{2}-Metallocryptands of Iron and Gallium: Synthesis, Structure, and Properties [1]

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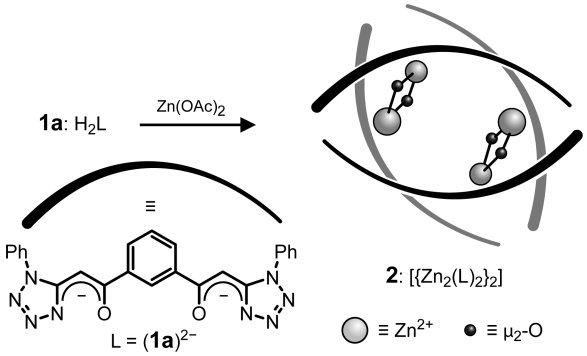
Starting from CH-acidic tetradentate ligands H_2L (**1**) and triethylamine, the synthesis and characterisation of four dinuclear iron(III) and gallium(III) cryptands $[M_2(L)_3]$ (**3**, **4**) are reported. The structures of the ligand H_2L (**1a**) and the triple helicate **3b** were determined by X-ray diffraction analysis. The ferric complexes **3** were further characterised by Mössbauer spectroscopy and cyclic voltammetry. NMR spectroscopy proved the diamagnetic gallium(III) cryptands **4** to remain stable in solution for several days.

Key words: N,O-Ligand, Metallocryptand, Triple Helicate, Self-assembly, Supramolecular Chemistry

Introduction

Recent developments on design and synthesis of supramolecular inorganic structures *via* self-assembly [2] exhibiting novel properties have provided exciting new prospects [3]. Over the years we have synthesised a multitude of supramolecular structures with different tetrazolyl enolate ions, ranging from coordination polymers with bidentate ligands [4] to metallocryptands with tetradentate ligands [5]. For instance, reaction of the bis-tetrazolyl ketone H_2L (**1a**) and zinc(II) acetate dihydrate yielded the bis(double helicate) $[\{Zn_2(L)_2\}_2]$ (**2**) (Scheme 1) which was crystallised as the cryptatoclathrate $[(thf)_2\subset(\{Zn_2(L)_2\}_2)_2] \equiv [(thf)_2\subset(\mathbf{2})_2]$.

Inspired by these results and our experiences in the field of supramolecular coordination chemistry, we became interested in the reaction of the bis-tetrazolyl ketones **1**, analogues [6] of the 1,3-diketo ligand system, with trivalent six-coordinate transition metal ions.



Scheme 1. Synthesis and schematic presentation of bis-(double helicate) **2**.

Results and Discussion

According to the literature procedure given in [5], the synthesis of H_2L (**1**) starts from 1,3-diacetylbenzene, sodium hydride, alkyl isothiocyanates and methyl iodide to give bis-ketene-*N*,*S*-acetals. Further reaction of the bis-ketene-*N*,*S*-acetals with sodium azide, cyclisation of the corresponding vinylazide intermediates and tautomerisation finally afford the bis-tetrazole ketones **1**. Vapour diffusion of diethyl ether into a dichloromethane solution of **1a** leads to transparent cuboids, crystallising in the achiral monoclinic space group $C2/c$ with four molecules in the unit cell [7, 8]. The molecular structure of **1a** is depicted in Fig. 1, top.

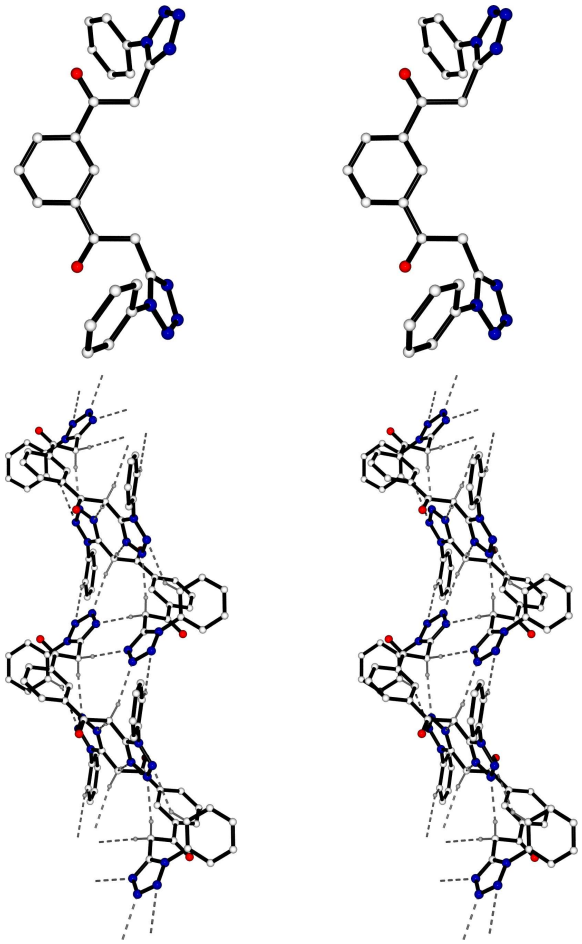
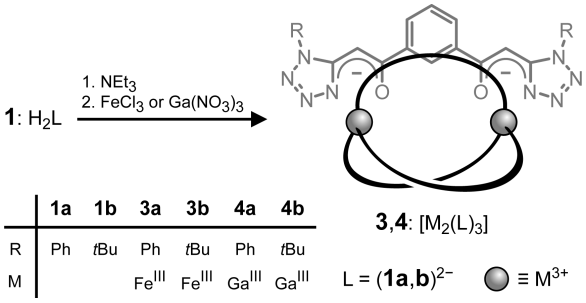


Fig. 1. Stereoviews (POVRAY presentation) of the molecular structure of (P,P)-(**1a**) (top) and *meso*-$(P,P)/(M,M)$-1D-$^{1}_{4}$(H$_2$L) (**1a**$_n$) (n = 4; bottom) [hydrogen atoms omitted for clarity, except hydrogen atoms involved in H bonding; O red, N blue, C white, H grey (small), H-bond grey (dotted) (colour online)].

It is worth to note that during crystallisation desymmetrisation of the intrinsically achiral bis-tetrazole ketones **1a** affords racemic crystals. In the crystal, the assembly of **1a** is dominated by twelve weak intermolecular H bonds ($d_{\varnothing}$(N···H–C) = 2.48 Å) [9] between alternating C_2-symmetric $(P,P)/(M,M)$-enantiomers of **1a** [10], which form racemic dimers with an inversion centre. These dimers are linked in parallels leading to a sinusoidal one-dimensional arrangement along the c axis to give the final solid state 1D polymer *meso*-$(P,P)/(M,M)$-1D-$^{1}_{\infty}$(H$_2$L) (**1a**$_\infty$) (Fig. 1, bottom).

Deprotonation of H$_2$L (**1**) with triethylamine in dichloromethane, reaction with iron(III) chloride under



	1a	1b	3a	3b	4a	4b
R	Ph	*t*Bu	Ph	*t*Bu	Ph	*t*Bu
M			Fe^{III}	Fe^{III}	Ga^{III}	Ga^{III}

Scheme. 2. Synthesis and schematic presentation of the triple helicates **3** and **4**.

reflux, and subsequent workup afforded a deep-violet microcrystalline material (Scheme 2). The formation of the {2}-ironcryptands [Fe$_2$(L)$_3$] (**3**) was suggested by elemental analysis and FAB mass spectroscopy (m/z = 1337 and 1457 for **3a** and **3b**, respectively).

In order to confirm the generation of the racemic {2}-ironcryptands **3**, a single-crystal X-ray structure analysis was carried out on dark-violet crystals of **3b**, obtained from an acetone/methanol/diethyl ether solution on standing for two weeks [7, 8]. According to this analysis, **3b** crystallises in the achiral monoclinic space group *Cc* with eight molecules in the unit cell. The asymmetric unit of **3b** contains two independent molecules forming pairs of enantiomers of the (Δ,Δ)-*fac* or (Λ,Λ)-*fac* {2}-ironcryptands, being related by pseudo centres of symmetry and differing only in terms of conformation and disorder. The molecular structure of {2}-ironcryptand (Δ,Δ)-[Fe$_2$(L)$_3$] (**3b**) is depicted in Fig. 2 (top) and consists of two slightly distorted octahedrally coordinated iron(III) centres bridged by three ligands (**1b**)$^{2-}$. The coordination sphere of the metal ions is built up by three carbonyl oxygen and three tetrazolyl nitrogen donors each. The intramolecular distances between the iron(III) ions amount to 6.803 and 6.950 Å, respectively. In addition, the {2}-metallocryptands are packed in the crystal lattice as racemic dimers (d(Ph-Ph) = 3.28 Å) with (Δ,Δ)- or (Λ,Λ)-stereochemistry at the iron(III) centres (Fig. 2, bottom).

Further characterisation of the complexes **3** was achieved by Mössbauer spectroscopy and cyclic voltammetry. Exemplarily, a Mössbauer spectrum of a powder sample of **3b** was recorded at 77 K in the absence of an applied magnetic field. It exhibits a broad and unresolved line pattern due to (temperature-independent) spin-spin relaxation with an isomeric shift δ(77 K) = 0.54 mm s^{-1} (not shown), typical for a high-spin iron(III) species with N,O liga-

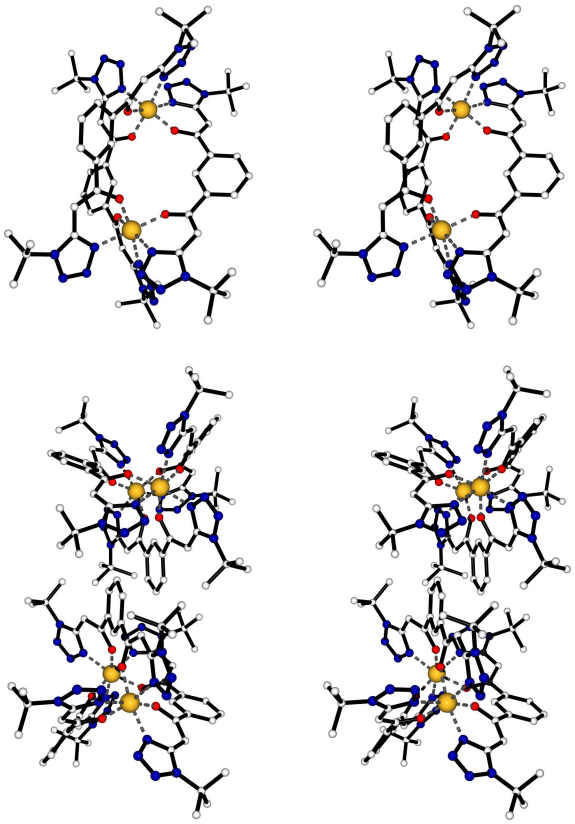


Fig. 2. Stereoviews (POVRAY presentation) of one independent molecule of the triple helicate (Δ,Δ)-$[Fe_2(L)_3]$ (**3b**) (top) and the dimeric racemic aggregate of **3b** with (Δ,Δ)- and (Λ,Λ)-stereochemistry at the ferric ions (bottom, view approximately along the Fe–Fe axes), highlighting the opposite helicity in the {2}-metallocryptands [hydrogen atoms, disorder, and non-coordinating solvent molecules omitted for clarity; Fe gold, O red, N blue, C white (colour online)].

tion [3m,n, 4a,b, 6a – c]. The reversible cyclic voltammogram of the metallocryptand **3b** was recorded in dichloromethane *versus* Fc/Fc^+ and displays a quasi-reversible, one-potential, two-electron transfer process (Fig. 3, scan rate 50 mV s^{-1}). The half-wave potential $E_{l/2} = -1265$ mV corresponds to the redox process $[Fe^{III}{}_2L_3]/[Fe^{II}{}_2L_3]^{2-}$. Comparable cyclic voltammograms were also obtained for analogous {2}-ironcryptands which possess ester functionalities instead of tetrazolyl groups [11].

White microcrystalline materials were obtained when gallium nitrate was treated with deprotonated **1** in a methanol/dichloromethane solution (Scheme 2). Elemental analysis and FAB MS data (*m/z* = 1366 and 1486 for **4a** and **4b**, respectively) indicate the formation of {2}-gallium(III) cryptands $[Ga_2(L)_3]$ (**4**).

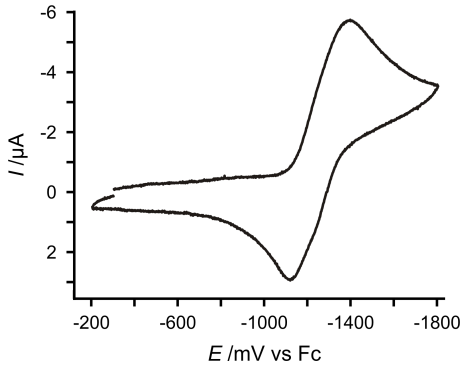


Fig. 3. Cyclic voltammogram of **3b**, scan rate 50 mV s^{-1}.

An X-ray diffraction analysis was carried out on colourless cuboidal crystals of **4a**, obtained from a dichloromethane solution by vapour diffusion of diethyl ether, but the poor data set did not allow complete refinement of the structure. However, it could be established that the molecular structure of the {2}-galliumcryptand **4a** is in principle isostructural to that of complex **3b**, and that complex **4a** is present in the crystal as a racemic mixture with homochiral (Δ,Δ)-*fac* or (Λ,Λ)-*fac* gallium centres. In contrast to the paramagnetic iron(III) complexes **3**, the gallium(III) cryptands **4** are amenable to NMR spectroscopic investigations. Due to symmetry, the ligands **1** and complexes **4** [12] show a reduced number of signals in the ^1H and ^{13}C NMR spectra (*e. g.* 5 ^1H and 9 ^{13}C NMR signals for **1b** and racemic **4b**). Clearly, cryptand **4b** remains intact in $[D_2]$methylene chloride solution for several days, as shown by the presence of the ^{13}C NMR carbonyl signal at δ = 174.31 ppm, approximately 20 ppm high-field shifted compared to the signal of the free ligand **1b** (δ = 194.14 ppm, $[D_6]$dimethyl sulfoxide).

Experimental Section

General information

Unless stated otherwise, all manipulations were carried out under dry dinitrogen atmosphere, and the solvents used were purified and dried according to standard procedures. All reagents employed (high-grade purity materials) were commercially available and used as supplied (Fluka, Aldrich, and Acros Organics). The bis-tetrazolyl ketones H_2L (**1**) were prepared according to the literature [5]. Melting points were determined on a Wagner-Munz apparatus and are not corrected. IR spectra were recorded on a Bruker IFS 25 spectrometer. NMR spectra were obtained from dilute solutions at approximately 25 °C and recorded on a Jeol EX400 spec-

trometer (^{1}H 400.1 MHz, ^{13}C 100.5 MHz). The residual solvent signals were used as internal standards: [D_6]dimethyl sulfoxide (^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm) and [D_2]methylene chloride (^{1}H: δ = 5.32 ppm, ^{13}C: δ = 53.8 ppm) [13]. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), or m (multiplet). Mass spectra were recorded on Varian MAT 311 A (70 Ev) (EI) or Micromass ZABSpec (Cs^+) spectrometers with *m*-NBA as matrix (FAB). Elemental analyses were performed on a Carlo Erba EA1110 CHN instrument and on a Heraeus CHN-Microautomat.

*H_2L (**1a**): cf.* Lit. [5]

*H_2L (**1b**):* Yield: 3.1 g (76 %) colourless needles. – M. p. 206 °C. – IR (KBr): ν = 2988, 2941, 1683, 1598, 1509. – ^{1}H NMR ([D_6]dimethyl sulfoxide): δ = 8.70 (s, 1H, Ar-*H*), 8.39 (d, 2H, Ar-*H*), 7.82 (t, 1H, Ar-*H*), 5.27 (s, 4H, 2 CH_2), 1.64 (s, 18H, 6 CH_3). – ^{13}C NMR ([D_6]dimethyl sulfoxide): δ = 194.14 (2 *C*=O), 149.12 (2 *C*N_2), 135.69 (2 Ar-C_{ipso}), 133.70 (2 Ar-*C*H), 128.68 and 128.62 (2 Ar-*C*H), 61.36 (2 *C*$(CH_3)_3$), 36.53 (2 *C*H_2), 29.12 (6 *C*H_3). – MS (EI): *m/z* (%) = 410 (5) $[M]^+$. – $C_{20}H_{26}N_8O_2$ (410.48) [14]: calcd. C 58.52, H 6.38, N 27.30; found C 57.65, H 6.43, N 27.32.

*General procedure for the synthesis of $[Fe_2(L)_3]$ (**3**)*

To a solution of the a bis-tetrazolyl ketone **1** (0.75 mmol) in dichloromethane (75 mL) was added triethylamine (0.21 mL, 1.5 mmol). This solution was then added to a clear solution of anhydrous iron(III) chloride (0.16 g, 1.0 mmol) in dichloromethane (200 mL) and diethyl ether (20 mL). The mixture was heated for 16 h under reflux, cooled to 20 °C, and washed with water (3 × 100 mL). The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. The crude reaction product was crystallised from the indicated solvent systems.

*$[Fe_2(L)_3]$ (**3a**):* H_2L (**1a**): 0.34 g. – Yield: 0.28 g (83 %) violet plates from acetone/methanol/diethyl ether. – M. p. > 250 °C (decomp). – IR (KBr): ν = 3020, 2938, 1540, 1524. – MS (FAB): *m/z* (%) = 1337 (100) $[Fe_2(L)_3]^+$. – $C_{60}H_{72}N_{24}O_6Fe_2$ (1337.09) [14]: calcd. C 53.90, H 5.43, N 25.14; found C 52.42, H 5.36, N 22.88.

*$[Fe_2(L)_3]$ (**3b**):* H_2L (**1b**): 0.31 g. – Yield: 0.30 g (81 %) violet microcrystals from chloroform/diethyl ether. – M. p. > 250 °C (decomp). – IR(KBr): ν = 2951, 1551, 1499. – MS (FAB): *m/z* (%) = 1457 (27) $[Fe_2(L)_3]^+$. – $C_{72}H_{48}N_{24}O_6Fe_2$ (1457.02) [14]: calcd. C 59.35, H 3.32, N 23.07; found C 57.47, H 3.27, N 20.77.

*General procedure for the synthesis of $[Ga_2(L)_3]$ (**4**)*

To a solution of a bis-tetrazolyl ketone **1** (0.75 mmol) in dichloromethane (50 mL) was added triethylamine (0.21 mL, 1.5 mmol). This solution was then added to a solution of gallium nitrate hydrate (0.21 g, ∼ 1.0 mmol) in methanol (50 mL). After stirring for 16 h at r. t., the reaction mixture was evaporated to dryness. The residue was taken up with dichloromethane and the organic phase washed with water (3 × 50 mL), dried over anhydrous magnesium sulfate, and evaporated to dryness. The crude reaction product was crystallised from the indicated solvent systems.

*$[Ga_2(L)_3]$ (**4a**)* [12]: H_2L (**1a**): 0.34 g. – Yield: 0.31 g (85 %) colourless cuboids from methylene chloride/diethyl ether. – M. p. > 250 °C (decomp). – IR (KBr): ν = 3065, 1595, 1541, 1500, 1459. – MS (FAB): *m/z* (%) = 1486 (4) $[Ga_2L_3+H]^+$. – $C_{72}H_{48}N_{24}O_6Ga_2$ (1484.77) [14]: calcd. C 58.24, H 3.26, N 22.64; found C 57.11, H 3.25, N 22.34.

*$[Ga_2(L)_3]$ (**4b**):* H_2L (**1b**): 0.31 g. – Yield: 0.31 g (90 %) white powder. – M. p. > 250 °C (decomp). – IR (KBr): ν = 2984, 1534, 1465. – ^{1}H NMR ([D_2]methylene chloride): δ = 8.96 (s, 3H, Ar-*H*), 7.57 (dd, 6H, Ar-*H*), 7.25 (t, 3H, Ar-*H*), 5.73 (s, 6H, 2 –C*H*=), 1.72 (s, 54H, 18 CH_3). – ^{13}C NMR ([D_2]methylene chloride): δ = 174.31 (6 *C*–O), 152.53 (6 *C*N_2), 142.01 (6 Ar-C_{ipso}), 128.32, 127.39 (6 Ar-*C*H), 126.79 (6 Ar-*C*H), 76.88 (6 –*C*H=), 60.85 (6 *C*$(CH_3)_3$), 29.06 (18 *C*H_3). – MS (FAB): *m/z* (%) = 1366 (100) $[Ga_2L_3+H]^+$. – $C_{60}H_{72}N_{24}O_6Ga_2$ (1364.84) [14]: calcd. C 52.80, H 5.32, N 24.63; found C 54.83, H 6.09, N 20.82.

Table 1. Crystal structure data for **1** and **3b**.

	1a	**3b**
Formula	$C_{24}H_{18}N_8O_2$	$C_{60}H_{72}Fe_2N_{24}O_6 \cdot 1.5$ $C_4H_{10}O \cdot 0.5\ CH_4O$ $\cdot C_3H_6O$
M_r	450.46	1522.40
Crystal size, mm^3	0.30×0.30×0.30	0.70×0.50×0.30
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	Cc
Temperature, K	173(2)	133(2)
a, Å	18.3762(7)	23.674(3)
b, Å	11.065(2)	23.425(3)
c, Å	12.1919(4)	28.424(3)
β, deg	114.27(2)	103.96(2)
V, Å^3	2260.0(5)	15297(3)
Z	4	8
D_{calcd}, g cm^{-3}	1.324	1.322
μ(MoK_α), mm^{-1}	0.090	0.450
F(000), e	936	6432
hkl range	$-23 \le h \le +23$ $-14 \le k \le +13$ $-15 \le l \le +15$	$-27 \le h \le +28$ $0 \le k \le +27$ $-33 \le l \le +33$
Refl. measured/unique	4720/2581	104127/24995
R_{int}	0.0187	0.0381
Param. refined	936	2031
$R(F)$ $[I \ge 2\sigma(I)]/wR(F^2)$ (all refls.)	0.0459/0.1462	0.0468/0.1224
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.211/−0.240	0.737/−0.520

Crystal structure determination

Details for crystal data, data collection, and refinement are given in Table 1. X-Ray data were collected on a Nonius Kappa CCD area detector (**1a**) and on a Stoe-Siemens-Huber four circle diffractometer equipped with a CCD area detector (**3b**) with MoK_α radiation (λ = 0.71073 Å). The structures were solved by Direct Methods with SHELXS-97 and refined with full-matrix least-squares against F^2 with SHELXL-97 [15]. Lorentz, polarisation, and absorption corrections [16] were applied for **1a**. All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms ideal positions were calculated. They were refined with a riding model. In structure **3b** some parts of the ligands were disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters. The OH hydrogen atom in the solvent molecule MeOH could not be found. The structure was refined as a racemic twin. The fractional contributions refined to 0.54 : 0.46(1).

Cyclic voltammetry

Cyclic voltammetry at a platinum electrode was performed in CH_2Cl_2 {0.2 M [(nBu)$_4$N](PF$_6$)} at r.t. under an argon atmosphere using a three-electrode set-up and an EG&G (potentiostat/galvanostat) model 283 [17]. Redox potentials were internally referenced against ferrocene/ferrocenium (Fc/Fc^+).

Acknowledgements

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