Synthesis and Structural Aspects of Two Trinuclear Cyano-bridged Heterometallic Complexes with Monodentate Coordination of Perchlorate and Acetate Anions

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Z. Naturforsch. **2010**, *65b*, 1106 – 1112; received December 12, 2009

Two new cyano-bridged trinuclear heterometallic complexes $[Ca_2(phen)_4(ClO_4)(H_2O)_3Fe(CN)_6]\cdot H_2O$ (**1**) and $[Ca_2(phen)_4(CH_3COO)(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ (**2**) (where phen = 1,10-phenanthroline) have been synthesized and characterized by single-crystal X-ray diffraction techniques, IR spectroscopy and thermogravimetric analysis. The structure of complex **1** features a central $[Fe(CN)_6]^{3-}$ unit that links a monocation $[Ca(phen)_2(H_2O)(ClO_4)]^+$ and a dication $[Ca(phen)_2(H_2O)_2]^{2+}$ *via* two *trans* cyanide bridges. Similarly, complex **2** also features a central $[Fe(CN)_6]^{3-}$ unit that links a monocation $[Ca(phen)_2(H_2O)(CH_3COO)]^+$ and a dication $[Ca(phen)_2(H_2O)_2]^{2+}$ *via* two *trans* cyanide bridges. In **1** and **2**, both Ca centers are seven-coordinated and achieve a pentagonal-bipyramidal geometry whereas the Fe center in both the complexes possesses a distorted octahedral geometry. Intra- and intermolecular hydrogen bonding networks are present in **1** and **2** that impart the overall molecular stability to both the systems.

Key words: Ca^{II}/Fe^{III} Complex, Cyano Bridge, Trinuclear, Thermal Analysis

Introduction

The effective approach of the cyano group to link different types of metal centers has been used in organometallic and coordination chemistry for the construction of supramolecular architectures or self assemblies [1 – 3]. In the past decade, there has been an impressive surge of the chemistry related to polynuclear cyano-bridged transition metal complexes [4 – 10]. In this regard, hexacyanometallate ions react with iron and other metal ions to produce Prussian Blue and its analogs [11 – 15], and with metal complexes to generate mixed-valence multidimensional networks [16 – 19]. When coordinatively unsaturated complexes are used instead of simple metal ions, the hexacyanometallate ions can adopt different bridging modes from η^1 to η^6 to form bimetallic assemblies of various network structures [17 – 20]. Recently, there has been a growing interest in the formation of coordination polymers using the $[Fe(CN)_6]^{3-}$ ion, and several bimetallic Fe-M (M = Cu^{II}, Ni^{II}, Mn^{II}) cyano-bridged polynuclear complexes have been reported [21 – 26]. The trinuclear cyano-bridged complex $[Nd(2,2'\text{-bipy})(H_2O)_4Fe(CN)_6Nd(2,2'\text{-bipy})_2(H_2O)_4][Fe(CN)_6]\cdot 8H_2O$ has also been synthesized [27]. In addition to using two convergent precursors to construct molecular squares, one can also envisage the use of $[M(CN)_6]^{n-}$ anions to connect *cis*-$[M(L\text{-}L)_2]^{n+}$ units. Although the hexacyanometallate building blocks can produce polymers *via trans* linkages, there is also a possibility for the self-assembly of molecular squares through *cis*-cyano interactions [28]. Nowadays, the cyano-bridged mixed valence complexes are studied because of their remarkable diversity of structural types. In most of these complexes, the bridging agent is $[M(CN)_6]^{n-}$(n = 2, 3, 4 and M = Mn, Fe, Cr, *etc.*). The coordination chemistry of alkaline earth cations, has received a strong impetus from bioinorganic chemistry [29] and attracted considerable interest through the preparation of cyano-bridged complexes. Recently, Westerhausen *et al.* [30] have extended these studies in case of alkaline-earth metals producing $(THF)_4Ca[M(CO)_5(CN)]_2$ (THF = tetrahydrofuran, M = Cr, Mo, W). Some cyano-bridged alkaline earth metal complexes, *i. e.* $([Sr_3(phen)_6(H_2O)_6\{Fe(CN)_6\}_2]\cdot phen\cdot 6.5H_2O)_n$ [31],

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$[Ca_2(phen)_4(H_2O)_3Fe(CN)_6(H_2O)(NO_3)]\cdot H_2O$ [32], and $[Ba_2(phen)_4(H_2O)_6Fe(CN)_6\cdot Cl_2(phen)\cdot 3H_2O]_n$ [33] have already been reported. In continuation of these studies, two cyano-bridged trinuclear seven-coordinated complexes of Ca(II), $[Ca_2(phen)_4(ClO_4)(H_2O)_3Fe(CN)_6]\cdot H_2O$ (**1**) and $[Ca_2(phen)_4(CH_3COO)(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ (**2**), are reported in the present contribution. Analytical, spectral and thermal data are fully consistent with the crystal structures obtained from X-ray studies.

Experimental Section

Materials

All the chemicals and solvents used for the synthesis were of reagent grade. $Ca(ClO_4)_2\cdot 4H_2O$ (Acros Organics), $Ca(CH_3COO)_2\cdot H_2O$ and $K_3[Fe(CN)_6]$ (Showa), and 1,10-phenanthroline monohydrate (Alfa Aesar) were obtained commercially and used as received without purification. All the solvents were dried using standard methods before use.

Physical techniques

Elemental analyses were carried out using a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center of the NCHU. The IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer in the range 4000 – 200 cm^{-1} with KBr pellets. Thermal analysis was carried out at a heating rate of 10 °C min^{-1} with a Mettler-Toledo Star TGA/SDTA-851e thermal analyzer system in a dynamic atmosphere of N_2 (flow rate 30 mL/min) in an alumina crucible for the range 25 – 350 °C.

Synthesis of $[Ca_2(phen)_4(ClO_4)(H_2O)_3Fe(CN)_6]\cdot H_2O$ (1)

An aqueous solution (15 mL) of $K_3Fe(CN)_6$ (0.33 g, 1 mmol) was added to a stirred mixture of 10 mL of an aqueous solution of $Ca(ClO_4)_2\cdot 4H_2O$ (0.62 g, 2 mmol) and 10 mL of a methanolic solution of 1,10-phenanthroline monohydrate (0.79 g, 4 mmol). On slow evaporation of the solvent at r. t., yellow crystals appeared after 4 – 5 d. The crystals were washed with water, dried in air, and used for X-ray analysis. Yield: 83 %. – Anal. for $C_{54}H_{32}Ca_2FeN_{14}O_8Cl$: calcd. C 55.13, H 2.74, N 16.67; found C 55.37, H 2.58, N 16.83 %.

Synthesis of $[Ca_2(phen)_4(CH_3COO)(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ (2)

The complex **2** was prepared in the same way as complex **1** by using $K_3[Fe(CN)_6]$ (0.33 g, 1 mmol), $Ca(CH_3COO)_2\cdot H_2O$ (0.35 g, 2 mmol), and 1,10-phenanthroline monohydrate (0.79 g, 4 mmol). Yield: 79 %. – Anal. for $C_{56}H_{45}Ca_2FeN_{14}O_7$: calcd. C 57.88, H 3.90, N 16.87; found C 57.94, H 3.72, N 17.11 %.

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{54}H_{32}Ca_2ClFeN_{14}O_8$	$C_{56}H_{45}Ca_2FeN_{14}O_7$
Formula weight	1176.40	1162.07
Crystal size, mm^3	0.32 × 0.27 × 0.26	0.12 × 0.18 × 0.44
Temperature, K	150(2)	100(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.985(3)	9.9141(2)
b, Å	12.616(3)	10.7637(3)
c, Å	19.744(5)	12.4831(3)
α, deg	77.960(5)	82.492(2)
β, deg	83.986(4)	77.204(2)
γ, deg	83.935(4)	83.122(2)
V, $Å^3$	2651.4(12)	1282.18(5)
Z	2	1
$D_{calcd.}$, g cm^{-3}	1.47	1.51
$\mu(MoK_\alpha)$, mm^{-1}	0.6	0.6
$F(000)$, e	1202	601
θ range, deg	1.06 – 28	2.97 – 31.51
Refl. collec. / indep. / R_{int}	39392 / 12635 / 0.0346	40169 / 8553 / 0.028
Data / restraints / ref. param.	12635 / 0 / 721	8553 / 51 / 410
Final indices $R1$ / $wR2$ [$I \geq 2\ \sigma(I)$]	0.0531 / 0.1477	0.032 / 0.086
Final indices $R1$ / $wR2$ (all data)	0.0697 / 0.1656	0.036 / 0.089
Goodness-of-fit on F^2	1.059	1.088
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	1.94 / −1.03	0.76 / −0.73

X-Ray crystallography

A good-quality air-stable orange block-type single crystal of **1** and a pale-yellow plate-type single crystal of **2** were selected and mounted on a Bruker SMART CCD area detector and an Oxford Diffraction Supernova diffractometer for complexes **1** and **2**, respectively. Graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) from a fine-focus sealed tube and the ω scan technique were used to collect the data sets. The stability of the crystals was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted. The data for **1** and **2** were corrected for Lorentz and polarization effects and for those of absorption (SADABS [34a]). Both structures were solved by Direct Methods using SHELXS-97 [34b] and refined by full matrix least-squares methods using SHELXL-97 [34c]. For both structures, the hydrogen atom positions were calculated, constrained to idealized geometries and treated as riding with the H atom displacement parameter calculated from the equivalent isotropic displacement parameter of the bound atom. The crystal structure of **2** was refined in the centrosymmetric space group $P\bar{1}$. It presents an occupational disorder of the acetate and one Ca-coordinated water molecule, with 50 % occupancy each in the asymmetric unit. This disorder has been efficiently accounted for in the refinement constraining the coordinating acetate and water oxygen atoms to identical positions and atomic displacement parameters. Structure refinement in the non-centrosymmetric sub-group *P*1 has been tried but it did not solve the disorder nor improve the structure quality. A summary of crystal data and parameters pertinent to intensity data collection and structure refinement is given in Table 1.

CCDC 734609 and 739109 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.

Results and Discussion

IR spectra

The IR spectra of the complexes **1** and **2** are consistent with the structural data presented in this paper. The absorption band at 3208 – 3510 cm^{-1} for both complexes is due to the ν(O-H) vibrations of water molecules present in the crystals [35]. The sharp bands at 1631 and 1647 cm^{-1} for complexes **1** and **2**, respectively, indicate the δ(H-OH) mode. Again bands at 403 and 416 cm^{-1} for complexes **1** and **2**, respectively, may be assigned to $\rho_w(H_2O)$, and the band at 847 cm^{-1} for both complexes $\rho_r(H_2O)$. These results show the presence of both coordinated and interstitial (lattice) water molecules [36]. For the ν(C≡N) mode of the $[Fe(CN)_6]^{3-}$ anion, two main band systems of comparable intensities are observed. The low-intensity bands at 2113 and 2108 cm^{-1} for complexes **1** and **2**, respectively, are assigned to the intermetallic C≡N stretching and the high-intensity bands around 2045 and 2076 cm^{-1} to the terminal C≡N stretching mode. The characteristic absorption bands at 1514, 1420, 1041, 728, and 619 cm^{-1} may be attributed to 1,10-phenanthroline [33]. The characteristic bifurcated absorption band at 1105 cm^{-1} for **1** indicates the presence of perchlorate anions [36]. The IR spectrum contains $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ bands for **2** at 1621 and 1347 cm^{-1}, giving a frequency difference ($\Delta\nu$) of 274 which reflects the unidentate nature of the carboxylate group [35]. The Ca-N stretching frequencies for **1** and **2** appear at 268, 247, 253, and 231 cm^{-1}, respectively [37].

Thermogravimetric analysis

The TGA trace shows complex **1** to be stable up to 60 °C. Beyond this temperature, the complex decomposes, and most of the mass loss occurs in two steps, 60 – 130 and 130 – 225 °C. The first step corresponds to the loss of one molecule of lattice water and the next step to the loss of three molecules of coordinated water. Above 270 °C the compound undergoes decomposition in two steps. The first step corresponds to the loss of perchlorate (255 – 370 °C), and the next step corresponds to the loss of four 1,10-phenanthroline molecules in a single step in the temperature range 390 – 445 °C. Complex **2** is stable up to 55 °C, and beyond this temperature most of the mass loss proceeds within two temperature ranges, 55 – 145 and 145 – 225 °C. The first process corresponds to the loss of two molecules of lattice water, and the next step is consistent with the loss of three molecules of coordinated water. Above 255 °C the compound looses one acetate ligand and four 1,10 phenanthroline molecules in the temperature ranges 255 – 325 and 325 – 360 °C, respectively, without any intermediate.

Crystal and molecular structure of $[Ca_2(phen)_4(ClO_4)(H_2O)_3Fe(CN)_6]\cdot H_2O$ *(**1**)*

The molecular structure of **1** with the atom numbering scheme and relevant bond lengths and angles are presented in Fig. 1 and Table 2, respectively. The asymmetric unit of **1** consists of one $[Ca(phen)_2(ClO_4)(H_2O)]^+$ monocation, the $[Fe(CN)_6]^{3-}$ anion, one $[Ca(phen)_2(H_2O)_2]^{2+}$ dication, and one solvate water molecule. The central $[Fe(CN)_6]^{3-}$ unit links the two cationic units *via* two *trans* cyano bridges. Within the complex, the $[Fe(CN)_6]^{3-}$ ion has the usual six-coordinated octahedral arrangement with slight distortions as indicated by the variation of the *cis* angles [84.61(11) – 94.87(11)°] and *trans* angles

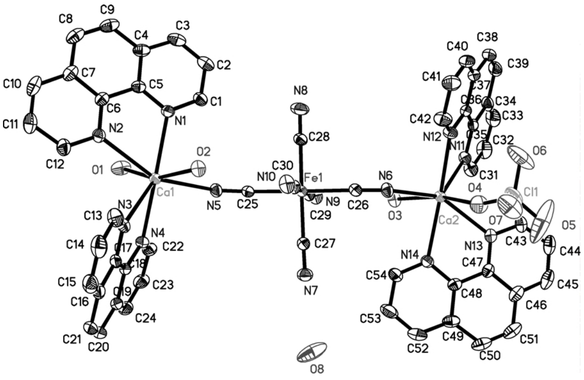

Fig. 1. ORTEP drawing of complex **1**. Ellipsoids are drawn at the 40 % probability level. Hydrogen atoms have been omitted for clarity.

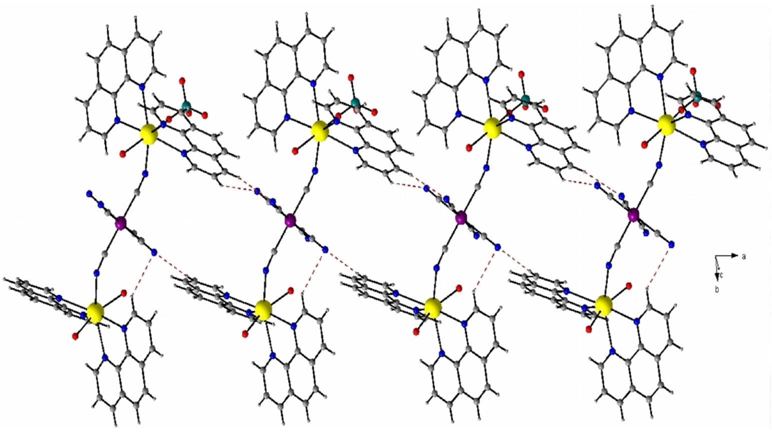

Fig. 2 (color online). Hydrogen bond contacts in crystals of **1**.

Table 2. Selected bond lengths (Å) and angles for **1** (deg).

Ca1 – O1	2.410(2)	Ca1 – O2	2.392(2)
Ca1 – N1	2.507(2)	Ca1 – N2	2.556(2)
Ca1 – N3	2.595(2)	Ca1 – N4	2.522(2)
Ca1 – N5	2.493(2)		
Ca2 – O3	2.366(2)	Ca2 – O4	2.399(2)
Ca2 – N6	2.486(2)	Ca2 – N11	2.575(3)
Ca2 – N12	2.515(3)	Ca2 – N13	2.555(3)
Ca2 – N14	2.520(3)		
N5 – C25 – Fe1	174.2(2)	N6 – C26 – Fe1	173.7(2)
N7 – C27 – Fe1	177.8(3)	N8 – C28 – Fe1	179.7(3)
N9 – C29 – Fe1	175.5(3)	N10 – C30 – Fe1	176.2(3)
Ca1 – N5 – C25	147.5(2)	Ca2 – N6 – C26	149.3(2)

Table 3. Weak hydrogen bond contacts (Å, deg) for **1**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H–A)
C3–H3···O4[#1]	0.95	2.59	3.357(5)	138.1
C23–H23···N8[#2]	0.95	2.46	3.186(4)	133.0
C41–H41···N7[#3]	0.95	2.54	3.305(5)	138.2
C44–H44···O6[#4]	0.95	2.59	3.382(7)	141.3

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $y+1$, z; #2 $x-1$, y, z; #3 $x+1$, y, z; #4 $-x+2$, $-y$, $-z$.

[178.09(12) – 179.15(12)°] away from the ideal value of 90 and 180°, respectively. The Fe–C and C≡N bond lengths are grouped together in the narrow ranges 1.932(3) – 1.948(3) Å and 1.146(4) – 1.155(4) Å, respectively. The Fe–C–N bond angles are almost linear, [173.7(2) – 179.7(3)°], whereas the Ca–N–C bond angles deviate strongly from linearity [147.5(2) – 149.3(2)°]. Though the geometry around the iron atom is found regular, the geometries around the calcium atoms are irregular. Four nitrogen donor atoms from two phen units, one nitrogen atom from the bridging CN of $[Fe(CN)_6]^{3-}$ and two oxygen atoms from two water molecules form a N_5O_2 donor environment around the Ca(1) atom in a pentagonal-bipyramidal geometry in which the five nitrogen atoms form a distorted pentagonal plane with the two oxygen atoms occupying the *trans* axial positions [O(1)–Ca(1)–O(2) = 161.12(9)°]. Seven-coordination is rather uncommon [38, 39] for calcium complexes, whereas eight-coordination is very common [40 – 43]. The Ca(1)–O(H_2O) and Ca(1)–N(phen) bond lengths lie in the ranges of 2.392(2) – 2.410(2), and 2.507(2) – 2.595(2) Å, respectively. Thus, the phen ligands are relatively weakly bonded to Ca(1), comparable with other previously reported Ca compounds [32, 44]. The Ca(2) atom is chelated by two phen ligands and directly bonded to one water molecule, one bridging cyano group and one perchlorate anion (ClO_4^-). The bond lengths Ca(2)–N(11), Ca(2)–N(12), Ca(2)–N(13), and Ca(2)–N(14) involving the phen ligands of 2.575(3), 2.515(3), 2.555(3), and 2.520(3) Å, respectively, are quite different from those in other complexes with Ca–N(phen) lengths in the range 2.512(2) – 2.586(2) and 2.531(2) – 2.571(2) Å [32], 2.557(2) – 2.596(2), and 2.567(3) – 2.617(3) Å [44]. The Ca(2)–O(H_2O) bond length [2.366(2) Å] is slightly shorter than Ca(2)–O(ClO_4), 2.399(2) Å. The Ca(2) atom also has a seven-coordinate geometry defined by a N_5O_2 donor environment similar to that of the Ca(1) center, but there is a significant distortion away from a pentagonal-bipyramidal geometry as indicated by the O–Ca(1)–O axial angle of 159.55(9)°. The Ca–N–C angle is 147.5(2)° for Ca(1) and 149.3(2)° for Ca(2).

An important structural aspect of **1** is the presence of a network of weak hydrogen bonds (Fig. 2). Table 3 summarizes key hydrogen bonding contacts for **1**. This bonding imparts stability to the system. Some C-H atoms of the phen rings in the structure act as donors, and the nitrogen atoms of the cyano groups which are non-bonded to Ca, as well as the oxygen atoms of the perchlorate anion, act as acceptors. These C–H$\cdots$acceptor interactions are in the range of 2.46–2.59 Å (H$\cdots$acceptor distances). The lengths and angles between the C atoms and the acceptor atoms are less than 3.450 Å and greater than 120°, respectively, and imply the presence of weak hydrogen bonds which are all unsymmetrical with different C–H$\cdots$acceptor angles.

Crystal and molecular structure of $[Ca_2(phen)_4(CH_3COO)(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ (**2**)

The molecular structure of **2** with the atom numbering scheme is presented in Fig. 3. Most of the structural data for **2** are very similar to those of **1** as summarized in Table 4. Complex **2** consists of a central $[Fe(CN)_6]^{3-}$ anion which links two cations, $[Ca(phen)_2(CH_3COO)(H_2O)]^+$ and $[Ca(phen)_2(H_2O)_2]^{2+}$, *via* two *trans* cyanide bridges.

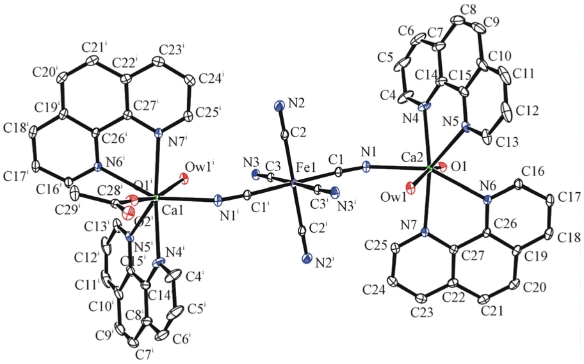

Fig. 3 (color online). ORTEP drawing of complex **2**. Ellipsoids are drawn at the 40 % probability level. Hydrogen atoms have been omitted for clarity. Only one component of the occupational disorder of the acetate molecule is shown. Symmetry code: (i) $-x$, $1-y$, $-z$.

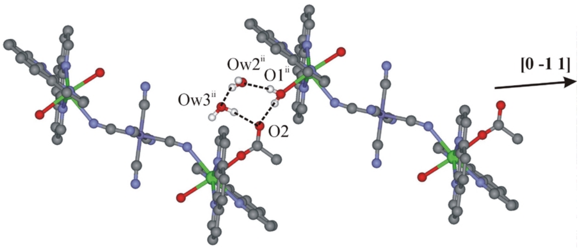

Fig. 4 (color online). Molecular packing in crystals of **2** with *intra*-chain hydrogen bonding. Symmetry code: (i) $-x$, $-y$, $1-z$.

Table 4. Selected bond lengths (Å) and angles for **2** (deg).

Ca1–Ow1	2.3837(8)	Fe1–C1	1.941(1)
Ca1–O1	2.3081(9)	Fe1–C2	1.950(1)
Ca1–N1	2.515(1)	Fe1–C3	1.936(1)
Ca1–N4	2.523(1)	C1–N1	1.158(1)
Ca1–N5	2.595(1)	C2–N2	1.157(2)
Ca1–N6	2.5418(9)	C3–N3	1.156(1)
Ca1–N7	2.520(1)	O1–C28	1.197(2)
		O2–C28	1.251(3)
		C28–C29	1.513(3)
N1–Ca1–N7	86.36(3)	O1–Ca1–N6	77.91(3)
N1–Ca1–N4	81.71(4)	O1–Ca1–N7	83.81(3)
N1–Ca1–O1	91.36(3)	N6–Ca1–N7	65.59(3)
Ow1–Ca1–N1	82.29(3)	N4–Ca1–N5	64.03(4)
Ow1–Ca1–N4	116.80(3)	N5–Ca1–N6	81.91(3)
Ow1–Ca1–N5	78.95(3)	Ca1–O1–C28	173.1(1)
Ow1–Ca1–N6	99.54(3)	C1–Fe1–C2	91.46(5)
Ow1–Ca1–N7	79.00(3)	C1–Fe1–C3	95.45(4)
O1–Ca1–N4	78.59(3)	C2–Fe1–C3	91.15(5)
O1–Ca1–N5	117.86(3)	C1–N1–Ca1	147.21(9)

Table 5. Hydrogen bond parameters (Å, deg) for **2**.

D–H$\cdots$A	D$\cdots$A	D–H$\cdots$A
Ow1–Hw1$\cdots$N3	2.8252(13)	177(2)
Ow1–Hw2$\cdots$N3	3.0003(13)	165.6(19)
Ow3–Hw5$\cdots$O2	2.900(3)	149(3)
Ow3–Hw6$\cdots$N1	3.319(2)	178(4)
Ow2–Hw3$\cdots$Ow3	2.883(3)	151(4)
Ow2–Hw4$\cdots$N2	3.084(2)	163(5)
O1–Hw8$\cdots$O2	2.685(2)	170(3)
O1–Hw7$\cdots$Ow2	2.870(2)	169(2)
C29–H29$\cdots$Ow3	2.167(4)	121(2)
C4–H4$\cdots$Ow3	3.221(3)	168(1)
C5–H5$\cdots$N2	3.206(2)	149(1)

The Fe(1) atom sits on an inversion center and accordingly is connected to two symmetry-equivalent cations. The difference between the cations $[Ca(phen)_2(CH_3COO)(H_2O)]^+$ and $[Ca(phen)_2(H_2O)_2]^{2+}$ arises from an occupational disorder of one acetate and one coordinated water molcule with 50 % occupancy each. In the following, we denote Ca(1) the calcium atom linked to one acetate and one water molecule (Ow1), and Ca(2) that linked to two water molecules (O1 and Ow1), although crystallographically Ca(1) and Ca(2) are symmetry-related in the space group $P\bar{1}$. The Fe(1) atom adopts a perfect octahedral geometry. The Fe–C and C–N(cyano) lengths lie in the narrow ranges 1.9356(11)–1.9499(12) Å and 1.1557(14)–1.1580(14) Å, respectively, and these values are relatively similar to those of **1**. The C–Fe–C angle involving the *trans* CN groups is perfectly 180° (by symmetry) and those involving the *cis* groups vary from 91.15(5) to 95.45(4)°. These values are in agreement with those obtained in other complexes [45–49]. Four

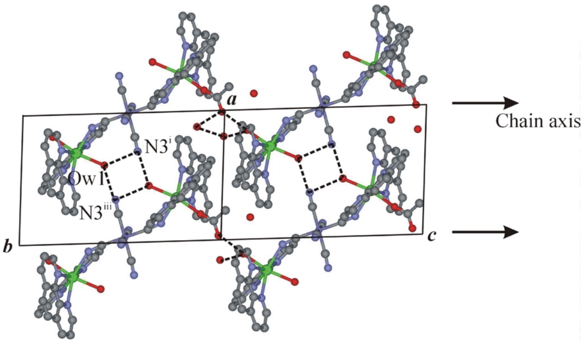

Fig. 5 (color online). Molecular packing in crystals of **2** as viewed along the crystallographic [0 1 1] axis, and *inter*-chain hydrogen bonding. Symmetry code: (i) $-x$, $1-y$, $-z$; (iii) $-1+x$, y, z.

nitrogen donor atoms from two phen units, one nitrogen and two oxygen atoms from the coordinated water and the acetate anion form a N_5O_2 donor environment around the Ca(1) atom in a pentagonal-bipyramidal geometry in which the five nitrogen atoms form a distorted pentagonal plane while the two oxygen atoms occupy the *trans* axial positions [O(1)–Ca(1)–Ow(1) = 161.99(3)°]. The structure is stabilized by a complicated network of hydrogen bond interactions and weak π-π stacking (Figs. 4 and 5). Table 5 summarizes key hydrogen bond contacts for **2**. The crystal packing may be described as infinite parallel chains of connected molecules running along the [0 −1 1] crystallographic direction. The intermolecular connection along the chains, as depicted in Fig. 4, is assisted by hydrogen bonds involving the non-coordinating oxygen atom O2 of the acetate, the coordinating O1 water molecule and the Ow2 and Ow3 solvate water molecules, resulting in the formation of an eight-membered ring. The *inter*-chain connection along the crystallographic [1 0 0] direction is assisted by the Ow1 water molecule, which thus bridges two cyanide nitrogen atoms, one intramolecularly to N3 and another one intermolecularly to a symmetry-equivalent N3, resulting in the formation of a centrosymmetric eight-membered (H–O–H···N···)$_2$ ring. The *inter*-chain connection along the crystallographic [0 1 1] direction is assisted by a weak C5–H5···N2 hydrogen bond and the donor interaction of the Ow2 water molecule with N2. Other *inter*-chain interactions involve rather weak π-π stacking of the phen groups. The donor-acceptor lengths are in the range of 2.167(4)–3.319(2) Å. This extensive network of hydrogen bonding imparts overall stability to the crystal system.

Conclusion

In this paper, we have described the structures of two new cyanide-bridged heterometallic assemblies based on hexacyanoferrate(III) as the building block, $[Ca_2(phen)_4(ClO_4)(H_2O)_3Fe(CN)_6]\cdot H_2O$ (**1**) and $[Ca_2(phen)_4(CH_3COO)(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ (**2**). The structural analyses have shown that both complexes consist of a trinuclear unit, $Ca(phen)_2(L)(H_2O)$-NC-$Fe(CN)_4$-CN-$Ca(phen)_2(H_2O)_2$ (L = ClO_4^- or CH_3COO^-, respectively), the calcium centers achieving pentagonal-bipyramidal geometries. Future work will explore the coordination mode and modification of the system using different metal ions, like alkaline earth metals such as Ba or Sr, and/or transition and lanthanide metal ions, and using Cr or Co hexacyanometallates as building blocks to develop new generations of cyanide-bridged heterometallic complexes and characterize their activities as well as the stereochemical control of the assembly.

Acknowledgement

The authors gratefully acknowledge financial support from the National Science Council of Taiwan.

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