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A $Fe^{III}O_4N_2$ co-ordination sphere assembled *via* an enolate–imine–amide ligand. Effect of amide protonation on the redox behaviour and stereochemistry of the iron(III) centre †

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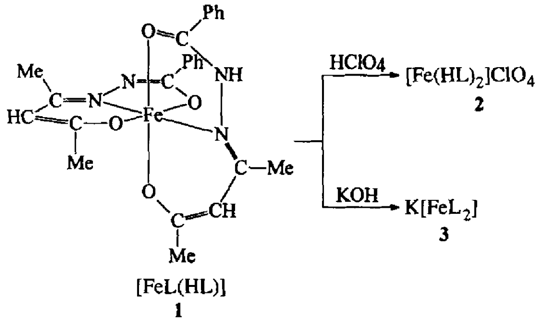
The reaction of anhydrous $FeCl_3$, acetylacetone benzoylhydrazone (H_2L) and KOH (1:2:3 mole ratio) in methanol produced an iron(III) complex, [FeL(HL)] **1**, the crystal structure of which was determined. Each ligand binds through enolate O, imine N and amide O atoms in meridional fashion. In the dianionic L both the enolic OH and the amide protons are dissociated, whereas in the monoanionic HL only the enolic OH is deprotonated. Addition of 1 equivalent of $HClO_4$ to **1** in MeOH gave $[Fe(HL)_2]ClO_4$ **2**. Similarly reaction of 1 equivalent of KOH with **1** yielded $K[FeL_2]$ **3**. All the complexes were characterized by analytical, spectroscopic, electrochemical and magnetic measurements. The metal centre in **1** is redox inactive. However, in cyclic voltammetric experiments **2** displayed $Fe^{III} \longrightarrow Fe^{II}$ reduction at −0.21 V and for **3** an oxidation at 0.40 V (*vs.* saturated calomel electrode) was observed due to $Fe^{III} \longrightarrow Fe^{IV}$ oxidation. Magnetic moments (at 298 K) of the three complexes reflect a $S = \frac{5}{2}$ spin state in each. The ESR spectra (at 298 K) of polycrystalline **1** and **2** are rhombic. On the other hand, an ideal axial spectrum was observed for **3**.

Higher-valent iron is of current interest because of its proven or postulated role in several biological processes.[1] Only a handful of co-ordination complexes of iron having oxidation state > +3 are known.[1d,2] Among these, biologically relevant O, N-co-ordinated species are extremely rare.[2f,g,i] Our original goal was to obtain a complex of higher-valent iron using the tridentate O,N,O-donor ligand, acetylacetone benzoylhydrazone MeC(OH)=CHC(CH$_3$)=NNHC(=O)Ph (H_2L), containing high-oxidation-state-promoting[3] amide and alcoholic hydroxy functionalities. During our attempts to prepare such a species we have isolated a mononuclear high-spin iron(III) complex, [FeL(HL)] **1** and found that the amide functions in it can be protonated or deprotonated. Reaction of **1** with $HClO_4$ or KOH results in facile conversion into $[Fe(HL)_2]ClO_4$ **2** or $K[FeL_2]$ **3** respectively. Further scrutiny of these complexes revealed unique relationships of the co-ordinated amide protonation states with the metal-centred redox properties and the stereochemistry of the iron(III) centre.

Proton-dependent electron-transfer processes are encountered quite often in biological redox systems.[4] In the above three complexes the protonation state of the co-ordinated amide functions dictates whether there will be any metal-centred redox process and if electron transfer is possible then in which direction the transfer will occur, *i.e.* whether reduction or oxidation of the iron(III) centre.

The ESR spectra of high-spin iron(III) species are extremely sensitive to the distortion of the co-ordination sphere around the metal centre. Because of this, ESR spectroscopy is being used as an efficient tool to establish the nature of iron(III) binding sites in biological systems.[5] For the present series of complexes the ESR results clearly indicate the strong dependence of the kind and extent of distortion of the iron(III) co-ordination sphere on the protonation states of the ligand amide functions.



Experimental

Materials

The compound H_2L was synthesized in 90% yield by condensing 1 equivalent of benzoylhydrazine and 1 equivalent of acetylacetone in methanol. Acetonitrile used for electrochemical experiments was purified by distillation from CaH_2 and stored over 3 Å molecular shieves. All other solvents and chemicals used were of analytical grade available commercially.

Physical measurements

Microanalytical data (C,H,N) were obtained with a Perkin-Elmer model 240C elemental analyser. Infrared spectra were recorded by using KBr pellets on a JASCO-5300 FT-IR spectrophotometer, electronic spectra on a JASCO-7800 UV/VIS spectrophotometer. Room-temperature magnetic susceptibilities were measured on a CAHN-3000 magnetic balance. Diamagnetic corrections calculated from Pascal's constants[6] were used to obtain the molar paramagnetic susceptibilities. The ESR spectra were recorded on a JEOL FE-3X spectrometer. An Elico digital conductivity meter was used to determine the solution electrical conductivity. A PAR model 370 electrochemistry system incorporating a model 175

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† *Non-SI units employed:* $G = 10^{-4}$ T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

universal programmer, model 174A polarographic analyser and model RE0074 X-Y recorder was employed for the electrochemical measurements. A platinum-disk working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used for the cyclic voltammetric experiments under a dry and purified dinitrogen atmosphere. The potentials reported are uncorrected for junction contributions.

Preparation of complexes

[FeL(HL)] 1. To a methanol solution (15 cm^3) of H_2L (550 mg, 2.52 mmol) and KOH (210 mg, 3.74 mmol) was added a solution (5 cm^3) of $FeCl_3$ (203 mg, 1.25 mmol) in methanol. The mixture was allowed to stir at room temperature in air for 3 h. The dark green solid which separated was filtered off, washed with water and dried in vacuum over anhydrous $CaCl_2$. Yield 340 mg (55%). Selected IR bands (cm^{-1}): 3331w, 1605m, 1561s, 1530s, 1431m, 1381s, 1329w, 1285m, 1138w, 1105w, 1069w, 1024m, 945m, 791m, 758m, 706s, 681m, 547m and 440m. Electronic spectral data in MeCN solution [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 608 (1050), 512 (sh), 480 (sh), 440 (sh), 351 (17 400) and 295 (19 300).

$[Fe(HL)_2]ClO_4$ 2. A methanol solution (10 cm^3) of 70% aqueous $HClO_4$ (1 cm^3) was prepared. Complex **1** (250 mg, 0.51 mmol) in methanol (5 cm^3) was treated with 0.44 cm^3 of the above $HClO_4$ solution. Immediately the mixture changed from brownish green to blue-green. It was allowed to stir at room temperature in air for 0.5 h, then filtered and to the filtrate CH_2Cl_2 (*ca.* 50 cm^3) was added followed by a large excess of hexane. The green solid precipitated was filtered off and dried under vacuum. Yield 240 mg (80%). Selected IR bands (cm^{-1}): 3281w, 1720w, 1603m, 1543s, 1506m, 1437m, 1348s, 1300m, 1225w, 1190w, 1100vs, 1020w, 945m, 793w, 706m, 683m, 623m, 548w and 455w. Electronic spectral data in MeCN solution [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 612 (1325), 440 (sh), 416 (sh), 347 (sh) and 304 (18 100).

$K[FeL_2]$ 3. To a methanol solution (30 cm^3) of complex **1** (300 mg, 0.61 mmol) was added KOH (35 mg, 0.62 mmol) in methanol (10 cm^3). The mixture was stirred magnetically at room temperature for 1 h, then filtered and left in air to evaporate slowly to 3–5 cm^3. The dark solid separated was filtered off and dried under vacuum. Yield 290 mg (90%). Selected IR bands (cm^{-1}): 1586m, 1526s, 1489s, 1431w, 1389s, 1281m, 1210w, 1171w, 1138w, 1069w, 1024m, 943m, 772m, 706s, 679w, 544w and 442w. Electronic spectral data in MeCN solution [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})]: 605 (880), 510 (sh), 475 (sh), 445 (sh), 350 (18 500) and 280 (20 200).

Crystallography

Single crystals of [FeL(HL)] **1** were obtained by slow evaporation of a MeOH–C_6H_6 (1 : 1) solution.

Crystal data. $C_{24}H_{25}FeN_4O_4$, $M = 489.3$, orthorhombic, space group $Pca2_1$, $a = 22.557(8)$, $b = 8.571(6)$, $c = 12.032(5)$ Å, $U = 2321(3)$ $Å^3$ (by least-squares refinement of 37 reflections having 2θ in the range 12–26°), $Z = 4$, $D_c = 1.400$ g cm^{-3}, dark plate (0.47 × 0.41 × 0.10 mm), μ(Mo-Kα) = 6.88 cm^{-1}, λ = 0.710 73 Å, $F(000) = 1020$.

Data collection and processing. Nicolet R3m/V diffractometer, ω-scan method ($3 < 2\theta < 45°$; crystal was weakly diffracting and few reflections with significant intensities were observed above 45°), graphite-monochromated Mo-Kα radiation; of 1811 reflections collected 1612 were independent and 961 observed [$F > 4\sigma(F)$]. No correction for absorption was applied. Two standard reflections measured after every 198 showed no significant variations during 19.98 h exposure to X-rays.

Solution and refinement. The position of the iron atom was determined from a Patterson map. The remainder of the structure emerged from a Fourier-difference map. The model was refined by full-matrix least-squares procedures. Owing to the limited size of the observed data set, only atoms Fe, N and O were refined anisotropically. Hydrogen atoms were included at calculated positions. Number of parameters 177, affording a data-to-parameter ratio of 5.4 : 1. The refinement on F converged (maximum shift/e.s.d. 0.001) to a final $R = 0.0652$, $R' = 0.0644$ and goodness of fit = 1.23 with the largest difference peak and hole 0.48 and −0.35 e $Å^{-3}$ respectively.

The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F) + 0.0009F^2]$. All calculations were carried out on a MicroVAXII computer using the SHELXTL PLUS programs.[7]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/107.

Results and Discussion

Synthesis and some properties

Complex **1** was prepared by treating $FeCl_3$, H_2L and KOH in 1 : 2 : 3 mole ratio in methanol. If the mole ratio is changed to 1 : 2 : 4 **1** is still precipitated but in considerably lower yield. Complex **3** can be recovered from the filtrate in the latter case. A more convenient method to prepare **3** is the addition of an equimolar amount of KOH to **1**. Similarly, **2** can be prepared by the reaction of **1** and $HClO_4$ in 1 : 1 mole ratio. Elemental analyses (Table 1) of the complexes are in satisfactory agreement with the proposed molecular formulae. Solution electrical conductivity values indicate the neutral character of **1** and 1 : 1 electrolytic nature[8] of **2** and **3**. The solid-state magnetic moments (Table 1) of the three complexes are very similar and correspond to a $S = \frac{5}{2}$ spin state of the iron(III) centre in each case. In the infrared spectra weak bands due to N–H stretches[9] were observed at 3331 and 3281 cm^{-1} for **1** and **2**, respectively. A medium-intensity band at ≈1604 cm^{-1} observed for these complexes is likely due to the C=O stretch of the co-ordinated protonated amide function.[10] No such band is observed for **3**. On the other hand, the electronic spectral features of the complexes are very similar. A peak at ≈610 nm followed by several shoulders and two intense high-energy (≈350 and ≈300 nm) absorptions are observed, due to charge transfer and intraligand transitions.[11]

Structure of complex 1

The structure of the [FeL(HL)] complex is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 2. The iron(III) ion has an O_4N_2 co-ordination sphere. Both ligands bind the metal ion in meridional fashion through the enolate O, the imine N, and the amide O atoms. A large distortion of the FeO_4N_2 octahedron is clearly evident from the bond distances and angles. The chelate bite angles in the five-membered rings formed by the amide O and imine N are smaller than those in the six-membered rings formed by the enolate O and imine N as expected. The Fe–O(2) distance is significantly larger than Fe–O(4). Also C(6)–O(2) is shorter than C(18)–O(4). Thus in the first ligand the amide group is protonated and the keto oxygen is connected to the metal ion. This is also reflected in the amide C–N distances of the two ligands (Table 2). The Fe^{III}–O (enolate)[12] and Fe^{III}–N (imine)[12b,13] distances are unusual.

Redox properties

The cyclic voltammograms of complexes **2** and **3** are shown in Fig. 2. Both display irreversible responses, at −0.21 and 0.40 V

Table 1 Elemental analysis,[a] bulk susceptibility[b] and electrical conductivity[c] data

Compound	Analysis (%) C	H	N	μ_{eff}/μ_B	Λ_M/Ω^{-1} cm^2 mol^{-1}
1	58.7	5.10	11.35	5.88	9
	(58.9)	(5.15)	(11.45)		
2	48.7	4.35	9.45	5.74	154
	(48.9)	(4.45)	(9.50)		
3	54.45	4.55	10.8	5.81	119
	(54.65)	(4.60)	(10.6)		

[a] Calculated values are in parentheses. [b] At 298 K. [c] In MeCN.

Table 2 Selected bond distances (Å) and angles (°) for [FeL(HL)] **1**

Fe–O(1)	1.943(11)	Fe–O(3)	1.969(12)
Fe–O(2)	2.127(11)	Fe–O(4)	1.952(12)
Fe–N(1)	2.168(12)	Fe–N(3)	2.066(13)
C(6)–O(2)	1.259(19)	C(18)–O(4)	1.322(18)
C(6)–N(2)	1.338(19)	C(18)–N(4)	1.295(20)
N(1)–N(2)	1.385(18)	N(3)–N(4)	1.409(18)
O(1)–Fe–O(2)	156.4(4)	O(2)–Fe–N(1)	73.5(4)
O(1)–Fe–O(3)	92.5(5)	O(2)–Fe–N(3)	96.1(4)
O(1)–Fe–O(4)	92.2(5)	O(3)–Fe–O(4)	162.8(4)
O(1)–Fe–N(1)	83.3(5)	O(3)–Fe–N(1)	94.5(5)
O(1)–Fe–N(3)	107.2(5)	O(3)–Fe–N(3)	84.6(5)
O(2)–Fe–O(3)	93.2(5)	O(4)–Fe–N(1)	102.5(5)
O(2)–Fe–O(4)	89.0(5)	O(4)–Fe–N(3)	78.2(5)
N(1)–Fe–N(3)	169.5(5)		

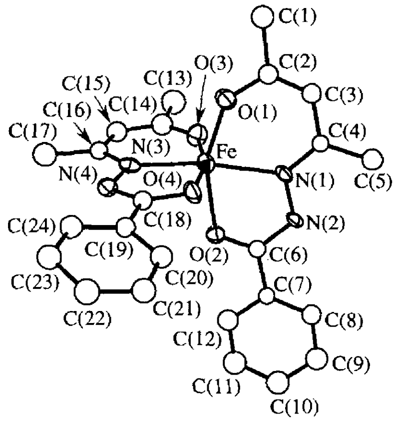

Fig. 1 Structure of [FeL(HL)] showing 30% probability thermal ellipsoids and the atom-labelling scheme. Hydrogen atoms are omitted for clarity

vs. SCE, respectively. However, the neutral [FeL(HL)] **1** is redox inactive in the potential range 0.60 to −0.60 V. The free H_2L also does not display any redox response in this potential range. All the complexes display an irreversible oxidation with very high current at ≈0.80 V most likely due to ligand oxidation. The response observed for **2** is assigned to $Fe^{III} \longrightarrow Fe^{II}$ reduction and that for **3** to $Fe^{III} \longrightarrow Fe^{IV}$ oxidation. Thus the metal centre can be reduced when both amide functions of the ligands are protonated and oxidized when the amide functions are deprotonated. In the intermediate situation metal-centred electron transfer is not possible. The origin of the observed redox behaviour of the three complexes is electrostatic. Addition of an electron to the metal centre is easier when a proton is added to neutral complex **1**. Similarly removal of a proton from **1** facilitates removal of an electron. Therefore, the amide protons are behaving like 'valves'[14] by allowing and controlling the electron transfer to or from the metal centre.

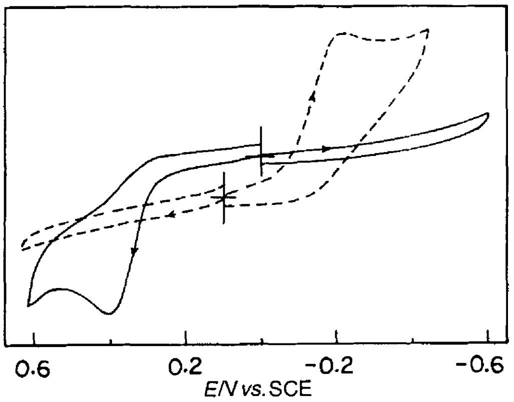

Fig. 2 Cyclic voltammograms (scan rate 0.100 V s^{-1}) of complexes **2** (– – –) and **3** (——) in MeCN (0.1 mol dm^{-3} NBu_4ClO_4) at a platinum electrode (298 K)

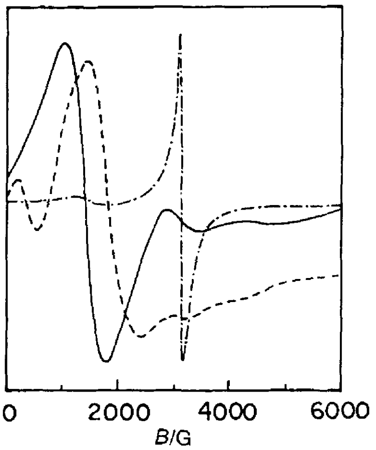

Fig. 3 X-Band (9.173 GHz) ESR spectra of polycrystalline complexes **1** (——), **2** (– – –) and **3** (– · – · –) at 298 K

ESR spectra

The X-band ESR spectra of the complexes are displayed in Fig. 3. The complexity of the ESR spectrum of a six-co-ordinated high-spin d^5 species depends upon the nature and extent of distortion from octahedral symmetry.[15] In a distorted-octahedral situation the magnetic levels consist of three Kramers doublets. The spectral features change as the ratio of the rhombic (E) and axial (D) zero-field splitting parameters ($\lambda = E/D$) and their values change. In a completely rhombic field ($\lambda = \frac{1}{3}$) a signal at $g = 30/7$ is expected from the middle Kramers doublet. Splitting and broadening of this signal can occur if λ deviates from $\frac{1}{3}$. The spectrum of [FeL(HL)] **1** is typical[15a] for large D and λ close to $\frac{1}{3}$. The splitting of the low-field signal in the case of $[Fe(HL)_2]ClO_4$ **2** indicates departure of λ from $\frac{1}{3}$. The completely deprotonated species $K[FeL_2]$ **3** displays the ideal spectrum for near-axial symmetry ($\lambda \approx 0$ and $D \geqslant 0.2$ cm^{-1}).[15a] Therefore the spectra of the complexes clearly display a dependence of the distortion of the $Fe^{III}O_4N_2$ co-ordination sphere on the protonation states of the ligand amide functions.

Conclusion

The metal centre in complex **1** is electrochemically inactive; however, it is prone to reduction in **2** and oxidation in **3**. In **1** and **2** the rhombicity of the FeO_4N_2 co-ordination sphere changes with charge in the amide protonation states. Complete deprotonation in **3** leads to axial symmetry. These observations may have some importance in the context of establishing the metal binding sites of enzymes containing high-spin Fe^{III}. The complexes reported in this work provide very good examples of the influence of the protonation state of co-ordinated amide on the metal-centred redox process and the nature of the distortion of the co-ordination sphere. To the best of our knowledge no other such example exists in iron(III) co-ordination chemistry.

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References

1 (*a*) T. J. McMurray and J. T. Groves, *Cytochrome P-450: Structure, Mechanism, and Biochemistry*, ed. P. R. Ortiz de Montellano, Plenum, New York, 1986, p. 1; (*b*) T. A. Dix and S. J. Benkovic, *Acc. Chem. Res.*, 1988, **21**, 101; (*c*) D. H. R. Barton and D. Doller, *Acc. Chem. Res.*, 1992, **25**, 504; (*d*) K. L. Kostka, B. G. Fox, M. P. Hendrich, T. J. Collins, C. E. F. Rickard, L. J. Wright and E. Münck, *J. Am. Chem. Soc.*, 1993, **115**, 6746.

2 (*a*) G. S. F. Hazeldean, R. S. Nyholm and R. V. Parish, *J. Chem. Soc. A*, 1966, 162; (*b*) R. L. Martin, N. M. Rhode, G. B. Robertson and D. Taylor, *J. Am. Chem. Soc.*, 1974, **96**, 3647; (*c*) E. A. Pasek and D. K. Straub, *Inorg. Chim. Acta*, 1977, **21**, 23; (*d*) D. Coucouvanis, F. J. Hollander and R. Pedelty, *Inorg. Chem.*, 1977, **16**, 2691; (*e*) D. Petridis, B. Niarchos and B. Kanellakopulos, *Inorg. Chem.*, 1979, **18**, 505; (*f*) G. T. Groves, R. C. Haushalter, N. Nakamura, T. E. Nemo and B. J. Evansk, *J. Am. Chem. Soc.*, 1981, **103**, 2884; (*g*) W. Hiller, J. Strahle, M. Hanack, W. E. Hatfield, L. W. Haar and P. Gutlich, *J. Am. Chem. Soc.*, 1984, **106**, 329; (*h*) T. J. Collins, K. L. Kostka, E. Münck and E. S. Uffelmann, *J. Am. Chem. Soc.*, 1990, **112**, 5637; (*i*) V. M. Leovac, R. Herak, B. Prelesnik and S. R. Niketic, *J. Chem. Soc., Dalton Trans.*, 1991, 2295; (*j*) D. Sellmann, M. Geck, F. Knock, G. Ritter and J. Dengler, *J. Am. Chem. Soc.*, 1991, **113**, 3819; (*k*) V. M. Leovac, L. S. Jovanovic, V. I. Cesljevic, L. J. Bjelica and N. J. Evic, *Polyhedron*, 1992, **11**, 1029; (*l*) N. V. Gerbeleu, Y. A. Simonov, V. B. Arion, V. M. Leovac, K. I. Turta, K. M. Indrichan, D. I. Gradinaru, V. E. Zavodnik and T. I. Malinovskii, *Inorg. Chem.*, 1992, **31**, 3264; (*m*) T. J. Collins, B. G. Fox, Z. G. Hu, K. L. Kostka, E. Münck, C. E. F. Rickard and L. J. Wright, *J. Am. Chem. Soc.*, 1992, **114**, 8724; (*n*) U. Knof, T. Weyhermüller, T. Wolter, K. Weighardt, E. Bill, C. Butzlaff and A. X. Trautwein, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1635.

3 D. W. Margerum, *Pure Appl. Chem.*, 1983, **55**, 23; D. P. Kessissoglou, X. Li, W. M. Butler and V. L. Pecoraro, *Inorg. Chem.*, 1987, **26**, 2487; S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1991, **30**, 4031.

4 C. Turró, C. K. Chang, G. E. Leroi, R. I. Cukier and D. G. Nocera, *J. Am. Chem. Soc.*, 1992, **114**, 4013.

5 R. Aasa and P. Aisen, *J. Biol. Chem.*, 1968, **243**, 2399; J. Peisach, W. E. Blumberg, E. T. Lode and M. J. Coon, *J. Biol. Chem.*, 1971, **246**, 5877; D. A. Folajtar and N. D. Chasteen, *J. Am. Chem. Soc.*, 1982, **104**, 5775; M. P. Weir, T. J. Peters and J. F. Gibson, *Biochim. Biophys. Acta*, 1985, **828**, 298; C. P. Thompson, B. M. McCarty and N. D. Chasteen, *Biochim. Biophys. Acta*, 1986, **870**, 530.

6 W. E. Hatfield, *Theory and Applications of Molecular Paramagnetism*, eds. E. A. Boudreaux and L. N. Mulay, Wiley, New York, 1976, p. 491.

7 G. M. Sheldrick, SHELXTL-PLUS 88, Structure Determination Software Programs, Nicolet Instrument Corp., Madison, WI, 1988.

8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

9 W. Kemp, *Organic Spectroscopy*, ELBS/Macmillan, Hong Kong, 1987, p. 65.

10 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986, p. 242.

11 C.-H. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond and H. J. Schugar, *Inorg. Chem.*, 1972, **11**, 990; J. A. Bertrand and P. G. Eller, *Inorg. Chem.*, 1974, 13, 927.

12 (*a*) B. Chiari, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem.*, 1984, **23**, 3398; (*b*) F. Corazza, C. Floriani and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 1987, 709.

13 R. N. Mukherjee, T. D. P. Stack and R. H. Holm, *J. Am. Chem. Soc.*, 1988, **110**, 1850.

14 D. Datta, P. K. Mascharak and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 1673.

15 (*a*) R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294; (*b*) R. Aasa, *J. Chem. Phys.*, 1970, **52**, 3919; (*c*) D. Collison and A. K. Powell, *Inorg. Chem.*, 1990, **29**, 4735.

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