

One-pot synthesis, physicochemical characterization and crystal structures of *cis*- and *trans*-(1,4,8,11-tetraazacyclotetradecane)-dichloroiron(III) complexes †

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The synthesis and characterization of *cis*- and *trans*-[Fe(cyclam)Cl₂]⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) are described. The assignment of geometrical configuration to these complexes has been made on the basis of their infrared spectra in the 800–900 cm⁻¹ region. In addition, the molecular structures of the *cis* and *trans* derivatives were determined by X-ray diffraction. Both complexes have a d⁵ electronic system, the *cis* and *trans* species being respectively in a high spin and a low spin configuration. These two isomers are fully characterized by electrochemistry and they are simultaneously observed in the reaction mixture by cyclic voltammetry. This study shows that the reactivity towards dioxygen of the two reduced isomers is different, and that the formation of the oxygenated species is not observed in some solvents.

Since the early 1960s, the synthesis of a very large number of metallated heterocycles have been reported.¹ These synthetic endeavors have provided the raw material for a multitude of research projects in many areas including biological studies, metal-ion catalysis, and metal-ion discrimination. Some of these studies have resulted in industrial and medical applications.²

Aza macrocycles generally act as strong field ligands with the disadvantage that they are usually not able to complete the ion co-ordination sphere.³ This is the case for iron(III), which is a very hard acidic metal ion. However, this ion has a reasonable affinity for 1,4,8,11-tetraazacyclotetradecane (cyclam).² Cyclam is a macrocyclic tetraamine possessing a 14-membered ring which forms stable complexes with many metal ions.^{4–7} Iron complexes possess a co-ordination number of six, as a result, the iron(III) cyclam complex has two anionic ligands. It is also well known that cyclic polyamines such as cyclam have a number of distinct conformations and for cyclam, five forms are possible.⁸ Moreover, the co-ordinated ligands can exist in a *cis* or *trans* configuration and both forms have been well described in the cobalt series.^{9–12} In the iron series, the corresponding *cis* and *trans* iron complexes have been identified and characterized by infrared spectroscopy.¹³ The *trans*-dichloro iron(III) cyclam complex was formed by warming the *cis* iron precursor in aqueous solution on a steam-bath.

Such complexes have already been utilized as olefinic epoxidation catalysts using dioxygen–aldehyde systems.^{14–17} Thus, it has been shown that the *trans* isomer exhibits the highest activity to activate dioxygen in the presence of linolenic acid [CH₃(CH₂CH=CH)₃(CH₂)₇CO₂H] in degrading tetraphenylcyclopentadienone; the activity of the corresponding *cis* isomer is almost negligible for the same reaction.^{15,16} To explain such a difference in reactivity towards dioxygen in the presence of reducing agents, Nishida and co-workers^{15,16} suggested that an intermediate should be formed only when aldehyde (benzaldehyde, isobutyraldehyde), dioxygen and the *trans* iron(III) cyclam complex are simultaneously present. This intermediate could be only formed in the presence of the *trans* iron complex due to the lability of the axial chloride ligand. In order to confirm this hypothesis, we decided to fully characterize the two iron cyclam isomers and to study their reactivity towards dioxygen.

We report here a one-pot synthesis in which the two isomers are simultaneously formed and then separated. The characterization is made on the basis of various analytical methods. The two isomers have been identified by electrochemistry and they are simultaneously observed in the reaction media by cyclic voltammetry. It is shown that the reactivity towards dioxygen of the two reduced isomers is different. Moreover, the formation of the oxygenated species depends upon the nature of the solvent. In addition, the molecular structures of the *cis* and *trans* derivatives were determined by X-ray diffraction.

Experimental

Chemicals

Cyclam was synthesized in our laboratory as previously reported.^{6,18,19} For all syntheses, chemicals were obtained commercially and used as received without further purification. For the electrochemical studies, methanol was purchased from the Carlo Erba Company and distilled over activated neutral alumina prior to use. Dimethyl sulfoxide (dmsO) was obtained from the SDS Company and dried over activated molecular sieves (4 Å), dimethyl sulfide obtained from Acros was used as received. The electrolyte salts, tetra-*n*-butylammonium hexafluorophosphate (NBu₄PF₆) and tetra-*n*-butylammonium tetrafluoroborate (NBu₄BF₄) were used as received from Fluka and Acros, respectively. Dioxygen gas was obtained from Air Liquide Company (grade C).

Preparation of the iron complexes

***cis*-(1,4,8,11-Tetraazacyclotetradecane)dichloroiron(III) chloride 1.** The *cis*-(1,4,8,11-tetraazacyclotetradecane)dichloroiron(III) chloride complex was prepared by the addition of methanolic FeCl₂ (100 mg in 5 cm³) to a stirred methanolic solution of cyclam (100 mg in 5 cm³) followed by the addition of concentrated HCl (2 cm³). Subsequently, air was bubbled through the reaction mixture for 1 h to oxidize the Fe^{II} complex to the Fe^{III} one. The yellow solid, which was formed on standing, was collected and recrystallized by adding water to the saturated methanolic solution of the complex (163 mg, 90%) (Found: C, 32.9; H, 6.9; Cl, 29.5; N, 15.3. C₁₀H₂₄Cl₃FeN₄ requires C, 33.1; H, 6.7; Cl, 29.3; N, 15.4%).

† Non-SI units employed: eV ≈ 1.602 × 10⁻¹⁹ J and G = 10⁻¹ T.

Table 1 X-Ray experimental parameters

Compound	1	2
Formula	C ₁₀ H ₂₄ Cl ₃ FeN ₄	C ₁₀ H ₂₄ Cl ₆ Fe ₂ N ₄
<i>M</i>	362.53	524.74
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.488(2)	6.407(2)
<i>b</i> /Å	14.450(3)	24.175(7)
<i>c</i> /Å	14.713(3)	13.524(3)
β/°	102.28(3)	99.82(3)
<i>U</i> /Å ³	1555	2064
<i>Z</i>	4	4
<i>F</i> (000)	756	1064
<i>D</i> /g cm ⁻³	1.548	1.689
Diffractometer	Siemens R3m/V	Enraf-Nonius CAD4
λ/Å	0.710 73	0.710 73
μ/cm ⁻¹	14.7	21.8
Absorption correction	XABS2 ²¹	Not corrected
Decay	No decay	3.8% corrected
<i>TK</i>	130	R.T.
sin θ/λ _{max}	0.756	0.703
<i>hkl</i> Ranges	0–11, –21 to 21, –22 to 22	0–8, 0–33, –18 to 18
Scan type	ω	ω–2θ
Reflections collected	11 163	6452
Independent reflections used, <i>N</i> _o	5636 (all data)	5973 (all data)
No. variables, <i>N</i> _v	179	199
<i>R</i> (<i>F</i>) ^a	0.046 (<i>I</i> > 2σ <i>I</i>)	0.031 (<i>I</i> > 2σ <i>I</i>)
<i>wR</i> 2(<i>F</i> _o ²) ^b	0.119 (all data)	0.083 (all data)
	0.106 (<i>I</i> > 2σ <i>I</i>)	0.076 (<i>I</i> > 2σ <i>I</i>)
Goodness of fit ^c	0.71	1.1

^a $R(F) = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $wR2(F_o^2) = [\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]$ where $w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 6.34P]$ for **1**, $1/[\sigma^2(F_o^2) + (0.03P)^2 + 1.53P]$ for **2** and $P = (F_o^2 + 2F_c^2)/3$. ^c Goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$.

trans-(1,4,8,11-Tetraazacyclotetradecane)dichloroiron(III) tetrachloroiron(III) **2**. *trans*-(1,4,8,11-Tetraazacyclotetradecane)dichloroiron(III) tetrachloroiron(III) was formed by slow evaporation of the filtrate of *cis*-(1,4,8,11-tetraazacyclotetradecane)dichloroiron(III) at room temperature (18 mg, 7%) (Found: C, 23.1; H, 4.7; Cl, 39.9; N, 10.8. C₁₀H₂₄Cl₆Fe₂N₄ requires C, 22.9; H, 4.6; Cl, 40.5; N, 10.7%).

The analogous perchlorate complex was obtained *via* thermal isomerization of the corresponding chloride salt of its *cis* analog as previously described.¹³ This isomerization reaction was carried out in a phosphate buffered solution (pH 7) to prevent demetallation of the macrocyclic complex.

Instrumentation

Infrared spectra were recorded on a Bruker IFS 66v Fourier-transform spectrometer and samples were prepared as 1% dispersions in CsI pellets. Microanalyses were performed by the Service Central d'Analyse du Centre National de la Recherche Scientifique (Vernaison, France). X-Band ESR spectra were obtained by the use of a Bruker ESP 300 spectrometer equipped with an Oxford Instrument Cryostat. The calibration of the ESR spectra was performed using the diphenylpicrylhydrazyl radical (dpph) as a standard. Electrochemical experiments were performed using a model 273A EG&G potentiostat controlled by a PC computer using the 270/250 Research Electrochemistry Software (version 4.23) marketed by EG&G. The actual experiments were performed in a three-electrode cell using a glassy carbon disc (GC) as the working electrode, a platinum spiral as the counter electrode, and a saturated calomel electrode (SCE) as the reference. The connection between the cell and the reference electrode was achieved by a bridge, fitted with a porous glass sintered disc, containing the same solvent–electrolyte as used in the cell except in the experiments where large quantities of dimethyl sulfide were present. In those particular experiments, the bridge contained 0.1 M NBu₄PF₆–MeOH. All potentials were referenced to the

SCE. Dioxygen was bubbled into solutions for at least 1 min, and up to 20 min in the studies performed in dmso.

Crystallography

Crystal structure of complex 1. An orange crystal of **1** (0.32 × 0.32 × 0.13 mm) was mounted on a Siemens R3m/v diffractometer. The data were collected at 130 K with graphite-monochromatized Mo-Kα radiation. A total of 11 163 intensities (5636 unique reflections), collected up to sin θ/λ = 0.756 Å⁻¹, were reduced with the XDISK data reduction programs,²⁰ no decay was observed in the standard reflections. The structure was solved *via* direct methods and refined (based on |*F*²| using all independent reflections) with full-matrix least-squares methods (Siemens SHELXTL, version 5.03²¹). An empirical absorption correction was applied.²² All non-hydrogen atoms were refined with anisotropic thermal parameters using all unique reflections. Hydrogen atoms attached to carbon were included in their calculated positions and refined with a riding model while hydrogen atoms attached to nitrogen were located on a Fourier-difference map and allowed to refine freely. Final agreement indices were *R*1 (observed data) = 0.046 and *wR*2 (all data) = 0.119. Experimental details are given in Table 1.

Crystal structure of complex 2. A brown crystal of **2** (0.25 × 0.20 × 0.18 mm) was mounted on a CAD4 Enraf-Nonius diffractometer. The data were collected at room temperature, with graphite-monochromatized Mo-Kα radiation. A total of 6452 intensities, collected up to sin θ/λ = 0.7 Å⁻¹, were reduced with the XCAD4PC data reduction programs.²³ A monotonic linear decay of 3.8% was observed and corrected. The structure was solved *via* direct methods and refined (based on |*F*²| using all independent reflections) with full-matrix least-squares methods.²⁴ All non-hydrogen atoms were refined with anisotropic thermal parameters using all unique reflections. Hydrogen atoms attached to carbon were included in their calculated positions and refined with a riding

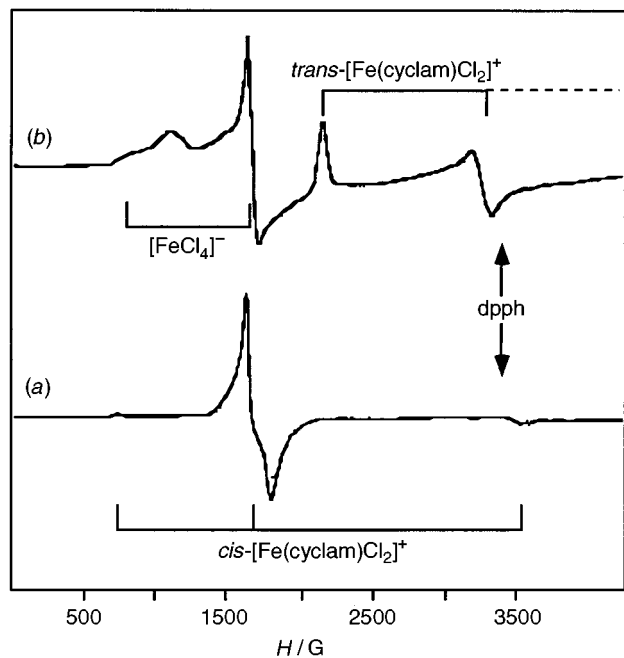


Fig. 1 X-Band ESR spectra recorded in MeOH at 4 K of (a) *cis*-[Fe(cyclam)Cl₂]⁺ and (b) *trans*-[Fe(cyclam)Cl₂]⁺ (the high field signal at *g* 1.15 is not shown)

model while hydrogen atoms attached to nitrogen were located on a Fourier-difference map. Final agreement indices were *R*1 (observed data) = 0.031 and *wR*2 (all data) = 0.083. Experimental details are given in Table 1.

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Results and Discussion

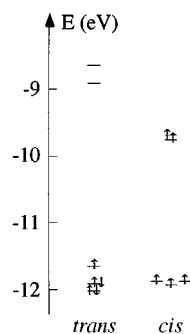
Characterization of the neutral compounds

The two complexes are highly coloured (orange for **1** and brown for **2**) and appear to be stable indefinitely in the solid state. The infrared spectra of complexes **1** and **2** in the 800–900 cm⁻¹ region are characteristic for the conformation of the macrocyclic amine ligand, and give information about the coordination scheme of the central metal ion. The other ligands or counter ions give no characteristic band in this region. The assignment of the geometrical configurations of [Fe(cyclam)Cl₂]⁺ in **1** and **2** are proposed on the basis of their infrared fingerprint pattern.¹³ The *trans* complex showed two groups of bands separated by 80 cm⁻¹. The main band at lower wavenumber, which is essentially due to the methylene group, consists of a sharp absorption close to 810 cm⁻¹, and the group at the highest wavenumbers, due to the secondary amine vibration, mainly consists of two bands close to 890 cm⁻¹. For the low symmetry *cis* isomer, the methylene vibration invariably shows two bands at around 800 cm⁻¹, and the amine vibrations give at least three bands in the range 850–870 cm⁻¹. The infrared spectrum of complex **2** shows two characteristic bands at 885 (broad) and 806 cm⁻¹; this is in good agreement with a *trans* configuration for the iron metal centre. In contrast, the presence of five bands between 790 and 870 cm⁻¹ [$\nu(\text{CH}_2) = 795$ and 805 cm⁻¹ and, $\nu(\text{NH}) = 850, 860$ and 865 cm⁻¹] is in good agreement with a *cis* co-ordination of the iron atom for complex **1**.

The ESR spectra of complexes **1** and **2** indicate that the *cis* and *trans* isomers have dissimilar electronic configurations. The *g* values (3.29, 2.19 and 1.15) for the *trans* isomer in frozen methanolic solutions at 4 K are in good agreement with a low-spin d⁵ iron center possessing rhombic symmetry, the ground state being ²T₂(t_{2g}⁵) [Fig. 1(a)]. In contrast, three signals at *g* 9.6, 4.2 and 2.0 are observed for the *cis* isomer [Fig. 1(b)]. This spectrum is characteristic of a high spin complex with axial

Table 2 Selected bond distances (Å) and bond angles (°) for complex **1**

Fe–Cl(1)	2.2982(8)	Fe–N(2)	2.200(2)
Fe–Cl(2)	2.3063(8)	Fe–N(3)	2.155(2)
Fe–N(1)	2.153(2)	Fe–N(4)	2.204(2)
N(1)–Fe–Cl(1)	97.32(6)	Cl(1)–Fe–Cl(2)	93.21(3)
N(2)–Fe–Cl(1)	176.96(6)	N(1)–Fe–N(2)	79.68(8)
N(3)–Fe–Cl(1)	97.39(6)	N(1)–Fe–N(3)	158.40(8)
N(4)–Fe–Cl(1)	88.64(6)	N(1)–Fe–N(4)	85.07(8)
N(1)–Fe–Cl(2)	98.42(6)	N(2)–Fe–N(3)	85.38(8)
N(2)–Fe–Cl(2)	87.70(6)	N(2)–Fe–N(4)	90.64(8)
N(3)–Fe–Cl(2)	96.46(6)	N(3)–Fe–N(4)	79.56(8)
N(4)–Fe–Cl(2)	175.80(6)		



Scheme 1

symmetry [$A_1(t_{2g}^3, e_g^2)$].²⁵ These ESR measurements agree well with the reported magnetic moment data {*trans*-[Fe(cyclam)Cl₂]⁺, $\mu_{\text{eff}} = 2.71 \mu_B$ and *cis*-[Fe(cyclam)Cl₂]⁺, $\mu_{\text{eff}} = 6.03 \mu_B$ }.¹³ In Fig. 1(a), a strong signal with a *g* value close to 4 and smaller absorptions at lower field are observed in the low-field range of the ESR spectrum. The comparison between the ESR spectra of **1** and **2** indicated that the low field signals are not due to the Fe(cyclam) moiety, but to the counter anion FeCl₄⁻. This was confirmed by the determination of the structures as described in the following paragraphs. Final verification was obtained by recording an ESR spectrum of FeCl₄H.²⁶

Simple extended Hückel transition metal calculations performed on both compounds indicate that the iron d orbital splitting is significantly larger for complex **2** than for **1**. Therefore, the *trans* ligands induce the strongest field around the iron center resulting in a low spin state (Scheme 1).

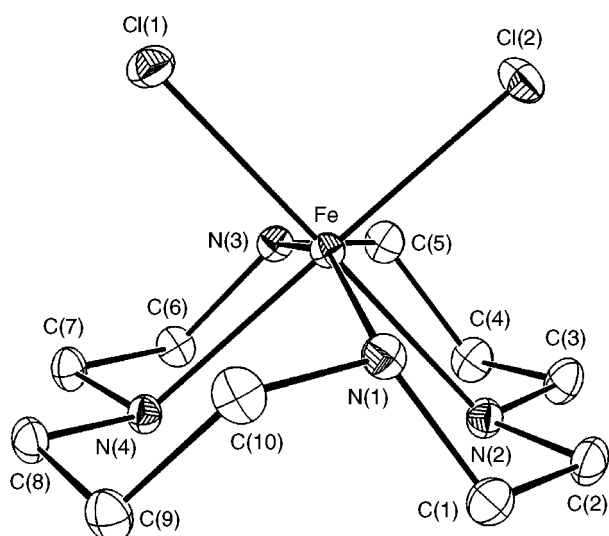
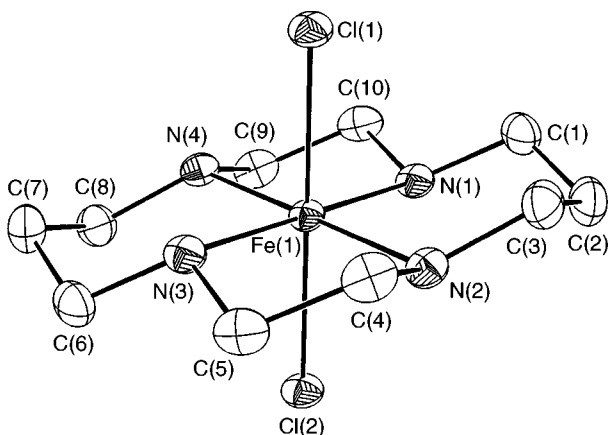
Crystal structure determination

The asymmetric unit of **1** contains a *cis*-[Fe(cyclam)Cl₂]⁺ cation and a chloride anion, Cl⁻. Selected distances and angles are listed in Table 2. As shown in Fig. 2, the cation adopts a *cis*-V conformation. The octahedrally co-ordinated iron(III) atom is bonded to the four nitrogen atoms of the cyclam and to the two *cis*-chlorine atoms. As expected for such a geometry, two significantly different Fe–N distances are found: 2.153(2), 2.155(2) Å for Fe–N(1) and Fe–N(3) and 2.200(2), 2.204(2) Å for Fe–N(2) and Fe–N(4). These values are close to the ideal M–N distances in the *cis*-V folded conformation²⁷ and are consistent with a high-spin state. As expected for a high-spin complex, the mean Fe–Cl distance of 2.302(5) Å is slightly larger than the Fe–Cl distances found in the *trans* complex.

The asymmetric unit of **2** contains a *trans*-[Fe(cyclam)Cl₂]⁺ cation and a FeCl₄⁻ anion. Selected distances and angles are listed in Table 3. As is usual for octahedral complexes, the cyclam exhibits a *trans*-III conformation (see Fig. 3).⁸ The iron atom lies exactly in the plane formed by the four nitrogen donor atoms which form a planar rectangular cavity of 2.96 × 2.72 Å². Two axial chlorine atoms bonded to the iron atom lead to a distorted octahedral co-ordination scheme. The mean (Fe–N) distance of 2.006(3) Å is close to the optimal M–N distances for

Table 3 Selected bond distances (Å) and bond angles (°) for complex **2**

Fe(1)–Cl(1)	2.290(1)	Fe(1)–N(4)	2.005(2)
Fe(1)–Cl(2)	2.288(1)	Fe(2)–Cl(3)	2.191(1)
Fe(1)–N(1)	2.003(2)	Fe(2)–Cl(4)	2.172(1)
Fe(1)–N(2)	2.009(2)	Fe(2)–Cl(5)	2.171(1)
Fe(1)–N(3)	2.007(2)	Fe(2)–Cl(6)	2.184(1)
Cl(1)–Fe(1)–Cl(2)	179.69(2)	N(1)–Fe(1)–N(4)	85.09(8)
N(1)–Fe(1)–Cl(1)	91.09(6)	N(2)–Fe(1)–N(3)	85.09(8)
N(2)–Fe(1)–Cl(1)	91.86(6)	N(2)–Fe(1)–N(4)	179.77(8)
N(3)–Fe(1)–Cl(1)	88.70(6)	N(3)–Fe(1)–N(4)	94.96(8)
N(4)–Fe(1)–Cl(1)	88.37(6)	Cl(3)–Fe(2)–Cl(4)	110.38(4)
N(1)–Fe(1)–Cl(2)	88.93(6)	Cl(3)–Fe(2)–Cl(5)	109.55(4)
N(2)–Fe(1)–Cl(2)	88.44(6)	Cl(3)–Fe(2)–Cl(6)	109.66(4)
N(3)–Fe(1)–Cl(2)	91.28(6)	Cl(4)–Fe(2)–Cl(5)	108.87(4)
N(4)–Fe(1)–Cl(2)	91.33(6)	Cl(4)–Fe(2)–Cl(6)	108.14(4)
N(1)–Fe(1)–N(2)	94.86(8)	Cl(5)–Fe(2)–Cl(6)	110.23(4)
N(1)–Fe(1)–N(3)	179.78(7)		

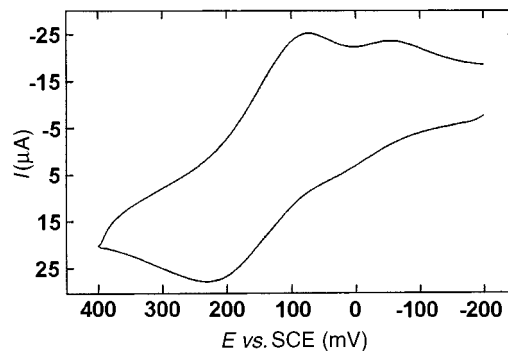
**Fig. 2** View of the *cis*-[Fe(cyclam)Cl₂]⁺ cation illustrated with 30% probability thermal ellipsoids**Fig. 3** View of the *trans*-[Fe(cyclam)Cl₂]⁺ cation illustrated with 30% probability thermal ellipsoids

a *trans*-III conformation.²⁷ Similar values have been reported for low-spin iron(III) cyclam complexes: 1.993(2) and 2.004(6) Å in *trans*-[Fe(H₂diac)Cl₂]⁺ and in *trans*-[Fe(diac)]⁺, respectively (H₂diac = *trans*-1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylic acid).²⁸ The mean (Fe–Cl) distance [2.289(1) Å] is in good agreement with the values observed for octahedral iron(III) complexes.²⁹ As shown in Table 3, the FeCl₄[−] anion does not exhibit distortion from tetrahedral geometry. The mean ⟨Fe–Cl⟩

Table 4 Electrochemical potentials (*E*_i) of the *cis* and *trans* isomers of [Fe(cyclam)Cl₂]⁺ in various solvents

Solvent	<i>cis</i> -[Fe(cyclam)Cl ₂]Cl <i>E</i> _i /V vs. SCE	<i>trans</i> -[Fe(cyclam)Cl ₂][ClO ₄] <i>E</i> _i /V vs. SCE
MeOH	0.154	−0.013*
dmsO	−0.033	−0.012
Pyridine	−0.177	−0.087

* Obtained with [Fe(cyclam)Cl₂]FeCl₄ in NBu₄BF₄–MeOH.

**Fig. 4** Cyclic voltammogram of the reaction mixture, FeCl₂·4H₂O and cyclam, in MeOH containing 0.1 M NBu₄PF₆. Scan rate 100 mV s^{−1}

distance of 2.18(1) Å observed in the anion compares well with values reported in literature.³⁰

Electrochemistry

As previously described, *cis*- and *trans*-[Fe(cyclam)Cl₂]⁺ are formed simultaneously in methanol by reaction of FeCl₂·4H₂O and cyclam (the cyclic voltammogram is shown in Fig. 4). On the basis of current intensities in cyclic voltammetry, the major species formed is the *cis*-[Fe(cyclam)Cl₂]⁺ complex. Only *trans*-[Fe(cyclam)Cl₂]FeCl₄, soluble in methanol, has been isolated; the corresponding chloride salt is not. The assignment of each isomer was made on the basis of the reduction potentials of *cis*-[Fe(cyclam)Cl₂]Cl (*E*_i = 0.154 V vs. SCE) and *trans*-[Fe(cyclam)Cl₂]FeCl₄ (*E*_i = −0.013 V vs. SCE). The diffusion coefficients of both species are assumed to be approximately equal. The two geometric isomers are readily prepared in the oxidized Fe(III) states as described previously by Chan and Poon.¹⁴

The electrochemical potentials of these iron(III) complexes, summarized in Table 4, depend on the nature of the solvent. Importantly, the half-wave potentials of the *cis* isomer are negatively shifted by approximately 320 mV when one changes the solvent from methanol to pyridine. The effective trend appears to be: the better the solvent donor, the more negative the reduction potential. This shift in reduction potential appears to be a bulk medium effect; for example, there is no exchange of chloride ions for the *cis* iron(III) complex dissolved in dmsO. The quantification of chloride ions was achieved by cyclic voltammetry using a chloride standard, bis(triphenylphosphoranylidene)ammonium chloride, N(PPh₃)₂Cl. Obviously, the presence of the open cavity for the *cis* complex provides an easily accessible co-ordination site. The corresponding *trans* compound has half-wave reduction potentials that are negatively shifted only by about 75 mV by replacing methanol with pyridine. Moreover, the reduction potentials are almost identical in MeOH and dmsO. Thus, the solvent has only a mild influence upon the reduction potential of the *trans* complex in organic solvents.

The solvent plays a significant role when the co-ordination of small molecules such as dioxygen occurs. Previously, it was noted by Nishida *et al.*¹⁵ that *trans*-[Fe(cyclam)Cl₂]ClO₄, when the iron centre is in a +2 oxidation state, co-ordinates dioxygen

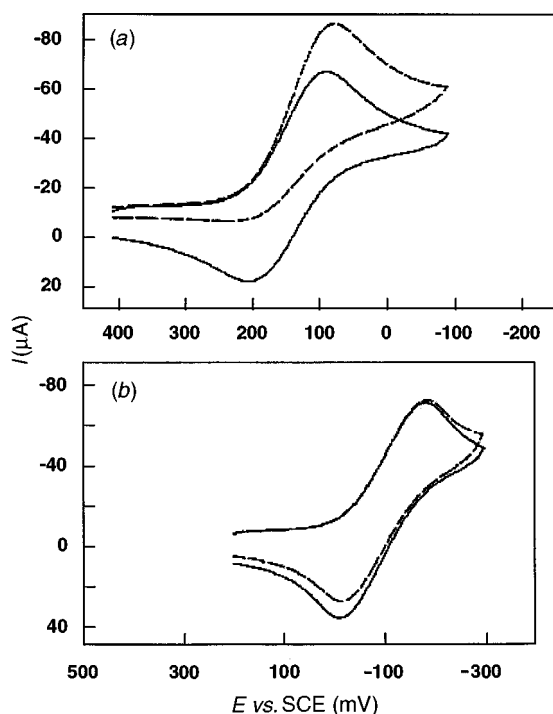


Fig. 5 Cyclic voltammogram of *cis*-[Fe(cyclam)Cl₂]Cl in methanol, 0.1 M NBu₄PF₆ (a) without and (b) with dmsu (5700 equivalents). Voltammograms obtained under an argon atmosphere (solid line) and in the presence of added dioxygen (broken line) are shown. Scan rate 100 mV s⁻¹

in dmsu. The *cis* complex does not co-ordinate dioxygen. Our first study was in agreement with these results. It is astonishing that the *trans* isomer, which has no apparent open co-ordination site for dioxygen, binds dioxygen. In contrast, a structural cavity exists in the *cis* isomer, suggesting an attractive binding site for dioxygen. Therefore, our electrochemical studies focused upon the question: 'Is the lack of co-ordination of dioxygen with the reduced *cis* isomer in dmsu attributable to blockage due to the dmsu molecules co-ordinated to the iron center, or does dmsu have a more significant role?'

Subsequent cyclic voltammetry was carried out in methanol which is a poor co-ordinating solvent. As expected, both isomers in their reduced Fe^{II} form co-ordinate dioxygen in methanol. The cyclic voltammogram of *cis*-[Fe(cyclam)Cl₂]Cl in methanol is presented in Fig. 5(a). In the presence of dioxygen, the peak potential at 0.082 V vs. SCE increases in magnitude and another reduction appears at -0.378 V vs. SCE (not shown). No peak potential corresponding to the reoxidation of Fe^{II} to Fe^{III} was detected in the presence of dioxygen. Another notable feature in the reduction of the *cis* isomer is the increase in cathodic current when dioxygen is present.

According to the high reactivity of the reduced *cis* Fe^{II} isomer in MeOH towards dioxygen, a lack of reactivity in dmsu is unexpected. As the methanol solvent is replaced by a potentially co-ordinative base like pyridine, the reduced *cis* isomer still reacts with dioxygen. The role of the sulfur atom in dmsu was investigated by recording cyclic voltammograms in solutions containing a large excess of dimethyl sulfide. In the presence of 5700 equivalents of Me₂S, the reduced *cis* isomer still reacts with dioxygen. An experiment was performed using the same experimental conditions with 5700 equivalents of dmsu, and the cyclic voltammetry of *cis*-[Fe(cyclam)Cl₂]Cl was unaffected by the presence of dioxygen [Fig. 5(b)].

Based upon the cyclic voltammetry study of *cis*-[Fe(cyclam)Cl₂]Cl, it is shown that dioxygen does not react with Fe^{III} in

the presence of dmsu which induces *a priori* a steric hindrance. With respect to the constraints of the cavity of this macrocyclic complex, it appears that the most favorable bonding mode should be an interaction with the macrocycle. Co-ordination to the iron center seems unlikely due to the large distance of the metal center from the macrocycle mean plane. Hydrogen bonding between the sulfur and oxygen atoms of the S=O group in dmsu and the hydrogen atoms associated with macrocyclic nitrogens could be the explanation for the lack of reactivity of the reduced *cis* isomer with dioxygen in the presence of dmsu.

To conclude our studies of the *cis*-[Fe(cyclam)Cl₂]Cl complex in dmsu, bulk electrolysis was conducted. The resulting reduced *cis* iron(II) complex seems to react with dioxygen. Therefore, the lack of reactivity noted in the cyclic voltammetry study could be attributed to a kinetically slow reaction rate compared to the reactivity of the *trans* species. However, during longer time-scales, a *cis* to *trans* isomerization cannot be ruled out.

References

- 1 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1st edn., 1989.
- 2 A. E. Martell and R. D. Hancock, *Modern Inorganic Chemistry*, ed. J. P. Fackler jun., Plenum Press, New York, 1996.
- 3 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
- 4 J. Van Alphen, *Recl.: J. R. Neth. Chem. Soc.*, 1936, **55**, 835.
- 5 J. Van Alphen, *Recl.: J. R. Neth. Chem. Soc.*, 1937, **56**, 343.
- 6 E. K. Barefield, *Inorg. Chem.*, 1972, **11**, 2273.
- 7 R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1995, **95**, 2529.
- 8 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
- 9 C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 2398.
- 10 C. K. Poon, *Inorg. Chim. Acta*, 1971, 322.
- 11 S. Yamaguchi, Y. Hayashi, M. Suzuki and A. Uehara, *Thermochim. Acta*, 1992, **208**, 191.
- 12 T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562.
- 13 P. K. Chan and C.-K. Poon, *J. Chem. Soc., Dalton Trans.*, 1976, 858.
- 14 W. Nam, R. Ho and J. S. Valentine, *J. Am. Chem. Soc.*, 1991, **113**, 7052.
- 15 Y. Nishida, N. Tanaka and S. Takahashi, *Chem. Lett.*, 1993, 411.
- 16 Y. Nishida and N. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1994, 2805.
- 17 W. W. Nam, H. J. Kim, S. H. Kim, R. Y. N. Ho and J. S. Valentine, *Inorg. Chem.*, 1996, **35**, 1045.
- 18 E. K. Barefield, F. Wagner and K. D. Hoges, *Inorg. Chem.*, 1976, **15**, 1370.
- 19 E. K. Barefield, D. Chueng and D. G. Van Derveer, *J. Chem. Soc., Chem. Commun.*, 1981, 302.
- 20 XDISK, Data reduction program, version 3.11, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1991.
- 21 G. M. Sheldrick, SHELXTL, Structure determination program, version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1996.
- 22 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.
- 23 K. Harms, XCAD4PC, Program for data reduction, University of Marburg, 1996.
- 24 G. M. Sheldrick, SHELX 97, Program for the solution of crystal structures, University of Göttingen, 1997.
- 25 A. Desideri, J. B. Raynor and C.-K. Poon, *J. Chem. Soc., Dalton Trans.*, 1977, 2051.
- 26 J. S. Avery, C. D. Burbridge and D. M. L. Goodgame, *Spectrochim. Acta, Part A*, 1968, **24**, 1721.
- 27 V. J. Thöm, C. C. Fox, J. C. A. Boeyens and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.
- 28 N. F. Curtis, L. Xin and D. C. Weatherburn, *Inorg. Chem.*, 1993, **32**, 5838.
- 29 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
- 30 F. A. Cotton and C. A. Murillo, *Inorg. Chem.*, 1975, **14**, 2467.

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