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Structural and spectroscopic studies of three novel two- and three-dimensional coordination polymers with benzenetricarboxylate ligands

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ABSTRACT

The synthesis, crystalline structure and vibrational characterisation of three new complexes with benzenetricarboxylate ligands are described in this work. Compound **1** $\{Na_5[Cu_3(C_9H_3O_6)_3(C_9H_4O_6)(H_2O)_{10})]\cdot(H_2O)_3\}$ was synthesised from 1,2,3-benzenetricarboxylic acid. This complex crystallised in a triclinic non-centrosymmetric space group (P1), and a three-dimensional coordination polymer was formed. This polymer displays an 8-connected uninodal net with the short Schläfli symbols $(4^{24}6^4)$. Conversely, compounds **2** $\{[CoK_2(C_9H_4O_6)_2(H_2O)_6]\}$ and **3** $\{[Zn_2(C_9H_4O_6)_2(H_2O)_6]\}$ were synthesised from 1,2,4-benzenetricarboxylic (4-btc). These complexes crystallised in the triclinic centrosymmetric group $P\bar{1}$, and, in both cases, two-dimensional coordination polymers were observed by X-ray diffraction. Compound **2** forms a 6,7-connected binodal net with the short Schläfli symbols $(3^9 4^9 5^3)_2(3^6 4^2 5^6 6)$. A 4,6-connected binodal net is also observed for compound **3**, and it presents Schläfli symbols equal to $(3^2 4^2 5^2)(3^4 4^4 5^4 6^3)$. In the infrared spectra, characteristic bands were observed at 1615 and 1459 cm^{-1} for **1**, at 1615 and 1264 cm^{-1} for **2** and at 1592 and 1260 cm^{-1} for **3** arising from the anti-symmetric and symmetric stretching modes of the carboxyl group (COO^-), respectively. The difference between these frequencies suggests that the metal coordination mode in the complexes is monodentate, which agrees well with the X-ray diffraction data.

1. Introduction

Supramolecular chemistry has become a focus of great scientific interest in recent years because supramolecular structures are related to the physical and chemical properties of several materials [1]. In this context, coordination polymers are very interesting systems because of their molecular topologies and potential applications as functional materials [2]. These polymers have various applications in several different areas such as non-liner optics [3], electronics [4], catalysis [5], magnetism [6,7], host–guest chemistry [8] and microporous materials [9].

Benzenepolycarboxylate ligands have proven to be great building blocks in the construction of metal–organic materials due to their different coordination modes [10–12]. The asymmetric polycarboxylic acids such as 1,2,4-benzenetricarboxylic acid (trimellitic acid) and 1,2,3-benzenetricarboxylic (hemimellitic acid) may result in asymmetric molecules, and they may also allow for the formation of supramolecular structures that may lead to more intriguing network topologies [13–23] and potential applications in non-linear optics. Some important characteristics of these polycarboxylic acids were described by Zhang et al. [24], such as the presence of neighbouring carboxyl groups, the possibility of rotation of the carboxyl group and the presence of hydrogen sites that can act as hydrogen-bond donors. In this context, 1,2,3-benzenetricarboxylic (3-btc) acid and 1,2,4-benzenetricarboxylic (4-btc) acid are good candidates to construct metal-oxygen clusters and coordination polymers.

The literature describes several investigations of symmetrical organic aromatic polycarboxylate ligands, such as 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate [19–22,24,25]. In contrast, few structures of complexes with asymmetrical acids have been published [13–24]. According to Xu et al. [21], this scarcity of structural data is primarily due to the asymmetry of the molecules, which may make the experimental crystallisation of the metallic complexes containing these acids difficult.

Some crystal structures of 3-btc and 4-btc derivatives are described in the literature, such as nickel [16], cobalt [18] and copper [17,26] complexes with 3-btc ligands. Crystalline structures of manganese [27–31], iron [32], cobalt [21,33,34], copper [20] and zinc [13,19,22,23,35–37] complexes with 4-btc ligands have been reported. In these compounds, the benzenetricarboxylate ligands are coordinated to the metal ions in several ways: monodentate, bidentate, chelate and bridging between two different metal ions. However, the monodentate and bidentate ligands in a sym–sym

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Table 1
Crystal data and refinement parameters for compounds **1**, **2** and **3**.

Compound	1	2	3
Formula	$C_{36}H_{39}O_{37}Cu_3Na_5$	$C_{18}H_{20}O_{18}CoK_2$	$C_{18}H_{20}O_{18}Zn_2$
Formula weight (g mol^{-1})	1369.24	661.47	655.08
Crystal system	triclinic	triclinic	triclinic
Space group	$P1$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.205(1)	6.813(3)	6.913(3)
b (Å)	10.820(1)	6.961(4)	7.197(2)
c (Å)	12.306(1)	13.826(7)	12.464(4)
α (°)	77.524(5)	92.68(4)	78.04(3)
β (°)	73.743(5)	95.19(4)	89.48(3)
γ (°)	89.201(5)	106.60(5)	64.92(4)
V (Å^3)	1272.1(2)	624.00(6)	547.36(3)
Z	1	2	1
Crystal size (mm)	0.03 × 0.13 × 0.16	0.57 × 0.19 × 0.13	0.40 × 0.15 × 0.11
Theta range for data collection (°)	5.11–27.49	2.97–32.78	3.21–29.38
D_{calc} (g cm^{-3})	1.787	1.912	1.987
μ (Mo Kα) (cm^{-1})	1.396	1.750	2.288
Transmission factors (mix/max)	0.8015/0.9014	0.8054/1.0000	0.7588/1.0000
Reflections measured/unique	17032	7380/4152	12146/2765
Observed reflections [$F^2_{obs} > 2\sigma(F^2_{obs})$]	9430	3223	2216
Number of parameters refined	729	185	186
$R(F_0)$ [$F^2_{obs} > 2\sigma(F^2_{obs})$]	0.0837	0.0464	0.0252
$wR(F_0^2)$ [$F^2_{obs} > 2\sigma(F^2_{obs})$]	0.1468	0.1522	0.0600
S	1.017	1.275	0.996
Largest difference in peak and hole (e Å^{-3})	0.786 and −0.622	0.792 and −0.554	0.484 and −0.462

configuration are the most common coordination modes. Despite the asymmetry of the ligand molecules, these complexes present a centrosymmetric unit cell in the solid state. In the literature, only one exception is observed for a zinc compound with 4-btc ligands [35], which crystallised in the non-centrosymmetric space group $P2_12_12_1$. This information is very important for the optical properties of crystals because the absence of a centre of inversion in the unit cell results in several nonlinear optical properties in these materials [38].

Thus, based on the aforementioned points, in this paper we report the synthesis and structural characterisation of compounds containing the asymmetrical acids 3-btc and 4-btc.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were supplied by Aldrich and Vetec. The elemental analyses for C, H and N were carried out on a Perkin-Elmer 2400 analyser. The infrared spectra were recorded on a Bomen Michelson 102 FTIR spectrophotometer using KBr pellets in the range of 4000–400 cm^{-1} with an average of 64 scans and 4 cm^{-1} of spectral resolution. Fourier-transform Raman spectroscopy was performed using a Bruker RFS 100 instrument, a Nd^{3+}/YAG laser operating at 1064 nm in the near-infrared and a CCD detector cooled with liquid nitrogen. Good signal-to-noise ratios were obtained by accumulating 256 scans using a spectral resolution of 4 cm^{-1} and a laser power of 100 mW.

2.2. Synthesis of $Na_5[Cu_3(C_9H_3O_6)_3(C_9H_4O_6)(H_2O)_{10})]\cdot(H_2O)_3$ (**1**)

An aqueous solution of Na_2CO_3 (330.0 mg, 1.04 mmol) was added dropwise to an ethanolic solution of 3-btc (440.0 mg, 1.05 mmol). After neutralisation at room temperature, an aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (590 mg, 0.81 mmol) was added slowly. The precipitate formed during the neutralisation was filtered and separated. After a few days, the formation of single crystals was observed in the remaining solution (yield less than 1%). Elemental analyses were not performed because only a few single crystals were obtained.

2.3. Synthesis of $CoK_2(C_9H_4O_6)_2(H_2O)_6$ (**2**)

An aqueous solution of KOH (100 mg, 1.78 mmol) was added to a solution of 4-btc (23 mg, 1.14 mmol) in an ethanol:water mixture (1:1). After neutralisation at room temperature, an aqueous solution of $CoCl_2\cdot 6H_2O$ (202 mg, 0.85 mmol) was slowly added. The pink precipitate formed during the neutralisation was dissolved in water with constant stirring. After a few months at room temperature, the formation of single crystals suitable for X-ray diffraction was observed in the final solution with a yield of 26%. Elemental *Anal.* Calc. for $C_{18}H_{20}O_{18}CoK_2$: C, 32.68; H, 3.05. Found: C, 32.90; H, 3.07%.

2.4. Synthesis of $[Zn_2(C_9H_4O_6)_2(H_2O)_6]$ (**3**)

An aqueous solution of KOH (99 mg, 1.77 mmol) was added to a solution of 4-btc (216 mg, 1.03 mmol) in an ethanol:water mixture (1:1). After neutralisation at room temperature, an aqueous solution of $Zn(NO_3)_2\cdot 6H_2O$ (328 mg, 1.12 mmol) was added by slow diffusion. After 7 days, single crystals were obtained, separated by filtration and dried at room temperature with a yield of 49%. Elemental *Anal.* Calc. for $C_{18}H_{20}O_{18}Zn_2$: C, 33.00; H, 3.08. Found: C, 33.06; H, 3.29%.

Table 2
Select bond lengths (Å) for (**1**), (**2**) and (**3**).

*Copper coordination sphere – **1***					
Cu1–O4	1.931(6)	Cu2–O1	1.972(6)	Cu3–O5	2.373(6)
Cu1–O5	1.944(7)	Cu2–O19	1.993(6)	Cu3–O16	1.998(7)
Cu1–O10	1.988(7)	Cu2–O7	1.973(7)	Cu3–O18	1.949(7)
Cu1–O11	1.947(7)	Cu2–O13	1.972(6)	Cu3–O22	1.950(8)
Cu1–O16	2.335(6)			Cu3–O23	1.962(8)
*Cobalt coordination sphere – **2***					
Co O3	2.063(2)	Co O7	2.091(2)	Co O8	2.156(3)
*Zinc coordination sphere – **3***					
Zn1–O2	2.036(12)	Zn1–O4	2.160(12)	Zn2–O6	2.112(12)
Zn1–O3	2.045(13)	Zn2–O5	2.065(12)	Zn2–O4	2.175(12)