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First-row transition-metal complexes of mixed 'pendant-arm' derivatives of 1,4,7-triazacyclononane containing phenolate and carboxylate functional groups†

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Three mixed pendant-arm azamacrocylic ligands of the 1,4,7-triazacyclononane backbone containing one N-bound phenolate and one or two N-bound carboxylate functionalities have been synthesized, namely 4-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1-acetate(2−), $[L^1]^{2-}$, 7-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-diacetate(3−), $[L^2]^{3-}$, and 7-(2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-diacetate(3−), $[L^3]^{3-}$. Their co-ordination chemistry with Fe^{III}, V^{III}, V^{IV}, Mn^{III} and Co^{III} has been investigated and the following complexes have been prepared as crystalline solids: $[Fe^{III}(L^1)Cl]$ **1**, $[Fe^{III}L^1(H_2PO_4)]$ **2**, $[Fe^{III}{}_2L^1{}_2(\mu\text{-}O)]\cdot H_2O$ **3**, $[V^{III}L^2]\cdot 1.5H_2O$ **4**, $[V^{IV}O(H^2L)]$ **5**, $[Mn^{III}L^2]\cdot 2H_2O$ **6**, $[Fe^{III}L^2]\cdot 1.5H_2O$ **7**, $[Co^{III}L^2]$ **8**, $[Fe^{III}L^3]\cdot 2H_2O$ **9** and $[Co^{III}L^3]\cdot 3H_2O$ **10**. Electronic spectra, magnetic properties and the electrochemistry of the new complexes are reported. The crystal structures **3**, **4**, **7** and **10** have been determined by X-ray crystallography.

Mono-,[1] di-[2] and tris-[3–7] N-functionalization of 1,4,7-triazacyclononane with organic pendant arms carrying carboxylate or phenolate groups affords tetra-, penta- and hexa-dentate derivatives, respectively, which in many instances form extraordinarily stable first-row transition-metal complexes. For example, the trianionic ligands 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (tcta)[3] and 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane derivatives[3–7] form neutral complexes with trivalent irons. Martell and co-workers[8–10] have determined the stability constants $K = [FeL]/[Fe^{3+}][L^{3-}]$ for $[Fe^{III}(tcta)]$ to be $10^{28.3}$ and 10^{52} dm^3 mol^{-1}(!) for [1,4,7-tris(2-hydroxy-3,5-dimethylbenzyl)-1,4,7-triazacyclononane]iron(III). It is the enormous stability of these complexes that has attracted our interest. In principle, a one-electron oxidation or reduction of such a species leads to complexes which should still display a large enough thermodynamic stability to enable their isolation and characterization, even if the actual stability constants of these forms are diminished by 20 orders of magnitude as compared to those of the parent complexes. Recently, we have been able to isolate species containing co-ordinated phenoxyl radicals by using one of the above [1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane]metal(III) complexes as precursors for a one-electron oxidation.[11,12] In this case the oxidation proved to be ligand- rather than metal-centred.

During this study we felt the necessity to synthesize hexadentate compounds with only one phenolate pendant arm and two redox-innocent, carboxylate-carrying, pendant arms attached to the 1,4,7-triazacyclononane backbone. Here we report the synthesis and co-ordination chemistry of three new compounds of this type, namely pentadentate 4-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1-acetate, $[L^1]^{2-}$, hexadentate 7-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-diacetate, $[L^2]^{3-}$, and hexadentate 7-(2-hydroxybenzl)-1,4,7-triazacyclononane-1,4-dipropanoate, $[L^3]^{3-}$; their structures are displayed in Scheme 1.

A general synthetic route to asymmetrically functionalized 1,4,7-triazacyclononane derivatives has recently been reported by Schröder and co-workers.[13]

Results and Discussion

Synthesis of the ligands

The synthetic routes to the mixed-pendant-arm macrocycles containing one phenolate and one or two carboxylate functionalities are summarized in Scheme 1.

N-(2-Hydroxybenzyl)-1,4,7-triazacyclononane has been prepared as described recently[1b] from the orthoamide derivative of 1,4,7-triazacyclononane, namely 1,4,7-triazatricyclo-$[5.2.1.0^{4,10}]$decane,[14] by reaction with 2-(bromomethyl)phenyl acetate in tetrahydrofuran and subsequent hydrolysis with aqueous NaOH. This compound reacts in methyl acrylate as solvent and reactant in the presence of acetic acid (Michael addition). The presence of acetic acid is necessary to suppress the addition of the ester to the phenolic OH group. Hydrolysis of the resulting diester was achieved with 3 equivalents of $LiOH\cdot H_2O$ in ethanol. A colourless solid of $Li_3[L^3]\cdot 1.25EtOH$ was obtained in good yields. The electronic spectrum in MeCN displays two absorption maxima at 240 ($\varepsilon = 7.5 \times 10^3$) and 292 nm ($3.4 \times 10^3$ dm^3 mol^{-1} cm^{-1}) which are assigned to π–π* transitions of the phenolate group.

The corresponding lithium precursor of 1-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane was obtained by the reaction of a large excess of 1,4,7-triazacyclononane with 2-bromomethyl-6-*tert*-butylphenyl acetate and $LiOH\cdot H_2O$ in ethanol as a colourless precipitate. In the above synthesis it is possible to recover the excess of 1,4,7-triazacyclononane *via* extraction of the reaction mixture with chloroform. Kaden and co-workers[1a] have introduced this synthetic procedure for the preparation of 1,4,7-triazacyclononane-1-acetate, for which we have recently published[1b] an improved synthesis by using 1,4,7-triazatricyclo$[5.2.1.0^{4,10}]$decane[14] as starting material.

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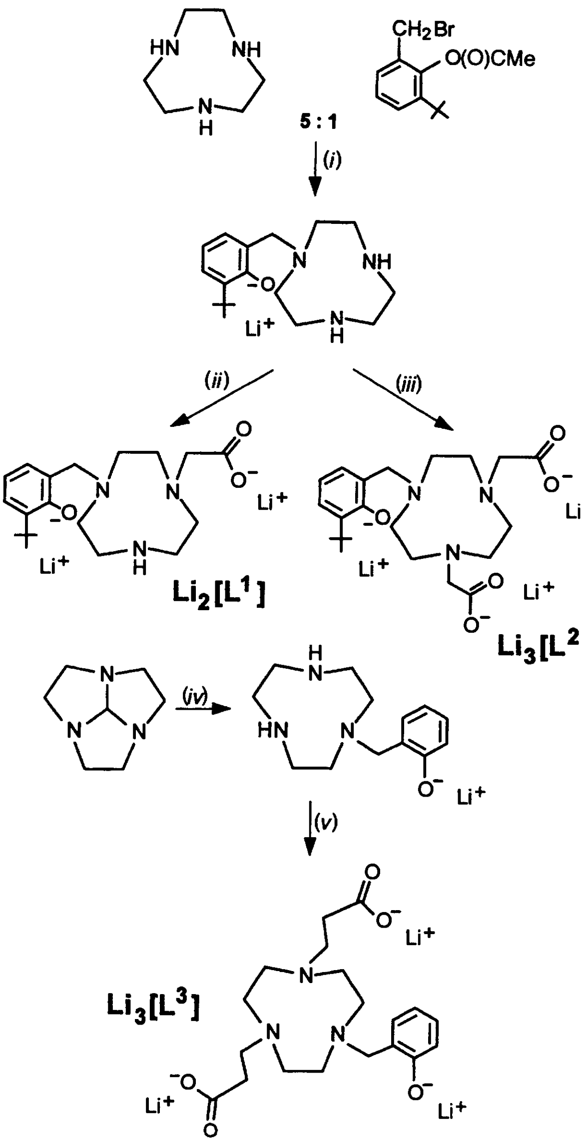
† *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, mmHg ≈ 133 Pa.

Table 1 Electronic spectra and magnetic properties of the complexes

Complex	Solvent	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	μ_{eff} (293 K)/μ_B
1	CH_2Cl_2	529 (2.6×10^3), 329 (4.4×10^3), 276 (9.5×10^3)	5.85
2	MeCN	485 (2.2×10^3), 318 (4.8×10^3), 278 (7.9×10^3)	5.85
3	MeCN	438 (2.4×10^3), 276 (8.1×10^3), 242 (8.9×10^3)	*a*
4	MeCN	570 (212), 378 (1.7×10^3), 325 (3.0×10^3)	2.63
5	MeCN	565 (140), 300 (sh), 290 (4.6×10^3)	1.98
6	MeCN	736 (370), 512 (1.4×10^3), 380 (1.9×10^3), 266 (8.8×10^3)	4.83
7	MeCN	505 (2.7×10^3), 327 (4.5×10^3), 243 (1.06×10^4)	5.92
8	MeCN	519 (465), 398 (550), 278 (1.14×10^4)	*b*
9	MeCN	484 (3.2×10^3), 319 (6.3×10^3), 274 (1.08×10^4)	5.6
10	MeCN	561 (620), 398 (610), 270 (2.0×10^4)	*b*

[a] Antiferromagnetic. [b] Diamagnetic.

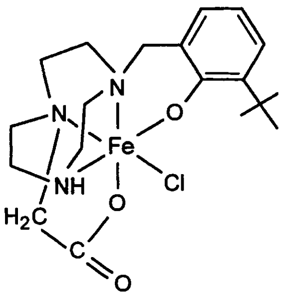


Scheme 1 (*i*) EtOH–water; LiOH·H_2O; (*ii*) MeOH–water, 1 equivalent $BrCH_2CO_2Et$, LiOH·H_2O; (*iii*) MeOH–water; 2 equivalents $BrCH_2CO_2$-Et, LiOH·H_2O; (*iv*) see ref. 1(*b*), (*v*) concentrated $MeCO_2H$, 2 equivalents $H_2C{=}CHCO_2Me$, EtOH, LiOH·H_2O

The lithium salt of 1-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane reacts readily in methanol with 1 or 2 equivalents of ethyl bromoacetate in the presence of LiOH yielding solutions containing 4-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1-acetate(2−) and 7-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-diacetate(3−), $[L^1]^{2-}$ and $[L^2]^{3-}$, respectively. We have not been able to isolate the corresponding lithium salts as solid materials but have used these solutions for the preparation of complexes.

Preparation and characterization of complexes

The pentadentate compound $[L^1]^{2-}$ provides two tertiary and one secondary amine nitrogen donor of the 1,4,7-triazacyclononane backbone, a phenolate and a carboxylate oxygen donor of the two pendant arms for co-ordination of metal ions. Thus, it binds to $FeCl_3$ in methanol with formation of red-violet microcrystals of $[Fe^{III}(L^1)Cl]$ **1**. Complex **1** is moderately soluble in common organic solvents but nearly insoluble in water. In the infrared spectrum a single sharp band at 3230 cm^{-1} is assigned to the ν(N–H) stretching frequency; a ν(C=O) band is observed at 1650 cm^{-1} indicating the presence of a monodentate carboxylate. At 1265 and 1339 cm^{-1} two ν(C–O) stretching modes of the co-ordinated phenolate and of the carboxylate group, respectively, are observed. The elemental analysis indicates the ratio of Fe : ligand : Cl as 1 : 1 : 1. Therefore, we propose the following structure for **1**.



The electronic spectrum and effective magnetic moment of complex **1** (Table 1) are in agreement with a formulation as an octahedral high-spin iron(III) species. A characteristic intense phenolate-to-iron charge transfer (c.t.) band is observed at 529 nm ($\varepsilon = 2.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}). A second transition at 329 nm ($\varepsilon = 4.4 \times 10^3$ dm^3 mol^{-1} cm^{-1}) is assigned to an amine-to-iron c.t. band.

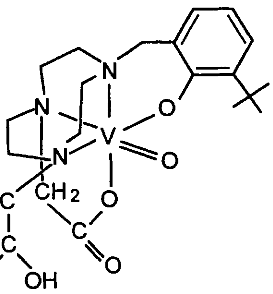
The chloride ligand in complex **1** is substitution labile and can be replaced by other monodentate ligands. Thus, **1** reacts in acetonitrile with an aqueous solution of an equimolar amount of $Na[H_2PO_4]$ with formation of red-violet crystals of $[Fe^{III}L^1(H_2PO_4)]$ **2**. The electronic spectrum and magnetic properties of **2** are very similar to those of **1** in accord with an octahedral high-spin iron(III) complex. In the infrared spectrum the monodentate $H_2PO_4^-$ ligand exhibits an intense, broad ν(P–O) stretching frequency at 1014 cm^{-1} which indicates that the P=O group is involved in intermolecular hydrogen bonding in the solid state.[15] This is corroborated by the observation that the effective magnetic moment of **2** decreases from 5.85 μ_B at 295 K to 3.47 μ_B at 10 K. This is typical for a small but significant intermolecular antiferromagnetic coupling.

Hydrolysis of complex **1** in an alkaline water–methanol mixture affords red-brown crystals of the μ-oxo dinuclear species $[Fe^{III}_2L^1_2(\mu\text{-}O)]\cdot H_2O$ **3**. In the infrared spectrum an intense band at 800 cm^{-1} is assigned to the $\nu_{asym}(Fe–O–Fe)$ stretching frequency.[16] From temperature-dependent magnetic susceptibility measurements (80–295 K) the usual strong intramolecular antiferromagnetic exchange coupling between two oxide-bridged high-spin iron(III) ions is observed. By using the spin Hamiltonian $H = -2JS_1S_2$ ($S_1 = S_2 = \frac{5}{2}$) a coupling constant J of ≈ -80 cm^{-1} [$g = 2.0$ (fixed)] was established. This value is not very precise but of similar magnitude to those found in many $Fe^{III}–O–Fe^{III}$ systems.[17]

Addition of $[V^{III}(MeCN)_3Cl_3]$ (under an argon atmosphere), $MnCl_2$ (in the presence of air), $FeCl_3$ or $Co(ClO_4)_2\cdot 6H_2O$ (again in the presence of air) to a water–methanol solution containing $Li_3[L^2]$ (solution A; see Experimental section) afforded microcrystalline green $[V^{III}L^2]\cdot 1.5H_2O$ **4**, red-brown $[Mn^{III}L^2]\cdot 2H_2O$ **6**, violet $[Fe^{III}L^2]\cdot 1.5H_2O$ **7**, and violet $[Co^{III}L^2]$ **8**, respectively. Complex **4** is oxidized by air in acidic ($HClO_4$) acetonitrile solution to produce violet crystals of $[V^{IV}O(HL^2)]$ **5**.

The anion $[L^2]^{3-}$ is hexadentate and provides three tertiary amine nitrogen donors and two carboxylate and one phenolate oxygen donor. The neutral complexes **4** and **6**–**8** are six-co-ordinate octahedral species. Their infrared spectra clearly show the presence of monodentate co-ordinated carboxylate groups [$\nu(C{=}O)$ 1630–1660 and $\nu(C–O)$ 1310–1350 cm^{-1}]. The $\nu(C–O_{phenolate})$ mode is observed in the range 1240–1280 cm^{-1} (Table 2). The effective magnetic moments summarized in Table 1 are in accord with octahedral V^{III} (d^2) in **4**, high-spin Mn^{III} (d^4) in **6**, high-spin Fe^{III} (d^5) in **7**, and diamagnetic low-spin Co^{III} (d^6) in **8**.

The infrared spectrum of complex **5** clearly shows that air oxidation of **4** yields a vanadyl species. The $\nu(V{=}O)$ stretching mode is observed at 950 cm^{-1}. Since the species is also six-co-ordinate, one of the three pendant arms of $[L^2]^{3-}$ must be unco-ordinated in **5**. The appearance of a strong band at 1736 cm^{-1} demonstrates that one carboxylate arm is not co-ordinated but protonated in **5**. A similar band has been observed for $[V^{IV}O(Htcta)]$.[3,18] Therefore, we propose the following structure for **5**.



The anion $[L^3]^{3-}$ is also hexadentate providing three tertiary amine nitrogen donors and two carboxylate and one phenolate oxygen donors. In contrast to $[L^2]^{3-}$, where the co-ordinated carboxylate arms form five-membered chelate rings M–O–C–C–N, the co-ordinated pendant carboxylate arms in $[L^3]^{3-}$ form more flexible six-membered chelate rings M–O–C–C–C–N. Reaction of $FeCl_3\cdot 6H_2O$ in an aqueous solution B of $Li[L^3]$ (see Experimental section) yields brown-violet crystals of $[Fe^{III}L^3]\cdot 2H_2O$ **9**. The electronic spectrum and the magnetic moment of **9** are very similar to those of **7**. From the reaction of solution B with $Co(ClO_4)_2\cdot 6H_2O$ and subsequent oxidation with H_2O_2 brown-violet crystals of $[Co^{III}L^3]\cdot 3H_2O$ **10** were obtained.

Crystal structures of complexes 3, 4, 7 and 10

Table 3 summarizes selected bond distances and angles of the neutral molecules in crystals of complexes **3**, **4**, **7** and **10**.

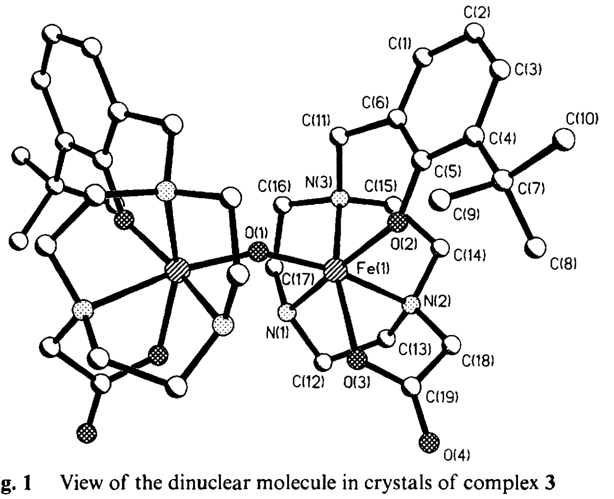


Fig. 1 View of the dinuclear molecule in crystals of complex **3**

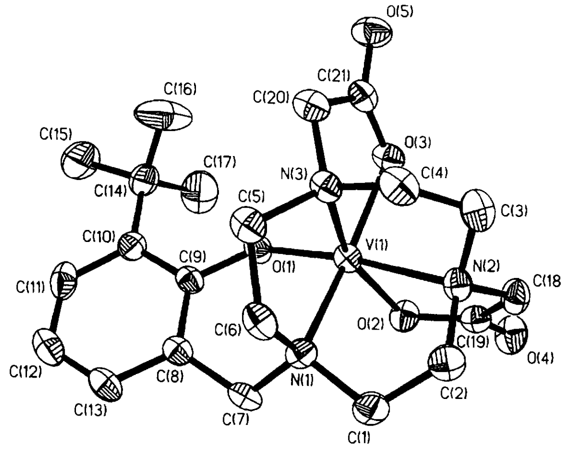


Fig. 2 Structure of one crystallographically independent molecule in crystals of complex **4**

Crystals suitable for X-ray crystallography were grown from an acetonitrile solution of complex **3** into which diethyl ether was allowed to slowly diffuse. These crystals contain three water molecules of crystallization per dinuclear unit and one diethyl ether solvate molecule. The position of the latter is not well defined because it slowly diffuses from the crystal during data collection.

Fig. 1 shows a ball-and-stick representation of the neutral dinuclear molecule in crystals of complex **3**. The dinuclear molecule possesses crystallographic C_2 symmetry where the bridging oxygen atom O(1) lies on this axis. Each iron(III) ion is co-ordinated to a pentadentate ligand $[L^1]^{2-}$; the sixth co-ordination site is occupied by an oxide bridge completing the respective octahedron. The $Fe–O_{oxo}$ bond distance at 1.787(1) Å is relatively short and indicates considerable double-bond character; the Fe–O–Fe angle is 155.3(3)°. The short $Fe–O_{oxo}$ bond exerts a pronounced *trans* influence and the Fe–N(2) bond at 2.270(3) Å is the longest $Fe–N_{amine}$ bond. In contrast, the $Fe–O_{phenolate}$ bond at 1.939(4) Å is relatively long in comparison with the analogous bond in mononuclear **7** at 1.882(5) Å. Consequently, this bond exerts a relative weaker *trans* influence on the Fe(1)–N(1) bond which is the second longest of the three Fe–N bonds. Thus, the oxide bridge is a stronger π donor at the expense of the phenolate π-donor capacity. The carboxylate oxygen is only weakly bound to iron [$Fe–O_{carboxylate}$ 2.028(4) Å] indicating the absence of π-donor bonding of this atom. As a consequence of this the $Fe–N_{amine}$ bond in *trans* position is the shortest [Fe(1)–N(3) 2.157(5) Å].

Crystals of complex **4** consist of the neutral molecule $[VL^2]$ and water molecules of crystallization. Fig. 2 shows this molecule and the atom labelling scheme. There are two

Table 2 Infrared spectroscopic data (cm^{-1}) for the complexes (KBr discs)

Complex	ν(C=O$_{\text{acetate}}$)	ν(C–O$_{\text{acetate}}$)	ν(C–O$_{\text{phenolate}}$)
1	1650	1339	1265
2	1630	1318	1274
3	1660	1320	1287
4	1635	1311, 1349	1245
5	1736, 1635	1320	1276
6	1660	1318	1278
7	1650	1312	1265
8	1650		1279

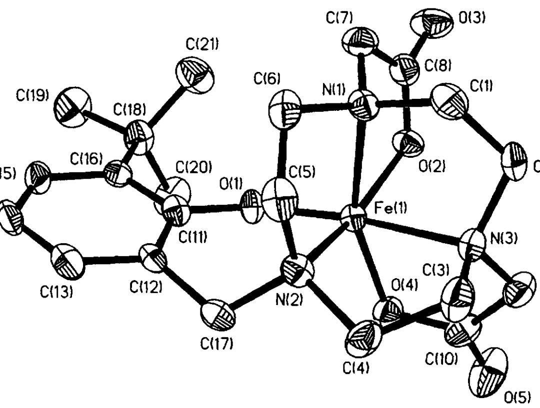


Fig. 3 Structure of one crystallographically independent molecule in crystals of complex 7

Table 3 Selected bond distances (Å) and angles (°) of the complexes

Complex **3**			
Fe(1)–O(1)	1.787(1)	Fe(1)–N(1)	2.242(5)
Fe(1)–O(2)	1.939(4)	Fe(1)–N(2)	2.270(3)
Fe(1)–O(3)	2.028(4)	Fe(1)–N(3)	2.157(5)
O(2)–C(5)	1.333(6)		
O(1)–Fe(1)–O(2)	103.3(1)	O(3)–Fe(1)–N(2)	77.4(1)
O(1)–Fe(1)–O(3)	103.0(2)	N(1)–Fe(1)–N(2)	75.3(1)
O(2)–Fe(1)–O(3)	94.6(2)	O(1)–Fe(1)–N(3)	99.0(2)
O(1)–Fe(1)–N(1)	88.8(1)	O(2)–Fe(1)–N(3)	89.5(2)
O(2)–Fe(1)–N(1)	164.4(1)	O(3)–Fe(1)–N(3)	156.1(1)
O(3)–Fe(1)–N(1)	92.1(2)	N(1)–Fe(1)–N(3)	78.8(2)
O(1)–Fe(1)–N(2)	164.1(1)	N(2)–Fe(1)–N(3)	78.9(1)
O(2)–Fe(1)–N(2)	92.4(1)	Fe(1)–O(1)–Fe(1A)	155.3(3)
Complex **4***			
V(1)–O(1)	1.863(3)	V(1)–N(1)	2.120(4)
V(1)–O(2)	1.974(3)	V(1)–N(2)	2.190(4)
V(1)–O(3)	2.042(3)	V(1)–N(3)	2.120(4)
O(1)–C(9)	1.354(6)		
O(1)–V(1)–O(2)	101.2(1)	O(1)–V(1)–O(3)	95.1(1)
O(2)–V(1)–O(3)	95.0(1)	O(1)–V(1)–N(1)	91.1(1)
O(2)–V(1)–N(1)	99.6(1)	O(3)–V(1)–N(1)	162.7(1)
O(1)–V(1)–N(2)	173.2(1)	O(2)–V(1)–N(2)	78.0(1)
O(3)–V(1)–N(2)	91.6(1)	N(1)–V(1)–N(2)	82.5(2)
O(1)–V(1)–N(3)	101.1(1)	O(2)–V(1)–N(3)	157.3(2)
O(3)–V(1)–N(3)	79.4(1)	N(1)–V(1)–N(3)	83.5(2)
N(2)–V(1)–N(3)	80.2(2)		
Complex **7***			
Fe(1)–O(1)	1.882(5)	Fe(1)–O(2)	1.974(5)
Fe(1)–O(4)	1.954(5)	Fe(1)–N(1)	2.216(6)
Fe(1)–N(2)	2.161(6)	Fe(1)–N(3)	2.209(6)
O(1)–C(11)	1.341(9)		
O(1)–Fe(1)–O(2)	98.7(2)	O(1)–Fe(1)–O(4)	100.7(2)
O(2)–Fe(1)–O(4)	96.7(2)	O(1)–Fe(1)–N(1)	101.8(2)
O(2)–Fe(1)–N(1)	78.4(2)	O(4)–Fe(1)–N(1)	157.5(2)
O(1)–Fe(1)–N(2)	89.1(2)	O(2)–Fe(1)–N(2)	158.1(2)
O(4)–Fe(1)–N(2)	102.0(2)	N(1)–Fe(1)–N(2)	80.0(2)
O(1)–Fe(1)–N(3)	169.7(2)	O(2)–Fe(1)–N(3)	91.5(2)
O(4)–Fe(1)–N(3)	79.5(2)	N(1)–Fe(1)–N(3)	78.6(2)
N(2)–Fe(1)–N(3)	80.9(2)		
Complex **10**			
Co(1)–N(1)	1.951(3)	Co(1)–N(2)	1.947(4)
Co(1)–N(3)	1.943(3)	Co(1)–O(1)	1.915(3)
Co(1)–O(2)	1.887(2)	Co(1)–O(3)	1.913(5)
O(2)–C(15)	1.324(5)		
N(1)–Co(1)–N(2)	88.2(1)	N(1)–Co(1)–N(3)	87.9(1)
N(2)–Co(1)–N(3)	88.3(1)	N(1)–Co(1)–O(1)	94.0(1)
N(2)–Co(1)–O(1)	90.4(1)	N(3)–Co(1)–O(1)	177.6(1)
N(1)–Co(1)–O(2)	176.7(1)	N(2)–Co(1)–O(2)	94.6(1)
N(3)–Co(1)–O(2)	90.5(1)	O(1)–Co(1)–O(2)	87.6(1)
N(1)–Co(1)–O(3)	89.7(1)	N(2)–Co(1)–O(3)	176.9(1)
N(3)–Co(1)–O(3)	93.9(1)	O(1)–Co(1)–O(3)	87.5(1)
O(2)–Co(1)–O(3)	87.5(1)		

* Bond distances and angles for only one crystallographically independent molecule are given. The dimensions of the second are very similar.

crystallographically independent molecules in the unit cell. The metrical details of these two molecules are very similar and in the following we will discuss only one of these. The vanadium(III) ion is co-ordinated to a hexadentate trianion [L^2]$^{3-}$. Three five-membered V–N–C–C–N chelate rings are formed by the co-ordinated 1,4,7-triazacyclononane backbone; the two acetate pendant arms also form five-membered chelate rings V–O–C–C–N whereas the phenolate arm forms a six-membered ring V–N–C–C–C–O. The V–O$_{\text{phenolate}}$ bond is short at 1.863(3) Å and similar to those found in [V$^{\text{III}}$L^4]PF at 1.887(3) Å[19] where L^4 represents the dianion of *N*,*N*′-bis-[(2-hydroxybenzyl)-*N*,*N*′-bis(2-methylpyridyl)]ethane-1,2-diamine. It displays the expected *trans* influence on the V–N(2) bond which is the longest V–N$_{\text{amine}}$ bond. The two V–O$_{\text{acetate}}$ bonds are inequivalent and significantly longer at 1.974(3) and 2.042(3) Å but are in the range observed for vanadium(III) carboxylate complexes; *e.g.* in [V(trdta)]$^-$ (trdta = 1,3-diaminopropenetetraacetate) at 2.011(2), 1.963(2), 1.951(2) and 1.986(2) Å.[20]

In crystals of complex **4** the two neutral molecules are connected by a series of intermolecular O–H···O hydrogen-bonding contacts. Thus, carbonyl oxygen atoms O(10) and O(5) form such a bond to two water molecules O(10)···H–O(13) 2.773(7) and O(5)···H–O(11) 2.889(8) Å, respectively. The water molecules also form contacts between each other: O(13)···O(12) 2.741(6), O(12)···O(11) 2.833(8) and O(13)···O(11) 2.801(8) Å.

Not surprisingly, complexes **4** and **7** are isostructural and the geometrical details and crystal packing are similar. Fig. 3 shows the structure of one of the two crystallographically independent neutral molecules in crystals of **7**. The Fe–O$_{\text{phenolate}}$ bond at 1.882(5) Å is short and indicates considerable double-bond character. It is very similar to those found in many iron(III) phenolate complexes.[21] The Fe–O$_{\text{acetate}}$ bonds are weaker [1.954(5) and 1.974(5) Å] and comparable to those in [Fe$^{\text{III}}$(tcta)] at 1.962(2) Å.[3] Rather surprisingly, the Fe–O$_{\text{phenolate}}$ bond does not exert the expected strong *trans* influence. The Fe–N(3) bond length in *trans* position is 2.209(6) Å, but Fe–N(1) with 2.216(6) is as long (or slightly longer) despite the fact that this bond is in *trans* position to a weakly bound carboxylate oxygen atom O(4). We have no explanation to offer for this behaviour.

Fig. 4 shows the structure of the neutral molecule in crystals of complex **10**. The cobalt(III) ion is bound to a hexadentate trianion [L^3]$^{3-}$. All the three pendant arms form six-membered chelates of the type M–O–C–C–C–N where the 1,4,7-triazacyclononane backbone provides three five-membered M–N–C–C–N rings. The Co$^{\text{III}}$ with a low-spin $t_{2g}{}^6$ electron configuration is in principle not capable of forming strong p$_\pi$–d$_\pi$ bonds and, therefore, the Co–O$_{\text{phenolate}}$ bond at 1.887(2) Å

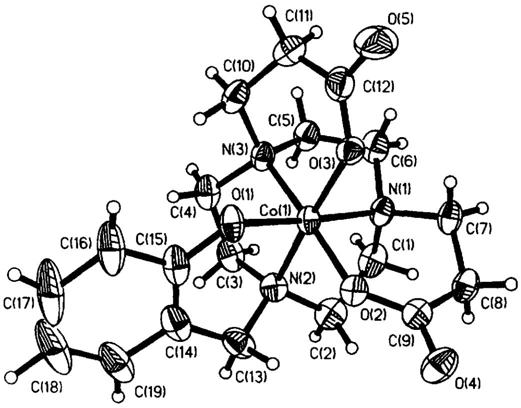


Fig. 4 Structure of the neutral molecule in crystals of complex **10**

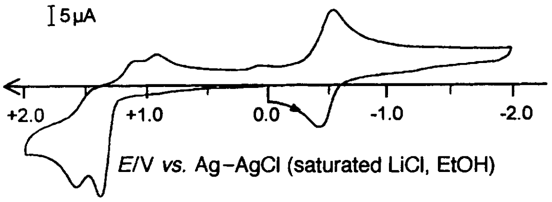


Fig. 5 Cyclic voltammogram of complex **1** in MeCN (0.10 mol dm^{-3} NBu_4PF_6 supporting electrolyte, 200 mV s^{-1} scan rate, glassy carbon electrode)

is about as long as the $Co-O_{carboxylate}$ bonds at an average of 1.914(3). A further indication of the lack of considerable π-donor bonding in **10** stems from the observation that the three $Co-N_{amine}$ bonds are within experimental error equidistant at 1.947(3) Å. It is also noteworthy that the O–C bond of the co-ordinated phenolate is the shortest in **10** [1.324(5) Å] and barely significantly longer in **4** [1.354(6)] and **7** [1.341(9) Å]. This again indicates weak (if any) π donation of the co-ordinated phenolate in **10** as compared to **4** and **7**.

The crystal packing in complex **10** again involves intermolecular O–H···O hydrogen-bonding contacts between the carbonyl oxygens O(4), O(5) and H_2O [O(4)···O(12) 2.909(5), O(4)···O(10) 2.739(5), O(5)···O(10), 2.720(6) and O(5)···O(11) 2.744(6) Å]. The water molecules also form O–H···O contacts among each other: O(10)···O(11) 2.716(5) and O(11)···O(12) 2.767(5) Å.

Electrochemistry

The cyclic voltammograms of the new complexes have been recorded in acetonitrile or dichloromethane solution containing 0.10 mol dm^{-3} tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Ferrocene was used as internal standard. The redox potentials discussed below are referenced *versus* the ferrocenium–ferrocene couple. The scan rates were varied between 20 and 200 mV s^{-1}. A glassy carbon working electrode and a Ag–AgCl (saturated LiCl in ethanol) electrode was used as the reference.

Complex **1** in CH_2Cl_2 in the potential range +1.5 to −2.5 V (Fig. 5) displays a quasi-reversible one-electron reduction wave at −0.92 V which is assigned to a metal-centred reduction Fe^{III}–Fe^{II}, and, in addition, two irreversible oxidation and two irreversible reduction waves at potentials >0.5 V which are ligand-centred oxidation-reduction processes associated with the co-ordinated phenolate.[12] The cyclic voltammogram of **2** displays a metal-centred reversible reduction wave at −1.5 V which indicates an enormous stabilization of the trivalent state by the co-ordinated $H_2PO_4^-$ in **2** as compared to **1**.

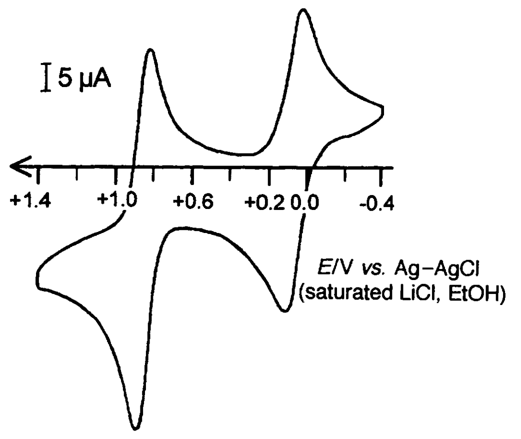


Fig. 6 Cyclic voltammogram of complex **6** in MeCN. Details as in Fig. 5

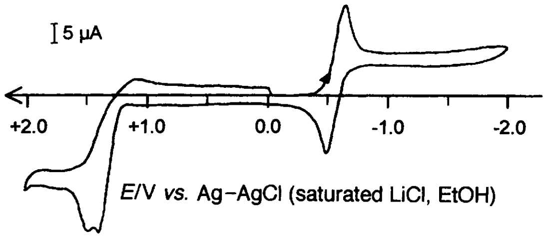


Fig. 7 Cyclic voltammogram of complex **7** in MeCN. Details as in Fig. 5

Complex **4** in MeCN exhibits two reversible one-electron-transfer waves at −1.98 and +0.04 V. Coulometric measurements at +1.5 V show that **4** is oxidized by a one-electron process yielding the monocation $[V^{IV}L^2]^+$. Therefore, we assign the two metal-centred processes as in equation (1). Interestingly,

$$[V^{IV}L^2]^+ \underset{-e}{\overset{-e}{\rightleftharpoons}} [V^{III}L^2] \underset{-e}{\overset{+e}{\rightleftharpoons}} [V^{II}L^2]^- \qquad (1)$$

corresponding octahedral vanadium(III) complexes containing a hexadentate ligand with two[19] or three[7] co-ordinated phenolate groups display a second reversible oxidation wave at very positive potentials: $V^{IV} \rightleftharpoons V^V + e^-$. Thus, in $[V^{III}L^4]PF_6$ (two phenolates)[19] the redox potential for this process is observed at +1.11 V and for $[V(tatp)]^+$ (three phenolates)[7] at +0.38 V [$tatp^{3-}$ = 1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane]. These results demonstrate the enormous, increasing stabilization of higher-valent vanadium species by one, two, three or even four[22] co-ordinated phenolates.

The corresponding manganese complex **6** (Fig. 6) in MeCN also displays two reversible one-electron-transfer waves at +0.315 and −0.475 V which are assigned as shown in equation (2). For $[Mn^{III}(tatp)]$ these potentials are at −0.25 and −0.88 V.[6]

$$[Mn^{IV}L^2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} [Mn^{III}L^2] \underset{-e}{\overset{+e}{\rightleftharpoons}} [Mn^{II}L^2]^- \qquad (2)$$

Thus, it is easier to oxidize this complex than **6** because three co-ordinated phenolates stabilize the oxidation state Mn^{IV} more efficiently than two in **6**. On the other hand, it is easier to reduce **6** to Mn^{II} than $[Mn^{III}(tatp)]$. The assumption that the phenolate groups predominantly stabilize Mn^{IV} in these complexes is nicely corroborated by the fact that $[Mn^{III}(tcta)]$ containing three co-ordinated acetate groups only is reversibly oxidized to $[Mn^{IV}(tcta)]^+$ at a much more positive potential of $E_{\frac{1}{2}}$ = +1.33 V.[3]

The cyclic voltammogram of complex **7** in MeCN is interesting because it again shows not only the expected reversible one-electron metal-centred reduction wave at −1.07 V but, in addition, two irreversible oxidation waves at ≈+1.08 V and, less developed, the corresponding reductions at ≈+0.8 V (Fig. 7). These latter processes are ligand-centred. Since the *para* position of the co-ordinated phenolate is not substituted in **6** by a bulky protecting group like a tertiary butyl group, the electrochemically generated phenoxyl radical rapidly undergoes side reactions (dimerization, further oxidation). A stable iron(III) complex containing a co-ordinated phenoxyl radical has recently been described.[12]

The cyclic voltammogram of complex **9** in MeCN is very similar to that of **7**. A reversible one-electron reduction at −1.14 V is assigned to the $[Fe^{III}L^3]$–$[Fe^{II}L^3]^-$ couple. It appears that the size of the chelate rings formed by the two carboxylate pendant arms in **7** and **9** does not have a significant effect on the Fe^{III}–Fe^{II} redox potentials. Two irreversible, probably phenolate-centred oxidations occur at $E_{p,ox} = +0.96$ and 0.74 V.

The cobalt complexes **8** and **10** did not produce reproducible cyclic voltammograms in the solvents water, CH_2Cl_2 or MeCN.

Experimental

The compounds 1,4,7-triazacyclononane,[23] its orthoamide derivative 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane[14] and *N*-(2-hydroxybenzyl)-1,4,7-triazacyclononane[1b] were prepared according to published procedures.

Preparations

Lithium salt of [1-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane]. To a mixture of 6-*tert*-butyl-*o*-cresol (20 g, 122 mmol) and acetic acid anhydride (25.9 g, 244 mmol) were added five drops of concentrated H_2SO_4. The solution was stirred at ambient temperature for 12 h. The reaction volume was reduced under reduced pressure by rotary evaporation and the resulting colourless liquid was distilled under reduced pressure at 75 °C (0.03 mmHg). The yield of 2-*tert*-butyl-6-methylphenyl acetate was 24 g (95%). This product (20 g, 97 mmol) was dissolved in dry CCl_4 (100 cm^3) and *N*-bromosuccinimide (17.2 g, 97 mmol) and azobisisobutyronitrile (0.2 g) were added. The solution was gently heated to reflux until the reaction started (effervescence of gas). The solution was filtered, the solvent stripped off by rotary evaporation and the resulting product distilled under reduced pressure (90 °C, 0.03 mmHg). After 5 d at 6 °C the colourless product crystallized; yield 23 g (83%).

A solution of 1,4,7-triazacyclononane (3.2 g, 25 mmol), 2-bromomethyl-6-*tert*-butylphenyl acetate (1.4 g, 5 mmol) and $LiOH\cdot H_2O$ (1.3 g, 30 mmol) in an ethanol (50 cm^3)–water (20 cm^3) mixture was stirred at 20 °C for 24 h. A colourless precipitate formed which was filtered off, washed with a small amount of ethanol and diethyl ether and air-dried. The excess of 1,4,7-triazacyclononane can be recovered by extraction of the above solution with chloroform. Yield: 1.0 g (61%). 80 MHz ^{1}H NMR ($CDCl_3$): δ 1.5 [s, 9 H, $C(CH_3)_3$]; 2.5 (s, 12 H, CH_2CH_2); 3.5 (s, 2 H, benzyl) and 7.1 (m, 3 H, aromatic).

Solution A containing the dianion 4-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1-acetate ($[L^1]^{2-}$). To a solution of $LiOH\cdot H_2O$ (0.08 g) and the lithium salt of *N*-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (0.30 g, 1.0 mmol) in a methanol (15 cm^3)–water (5 cm^3) mixture was added $BrCH_2CO_2Et$ (0.17 g, 1.0 mmol). The solution was heated to reflux for 2 h. This solution was used for the preparation of complexes $[Fe(L^1)Cl]$, $[FeL^1(H_2PO_4)]$ and $[Fe_2L^1_2(\mu\text{-}O)]$.

Solution B containing the trianion 7-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-diacetate ($[L^2]^{3-}$). To a solution of $LiOH\cdot H_2O$ (0.21 g) and the lithium salt of *N*-(3-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (0.30 g, 1.0 mmol) in a methanol (15 cm^3)–water (5 cm^3) mixture was added $BrCH_2CO_2Et$ (0.40 g, 2.4 mmol). The solution was heated to reflux for 2 h. This solution was used for the preparation of complexes $[VL^2]$, $[V^{IV}O(HL^2)]$, $[MnL^2]$, $[FeL^2]$ and $[CoL^2]$.

Trilithium 7-(2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-dipropanoate ($Li_3[L^3]$). A solution of 1-(2-hydroxybenzyl)-1,4,7-triazacyclononane[1b] and concentrated acetic acid (12.5 cm^3) in acrylic acid methyl ester (175 cm^3) was stirred at 20 °C for 3 d. After filtration, the solvent was stripped off by rotary evaporation at 75 °C (**CAUTION**: hood). The viscous yellow-brown residue was dissolved in $CHCl_3$ (175 cm^3) and washed with the minimum volume of an aqueous solution of $NaHCO_3$. The aqueous phase was separated and extracted with $CHCl_3$ (3 × 50 cm^3). The combined $CHCl_3$ phases were dried over $MgSO_4$. After filtration and removal of the solvent a brown viscous oil of dimethyl 7-(2-hydroxybenzyl)-1,4,7-triazacyclononane-1,4-dipropanoate was obtained. Yield: 26.7 g (76%). To the crude product (26.7 g, 65.5 mmol) dissolved in ethanol (300 cm^3) was added solid $LiOH\cdot H_2O$ (8.25 g, 197 mmol) and the solution stirred for 55 °C for 16 h. A colourless precipitate of $Li_3[L^3]\cdot 1.25EtOH$ formed which was filtered off. Yield: 18.8 g (63%) (Found: C, 56.4; H, 7.3; N, 7.3. Calc. for $C_{19}H_{26}Li_3N_3O_5\cdot 1.25EtOH$: C, 56.8; H, 7.4; N, 7.4%).

$[Fe^{III}(L^1)Cl]$. To solution A (20 cm^3) was added $FeCl_3$ (0.16 g, 1.0 mmol). The clear violet solution was heated to 80 °C for 1 h and then stirred for 24 h at room temperature during which time red-violet microcrystals of complex **1** precipitated. Yield: 0.27 g (62%) (Found: C, 53.0; H, 7.4; Cl, 8.5; N, 8.7. Calc. for $C_{19}H_{29}ClFeN_3O_3$: C, 52.0; H, 6.7; Cl, 8.1; N, 8.5%).

$[Fe^{III}L^1(H_2PO_4)]$ 2. To a solution of complex **1** (0.44 g, 1.0 mmol) in acetonitrile (20 cm^3) was added a solution of NaH_2PO_4 (0.12 g) dissolved in water (5 cm^3). The solution was heated to reflux for 2 h after which time the reaction volume was reduced to ≈10 cm^3 by evaporation of the solvent. At 5 °C red-violet crystals of **2** precipitated. Yield: 0.30 g (60%) (Found: C, 46.0; H, 5.6; N, 8.5. Calc. for $C_{19}H_{31}FeN_3O_7$: C, 45.6; H, 5.4; N, 8.4%).

$[Fe^{III}_2L^1_2(\mu\text{-}O)]\cdot H_2O$ 3. A solution of complex **1** (0.44 g, 1.0 mmol) in a mixture of methanol (20 cm^3) and water (5 cm^3) to which NaOH (0.20 g, 5.0 mmol) had been added was heated to reflux for 5 h. The filtered solution was allowed to stand at ambient temperature for a few days during which time red-brown crystals of **3** precipitated. Crystals suitable for X-ray crystallography were grown from an acetonitrile solution of **3** into which diethyl ether was allowed slowly to diffuse. Yield: 0.18 g (44%) (Found: C, 53.4; H, 7.0; N, 10.2. Calc. for $C_{38}H_{60}Fe_2N_6O_8$: C, 55.5; H, 7.1; N, 10.2%).

$[V^{III}L^2]\cdot 1.5H_2O$ 4. The solvent of methanol solution B (15 cm^3) was stripped off by rotary evaporation and the solid residue dissolved in acetonitrile and flushed with argon. A deoxygenated solution of VCl_3 (0.16 g, 1.0 mmol) in acetonitrile (15 cm^3) was heated to reflux under argon {formation of green $[V(MeCN)_3Cl_3]$} and then added to the above solution and heated to 60 °C for 1 h. Upon reduction of the reaction volume by evaporation, a green crystalline product **4** precipitated which was filtered off under argon, washed with diethyl ether and dried. Yield: 0.18 g (43%) (Found: C, 54.8; H, 6.6; N, 9.1. Calc. for $C_{21}H_{30}N_3O_5V\cdot 1.5H_2O$: C, 55.4; H, 6.6; N, 9.2%).

$[V^{IV}O(HL^2)]$ 5. To the above acetonitrile solution prepared for the synthesis of complex **4** were added a few drops of concentrated $HClO_4$ (60%) and the resulting solution was stirred at room temperature in the presence of air for a few hours until a change to violet had occurred. Upon standing in an open vessel for 2 d crystals of **5** precipitated. Yield: 0.15 g (32%) (Found: C, 50.8; H, 6.5; N, 8.6. Calc. for $C_{21}H_{31}N_3O_6V$: C, 51.1; H, 6.7; N, 8.6%).

$[Mn^{III}L^2]\cdot 2H_2O$ 6. To solution B (15 cm^3) was added $MnCl_2$ (0.13 g, 1.0 mmol) and the solution was heated to reflux for 2 h in the presence of air. A red-brown precipitate of complex **6** formed which was filtered off. Yield: 0.18 g (39%) (Found: C, 52.0; H, 7.1; N, 8.4. Calc. for $C_{21}H_{30}MnN_3O_5\cdot 2H_2O$: C, 51.0; H, 7.1; N, 8.5%).

Table 4 Crystallographic data for complexes **3**, **4**, **7** and **10**

	3	**4**	**7**	**10**
Formula	$C_{38}H_{62}Fe_2N_6O_9$	$C_{21}H_{33}N_3O_{6.5}V$	$C_{21}H_{33}FeN_3O_{6.5}$	$C_{19}H_{32}CoN_3O_8$
M	858.6	482.3	487.3	489.4
Crystal symmetry	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*C*2/*c* (no. 15)	*Pcab* (no. 61)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)
a/Å	25.25(1)	12.873(4)	21.901(3)	14.527(3)
b/Å	14.490(6)	21.910(7)	12.959(4)	11.514(2)
c/Å	13.513(6)	32.68(1)	32.682(7)	12.900(3)
β/°	114.19(3)			96.66(3)
U/Å	4509.9(8)	9217(4)	9276(4)	2143.1(8)
Z	4	16	16	4
F(000)	1824	4080	4128	1032
D_c/g cm^{-3}	1.4	1.26	1.40	1.52
Crystal size/mm	0.2 × 0.18 × 0.45	0.15 × 0.25 × 0.6	0.25 × 0.30 × 0.50	0.42 × 0.51 × 0.45
μ(Mo-Kα)/mm^{-1}	0.71	0.46	0.69	0.85
Data measured	4604	8917	8539	4133
No. unique	2554 [$I \geqslant 2.5\sigma(I)$]	4604 [$I \geqslant 2.5\sigma(I)$]	3658 [$I \geqslant 2.0\sigma(I)$]	2643 [$I \geqslant 2.0\sigma(I)$]
No. parameters	259	578	597	400
R^a	0.058	0.057	0.058	0.047
R'^b	0.050	0.047	0.053	0.042
Weighting scheme, w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$	$\sigma^2(F) + 0.0005F^2$	$\sigma^2(F) + 0.0001F^2$
Largest peak/e Å^{-3}	0.50	0.35	0.46	0.69

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

$[Fe^{III}L^2]\cdot 1.5H_2O$ 7. This violet complex was prepared as described above for **6** by using $FeCl_3$ (0.16 g, 1.0 mmol) instead of $MnCl_2$. Yield: 0.30 g (62%) (Found: C, 51.9; H, 6.9; N, 8.5. Calc. for $C_{21}H_{30}FeN_3O_5\cdot 1.5H_2O$: C, 51.8; H, 6.8; N, 8.6%).

$[Co^{III}L^2]$ 8. This violet complex was prepared as described above for **6** and **7** in the presence of air by using $Co(ClO_4)_2\cdot 6H_2O$ (0.37 g, 1.0 mmol) instead of $FeCl_3$ or $MnCl_2$. Yield: 0.20 g (43%) (Found: C, 54.5; H, 6.6; N, 9.1. Calc. for $C_{21}H_{30}CoN_3O_5$: C, 54.4; H, 6.5; N, 9.1%).

$[Fe^{III}L^3]\cdot 2H_2O$ 9. To a solution of $FeCl_3\cdot 6H_2O$ (0.67 g, 2.5 mmol) in acetonitrile (40 cm^3) was added dropwise a solution of $Li_3[L^3]$ (1.11 g, 2.4 mmol) in water (20 cm^3). The solution was heated to reflux for 2 h. From this solution brown-violet crystals of complex **9** precipitated within a few days at room temperature. Yield: 0.96 g (82%) (Found: C, 48.3; H, 6.6; Fe, 12.0; N, 9.0). Calc. for $C_{19}H_{30}FeN_3O_7$: C, 48.7; H, 6.5; Fe, 11.9; N, 9.0%).

$[Co^{III}L^3]\cdot 3H_2O$ 10. To a solution of $CoCl_2\cdot 6H_2O$ (0.36 g, 1.5 mmol) in water (20 cm^3) was added an aqueous solution (20 cm^3) of $Li_3[L^3]$ (0.66 g, 1.45 mmol). The solution was heated to 60 °C and H_2O_2 (35%, 2.5 cm^3) was added dropwise. The solution was allowed to stand in an open vessel at ambient temperature for 7 d. Brown-violet crystals of complex **10** were obtained. Yield: 0.54 g (73%) (Found: C, 46.8; H, 7.1; Co, 11.8; N, 8.6. Calc. for $C_{19}H_{32}CoN_3O_8$: C, 46.7; H, 6.6; Co, 12.0; N, 8.6%).

Physical measurements

Infrared spectra were recorded as KBr discs on a Perkin-Elmer FTIR model 1720X spectrometer, UV/VIS spectra on a Perkin-Elmer Lambda 9 spectrophotometer. The magnetic susceptibilities of powdered samples of complexes were measured in the temperature range 80–295 K by the Faraday method. The diamagnetism of the sample was taken into account using Pascal's constants. Cyclic voltammetric measurements were carried out by use of PAR equipment (potentiostat M173, universal programmer M175) on solutions (MeCN or CH_2Cl_2) containing 0.10 mol dm^{-3} NBu_4PF_6 as supporting electrolyte and ferrocene as internal standard.

X-Ray crystallography

The crystallographic data for complexes **3**, **4**, **7** and **10** are summarized in Table 4. A brown crystal of **3** and a green one of **4** were mounted on a glass fibre and placed on a Syntex R3 diffractometer, whereas dark red crystals of **7** and **10** were placed on a Siemens P4 diffractometer, respectively. Graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å) was used throughout. Intensity data were collected at 293(2) K and were corrected for Lorentz, polarization, and absorption effects (for **3** and **4** only; ψ scans) in the usual manner. The structures were solved by conventional Patterson (**3**, **4**), Fourier-difference and direct (**7**, **10**) methods by using the Siemens SHELXTL PLUS program package.[24] The function minimized during full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_o|)^2$, where *w* is as indicated in Table 4. Neutral atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 25. The positions of the hydrogen atoms of the methylene and phenyl groups were placed at calculated positions with group isotropic thermal parameters for **3**, **4** and **7**. For **10** all H atoms were located in the final Fourier difference map and included in the refinement. The methyl groups were treated as rigid bodies. All non-hydrogen atoms were refined with anisotropic thermal parameters.

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 186/256.

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