SYNTHESIS OF [N,N'-PHENYLENEBIS(SALICYLIDENIMINATO)] MONONITROSYLIRON AND ITS CHARACTERIZATION IN THE SOLID STATE (IR, EPR, MÖSSBAUER, X-RAY ANALYSIS AND MAGNETIC SUSCEPTIBILITY)

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Abstract—Appreciable changes in effective magnetic moment, isomer shift (I_s) and quadrupole splitting (ΔE_a) (Mössbauer spectra) as well as in the EPR spectra occur upon cooling a sample of the title compound [Fe(salophen)NO] at a temperature of about 180 K. The observed changes are consistent with a $S = 3/2 \rightleftharpoons S = 1/2$ spin crossover. At 300 K $I_s = 0.29$ and $\Delta E_q = 0.198$ mm s⁻¹, while for a sample temperature of 100 K values are observed of 0.15 and 1.738 mm s⁻¹, respectively. In the EPR spectrum of polycrystalline samples a broad signal is observed. At 100 K two sharp lines corresponding to $g_{\perp} = 2.108$ and $g_{\parallel} = 2.211$ are present. The EPR spectrum for 12 K is nearly identical to the spectrum obtained at 100 K. The physicochemical properties of the complex resemble strongly those of the analogue [Fe(salen)NO] and consequently rationalization of the results in terms of the MO diagram for the latter complex can be given. From the magnetic susceptibility and Mössbauer data a separation of the orbitals — involved in the spin-crossover process of about 300 cm⁻¹ was calculated. Analysis of the magnetic-susceptibility data further reveals, via the large values found for ΔS^{\ominus} (286.2 J mol⁻¹ K⁻¹) and ΔH^{\ominus} (28.9 kJ mol⁻¹), that the spin crossover is accompanied by a relative large change in the bonding distances and/or angles. In oxygen- and/or water-containing solutions the complex is rapidly transformed into the μ -oxo-dimer [Fe(salophen)]₂O.

The pentacyanonitrosylferrate or nitroprusside dianion is very interesting from several points of view. The properties of this anion have been recently reviewed.¹ Nitroprusside is frequently used as a reagent for detection and/or determination of a wide variety of nucleophillic species—generated in (strongly) alkaline medium from compounds such as thiols, ketones, aldehydes, phenols, pyrrols, indols and thioureas—and sulphite. Moreover, nitroprusside is a potent hypotensive drug. Unfortunately, a number of drawbacks limits its therapeutic use. Nitroprusside is administered by (intravenous) infusion (in the clinic), because the drug is not absorbed after oral administration. Secondly, nitroprusside is especially light-sensitive in (infusion) solutions. On the other hand, the drug is toxic due to the *in vivo* loss of the cyanide ligands. Reactivity, and most probably the biological activity as well, are related to the $Fe(II)-NO^+$ moiety.

Therefore, our ultimate aim was the synthesis of

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Fig. 1. Structure of [Fe(salophen)NO].

stable and less toxic (mono)nitrosyl analogues of nitroprusside with at least a comparable hypotensive action. In general the separations of the orbitals involved in the ligand coordination in iron nitrosyl complexes are small.² As a consequence both the stability of iron mononitrosyl complexes and the character of the nitrosyl group (NO^+ , NO^0) or NO⁻) are sensitive to subtle changes in the properties of the coordinated ligands. A survey of the literature on mononitrosyl iron complexes reveals that only a minority of these compounds are to a certain extent stable in the solid state and in solution. On the basis of the anionic multidentate ligands present in the relatively stable complexes porphinato,³ phthalocyanato,⁴ dithiolato,⁵ dithiocarbamato⁶ and Schiff base⁷⁻⁹ mononitrosyl coordination compounds can be distinguished. Apparently, π -extended systems possess stabilizing properties towards iron nitrosyl complexes. This is not surprising, since cyanide present in the comparatively stable nitroprusside ion is a strong field ligand with an exceptional $d\pi$ -accepting ability.

An alternative approach to the preparation of nitroprusside analogues is the replacement of the central metal ion by Ru(II). In this ion the fully occupied t_{2g}^6 -orbitals extend far more into space and consequently strong back-bonding interactions with common π -acceptor ligands such as NO⁺ occur.¹⁰⁻¹³ For this reason Ru(II) nitrosyl complexes can be formally regarded as Ru-NO⁺ and are in general relatively stable. Unfortunately, Ru(II) complexes are both mutagenic and carcinogenic.¹⁴

In order to obtain more insight into the role of conjugation in stabilizing mononitrosyl iron complexes, the phenylene analogue of [N,N'-ethylenebis(salicylideniminato)]nitrosylferrate, [Fe(salophen)NO] (Fig. 1), was prepared and its physicochemical features were compared to those of [Fe(salen)NO] which was recently characterized by Wells *et al.*⁸

Finally, the stability of [Fe(salophen)NO] was investigated in the solid state and in solution, employing the intensity of the characteristic nitrosyl stretching frequency in the IR spectrum as criterion.

EXPERIMENTAL

Reagents and ligands

Sodium acetate, sodium nitrite, o-phenylenediamine and sulfuric acid (Merck analytical grade), ferrous perchlorate hexahydrate (Ventron), salicylaldehyde (Baker reagent grade), methanol and ethanol (Baker analytical grade) were used in the synthetic procedures. The ligands o-ethylene- and o-phenylenebissalicylideniminato were obtained by condensation of the respective diamines with salicylaldehyde (1:2) in refluxing ethanol. The crop of yellow and orange crystals was subsequently thoroughly washed with ethanol and recrystallized from ethanol.

Preparation of [Fe(salophen)NO]

Earnshaw et al.⁷ prepared [Fe(salen)NO] via the extremely air-sensitive [Fe(salen)] complex. In our method the desired nitrosyl complex is produced in one step, circumventing the unstable intermediate. 0.32 g powdered ligand was added to 30 cm³ methanol, which was deoxygenated by purging with nitrogen purified via a BTS tower. Thereafter, a 0.16 g sodium acetate (0.02 M) and 0.36 g ferrous perchlorate (0.01 M) were added. Immediately NO gas, generated from sodium nitrite by dropwise addition of 2 M sulfuric acid and purified by passage through a 30% KOH solution and a column of KOH pellets,¹⁵ was bubbled through the wellstirred reaction medium. The solution turned black and a black product precipitated. After 1.5 h the excess NO gas was removed by purging with nitrogen and the black microcrystalline material was filtered, washed with 30 cm³ deoxygenated methanol under a stream of nitrogen and finally dried in vacuo for 1.5 h.

Found: Fe; 13.7%. Calc. for [Fe(salophen)NO] (FeC₂₀H₁₄N₃O₃): Fe, 14.0%. $v_{NO} = 1720 \text{ cm}^{-1}$ (KBr, Nujol mull).

Preparation of [Fe(salen)NO] and [Co(salophen)-NO]

The complex [Fe(salen)NO] was prepared in an analogous way. In the synthesis of [Co(salophen)NO] Co(II) acetate tetrahydrate was used, while sodium acetate was omitted.

[Fe(salen)NO]: $v_{NO} = 1710 \text{ cm}^{-1}$ (KBr); [Co(salophen)NO]: $v_{NO} = 1640 \text{ cm}^{-1}$ (KBr).

Physical measurements

Powder X-ray diffractograms were recorded by means of a Philips diffractometer, type PW 1025/25 using Cu- K_{α} radiation ($\lambda = 1.5418$ Å).



Fig. 2. Effective magnetic moment (μ_{eff}) for [Fe(salophen)NO] in the temperature range 80-300 K.

The magnetic properties of [Fe(salophen)NO] were determined in the temperature range 2-300 K. The high-temperature susceptibility (T > 77 K) was measured using a Faraday balance. In the lowtemperature range susceptibility and magnetization measurements were performed using a PAR vibrating sample magnetometer. Field-dependent magnetization curves were recorded at liquid-He temperature applying fields up to 5.6 T. All susceptibility data were corrected for diamagnetism of the samples¹⁶ and the sample holder.

The IR spectra were recorded for both the KBr pellet and the Nujol mull by means of a Beckman IR-10 spectrometer in the frequency range 4000–200 cm⁻¹. For the Mössbauer experiments a conventional constant-acceleration type spectrometer was applied. The source was 57 Co diffused in rhodium. All isomer shifts (I_s) are relative to sodium nitroprusside.

The EPR spectra for a polycrystalline sample of [Fe(salophen)NO] were recorded at room temperature, and 100 and 12 K on a Varian E 3 at X-band frequencies, employing a 9.22-GHz field modulation.

RESULTS

Magnetic susceptibility

The data for polycrystalline [Fe(salophen)NO] are represented in Fig. 2.

These results closely resemble those for [Fe(salen)NO]. At about 180 K a spin crossover occurs. Above the crossover temperature (T_c) the effective magnetic moment (μ_{eff}) is approximately 3.9, while at temperatures below T_c the effective magnetic moment is about 1.9. These values are

very close to the spin-only values for $S = \frac{3}{2}$ (3.88) and $S = \frac{1}{2}$ (1.73), respectively. In addition a magnetic phase transition due to antiferromagnetic coupling of the Fe centres is observed at T = 6 K (Fig. 3).

The magnetic-susceptibility data can be treated according to eqn (1):

$$\mu_{\rm eff}^2 = \alpha \cdot \mu_{\rm S=3/2}^2 + (1-\alpha)\mu_{\rm S=1/2}^2, \qquad (1)$$

in which $\mu_{S=3/2}$ and $\mu_{S=1/2}$ are the theoretical spinonly values of 3.88 and 1.73. The equilibrium constant at various temperatures for the spin crossover (K_{eq}^{T}) can be calculated by eqn (2):

$$K_{eq}^{T} = \alpha / (1 - \alpha), \qquad (2)$$

where α denotes the fraction in the high-spin state. Subsequently, eqn (3):

$$\ln K_{eq}^{T} = \Delta S^{\Theta} / R - \Delta H^{\Theta} / RT$$
 (3)

offers the possibility of calculating both enthalpic and entropic changes accompanying the spin transition. In Fig. 4 the plot of $\ln K_{eq}^{T}$ vs T^{-1} is given. From this plot values of $286.2 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ and 28.9 kJ mol⁻¹ were calculated for ΔS^{Θ} and ΔH^{Θ} . The ΔS^{Θ} value comprises an electronic entropy change related to a difference in spin multiplicity and state degeneracy for the high- and low-spin states. In theory the electronic entropy change for the present case equals $R \ln (\frac{4}{2}) = 5.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus the calculated value for ΔS^{\ominus} may almost entirely be ascribed to changes in bond distances and/or bond angle occurring concomitantly with spin-crossover process. The value the of $286.2 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ is very high. Petty et al.¹⁷ found



Fig. 3. Reciprocal magnetic susceptibility $(1/\chi)$ for [Fe(salophen)NO] in the temperature range 2-80 K.



a value of $112.2 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ for an iron(II) complex. Apparently, large changes in bonding distances and/or angles occur during the spin crossover. A change in bonding distance of 0.1-0.2 Å is reasonable.¹⁶ Assuming a change equal to 0.2 Å, the expected inner coordination sphere reorganization energy is $25.1 \text{ kJ} \text{ mol}^{-1}$.¹⁸ As a consequence, the estimated electronic contribution to the observed enthalpic change amounts to $28.9 - 25.1 = 3.8 \text{ kJ} \text{ mol}^{-1}$. This value reflects the separation of the electronic levels involved in the spin transition and is estimated as 300 cm^{-1} .

Mössbauer spectroscopy

In the Mössbauer experiments performed at various temperatures the spin transition is also observed at $T_c = 180$ K. The Mössbauer data are summarized in Table 1. In Fig. 5 the variation in the quadrupole splitting (ΔE_q) and I_s with temperature is depicted. Representative Mössbauer spectra

data for [Fe(salophen)NO]		
Т	ΔE_q	I,
(K)	$(mm s^{-1})$	(mm s ⁻¹) ^a
300	0.198	-0.29
220	0.292	-0.30
200	0.364	-0.29
180	1.231	-0.19
160	1.576	-0.15
130	1.705	-0.15
100	1.738	-0.15

Table 1. Mössbauer spectroscopy

"Relative to sodium nitroprusside.



Fig. 5. Variation of quadrupole splitting (ΔE_q) (open circles) and isomer shift (I_s) (closed circles) with temperature in the range 100-300 K.

for T = 293, 200, 160 and 100 K are given in Fig. 6. The magnetic-susceptibility and Mössbauer data are thus in good agreement. The quadrupolesplitting values at each temperature $[\Delta E_q(T)]$ are related to the quadrupole splitting at T = 0 K $[\Delta E_q(0)]$ via eqn (4):¹⁹

$$\Delta E_q(T) = \Delta E_q(0) \tanh\left(\Delta \frac{1}{2}kT\right). \tag{4}$$



Fig. 6. Mössbauer spectra for [Fe(salophen)NO] at the indicated temperatures.

In eqn (4) Δ represents the separation of the levels playing a role in the spin crossover. Using for $\Delta E_q(0)$ the extrapolated value of 1.83 mm s⁻¹ a reasonable fit between experimental and calculated values is obtained for $\Delta = 280 \text{ cm}^{-1}$. This value is relatively close to the value of 300 cm⁻¹ derived from the susceptibility data.

X-ray analysis

The X-ray powder diffraction pattern of [Fe(salophen)NO] can be indexed in an orthorhombic space group. The cell parameters are a = 16.74 Å, b = 17.32 Å and c = 10.65 Å. Systematic absences indicate P222 to be the most likely space group. Data for the observed reflections with 2 θ between 10 and 25° are presented in Table 2. The results agree qualitatively with the reported structure for one of the modifications of the related Co complex [Co(salophen)].²⁰ The cell parameters are about the same for both complexes, but in the case of the iron compound the *c*-parameter is doubled with respect to the value for the Co compound. This is probably due to the presence of the NO moiety in the Fe complex and to the larger size of the central Fe ion. Both conditions may give rise to a shift

Table 2. X-ray powder diffraction data for [Fe(salophen)NO]

2θ	
(°)	hkl
10.22	020
13.20	021
13.45	201
14.18	121
14.52	211
16.07	130
17.35	012
17.47	102, 031
17.97	301
19.51	022
20.23	122
20.48	040, 212, 231
21.06	400
23.54	420
24.48	241

DISCUSSION

Comparison of the magnetic behaviour, EPR, IR and Mössbauer parameters of [Fe(salen)NO] and [Fe(salophen)NO] leads to the conclusion that only minor changes occur upon extension of the conjugation in the equatorial Schiff base ligand. This is consistent with the observation that μ_{eff} for the $S = \frac{1}{2}$ and $\frac{3}{2}$ spin states approximates the theoretical spin-only values, suggesting a limited admixture of the salophen orbitals and the metal d-orbitals. Lack of suitable orbitals on the phenolic oxygen may account for a slight degree of delocalization involving the equatorial ligand. Because of the similarities in the properties of [Fe(salen)NO] and [Fe(salophen)NO] the MO description proposed by Wells et al.⁸ (Fig. 8) might be used for the explanation of the observed features of [Fe(salophen)NO]. The relatively low nitrosyl stretching frequency of $1720 \,\mathrm{cm}^{-1}$ is, according to Gaughan et al.,²¹ indicative either of an Fe(II)-NO⁰ or an



Fig. 7. Polycrystalline EPR spectra for [Fe(salophen)]NO]. The sample temperatures are indicated.

coordination. In the structure of the orthorhombic modification of the Co complex the c-axis is perpendicular to the almost planar ligand. Alternation of the assumed out-of-plane shift of the Fe atom in the positive and negative direction will result in a doubling of the translation symmetry along the c-axis with respect to the original structure.

EPR spectroscopy

Figure 7 shows the EPR spectra for polycrystalline [Fe(salophen)NO]. At T = 295 K a broad polycrystalline EPR signal is observed. Upon lowering the sample temperature the EPR spectrum changes markedly at about 180 K. At T = 100 K two sharp lines are observed which correspond to $g_{\perp} = 2.108$ and $g_{\parallel} = 2.211$. The EPR spectrum for T = 12 K is practically the same with $g_{\perp} = 2.090$ and $g_{\parallel} = 2.195$.



Fig. 8. MO diagram for an {FeNO}⁷ complex with a bent geometry.

Fe(III)-NO⁻ moiety. In the given MO diagram six *d*-electrons are placed in orbitals with a predominant *d*-character, while one electron resides mainly in the antibonding π_y^* -orbital. Thus, the hightemperature state can be formally regarded as temperature state can be formally regarded as Fe(II)-NO. Furthermore, the NO stretching frequency for [Co(salophen)NO] is 1640 cm⁻¹. The decline in the NO stretching frequency, going from d^6 [Fe(salophen)NO] to d^8 [CO(salophen)NO] is in agreement with the orbital leveling as given by Wells *et al.*⁸ In the Co analogue a second *d*-electron is placed in the π_y^* -orbital leading to substantial weakening of the bond between the N and the O atom in the nitrosyl group.

As suggested by the large values found for ΔH^0 and ΔS^0 , the spin-crossover process is accompanied by structural changes, i.e. changes in bond distances and/or angles. X-ray analysis of [Fe(salophen)NO] at 293 K suggests that in the high-spin state the Fe ion is displaced out of the plane of the Schiff base ligand. Wells et al.8 derive from their Mössbauer experiments that on going from the $S = \frac{3}{2}$ state to the $S = \frac{1}{2}$ state the recoil-free fraction increases. These authors attribute this phenomenon to the movement of the iron atom from an out-of-plane position to an in-plane position. It is clear that this implies a change in bond distances and angles. Therefore, changes in the bond distances and angles must be taken into account in the interpretation of the Mössbauer parameters. Wells et al.,8 however, neglect these changes in their explanation given for the variation of Mössbauer parameters with temperature. According to the MO diagram, the spin crossover consists in the transfer of electron density from the d_{xy} -orbital to the d_{z^2} -orbital. The d_{z^2} -orbital possesses less d-character because of overlap between the d_{z^2} and the σ^* -orbital. As a consequence the electric field gradient (EFG) and thus the quadrupole splitting is larger for the $S = \frac{1}{2}$ state. At the same time the Fe atom moves into the plane of the equatorial salophen ligand and consequently the bond distances (r) become shorter. This effect will also lead to an increase in the EFG, since the EFG is proportional to r^{-3} . As a result of these two cooperative effects the quadrupole splitting will greatly change in the neighbourhood of the spin conversion temperature (180 K). On the other hand a relatively small decrease in I_{x} is observed. This indicates the effective s-electron density as experienced by the iron nucleus in the $S = \frac{1}{2}$ state to be smaller. The spin crossover is apparently associated with an increase in shielding of the s-type iron electrons due to transfer of electron density from the σ^* -type d_{z^2} -orbital to the d_{xy} -orbital.

The complex [Fe(salophen)NO] is relatively stable in the solid state. No decrease in the intensity of the nitrosyl stretching frequency (1720 cm^{-1}) was observed over a period of 2 months. By contrast, in oxygen- and/or water-containing solutions a red precipitate is rapidly formed. The observed peak at 820 cm^{-1} in the IR spectrum of the red material points to the formation of the μ -oxo-dimer [Fe(sal-ophen)]₂O.^{22,23} Gulotti *et al.*²⁴ have reported that the μ -oxo-dimer [Fe(salen)]₂O is cleaved in the presence of excess cyanide, while [Fe(salen)(CN)₂] is slowly converted into the oxygen-bridged species. Most probably this type of dimirization can be prevented by a (strong) ligand at the sixth position. Placing a sixth ligand along the z-axis will lift the d_{xz} -, d_{yz} - and especially the d_{z2} -orbital. This may result in an orbital leveling very similar to the orbital configuration in the nitroprusside ion.²⁵

In conclusion [Fe(salophen)NO] is not a suitable nitroprusside analogue. Most probably replacement of the four equatorial cyanide ligands in nitroprusside by an anionic multidentate with exceptional $d\pi$ -accepting ability may result in a stable Fe(II)-NO⁺ complex.

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