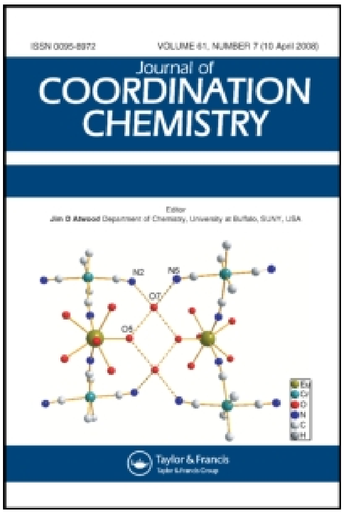

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New mixed-anion zinc(II) complexes, $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ and $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$; synthesis, characterization and crystal structures

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Zinc(II) complexes with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) containing two different anions have been synthesized and characterized by elemental analysis, IR-, ^1H NMR-, ^{13}C NMR spectroscopy. The single crystal X-ray data of $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ show the complex to be monomeric and the Zn atom with an unsymmetrical six-coordinate geometry, coordinated by four nitrogen atoms of "phen", one trichloroacetate and one water. The crystal structure of $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ shows each zinc atom chelated by the nitrogen atoms of "bpy" and also two oxygen atoms of acetate. From the infrared spectra and X-ray crystallography, it is established that coordination of the carboxylate group to zinc is different for trichloroacetate and acetate.

Keywords: Zinc(II) complex; Mixed-anion complex; 1,10-Phenanthroline; 2,2′-Bipyridine

1. Introduction

The carboxylate group is a multifunction coordination mode ligand with a variety of binding geometries: monodentate and bidentate either by chelation, or by forming a bridge. A great variety of complexes containing carboxylate groups exist and play a key role in many biochemical systems involving mono- or polymetallic sites [1]. Infrared spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. In complexes where carboxylate is bidentate, there is a decrease in the anti-symmetric $–COO^-$ frequency [2], resulting in decrease of $\Delta\nu$ value $(\nu_{as} - \nu_{sym})$, but when only one oxygen of the $–COO^-$ group bonds, the two C–O bond lengths are different leading to an increase of the $–COO^-$ antisymmetric stretching frequency. Preparing new complexes of zinc(II) with two different carboxylate ions as a route

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to control physical properties is of interest. Recently, we reported the syntheses and crystal structures of 1 : 1 adducts of [Pb(phen)(O_2CCH_3)(O_2ClO_2)] [3], [Pb(phen)(O_2CCH_3)(O_2NO)] [4], [Pb(phen)(O_2CCH_3)(NCS)] [5], [Pb(bpy)(O_2CCH_3)(NCS)] [6] and 1 : 2 adducts of [Pb(phen)$_2$(CH_3COO)]X (X = NCS^-, NO_3^- and ClO_4^-) [7]. In the present article we report the preparation, full structural characterization and crystal packing of two new mixed-anion zinc(II) complexes, [Zn(phen)$_2$(CCl_3COO)(H_2O)](NO_3) and [Zn(bpy)$_2$(CH_3COO)](ClO_4) · H_2O.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

2.2. *Preparation of the complex [Zn(phen)$_2$(CCl_3COO)(H_2O)](NO_3) (1)*

To a magnetically stirred solution of phen (0.400 g, 2 mmol) in methanol (10 mL) was added dropwise a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol) and $NaCCl_3COO$ (0.371 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. 160°C. Yield: 0.33 g, 50%.

Anal. Calcd for $C_{26}H_{18}Cl_3N_5O_6Zn$: C, 46.67; H, 2.69; N, 10.47. Found: C, 46.10; H, 2.70; N, 10.70%.

IR (cm^{-1}) selected bands: ν(O–H) 3325–3440 m, $\nu(C{-}H)_{ar}$ 3130 m, ν(C=C), ν(C=N) 1618 s, 1418 m, $\nu_s(COO^-)$ 1323 s, $\nu_{as}(COO^-)$ 1659 s, $\nu(NO_3^-)$ 1377 vs and ν(C–Cl) 836 s.

^{1}H NMR (DMSO; δ): 8.05 (m, 1H), 8.32 (m, 1H), 8.31 (m, 1H), 8.78 (m, 1H) and 8.93 (m, 1H).

^{13}C-{^{1}H} NMR (DMSO; δ): 79.14, 124.16, 125.74, 127.29, 129.01, 139.86, and 148.88.

2.3. *Preparation of the complex [Zn(bpy)$_2$(CH_3COO)](ClO_4) · H_2O (2)*

We prepared complex **2** via the analogous method used for synthesis of complex **1**.

2.3.1. Product (2). [Reactant materials: "bpy", zinc(II) acetate, sodium perchlorate (2 : 1 : 2)]. (White crystals). M.p. 220°C. Yield: 0.271 g, 49%.

Anal. Calcd for $C_{22}H_{21}ClN_4O_7Zn$: C, 47.63; H, 3.78; N, 10.10. Found: C, 48.10; H, 3.60; N, 10.50%.

IR (cm^{-1}) selected bands: ν(O–H) 33102–3505 w, $\nu(C{-}H)_{ar}$ 3063 m, $\nu(C{-}H)_{al}$ 2928 m, ν(C=C), ν(C=N) 1592 s, 1469 m, $\nu_s(COO^-)$ 1431 s, $\nu_{as}(COO^-)$ 1564 s, and $\nu(ClO_4^-)$ 1087 vs.

^{1}H NMR (DMSO, δ): 1.82 (s, 3), 7.60 (m, 4H), 8.10 (m, 4H), and 8.65 (m, 8H).

^{13}C-{^{1}H} NMR (DMSO, δ): 22.60, 109.60, 122.54, 126.87, 140.50, 140.83, and 149.14.

2.4. *Crystallography*

Intensity data measurements were carried out using a Siemens *R*3*m*/*V* diffractometer. Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2.

Hydrogen atom positions were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic displacement parameter. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs were applied. All structural calculations were carried out with a PDP–11/23+ computer using the SDP–PLUS program package [8, 9].

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in tables 2 and 3. Anisotropic displacement parameters observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are available from CCDC. ORTEP diagrams and perspective views of the packing in the unit cells are shown in figures 1–4.

Table 1. Crystal data and structure refinement of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](NO$_3$) and [Zn(bpy)$_2$(CH$_3$COO)](ClO$_4$) · H$_2$O.

Empirical formula	$C_{26}H_{18}Cl_3N_5O_6Zn$	$C_{22}H_{21}ClN_4O_7Zn$
Formula weight	668.17	554.25
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 8.7833(18)$ $b = 16.168(4)$ $c = 18.414(4)$ $\alpha = 90$ $\beta = 93.658(7)$ $\gamma = 90$	$a = 8.2309(17)$ $b = 9.500(2)$ $c = 14.933(3)$ $\alpha = 79.500(4)$ $\beta = 84.260(4)$ $\gamma = 85.128(4)$
Volume (Å^3)	2609.6(10)	1139.6(4)
Z	4	2
Density (calculated) (Mg m^{-3})	1.701	1.615
Absorption coefficient (mm^{-1})	1.302	1.248
F(000)	1352	568
Crystal size (mm^3)	0.34 × 0.28 × 0.27	0.30 × 0.25 × 0.25
θ range for data collection (°)	2.22 to 30.00	1.39 to 27.00
Index ranges	$-12 \le h \le 11$ $-20 \le k \le 22$ $-25 \le l \le 25$	$-10 \le h \le 10$ $-12 \le k \le 12$ $-19 \le l \le 19$
Reflections collected	25382	10303
Independent reflections	7518	4891
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.704600 and 0.652528	0.745988 and 0.416652
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7518/0/372	4891/0/353
Goodness-of-fit on F^2	1.011	1.015
Final R [$I > 2\sigma(I)$]	Indices for 6339 refl	Indices for 3978 refl
R indices (all data)	$R_1 = 0.0377$, $wR_2 = 0.0924$ $R_1 = 0.0462$, $wR_2 = 0.0974$	$R_1 = 0.541$, $wR_2 = 0.1339$ $R_1 = 0.0655$, $wR_2 = 0.1394$
Largest diff. peak, hole (e Å^{-3})	1.061, −0.995	0.726, −0.599

Table 2. Bond lengths (Å) and angles (°) for $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$.

Zn(1)–O(1W)	2.1034(14)	N(1′)–Zn(1)–O(2)	89.43(6)
Zn(1)–N(1′)	2.1277(15)	O(1W)–Zn(1)–N(1)	89.80(6)
Zn(1)–O(2)	2.11401(14)	N(1′)–Zn(1)–N(1)	174.37(6)
Zn(1)–N(1)	2.1538(15)	O(2)–Zn(1)–N(1)	85.64(5)
Zn(1)–N(12)	2.1596(16)	O(1W)–Zn(1)–N(12)	167.19(6)
Zn(1)–N(12′)	2.1644(16)	N(1′)–Zn(1)–N(12)	99.67(6)
		O(2)–Zn(1)–N(12)	88.61(6)
		N(1)–Zn(1)–N(12)	77.52(6)
		O(1W)–Zn(1)–N(12′)	93.49(6)
		N(1′)–Zn(1)–N(12′)	77.83(6)
		O(2)–Zn(1)–N(12′)	166.28(5)
		N(1)–Zn(1)–N(12′)	106.81(6)
		N(12)–Zn(1)–N(12′)	88.53(6)
		O(1W)–Zn(1)–N(1′)	93.12(6)
		O(1W)–Zn(1)–O(2)	92.27(6)

Table 3. Intermolecular H-bonds in $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$.

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	DHA (°)
O(lW)–H(2W)···O(1S) $[-x+1, -y+1, -z]$	2.685	0.838	1.848	176.82
O(lW)–H(1W)···O(1)	2.691	0.892	1.879	150.52

3. Discussion

3.1. *Syntheses*

Reaction between phen and mixtures of zinc(II) nitrate with sodium trichloroacetate provided crystalline material analyzing as $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ while reaction between bpy and mixtures of zinc(II) acetate with sodium perchlorate provided crystalline material analyzing as $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$. The IR spectrum of the $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ complex shows $\nu(ClO_4^-)$ at ca. 1087 cm^{-1} and $\nu(NO_3)$ in the $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ complex appears at ca. 1377 cm^{-1}. The IR spectra of both complexes show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1615 cm^{-1} range. The absorption band for ν(HOH) at 3320–3430 cm^{-1}, indicates the presence of water in both complexes. The broad band for ν(HOH) in $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ indicates hydrogen bonds, which is confirmed by the crystal structure. The characteristic bands of the carboxylate group in $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ appear about 1659 $\nu_{as(C–O)}$ and 1323 $\nu_{sym(C–O)}$ cm^{-1} and the $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ appear about 1564 $\nu_{as(C–O)}$ and 1431 $\nu_{sym(C–O)}$ cm^{-1}. The $\Delta\nu$ value ($\nu_{as} - \nu_{sym}$) in the $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ is 135 cm^{-1}, is significantly lower than the value of $\Delta\nu = 336\,cm^{-1}$ in the $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$, indicating that the carboxylate group coordinates Zn in a bidentate fashion in $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ and monodentate fashion in $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ [10–14]. This is confirmed by the crystal structure.

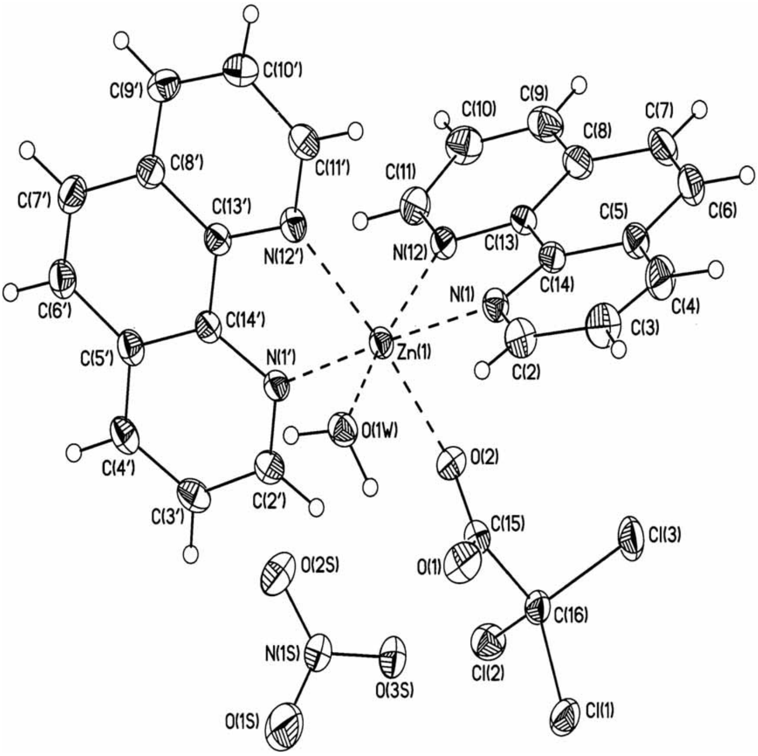

Figure 1. ORTEP diagram of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](NO$_3$).

3.2. *Crystal structure of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](NO$_3$)*

An ORTEP diagram and unit cell of [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)](NO$_3$) are shown in figures 1 and 2. The selected bond distances and angles around Zn(II) are shown in table 2. The structure of the complex consists of discrete [Zn(phen)$_2$(CCl$_3$COO)(H$_2$O)]$^+$ cations and NO_3^- anions. Each zinc atom is chelated by four nitrogen atoms of two phen ligands with Zn–N distances of 2.1277(15), 2.1538(15), 2.1596(16), and 2.1644(16) Å, and one oxygen atom of the trichloroacetate anion with a Zn–O distance of 2.11401(14) Å and also oxygen atom of one water molecule with a Zn–O(W) distance of 2.1034(14) Å. The coordination environment around the Zn(II) ion is distorted octahedral [ZnN$_4$O$_{(\text{trichloroacetate})}O_{\text{water}}$] and the carboxylate (trichloroacetate) ligand is monodentate. The complex is linked by inter-molecular hydrogen bonding (figure 2 and table 3). The coordinated water molecules are involved in hydrogen bonding as hydrogen-bond acceptors with O atoms from trichloroacetate as hydrogen-bond donors.

3.3. *Crystal structure of [Zn(bpy)$_2$(CH$_3$COO)](ClO$_4$) · H$_2$O*

An ORTEP diagram and unit cell of [Zn(bpy)$_2$(CH$_3$COO)](ClO$_4$) · H$_2$O are shown in figures 3 and 4. Selected bond distances and angles around Zn(II) are

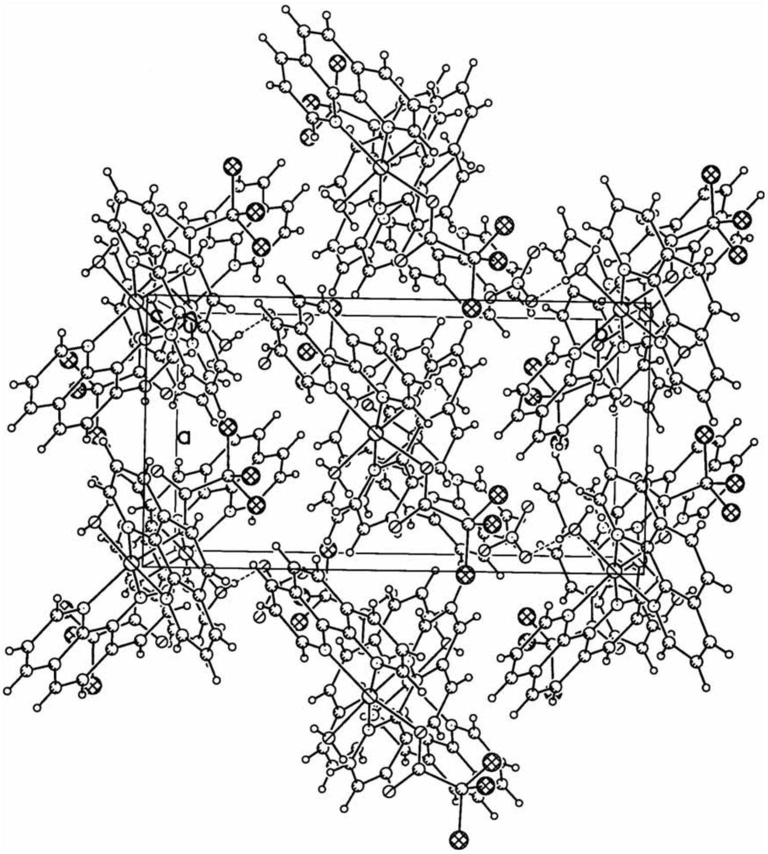

Figure 2. The unit cell of $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$.

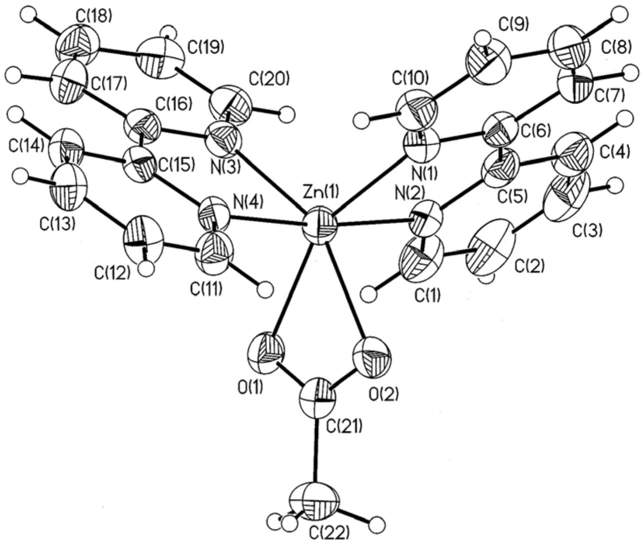

Figure 3. ORTEP diagram of $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$.

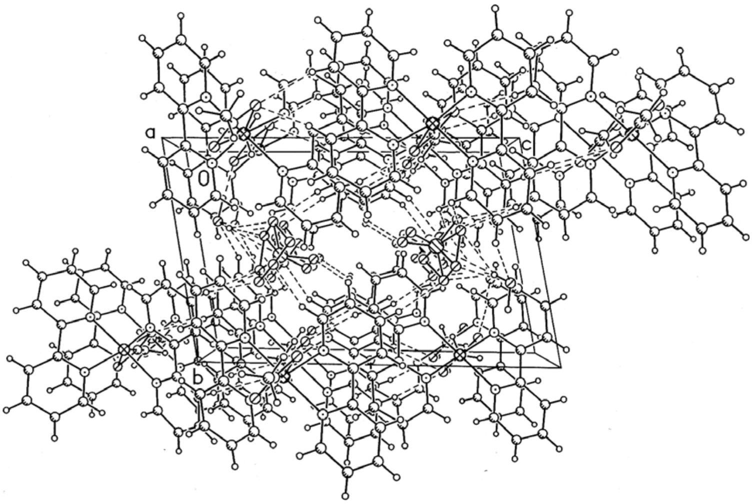

Figure 4. The unit cell of $[Zn(bpy)_2(CH_3COO)](ClO_4)\cdot H_2O$.

Table 4. Bond lengths (Å) and angles (°) for $[Zn(bpy)_2(CH_3COO)](ClO_4)\cdot H_2O$.

Zn(1)–N(4)	2.100(3)	N(4)–Zn(1)–N(2)	173.18(12)
Zn(1)–N(2)	2.109(3)	N(3)–Zn(1)–N(4)	77.76(12)
Zn(1)–N(3)	2.123(3)	N(3)–Zn(1)–N(2)	97.81(11)
Zn(1)–N(1)	2.123(3)	N(1)–Zn(1)–N(4)	98.90(12)
Zn(1)–O(1)	2.156(3)	N(2)–Zn(1)–N(1)	77.59(12)
Zn(1)–O(2)	2.207(3)	N(3)–Zn(1)–N(1)	109.86(12)
		N(4)–Zn(1)–O(1)	92.46(11)
		N(2)–Zn(1)–O(1)	93.16(11)
		N(3)–Zn(1)–O(1)	95.87(11)
		N(1)–Zn(1)–O(1)	153.50(11)
		N(4)–Zn(1)–O(2)	94.38(11)
		N(2)–Zn(1)–O(2)	91.78(11)
		N(3)–Zn(1)–O(2)	154.63(11)
		N(1)–Zn(1)–O(2)	95.09(11)
		O(2)–Zn(1)–O(1)	60.03(10)

shown in table 4. The structure of the complex consists of discrete $[Zn(bpy)_2(CH_3COO)]^+$ cations and ClO_4^- anions. The ClO_4^- anions were disordered. Each zinc atom is chelated by four nitrogen atoms of two "bpy" ligands with Zn–N distances of 2.100(3), 2.109(3), 2.123(3), and 2.123(3) Å, and two oxygen atoms of the acetate anion with Zn–O distances of 2.156(3) and 2.207(3) Å. There is an uncoordinated water molecule in this complex. The coordination number environment around the Zn(II) is distorted octahedral, $[ZnN_4O_{2acetate}]$, with the acetate ligand bidentate. Weak C–H···O interactions, between hydrogen atoms of phen and the oxygen atoms of perchlorates are shown in figure 4. The structure of this complex is controlled by weak hydrogen bonding, C–H···O interactions.

The striking difference feature between $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ and $[Zn(bpy)_2(CH_3COO)](ClO_4)\cdot H_2O$ is that the carboxylate is monodentate in the former and bidentate in the latter; decrease in coordination strength of the carboxylate from acetate to trichloroacetate may be responsible. The other difference between

$[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ and $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$ is that, in the former, normal hydrogen bonding is observed O–H···O, and in the latter only weak C–H···O hydrogen bonding is observed.

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 253687 for $[Zn(phen)_2(CCl_3COO)(H_2O)](NO_3)$ and 253684 for $[Zn(bpy)_2(CH_3COO)](ClO_4) \cdot H_2O$.

Acknowledgement

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