

Spin State Equilibria in Fe(NO)(salphen)

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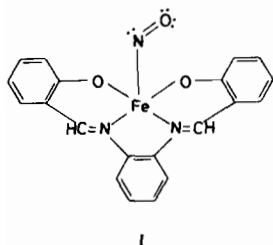
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The structures [1] of the magnetically distinct forms ($S = 3/2$ and $S = 1/2$) [2] of Fe(NO)(salen) {salenH₂ = NN'-ethylenebis(salicylideneimine)} have recently been described. The average Fe–N–O angle in the $S = 3/2$ form is 147°, and low temperature X-ray diffraction studies show that in the $S = 1/2$ form this angle is 127°, and the Fe atom is 0.1 Å closer to the mean coordination plane of the salen ligand. We wish to report that Fe(NO)(salphen), where salphen-H₂ = NN'-o-phenylenebis(salicylideneimine), shows very similar magnetic and infrared behaviour



Like Fe(NO)(salen), the salphen nitrosyl (I) was prepared by reaction of gaseous nitric oxide with the iron(II) complex [3] suspended in 96% ethanol. Approximately one mol of nitric oxide was absorbed per mol of iron(II) salphen. Satisfactory microanalyses were obtained (Found: C, 60.02; H, 3.64; N, 10.41; Fe, 13.76%. C₂₀H₁₄N₃O₃Fe requires C,

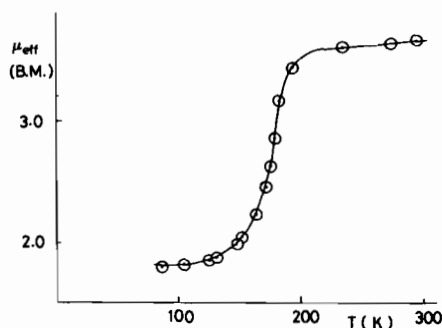


Fig. 1. Variation of magnetic moment of Fe(NO)(salphen) with temperature.

60.02; H, 3.53; N, 10.50; Fe, 13.95%). The preparations were carried out under nitrogen, but the dry, greyish-brown nitrosyl is air-stable.

The magnetic data are given in Table I and illustrated in Fig. 1. The effective magnetic moment, μ_{eff}, of Fe(NO)(salphen) decreased from 3.65 B.M. at 295 K to approximately 1.80 B.M. at 88 K, consistent with a change in spin state from $S = 3/2$ to $S = 1/2$. The change of spin state took place between approximately 160 and 180 K but is not so precipitous as with Fe(NO)(salen).

Infrared spectra have been recorded over the same temperature range as the magnetic measurements. At room temperature (Fig. 2) Fe(NO)(salphen) has a strong nitric oxide stretching frequency at 1724 cm⁻¹, with a very weak band at 1660 cm⁻¹. In the region of the spin state transition the former band rapidly weakened while the latter intensified, and at liquid nitrogen temperature only the latter was visible (1643 cm⁻¹). The bands are assigned to the stretching frequencies of the $S = 3/2$ and $S = 1/2$ spin states respectively. The band of the $S = 1/2$ isomer of Fe(NO)(salen) could not be identified in the low temperature i.r. spectrum [2] because it apparently co-incided with double bond absorptions of the

TABLE I. Variation of Magnetic Moment (μ_{eff}) and Magnetic Susceptibility of Fe(NO)(salphen) with Temperature.

T (K)	294.8	274.9	234.5	194.2	184.1	180.0	175.8	172.0
10 ⁶ χ _A	5647	6005	6857	7622	6842	5664	4899	4376
μ _{eff} (B.M.)	3.65	3.63	3.58	3.44	3.17	2.86	2.62	2.45
T (K)	164.4	153.0	147.5	129.5	125.6	105.5	87.8	
10 ⁶ χ _A	3792	3428	3379	3384	3434	3940	4607	
μ _{eff} (B.M.)	2.23	2.05	2.00	1.87	1.86	1.82	1.80	
Diamagnetic Correction = 179.5 × 10 ⁻⁶ c.g.s.u.								

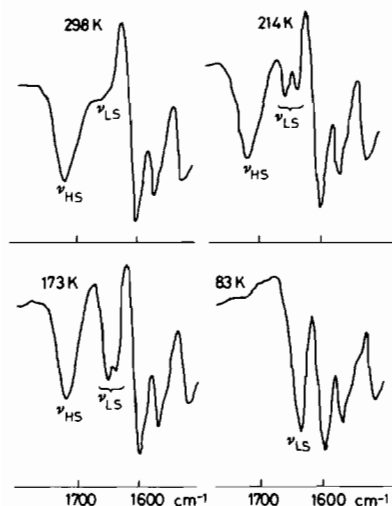


Fig. 2. Infrared spectra of Fe(NO)(salphen) at various temperatures.

quadridentate ligand, but it is clearly visible in the spectrum of Fe(NO)salphen. The magnetic and infrared changes were reversed on warming to room temperature. The splitting of the $S = \frac{1}{2}$ absorption at intermediate temperatures (Fig. 2) suggests that two polymorphs of the low spin form may exist.

The 5,5'-dinitro-substituted derivative of Fe(NO)-salen, Fe(NO)(salen NO₂), has been re-prepared and again found [2] to have a temperature-dependent magnetic moment, but the values (3.69 B.M. at 300 K and 3.41 B.M. at 90 K) were higher than obtained earlier (3.08 and 2.60 B.M.), and the Curie Weiss constant was 20° instead of ~65°. The earlier preparations lost nitric oxide, as judged from the infrared spectra, but this difficulty was not found with the present product. The infrared behaviour was as before [2], confirming that the relative proportions of $S = 3/2$ and $S = \frac{1}{2}$ spin states change only slowly with temperature.

The Mössbauer spectra of the nitrosyls have been recorded at room and liquid nitrogen temperatures (Table II). The chemical isomer shifts δ , as reported earlier [2] for Fe(NO)salen, are in the range expected for iron(III) and an $S = 3/2$ spin state [4]. The isomer shift normally increases as the temperature is lowered because of the second order Doppler effect, but the values for the salen and salphen nitrosyls decrease. This is compatible with the formation of the $S = \frac{1}{2}$

TABLE II. Mössbauer Parameters of Nitrosyls.

Nitrosyl	T (K)	δ^a (mm s ⁻¹)	ΔE (mm s ⁻¹)
Fe(NO)(salen)	300	0.39	0.29
	77	0.25	1.92
Fe(NO)(salphen)	300	0.36	0
	77	0.27	1.72
Fe(NO)(salphen NO ₂)	300	0.50	0.50
	77	0.50	0.50

^aWith respect to natural iron.

spin state. On cooling, the quadrupole splittings, ΔE , for these two nitrosyls increased dramatically. From the molecular orbital diagram developed by Mingos [5] for systems in which the M-N-O angle varies from 180 to 90°, it would appear that in the $S = 3/2$ state the electronic configuration is $(d_{yz}, \pi^*(NO))^2, (d_{xz}, \pi^*(NO))^2, (d_{xy})^1, (\pi^*(NO), d_{z^2})^1, (\pi^*(NO), d_{yz})^1$ whereas in the $S = \frac{1}{2}$ state, with a smaller M-N-O angle, the separation between the last two orbitals is much increased leading to the configuration $(d_{yz}, \pi^*(NO))^2, (d_{xz}, \pi^*(NO))^2, (d_{xy})^2, (\pi^*(NO), d_{z^2})^1$. The filling of orbitals introduces little net charge along the z axis in the $S = 3/2$ state so ΔE is small whereas in the $S = \frac{1}{2}$ state the additional electron in the d_{xy} orbital produces a greater valence contribution to the electric field gradient and a moderate ΔE . The Mössbauer spectrum of Fe(NO)(salen NO₂) showed little change on cooling, but from the magnetic data it can be calculated that only 25% is in the low-spin form at 80 K. It would seem likely that on cooling Fe(NO)(salphen) and Fe(NO)(salen NO₂) undergo similar structural changes to those reported for Fe(NO)(salen).

References

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