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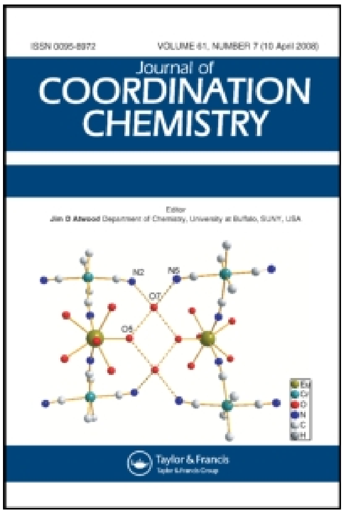

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Unusual coordination features and self-assembly of a crown ether complex $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)][Cu(NO_3)_3(H_2O)]$

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Unusual coordination features and self-assembly of a crown ether complex $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)][Cu(NO_3)_3(H_2O)]$

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A novel supramolecular complex, $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)][Cu(NO_3)_3(H_2O)]$ (**1**), has been prepared and characterized by X-ray single crystal diffraction. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 11.233(6)$, $b = 13.342(7)$, $c = 16.601(8)$ Å, $\alpha = 89.836(7)$, $\beta = 79.132(8)$, $\gamma = 66.545(7)^\circ$, $V = 2234(2)$ Å^3, $Z = 2$ and final $R_1(wR_2) = 0.0467(0.1164)$. Novel coordination features and supramolecular architectures are found in the solid state of **1**. Two $[Na(2,3\text{-naphtho-15-crown-5})]^+$ cations containing two different sodium coordination numbers (six and seven) are bridged by a tridentate nitrate group, to form a larger complex cation, $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)]$, which is assembled into a novel 1D zigzag chain-like structure through aromatic $C–H\cdots\pi$ interactions.

Keywords: 2,3-Naphtho-15-crown-5; Sodium; Copper; $C–H\cdots\pi$ interactions

1. Introduction

Coordinating behavior of ligands to metal ions is the main motif of coordination chemistry and the rise of supramolecuar chemistry injects new energy into coordination chemistry. Crown ethers as one kind of organic ligand, have attracted much attention, not only because crown ethers are able to impose unusual coordination numbers and arrangements on various metal ions, but also because they and their cations can act as building blocks to form 1D–3D supramolecular structures by coordinate covalent bonds and other weak interactions, such as hydrogen bonds, $\pi–\pi$ stacking interactions and so on [1–4]. In recent years, the aromatic $C–H\cdots\pi$ interaction, also named as edge-to-face, edge-on or T-shape $\pi–\pi$ stacking interaction, has been extensively studied both in theory and experiments [5–10]. These attractive interactions contribute to the folding of proteins [11] and play an important role in determining the configuration of coordination complexes [12]. We have reported two

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2,3-naphtho-15-crown-5 sodium complexes [Na(2,3-naphtho-15-crown-5)][M(SCN)$_2$] (M = Pd, Pt) [13], which are assembled into 1D zigzag chains by strong intermolecular π–π stacking interactions, affording a roughly face-to-face stacking model for naphthylene moieties. Herein, we report a new 1D zigzag, chain-like, supramolecular complex, [Na$_2$(2,3-naphtho-15-crown-5)$_2$(NO$_3$)][Cu(NO$_3$)$_3$(H$_2$O)] (**1**), assembled by intercationic aromatic C–H $\cdots$ π interactions and electrostatic interactions.

2. Experimental

2.1. *Preparation*

N15C5 [14] and Na$_2$(i-mnt) [15] were prepared as described in the literature. All reagents and solvents were AR grade and used without further purification. Complex **1** was synthesized as an unexpected product when carrying out the synthesis of [Na(2,3-naphtho-15-crown-5)]$_2$[Cu(i-mnt)$_2$]. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (121 mg, 0.5 mmol) and Na$_2$(i-mnt)$_2$ (70 mg, 0.5 mmol) in methanol (10 mL) was stirred for 2 h, then a solution of 2,3-naphtho-15-crown-5 (318 mg, 1.0 mmol) in methanol (10 mL) was added and continuously stirred for another 2 h. Filtering off the brown precipitation ([Na(2,3-naphtho-15-crown-5)]$_2$[Cu(i-mnt)$_2$]), the filtrate was gradually removed by evaporation under vacuum until deep green solid was obtained. The solid was dissolved in 1,2-dichloroethane and the blue lamellar single crystal was obtained from diethyl ether/1,2-dichloroethane (V : V = 4 : 1) solution after two weeks. Yield: 197 mg, 39.5% (based on Cu). Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 II analyser. Calcd for $C_{36}H_{46}CuN_4Na_2O_{23}$ (%): C, 42.68; H, 4.54; N, 5.53. Found: C, 42.79; H, 4.46; N, 5.64. FT-IR spectra of the complex in KBr pellets were measured on a Nicolet-460 FT-IR spectrometer in the range 4000–400 cm^{-1}. Selected FT-IR absorptions (cm^{-1}): 3057 (ν(Ar–H), w), 2918 (ν(CH$_2$CH$_2$), m), 2872 (m), 1630 (ν(Ar C=C), m), 1509 (m), 1487 (s), 1452 (δ(CH$_2$CH$_2$), m), 1384 (vs), 1358 (ν(NO), m), 1291 (m), 1258 (ν(C–O–C), s), 1172 (m), 1118 (s), 1055 (m), 871 (m), 838 (ν(NO), w), 758 (δ(Ar–H), m).

2.2. *Crystal structure determination*

Crystallographic data of **1** were collected on a Bruker Smart-1000 CCD diffractometer at 298 ± 2 K with Mo-Kα radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods and expanded using Fourier techniques with SHELXL-97 program [16]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The water H atoms were located in a difference map, the O–H distances were restrained to about 0.90 Å and the U_{iso}(H) values were not refined; all other hydrogen atoms were added theoretically, riding on the concerned atoms and not refined. A total of 11850 reflections collected (θ range 2.01–25.03°) give all the data for $R_1 = 0.0851$ and $wR_2 = 0.1413$, 7784 of which were used in the refinement to give the final $R_1 = 0.0467$ and $wR_2 = 0.1164$ [$I > 2\sigma(I)$]. Residual electron density: 0.377 and −0.604 e Å^{-3}.

2.3. *Crystal data*

For **1**, $C_{36}H_{46}CuN_4Na_2O_{23}$, $M = 1012.29$, triclinic, space group $P\bar{1}$, $a = 11.233(6)$, $b = 13.342(7)$, $c = 16.601(8)$ Å, $\alpha = 89.836(7)$, $\beta = 79.132(8)$, $\gamma = 66.545(7)°$,

Table 1. Selected bond lengths (Å) and angles (°) of complex **1**.

Cu(1)–O(23)	1.924(3)	Na(1)–O(2)	2.435(3)	Na(2)–O(6)	2.358(3)
Cu(1)–O(17)	1.956(3)	Na(1)–O(3)	2.446(3)	Na(2)–O(9)	2.359(3)
Cu(1)–O(11)	2.012(3)	Na(1)–O(5)	2.447(3)	Na(2)–O(10)	2.361(3)
Cu(1)–O(15)	2.042(4)	Na(1)–O(4)	2.522(3)	Na(2)–O(8)	2.368(3)
Cu(1)–O(14)	2.465(4)	Na(1)–O(1)	2.545(3)	Na(2)–O(22)	2.391(3)
Na(1)–O(20)	2.347(3)	Na(2)–O(7)	2.356(3)	Na(2)–O(21)	2.526(3)
O(23)–Cu(1)–O(17)	175.53(13)	O(2)–Na(1)–O(1)	62.67(8)		
O(23)–Cu(1)–O(11)	87.66(11)	O(3)–Na(1)–O(1)	125.98(10)		
O(17)–Cu(1)–O(11)	94.17(11)	O(5)–Na(1)–O(1)	66.39(9)		
O(23)–Cu(1)–O(15)	86.60(13)	O(4)–Na(1)–O(1)	134.01(12)		
O(17)–Cu(1)–O(15)	90.33(13)	O(7)–Na(2)–O(6)	64.78(8)		
O(11)–Cu(1)–O(15)	160.30(13)	O(7)–Na(2)–O(9)	126.38(11)		
O(23)–Cu(1)–O(14)	86.79(13)	O(6)–Na(2)–O(9)	127.79(11)		
O(17)–Cu(1)–O(14)	93.99(14)	O(7)–Na(2)–O(10)	131.70(10)		
O(11)–Cu(1)–O(14)	145.14(11)	O(6)–Na(2)–O(10)	69.96(9)		
O(15)–Cu(1)–O(14)	53.19(13)	O(9)–Na(2)–O(10)	71.63(11)		
O(2)–Na(1)–O(3)	67.16(10)	O(7)–Na(2)–O(8)	69.95(10)		
O(2)–Na(1)–O(5)	99.91(10)	O(6)–Na(2)–O(8)	132.52(11)		
O(3)–Na(1)–O(5)	105.26(11)	O(9)–Na(2)–O(8)	71.01(11)		
O(2)–Na(1)–O(4)	127.31(11)	O(10)–Na(2)–O(8)	142.18(11)		
O(3)–Na(1)–O(4)	67.76(12)	O(22)–Na(2)–O(21)	50.47(10)		
O(5)–Na(1)–O(4)	67.62(12)				

$V = 2234(2)$ Å^3, $Z = 2$, $D_c = 1.505\,\mathrm{g\,cm^{-3}}$, $F(000) = 1050$, $\mu(\mathrm{Mo\ K}\alpha) = 0.598\,\mathrm{mm^{-1}}$, GoF = 1.007. Selected bond lengths and angles are given in table 1.

3. Results and discussion

3.1. *Description of the crystal structure*

Complex **1** consists of one [Na_2(2,3-naphtho-15-crown-5)$_2$(NO_3)]$^+$ complex cation and one [Cu(NO_3)$_3$(H_2O)]$^-$ complex anion (see figure 1) with no obvious interactions between the complex cation and anion. In the [Na_2(2,3-naphtho-15-crown-5)$_2$(NO_3)]$^+$ complex cation, nitrate N(4) as a tridentate bridging ligand attaches two [Na(2,3-naphtho-15-crown-5)]$^+$ cations through Na–O(nitrate) interactions. In [Na(1)(2,3-naphtho-15-crown-5)]$^+$ cation, Na(1) is six-coordinated by five ether oxygen atoms and one nitrate oxygen atom from the nitrate N(4). The Na(1)–O (ether) distances are in the range 2.435(3)–2.545(3) Å, on average longer than those of [Na(2,3-naphtho-15-crown-5)][M(SCN)$_2$] (M = Pd, Pt) (2.374(5)–2.484(5) Å) [13]. However, the Na(1)–O(20) contact (2.347(3) Å) is even tighter, which might in part lead to the large deviation of Na(1) from the ether plane (O(1)–O(5)) and the longer Na(1)–O(ether) distances. The Na(2) atom of the [Na(2)(2,3-naphtho-15-crown-5)]$^+$ cation is coordinated to seven oxygen atoms, five on the ether, and two on nitrate N(4). The Na(2)–O(ether) distances range from 2.356(3) to 2.391(3) Å, much shorter than those of [Na(2,3-naphtho-15-crown-5)]$_2$[Pt(i-mnt)$_2$] (2.444(5)–2.609(5) Å) [17], indicating strong Na–O contacts. The two asymmetric Na(2)–O(nitrate) distances are 2.391(3) and 2.526(3) Å, with a chelating angle of 50.47(10)°.

In the complex anion [Cu(NO_3)$_3$(H_2O)]$^-$, the Cu(1) atom is five-coordinate with one water molecule and three nitrates, two monodentate (N(1) and N(3)) and a chelating

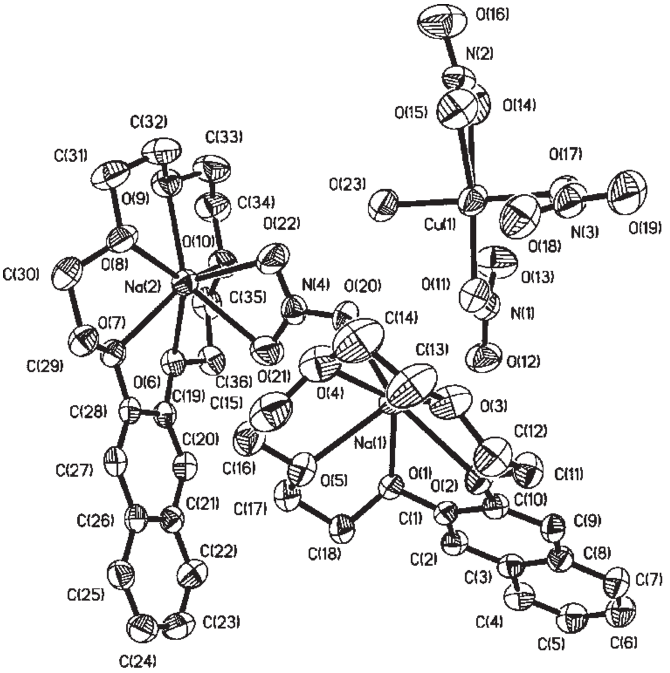

Figure 1. Molecular structure of **1** with 30% probability ellipsoids.

one (N(2)). In the CuO_5 group, the Cu–O bond lengths vary from 1.924(3) to 2.465(4) Å, in which even the longest value (2.465(4) Å) is much shorter than the sum of the van der Waals radii of Cu and O atoms (2.90 Å) [18], indicating strong Cu–O contacts. The Cu(1) atom is constrained to lie on the least-squares plane defined by O(11), O(14) and O(15), the sum of the bond angles within the plane is 358.63°, near 360°. The bond angle O(23)–Cu(1)–O(17) is 175.53(13), close to 180°, and the axial Cu–O bonds, i.e. Cu(1)–O(17) and Cu(1)–O(23) are short, both less than 2.00 Å. Thus, a distorted trigonal bipyramidal configuration (a $3+2$ model) is observed.

Novel supramolecular architectures in **1** were shown in figure 2. The complex cations, $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)]^+$, are assembled into a 1D zigzag cationic chain by aromatic $C\text{–}H\cdots\pi$ interactions. The $C\text{–}H\cdots\pi$ distances between H(24) and the centers of the stacking naphthylene ring and its outer phenyl ring are 2.98 Å and 3.053 Å, respectively, which both lie within the common reported values for aromatic $C\text{–}H\cdots\pi$ interactions (2.59–3.39 Å) [8–10] and the corresponding $C(24)\text{–}H(24)\cdots\pi$ angles are 169.6 and 167.0°, respectively, near the ideal angle of 180°.

3.2. *Thermal properties*

The combined TG/DTA measurements were carried out between 50 and 500°C on crystalline sample in a N_2 stream using Perkin-Elmer PYRTSI TG/DTA equipment with a heating rate of $10^\circ C\,min^{-1}$. As displayed in figure 3, TGA data for crystalline sample **1** indicate four steps of weight loss; the first weight loss of coordinated water, ended at 157°C (observed 1.75%, calculated 1.78%), the second weight loss of

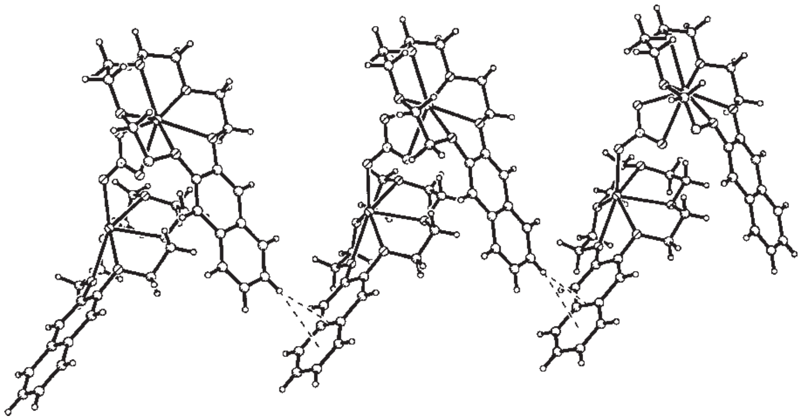

Figure 2. The 1D zigzag cationic chain of **1** along b-axis and assembled by C–H $\cdots\pi$ interactions.

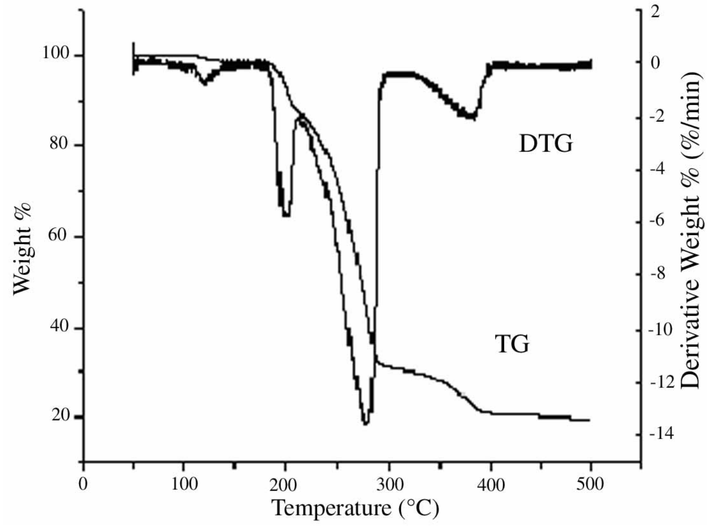

Figure 3. TG and DTA curves for complex **1** in nitrogen atmosphere.

NO_2 and O_2 corresponding to the decomposition of $Cu(NO_3)_2$, stopped at 214°C (observed 11.10%, calculated 10.67%), the third of 56.51%, ended at 310°C, indicating 9/10 of 2,3-naphtho-15-crown-5 ligand was lost and the last ended at 441°C, giving a weight loss of 10.19%, corresponding to decomposed $NaNO_3$ (expected 10.67%).

4. Conclusion

We have synthesized and characterized a novel supramolecular complex, $[Na_2(2,3\text{-naphtho-15-crown-5})_2(NO_3)][Cu(NO_3)_3(H_2O)]$ (**1**), in which two $[Na(2,3\text{-naphtho-15-crown-5})]^+$ cations with sodium coordination numbers of six and seven are linked by a tridentate bridging nitrate group. The resulting larger complex cations, [Na_2(2,3-naphtho-15-crown-5)$_2$(NO_3)], are further assembled into a novel 1D zigzag chain-like structure by aromatic C–H$\cdots\pi$ interactions. Complex **1** can be seen as a 1D structure stabilized by aromatic C–H$\cdots\pi$ interactions and electrostatic interactions.

Supplementary material

Crystallographic data for the structure in this article have been deposited with Cambridge Crystallographic Data Center, CCDC-239863 (**1**). A copy of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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