

Coordination chemistry of 1,4-bis(carboxymethyl)-1,4,7-triazacyclononane: Synthesis and characterization of mononuclear and binuclear μ -oxo-bridged iron(III) complexes, and a 1D-helical copper(II) chain

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Abstract

The syntheses of the pentadentate ligand 1,4-bis(carboxymethyl)-1,4,7-triazacyclononane (**LH**₂) and its use in the preparation of [LHCu]ClO₄ (**1**), and a mononuclear iron(III) complex ([LFeCl] (**2**)) are reported. The hydrolysis of **2** in the presence of an excess of NaClO₄ resulted in the crystallization of a binuclear complex, [Fe₂(μ -O)L₂] · (NaClO₄)₃ · CH₃OH · 3H₂O (**3**). The crystal structures of **1–3** have been determined by single-crystal X-ray crystallography. In complex **1**, the Cu(II) centre is in square based pyramidal environment, with two nitrogen atoms from the tacn ring and two oxygen atoms from two different carboxylate groups lying in the basal plane and the third nitrogen atom occupying the apical position. One pendant acetic acid group is protonated and, instead of coordinating to the copper(II) centre, participates in hydrogen bonding interactions with the perchlorate counter-ion. The coordinated carboxylate group forms a bridge to the copper atom of an adjacent [LHCu]⁺ molecule, thus generating 1D-helical chains. The compound exhibits weak ferromagnetic coupling probably due to weak interactions between [LHCu]⁺ molecules. In complex **2**, the iron(III) centre is in a distorted octahedral geometry, with the *fac*-coordinated triamine ring, two carboxylate groups and one chloride ligand occupying the coordination sphere. In the binuclear complex **3**, two iron(III) centres are bridged by one oxygen atom to form a μ -oxo-diron(III) complex with an Fe · · Fe distance of 3.423(3) Å and a non-linear Fe–O–Fe angle of 144.4°. This binuclear complex features strong antiferromagnetic coupling between the two iron(III) centres. Crown Copyright © 2007 Published by Elsevier Ltd. All rights reserved.

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1. Introduction

Binuclear (and higher nuclearity) transition metal complexes featuring bridging groups between the metal centres have been widely studied over the past few decades. The drive for these studies derives from many quarters, with one major focus being complexes with novel molecular

structures and magnetic behaviour [1–6]. Polynuclear complexes have also been actively pursued as models for multi-metal centre units found at the active sites of important enzymes [7–10]. For example, oxo-bridged iron complexes have attracted considerable interest because diiron centres have been found at the active site of a variety of non-heme proteins (hemerythrin, purple acid phosphatase, ribonucleotide reductase, methane monooxygenase) [11–16].

Ligands based on 1,4,7-triazacyclononane, tacn, are particularly effective for forming binuclear (and higher nuclearity) complexes because they bind strongly to one

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face of the metal polyhedron while at the same time leaving one or more accessible coordination sites for the introduction of bridging ligands. The tacn macrocycle also lends itself readily to further structural elaboration through attachment of potentially coordinating pendant arms (e.g. pyridyl, carboxylate, phosphonate) or non-coordinating organic groups to one or more of the three secondary nitrogens of the tacn ring. Variation in the number and types of pendant groups incorporated into the ligand framework therefore offers a potential means of controlling metal complex stability, selectivity for particular metal ions, as well as the redox potential and stereochemistry of coordinated metal ions. In terms of the formation of multinuclear complexes, the number of pendant groups dictates the number of coordination sites left available for auxiliary ligands to bridge between the metal centres. In some cases, the pendant groups may themselves act as endogenous bridging groups.

Complexes featuring ligands with pendant carboxylate groups [1,2] are of interest because the carboxylate moiety is found in many metalloproteins where aspartate or glutamate side chains act as coordinating groups. In addition, the presence of carboxylate groups increases the probability of forming complexes with interesting magnetic properties because these groups can adopt a variety of coordination modes, ranging from terminal monodentate to several different bridging configurations (*syn-syn*, *syn-anti*, etc.) [17].

We, and others, recently described the synthesis and characterization of stable metal complexes of the ligand, 1,4,7-triazacyclononane-*N*-acetate, that include mononuclear complexes [1,18–20], binuclear complexes [1,20] and helical chains, in which copper(II) atoms are bridged by the carboxylate pendant arms [21]. We have now begun to investigate the coordination behaviour of another carboxylate-bearing tacn ligand, 1,4-bis(carboxymethyl)-1,4,7-triazacyclononane (**LH**₂). Herein we report an efficient and high yielding synthetic route to **LH**₂, together with the synthesis and properties of a Cu(II) complex, [(**LH**)Cu](ClO₄) (**1**) and two novel Fe(III) complexes, [LFeCl] (**2**) and [Fe₂(μ-O)L₂] · (NaClO₄)₃ · CH₃OH · 3H₂O (**3**) of this ligand.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial suppliers and used without purification with the exception of 1,4,7-triazacyclononane trihydrochloride (tacn · 3HCl) [22] and 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (tacn ortho-amide) [23,24], which were prepared by literature methods.

2.2. Physical measurements

NMR spectra were obtained on a Bruker AV 200 or DPX 300 (CDCl₃) spectrometer, IR spectra were recorded

using KBr pellets on a Perkin–Elmer 1600 FTIR spectrometer at a resolution of 8 cm^{−1}. Electronic spectra were recorded on a Cary 5G UV–Vis–NIR spectrophotometer in 1 cm quartz cells. Mass spectra were obtained using a Micromass platform mass spectrometer with an electrospray source. Microanalyses were performed by the Campbell Microanalytical Service, University of Otago, New Zealand. Magnetic susceptibilities were measured on powdered samples contained in calibrated gelatine capsules using a Quantum Design MPMS 5 Squid magnetometer operating in a field of 1 T. The instrument was calibrated against a standard Pd sample supplied by the company and against a chemical calibrant (CuSO₄ · 5H₂O).

2.3. Syntheses

Caution: Although no problems were encountered during this work, perchlorate salts of transition metal complexes are potentially explosive and should be handled with extreme care and be prepared only in small quantities.

2.3.1. 1-Ethylacetato-4-formyl-1,4,7-triazacyclononane (**II**)

A solution of bromoethylacetate (3.6 g, 22 mmol) in acetonitrile (40 mL) was added to a solution of tacn ortho-amide (3 g, 22 mmol) in acetonitrile (40 mL). The mixture was stirred at room temperature overnight. The resulting white product **I** was collected by filtration, washed with diethyl ether (2 × 30 mL) and air dried. The solid was then dissolved in water (100 mL) and heated to reflux for 4 h. After removal of the solvent by rotary evaporation and drying at 90 °C for 2 h, a dark red-orange oil of **II** was obtained. Yield: 2.50 g, 93%. Selected IR bands (KBr, cm^{−1}): 3426 [ν(O–H)], 2935 [ν(C–H)], 1730 [ν(CO ester)], 1660 [ν(CO formyl)]. ¹H NMR spectrum (CDCl₃): δ (ppm) 1.28 and 1.29* (3H, t, CH₃–CH₂), 2.93–3.89 (12H, m, CH₂-ring), 3.55 and 3.7* (2H, s, N–CH₂–COOEt), 4.2 and 4.18* (2H, q, CH₃–CH₂), 8.38 and 8.18* (1H, s, CHO), 9.18 (1H, s, N–H). * splitting of signals due to two resonance forms of the formyl group.

2.3.2. 1,4-Bis(ethylacetato)-7-formyl-1,4,7-triazacyclononane (**III**)

Compound **II** (2.8 g, 10 mmol) was dissolved in acetonitrile (40 mL) and a solution of bromoethylacetate (2.02 g, 10 mmol) in acetonitrile (40 mL) slowly added. Sodium carbonate (7 g) was added and the mixture stirred overnight under reflux. The suspension was filtered to remove the insoluble inorganic salts and the solvent was removed from the filtrate under reduced pressure to yield a very viscous brown oil. This was placed under high vacuum to remove volatile impurities. Yield: 3.1 g, 89%. ¹H NMR spectrum (CDCl₃): δ (ppm) 1.26 and 1.27* (6H, t, CH₃–CH₂–O), 2.68, 2.76, 3.00, 3.21, 3.31, 3.51 (6 × 2H, 6m, ring-NCH₂), 3.4 (4H, s, N–CH₂–COOEt), 4.15 and 4.16* (4H, q, CH₂–CH₃), 8.06 (1H, s, N–CHO). ¹³C NMR spectrum (CDCl₃): δ (ppm) 14.57 CH₃–CH₂–O, 47.33 and 50.44* ring-NCH₂ next to CHO, 54.4 and 58.11*, 55.03

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