Metal–betaine interactions
VII. Crystal and molecular structures of aquadichloro(pyridine betaine)zinc(II), dichlorobis(pyridine betaine)zinc(II) and dichlorobis(betaine)zinc(II) monohydrate*

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Abstract

Three Zn(II) complexes of betaine (Me$_3\overset{+}{N}$CH$_2$COO$^-$, abbreviated as BET) and pyridine betaine (C$_5$H$_5\overset{+}{N}$CH$_2$COO$^-$, pyBET) have been prepared and characterized by X-ray crystallography. The results reveal that all three complexes are monomeric with tetrahedrally coordinated Zn(II) atoms. The Zn(II) atom is coordinated by two chloro ligands (Zn–Cl = 2.231(1), 2.219(1) Å), one unidentate pyBET ligand (Zn–O(carboxy) = 1.936(1) Å) and one aqua ligand (Zn–O(aqua) = 2.051(1) Å) in aquadichloro(pyridine betaine) zinc(II), [Zn(pyBET)(H$_2$O)Cl$_2$] **(1)**, whereas the coordination sphere of the Zn(II) atom comprises two chloro ligands (Zn–Cl = 2.261(1), 2.238(2) Å) and two unidentate pyBET ligands (Zn–O(carboxy) = 1.988(3), 1.964(2) Å) in dichlorobis(pyridine betaine) zinc(II), [Zn(pyBET)$_2$Cl$_2$] **(2)**. In dichlorobis(betaine)zinc(II) monohydrate, [Zn(BET)$_2$Cl$_2$]·H$_2$O **(3)**, the Zn(II) atom is bonded to two chloro ligands (Zn–Cl = 2.231(3) Å) and two unidentate BET ligands (Zn–O(carboxy) = 1.965(7) Å), and the water molecule participates only in linking the tetrahedral complexes into a zigzag chain.

Introduction

The crystal structures of Zn(II) carboxylates have been widely studied [2]. In the octahedral zinc carboxylates, the Zn(II) atom is commonly coordinated either by two unidentate carboxylato groups and four neutral ligands, as in [Zn(C$_6$H$_3$Cl$_2$OCH$_2$COO)$_2$(H$_2$O)$_4$] [3], or by two chelating carboxylato groups and two neutral ligands, as in [Zn(MeCOO)$_2$(H$_2$O)$_2$] [4] and [Zn(C$_6$H$_5$OCH$_2$COO)$_2$(H$_2$O)$_2$] [5]. In contrast, the crystal structures of tetrahedral Zn(II) carboxylates are relatively less well studied [6]; in such complexes the Zn(II) atom is commonly coordinated by two unidentate carboxylato groups and two neutral ligands, two examples being [Zn(C$_6$H$_3$Cl$_2$OCH$_2$COO)$_2$(H$_2$O)$_2$] [3] and [Zn(MeCOO)$_2$(SC(NH$_2$)$_2$)$_2$] [7].

As zwitterionic ligands, betaine compounds can be used to prepare metal carboxylate-like complexes in which the metal center can bear additional anionic ligands. Previously we have reported crystal structures of several metal complexes in this series, e.g.

[Cd(BET)(μ-Cl)$_2$]$_n$, [Cd(BET)(H$_2$O)Cl(μ-Cl)]$_2$ [8], [Cd$_3$(pyBET)$_4$Cl$_6$] [9], and [Rh$_2$(BET)$_4$Cl$_2$]Cl$_2$·4H$_2$O [10] (BET = betaine, Me$_3\overset{+}{N}$CH$_2$COO$^-$; pyBET = pyridine betaine, C$_5$H$_5\overset{+}{N}$CH$_2$COO$^{-\dagger}$. The present work deals with the preparation and structural characterization of three new monomeric zinc(II) complexes of betaine compounds, namely aquadichloro(pyridine betaine)zinc(II) [Zn(pyBET)(H$_2$O)Cl$_2$] **(1)**, dichlorobis(pyridine betaine) zinc(II) [Zn(pyBET)$_2$Cl$_2$] **(2)** and dichlorobis(betaine)zinc(II) monohydrate [Zn(BET)$_2$Cl$_2$]·H$_2$O **(3)**. Single-crystal X-ray analysis reveals that in all three complexes the Zn(II) atoms are tetrahedrally coordinated and the carboxy group of the betaine ligands exhibits the unidentate mode.

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*For Part VI, on [Cu(BET)$_4$](NO$_3$)$_2$, see ref. 1.
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$\dagger$The IUPAC names for BET and pyBET are 1-carboxy-*N,N,N*-trimethylmethanaminium hydroxide inner salt and 1-(carboxymethyl)pyridinium hydroxide inner salt, respectively.

Experimental

Preparation

Complex 1 was prepared by dissolving $ZnCl_2$ (0.272 g, 2.0 mmol) and pyridine betaine (0.276 g, 2.0 mmol) [11] in water (2 ml). After evaporation at room temperature for a week, colorless grain-like crystals were obtained. Complex 2 was prepared by dissolving $ZnCl_2$ (0.204 g, 1.5 mmol) and pyridine betaine (0.414 g, 3.0 mmol) in water (3 ml), and slow evaporation at room temperature for 10 days yielded colorless prismatic crystals. Complex 3 was prepared by dissolving $ZnCl_2$ (0.136 g, 1.0 mmol) and betaine monohydrate (0.270 g, 2.0 mmol; Sigma) in water (1.5 ml). After evaporation at room temperature for a week, colorless polyhedral crystals were obtained.

Physical measurement

Densities of the crystals were measured by flotation in 1,2-di-bromoethane/n-hexane. Infrared spectra (KBr pellets) were recorded on a Nicolet 20SXC FT-IR spectrometer in the range 4000–400 cm^{-1}. The three complexes exhibit the following carboxy group absorptions (v = very, s = strong, m = medium; cm^{-1}): for complex 1, $\nu(COO)$ at 1645vs, 1378s, and $\delta(COO)$ at 710m; for complex 2, $\nu(COO)$ at 1647 vs, 1377vs, 1363vs, and $\delta(COO)$ at 775vs; for complex 3, $\nu(COO)$ at 1652vs, 1398vs, and $\delta(COO)$ at 727m. The values of the separation (Δ) between the $\nu(COO)$ absorptions are 267, 277 (av.) and 255 cm^{-1} for complexes 1, 2, and 3, respectively. The Δ values in 1 and 2 are significantly larger than that in uncomplexed pyridine betaine ($\Delta = 253$ cm^{-1}) [11], thus

TABLE 1. Data collection and processing parameters

Complex	1	2	3
Molecular formula[a]	$Zn(pyBET)(H_2O)Cl_2$	$Zn(pyBET)_2Cl_2$	$Zn(BET)_2Cl_2 \cdot H_2O$
Molecular weight	291.44	410.48	388.58
Color and habit	colorless prism	colorless polyhedron	colorless polyhedron
a (Å)	6.1663(3)	7.313(1)	9.269(5)
b (Å)	8.6674(9)	8.734(3)	11.860(6)
c (Å)	9.783(1)	13.667(4)	8.137(4)
α (°)	82.944(9)	75.86(2)	90
β (°)	89.010(7)	76.66(2)	90
γ (°)	83.740(7)	81.40(2)	90
V (Å^3)	515.79(9)	819.6(4)	894.5(3)
Z	2	2	2
ρ_{meas} (g/cm^3)	1.870	1.667	1.439
ρ_{calc} (g/cm^3)	1.876	1.663	1.443
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$Imm2$ (No. 44)
Radiation		graphite-monochromatized Mo Kα, $\lambda = 0.71073$ Å	
Standard reflections	(311), (0$\bar{3}\bar{3}$)	(3$\bar{2}$2), (2$\bar{1}$4)	(12$\bar{2}$), (341)
Intensity variation	$\pm 0.7\%$	$\pm 3\%$	$\pm 1.5\%$
R_{int} (from merging of equiv. reflections)	0.012	0.025	0.043
Absorption coefficient (mm^{-1})	2.95	1.88	1.73
Crystal size (mm^3)	$0.25 \times 0.30 \times 0.26$	$0.25 \times 0.30 \times 0.25$	$0.24 \times 0.30 \times 0.34$
Transmission factors	0.356–0.420	0.586–0.631	0.686–0.863
Scan type	ω	ω–2θ	ω–2θ
Scan range		0.65° below Kα_1 to 0.65° above Kα_2	
Background counting		stationary counts for one-fifth of scan time at each end of scan range	
Collection range, $2\theta_{max}$	$h, \pm k, \pm l, 65°$	$h, \pm k, \pm l, 62°$	$h, k, l, 55°$
Unique data measured	3741	5429	617
Observed data $[|F_o| \geqslant 6\sigma(|F_o|)]$, n	3001	4209	597
No. variables, p	127	209	61
$R_F = \Sigma\Delta/\Sigma|F_o|$[b]	0.031	0.072	0.057
Weighting scheme[c], w		$[\sigma^2(F_o) + A|F_o|^2]^{-1}$	
$R_G = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$	0.026	0.090	0.067
$S = [\Sigma w\Delta^2/(n-p)]^{1/2}$	1.554	1.449	1.796
Residual extrema in final difference map (e/Å^3)	$+0.34$ to -0.27	$+1.20$ to -2.77	$+1.09$ to -1.37

[a]$BET = (CH_3)_3\overset{+}{N}CH_2COO^-$, $pyBET = C_5H_5\overset{+}{N}CH_2COO^-$. [b]$\Delta = ||F_o| - |F_c||$. [c]$A = 0.0001, 0.003$ and 0.0009 for 1, 2 and 3, respectively.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters[a] ($\text{Å}^2 \times 10^4$ for Zn and Cl; 10^3 for others)

	x	y	z	U_{eq}
Complex 1				
Zn(1)	4955(1)	2224(1)	1152(1)	287(1)
Cl(1)	1518(1)	3084(1)	557(1)	365(1)
Cl(2)	5391(1)	708(1)	3149(1)	366(1)
O(1w)	6259(2)	4231(2)	1459(1)	35(1)
O(1)	6833(2)	1320(2)	−215(1)	38(1)
O(2)	6659(2)	3311(2)	−1916(1)	40(1)
C(1)	7415(3)	2016(2)	−1354(2)	28(1)
C(2)	9249(3)	1060(2)	−2028(2)	30(1)
N(1)	10068(2)	1911(2)	−3295(1)	27(1)
C(3)	11821(3)	2690(2)	−3221(2)	34(1)
C(4)	12623(3)	3489(2)	−4382(2)	44(1)
C(5)	11623(4)	3492(2)	−5627(2)	46(1)
C(6)	9824(4)	2685(3)	−5682(2)	45(1)
C(7)	9065(3)	1895(2)	−4502(2)	37(1)
Complex 2				
Zn(1)	1383(1)	63(1)	2533(1)	277(1)
Cl(1)	3775(1)	−1725(1)	2034(1)	409(3)
Cl(2)	2583(2)	1946(1)	2977(1)	479(4)
O(11)	−5(4)	1057(3)	1408(2)	37(1)
O(12)	−970(4)	−1231(3)	1333(2)	42(1)
C(11)	−1063(5)	225(4)	1183(3)	31(1)
C(12)	−2688(5)	1146(4)	676(3)	37(1)
N(1)	−2729(4)	2878(3)	535(2)	31(1)
C(13)	−2155(6)	3769(5)	−409(3)	42(1)
C(14)	−2128(8)	5386(5)	−542(4)	55(2)
C(15)	−2705(7)	6079(5)	290(4)	56(2)
C(16)	−3284(8)	5133(6)	1244(4)	58(2)
C(17)	−3271(6)	3520(5)	1357(3)	46(1)
O(21)	−516(3)	−1067(3)	3622(2)	36(1)
O(22)	−2695(4)	1052(3)	3682(3)	50(1)
C(21)	−2198(5)	−373(4)	3810(3)	33(1)
C(22)	−3769(5)	−1473(4)	4205(3)	39(1)
N(2)	−3074(4)	−3173(3)	4361(2)	33(1)
C(23)	−2250(6)	−3792(5)	3537(3)	39(1)
C(24)	−1547(7)	−5351(5)	3662(4)	50(2)
C(25)	−1664(8)	−6293(5)	4646(4)	57(2)
C(26)	−2480(8)	−5660(6)	5470(4)	56(2)
C(27)	−3207(6)	−4091(5)	5322(3)	45(1)
Complex 3				
Zn(1)	0	0	2902	329(4)
Cl(1)	2037(3)	0	1439(4)	574(9)
O(1)	0	1194(5)	4577(10)	63(3)
O(2)	0	2741(6)	3052(13)	61(2)
C(1)	0	2252(7)	4366(11)	35(2)
C(2)	0	2995(7)	5889(11)	40(3)
N(1)	0	2442(7)	7528(9)	44(3)
C(3)	1353(13)	1782(9)	7772(18)	93(4)
C(4)	0	3319(11)	8826(15)	71(5)
O(1w)	541(20)	5000	1850(24)	78(7)[b]

[a]Equivalent isotropic temperature factor U_{eq} defined as one third of the trace of the orthogonalized U tensor. [b]Site occupancy factor is 0.5.

indicating that in both complexes the carboxy group acts in the unidentate mode [12]. Similarly the Δ value in complex 3 is significantly larger than that

TABLE 3. Selected bond lengths (Å) and bond angles (°)

Complex 1			
Cl(1)–Zn(1)	2.231(1)	Cl(2)–Zn(1)	2.219(1)
O(1w)–Zn(1)	2.051(1)	O(1)–Zn(1)	1.936(1)
Cl(1)–Zn(1)–Cl(2)	115.9(1)	Cl(1)–Zn(1)–O(1w)	103.1(1)
Cl(2)–Zn(1)–O(1w)	104.6(1)	Cl(1)–Zn(1)–O(1)	117.8(1)
Cl(2)–Zn(1)–O(1)	109.0(1)	O(1w)–Zn(1)–O(1)	104.7(1)
Zn(1)–O(1)–C(1)	126.4(1)		
O(1)–C(1)	1.266(2)	O(2)–C(1)	1.234(2)
C(1)–C(2)	1.518(2)	C(2)–N(1)	1.473(2)
O(1)–C(1)–O(2)	127.3(2)	O(1)–C(1)–C(2)	112.0(1)
O(2)–C(1)–C(2)	120.6(2)	C(1)–C(2)–N(1)	112.6(1)
Hydrogen bonding			
O(2)···O(1wa)	2.710(2)	C(1)–O(2)···O(1wa)	140.7(2)
Complex 2			
Zn(1)–Cl(1)	2.262(1)	Zn(1)–Cl(2)	2.238(2)
Zn(1)–O(11)	1.988(3)	Zn(1)–O(21)	1.964(2)
Cl(1)–Zn(1)–Cl(2)	108.7(1)	Cl(1)–Zn(1)–O(11)	111.4(1)
Cl(2)–Zn(1)–O(11)	109.4(1)	Cl(1)–Zn(1)–O(21)	108.7(1)
Cl(2)–Zn(1)–O(21)	114.9(1)	O(11)–Zn(1)–O(21)	103.9(1)
Zn(1)–O(11)–C(11)	118.2(2)	Zn(1)–O(21)–C(21)	118.4(2)
O(11)–C(11)	1.268(5)	O(12)–C(11)	1.231(4)
C(11)–C(12)	1.537(5)	C(12)–N(1)	1.475(4)
O(21)–C(21)	1.286(4)	O(22)–C(21)	1.224(4)
C(21)–C(22)	1.525(5)	C(22)–N(2)	1.475(4)
O(11)–C(11)–O(12)	128.2(3)	O(11)–C(11)–C(12)	116.0(3)
O(12)–C(11)–C(12)	115.8(4)	C(11)–C(12)–N(1)	112.8(3)
O(21)–C(21)–O(22)	128.2(3)	O(21)–C(21)–C(22)	115.4(3)
O(22)–C(21)–C(22)	116.3(3)	C(21)–C(22)–N(2)	113.6(3)
Complex 3			
Zn(1)–Cl(1)	2.231(3)	Zn(1)–O(1)	1.965(7)
Cl(1)–Zn(1)–O(1)	111.7(1)	Cl(1)–Zn(1)–Cl(1a)	115.5(2)
O(1)–Zn(1)–O(1b)	92.2(4)	Zn(1)–O(1)–C(1)	128.3(7)
O(1)–C(1)	1.27(1)	O(2)–C(1)	1.22(1)
C(1)–C(2)	1.52(1)	C(2)–N(1)	1.49(1)
O(1)–C(1)–O(2)	126.3(9)	O(1)–C(1)–C(2)	117.6(8)
O(2)–C(1)–C(2)	116.1(8)	C(1)–C(2)–N(1)	118.4(7)
Hydrogen bonding			
O(2)···O(1w)	2.90(1)	O(2)···O(1w)···O(2c)	135(1)

Symmetry codes for 1: (a) $1-x$, $1-y$, $-z$; for 3: (a) $-x$, y, z; (b) x, $-y$, z; (c) x, $1-y$, z.
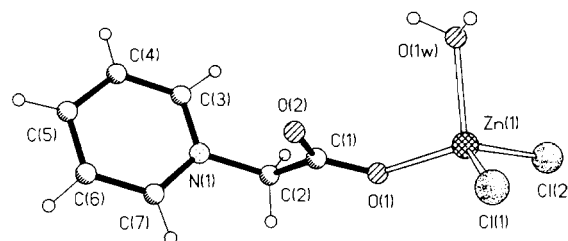
Fig. 1. Perspective view showing the molecular structure of [Zn(pyBET)(H$_2$O)Cl$_2$] (1) and the atom numbering scheme.
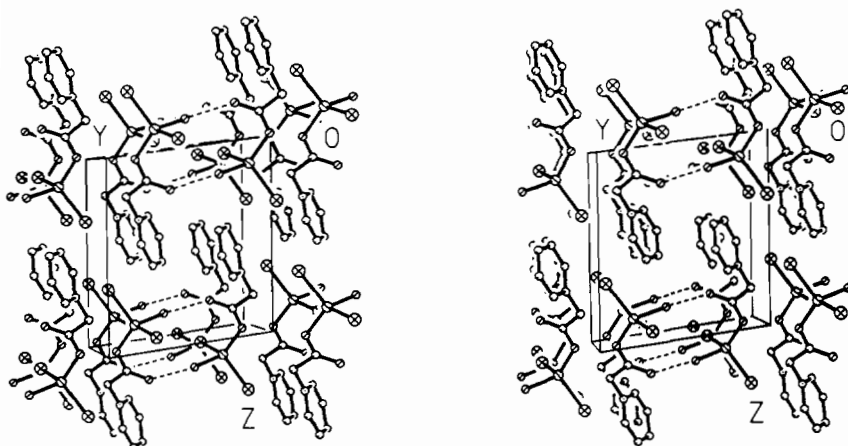
Fig. 2. Stereoview of the crystal structure of [Zn(pyBET)(H₂O)Cl₂] (**1**). The origin of the unit cell lies at the upper right corner, with *a* pointing towards the reader, *b* for right to left at a slant, and *c* downwards. Hydrogen bonds are represented by broken lines.
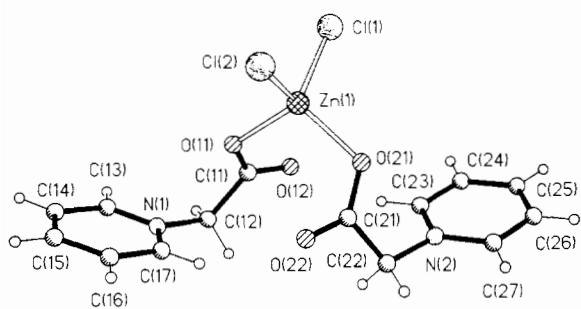

Fig. 3. Perspective view showing the molecular structure of [Zn(pyBET)₂Cl₂] (**2**) and the atom numbering scheme.

in uncomplexed betaine ($\Delta = 236$ cm^{-1}) [13] and thus indicative of the unidentate mode.

Crystal structure determination and refinement

For each complex, determination of the crystal class, orientation matrix and cell dimensions on a

Nicolet R3m/V diffractometer were performed according to established procedures [14]. Diffraction intensities were collected at 21 °C, and the details are summarized in Table 1. The raw data were processed with the learnt-profile procedure [15], and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected reflections over a range of 2θ angles [16].

The three crystal structures were solved with the Patterson superposition method and subsequent difference Fourier synthesis. The lattice water molecule of complex **3**, found to be disordered over two positions related by a mirror plane, was assigned half site occupancy. All hydrogen atoms of the betaine ligands were generated geometrically (C–H = 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms;

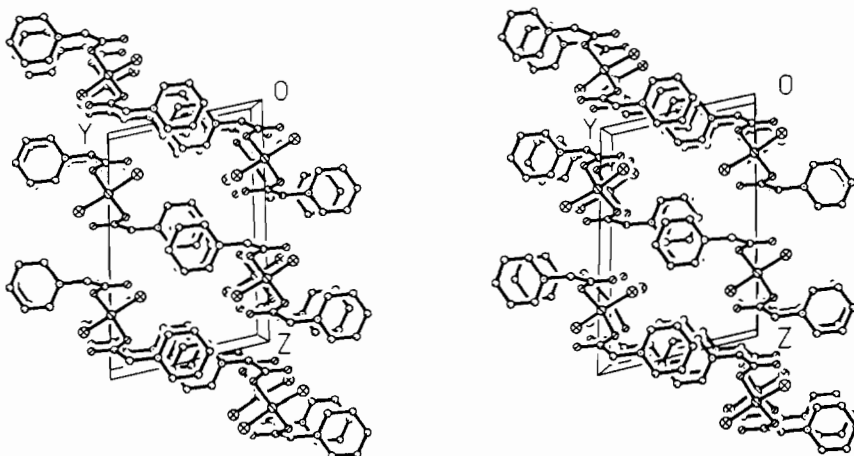Fig. 4. Stereoview of the crystal structure of [Zn(pyBET)₂Cl₂] (**2**). The origin of the unit cell lies at the upper right corner, with *a* pointing towards the reader, *b* from right to left at a slant, and *c* downwards.
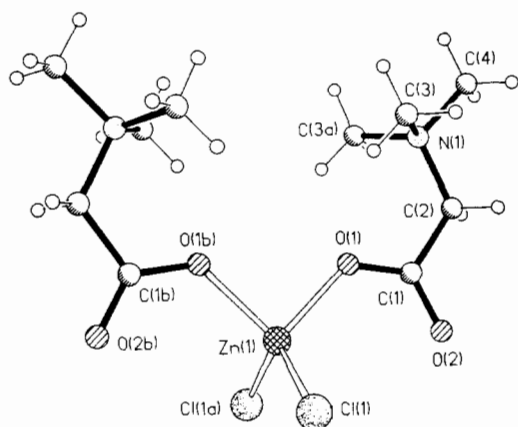
Fig. 5. Perspective view showing the structure and atom numbering of the [Zn(BET)₂Cl₂] molecule in (3).

the aqua H atoms of complex **1**, as located in a difference map, were held stationary and included in structure-factor calculations in the last stage of full-matrix least-squares refinement.

All computations were performed on a DEC MicroVAX-II computer with the SHELXTL-PLUS program package [17, 18]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [19]. The final discrepancy indices and other parameters at the conclusion of refinement are listed in Table 1, the atomic coordinates and thermal parameters in Table 2, and selected bond distances and angles in Table 3.

Results and discussion

[Zn(pyBET)(H₂O)Cl₂] (1)

Complex **1** exists primarily as a discrete [Zn(pyBET)(H₂O)Cl₂] molecule (Fig. 1). The Zn(II) atom is coordinated by a unidentate pyBET ligand (Zn–O(carboxy) = 1.939(1) Å), two chloro ligands (Zn–Cl = 2.231(1) and 2.219(1) Å) and one aqua

ligand (Zn–O(aqua) = 2.051(1) Å) in a distorted tetrahedral environment. The most distorted angle is O(1)–Zn(1)–Cl(1) at 177.8(1)°. The Zn–O(aqua) bond length is significantly longer than that of the Zn–O(carboxy) bond. On the other hand the Zn–Cl bond lengths are significantly shorter than the average Zn–Cl bond length of 2.359 Å in tetrahedral Zn(II) complexes [6].

A stereoview of the crystal structure of complex **1** is shown in Fig. 2. Each pair of adjacent molecules are linked through two intermolecular hydrogen bonds between the uncoordinated carboxy oxygen and the aqua ligand (O(2)···O(1wa) = 2.710(4) Å) into a centrosymmetric, hydrogen-bonded dimer.

[Zn(pyBET)₂Cl₂] (2)

As illustrated in Fig. 3, the Zn(II) atom in complex **2** is coordinated by two unidentate carboxy groups of pyBET (Zn–O = 1.964(2), 1.988(3) Å) and two chloro ligands (Zn–Cl = 2.238(2), 2.262(1) Å). The [Zn(pyBET)₂Cl₂] molecule has an approximate two-fold axis parallel to the *a* axis (see Fig. 4). Both the Zn–O(carboxy) and Zn–Cl bond lengths are slightly longer than the respective values in complex **1**. These bond lengths are comparable to those found in [Zn(glycine)₂Cl₂]·(glycine) [20] in which the Zn(II) atom is tetrahedrally coordinated by two chloro ligands and two unidentate carboxy groups. It is of interest to note that the torsion angles Zn(1)–O(11)–C(11)–C(12) and Zn(1)–O(21)–C(21)–C(22) are 155.1(2) and 149.8(3)°, respectively, which deviates markedly from the idealized value (180°) for the *syn* mode of coordination. This may be ascribed to mutual repulsion between the two carboxy groups in the molecule. The two pyridine rings are fully extended away from each other, the torsion angles O(11)–C(11)–C(12)–N(1) and O(21)–C(21)–C(22)–N(2) being 3.3(5) and −178.9(4)°, respectively.

[Zn(BET)₂Cl₂]·H₂O (3)

The crystal structure of complex **3** consists of discrete [Zn(BET)₂Cl₂] molecules (Fig. 5), which are
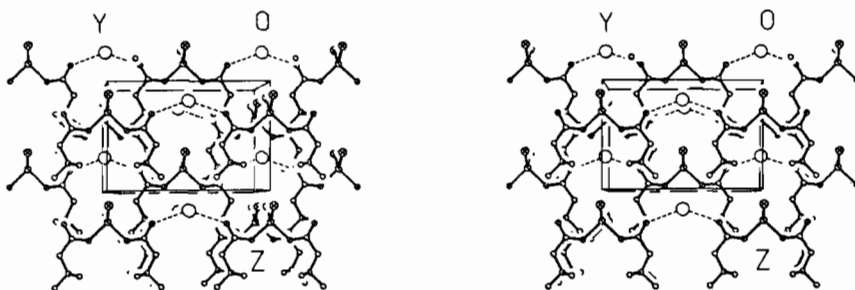
Fig. 6. Stereoview of the crystal structure of [Zn(BET)₂Cl₂]·H₂O (3). The origin of the unit cell lies at the upper right corner, with *a* pointing toward the reader, *b* from right to left, and *c* downwards. The disordered water molecules are represented by large circles located at their idealized positions, and hydrogen bonds by broken lines.

structurally very similar to complex 2. The Zn(II) atom, being located at Wyckoff position (2a) of symmetry mm, is tetrahedrally coordinated by two chloro ligands (Zn–Cl = 2.231(3) Å) and two unidentate carboxy groups (Zn–O = 1.965(7) Å). The most distorted angle in the tetrahedron is Cl(1)–Zn(1)–Cl(1a) at 115.5(2)°. The main difference between complexes 2 and 3 is that the latter has higher symmetry, uncoordinated oxygen of the carboxy group being outstretched and the torsion angle Zn(1)–O(1)–C(1)–C(2) exactly equal to 180°.

The lattice water molecule (in Wyckoff position 4(c) of symmetry m) is disordered over two positions related by the mirror plane at $x = 0$. As illustrated in Fig. 6, the water molecule (represented by a large circle) is weakly hydrogen-bonded to two adjacent uncoordinated carboxy oxygen atoms (O(1w)···O(2) = 2.90(1) Å), building up a one-dimensional chain running parallel to the b axis. The structure is thus of the layer type with its molecular components concentrated about the (200) family of planes.

Conclusions

Owing to the presence of the weak aqua ligand in complex 1, the Zn–O(carboxy) and Zn–Cl bond lengths are slightly shorter than the respective ones in complexes 2 and 3. As compared to complex 2, the outstretched carboxy groups in complex 3 reduce their mutual repulsion in the molecule, resulting in slightly shorter Zn–Cl and Zn–O(carboxy) bonds and less distorted bond angles (see Table 3). Reference to Fig. 5 shows that the greater steric bulk of the pyridine ring relative to the trimethylamino group accounts for a reduction in molecular symmetry of the complex from C_{2v} to C_2 (idealized) in 2.

Both the chelating and unidentate modes of carboxylato coordination occur commonly in Zn(II) carboxylates [5]. Moreover, the betaine ligand has been found acting in the unsymmetrical chelating mode in [Cd(BET)(H₂O)Cl(μ-Cl)] [7]. In contrast, the carboxy group of betaine ligands in the present complexes exhibits the unidentate mode, which may be ascribed to the fact that owing to the effect of the positively-charged nitrogen atom, the O–C–O angle in betaine ligands is significantly larger than that in metal complexes of common carboxylic acids. Presumably the carboxy group of betaine ligands may only exhibit the chelating mode when it co-

ordinates to metal ions of large radii, or when the effect of the quaternary ammonium moiety is reduced, for instance, by inserting additional methylene units between the nitrogen atom and the carboxy group.

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