

Topologic Equivalents of Coronands, Cryptands and Their Inclusion Complexes: Synthesis, Structure and Properties of {2}-Metallacryptands and {2}-Metallacryptates**

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 68th birthday

Abstract: The synthesis and structural characterisation of two dinuclear iron(III) complexes are reported. The compounds of general structure $[\text{Fe}_2\text{L}_3^1]$ [**8**; $\text{L}^1 =$ dianion of 2,2'-dicyano-2,2'-isophthaloyldi(isopropylidicarboxylate)] and $[\text{K} \subset \text{Fe}_2\text{L}_3^2]^+$ (PF_6^-) [**10**; $\text{L}^2 =$ dianion of 1,1'-(2,6-pyridylene)bis-1,3-(4-dimethyl)pentanedione] are formed by the deprotonation of ligands **7** and **9** with triethylamine and potassium hydride respectively, followed by addition of iron(III) chloride and work up with water or aqueous potassium hexafluorophosphate. X-ray crystallographic studies reveal that **8** is a

racemic mixture composed of triple helicates with (Δ, Δ)-*fac* and (A, A)-*fac* configuration at the two iron bridgeheads. In contrast to racemic **8**, the two iron centres in the *meso*-**10** [(Δ, A) -*fac*] have opposite configuration. Investigations of the redox-active iron centres in {2}-metallacryptand **8** and {2}-metallacryptate **10**

by cyclic voltammetry show slightly different behaviour. The peaks for the two consecutive reductions of the two iron centres of **8** can hardly be resolved, whereas **10** shows two well-separated peaks. Mössbauer measurements were performed on **8** and **10** between 4.2 and 300 K, with and without a field applied perpendicular or parallel to the γ -beam. All zero-field and 20 mT spectra exhibit a broad and unresolved absorption pattern. Application of 5.3 T at 4.2 K results in well-resolved magnetic hyperfine patterns which are practically the same for **8** and **10**.

Keywords

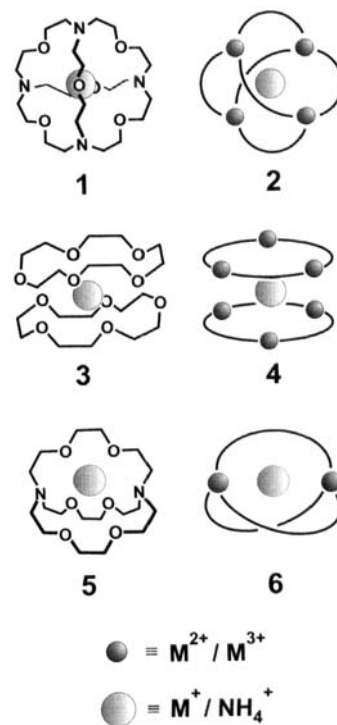
iron · metallacryptands · metallacryptates · self-assembly · structure elucidation

Introduction

The chemistry of coronands, cryptands and their inclusion complexes is extensively documented in countless monographs,^[1] reviews^[2] and communications.^[3] Some years ago, we found that there exist {3}-metallacryptates **2**, which are topologically equivalent to the {3}-cryptates **1**.^[4,5] The metalla-topomers

2 essentially differ only in the substitution of the nitrogen bridgehead atoms of **1** by metal ions in **2**. An advantage is that the {3}-metallacryptates **2** are obtainable by spontaneous self-assembly^[6] in a one-pot reaction with yields of about 80%.

Recently, we were successful in obtaining the corresponding topologic equivalents **4** of the crown ether sandwich complexes **3**.^[7] Therefore, we assumed that the use of suitable tailor-made ligands would make available not only the {2}-cryptates **5**, but also the corresponding topologically equivalent {2}-metallacryptates **6**.^[8]



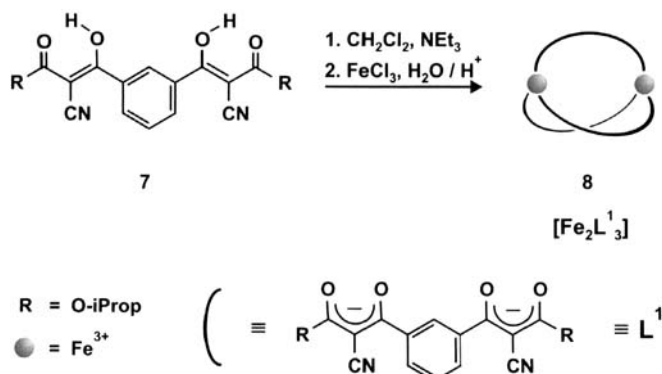
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Results and Discussion

In order to test the above hypothesis, we added iron(III) chloride and triethylamine to 2,2'-dicyano-2,2'-isophthaloyldi(isopropylidencarboxylate) **7**^[9, 10] in dichloromethane as a one-pot reaction. After aqueous work-up, we obtained dark red microcrystals in a yield of 92%. Microanalysis and the FAB–MS spectra (FAB = fast atom bombardment) indicated that the isolated product is an iron chelate of the general composition $[\text{Fe}_2\text{L}_3^1]$, formed by self-assembly (Scheme 1).

X-ray crystallographic analysis of the molecular structure of complex $[\text{Fe}_2\text{L}_3^1]$ (**8**)^[11] revealed that **8** is a {2}-metallacryptand (= triple helicate)^[15] without any characteristic symmetry elements (Figure 1).



Scheme 1. Synthesis of metallacryptand **8**.

Each of the two iron centres ($d_{\text{Fe}-\text{Fe}} = 709$ pm) is octahedrally surrounded by six oxygen atoms. With octahedral coordination centres of the type MA_3B_3 [for bidentate ligands $\text{M}(\text{AB})_3$], two pairs of enantiomers $[(\Delta), (\Lambda)\text{-fac}]$; $(\Delta), (\Lambda)\text{-mer}]$ are possible.^[16] In the chiral, racemic complex **8** both iron centres are coordinated identically. Therefore, the {2}-metallacryptand is either a $(\Delta, \Delta)\text{-fac}$ or $(\Lambda, \Lambda)\text{-fac}$ triple helicate. The crystals obtained (triclinic, space group $P\bar{1}$) are composed of the homochiral {2}-metallacryptand **8**. The donating power in the interior of the metallacryptand is insufficient for the complexation of alkali metal cations. Above all, the three hydrogen atoms in **8** are directed towards the empty cavity in the centre.

In order to synthesise the topologically equivalent metallacryptate **6** in an analogous manner to **5**, we substituted the *m*-phenylene spacer for a *m*-pyridylene spacer. By deprotonation of 1,1'-(2,6-pyridylene)bis-1,3-(4-dimethyl)pentanedione

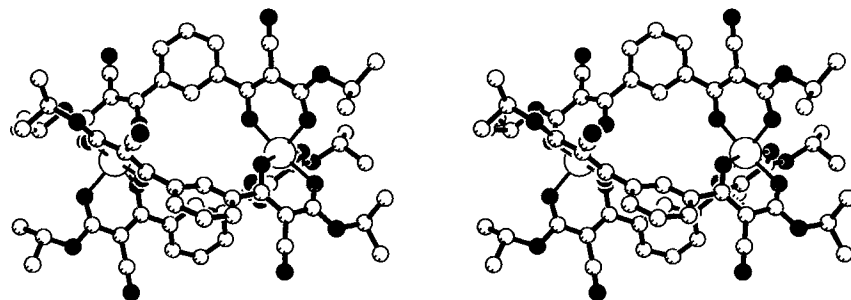
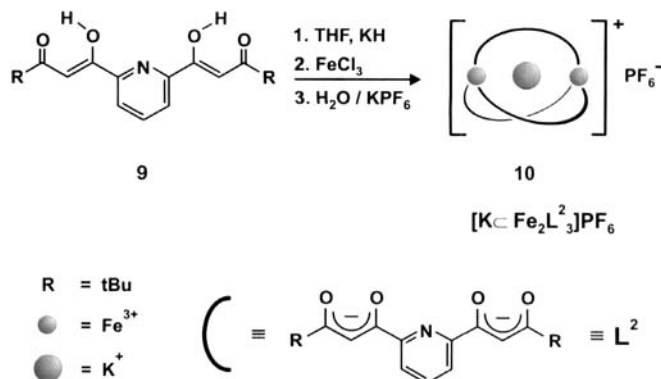


Figure 1. Stereoview of **8** perpendicular to the Fe–Fe axis (hydrogen atoms and solvent molecules have been omitted for clarity).



Scheme 2. Synthesis of metallacryptate **10**.

(**9**)^[17, 18] with potassium hydride in THF, addition of iron(III) chloride and subsequent work-up with aqueous potassium hexafluorophosphate, we were able to isolate rust-coloured microcrystals of general composition $[\text{K} \subset \text{Fe}_2\text{L}_3^2]^+(\text{PF}_6)^-$ (**10**, Scheme 2).

According to an X-ray crystallographic structure analysis,^[11] **10** is a C_{3h} -symmetric {2}-metallacryptate (= metallapaddlane), an idealised view of which is shown in Figure 2.

In the centre of the $[\text{Fe}_2\text{L}_3^2]$ cavity of **10** is a potassium ion with ninefold coordination to six ligand oxygens and to three pyridine nitrogen atoms; 3 molecules of solvent dichloromethane are incorporated in the space between the individual molecules. A hexafluorophosphate ion acts as counterion and an additional solvent molecule is intercalated in the crystal lattice. Complex **10** also crystallises in the space group $P\bar{1}$, and the two iron atoms ($d_{\text{Fe}-\text{Fe}} = 715$ pm) are octahedrally surrounded by six oxygen atoms. However, in contrast to racemic $[(\Delta, \Delta)/(\Lambda, \Lambda)\text{-fac}]\text{-8}$, the two iron centres in *meso*-**10** $[(\Delta, \Delta)\text{-fac}]$ have opposite configuration (Figure 3). It is noticeable that the empty metallacryptand **8** forms a chiral triple helix, whereas the metallacryptate **10** is achiral. Further investigations are necessary to clarify whether there is a general relationship between the inclusion of cations and the stereochemistry of the cryptate.

Cyclic voltammetry of the {2}-metallacryptand **8** and the {2}-metallacryptate **10** under aprotic conditions^[19] shows slight differences in the behaviour of the redox-active iron centres. Cyclic voltammograms of the metallacryptand **8** display a quasireversible, one-potential, two-electron transfer process (chart speed: 50 mVs^{-1} , Figure 4a). The half-wave potential $E_{1/2} = -430$ mV corresponds to the redox process $[\text{Fe}_2^{\text{III}}\text{L}_3^1]/[\text{Fe}_2^{\text{II}}\text{L}_3^1]^{2-}$. However, thin-layer cyclic voltammograms at chart speeds below 20 mVs^{-1} show a weakly structured signal indicating a stepwise electron transfer with a potential separation of approximately 60 mV (Figure 4b). Metallacryptate **10** undergoes two well-separated, quasireversible one-electron transfer processes (chart speed 50 mVs^{-1} , Figure 4c). The half-wave potential $E_{1/2} = -895$ mV corresponds to the redox process $[\text{K} \subset \text{Fe}^{\text{III}}\text{L}_3^2]^+ / [\text{K} \subset \text{Fe}^{\text{II}}\text{L}_3^2]$, whereas the reduction of $[\text{K} \subset \text{Fe}^{\text{II}}\text{L}_3^2]$ to $[\text{K} \subset \text{Fe}^{\text{II}}\text{L}_3^2]^-$ occurs at $E_{1/2} = -1130$ mV. This behaviour clearly demonstrates a sen-

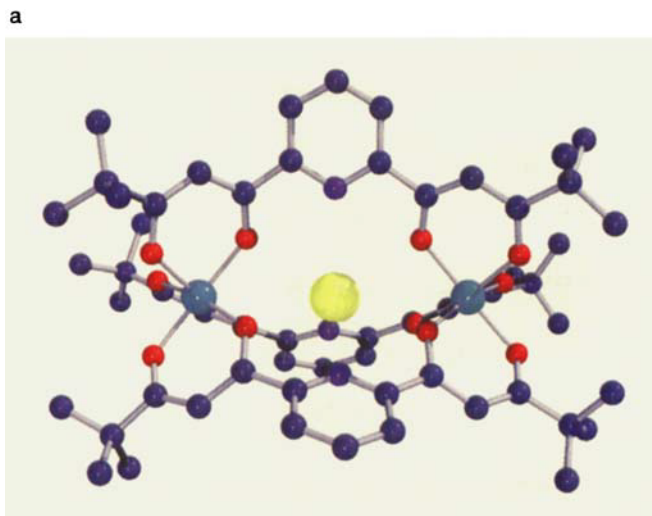


Figure 2. a) View of **10** perpendicular to the Fe–Fe axis (hydrogen atoms, counterion and solvent molecules have been omitted for clarity). Iron: green, potassium: yellow, oxygen: red, nitrogen: blue, carbon: grey.

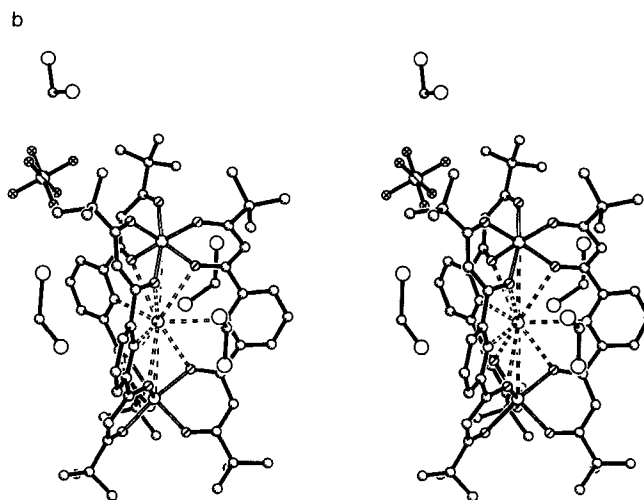


Figure 2. b) Stereoview of **10** perpendicular to the Fe–Fe axis, including the $(PF_6)^-$ counterion and dichloromethane solvent molecules (hydrogen atoms have been omitted for clarity).

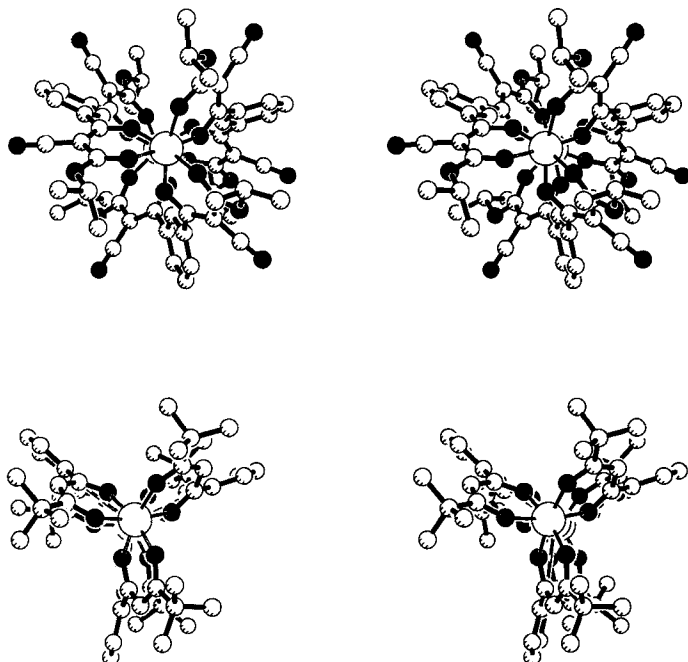


Figure 3. Top: stereoview of **8** along the Fe–Fe axis. Bottom: stereoview of **10** along the C_3 axis (hydrogen atoms, solvent molecules and counterion have been omitted for clarity).

sitive dependence of the electrochemical properties on electrostatic interactions which are increased by the inclusion of potassium in **10**.

Mössbauer measurements were performed on the {2}-metallacryptand **8** and on the K^+ -{2}-metallacryptate **10**^[20] at 4.2–300 K with and without a field applied perpendicular (20 mT and 5.3 T) or parallel (5.3 T) to the γ -beam. All zero-field and 20 mT spectra exhibit a broad and unresolved absorption pattern (Figure 5a) due to (temperature-independent) spin–spin relaxation. Application of 5.3 T at 4.2 K results in well-resolved magnetic hyperfine patterns, which were analysed with the spin-

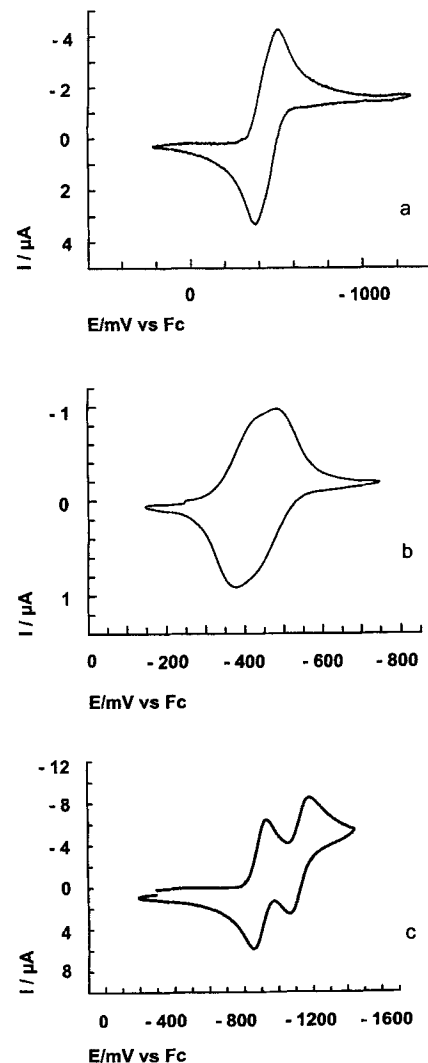


Figure 4. Cyclic voltammograms of a) the metallacryptand **8** (scan rate: 50 mVs^{-1}); b) metallacryptand **8** under thin-layer conditions (scan rate: 10 mVs^{-1}); c) metallacryptate **10** in CH_2Cl_2 (0.1 M TBAHFP; scan rate: 50 mVs^{-1}) vs. Fc/Fc^+ .

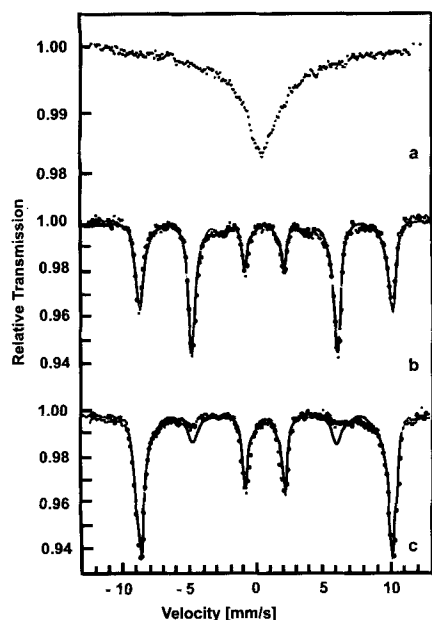


Figure 5. Experimental Mössbauer spectra of **10**, recorded at a) 4.2 K, 20 mT $\perp \gamma$; b) 5.3 T $\perp \gamma$; c) 5.3 K $\parallel \gamma$. Solid lines result from spin-Hamiltonian simulations which used the parameters summarised in Table 1.

Table 1. Spin-Hamiltonian parameters resulting from simulations of 5.3 T spectra (\parallel and $\perp \gamma$) of **8** and **10**, recorded at 4.2 K.

	δ [a]	ΔE_Q [b]	η [c]	Γ [d]	D [e]	E/D [f]	$A_{xx}/g_n\mu_n$ [g]	$A_{yy}/g_n\mu_n$ [g]	$A_{zz}/g_n\mu_n$ [g]	$g_{x,y,z}$ [h]
8	0.56	+0.13	0	0.35	-1.1	0	-18.7	-24.3	-22.7	2
10	0.56	+0.10	0	0.35	-1.1	0	-18.9	-23.4	-21.8	2

[a] Isomeric shift relative to α -Fe at room temperature (mm s^{-1}). [b] Quadrupole splitting; sign corresponds to main compound of electric field gradient tensor (mm s^{-1}). [c] Asymmetry parameter of electric field gradient. [d] Line width at half height (mm s^{-1}). [e] Zero-field splitting parameter (cm^{-1}). [f] Rhombicity parameter. [g] Magnetic hyperfine coupling components (T). [h] g-Factors.

Hamiltonian formalism (Figure 5b,c).^[21] The hyperfine patterns of **8** and **10** are practically the same; this is also reflected by the spin-Hamiltonian parameters as summarised in Table 1. From the isomer shifts δ and quadrupole splittings ΔE_Q we conclude that each individual iron atom in **8** and **10** is hexacoordinated by oxygen atoms in a nearly perfect octahedral arrangement. The magnetic hyperfine patterns are successfully simulated by neglecting exchange interactions between the iron(III) sites; this result is plausible considering the relatively large Fe–Fe distances. Obviously, the presence of potassium in **10** has no measurable effect on the local electronic structure of each of the two irons nor on the exchange interaction between them as compared to **8**.

Conclusion

The importance of these results beyond this work is the realisation that there exists parallel to the family of the classical crown ethers, cryptands and their complexes, a topologically equivalent family of metallacrowns, metallacryptands and their inclusion complexes. Their representatives are available in very good yields from one-pot reactions or in two steps respectively by self-assembly.

Experimental Section

Complex 8: Triethylamine (0.83 mL, 6 mmol) was added to a solution of ligand **7** (1.16 g, 3 mmol) in dry CH_2Cl_2 (100 mL). The mixture was stirred for 30 min at 20 °C. After addition of iron(III) chloride (324 mg, 2 mmol) the solution turned red. The mixture was stirred for 3 h at 20 °C, followed by addition of water (75 mL). The two phases were separated, the aqueous layer extracted with CH_2Cl_2 (3×50 mL), and the combined organic phases dried over anhydrous sodium sulfate. After filtration the solvent was removed. Red crystals were obtained by the diffusion of diethyl ether into a chloroform solution. Yield: 1.15 g (91%); m.p. > 250 °C (decomp.); IR (KBr): $\tilde{\nu} = 2220$ (CN), 1590, 1560 (C=C) cm^{-1} ; FAB-MS (3-nitrobenzyl alcohol matrix): $m/z = 1305$ ($\text{Fe}_2\text{L}_3^+ + 2\text{Na}^+$), 1282 ($\text{Fe}_2\text{L}_3^+ + \text{Na}^+$), 1259 (Fe_2L_3^+); $\text{C}_{60}\text{H}_{54}\text{Fe}_2\text{N}_6\text{O}_{18}$ (1258.81): calcd C 57.25, H 4.32, N 6.68; found: C 57.27, H 4.30, N 6.61

Complex 10: Ligand **9** (994 mg, 3 mmol) was added to a suspension of potassium hydride (241 mg, 6 mmol) in dry THF (100 mL) and the mixture stirred for 15 min at 20 °C. After addition of iron(III) chloride (324 mg, 2 mmol) the solution turned dark red. The solution was stirred for 4 h at 20 °C, and then treated with aqueous $[\text{KPF}_6]$ (4.5 g, 24 mmol) in water (100 mL). The two phases were separated, the aqueous layer extracted with CH_2Cl_2 (3×50 mL), and the combined organic phases dried over anhydrous potassium sulfate. After filtration the solvent was removed. Rust-coloured crystals were obtained by diffusion of diisopropyl ether and CH_2Cl_2 . Yield: 926 mg (72%); m.p. > 250 °C (decomp.); IR (CHBr₃): $\tilde{\nu} = 1590, 1550, 1515$ cm^{-1} (C=O); FAB-MS (3-nitrobenzyl alcohol matrix): $m/z = 1138.0$; $\text{C}_57\text{H}_{69}\text{F}_6\text{Fe}_2\text{KN}_3\text{O}_{12}\text{P}$ (1283.94): calcd C 53.32, H 5.42, N 3.27; found: C 53.33, H 5.49, N 3.23 ($\text{K}^+ \leftarrow \text{Fe}_2\text{L}_3^+$), 808.9 ($\text{K}^+ \leftarrow \text{Fe}_2\text{L}_2^+$).

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- [11] Crystal data for **8**: $\text{C}_{60}\text{H}_{54}\text{Fe}_2\text{N}_6\text{O}_{18} \cdot 2.75\text{C}_4\text{H}_{10}\text{O} \cdot 0.25\text{CHCl}_3$; $M = 1258.79 + (2.75 \times 74.12) + (0.25 \times 119.38)$; crystal dimensions: $0.80 \times 0.70 \times 0.70\text{ mm}^3$; triclinic; space group $P\bar{1}$; $a = 1442.7(15)$, $b = 1613.8(16)$, $c = 1792.4(17)\text{ pm}$; $\alpha = 105.44(3)$, $\beta = 107.13(3)$, $\gamma = 90.55(3)^{\circ}$; $V = 3.826(7)\text{ nm}^3$; $Z = 2$; $\rho_{\text{calc}} = 1.295\text{ Mg m}^{-3}$; $F(000) = 1564$; $\lambda = 71.073\text{ pm}$; $T = 153\text{ K}$; $\mu(\text{MoK}\alpha) = 0.478\text{ mm}^{-1}$; min/max transmission: 0.679/0.862; $2.96^{\circ} \leq 2\theta \leq 51.58^{\circ}$; 26983 collected reflections, of which 12724 were independent ($R_{\text{int}} = 0.0276$) and used in the structure refinement (1094 parameters, 639 restraints). The R -values are $R1 = \sum |F_o - F_c| / \sum F_o = 0.0486$ ($1 > 2\sigma(I)$) and $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2} = 0.1155$ (all data); min/max residual electron density: $-660\text{ e nm}^{-3} / 436\text{ e nm}^{-3}$. Two sites are occupied by diethyl ether molecules at two positions with occupancies of 0.55:0.45 each. The third position of solvent molecule in the asymmetric unit is occupied by diethyl ether at two positions and by CHCl_3 at the third position (0.37:0.38:0.25). Crystal data for **10**: $\text{C}_{57}\text{H}_{69}\text{F}_6\text{Fe}_2\text{KN}_3\text{O}_{12}\text{P} \cdot 2.5\text{CH}_2\text{Cl}_2$; $M = 1283.92 + (2.5 \times 84.93)$; crystal dimensions: $0.65 \times 0.50 \times 0.45\text{ mm}^3$; triclinic; space group $P\bar{1}$; $a = 1515.0(3)$, $b = 1519.9(3)$, $c = 1734.6(4)\text{ pm}$; $\alpha = 90.82(3)$, $\beta = 96.03(3)$, $\gamma = 118.61(3)^{\circ}$; $V = 3.4775(13)\text{ nm}^3$; $Z = 2$; $\rho_{\text{calc}} = 1.429\text{ Mg m}^{-3}$; $F(000) = 1546$; $\lambda = 71.073\text{ pm}$; $T = 133\text{ K}$; $\mu(\text{MoK}\alpha) = 0.766\text{ mm}^{-1}$; min/max transmission: 0.759/0.780; $3.64^{\circ} \leq 2\theta \leq 54.00^{\circ}$; 66986 collected reflections of which 15082 were independent ($R_{\text{int}} = 0.0271$) and used in the structure refinement (958 parameters, 706 restraints). The R values are $R1 = 0.0376$ ($1 > 2\sigma(I)$) and $wR2 = 0.0944$ (all data); min/max residual electron density: $-625\text{ e nm}^{-3} / 584\text{ e nm}^{-3}$. Two *t*-butyl groups are disordered over two positions with occupancies of 0.54:0.46 and 0.82:0.18. One *t*-butyl group shows two different rotameric conformations with occupancies of 0.50:0.50. The three dichloromethane molecules coordinated to the complex cavities are disordered around inversion centres.
- The intensities of **8** and **10** were collected on a Stoe–Siemens–Huber four-circle diffractometer with Siemens CCD area detector by using φ - and ω -scans on a shock-cooled crystal in an oil drop.^[12] Data integration was performed with the program SAINT. For all data, a semiempirical absorption correction was applied. The structure of **8** was solved by Patterson methods and that of **10** by direct methods (SHELXS-96).^[13] Refinement of F^2 was accomplished by the least-squares method (SHELXL-96).^[14] All non-hydrogen atoms were refined anisotropically and the riding model was used for the hydrogen atoms. All disordered components were refined anisotropically with the assistance of distance and ADP restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100076. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code + (1223)336-033, e-mail: deposit@chemcryst.cam.ac.uk).
- For red-green stereoviews of **8** and **10**, see <http://www.organik.uni-erlangen.de/saalfrank.index.html>
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