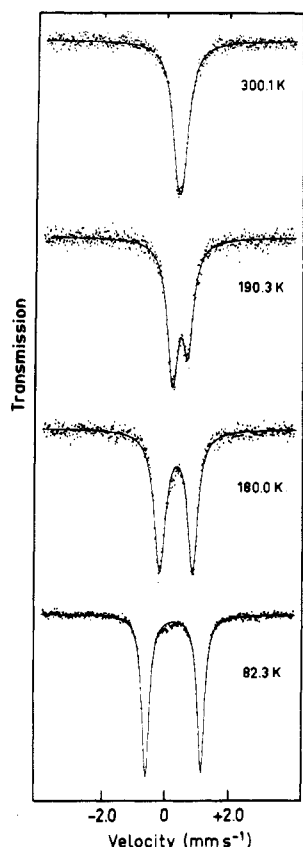


Figure 1. ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{salphen})\text{NO}]$ at 82.3, 180.0, 190.3 and 300.1 K. The full lines correspond to a least-squares fit to Lorentzian line shape.

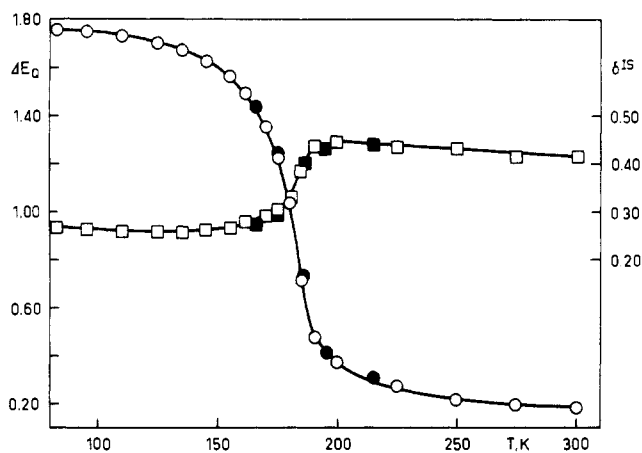


Figure 2. Quadrupole splitting ΔE_Q (○ and ●, left-hand scale) and isomer shift $\delta^{1\text{S}}$ (□ and ■, right-hand scale) of $[\text{Fe}(\text{salphen})\text{NO}]$ as a function of temperature. Open signs correspond to decreasing temperature; solid signs correspond to increasing temperature.

isomer shift value $\delta^{1\text{S}} = +0.265 \text{ mm s}^{-1}$, particularly if taken in conjunction with the magnetic data (viz, $\mu_{\text{eff}} = 1.80 \mu_{\text{B}}$ at 87.8 K⁴). On the other hand, the value $\delta^{1\text{S}} = +0.416 \text{ mm s}^{-1}$ for the unresolved Mössbauer doublet at 300.1 K is consistent with an $S = 3/2$ state of iron,⁷ which is suggested by the measured magnetic data (viz, $\mu_{\text{eff}} = 3.65 \mu_{\text{B}}$ at 294.8 K⁴). In the temperature range studied, the compound is therefore involved in a spin-state transition between $S = 3/2$ and $S = 1/2$ states. One might expect to find a superposition of the separate quadrupole doublets of the two spin states in the intermediate range of temperature; however, only one quadrupole doublet is observed. This phenomenon is

Table I. ^{57}Fe Mössbauer Effect Data for $[\text{Fe}(\text{salphen})\text{NO}]^a$

T, K	$\Delta E_Q,^b$ mm s^{-1}	$\delta^{1\text{S}},^c$ mm s^{-1}	A^d
300.1	0.182	+0.416	0.23
274.7	0.194	+0.415	0.27
250.0	0.217	+0.433	0.30
224.9	0.260	+0.413	0.33
199.7	0.376	+0.447	0.35
190.3	0.480	+0.434	0.37
184.8	0.716	+0.386	0.44
180.0	1.040	+0.333	0.55
175.2	1.227	+0.306	0.63
170.0	1.355	+0.291	0.71
161.4	1.495	+0.279	0.80
155.1	1.565	+0.266	0.88
145.2	1.629	+0.263	0.96
135.0	1.676	+0.259	1.04
124.8	1.705	+0.259	1.12
110.2	1.733	+0.260	1.18
95.0	1.751	+0.264	1.28
82.3	1.756	+0.265	1.38
165.8*	1.441	+0.278	0.76
175.0*	1.244	+0.306	0.63
185.3*	0.735	+0.401	0.44
194.9*	0.412	+0.436	0.35
215.1*	0.313	+0.444	0.33

^aData are listed in the order of measurement. Those for increasing temperatures are marked with an asterisk in the T column. For temperatures of 199.7 K and higher, line positions and line widths are strongly correlated. ^bExperimental uncertainty $\pm 0.005 \text{ mm s}^{-1}$. ^cRelative to metallic iron at 298 K. Experimental uncertainty $\pm 0.005 \text{ mm s}^{-1}$. ^dThe total area is defined as $A = 2(A_{\text{meas}} - A_{\text{impurity}})/(\pi f_{\text{S}} \Gamma_0)$ where f_{S} is the Debye-Waller factor of the source and Γ_0 is the natural line width. Experimental uncertainty ± 0.02 .

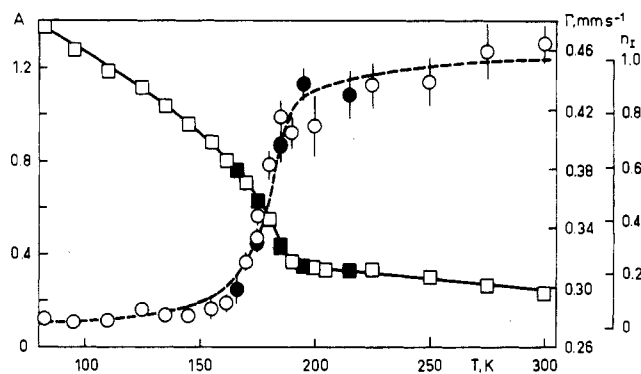


Figure 3. Line width Γ (mm s^{-1} ; ○ and ●, right-hand innermost scale) and total area of the Mössbauer spectrum A (□ and ■, left-hand scale) as functions of temperature. Open signs correspond to decreasing temperature; solid signs correspond to increasing temperature. The dashed curve represents the intermediate-spin $S = 3/2$ fraction n_I , cf. eq. 1 (right-hand outermost scale). The values of A have been corrected for the contribution of an unidentified impurity. The experimental uncertainty of Γ is indicated for the individual points, that of A is ± 0.02 .

encountered if the relaxation from the $S = 1/2$ to the $S = 3/2$ state and vice versa is rapid as compared to the time scale of Mössbauer spectroscopy ($\tau \lesssim 1 \times 10^{-8} \text{ s}$). The nucleus thus "sees" only the average of the ΔE_Q and $\delta^{1\text{S}}$ values characteristic of the two spin states. It should be noted that the fractions n_I and n_L of the intermediate-spin ($S = 3/2$) and low-spin ($S = 1/2$) states, respectively, which will be used below, should in fact represent the probability of the system to be found in the corresponding state.

Detailed calculations of Mössbauer spectra for various relaxation times have been recently performed by Maeda and Takashima⁸ on the basis of a stochastic model. In order to compare the present results with this type of calculations, the dependence of the quadrupole splitting ΔE_Q on the intermediate-spin fraction

(7) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971.

(8) Maeda Y.; Takashima, Y. *Mem. Fac. Sci. Kyushu Univ., Ser. C* **1983**, 14, 107.

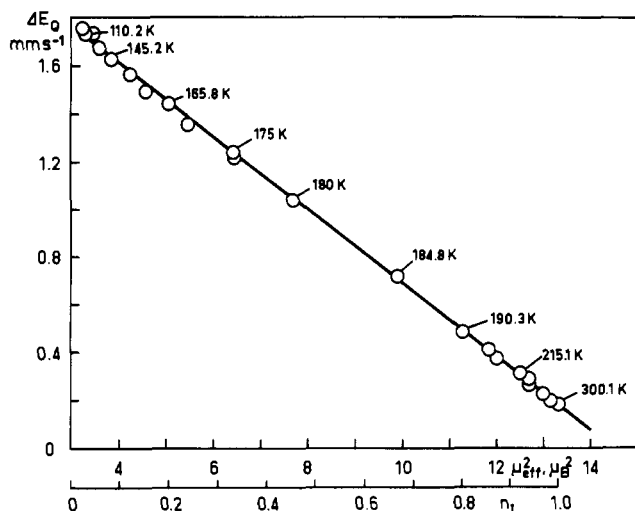


Figure 4. Quadrupole splitting ΔE_Q (mm s^{-1}) as a function of the effective magnetic moment squared μ_{eff}^2 (μ_B^2). For the scale of the intermediate-spin ($S = 3/2$) fraction n_1 on the abscissa, refer to the text.

n_1 is required. The fraction n_1 can be calculated from the measured values of the effective magnetic moment μ_{eff} according to

$$n_1 = \frac{\mu_{\text{eff}}^2 - \mu_L^2}{\mu_1^2 - \mu_L^2} \quad (1)$$

In eq 1, we have assumed, for the effective magnetic moments of the spin states involved, the values $\mu_L = \mu(S = 1/2) = 3^{1/2} = 1.73 \mu_B$ (spin-only value) and $\mu_1 = \mu(S = 3/2) = 3.65 \mu_B$. These assumptions seem to be reasonable, since the measured values are $\mu_{\text{eff}} = 1.80 \mu_B$ at 87.8 K and $3.65 \mu_B$ at 294.8 K. Here the effective magnetic moment values of the pure compound have been utilized.⁴ Moreover, the magnetic moment where the fraction of the $S = 3/2$ state assumes the value $n_1 = 0.50$ obtains as $\mu_{\text{eff}} = 8.2^{1/2} \mu_B$, and this value corresponds to the virtual transition temperature $T_c \approx 180$ K in good agreement with the results of Mössbauer effect measurements (see below).

The quadrupole splitting ΔE_Q appears to parallel the increase of the measured values of μ_{eff}^2 in the transition region. This is demonstrated in Figure 4 where ΔE_Q is plotted as a function of μ_{eff}^2 . Evidently, the observed quadrupole splitting ΔE_Q is a linear function of μ_{eff}^2 over the complete transition region where ΔE_Q is well represented by

$$(\Delta E_Q)_{\text{meas}} = 2.227 (\text{mm s}^{-1}) - 0.154 (\text{mm s}^{-1}/\mu_B^2) \mu_{\text{eff}}^2 \quad (2)$$

where the relative error of the coefficients as given by the numerical fit is $\pm 5 \times 10^{-3}$. According to the results of Maeda and Takashima,⁸ this behavior is expected on condition that (i) the relaxation between the states $S = 1/2$ and $S = 3/2$ is rapid and (ii) the maximum components V_{zz} of the EFG tensors of the $S = 1/2$ and $S = 3/2$ states are parallel and of equal sign. This is, in fact, the most simple case where the observed value ΔE_Q is the weighted average of the ΔE_Q values of the two spin states and can thus be written as

$$\overline{\Delta E_Q} = n_1 \Delta E_Q^1 + (1 - n_1) \Delta E_Q^L = \Delta E_Q^L - n_1 (\Delta E_Q^L - \Delta E_Q^1) \quad (3)$$

Employing eq 1 for n_1 , one immediately obtains

$$\overline{\Delta E_Q} = \left[\Delta E_Q^L + \frac{\Delta E_Q^L - \Delta E_Q^1}{\mu_1^2 - \mu_L^2} \mu_L^2 \right] - \frac{\Delta E_Q^L - \Delta E_Q^1}{\mu_1^2 - \mu_L^2} \mu_{\text{eff}}^2 \quad (4)$$

in the range $\mu_L^2 \leq \mu_{\text{eff}}^2 \leq \mu_1^2$. If ΔE_Q^L and ΔE_Q^1 are independent of temperature over the complete transition region, eq 4 represents exactly the observed behavior. This result demonstrates that the V_{zz} components are indeed parallel and of equal sign. Moreover, from eq 2 and 4 one obtains the temperature-independent values $\Delta E_Q^L = 1.765 \text{ mm s}^{-1}$ and $\Delta E_Q^1 = 0.175 \text{ mm s}^{-1}$. These values

may be compared with the measured values of the quadrupole splitting at the two limiting temperatures, viz. $\Delta E_Q = 0.182 \text{ mm s}^{-1}$ at 300.1 K and $\Delta E_Q = 1.756 \text{ mm s}^{-1}$ at 82.3 K. The center of the change of ΔE_Q provides an estimate for the transition temperature $T_c \approx 181$ K, viz. Figure 2, which value is consistent with the value of T_c obtained on the basis of magnetic data.

The temperature dependence of the isomer shift exhibits no unusual behavior apart from the region of the spin-state transition. It is reasonable to expect, for spin-invariant complexes, that the isomer shift should increase with decreasing temperature, thus reflecting the temperature dependence of the second-order Doppler shift. This is indeed observed in the temperature range below ~ 130 K for the $S = 1/2$ state and above ~ 200 K for the $S = 3/2$ state; cf. Figure 2. In the intermediate region, the δ^{IS} values for the $S = 1/2$ and $S = 3/2$ states experience a continuous transformation into each other due to the spin-state transition. From the mean value of the isomer shift in this interval, the transition temperature is again estimated as $T_c \approx 181$ K.

The line widths (Γ) for the two Mössbauer lines of the practically pure $S = 1/2$ state at low temperatures are close to 0.280 mm s^{-1} and almost identical; similarly, for the pure $S = 3/2$ state at high temperatures, values of Γ close to 0.46 mm s^{-1} are obtained. The temperature dependence of Γ in the transition region is displayed in Figure 3 and corresponds closely to the behavior of the intermediate ($S = 3/2$) spin fraction, n_1 . The apparent asymmetry of the 190.3 K spectrum in Figure 1 is not due to relaxation effects as one could assume but is rather caused by a small amount of impurity. This impurity contributes at low temperature $\sim 4\%$ to the total area, its relative amount increasing at higher temperatures due to the rapid decrease of the total area, which is likewise displayed in Figure 3. In addition, the position of the impurity line at about 190 K coincides with the low-velocity line of the compound, thus producing the observed asymmetric total spectrum. The values of Γ shown in Figure 3 have been obtained by a numerical fit of the Mössbauer spectra taking account of the mentioned impurity. Different line widths for the pure $S = 1/2$ and $S = 3/2$ states have been also encountered in the slowly relaxing compound [Fe(salen)NO].²

The temperature dependence of the total area A of the Mössbauer lines displayed in Figure 3 shows that the recoil-free fraction f decreases considerably on transition from the $S = 1/2$ to the $S = 3/2$ state. This is in close correspondence to the findings for [Fe(salen)NO].² The behavior of A in the region of T_c indicates that some kind of modification of the lattice accompanies the change of spin state. On the basis of the analysis of multi-temperature structure data for spin transition compounds,⁶ it may be assumed that this behavior is caused by the modification of unit cell dimensions or the changes of metal-ligand bond lengths and bond angles at the transition or both. Similar changes of the recoil-free fraction at a spin-state transition have been encountered before.

An attempt has been made to follow the expected structural modification by measurements of the powder X-ray diffraction of [Fe(salphen)NO] over the transition region. Unfortunately, the diffraction patterns did not show sufficient details, possibly due to the poor size of the crystals of the substance.

Although in most spin-state transitions the relaxation between the two states is slow as compared to the time scale of Mössbauer spectroscopy, examples for rapid relaxation are known. These examples comprise, in particular, systems involving the spin states $^6A_1(t_2^3e^2)$ and $^2T_2(t_2^5)$ of iron(III) such as a number of dithiocarbamate,⁹ monothiocarbamate,¹⁰ and diselenocarbamate¹¹ complexes. More recently, rapid interconversion of spin states has been reported for various FeN_4O_2 complexes with Schiff base ligands.¹²⁻¹⁷ In some of these systems, the relaxation rates seem

- (9) Merrithew, P. B.; Rasmussen, P. G. *Inorg. Chem.* **1972**, *11*, 325.
- (10) Kunze, K. R.; Perry, D. L.; Wilson, L. J. *Inorg. Chem.* **1977**, *16*, 594.
- (11) DeFilipo, D.; Depalano, P.; Diaz, A.; Steffe, S.; Trogu, E. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1566.
- (12) Maeda, Y.; Tsutsumi, N.; Takashima, Y. *Chem. Phys. Lett.* **1982**, *88*, 248.
- (13) Maeda, Y.; Ohshio, H.; Takashima, Y. *Chem. Lett.* **1982**, 943.

to be rather sensitive to slight changes in the constituents of the complex that are rather distant from the metal atom primarily concerned with the change of spin state. Thus changes in the counterion¹⁷ and in ligand substituents¹⁶ may drastically alter the character of the observed Mössbauer spectra. The exact origin of these effects, whether electronic, steric, or other in nature, is not known with certainty.

As far as iron nitrosyl complexes are concerned, the only reported example of a rapid $S = 3/2 \rightarrow 1/2$ spin-state transition is [Fe(TMC)NO](BF₄)₂ where TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam).¹⁸ However, this compound exhibits Mössbauer parameters considerably different from those of [Fe(salphen)NO]. Thus at 300 K, the quadrupole splitting and the isomer shift of [Fe(TMC)NO](BF₄)₂ have been reported as $\Delta E_Q = 0.53 \text{ mm s}^{-1}$ and $\delta^{IS} = +0.46 \text{ mm s}^{-1}$, respectively, whereas at 10 K, the values $\Delta E_Q = 0.645 \text{ mm s}^{-1}$ and $\delta^{IS} = +0.588 \text{ mm s}^{-1}$ have been obtained. The high-temperature values may be compared with the magnetic moment $\mu_{\text{eff}} = 3.62 \mu_B$ at 286 K where the intermediate-spin (i.e. $S = 3/2$)

fraction may be estimated as $n_1 \approx 0.84$; the low temperature values may be set against the moment value $\mu_{\text{eff}} = 2.66 \mu_B$ at 4.2 K where $n_1 \approx 0.34$. It should be noted that the [Fe(TMC)NO](BF₄)₂ complex has a nearly linear FeNO group, a high NO stretching frequency of 1840 cm⁻¹, and a geometry intermediate between a square pyramid and a trigonal bipyramid.¹⁸ On the other hand, the [Fe(salphen)NO] complex, which shows a $S = 3/2 \rightarrow 1/2$ transition of the discontinuous type, is characterized by Mössbauer parameters much more similar to those found for [Fe(salphen)NO], although the relaxation between the spin states is slow. Thus for the $S = 3/2$ state, $\Delta E_Q = 0.352$ and $\delta^{IS} = +0.440 \text{ mm s}^{-1}$, whereas for the $S = 1/2$ state, $\Delta E_Q = 1.950$ and $\delta^{IS} = +0.281 \text{ mm s}^{-1}$ have been reported.² In [Fe(salphen)NO], the FeNO group is strongly bent,³ the NO stretching frequency is low¹ at 1712 cm⁻¹, and the coordination unit is not noticeably distorted toward trigonal-bipyramidal geometry. It may be therefore assumed that the most significant structural characteristics in [Fe(salphen)NO] are similar to those of [Fe(salphen)NO] rather than to those observed for [Fe(TMC)NO](BF₄)₂. The rapid relaxation between the spin states $S = 3/2$ and $S = 1/2$ in the [Fe(TMC)NO](BF₄)₂ complex is therefore not a consequence of different coordination geometry of this complex and must be rather determined by other factors.

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Registry No. [Fe(salphen)NO], 73288-79-6.

- (14) Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1984**, *23*, 3861.
 (15) Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1984**, *23*, 3870.
 (16) Ohshio, H.; Maeda, Y.; Takashima, Y. *Inorg. Chem.* **1983**, *22*, 2684.
 (17) Maeda, Y.; Tsutsumi, N.; Takashima, Y. *Inorg. Chem.* **1983**, *23*, 2440.
 (18) Hodges, K. D.; Wollmann, R. G.; Kessel, S. L.; Hendrickson, D. N.; Van Derveer, D. G.; Barefield, E. K. *J. Am. Chem. Soc.* **1979**, *101*, 906.

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Orbital Description of the Emitting Doublet States in Quadrate and Trigonal Chromium(III) Complexes

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The paper presents a simple orbital description of the emitting doublet states in hexacoordinated chromium(III) amine complexes of effective quadrate or trigonal symmetry. The principal parameter in this description is the energy splitting of the three t_{2g} -type d orbitals under the tetragonal or trigonal component of the ligand field. It is shown how this splitting affects the energies and wave functions of the lowest excited doublet states, from which emission occurs. The orbital characteristics of these wave functions are analyzed in terms of orbital occupation numbers. These numbers provide a simple orbital rationale for various excited-state properties, such as charge density distribution, metal-ligand bonding energies, Jahn-Teller instability, and solvent influence. The analysis attempts to clarify the phenomenological differences between the emission spectra of so-called ²E and ²T emitters of tetragonal symmetry. It also offers specific predictions with regard to the nature of the emitting states in trigonal complexes, such as Cr(acac)₃ and Cr(bpy)₃³⁺.

I. Introduction

Recently Forster and co-workers¹ examined the emission spectra of over 40 quadrate mono- and disubstituted chromium(III) amine complexes in glassy solutions at 77 K. All these complexes were found to emit from their lowest doublet excited state. Depending on the octahedral parentage of the luminescent state, two quite different types of emission spectra were observed. So-called ²E emitters, i.e. complexes emitting from levels that are derived from the octahedral ²E_g state, produce sharp emission spectra in the 650-710-nm region. On the other hand, ²T emitters, i.e. complexes that emit from doublet components of octahedral ²T_{1g} parentage, are characterized by broad spectra, usually shifted to longer wavelengths.

It has also been found that at 77 K the nonradiative relaxation rates of the ²E emitters are confined to a narrow range, (0.9-3.5) × 10⁴ s⁻¹, while a greater variation in decay rate prevails when the emission is due to a component of ²T_{1g} origin.²

Finally, these two classes of emitters also display different solvent effects.³ ²E emitting states are only slightly affected by the solvent, whereas ²T emission shifts to shorter wavelengths in hydroxylic solvents.

As it appears, ligand field calculations based on parameters that are extracted from the quartet region of the optical spectrum score reasonably well in predicting the nature of the emitting doublet state. Considerably less clarity is available as to the reasons the two types of emitters show such pronounced differences in spectral width, Stokes shift, lifetime, and solvent influence.

In an early paper, Hoggard and Schmidtke⁴ have pointed to configurational differences between both emitting levels, without however providing a detailed description of these differences. As we have shown before,⁵ such a description is not a trivial matter

(1) Forster, L. S.; Rund, J. V.; Fucaloro, A. F. *J. Phys. Chem.* **1984**, *88*, 5012. See also: Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

(2) Forster, L. S.; Rund, J. V.; Fucaloro, A. F.; Lin, S. H. *J. Phys. Chem.* **1984**, *88*, 5017.
 (3) Fucaloro, A. F.; Forster, L. S.; Glover, S. G.; Kirk, A. D. *Inorg. Chem.* **1985**, *24*, 4242.
 (4) Schmidtke, H.-H.; Hoggard, P. E. *Chem. Phys. Lett.* **1973**, *20*, 119.
 (5) Ceulemans, A.; Beyens, D.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 2988.