



Note

A trinuclear copper(II) complex with 2,5-pyridine-dicarboxylato bridges – $[\text{Cu}_3(2,5\text{-pydc})_2(\text{Me}_5\text{dien})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2] \cdot \text{H}_2\text{O}$: Synthesis, crystal structure and magnetic properties

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ABSTRACT

A trinuclear copper(II) complex, $[\text{Cu}_3(2,5\text{-pydc})_2(\text{Me}_5\text{dien})_2(\text{BF}_4)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ **1**, has been constructed from 2,5-pyridine-dicarboxylato bridges (2,5-pydc²⁻) and *N,N,N',N',N'*-pentamethyl-diethylenetriamine (Me_5dien) acting as a blocking ligand. The copper ions, within the centrosymmetric trinuclear cations, are connected by two 2,5-pydc²⁻ bridges, with an intramolecular Cu...Cu separation of 8.432 Å. The central copper ion exhibits an elongated octahedral geometry, with semicoordinated (BF_4^-) ions, while the terminal ones are pentacoordinated (distorted square-pyramidal geometry). The cryomagnetic investigation of **1** reveals an antiferromagnetic coupling of the copper(II) ions ($J = -5.9 \text{ cm}^{-1}$, $\mathbf{H} = -J\mathbf{S}_{\text{Cu1}}\mathbf{S}_{\text{Cu2}} - J\mathbf{S}_{\text{Cu2}}\mathbf{S}_{\text{Cu1a}}$).

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1. Introduction

Polycarboxylato anions, both aliphatic and aromatic, are largely employed as spacers in obtaining coordination polymers with various dimensionalities and network topologies [1]. The rich structural variety of the coordination polymers constructed from polycarboxylato ligands arises from: (i) the number of the carboxylato groups attached to the organic ligand; (ii) the spatial orientation of the carboxylato groups; (iii) the various coordination modes exhibited by each COO^- group; (iv) the presence of the coligands in the coordination sphere of the metal ions. The case of the polycarboxylato ligands derived from pyridine is particularly interesting, since the pyridinic nitrogen atom cooperates with the carboxylato groups in the interaction with the metal ions. Such an example is the 2,5-pyridine-dicarboxylato anion whose coordination modes are illustrated in Scheme 1. Taking the case of the copper(II) ion, the search of the literature reveals two types of complexes: (1) mononuclear dianionic species, $[\text{Cu}(2,5\text{-pydc})_2]^{2-}$ and $[\text{Cu}(2,5\text{-pydc})_2(\text{H}_2\text{O})_2]^{2-}$ [2]; (2) one dimensional coordination polymers, $[\text{Cu}(2,5\text{-pydc})_n]$ and $[\text{Cu}(2,5\text{-pydc})(\text{H}_2\text{O})_n]$ [3]. Recent papers show that the 2,5-pyridine-dicarboxylato anion is also appropriate for constructing heterometallic coordination polymers [4]. When such

divergent ligands are employed, oligonuclear complexes can be obtained by adding blocking ligands (most frequently chelating species). Here we describe a trinuclear copper(II) complex constructed from 2,5-pyridine-dicarboxylato bridges and *N,N,N',N',N'*-pentamethyl-diethylenetriamine (Me_5dien) as a blocking ligand: $[\text{Cu}_3(2,5\text{-pydc})_2(\text{Me}_5\text{dien})_2(\text{H}_2\text{O})_2(\text{BF}_4)_2] \cdot \text{H}_2\text{O}$.

2. Experimental part

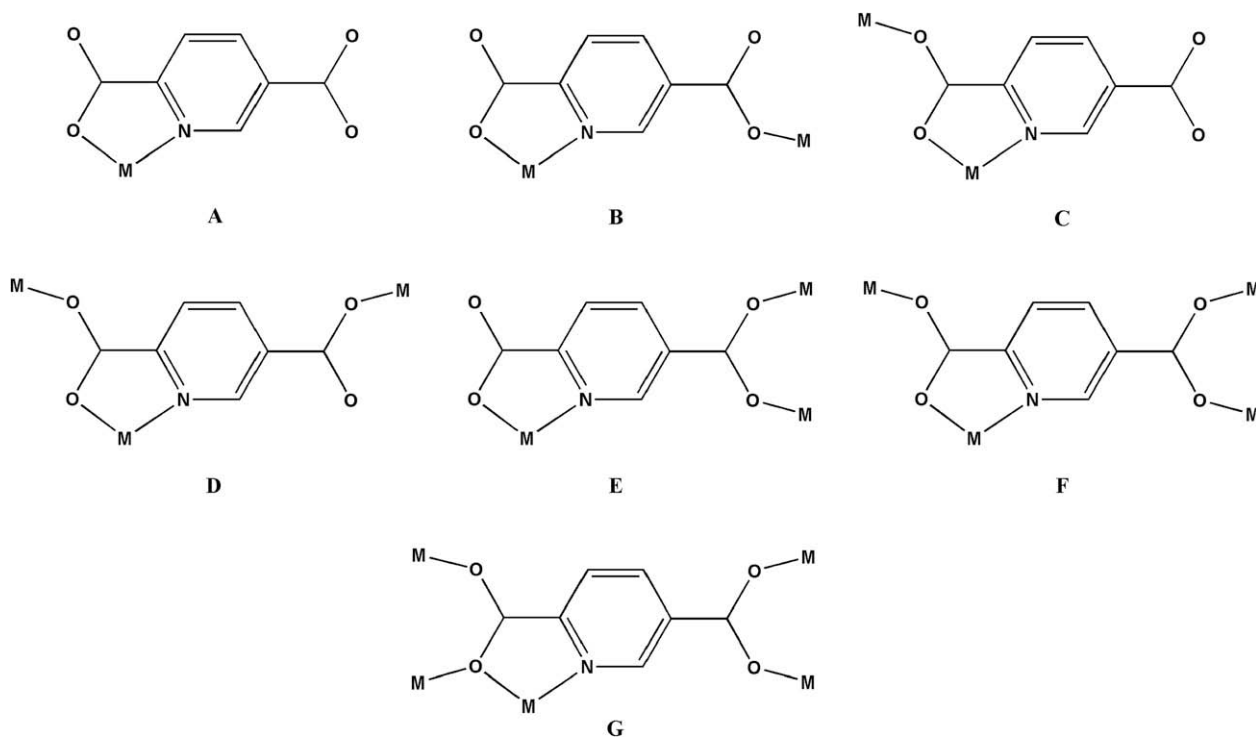
2.1. Synthesis

The starting complex, $[\text{Cu}(\text{Me}_5\text{dien})(\text{acac})]\text{BF}_4$, was obtained following the method described for $[\text{Cu}(\text{Me}_5\text{dien})(\text{acac})]\text{ClO}_4$ [5], and using $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ instead of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The $\text{Cu}(2,5\text{-pydc})_2$ complex was synthesised through a procedure resembling that of the pyridine-2,4-dicarboxylato analogue [6].

$[\text{Cu}_3(\text{Me}_5\text{dien})_2(\text{H}_2\text{O})_2(\text{pydc})_2(\text{BF}_4)_2] \cdot \text{H}_2\text{O}$ **1**: A water/methanol (1:2, v/v) solution (15 mL) of $\text{Cu}(2,5\text{-pydc})_2$ (98.9 mg, 0.25 mmol) and triethylamine (50.8 mg, 0.5 mmol) was gently added to a methanol solution (10 mL) of $[\text{Cu}(\text{Me}_5\text{dien})(\text{acac})]\text{BF}_4$ (211.5 mg, 0.5 mmol). The resulted mixture was allowed to slowly evaporate at room temperature yielding a blue crystalline compound. Single crystals suitable for X-ray diffraction were obtained by recrystallisation from an acetonitrile/methanol (1:1, v/v) solution. The crystals were collected by filtration and washed with small amounts

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Scheme 1.

of acetonitrile (yield: 65%). Elemental chemical *Anal. Calc.*: C, 35.13; H, 5.12; N, 10.24. Found: C, 34.8; H, 5.6; N, 9.9%. Selected IR data (KBr, cm^{-1}): 3396 mb, 2982 m, 2827 w, 1641 s, 1617 s, 1596 s, 1468 m, 1388 s, 1349 s, 1278 m, 1033 s, 766 s, 690 m, 515 m. Diffuse reflectance spectrum: 260 nm; 350 nm, and a large band between 450 and 900 nm.

2.2. Physical measurements

The IR spectra were recorded on KBr pellets with a Bio-Rad FTS 135 spectrophotometer in the 4000–400 cm^{-1} range. Solid state (diffuse reflectance) spectra in the 200–900 nm range were recorded on an JASCO V-570 spectrometer using MgO as a standard.

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer. Magnetic susceptibility measurements were performed in the 1.95–300 K temperature range in a 1000 G applied magnetic field, and diamagnetic corrections were applied by using Pascal's constants.

2.3. X-ray crystallography

X-ray data for crystal **1** were collected at room temperature on Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinement for crystal **1** is given in Table 1.

3. Results and discussion

In order to obtain the oligonuclear complex with 2,5-pyridine-dicarboxylato bridges, we have chosen $[\text{Cu}(\text{Me}_5\text{dien})(\text{acac})]\text{BF}_4$ as a starting material. Our synthetic approach is based on the obser-

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compound **1**

Chemical formula	$\text{C}_{32}\text{H}_{56}\text{B}_2\text{Cu}_3\text{F}_8\text{N}_8\text{O}_{11}$
M (g mol^{-1})	1093.08
Temperature (K)	293
Wavelength (\AA)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a (\AA)	8.1018(3)
b (\AA)	13.6706(15)
c (\AA)	20.3788(19)
β ($^\circ$)	91.944(5)
V (\AA^3)	2255.8(3)
Z	4
D_{calc} (g cm^{-3})	1.609
μ (mm^{-1})	1.497
$F(000)$	1122
Goodness-of-fit on F^2	1.039
Final R_1 , wR_2 [$I > 2\sigma(I)$]	0.0377, 0.0747
R_1 , wR_2 (all data)	0.0650, 0.0831
Largest difference in peak and hole (e \AA^{-3})	0.468, -0.337

vation that mixed-ligand (acetylacetonato–polyamine) copper(II) complexes react with carboxylato ligands losing the acetylacetonato group [7]. At the same time, the polyamine ligand prevents the formation of a coordination polymer.

3.1. Description of structure

The crystal structure of **1** consists of centrosymmetric trinuclear species, $[\text{Cu}_3(2,5\text{-pydc})_2(\text{Me}_5\text{dien})_2(\text{BF}_4)_2(\text{H}_2\text{O})_2]$, and crystallization water molecules (Fig. 1). The copper ions are connected by two 2,5-pyridine-dicarboxylato anions, which exhibit the bridging mode **B** (Scheme 1). The central copper(II) ion displays an elongated octahedral geometry with the two pyridyl nitrogen atoms and two carboxylato oxygens describing the basal plane

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