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Crystal structure, electrochemical and spectroscopic properties of the *trans*-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO^+)(cyclam)]$_2$}(PF_6)$_6$ complex

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The *trans*-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO^+)(cyclam)]$_2$}(PF_6)$_6$ complex was prepared from the reaction of *trans*-[Fe(cyclam)Cl_2]Cl and nitric oxide. The molecular structure of the complex was determined by X-ray diffraction (space group $P2_1/c$; a = 10.3560(3) Å; b = 17.7110(6) Å; c = 17.9480(6) Å; β = 91.052(2)°). Crystal and spectroscopic evidence indicates the existence of two independent complexes with participation of different forms of nitric oxide: NO^+ and NO^0. The IR spectrum shows the presence of two ν(NO) stretching modes at 1863 and 1610 cm^{-1} which are characteristic of these NO species, respectively. Upon reduction by zinc amalgam, the ν(NO^+) band at 1863 cm^{-1} disappears and the band at 1610 cm^{-1} becomes more intense. The EPR measurements indicate the presence of the NO^0 group. No signal for paramagnetic species of Fe(III) was observed.

Introduction

Due to the clinical importance of the nitric oxide species, several nitrosyl transition metal complexes are currently under investigation by the inorganic and biomedical communities.[1–5] The role of these complexes as NO carriers which can release NO upon photolysis,[1,5] their applications in photodynamic therapy for antitumor purposes and as NO delivery agents of vascular NO,[6,7] as well as biodistribution inside the cells, are important recent areas of research. Particularly, ruthenium complexes with the edta class of ligands have been reported as examples of important clinical antisepsis agents in the scavenging of excess NO in the blood stream or in cells.[8–10] In this context the [Ru_2(ttha)(H_2O)$_2$]$^{2+}$ (ttha = triethylenetetraminehexaacetate) binuclear complex has been reported as an efficient scavenger of free NO.[11] The [Ru^{II}(hedta)L] complex (hedta = *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid), with L = NO^+, NO and NO^-, was the first and most interesting example wherein the entire electron transfer ligand series of $NO^{+/0/-}$ is clearly present.[12] The little difference observed in the N–O bond order of the coordinated group of Ru^{II}(NO^+) and Ru^{II}(NO) was ascribed to the compensating π-donation and σ-withdrawal by the metal center.[12] On the other hand, iron nitrosyl complexes with edta and azide ligands are reported in the literature as typical {Fe–NO}^{7} paramagnetic nitrosyl-iron centers.[13–15]

The apparently simple {Fe–NO}^{n} moieties show intriguing and complex properties concerning conformation and oxidation states of the iron metal center and NO species.[16–19] To better understand the electronic structures of these important species, great experimental and theoretical efforts have been devoted to fully characterize them.[15,16–20] Recently, Hauser and coworkers[16] reported the properties of *trans*-[(cyclam)Fe(NO)Cl](ClO$_4$) and *cis*-[(cyclam)Fe(NO)I]I that were isolated from the reaction of the *cis*-[(cyclam)Fe(Cl)$_2$]Cl complex and hydroxylamine in aqueous solutions. The authors concluded that both species are of the {Fe–NO}^{7} type. In spite of the care adopted in using redox-innocent macrocycles as co-ligands so as not to perturb electronically the metal center, remarkable changes in the properties of the complexes were observed, demonstrating that the versatility of the {Fe–NO}^{n} species seems to be inexhaustible.[15–20]

We report here a novel crystal form of the {Fe–NO}^{n} unit, obtained by direct reaction of the *trans*-[(cyclam)Fe(Cl)$_2$]Cl complex with a gaseous stream of nitric oxide, in which both values, n = 6 and n = 7, are simultaneously present in the unit cell.

Experimental

All manipulations were carried out under an inert atmosphere (N_2 or Ar) following conventional techniques. Milli-Q grade or doubly distilled water was used throughout. Cyclam (1,4,8,11-tetrazacyclotetradecane) was obtained from Aldrich and used without further purification. The *trans*-[(cyclam)FeCl_2](BF_4) complex was prepared according to the literature procedure.[21] Electronic spectra were acquired with a Hewlett-Packard 8453 diode-array scanning spectrophotometer in the 1100–200 nm range. A quartz cell (1.0 cm pathlength) was used, keeping concentrations of samples between 1.0×10^{-3} and 1.0×10^{-2} M. Infrared spectra were taken on a Shimadzu FTIR-8300 spectrophotometer, using solid samples dispersed in KBr pellets. Electrochemical experiments were performed on a BAS 100BW electrochemical analyzer (Bioanalytical Systems-BAS, West Lafayette, IN). A conventional three-electrode glass configuration cell with glassy carbon of 0.126 cm^2 geometrical area, and a Pt foil were used as working and auxiliary electrodes, respectively. A 0.1 M NaTFA, pH = 4.0, was used as electrolyte,

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Table 1 Crystal data and structure refinement for the *trans*-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO^+)(cyclam)]$_2$}(PF_6)$_6$ complex

Empirical formula	$C_{30}H_{72}Cl_3F_{36}Fe_3KN_{15}O_3P_6$
Formula weight	1873.84
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.3560(3)
b/Å	17.7110(6)
c/Å	17.9480(6)
β/°	91.052(2)
V/Å^3	3291.4(2)
Z	2
μ/mm^{-1}	1.133
Reflections collected	38116
Independent reflections	5793 [R(int) = 0.0751]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0461$, $wR2 = 0.1284$
R indices (all data)	$R1 = 0.0694$, $wR2 = 0.1538$

at 25 ± 0.2 °C. Potential values were measured *versus* Ag/AgCl (3.0 M KCl) as reference electrode. The EPR spectrum of the powder sample was acquired with a Varian E109–110 EPR spectrometer at X and Q bands at two temperatures, room temperature and 100 K.

trans-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO^+)(cyclam)]$_2$}(PF_6)$_6$ 1

Complex **1** was prepared by dissolving 0.132 g (0.309 mmol) of *trans*-[(cyclam)FeCl$_2$](BF_4) in 100 mL of water, under argon and stirring. A nitric oxide gas flow was passed through the solution for 3 h. The solution was then rotary-evaporated to 4 mL, and the *trans*-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO^+)(cyclam)]$_2$}(PF_6)$_6$ complex was precipitated by the addition of 5 mL of a KPF_6 saturated aqueous solution. Yield: 85%. Calc. C: 19.2, H: 3.8, N: 11.2. Found C: 19.4, H: 3.7, N: 11.3%.

Slow recrystallization of the crude material from aqueous solution produced single crystals of the complex suitable for X-ray crystallography.

Structure determination and refinement

A prismatic crystal of dimensions 0.16 × 0.08 × 0.06 mm was used for data collection. All measurements were made on an Enraf-Nonius Kappa-CCD difractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Data were collected up to 50° in 2θ with a redundancy of 4. The final unit cell parameters were based on all reflections. Data collection was made using the COLLECT program;[22] integration and scaling of the reflections were done with the HKL Denzo-Scalepack system of programs.[23] Absorption corrections were applied to the data using the multi-scan method.[24] The structure was solved by Patterson methods with SHELXS-97.[25] The Fourier map showed both Fe atoms. All other non-hydrogen atoms were found in successive difference Fourier maps. Hydrogen atoms were positioned on stereochemical grounds and refined with the riding model. The structure was refined by full-matrix least-squares on F^2 using SHELXL-97.[26] The program WINGX was used to analyze and prepare the data for publication.[27] Crystal data, data collection procedures, structure determination method and refinement results are summarized in Table 1.

CCDC reference number 174763.

See http://www.rsc.org/suppdata/dt/b1/b111029b/ for crystallographic data in CIF or other electronic format.

Results and discussion

The electronic spectrum of complex **1** shows two bands at 232 nm ($\varepsilon = 2.9 \times 10^3$ M^{-1} cm^{-1}) and 331 nm ($\varepsilon = 2.3 \times 10^2$ M^{-1} cm^{-1}). Since the complex is structurally and electronically similar to the *trans*-[(cyclam)Ru(NO)Cl]$^{2+}$ species, it is likely that their UV-visible spectra would be similar.[3] Based on this analogy, the relatively intense band at 232 nm was assigned to the LMCT charge transfer band [$\pi_p(Cl^-) \longrightarrow e_g(Fe)$] and the band at 331 nm was assigned to a spin-allowed d–d transition $^1A_1 \longrightarrow {}^1T_1$.[3,28]

The infrared spectrum of the title complex showed bands in the range 3190–2856 cm^{-1} that are characteristic of νNH and those in the range 1460–1430 cm^{-1} characteristic of νCH and νCN stretching modes of the cyclam ligand.[29,30] The bands at 810 and 896 cm^{-1} that are currently attributed to the vibrational modes of the cyclam moiety in the *trans* conformation are overlapped by the intense νPF_6^- band. The most prominent feature of the IR spectrum is the presence of two bands assigned to the νNO stretching frequencies: a sharp and strong peak at 1893 cm^{-1} and a weak one at 1610 cm^{-1}. These νNO frequency values are consistent with the simultaneous presence of nitrosyl groups in the NO^+ {FeNO}^{6} and NO^0 {FeNO}^{7} oxidation forms.[31]

In a further experiment, an aqueous solution of complex **1** was reduced by a freshly prepared zinc amalgam under an argon atmosphere, which was followed by precipitation. Upon reduction, the infrared spectrum of the fully reduced solid species (Fig. 1) showed an increase in the intensity of the band at 1610 cm^{-1}. Conversely, the band at 1893 cm^{-1} disappeared.

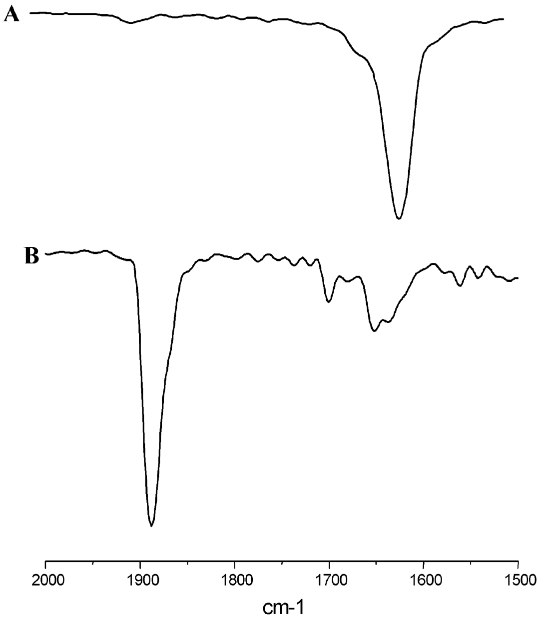

Fig. 1 Infrared spectra of complex **1**: (A) fully reduced, (B) freshly prepared.

The cyclic voltammetry of complex **1** in aqueous medium presented a strong dependence on the potential range investigated, as well as on the initial sweep direction. Fig. 2 shows the cyclic voltammetry for a scan starting at −0.80 V with initial anodic sweep, in which three electrochemical processes are evidenced. The process centered at approximately −0.70 V, *versus* Ag/AgCl, is attributed to the reduction of the *trans*-{FeNO}^{7} species. The higher potential waves ($E_{1/2}$ = 0.40 V) are attributed to the *trans*-{FeNO}$^{6/7}$ redox process centered at the metal (Fe$^{III/II}$), whereas the one centered at 0.08 V is assigned[21] to the Fe$^{III/II}$ couple of *trans*-[(cyclam)FeCl(OH_2)]$^+$, which is generated following dissociation of NO from the *trans*-{FeNO}^{7} complex. The fact that the process centered around 0.08 V only appears when the scan extends to −0.80 V (Fig. 2), makes reasonable the assignment of the generating aqua species *trans*-[(cyclam)FeCl(OH_2)]$^+$. To confirm this assignment, a small amount of the *trans*-[(cyclam)FeCl$_2$](BF_4) complex was added to the electrochemical probe solution, resulting in an increase in the intensity of the current peak observed for the process centered at 0.08 V.

To investigate the occurrence of the NO thermal labilization, a freshly prepared sample solution of complex **1** was kept under

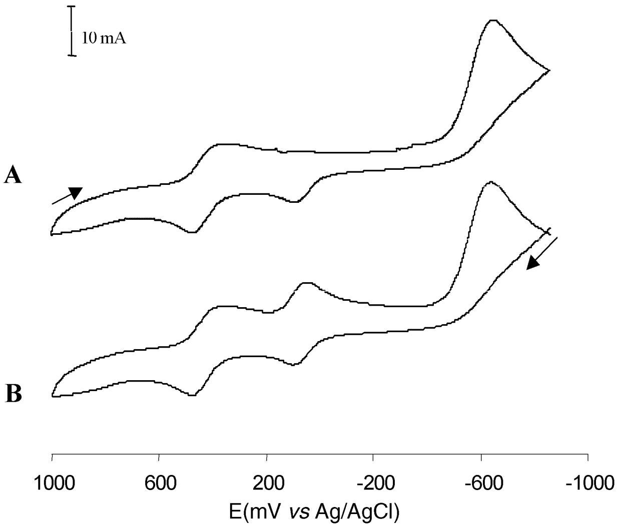

Fig. 2 Cyclic voltammetry at 50 mV s^{-1} of 10^{-3} M of complex **1** in 0.1 M CF_3CO_2Na, pH 4.0. (A) Scan starts at 1000 mV with initial cathodic sweep. (B) Scan starts at −800 mV with initial anodic sweep. Potentials are quoted *versus* Ag/AgCl (3.0 M KCl).

argon for 24 h, and the complex reactivity monitored by differential pulse voltammetry. To avoid the induced electrochemical nitric oxide labilization, the potential sweep scale was fixed in the range from −0.30 to 0.80 V. A current intensity decreasing with time was observed for the *trans*-$\{FeNO\}^{6/7}$ process (E_{pa} = 0.44 V), at the expense of the current intensity increase for the *trans*-$[(cyclam)FeCl(OH_2)]^{2+/+}$ (E_{pa} = 0.08 V) process. After 24 h, the solution was rotary-evaporated and the IR spectrum of the resulting compound showed no NO peaks (1893 and 1610 cm^{-1}), indicating that the NO dissociation also occurs thermally. Both electrochemical and thermal NO labilization observed for the title complex are important properties that are currently under investigation in our laboratories concerning the ability of the complex to act as an NO carrier or scavenger.

The presence of two differently charged nitrosyl groups in complex **1** was confirmed by X-ray diffraction studies. Indeed, the crystal structure determination reveals that two crystallographically independent ion complexes are present in the crystal. The compound crystallizes in the monoclinic space group $P2_1/c$, with two independent Fe^{2+} ions, one sited on a general position (Fe1) and another one sited on a crystallographic inversion center (Fe2). The first one is at the center of a cyclam group and in the plane of the nitrogen atoms to which it is bonded (rms deviation of atoms Fe1, N12, N13, N14, N15 from least squares plane is 0.035) and its approximate octahedral configuration is completed by the N atom of a nitrosyl group and a Cl^- ion, at opposite vertices of the axial direction which is nearly perpendicular to the cyclam nitrogen atoms plane. The second Fe^{2+} ion has a configuration similar to that of the first one, except for the fact that the Cl^- ion and the NO group are disordered, both sited in both vertices of the axial direction with one half occupation factors. The structure is completed by three independent PF_6^- groups (one in two disordered orientations as often occurs for these systems) all sited on general positions, and a disordered potassium cation, with an occupation number of one half. The first cation corresponds to *trans*-$[(cyclam)Fe(NO^+)Cl)]^{2+}$ (I) and the second one to *trans*-$[(cyclam)Fe(NO^0)Cl]^+$ (II). ORTEP projections are shown in Fig. 3. Bond lengths and angles are given in Table 2.

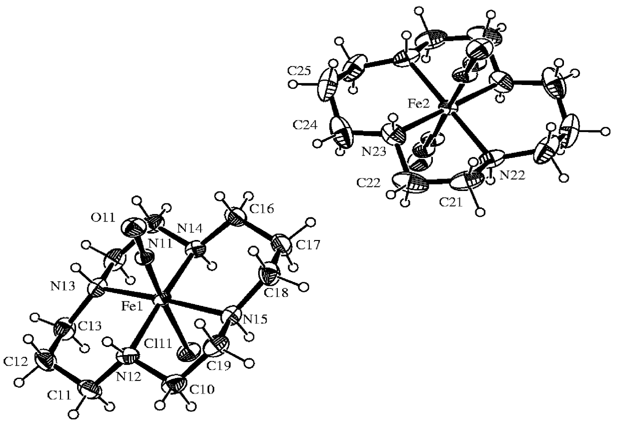

Fig. 3 ORTEP view of the two complex cations, showing the atom labeling and the 30% probability ellipsoids.

Table 2 Selected bond lengths (Å) and angles (°) for the *trans*-K$\{[FeCl(NO^0)(cyclam)]\cdot[FeCl(NO^+)(cyclam)]_2\}(PF_6)_6$ complex, e.s.d.s in parentheses

Fe(1)–Cl(11)	2.2476(11)	O(11)–N(11)	1.131(4)
Fe(1)–N(11)	1.648(3)	Fe(2)–Cl(21)	2.197(4)
Fe(1)–N(12)	2.021(3)	Fe(2)–N(21)	1.630(10)
Fe(1)–N(13)	2.016(3)	Fe(2)–N(22)	2.006(4)
Fe(1)–N(14)	2.002(3)	Fe(2)–N(23)	2.007(4)
Fe(1)–N(15)	2.014(3)	O(21)–N(21)	1.194(11)
N(14)–Fe(1)–N(15)	94.49(13)	N(13)–Fe(1)–N(12)	94.14(14)
N(14)–Fe(1)–N(13)	85.36(13)	O(11)–N(11)–Fe(1)	177.8(3)
N(15)–Fe(1)–N(13)	174.66(13)	N(23)–Fe(2)–N(22)^i	94.30(18)
N(14)–Fe(1)–N(12)	175.48(13)	N(23)–Fe(2)–N(22)	85.70(18)
N(15)–Fe(1)–N(12)	85.59(14)	O(21)–N(21)–Fe(2)	177(2)

The Fe–N(cyclam) bond lengths are similar in the two moieties and in excellent agreement with those of Fe–N(amine) found in the *trans*-$[(cyclam)Fe(NO)Cl)](ClO_4)$ complex (III) reported by Hauser and coworkers.[16] However, the Fe1–N(11) and Fe(2)–N(21) bond lengths in complex **1** are 1.648(3) and 1.630(10) Å, respectively, both shorter than in compound (III) [1.820(4) Å] in which it is considered to be of the $\{Fe–NO\}^7$ type. The coordinated nitric oxide forms a bent Fe–NO moiety with a bond angle of 144.0(4)° in (III) and is approximately linear in (I) [177.8(3)°] and (II) [177(2)°]. While these bond angles are quite similar in complexes (I) and (II), their NO bond lengths of 1.131(4) and 1.194(11) Å suggest that the nitric oxide groups are coordinated to the iron(II) centers in the different oxidation states NO^+ and NO^0, respectively. The shorter N–O bond, 1.131(4) Å, is comparable to the correspondent distance of 1.128(5) Å found in *trans*-$[(cyclam)RuCl(NO)]^{2+}$, to which the NO^+ character was also attributed.[3] The two *ν*NO stretching frequencies observed in the IR spectrum are consistent with the presence of these different species. The interpretation of the two independent differently charged NO groups and the presence of the disordered potassium ion with the same occupation factor as that of the *trans*-$[(cyclam)Fe(NO^0)Cl]^+$ species, gives the correct charge balance for the structure. This requires that both iron atoms are present in the Fe^{2+} oxidation state, a fact that is also supported by the lack of an Fe^{3+} EPR signal.

The EPR spectra of a powder sample of the *trans*-K$\{[FeCl(NO^0)(cyclam)]\cdot[FeCl(NO^+)(cyclam)]_2\}(PF_6)_6$ complex in X (9.268 GHz) and Q (34.331 GHz) bands, are shown in Figs. 4A and B, respectively.

Measurements were performed at two different temperatures, RT and 100 K. At RT the X band spectrum is typical of a radical, with anisotropic *g* factor values around 2.029 and a line width of 8.38 mT. The spectrum at 100 K clearly shows a hyperfine splitting structure. This splitting is more evident in the Q band spectrum at both temperatures. Tentative spectral simulations at both frequencies and temperatures were unsuccessful, probably due to the intermolecular dipolar spin couplings that broaden the spectra and reduce the spectral resolution.[16]

The *g* value and nitrogen hyperfine structure are consistent with an unpaired electron occupying a NO *π** orbital in the

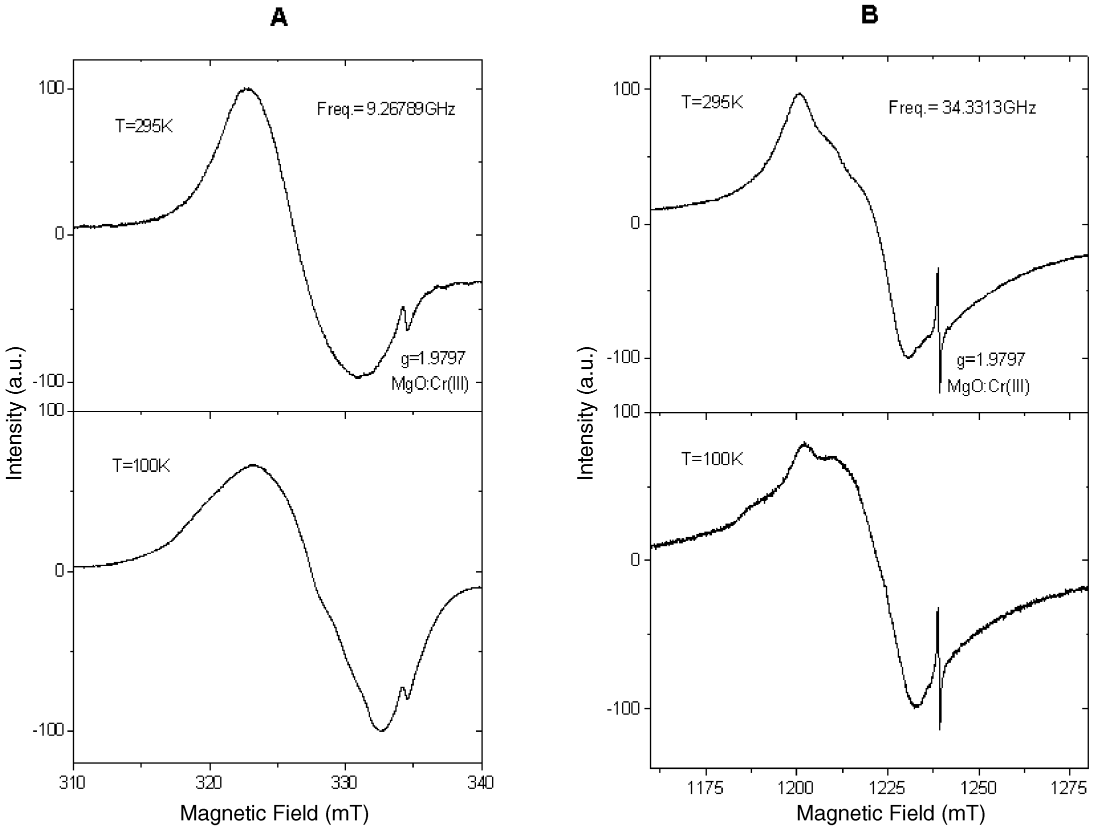

Fig. 4 EPR spectra of the powder sample of *trans*-K{[FeCl(NO^0)(cyclam)]·[FeCl(NO$^+$)(cyclam)]$_2$}(PF$_6$)$_6$ in (A) the X band (9.268 GHz) and (B) the Q band (34.331 GHz) measured at 295 and 100 K, respectively. The sharp line is a *g* marker as indicated.

{FeNO}^{7} moiety with significant NO$^•$ character which explains the appearance of the observed splitting. Measurements in a wide range of magnetic field and different temperatures, including 4.3 K, demonstrated the non-existence of a paramagnetic species with the Fe(III) ion.

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