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Bimetallic copper(II) and zinc(II) complexes of acyclic Schiff base ligands derived from amino acids

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ABSTRACT

The acyclic Schiff-base ligands (2-(OH)-5-(R³)C₆H₂-1,3-(HC=NC(R¹)(R²)CO₂H), derived from the dialdehyde 2-hydroxy-5-R-1,3-benzenedicarboxaldehyde (R = Me or *t*-Bu) and two equivalents of the amino acids glycine, 2,2-diphenylglycine or phenylalanine, have been reacted with the metal acetates $M(OAc)_2$ (M = Cu, Zn) in the presence of triethylamine, affording the complexes [HNEt₃][M₂(CH₃CO₂)₂-(2-(O)-5-(*t*-Bu)C₆H₂-1,3-(HC=NC(R¹)(R²)CO₂)₂] (M = Cu, R¹ = R² = C₆H₅, R³ = Me (**1**); M = Zn, R¹ = R² = H, R³ = *t*-Bu (**2**); M = Zn, R¹ = R² = C₆H₅, R³ = *t*-Bu (**3**); M = Zn, R¹ = H, R² = CH₂C₆H₅, R³ = *t*-Bu (**4**)) in good yields. The crystal structures of **1**-MeCN, **2**·1 $\frac{1}{2}$ MeOH, **3**·2MeOH, and **4**·3MeOH have been determined. © 2010 Elsevier B.V. All rights reserved.

1. Introduction

There is currently much academic and industrial interest in biocompatible catalytic systems for the ring opening polymerisation of lactides and lactone [1–8]. Recently, Hillmyer and Tolman drew an interesting analogy between the coordination/insertion mechanism in lactone polymerisation and the mechanism of hydrolysis by some metalloenzymes [9]. In a commonly accepted mechanism pathway, one of the two or more metals in the active site of the enzyme coordinates a water molecule enhancing its nucleophilic ability by lowering its pK_a and generating a metal bound hydroxide species; while another metal coordinates to the substrate rendering it more electrophilic and more susceptible to nucleophilic attack. Considering this, Hillmyer and Tolman studied lactone polymerisation catalysts containing a Zn–O–Zn motif as metalloenzyme mimics, with the intention of promoting potential cooperative effects between metal centres [9–12].

With this in mind, we have decided to investigate the synthesis and catalytic behaviour of zinc complexes supported by acyclic Schiff base ligands. Using a phenolate residue as the central motif of our ligand framework, we hoped to promote the formation of the desired Zn–O–Zn motif. After failing to prepare this ligand framework in a template-free fashion, a strategy that was recently

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employed for the synthesis of a number of new macrocyclic Schiff base ligand systems [13], we decided to employ a template strategy which led to the one-pot synthesis of complexes **1–4** (Scheme 1).

2. Results and discussion

2.1. Copper

The reaction of the dialdehyde 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde with the amino acid 2,2-diphenylglycine and copper diacetate in the presence of triethylamine in refluxing methanol afforded the green complex [HNEt₃][Cu₂(CH₃CO₂)₂-(2-(0)-5-(Me)C₆H₂-1,3-(HC=NC(Ph₂CO₂)₂] in high yield (ca. 64%). Crystals suitable for a single crystal X-ray diffraction study were grown from a saturated acetonitrile solution on prolonged standing at 0 °C. The crystal structure of **1** is shown in Fig. 1 with selected bond lengths and angles given in the caption. Crystallographic data are given in Table 1. The asymmetric unit comprises two cation/anion pairs and two acetonitrile lattice solvent molecules. The cation hydrogen bonds to the anion *via* N-H···O(carboxylate) interactions that are bifurcated in one case and mono-furcated in the other. One cation is disordered such that it forms H-bonds to one anion or the other.

The copper metal centres in complex **1** are five coordinate and adopt a distorted square-based pyramidal geometry (Reedijk criteria τ = 0.4 for Cu(1) and Cu(2)) [14] with O(6) and O(9) at the apex





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Scheme 1. Synthesis of complexes 1 (M = Cu, $R^1 = R^2 = C_6H_5$, $R^3 = Me$), 2 (M = Zn, $R^1 = R^2 = H$, $R^3 = t$ -Bu), 3 (M = Zn, $R^1 = R^2 = C_6H_5$, $R^3 = t$ -Bu) and 4 (M = Zn, $R^1 = H$, $R^2 = C_1C_2C_6H_5$, $R^3 = t$ -Bu). Conditions: M(OAc)₂ (2 equivalents wrt the dialdehyde), triethylamine (5 equivalents wrt the dialdehyde), methanol or ethanol, reflux 12 h.



Fig. 1. Crystal structure of one of two cation/anions pairs in the asymmetric unit of **1**·2MeCN. The solvent of crystallisation is omitted for clarity. Selected bond lengths and angles (Å, °): Cu(1)–O(1) 1.934(6), Cu(1)–N(1) 1.960(8), Cu(1)–O(3) 1.978(6), Cu(1)–O(6) 2.125(6), Cu(1)–O(8) 1.918(7), Cu(2)–O(3) 1.977(6), Cu(2)–N(2) 1.926(8), Cu(2)–O(4) 1.943(7), Cu(2)–O(7) 1.905(7), Cu(2)–O(9) 2.191(7), Cu(1)–O(3)–Cu(2) 112.2(3), O(3)–Cu(1)–O(1) 173.8(3), O(7)–Cu(2)–N(2) 150.1, O(8)–Cu(1)–N(1) 149.5(3), O(3)–Cu(2)–O(4) 173.4(3), H(5)···O(4) 2.11, N(5)–H(5)···O(4) 143, H(5)···O(5) 2.15, N(5)–H(5)···O(5) 154.

for Cu(1) and Cu(2), respectively. Cu(1) and Cu(2) lie ca. 0.274 and 0.245 Å respectively above the mean planes defined by N(1), O(1), O(3) and O(8) for Cu(1) and N(2), O(3), O(4) and O(7) for Cu(2). The copper centres are bridged through a Cu–O–Cu bond and through two acetate moieties.

2.2. Zinc

The reaction of the dialdehyde 2-hydroxy-5-*tert*-butyl-1,3benzenedicarboxaldehyde with the amino acids glycine, 2,2diphenylglycine or phenylalanine, and zinc diacetate in the presence of triethylamine in refluxing ethanol or methanol readily afforded the complexes $[HNEt_3][Zn_2(CH_3CO_2)_2(2-(O)-5-(t-Bu)C_6H_2-1,3-(HC=NC(R^1)(R^2)CO_2)_2]$ (R¹ = R² = H (**2**); R¹ = R² = C₆H₅ (**3**); R¹ = H, R² = CH₂C₆H₅ (**4**)) in excellent yields (75%, 93% and 96%, respectively). Crystals of **2**.1 $\frac{1}{2}$ MeOH, **3**.2MeOH, and **4**.3MeOH suitable for single crystal X-ray diffraction studies were grown from saturated methanol solutions at -25 °C. Crystals of $2.1\frac{1}{2}$ MeOH and 4.3MeOH were small and required the use of synchrotron radiation [15,16].

The X-ray crystal structure of complexes 2 and 3 and that of the anion of 4 are presented in Figs. 2–4, respectively, with selected bond lengths and angles given in the captions. Crystallographic data are collated in Table 1.

Crystals of complex $2 \cdot 1 \frac{1}{2}$ MeOH formed as small, thin needles and the resulting diffraction was weak even at the synchrotron. The cations and methanol molecules were subject to substantial disorder and the structure refinement was good enough only for a confirmation of the connectivity. The asymmetric unit comprises two cation/anion pairs and three methanol molecules. As in the case of **1**, the cations hydrogen bond to the anions *via* N-H···O(carboxylate) interactions. The two zinc ions Zn(1) and Zn(2) adopt a

Table 1

Crystallographic data for 1.MeCN, 2.1¹/₂MeOH, 3.2MeOH, and 4.3MeOH.

Compound	1 ⋅MeCN	$2 \cdot 1 \frac{1}{2}$ MeOH	3 ·2(CH ₃ OH)	4 ·3(CH ₃ OH)
Formula	$[C_{41}H_{33}Cu_2N_2O_9][C_6H_{16}N] \cdot C_2H_3N$	$[C_{20}H_{21}Zn_2N_2O_9][C_6H_{16}N]\cdot 1\frac{1}{7}CH_4O$	$[C_{44}H_{39}N_2O_9Zn_2][C_6H_{16}N] \cdot 2(CH_4O)$	$[C_{32}H_{35}N_2O_9Zn_2][C_6H_{16}N]\cdot 3(CH_4O)$
Formula weight (g/mol)	968.03	714.39	1036.79	930.76
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	PĪ	P2 ₁	$P2_1/c$	ΡĪ
Unit cell dimensions				
a (Å)	10.459(5)	14.176(9)	10.3992(2)	11.516(4)
b (Å)	15.366(7)	14.524(9)	16.2391(3)	12.909(5)
c (Å)	28.666(13)	17.073(10)	29.9788(6)	16.327(6)
α (°)	96.789(6)	90	90	87.411(4)
β(°)	92.233(6)	105.501(8)	96.676(2)	70.978(3)
γ(°)	104.282(6)	90	90	72.015(3)
V (Å ³)	4422(4)	3397(4)	5028.30(17)	2178.5(13)
Ζ	4	4	4	2
Temperature (K)	160(2)	150(2)	140(1)	150(2)
Wavelength (Å)	0.71073	0.6939	0.71073	0.7848
Calculated density $(\alpha \text{ cm}^{-3})$	1.454	1.401	1.370	1.419
Absorption coefficient (mm ⁻¹)	1.025	1.472	1.016	1.165
Transmission factors; maximum, minimum	0.960, 0.762	0.985, 0.683	0.771, 0.615	0.966, 0.854
Crystal size (mm)	$0.28 \times 0.10 \times 0.04$	$0.28 \times 0.03 \times 0.01$	$0.53 \times 0.35 \times 0.27$	$0.14 \times 0.08 \times 0.03$
θ (maximum) (°)	22.5	22.5	29.0	25.0
Reflections	25 409	21 390	72 107	11 424
Unique reflections	11 558	9421	13 277	5643
Reflections with $F^2 > 2\sigma(F^2)$	5275	6485	9155	3215
Rint	0 1223	0.0626	0.0595	0.0521
Number of	1203	728	709	430
$R_1 [F^2 > 2\sigma(F^2)]$	0.0722	0.0880	0.0403	0.0660
wR_2 (all data)	0.1838	0.2499	0.1008	0.1866
Goodness-of-fit	0.983	1.036	0.992	0.936
Largest difference peak and hole (e Å ⁻³)	0.674 and -0.739	0.945 and -0.714	0.599 and -0.497	0.554 and -0.360

trigonal bipyramidal geometry with the phenolic oxygen (O(3)) and the oxygen from the glycine residue (O(1) and O(4), respectively) occupying the axial positions.

In the structure of **3**-2MeOH the asymmetric unit comprises one anion, one disordered cation and two methanol molecules of crystallisation, one of which is also disordered. The cation and anion hydrogen bond as seen for the previous two examples, while the two methanol molecules hydrogen bond to each other and one hydrogen bonds to the anion.

The asymmetric unit of **4**·3MeOH comprises one cation, one anion and probably three MeOH of crystallisation. The cation and methanol molecules were so badly disordered they were modelled with the Platon Squeeze procedure [17] as areas of diffuse electron density. However, during the development of the structural model it was clear that the cation and anion formed a hydrogen bonded interaction in tune with those of the other compounds reported here.

For complex **4**, the zinc centres are five coordinate and their geometry is best described as trigonal bipyramidal (Reedijk criteria $\tau = 0.7$ for Zn(1) and Zn(2)) [14] with the phenolic oxygen and the oxygen from the amino acid residue occupying the axial positions. In the case of Zn(1) in complex **3**, the geometry adopted by the ion is intermediate between trigonal bipyramidal and square base pyramidal as demonstrated by the calculated Reedijk criteria ($\tau = 0.5$). In the case of Zn(2) in complex **3**, the hydrogen bond between the triethyl ammonium cation and the carboxylic oxygen somehow perturbs the geometry around the zinc centre: the

geometry is closer to a distorted square base pyramid ($\tau = 0.4$) with O(9) at the apex. In each complex, the two zinc centres are bridged through a Zn–O–Zn bond and through two acetate moieties thus forming a distorted eight membered ring in a boat conformation. Each zinc centre is also bound to the imino nitrogen and an oxygen atom from the amino acid residue.

The Zn–O_{phenolate} bond lengths range from 2.0619(15) to 2.100(5) Å and are similar to those found in related dinuclear zinc complexes supported by phenolate ligands (1.997(3)-2.112(4) Å). The Zn–O–Zn angles (101.39(6) (3) and $100.8(2)^{\circ} (4)$) are also comparable to those found in related dinuclear complexes $(100.92(7) \text{ and } 101.19(15)^{\circ})$ [6,18].

2.3. ε-Caprolactone polymerisation

As mentioned for the iron complexes studied by Gibson [3] and ourselves [19], the initiating metal alkoxide (obtained *via* alkoxy/ carboxylate exchange), obtained by mixing complexes **1–4** with benzyl alcohol, may exhibit enhanced nucleophilicity due to the anionic nature of the metal complex [20]. Complexes **1–4** were therefore screened for the ring opening polymerisation of ε -caprolactone in toluene at room temperature and at 80 °C and in the presence of benzyl alcohol. In all cases however, only traces of polymers were isolated. Due to these disappointing results, no further investigation of the potential of these complexes for ring opening polymerisation was attempted.



Fig. 2. Crystal structure of one of two cation/anion pairs in the asymmetric unit of 2.1 ½MeOH. The solvent of crystallisation is omitted for clarity.

In conclusion, four copper and zinc di-nuclear complexes supported by acyclic Schiff base ligands were synthesised and structurally characterised. Surprisingly, these anionic complexes were found to be inactive for the ring opening polymerisation of ε -caprolactone in the presence of benzyl alcohol.

3. Experimental

3.1. General

All manipulations, unless otherwise stated, were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Hexane, diethyl ether and tetrahydrofuran were refluxed over sodium and benzophenone. Toluene, octane and methanol were refluxed over sodium. Dichloromethane and acetonitrile were refluxed over calcium hydride. All solvents were distilled and degassed prior to use. Dry methanol or ethanol was stored over activated 4 Å molecular sieves. E-Caprolactone was dried over calcium hydride, vacuum distilled and degassed prior to use. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer; ATR spectra were recorded on a Spectrum BX FT IR system equipped with an ATR probe. ¹H NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz and a Gemini 300 NMR spectrometer or a Bruker Advance DPX-300 spectrometer at 300 MHz. The ¹H NMR spectra were calibrated against the residual portio impurity of the deuterated solvent. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University. All other chemicals were obtained commercially from Aldrich and used without further purification.

3.2. Synthesis of [HNEt₃][Cu₂(CH₃CO₂)₂(2-(0)-5-(Me)C₆H₂-1,3-(HC=NCPh₂CO₂)₂] (**1**)

A solution of 2,2-diphenyl glycine (0.42 g, 1.8 mmol), copper diacetate (0.37 g, 2.0 mmol) and 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (0.15 g, 0.92 mmol) in methanol (30 mL) was stirred at room temperature for 30 min. Triethylamine (0.28 mL, 2.0 mmol) was then added and the solution brought to reflux for 12 h. The solvent was then removed *in vacuo* and the residue extracted in hot acetonitrile. Recrystallisation from a saturated acetonitrile solution afforded **1** as green needles. Yield: 0.54 g, 64%; m.p. > 350 °C; elemental analysis calculated for C₄₇H₄₉Cu₂-N₃O₉: C, 60.90; H, 5.33; N, 4.53. Found: C, 60.68; H, 5.62; N, 4.61%. IR (nujol mull, KBr): 1662(w), 1623(m), 1569(w), 1539(w), 1303(w), 1259(w), 1169(m), 1073(w), 1026(m), 972(m), 815(s), 768(w), 738(s), 698(m), 665(w) cm⁻¹; MS (MAL-DI): *m/z* 822.2 [M–H–HNEt₃].

3.3. Synthesis of [HNEt₃][Zn₂(CH₃CO₂)₂(2-(O)-5-(t-Bu)C₆H₂-1,3-(HC=NCH₂CO₂)₂] (**2**)

A solution of glycine (79 mg, 1.1 mmol), zinc diacetate (196 mg, 1.1 mmol) and 2-hydroxy-5-*tert*-butyl-1,3-benzenedicarboxalde-hyde (95 mg, 0.46 mmol) in methanol (50 mL) was stirred at room temperature for 30 min. Triethylamine (0.35 mL, 2.5 mmol) was then added and the solution brought to reflux for 12 h. Yield: 230 mg, 75%; m.p. > 350 °C; elemental analysis calculated for C₂₆H₃₉N₃O₉Zn₂: C, 46.72; H, 5.88; N, 6.29. Found: C, 46.81; H, 5.93; N, 6.21%; IR (nujol mull, KBr): 1653(s), 1587(s), 1297(w), 1261(w), 1228(w), 1157(w), 1076(m), 1020(m), 893(w), 807(w), 777(m), 734(m), 668(m), 618(w), 589(w) cm⁻¹; ¹H NMR (C₆D₆,



Fig. 3. X-ray crystal structure of complex **3** showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonding, and minor disorder components have been omitted for clarity. Selected bond lengths and angles (Å, °): Zn(1)-O(3) 2.0696(15), Zn(1)-N(1) 2.0501(17), Zn(1)-O(1) 2.0268(16), Zn(1)-O(6) 1.9707(18), Zn(1)-O(8) 1.985(17), Zn(2)-O(3) 2.0623(15), Zn(2)-N(2) 2.0517(18), Zn(2)-O(4) 2.0475(15), Zn(2)-O(7) 1.9746(18), Zn(2)-O(9) 1.9721(17), Zn(1)-O(3)-Zn(2) 101.39(6), O(1)-Zn(1)-O(3) 164.91(6), O(8)-Zn(1)-N(1) 136.49(7), O(3)-Zn(2)-O(4) 160.13(7), O(7)-Zn(2)-N(2) 138.62(9), $H(3)\cdots O(4) 1.92$, $N(3)-H(3)\cdots O(4) 155$, $H(11)\cdots O(10) 1.94$, $O(11)-H(11)\cdots O(2) 1.74$, $O(10)-H(10)\cdots O(2) 164$.

400 MHz) δ 8.38 (s, 2H, *CH*=N), 7.37 (s, 2H, *C*₆*H*₂), 4,25 (s, 4H, N-*CH*₂), 3.11 (q, 6H, *J* = 7.3 Hz, HN(*CH*₂*CH*₃)₃), 2.04 (s, 6H, *CH*₃*CO*₂), 1.31 (t, 9H, *J* = 7.3 Hz, HN(*CH*₂*CH*₃)₃), 1.29 (s, 9H, *C*(*CH*₃)₃) ppm; MS (ES⁺): *m/z* 102.2 [HNEt₃⁺]⁺ 567.0 [M-HNEt₃+2H]⁺ 668.1 [M+H]⁺; (ES⁻): *m/z* 567.0 [M-HNEt₃⁻]⁻.

3.4. Synthesis of [HNEt₃][Zn₂(CH₃CO₂)₂(2-(O)-5-(t-Bu)C₆H₂-1,3-(HC=NCPh₂CO₂)₂] (**3**)

A solution of 2,2-diphenyl glycine (1.10 g, 4.8 mmol), zinc diacetate (0.98 g, 5.3 mmol) and 2-hydroxy-5-tert-butyl-1,3-benzenedicarboxaldehyde (0.50 g, 2.4 mmol) in methanol (50 mL) was stirred at room temperature for 30 min. Triethylamine (1.7 mL, 12 mmol) was then added and the solution brought to reflux for 12 h. The solvent volume was reduced to 3 mL. After prolonged standing at room temperature, **3** was isolated as yellow crystals. Yield: 2.20 g, 93%; m.p.: 192 °C; elemental analysis calculated for C₅₀H₅₅N₃O₉Zn₂: C, 61.74; H, 5.70; N, 4.32. Found: C, 61.65; H, 5.61; N, 4.25%. IR (nujol mull, KBr): 2719(w), 2660(w), 1661(m), 1643(m), 1608(m), 1587(w), 1340(w), 1261(m), 1159(w), 1097(m), 1024(m), 800(s) cm⁻¹; ¹H NMR (C₆D₆, 400 MHz) δ 7.99 (s, 2H, N=CH), 7.20-7.77 (m, 20H, C₆H₅), 7.07 (s, 2H, C₆H₂), 2.62 $(m, 6H, HN^+CH_2CH_3)$, 2.01 $(s, 6H, CH_3CO_2)$, 0.93 (t, l = 6.5 Hz, 9H) $HN^{+}CH_{2}CH_{3}$), 0.88 (s, 9H, C(CH_{3})_{3}) ppm; MS (ES-): m/z 870.3 $[M-HNEt_3^+]^-$, (ES+): m/z 102.1 $[HNEt_3^+]$.

3.5. Synthesis of [HNEt₃][Zn₂(CH₃CO₂)₂(2-(O)-5-(t-Bu)C₆H₂-1,3-(HC=NCHCH₂PhCO₂)₂] (**4**)

A solution of phenylalanine (0.80 g, 4.8 mmol), zinc diacetate (0.98 g, 5.3 mmol) and 2-hydroxy-5-tert-butyl-1,3-benzenedicarboxaldehyde (0.50 g, 2.4 mmol) in methanol (50 mL) was stirred at room temperature for 30 min. Triethylamine (1.7 mL, 12 mmol) was then added and the solution brought to reflux for 4 h. The solvent volume was reduced to 3 mL. After prolonged standing at -25 °C, **4** was isolated as yellow crystals. Yield: 1.98 g, 96%; m.p.: 252 °C; elemental analysis calculated for C₄₀H₅₁N₃O₉Zn₂: C, 56.61; H, 6.06; N, 4.95. Found: C, 56.72; H, 5.96; N, 4.90. IR (nujol mull, KBr): 2724(m), 2663(w), 1629(w), 1588(w), 1260(m), 1169(w), 1084(w), 1021(s), 805(m), 700(w), 665(w) cm⁻¹; ¹H NMR (C₆D₆, 400 MHz) δ 7.41 (s, 2H, CH=N), 6.89-6.72 (m, 10H, C₆H₅), 6.42(br s, 2H, Ar-H), 3.92 (d, 2H, J = 10.8 Hz, CH₂C₆H₅), 3.77 (d, 2H, J = 12.8 Hz, CH₂C₆H₅), 3.49 (m, 1H, C=N-CH), 3.03 (m, 1H, C=N-CH), 2.85 (m, 6H, HNCH₂CH₃⁺), 2.17 (br s, 6H, CH₃CO₂), 1.35 (s, 9H, C(CH₃)₃), 1.04 (m, 9H, HNCH₂CH₃⁺) ppm; MS (ES-): m/z 747.1 [M-HNEt₃⁺]⁻.

3.6. X-ray crystallography

Diffraction data were collected using CCD diffractometers with sealed tube sources for 1 MeCN [21] and 3 MeOH [22], and with synchrotron radiation for $2.1\frac{1}{2}$ MeOH, and 4.3 MeOH [21].



Fig. 4. X-ray crystal structure of the anion of complex **4** showing the atom numbering scheme. Hydrogen atoms, the cation and three methanol solvent molecules have been omitted for clarity. Selected bond lengths and angles (Å, °): Zn(1)-O(1) 2.100(5), Zn(1)-N(1) 2.012(7), Zn(1)-O(2) 2.087(6), Zn(1)-O(6) 1.969(6), Zn(1)-O(8) 1.975(7), Zn(2)-O(1) 2.100(5), Zn(2)-N(2) 2.027(6), Zn(2)-O(4) 2.076(5), Zn(2)-O(7) 1.967(5), Zn(2)-O(9) 1.988(7), Zn(1)-O(1)-Zn(2) 100.8(2), O(1)-Zn(1)-O(2) 165.6(2), O(8)-Zn(1)-N(1) 124.8(3), O(1)-Zn(2)-O(4) 168.0(2), O(7)-Zn(2)-N(2) 127.2(2).

Narrow-frame exposures were employed. Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetryequivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix-least squares on F^2 values for all unique data [23,24]. All non-hydrogen atoms were refined anisotropically. H atoms were included in a riding model with U_{iso} set to be 1.2 times (1.5 times for methyl-H) U_{eq} for the carrier atom. Further details are presented in Table 1. In 1 MeCN one of the cations is disordered over two sets of positions with some atoms common, major component 52.4(11)%. The data for **2** $1\frac{1}{2}$ MeOH were rather weak and hampered by the needle crystal habit. Both cations and parts of the anions suffered from unresolved disorder while the highly disordered methanol molecules were modelled as areas of diffuse electron density by the Platon Squeeze procedure [17]. In 3-2MeOH twofold disorder was modelled in the methyl group C(42) (major component 62.5(18)%), all of the ethyl groups in the cation (major component 76.0(4)%) and the methanol molecule, O(10)/C(51) (major component: 84.7(9)%). In each case the point atom disorder was modelled using restraints on geometry and anisotropic displacement parameters. In 4-3MeOH the cation and the methanol of crystallization were badly disordered and modelled as diffuse regions of electron density [17].

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Appendix A. Supplementary material

CCDC 767782–767785 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.08.043.

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