
Rolf W. Saalfrank a, Uwe Reimann a, Andreas Scheurer a, Frank Hampel b, Cornelia Goebel c, and Regine Herbst-Irmer c

a Department Chemie und Pharmazie, Lehrstuhl für Anorganische und Allgemeine Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 1, 91058 Erlangen, Germany
b Department Chemie und Pharmazie, Organische Chemie, Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany
c Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany

Reprint requests to Prof. Dr. R. W. Saalfrank. Fax: (+49) 9131-85-27367.
E-mail: rolf.saalfrank@chemie.uni-erlangen.de

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Starting from CH-acidic tetradentate ligands H2L (1) and triethylamine, the synthesis and characterisation of four dinuclear iron(III) and gallium(III) cryptands [M2(L)3] (3, 4) are reported. The structures of the ligand H2L (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 tetracyclo enolate ions, ranging from coordination polymers with bidentate ligands [4] to metallocryptands with tetratate ligands [5]. For instance, reaction of the bis-tetrazolyl ketone H2L (1a) and zinc(II) acetate dihydrate yielded the bis(double helicate) [(Zn2(L)2)2] (2) (Scheme 1) which was crystallised as the cryptato-clathrate [(thf)2⊂{(Zn2(L)2)2}] ≡ [(thf)2⊂(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.

Results and Discussion

According to the literature procedure given in [5], the synthesis of H2L (1) starts from 1,3-diacetylbenzene, sodium hydride, alkyl isothiocyanates and methyl iodide to give bis-ketene-N,S-acets. Further reaction of the bis-ketene-N,S-acets 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.
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 ($d(\text{N} \cdots \text{H} - \text{C}) = 2.48 \text{ Å}$) [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 $\text{meso-}(P,P)/(M,M)-1\text{D}(\text{H}_2\text{L})$ (1a$_n$) (Fig. 1, bottom).

Deprotonation of $\text{H}_2\text{L}$ (1) with triethylamine in dichloromethane, reaction with iron(III) chloride under reflux, and subsequent workup afforded a deep-violet microcrystalline material (Scheme 2). The formation of the $\{2\}$-ironcryptands $[\text{Fe}_2\text{L}_3]$ (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 $(\Delta,\Delta)$-fac or $(\Lambda,\Lambda)$-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 $(\Delta,\Delta)$-$[\text{Fe}_2\text{L}_3]$ (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 ($d(\text{Ph-Ph}) = 3.28 \text{ Å}$) with $(\Delta,\Delta)$- or $(\Lambda,\Lambda)$-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 $\delta(77 \text{ K}) = 0.54 \text{ mm s}^{-1}$ (not shown), typical for a high-spin iron(III) species with $N,O$ liga-
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Fig. 2. Stereoviews (POVRAY presentation) of one independent molecule of the triple helicate (Δ,Δ)−[Fe₂(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)].

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 ¹³C NMR spectra (e.g. 5 ¹H and 9 ¹³C NMR signals for 1b and racemic 4b). Clearly, cryptand 4b remains intact in [D₂]methylene chloride solution for several days, as shown by the presence of the ¹³C 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, [D₆]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 H₂L (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-
trameter (1H 400.1 MHz, 13C 100.5 MHz). The residual solvent signals were used as internal standards: [D8]dimethyl sulfoxide (1H: δ = 2.50 ppm, 13C: δ = 39.52 ppm) and [D2]methylen chloride (1H: δ = 5.32 ppm, 13C: 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.

**H2L (1a):** cf. Lit. [5]

H2L (1b): Yield: 3.1 g (76%) colourless needles. – M. p. 206 °C. – IR (KBr): ν = 2988, 2941, 1683, 1598, 1509. – 1H NMR ([D8]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 CH2), 1.64 (s, 18H, 6 CH3). – 13C NMR ([D8]dimethyl sulfoxide): δ = 194.14 (2 C=O), 149.12 (2 CN2), 135.69 (2 Ar-Cipso), 133.70 (2 Ar-CH), 128.68 and 128.62 (2 Ar-CH), 61.36 (2 CH(2)H), 56.53 (2 CH2), 29.12 (6 CH3). – MS (EI): m/z (%) = 410 (5) [M]+, – C29H26N2O2 (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 [Fe2L]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 the a bis-tetrazolyl ketone 1 (0.75 mmol) in dichloromethane (200 mL) and diethyl ether (20 mL). The mixture was stirred for 16 h and refluxed, cooled to 20 °C, and washed with water (3 × 50 mL). The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. The crude reaction product was crystallised from the indicated solvents.

[Fe2L]3 (3a): H2L (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) [Fe2L3]+, – C60H27N22O24Fe2 (1337.09) [14]; calcd. C 53.90, H 5.43, N 20.65; found C 52.42, H 5.36, N 22.88.

[Fe2L]3 (3b): H2L (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) [Fe2L3]+, – C72H48N24O24Fe2 (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 [Ga2L3]4 (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 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.

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

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<tr>
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<th>1a</th>
<th>3b</th>
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<tr>
<td><strong>Formula</strong></td>
<td>C24H19N3O2</td>
<td>C60H27Fe2N24O24 · 1.5 C10H11O · 0.5 CH3O · C7H4O</td>
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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 MoKα radiation (λ = 0.71073 Å). The structures were solved by Direct Methods with SHELXS-97 and refined with full-matrix least-squares against F² 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 anisotropically. For the hydrogen atoms 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 CH₂Cl₂ {0.2 M [nBu₄N][PF₆]} 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/ferroacenium (Fc/Fc⁺).

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[14] The microanalytical data for 1b, 3, and 4 deviate from theory due to varying amounts of crystal solvents.


[12] Recrystallised complex 4a showed only a very poor solubility in common deuterated solvents and therefore no NMR data could be recorded.