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Covalent and ionic Cu(II) complexes with cyclam and substituted benzoato ligands: structural, thermal, redox and mesomorphic properties

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ABSTRACT

A covalent mononuclear complex, $[Cu(p-HOC_6H_4COO)_2(cyclam)]$ (1), and two ionic mononuclear complexes, $[Cu(cyclam)(H_2O)_2](p-CH_3OC_6H_4COO)_2$ (2) and $[Cu(cyclam)(H_2O)_2](p-CH_3(CH_2)_{15}OC_6H_4COO)_2 H_2O$ (3), were formed from reaction of cyclam with $[Cu_2(p-HOC_6H_4COO)_4(H_2O)_2]$, $[Cu_2(p-CH_3OC_6H_4COO)_4(H_2O)_2]$ and $[Cu_2(p-CH_3(CH_2)_{15}OC_6H_4COO)_4(H_2O)_2]$, respectively. These complexes were isolated as purple crystals with molecular structures showing distorted octahedral N₄O₂ geometry. Complexes 1 and 2 were irreversibly reduced to Cu(I) and oxidized to Cu(III), while 3 was redox inactive. Complex 2 reacted with *N*-(hexadecyl)isonicotinamide (L) to form $[Cu(cyclam)(L)_2](p-CH_3OC_6H_4COO)_2$ (4). These complexes were thermally stable ($T_{dec} > 200$ °C for 1–3 and 174 °C for 4). Complexes 3 and 4 behaved as ionic liquids (melting temperatures lower than 100 °C) and exhibited mesomorphism.

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1. Introduction

Most Cu(II) carboxylates are dimeric with a paddle-wheel structure [1–16]. In the absence of solvent molecules at the axial positions, the dimers are linked into a one-dimensional oligomeric chain in the solid state [17] and remain intact in solution [18, 19]. The two Cu(II) ions in the dimer are separated by about 2.61 Å [20], and experience a strong antiferromagnetic interaction (-2 J about 300 cm⁻¹ [5, 21]), postulated to occur indirectly through the bridging carboxylato ligands (the super-exchange pathway) [5]. Previous research on these complexes was focused on their potential as molecular sieves, molecular magnets, and redox catalysts [22–24], and less on their chemical properties, even though both Cu(II) ions in the dimeric structure are readily accessible for attack by Lewis bases.

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a macrocyclic N₄-donor with the ability to form kinetically and thermodynamically stable complexes with many transition metal ions [25-27]. These complexes are of interest as redox catalysts [28–34], sensors [35], and as pharmaceutical materials [36]. Structurally, most of these complexes are mononuclear with cyclam occupying the four basal sites of the metal ion, while the two axial sites are occupied by other ligands [37].

We noted that $[Cu_2(4-XC_6H_4COO)_4]$ (X = H [37], *tert*-butyl [37], and CI [38]) reacted with cyclam to form ionic complexes, $[Cu(cyclam)(H_2O)_2](4-XC_6H_4COO)_2$. In these complexes, the axial sites were weakly coordinated by H₂O molecules, resulting in an elongated octahedral N₄O₂ geometry at Cu(II).

This article reports the synthesis, structures, thermal, and redox properties of a covalent complex, $[Cu(p-HOC_6H_4COO)_2(cyclam)]$ (1), and two ionic complexes, $[Cu(cyclam)(H_2O)_2](p-CH_3OC_6H_4COO)_2$ (2) and $[Cu(cyclam)(H_2O)_2](p-CH_3(CH_2)_{15}OC_6H_4COO)_2 H_2O$ (3), formed from reactions of the corresponding Cu(II) substituted benzoates with cyclam. Also reported is an ionic complex, $[Cu(cyclam)(L)_2](p-CH_3OC_6H_4COO)_2 H_2O$ (3), formed from reactionamide (L). L was chosen as it was a monodentate, N-donor expected to form complexes with mesomorphic properties, lower melting temperatures, and higher solubility in non-polar organic solvents (lipophilic cyclam complexes were found to possess good anti-tumor activity [39]). The synthetic steps for these complexes are shown in scheme 1. Complexes 1–3 were isolated as purple crystals and their molecular structures were determined by X-ray crystallography. 1 is the first example of a molecular Cu(II) complex reported from such reaction, while the ionic structures of 2 and 3 are similar to those reported [37]. Finally, this article reports the mesomorphic properties of 3 and 4.



Scheme 1. (a) Structural formula of N-(hexadecyl)isonicotinamide (L); (b) syntheses of 1-4.

2. Experimental

2.1. Materials and measurements

All chemicals were analaR grade and used without purification. Elemental analyses were carried out on a Thermo Finnigan Flash EA 1112. ¹H NMR spectra were recorded on a JEOL FT-NMR lambda 400 MHz spectrometer. FTIR spectra were recorded from 4000 to 450 cm⁻¹ on either a Perkin Elmer Spectrum 400 spectrophotometer or Perkin Elmer Frontier FTIR spectrophotometer equipped with a diamond attenuated total reflectance attachment. Electronic spectra were recorded on a Shimadzu UV-vis-NIR 3600 spectrophotometer. Magnetic susceptibilities of solid samples were measured at room temperature on a Sherwood automagnetic susceptibility balance by the Gouy method, using Hg[Co(NCS),] as the calibrant. Molar susceptibility values were corrected for the diamagnetism of the constituent atoms using Pascal's constants. Thermogravimetry (TG) was done on a Perkin Elmer Pvris Diamond TG/DTA instrument under N₂ at a flow rate of 10 cm³ min⁻¹. The temperature range was 50–900 °C and the scan rate was 20 °C min⁻¹. Differential scanning calorimetry (DSC), was done on a Mettler Toledo DSC 822 calorimeter under N₂ at a flow rate of 20 cm³ min⁻¹ and scan rate of 10 °C min⁻¹. The onset temperatures were guoted for all peaks observed. The photomicrographs were captured on an Olympus polarizing optical microscopy (POM) equipped with a Mettler Toledo FP90 central processor and a Linkam THMS 600 hot stage. The samples were finely ground and any moisture absorbed from the atmosphere was removed prior to analysis by heating in an oven at 60 °C overnight in order to obtain clear photomicrographs of the optical textures. The heating and cooling rates were 10 and 2 °C min⁻¹, respectively, and the magnification was 50x. Cyclic voltammetry (CV) was performed on a Gamry Potentiostat/Galvanostat 600 instrument at 25 °C. A standard three-electrode set up (glassy carbon working electrode, Ag/AgCl reference electrode, and platinum wire counter electrode) was used. For 1 and 2, the solvent was H₂O, and the supporting electrolyte was Na₂SO₄. For **3**, the solvent was CHCl₂, and the supporting electrolyte was tetrabutylammonium tetrafluoroborate. The molarities of complexes were 1 mM, while those of the electrolytes were 0.5 M. The scan rate was 100 mV s⁻¹, and the quoted E values were versus Ag/ AgCl. The solutions were bubbled with N₂ prior to measurements.

2.2. Synthesis of $[Cu_2(p-HOC_6H_4COO)_4(H_2O)_2]$

 $[Cu_{2}(CH_{3}COO)_{4}(H_{2}O)_{2}] (12.5 \text{ mmol}, 4.99 \text{ g}) \text{ was added portionwise to an ethanolic solution of } p-HOC_{6}H_{4}COOH (50.0 \text{ mmol}, 6.91 \text{ g}) \text{ at } 60 ^{\circ}C, \text{ and the reaction mixture was further heated at this temperature for 30 min. The blue powder formed was filtered from the hot reaction mixture, washed with distilled water, and dried in a warm oven (60 ^{\circ}C). Yield: 7.18 g (80.7%). IR (KBr disk, cm⁻¹): 3446 (br), 3210 (br), 1609 (vs), 1580 (s), 1548 (s), 1406 (vs), 1237 (s). Anal. Calcd for C_{28}H_{24}Cu_{2}O_{14} (\%): C, 47.3; H, 3.4. Found: C, 46.9; H, 3.3.$

2.3. Synthesis of $[Cu_2(p-CH_3OC_6H_4COO)_4(H_2O)_2]$

The procedure was the same as for $[Cu_2(p-HOC_6H_4COO)_4(H_2O)_2]$, using $[Cu_2(CH_3COO)_4(H_2O)_2]$ (12.5 mmol, 4.99 g) and $p-CH_3OC_6H_4COOH$ (50.0 mmol, 7.61 g). The product was a greenish blue powder. Yield: 8.4 g (87.5%). IR (KBr, disk, cm⁻¹): 3603 (vw), 2953 (vw), 2829 (vw), 1595 (s), 1544 (vs), 1428 (s), 1403 (s), 1251 (vs). Anal. Calcd for $C_{32}H_{32}Cu_2O_{14}$ (%): C, 50.1; H, 4.2. Found: C, 49.5; H, 4.0.

2.4. Synthesis of $[Cu_2(p-CH_3(CH_2)_{15}OC_6H_4COO)_4(H_2O)_2]$

CH₃(CH₂)₁₅Br (50.0 mmol, 15.27 g) was added dropwise to a mixture of p-HOC₆H₄COOC₂H₅ (50.1 mmol, 8.33 g), K₂CO₃ (100.0 mmol, 13.84 g), and a catalytic amount of KI in DMF at room temperature. The reaction mixture was then refluxed for 24 h and cooled to room temperature. The white powder (p-CH₃(CH₂)₁₅OC₆H₄COOC₂H₅) obtained was washed several times with distilled water and recrystallized from hot CH₃CH₂OH. Yield: 9.55 g (48.9%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.83 (t, 3 H, **CH**₃(CH₂)₁₅O),

1.2–1.3 (*m*, 30 H, $CH_3(CH_2)_{15}O$), 3.9 (*t*, 3 H, $COOCH_2CH_3$), 4.3 (*q*, 2 H, $COOCH_2CH_3$), 6.8 (*d*, 2 H, C_6H_4), 7.9 (*d*, 2 H, C_6H_4). IR (neat, cm⁻¹): 2915 (vs), 2848 (s), 1712 (vs), 1606 (m), 1509 (m), 1470 (s), 1314 (m), 1248 (vs), 768 (s), 696 (m).

An aqueous solution of KOH was added in excess to a hot ethanolic solution of p-CH₃(CH₂)₁₅OC₆H₄COOC₂H₅ (14.3 mmol, 5.6 g). The mixture was refluxed for 4 h and then cooled to room temperature. The white powder (p-CH₃(CH₂)₁₅OC₆H₄COOK) obtained was filtered, washed thoroughly with distilled water, and dried in an oven. Yield: 4.15 g (72.4%). IR (neat, cm⁻¹): 2917 (vs), 2848 (s), 1601 (m), 1541 (m), 1393 (s), 1252 (s), 791 (s), 651 (m). Anal. Calcd for C₂₃H₃₇KO₃ (%): C, 68.9; H, 9.3. Found: C, 69.4; H, 10.1.

CuSO₄·5H₂O (5.0 mmol, 1.26 g) was added to a warm ethanolic solution of p-CH₃(CH₂)₁₅OC₆H₄COOK (10.0 mmol, 4.02 g). The reaction mixture was stirred for 30 min, and the blue powder formed was filtered, washed with distilled water, and dried in a warm oven. Yield: 3.0 g (74.6%). IR (neat, cm⁻¹): 3400 (br), 2916 (vs), 2849 (s), 1609 (m), 1593 (m), 1499 (s), 1435 (vs), 1256 (s), 785 (s), 664 (m). Anal. Calcd for C₉₃H₁₅₂Cu₂O₁₄ (%): C, 68.7; H, 9.5. Found: C, 68.1; H, 9.2.

2.5. Synthesis of $[Cu(p-HOC_6H_4COO)_2(cyclam)]$ (1)

An ethanolic solution of cyclam (0.89 mmol, 0.18 g) was added portionwise to an ethanolic suspension of $[Cu_2(p-HOC_6H_4COO)_4(H_2O)_2]$ (0.42 mmol, 0.30 g). The purple solution formed was heated at 60 °C for 1 h and filtered hot. Dark-purple prismatic crystals were deposited after 2 days at room temperature. Yield: 0.40 g (78.4%). IR (neat, cm⁻¹): 3239 (m), 3122 (m), 2933 (m), 2870 (m), 1605 (m), 1585 (s), 1539 (vs), 1351 (vs), 1272 (vs), 789 (vs), 617 (s).

2.6. Synthesis of $[Cu(cyclam)(H_2O)_2](p-CH_3OC_6H_4COO)_2(2)$

The procedure was the same as for **1**, using cyclam (2.5 mmol, 0.50 g) and $[Cu_2(p-CH_3OC_6H_4COO)_4(H_2O)_2]$ (1.19 mmol, 0.91 g). The product was isolated as purple needles. Yield: 0.87 g (60.8%). IR (neat, cm⁻¹): 3133 (m), 2934 (m), 1599 (s), 1549 (s), 1382 (s), 1255 (s), 791 (vs).

2.7. Synthesis of $[Cu(cyclam)(H_2O)_2](p-CH_3(CH_2)_{15}OC_6H_4COO)_2 H_2O(3)$

The procedure was the same as for **1**, using cyclam (0.05 mmol, 0.01 g) and $[Cu_2(p-CH_3(CH_2)_{15}OC_6H_4COO)_4(H_2O)_2]$ (0.11 mmol, 0.17 g). The product was isolated as purple crystals. Yield: 0.046 g (88.4%). IR (neat, cm⁻¹): 3193 (br), 2917 (s), 2851 (m), 1604 (s), 1583 (s), 1546 (s), 1472 (m), 1376 (vs), 1241 (s), 788 (s), 647 (s).

2.8. Synthesis of N-(hexadecyl)isonicotinamide (L)

A solution of isonicotinic acid (51.6 mmol, 6.35 g) and $CH_3(CH_2)_{15}NH_2$ (50.5 mmol, 12.2 g) in $CHCI_3$ (100 cm³) was refluxed in the presence of anhydrous $MgSO_4$ for 3 h. The hot reaction mixture was filtered, and a pale yellow powder was obtained from the filtrate on cooling. It was recrystallized from hot CH_3CH_2OH . Yield: 12.3 g (70.3%). ¹H NMR (400 MHz, $CDCI_3$, ppm): $\delta = 0.83$ (t, 3 H, **CH**₃), 1.1–1.2 (m, 26 H, $CH_2(CH_2)_{13}CH_3$), 1.6 (m, 2 H, $CH_2CH_2(CH_2)_{13}CH_3$), 2.8 (m, 2 H, **CH**_2CH_2(CH_2)_{13}CH_3), 3.4 (b, 1 H, **NH**CH₂CH₂(CH₂)₁₃CH₃), 7.7 (d, 2 H, C_6H_4), 8.6 (d, 2 H, C_6H_4). IR (KBr disk, cm⁻¹): 2918 (s), 2853 (s), 1636 (m), 1529 (s).

2.9. Synthesis of $[Cu(cyclam)(L)_2](p-CH_3OC_6H_4COO)_2$ (4)

A mixture of **2** (0.39 mmol, 0.26 g) and L (0.87 mmol, 0.30 g) in $CH_3CH_2OH-CHCl_3$ (1 : 1) was stirred at room temperature for 30 min. The purple powder formed was isolated by filtration and washed with CH_3OH . Yield: 0.28 g (65.7%). Anal. Calcd for $C_{70}H_{114}CuN_8O_8$ (%): C, 66.77; H, 9.12; N, 8.90. Found: C, 66.35;

Complex	1	2	3
Chemical formula	$C_{24}H_{34}CuN_4O_6$	$C_{26}H_{42}CuN_4O_8$	$C_{56}H_{104}CuN_4O_9$
Formula mass (g mol ⁻¹)	538.1	602.19	1040.97
Т (К)	100(2)	100(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	P2,/c	Pbca	<i>P</i> ⁻1
a (Å)	8.2488(1)	15.5810(6)	9.1310(11)
b (Å)	13.2976(2)	7.0534(2)	14.3849(16)
c (Å)	11.1659(2)	25.8128(9)	22.192(3)
a (°)	90	90	89.533(2)
β (°)	102.725(1)	90	88.267(2)
γ (°)	90	90	82.150(2)
Volume (ų)	1194.70(3)	2836.80(17)	2886.2(6)
Ζ	2	4	2
D_{Calcd} (g cm ⁻³)	1.496	1.41	1.198
F(0 0 0)	566	1276	1138
μ (Mo Kα) (mm ⁻¹)	0.963	0.824	0.434
Measured data	12,947	15,747	37,551
Unique data	2751	2501	13,243
Observed data ($l \ge 2.0\sigma(l)$)	2481	1842	8642
R, obs. data; all data	0.024; 0.065	0.035; 0.079	0.049, 0.091
<i>a</i> , <i>b</i> in weighting scheme	0.033, 0.636	0.046, 0.726	0.064, 0.222
$R_{\rm w}$, obs. data; all data	0.028; 0.067	0.057; 0.089	0.116, 0.137

Table 1. Crystal data and structure refinement for 1-3.

Table 2. Selected bond lengths (Å) for 1-3.

Complex	1	2	3
Cu–N1	2.0235(11)	2.0095(19)	2.0176(19)
Cu–N2	2.0168(11)	2.0187(19)	2.035(2)
Cu2–N3	_	_	2.017(2)
Cu2–N4	_	_	2.0140(19)
Cu-01	2.3830(10)	2.5355(17)	_
Cu…02	3.6304(11)	_	_
Cu1–O1w	_	_	2.4800(18)
Cu2-02w	-	-	2.4587(18)

H, 9.05; N, 8.01. IR (neat, cm⁻¹): 2917 (vs), 2851 (vs), 1636 (s), 1599 (vs), 1543 (vs), 1473 (m), 1382 (vs), 1250 (s), 961 (s), 792 (s), 615 (m).

2.10. Crystallographic data collection and structural determination

Intensity data for **1–3** were collected at reduced temperature on a Bruker SMART APEX II CCD fitted with Mo K*a* radiation. Each data set was corrected for absorption based on multiple scans [40] and reduced using standard methods [41]. The structures were solved by direct methods with SHELXS97 [42] and refined by a full-matrix least-squares procedure on F^2 using SHELXL97 with anisotropic displacement parameters for non-hydrogen atoms and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$). All hydrogens in **1** were included in the final refinement in their calculated positions. For **2** and **3**, C-bound hydrogens were treated similarly but the O- and N-bound hydrogens were located from a difference map and refined with distance restraints $O-H = 0.84 \pm 0.01$ Å and $N-H = 0.88 \pm 0.01$ Å; for **3**, N–H was fixed at 0.88 Å. Crystal data and refinement details are given in table 1, selected bond lengths and angles are given in table 2, and hydrogen bonding data are given in table 3. Figures 1, 3 and 5, showing the atom labeling schemes, were drawn with 50% displacement ellipsoids using ORTEP-3 for Windows [43], and the packing diagrams were drawn with DIAMOND [44]. Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center.

Table 3. Summary o	of selected intermolecular interactions	(D–H···A; Å, °) o	perating in the cr	ystal structures of 1–3.
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D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)	Symmetry operation
Complex 1					
N1–H1n…O2	0.930(1)	2.076(1)	2.950(2)	155.83(7)	1− <i>x</i> , 1− <i>y</i> , − <i>z</i>
03–H30…02	0.840(1)	1.7789(9)	2.618(1)	176.45(8)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
Complex 2					
01w–H2w…02	0.83(2)	2.02(2)	2.848(2)	174(2)	x, y, z
N1-H1n…01	0.87(1)	2.04(1)	2.864(3)	156(2)	1-x, -y, -z
01w-H1w…01	0.84(2)	1.92(2)	2.757(2)	171(2)	1-x, 1-y, -z
N2–H2n…O2	0.87(1)	2.10(1)	2.921(3)	157(2)	x, 1+y, z
Complex 3					
01w-H1w1…01	0.84(2)	1.93(2)	2.767(2)	175(2)	x, y, z
01w-H1w2…04	0.84(2)	2.00(2)	2.797(3)	158(2)	x, y, z
02w-H2w1…01	0.84(2)	1.93(2)	2.772(2)	172(2)	x, y, z
02w-H2w2…05	0.83(2)	1.92(2)	2.735(3)	165(2)	x, y, z
03w-H3w1…02	0.84(2)	1.96(2)	2.796(3)	174(2)	x, y, z
03w-H3w2…04	0.83(2)	2.07(2)	2.900(2)	174(2)	x, y, z
N1-H1n…02	0.930(2)	2.134(2)	2.978(3)	150.4(1)	x, y, z
N2–H2n…O4	0.930(2)	2.079(2)	2.987(3)	165(1)	1 <i>—x</i> , <i>—y</i> , 1 <i>—z</i>
N3–H3n…O3w	0.930(2)	2.045(2)	2.959(3)	167.2(1)	<i>-x</i> , 1 <i>-y</i> , 1 <i>-z</i>
N4–H4n…05	0.930(2)	1.961(2)	2.888(2)	174.6(1)	x, y, z



Figure 1. Coordination environment of Cu(II) in **1**. The atoms comprising the asymmetric unit are labeled. The unlabeled atoms are related by the symmetry operation *i*: 1-x, 1-y, -z.

Complex	Δ^{a} (cm ⁻¹)	λ /nm (ϵ /M ⁻¹ cm ⁻¹)	$\mu_{ m eff}$ /BM	Reference
$[Cu_2(R1)_4(H_2O)_2]$	174	715 (65) ^b	2.2	This work
[Cu ₂ (R2) ₄ (H ₂ O) ₂]	141	677 (431) ^c	2.8	This work
[Cu ₂ (R3) ₄ (H ₂ O) ₂]	158	682 (388) ^c	2.9	This work
[Cu ₂ (R4) ₄ (EtOH) ₂]	144	694 ^d	na	[7]
[Cu, (R5), (H, O),]. 3dmf	206	704 ^d	2.1	[10]
[Cu ₂ (CH ₃ (CH ₂),COO) ₄]	173	671 (375) ^c	1.6	[15]
[Cu ₃ (R6) ₆]	177	na	2.5	[48]
[Cu ₆ (R7) ₁₂]	162	685 (505) ^c	10.2	[49]

Table 4. Instrumental data for complexes of copper(II) with substituted benzoates in comparison with published crystals of dimeric paddle-wheel, trinuclear and hexanuclear complexes.

 ${}^{a}\Delta = \bar{U}_{as}COO - \bar{U}_{s}COO.$

^bln DMSO. In CHCl_a.

^dReflectance.

 $R1 = p-HOC_6H_4COO; R2 = p-CH_3OC_6H_4COO; R3 = p-CH_3(CH_2)_{15}OC_6H_4COO; R4 = 1-phenylcyclopropane-1-carboxylato; R5 = 2,6-(CH_3O)_nicotinato; R6 = 2,4,6-triisopropylbenzoato; R7 = 3,4,5-triethoxybenzoato; na = not available.$

3. Results and discussion

3.1. Syntheses and structures of $[Cu_2(p-ROC_6H_4COO)_4(H_2O)_2]$ (R=H, CH₃, CH₃(CH₂)₁₅)

Three Cu(II) carboxylates, $[Cu(p-ROC_{e}H_{a}COO)_{2}(H_{2}O)]$ (R=H, CH₂, CH₂(CH₂)₁₅), were synthesized according to published methods [1–16]. In order to deduce their structural formulas, we compared their IR, UV-vis, and magnetic data with crystals of dimeric [7, 10, 15], a trinuclear [45] and a hexanuclear [46] copper(II) carboxylates (table 4). Based on these data and the following arguments, we inferred that our complexes were likely dinuclear ($[Cu_2(p-ROC_eH_2COO)_4(H_2O)_2]$) adopting the paddle-wheel structure: (a) the difference in values of the COO(asym) and COO(sym) vibrations of the carboxylate ligands $(\Delta = \cup COO, asym - \cup COO, sym)$ from IR spectra have been extensively used by many authors to probe the binding modes of carboxylate ligands [47]. The Δ value for [Cu(p-HOC₆H₄COO)₂(H₂O)] (174 cm⁻¹) was similar to the dimeric paddle-wheel $[Cu_2(CH_3(CH_3)_5COO)_4]$ (173 cm⁻¹) [15], while the lower values for $[Cu(p-ROC_{k}H_{4}COO)_{2}(H_{2}O)]$ (141 cm⁻¹ for R=CH₃; 158 cm⁻¹ for R=CH₃(CH₂)₁₅) can be indicative of a bridging bidentate coordination geometry, very likely of the paddle-wheel type, (b) the similar λ_{max} value (685 nm) from the UV-vis spectrum of the hexanuclear complex with our complexes (682–715 nm) may arise from the dissociation of the former complex in solution, (c) the trinuclear and hexanuclear complexes were formed from trisubstituted benzoato ligands and their colors were dark green, while our complexes were formed from monosubstituted benzoato ligands and their colors were blue, and (d) the hexanuclear complex was sparingly soluble in both polar and nonpolar solvents, while our complexes were quite soluble in solvents such as hot ethanol, DMSO, and THF.

The value for the effective magnetic moment (μ_{eff}) for [Cu₂(p-HOC₆H₄COO)₄(H₂O)₂] (2.2 BM) was in agreement with most dinuclear Cu(II) complexes adopting paddle-wheel structures [1.6–2.1 BM [10, 15]). However, the values obtained for [Cu₂(p-CH₃OC₆H₄COO)₄(H₂O)₂] (2.8 BM) and [Cu₂(p-CH₃(CH₂)₁₅OC₆H₄COO)₄(H₂O)₂] (2.9 BM) were slightly higher and cannot be currently rationalized in the absence of variable-temperature magnetic data.

3.2. Reactions of cyclam with $[Cu_2(p-ROC_6H_4COO)_4(H_2O)_2]$ (R=H, CH₃, CH₃(CH₂)₁₅)

Cyclam reacted with $[Cu_2(p-ROC_6H_4COO)_4(H_2O)_2]$ (R=H, CH₃, CH₃(CH₂)₁₅) (mole ratio = 2 : 1) to form a mononuclear covalent complex, $[Cu(p-HOC_6H_4COO)_2(cyclam)]$ (1), and two mononuclear ionic complexes, $[Cu(cyclam)(H_2O)_2](p-CH_3OC_6H_4COO)_2$ (2) and $[Cu(cyclam)(H_2O)_2](p-CH_3(CH_2)_{15}OC_6H_4COO)_2 \cdot H_2O$ (3), respectively. Complexes 1–3 were purple crystals and their molecular structures were determined by X-ray crystallography. In the presence of cyclam, the dimeric structure of $[Cu_2(p-ROC_6H_4COO)_4(H_2O)_2]$ dissociated in hot ethanol, and the 'free' ions formed, self-assembled to form the monomeric complexes, though the concept of an 'assembly effect' proposed by Lindoy *et al.* [37] may also apply, especially for 1.



Figure 2. Supramolecular association operating in **1**. The O–H···O hydrogen bonding (orange dashed lines) leads to chains along the *b*-axis. Intramolecular N–H···O hydrogen bonds are shown as blue dashed lines. Color code: Cu, orange; O, red; N, blue; C, gray; and H, green (see http://dx.doi.org/10.1080/00958972.2016.1147032 for color version).

3.3. Structures of 1–3

The molecular structure of **1** (figure 1) shows a Cu(II) located on a crystallographic center of inversion which exists within a *trans*-N₄O₂ donor set, being four-coordinate by the four N atoms of cyclam and two carboxylate-O1 atoms. The resulting coordination geometry was based on a tetragonally distorted octahedron (table 2). O2 was aligned over the Cu–N1ⁱ bond but was oriented away from the Cu ion to allow for formation of an intramolecular N1–H···O hydrogen bond. As a result, the Cu···O2 separation was 3.6304(11) Å, a distance too long to be considered as significant bonding interaction. There was a small twist of the COO group out of the plane of the aromatic ring to which it was connected (O1/C1/C2/C3 torsion angle = -167.24(12)°). The *p*-HOC₆H₄COO ligand was folded towards the plane through the four N atoms with the dihedral angle formed between the CuN₄ and C₆ planes being 49.11(5)° (*p*-HOC₆H₄COO adopted an orthogonal disposition to the CuN₄ plane).

The crystal packing in **1** was dominated by O–H···O hydrogen bonds (table 3). The hydroxyl–O3–H forms a hydrogen bond to the carbonyl-O2 so that the latter, which also participates in an N–H···O interaction, is bifurcated. The O–H···O hydrogen bonds link the *p*-HOC₆H₄COO ligand into a supramolecular chain along the *b*-axis. Successive chains were interspersed by [Cu(cyclam)] units via the coordinate Cu–O bonds and N–H···O hydrogen bonds. The resulting layers, which have a flattened topology, lie



Figure 3. Coordination environment of Cu(II) in **2** extended to include the hydrogen-bonded p-CH₃OC₆H₄COO⁻ ions. The atoms comprising the asymmetric unit are labeled. The unlabeled atoms are related by the symmetry operation *i*: 1–*x*, 1–*y*, –*z*.

parallel to the (102) plane (figure 2). The hydroxyl–OH...O(carboxylate) hydrogen bonding results in the formation of rather large 40-membered { \cdots OCOCuOC₅OH \cdots OC₅OH \cdots }₂ synthons which are stabilized by two internal six-membered { \cdots HNCuOCO} synthons. The supramolecular layers stack in a \cdots ABA \cdots fashion with the primary contacts between the layers being of the type C–H \cdots O.

For **2**, a similar centrosymmetric and octahedral *trans*-N₄O₂ donor set (table 2) is observed, but in this case the *trans*-oxygens are derived from coordinating water (figure 3). The *p*-CH₃OC₆H₄COO⁻ ions are associated with $[Cu(cyclam((H_2O)_2)^{2+} by aqua-OH\cdotsO2 hydrogen bonds. The$ *p* $-CH₃OC₆H₄COO⁻ ions form an intramolecular N1-H\cdotsO1 hydrogen bond, and so in a sense, the structure of$ **2**differs from**1**by the insertion of two H₂O molecules between Cu(II) and*p*-CH₃OC₆H₄COO⁻. As for**1**, the COO group of*p*-CH₃OC₆H₄COO⁻ is twisted out of the plane of the aromatic ring to which it is connected [O1/C1/C2/C3 torsion angle = 8.0(3)°].

Significant hydrogen bonding is also apparent in the crystal structure of **2** (table 3). Thus, the second aqua-H1w is hydrogen bonded to the carboxylate-O1, and the amine-N2-H is hydrogen bonded to carboxylate-O2, so that each carboxylate oxygen is bifurcated. As a result, each $[Cu(cyclam((H_2O)_2)^{2+}]^{2+}$ is surrounded by four $p-CH_3OC_6H_4COO^-$ ions, with each of these associations stabilized by an eight-membered {···HNCuOH···OCO} synthon. A supramolecular chain along the *b*-axis occurs as $[Cu(cyclam((H_2O)_2)^{2+}]^{2+}$ ions are bridged by centrosymmetric 12-membered {...OHO...OCO}₂ synthons involving $p-CH_3OC_6H_4COO^-$ ions and coordinated H_2O molecules (figure 4). The chains are connected into layers in the *ab*-plane via C-H···O interactions occurring between the CH₃O groups, and the layers interdigitated along the *c*-axis with no specific interactions between them.

For **3**, the crystallographic asymmetric unit is made up of two half $[Cu(cyclam)(H_2O)_2]^{2+}$ ions (each ion is disposed about a center of inversion), two $p-CH_3(CH_2)_{15}OC_6H_4COO^-$ ions and a lattice H_2O (figure 5). Each Cu(II) is located within a *trans*-N₄O₂ donor set (table 2). The alkyl chains in $p-CH_3(CH_2)_{15}OC_6H_4COO^-$ adopt



Figure 4. Supramolecular association in 2. The O-H···O and N-H···O hydrogen bonding (orange and blue dashed lines, respectively) lead to a chain along the *b*-axis. Color code: Cu, orange; O, red; N, blue; C, gray; and H, green (see http://dx.doi.org/10.1080/00958 972.2016.1147032 for color version).



Figure 5. (a), (b) The coordination environments of Cu(II) in the two independent cations in **3**. The atoms comprising the asymmetric unit are labeled. The unlabeled atoms are related by the symmetry operations: 1-x, -y, 1-z in (a) and -x, 1-y, 1-z in (b); (c), (d) The two independent carboxylate anions highlighting the extended conformations of the alkyl chains.

an extended, all-*trans* conformation. The major difference between the ions is the relative orientations of the COO group with respect to the C_6H_4 ring, being either twisted (O1–C11–C12–C13 torsion angle = 17.3(3)°) or co-planar (O4–C34–C35–C36 = -3.5(3)°).

The components of the crystallographic asymmetric unit in **3** (figure 6) are connected via $O-H\cdots O$ hydrogen bonds (table 3), whereby coordinated and lattice H₂O molecules bridge the carboxylate-O.



Figure 6. Supramolecular association in **3**. (a) $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds between the components of the asymmetric unit, (b) supramolecular chain along [1 –1 0] (most of the alkyl chains and all non-acidic hydrogens were removed for clarity) and (c) a view in projection down the *b*-axis of the unit cell contents. The $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds (shown as orange and blue dashed lines, respectively) led to a chain. Color code: Cu, orange; O, red; N, blue; C, gray; and H, green (see http://dx.doi.org/10.1080/00958972.2016.1147032 for color version).

Each N–H forms a N–H···O hydrogen bond to a carboxylate-O, with the result that three of the carboxylate-O atoms are bifurcated and the other trifurcated (figure 6(a)). As each $[Cu(cyclam)(H_2O)_2]^{2+}$ ion lies on a center of inversion, similar hydrogen bonds are formed on the other side of each CuN_4 plane, leading to a supramolecular chain with base vector [1 - 1 0] (figure 6(b)). The chains align in the *ab*-plane, with the carboxylate substituents lying to either side (figure 6(c)). The only notable contact between chains is of the type C–H··· π .

Liu *et al.* found that, for Cu(II) complexes of a 22-membered symmetric macrocyclic ligand, the smaller NO_3^- is coordinated to Cu(II) while the bigger CIO_4^- is not coordinated, and related the differences to anion size [48]. However, the size effect may not account for the difference in the structures of **1** and **2**, since similar complexes reported by Lindoy *et al.*, show that $C_6H_5COO^-$ (smaller than *p*-HOC₆H₄COO⁻ in

1) was not coordinated to Cu(II) [37]. The difference was actually surprising given the analogous crystallization conditions employed (see Experimental) and similar pK_a values for the parent carboxylic acids (pK_a = 4.55 for *p*-HOC₆H₄COOH and 4.47 for *p*-CH₃OC₆H₄COOH). Even more perplexing is the fact that, when these are compared with two closely related complexes available in the Cambridge Structural Database (CSD) [49]: [Cu(*en*)₂(H₂O)₂](*p*-HOC₆H₄COO)₂·2H₂O (*en* = ethylene-1,2-diamine) [50] (an analog of **1**) is similar to **2**, and [Cu(*pn*)₂(*p*-CH₃OC₆H₄COO)₂] (*pn* = 1,3-propanediamine) [51] (an analog of **2**) is similar to **1**. Clearly, the observed molecular structures for **1** and **2** arose as a result of the subtle interplay of chemical composition and supramolecular aggregation patterns, in particular the ability of the -OH in **1** to form hydrogen bonds to the carboxylate, a feature absent in **2**. We are currently collecting theoretical data to further rationalize the difference. We note that there were no Cu(II) complexes in the CSD [49] with similar structure as **3** for comparison.

Finally, based on the crystal structures of **1** and **2**, and on the fact that Cu(II) has a preference for N-donor ligands than O-donor ligands, we decided to treat these complexes with *N*-(hexadecyl)ison-icotinamide (L) to form magnetic complexes with liquid crystal properties. We found that under similar conditions, **1** hardly reacted with L, but **2** reacted to form a purple powder (**4**) in good yield. The chemical formula of **4**, $[Cu(cyclam)(L)_2](p-CH_3OC_6H_4COO)_2$, was deduced from elemental analyses (see Experimental) and comparison of its spectroscopic data with **1–3** (table 5). Due to solubility differences, the UV-vis spectra for **1–4** were recorded in different solvents: **1** in H₂O (slightly soluble), **2** in CH₃CH₂OH, and **3** and **4** in CHCl₃.

IR spectra for these complexes show peaks for coordinated H_2O and N-H(cyclam) at 3200–3700 cm⁻¹, C–C(aromatic) at 1600 cm⁻¹, COO(asym) at 1585 cm⁻¹ (for **1**) and 1545 cm⁻¹ (for **2**–**4**), N–H(cyclam) at 1540 cm⁻¹, and COO(sym) at 1531 cm⁻¹ (for **1**) and 1380 cm⁻¹ (for **2**–**4**). In addition, there are strong peaks for CH₂(asym) at 2922 cm⁻¹ and CH₂(sym) at 2850 cm⁻¹ for **3** and **4**, and for C=O(amide) at 1636 cm⁻¹ for **4**. The Δ values for **1**–**3** are in agreement with the carboxylate binding modes as revealed from their crystal structures (Δ = 234 cm⁻¹ for monodentate in **1**; 167 cm⁻¹ for ionic in **2**, and 170 cm⁻¹ for ionic in **3**). For **4**, the Δ value is 161 cm⁻¹, from which we infer that *p*-CH₃OC₆H₄COO⁻ ion is not coordinated to Cu(II).

The UV-vis spectrum for **1** shows a broad d-d band at 505 nm ($\varepsilon_{max} = 155 \text{ M}^{-1} \text{ cm}^{-1}$), suggesting a *trans* III square planar geometry [52, 53]. For **2–4**, the bands are at lower energies ($\lambda_{max} = 528-546 \text{ nm}$; $\varepsilon_{max} = 30-119 \text{ M}^{-1} \text{ cm}^{-1}$), suggesting a *trans* III octahedral geometry [53–55]. The geometries for **2–4** were expected based on their structures, but the geometry for **1** was unexpected as this means that both coordinated p-HOC₆H₄COO⁻ ligands dissociated in aqueous solution. However, the result for **1** is actually supported by its molar conductance value of 137 S cm² mol⁻¹ in H₂O, indicating a 1 : 2 electrolyte [56].

3.4. Magnetic properties of 1-3

The μ_{eff} values for **1–3** were determined at room temperature by the Gouy method. The values for **1** (1.72 BM) and **2** (1.67 BM) are lower than the values reported for several Cu(II) octahedral complexes (1.9–2.2 BM) [57–62]. The results suggest weak antiferromagnetic interactions between the Cu(II) ions in both molecules, which are linked by H-bonds. A similar suggestion was proposed by Bhargavi *et al.*, for Mn(acphpn)(H₂O)NCS]·2H₂O (acphpn = *N*,*N*′-bis(2-hydroxyacetophenone)-1,3-diaminopropane [63]. However, the value for **3** (2.15 BM) is in agreement with the reported values. From these, we infer that the magnetic properties of these complexes are independent of the different coordination modes of the carboxylate ions and the alkyl chain length.

Complex	IR Δ (cm ⁻¹)	UV-vis $\lambda_{\rm max}$ (nm) ($\epsilon_{\rm max}/{ m M}^{-1}~{ m cm}^{-1}$)	$\mu_{ m eff}$ (BM)	TG T _{dec} /°C	DSC T _{onset} (°C) (ΔH/kJ mol ⁻¹)
1	234	505 (155)	1.72	262	58.9 (+22.9), 120.3 (+9.1)
					241.8 (+22.2)
2	167	536 (119)	1.67	249	53.2 (+77.7), 101.8 (+5.2)
3	170	546 (85)	2.15	210	58.2 (+56.4), 86.5 (+34.7)
					100.5 (+19.8), 137.8 (+30.7)
4	161	528 (30)	-	174	72.8 (+37.9), 86.7 (1.8)

Table 5. Characterization data for 1-4.

Figure 7. CV of an aqueous solution of (a) 1 and (b) 2.

3.5. Redox properties of 1-3

Cyclam is structurally flexible. Hence, it is able to stabilize unusual oxidation states of metal ions, resulting in their uses as homogeneous redox catalysts. Examples include electrocatalytic reduction of carbonyl groups [34] and oxidation of alkenes [28–33]. An important parameter for such applications is the redox potential of the complex, which may be determined by CV.

For **1**, its CV scan in H₂O (figure 7(a)) shows a weak cathodic peak (E_{pc}) at -0.25 V and a strong anodic peak (E_{pa}) at + 0.89 V. The cathodic peak is assigned to the reduction of $[Cu(cyclam)]^{2+}$ to $[Cu(cyclam)]^{+}$ as its value is in the region normally observed for most mononuclear copper(II) complexes (about -0.13 V) [64]. The anodic peak is assigned to the oxidation of $[Cu(cyclam)]^{2+}-[Cu(cyclam)]^{3+}$ as the value is similar to that reported by Zhang et al. for the Cu(II) complex of 1,4,8,11-tetraazacyclotetradecane-5,7-dione in aqueous solution (+0.83 V) [65]. The stronger anodic peak suggests a more facile oxidation compared to the reduction process, but both redox processes were irrreversible. Under similar conditions, the CV scan for 2 (figure 7(a)) shows a weak cathodic peak at -0.2 V and two strong anodic peaks at +0.18 V and + 1.0 V. The first anodic peak may be due to oxidation of cyclam, while the other two peaks may be similarly assigned as for 1. There were no cathodic or anodic peaks in the CV scan for 3 in CHCl, which is ascribed to the presence of insulating long alkyl chains [15]. In CHCl., the long alkyl chains were expected to result in the formation of micelle-like structures, with the hydrophobic part on the outside and the hydrophilic part ([Cu(cyclam)(H,O),]²⁺) on the inside. In this structure, the electrons from the electrode were unable to reach the 'insulated' Cu(II) ions to reduce them, and electrons from the 'insulated' Cu(II) ions were unable to reach the electrode to oxidize it. According to these results, these complexes were unsuitable as homogeneous catalysts.

3.6. Thermal and mesomorphic properties of 1-4

The thermal properties of **1–4** (table 5) were studied by TG, while the mesomorphic properties of **3** and **4** were studied by DSC and POM, as the latter complexes were expected to be liquid crystals due to their anisotropic molecular shapes and the presence of long alkyl chains.

For **1**, the TG trace showed an initial mass loss of 83.9% (Calcd 88.2%) from 262 °C to about 500 °C due to decomposition of p-HOC₆H₄COO⁻ and cyclam. Its DSC scan showed three endothermic peaks at 58.9 °C ($\Delta H = + 22.9 \text{ kJ mol}^{-1}$), 120.3 °C ($\Delta H = + 9.1 \text{ kJ mol}^{-1}$), and 241.8 °C ($\Delta H = + 22.2 \text{ kJ mol}^{-1}$), assigned to breaking of p-HOC₆H₄COO-Cu and both inter- and intramolecular hydrogen bonds, respectively.

For **2**, the TG trace showed an initial mass loss of 6.8% (Calcd 6.0%) from 104 °C to 195 °C due to evaporation of coordinated H₂O, followed by 82.4% (Calcd 83.5%) from 249 °C to about 600 °C due to decomposition of $p-CH_3OC_6H_4COO^-$ and cyclam. Its DSC scan showed two endothermic peaks at 53.2 °C ($\Delta H = +77.7$ kJ mol⁻¹) and 101.8 °C ($\Delta H = +5.2$ kJ mol⁻¹), assigned to breaking of both interand intramolecular hydrogen bonds and dissociation of coordinated H₂O molecules, respectively. The significantly higher enthalpy change for **2** compared to **1** suggests stronger hydrogen bonds in the

Figure 8. Photomicrographs of (a) 3 on cooling at 141 °C, (b) L on cooling at 98.0 °C, (c) 4 on heating at 84.3 °C, and (d) 4 on cooling at 74.2 °C.

former complex, which is to be expected since these bonds involved free p-CH₃OC₆H₄COO⁻, coordinated H₂O and cyclam-NH in **2**, but only coordinated p-HOC₆H₄COO and cyclam-NH in **1**.

The TG trace for **3** showed an initial mass loss of 2.3% (Calcd 1.7%) from 67 °C to about 100 °C due to evaporation of lattice H₂O, followed by 87.4% (Calcd 92.2%) from 210 °C to about 500 °C due to evaporation of coordinated H₂O and decomposition of p-CH₃(CH₂)₁₅OC₆H₄COO⁻ and cyclam. Its DSC scan showed four endothermic peaks at 58.2 °C ($\Delta H = + 56.4$ kJ mol⁻¹), 86.5 °C ($\Delta H = + 34.7$ kJ mol⁻¹), 100.5 °C ($\Delta H = + 19.8$ kJ mol⁻¹) and 137.8 °C ($\Delta H = + 30.7$ kJ mol⁻¹). These are assigned to the breaking of hydrogen bonds and van der Waals forces, dissociation of coordinated H₂O molecules, and crystal-to-mesophase transition, respectively. Under POM, dendritic textures (figure 8(a)) were observed at 141 °C on cooling from its isotropic liquid phase (145 °C). This mesophase then coalesced on further cooling until it crystallized at 89.9 °C.

Finally, the TG trace for **4** showed an initial mass loss of 96.4% (calcd. 95.0%) from 174 °C to 568 °C due to decomposition of L, $p-CH_3OC_6H_4COO^-$ and cyclam. Its DSC scan showed two endothermic peaks at 72.8 °C ($\Delta H = +37.9$ kJ mol⁻¹) and 86.7 °C ($\Delta H = +1.8$ kJ mol⁻¹). Under POM the sample started to melt at 74.3 °C, forming a needle-like texture (figure 8(c)) similar to L (figure 8(b)) on further heating at 93.2 °C, but did not clear to the isotropic liquid, even on heating to near its decomposition temperature (174 °C). We repeated the POM experiment and found that when the fluid phase at 100 °C was cooled, a brush-like texture (figure 8(d)), consistent with mesomorphic ionic liquids [66], rapidly formed

at 78.9 °C. Combining the DSC and POM data, it seems that the complex melted at 72.8 °C, and then the axially coordinated L ligands dissociated at 86.7 °C. On cooling, its components reassembled to a mesophase at 78.9 °C. A similar dissociation of N-donor ligands (pyridine, pyrazine and 4,4'-bipyridine) coordinated at the axial positions of Cu(II) alkylcarboxylates was suggested by Attard and Cullum [67].

The amount of residue found at 600 °C for these complexes (16.1% for **1**, 10.8% for **2**, 10.3% for **3**, and 3.6% for **4**) were in agreement with the calculated values, assuming pure CuO [68, 69].

Based on the above data, the thermal stability of these complexes follows the order: 1 > 2 > 3 > 4. Hence, it may be inferred that the molecular complex is thermally more stable than the ionic complexes. Also, **3** and **4** exhibit mesomorphisms as expected for ionic complexes.

4. Conclusion

Three dimeric complexes, $[Cu_2(p-ROC_6H_4COO)_4(H_2O)_2]$ (R=H, CH₃, CH₃(CH₂)₁₅), were formed from reactions of Cu(II) with the corresponding carboxylate. In the reaction with cyclam, these complexes formed a mononuclear covalent complex, $[Cu(p-HOC_6H_4COO)_2(cyclam)]$ (1), and two mononuclear ionic complexes, $[Cu(cyclam)(H_2O)_2](p-CH_3OC_6H_4COO)_2$ (2) and $[Cu(cyclam)(H_2O)_2](p-CH_3(CH_2)_{15}OC_6H_4COO)_2$ ·H₂O (3), respectively. Complexes 1–3 show differences in supramolecular association due to extensive hydrogen bonding interactions. The Cu(II) ions in 1 and 2 are irreversibly reduced to Cu(I) and oxidized to Cu(III), while 3 is redox inactive due to the insulating long alkyl chains. Complex 2 reacted with *N*-(hexadecyl)isonicotinamide (L) to form $[Cu(cyclam)(L)_2](p-CH_3OC_6H_4COO)_2$ (4). These complexes have high decomposition temperatures (>200 °C for 1–3, and 174 °C for 4); the covalent 1 is the most thermally stable, while the lower thermal stability of 4 arose from the presence of N-donor ligands at the axial sites of Cu(II). Complexes 3 and 4 have melting temperatures lower than 100 °C, defining them as ionic liquids, and both exhibit mesomorphism characteristics of ionic liquid crystals.

Supplementary material

CCDC-765498 (1), 912696 (2) and 985198 (3) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Disclosure statement

No potential conflict of interest was reported by the authors.

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