$[Zn(phen)_2(CX_3COO)]^+$, X = H or Cl; Influence of X on the Coordination Mode of the Carboxylate Group (phen = 1,10-Phenanthroline)

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Two new $Zn^{II}(phen)_2$ complexes with trichloroacetate and acetate anions, $[Zn(phen)_2(CCl_3COO)(H_2O)](ClO_4)$ and $[Zn(phen)_2(CH_3COO)](ClO_4)$, have been synthesized and characterized by elemental analysis, IR, ^1H NMR, ^{13}C NMR spectroscopy. The single crystal X-ray data of these compounds show the Zn atoms to have six-coordinate geometry. From IR spectra and X-ray crystallography it is established that the coordination of the COO^- group is different for trichloroacetate and acetate. The former acts as a monodentate whereas the latter acts as a bidentate ligand.

Key words: Zinc(II) Complexes, Mixed-Anion Complexes, 1,10-Phenanthroline, Trichloroacetate, Acetate.

Introduction

The carboxylate group is a multifunctional ligand that acts with a variety of binding geometries: Monodentate coordination **a**, bidentate coordination either by chelation **b**, or by forming a bridge **c, d** and **e**. With the three latter forms (**c**, **d** and **f**), the compounds can be polymeric. For these reasons, there is a great variety of complexes containing carboxylate groups ligand. The general structure modes are shown below (Chart 1).

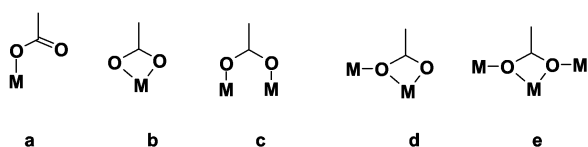**a** **b** **c** **d** **e**

Chart 1.

IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. Building and structural design of new species of zinc(II) with different carboxylate ions which modify the architectures and control the physical properties is an interesting topic. We report here on the preparation, full structural characterization and molecule packing of two new mixed-anion zinc(II) complexes, $[Zn(phen)_2(CCl_3COO)(H_2O)](ClO_4)$ (**1**) and $[Zn(phen)_2(CH_3COO)](ClO_4)$ (**2**).

Results and Discussion

Syntheses

Reactions between the "phen" ligand and mixtures of zinc(II) acetate or zinc(II) trichloroacetate with sodium perchlorate in methanol provided crystalline materials analyzing as $[Zn(phen)_2(CCl_3COO)(H_2O)]$- (ClO_4) (**1**) and $[Zn(phen)_2(CH_3COO)](ClO_4)$ (**2**), respectively. The IR spectra of the these complexes show $v(ClO_4^-)$ at *ca.* 1100 and 1083 cm^{-1} in **1** and **2**, respectively, and absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400– 1616 cm^{-1} range. The broad absorption band for $v(HOH)$ at 3320–3430 cm^{-1} indicates the presence of a water molecule in **1**. The broad band is perhaps attributable to $v(O\text{-}H\ldots X)$, indicating the presence of hydrogen bonds in the **1**, which is confirmed by the crystal structure of this complex. The characteristic bands of the carboxylate groups in **1** appear at $1569 v_{as(C\text{-}O)}$ and $1416 v_{sym(C\text{-}O)}$ cm^{-1} and in **2** at $1661 v_{as(C\text{-}O)}$ and $1331 v_{sym(C\text{-}O)}$ cm^{-1}. The Δv value (v_{as}-v_{sym}) for **1** is 153 cm^{-1}, significantly lower than the value of $\Delta v = 330$ cm^{-1} for **2**, indicating that the carboxylate group is coordinating with Zn in a bidentate fashion in **2** and in a monodentate fashion in **1** [1–5], which is unambiguously confirmed by the crystal structures of the two complexes.

*Crystal structure of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)]-
(ClO$_4$) (**1**) and [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$) (**2**)*

The structure of complex **1** consists of discrete
[Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)]$^+$ cations and ClO$_4$$^-$
anions. Each zinc atom is chelated by four nitro-
gen atoms of two "phen" ligands with Pb–N dis-
tances of 2.0963(16), 2.1327(16), 2.1352(16), and
2.1426(16) Å, one oxygen atom of the trichloroacetate

Fig. 1. ORTEP diagram of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)]-
(ClO$_4$) (**1**).

Fig. 2. The unit cell of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](ClO$_4$)
(**1**).

Fig. 3. ORTEP diagram of [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$)
(**2**).

Fig. 4. The unit cell of [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$) (**2**).

anion with a Zn–O distance of 2.1380(14) Å, and also
the oxygen atom of a water molecule with a Zn–O(W)
distance of 2.0996(14) Å. The coordination number is
six and the coordination environment around the Zn(II)
ion is distorted octahedral. The carboxylate moiety of
the trichloroacetate ligand is monodentate. Cation and
anion are linked by hydrogen bonding (Fig. 1 and Ta-
ble 3).

The structure of [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$) **2**
consists of discrete [Zn(phen)$_2$(CH$_3$COO)]$^+$ cations
and ClO$_4$$^-$ anions. Each zinc atom is chelated by
four nitrogen atoms of two "phen" ligands with Zn–N
distances of 2.1238(16), 2.1466(17), 2.1615(17), and

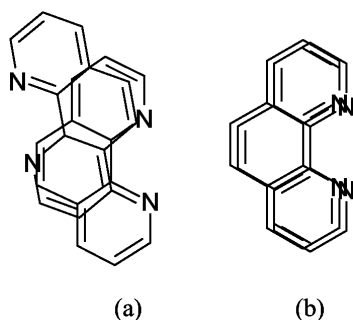| Empirical formula	$C_{26}H_{18}Cl_4N_4O_7Zn$	$C_{26}H_{19}ClN_4O_6Zn$	Table 1 Crystal data and struc-
Formula weight	705.61	584.27	ture refinement of [Zn(phen)$_2$-
Temperature [K]	120(2)	120(2)	(CCl$_3$COO)(H$_2$O)](ClO$_4$) (**1**)
Wavelength [Å]	0.71073	0.71073	and [Zn(phen)$_2$(CH$_3$COO)]-
Crystal system	monoclinic	monoclinic	(ClO$_4$) (**2**).
Space group	$P2_1/c$	$P2_1/c$	
Unit cell dimensions	$a = 8.8154(4)$ Å	$a = 8.1559(16)$ Å	
	$b = 16.3009(8)$ Å	$b = 19.256(4)$ Å	
	$c = 18.6521(9)$ Å	$c = 15.552(3)$ Å	
	$\beta = 94.3790(10)°$	$\beta = 95.40(3)°$	
Volume	2672.5(2) Å^3	2431.6(8) Å^3	
Z	4	4	
Density (calculated)	1.754 g/cm^3	1.596 g/cm^3	
Absorption coefficient	1.38 mm^{-1}	1.17 mm^{-1}	
$F(000)$	1424	1192	
Crystal size	$0.40 \times 0.35 \times 0.35$ mm^3	$0.70 \times 0.5 \times 0.3$ mm^3	
θ Range for data collection	1.66 to 30.01°	2.12 to 30.03°	
Index ranges	$-12 \leq h \leq 12$	$-11 \leq h \leq 11$	
	$-22 \leq k \leq 22$	$-27 \leq k \leq 18$	
	$-26 \leq l \leq 26$	$-20 \leq l \leq 21$	
Reflections collected	31130	20089	
Independent reflections	7765	7053	
Absorption correction	— Semi-empirical from eqivalents —		
Max. and min. transmission	0.0615 and 0.589	0.928 and 0.644	
Refinement method	– Full-matrix least-squares on F^2 –		
Data / restraints / parameters	7765/0/381	7053/0/343	
Goodness-of-fit on F^2	1.068	1.034	
Final $R[I > 2\sigma(I)]$	indices for 6215 ref1	indices for 5673 ref1	
	$R1 = 0.0372$, $wR2 = 0.0759$	$R1 = 0.0404$, $wR2 = 0.0914$	
R Indices (all data)	$R1 = 0.0481$, $wR2 = 0.0789$	$R1 = 0.0503$, $wR2 = 0.0953$	
Largest diff. Peak, hole	0.530, -0.403 e/Å^3	0.739, -0.368 e/Å^3	

Fig. 5. Projection of nearest neighbor pairs in the π-π stacks of the heteroaromatic bases (a) in **2** and (b) in **1**.

2.1637(17) Å, and two oxygen atoms of the acetate anion with Zn–O distances of 2.11533(15) and 2.2531(16) Å. The coordination number is six and the coordination environment around the Zn(II) ion is also distorted octahedral. The carboxylate moiety acts as a bidentate ligand.

The packing of complexes **1** and **2** is similar in that there are π-π stacking [6] interactions between the parallel aromatic rings as shown in Figs 2, 4 and 5. The mean molecular planes are close to parallel and sepa-

rated by a distance of ~ 3.5 Å, similar to that of the planes in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "π-stacking" type, rather than "edge-to-face" or "vertex-to-face" types [7 – 11]. It has been shown that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups [12]. Hence, it can be expected that in complexes **1** and **2** the interaction of the electron-poor pyridyl rings with less electron-poor rings such as phenyl groups must be favored (Fig. 5a). The interplanar distances in **1** and **2** are 4.45, excluding π-π stacking [11 – 12] and in **2** they are 3.6 Å, that is normal π-π stacking [11 – 12].

The fact that the carboxylate moiety acts as a monodentate ligand in **1** and as a bidentate in **2**, can be explained by the different electronegative influence of the X atoms in the [Zn(phen)$_2$(CX$_3$COO)]$^+$ cation, and the water molecule in **1** may also be responsible for the unexpected structural variation.

Experimental Section

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Micro-

Table 2. Bond lengths (Å) and angles (°) for [Zn(phen)$_2$-(CCl$_3$COO)(H$_2$O)](ClO$_4$) (**1**).

Zn(1)–O(1W)	2.0996(14)	Zn(1)–N(2A)	2.1238(16)
Zn(1)–O(1)	2.1380(14)	Zn(1)–N(1)	2.1466(17)
Zn(1)–N(1A)	2.1615(17)	Zn(1)–N(2)	2.1637(17)
C(13)–O(1)	1.251(2)	C(13)–O(2)	1.230(2)
O(1W)–Zn(1)–N(2A)	94.09(6)	O(1W)–Zn(1)–O(1)	91.04(6)
N(2A)–Zn(1)–O(1)	89.58(6)	O(1W)–Zn(1)–N(1)	163.99(6)
N(2A)–Zn(1)–N(1)	101.92(6)	O(1)–Zn(1)–N(1)	88.94(6)
O(1W)–Zn(1)–N(1A)	92.72(6)	N(2A)–Zn(1)–N(1A)	78.20(6)
N(1A)–Zn(1)–O(1)	167.43(6)	O(1W)–Zn(1)–N(2)	86.93(6)
N(2A)–Zn(1)–N(2)	173.67(6)	N(2)–Zn(1)–O(1)	84.16(6)
N(2)–Zn(1)–N(1)	77.14(6)	N(2)–Zn(1)–N(1A)	108.01(6)
N(1)–Zn(1)–N(1A)	90.72(6)		

Table 3. Intermolecular H-bonds in the structure of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](ClO$_4$) (**1**).

D-H⋯A	D⋯A, Å	D-H, Å	H⋯A, Å	DHA, deg
O(1W)–H(1WA)⋯O(2)	2.637(3)	0.79	1.90	155
O(1W)–H(1WB)⋯O(2S)	2.817(3)	0.82	2.03	160

analyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

*Preparation of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](ClO$_4$) (**1**)*

To a magnetically stirred solution of the "phen" ligand (0.400 g, 2 mmol) in methanol (10 ml) was added dropwise a mixture of Zn(NO$_3$)$_2$ · 6H$_2$O (0.297 g, 1 mmol), NaCCl$_3$COO (0.371 g, 2 mmol) and NaClO$_4$· H$_2$O (0.280 g, 2 mmol) in methanol (20 ml) at room temperature over 30 min. The reaction mixture was stirred for 2 h at room temperature. A single crystal suitable for X-ray analysis was obtained by slow evaporation of this solution at room temperature. M. p. 150 °C. Yield: 0.38 g, 55%, calcd. C 44.21, H 2.55, N 7.94; found C 44.95, H 2.80, N 8.25. – IR (KBr) selected bands: $\nu = 3320 – 3430$ m, 3135 m, 1616 (s), 1415 (m), 1331 (s), 1661 (s), 1100 (vs) and 830 (s) cm^{-1}. – ^{1}H NMR (500.14 MHz, [D$_6$]-DMSO): $\delta = 8.01$ (m, 1H), 8.29 (m, 1H), 8.31 (m, 1H), 8.77 (m, 1H) and 8.93 (m, 1H) ppm. – ^{13}C-{^{1}H} NMR (125.76 MHz, [D$_6$]-DMSO): $\delta = 79.65$, 125.92, 127.67, 129.34, 139.92, 149.28, and 182.25 ppm.

*Preparation of [Zn(phen)$_2$(CH$_3$COO)](ClO$_4$) (**2**)*

We prepared complex **2** *via* the method used for the synthesis of complex **1**, using phen, zinc(II) acetate and sodium perchlorate (2:1:2); White crystals, M.p 213 °C. Yield: 0.321 g, 55%. cacld. C 53.39, H 3.25, N 9.58; found C 54.05, H 3.75, N 9.70. – IR (KBr) selected bands: $\nu = 3130$ (m), 2980 (m), 1610 (s), 1505 (m), 1416 (s), 1569 s, and 1083 (vs). – ^{1}H NMR (500.14 MHz, [D$_6$]-DMSO): $\delta = $

Table 4. Bond lengths (Å) and angles (°) for [Zn(phen)$_2$-(CH$_3$COO)](ClO$_4$) (**2**).

Zn(1)–N(1)	2.0963(16)	Zn(1)–N(3)	2.1327(16)
Zn(1)–N(4)	2.1352(16)	Zn(1)–N(2)	2.1426(16)
Zn(1)–O(2)	2.1533(15)	Zn(1)–O(1)	2.2531(16)
Zn(1)–C(25)	2.5329(19)	C(25)–O(1)	1.251(2)
C(25)–O(2)	1.267(2)		
N(1)–Zn(1)–N(3)	113.59(6)	N(1)–Zn(1)–N(4)	99.61(6)
N(3)–Zn(1)–N(4)	78.29(6)	N(1)–Zn(1)–N(2)	79.21(6)
N(2)–Zn(1)–N(3)	97.83(6)	N(4)–Zn(1)–N(2)	175.17(6)
N(1)–Zn(1)–O(2)	146.31(6)	N(3)–Zn(1)–O(2)	99.66(6)
N(4)–Zn(1)–O(2)	91.99(6)	N(2)–Zn(1)–O(2)	91.50(6)
N(1)–Zn(1)–O(1)	88.26(6)	N(3)–Zn(1)–O(1)	157.36(6)
N(4)–Zn(1)–O(1)	92.82(6)	N(2)–Zn(1)–O(1)	91.82(6)
O(2)–Zn(1)–O(1)	59.47(5)		

1.78 (s, 3H), 8.08 (m, 4H), 8.29 (m, 2H), and 8.90 (m, 8H). – ^{13}C-{^{1}H} NMR (125.76 MHz, [D$_6$]-DMSO): $\delta = 22.68$, 126.30, 127.70, 129.31, 140.50, 149.86, and 179.25.

Determination of the structure

Crystallographic measurements were made at 120(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $1.66 \leq \theta \leq 30.01°$ for **1** and $2.12 \leq \theta \leq 30.03°$ for **2** using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinements. Intensities of 31130 and 20089 unique reflections were measured, of which 7765 and 7053 with $I > 2\sigma(I)$ were used in the refinement for **1** and **2**, respectively. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic displacement parameter. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [13 – 14].

Crystal data and data of structure refinement are given in Table 1, selected bond lengths and angles in Tables 2 and 4. Anisotropic displacement parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are presented in the supplementary material. ORTEP diagrams and perspective views of the packing in the unit cells are shown in Figs 1, 2, 3, and 4.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 253685 for **1** and 253683 for **2**.

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