

Synthesis, Characterisation and Structural Studies of $[\text{Zn}(\text{phen})_3][\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O} \cdot 0.25\text{MeOH}$ and $[(\text{bipy})_2(\text{H}_2\text{O})\text{Zn}(\mu\text{-NC})\text{Fe}(\text{CN})_4(\text{NO})] \cdot 0.5\text{H}_2\text{O}$

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Two new bimetallic complexes $[\text{Zn}(\text{phen})_3][\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O} \cdot 0.25\text{MeOH}$, (**1**) and $[(\text{bipy})_2(\text{H}_2\text{O})\text{Zn}(\mu\text{-NC})\text{Fe}(\text{CN})_4(\text{NO})] \cdot 0.5\text{H}_2\text{O}$, (**2**), have been isolated (where phen = 1,10-phenanthroline and bipy = bipyridyl) and characterised by X-ray crystallography [as the $2\text{H}_2\text{O} \cdot 0.25\text{CH}_3\text{OH}$ solvate for (**1**) and hemihydrate for (**2**)] infrared spectroscopy and thermogravimetric analysis. Substitution of phenanthroline for bipyridyl resulted in a cyano-bridged bimetallic species rather than two discrete mononuclear metal complexes. The bond angles of Fe-N-O were shown to be practically linear for both **1** [$179.2(7)^\circ$] and **2** [$178.3(3)^\circ$], and the Zn atoms have distorted octahedral geometry. The solvent molecules in both crystal lattices take part in forming hydrogen-bonded networks.

Key words: Zinc(II) Nitrate, Crystal Structures, Spectral Studies

Introduction

There is considerable interest in designing poly-metallic molecular systems with extended structures which possess catalytic and electronic properties, mainly molecular based magnets and inorganic materials [1–10] with channels mimicking zeolites [1, 2] or inner cavities [3, 6–9]. The most successful and often the sole strategy for preparing these materials still consists in assembling building blocks, usually transition metal complexes, one having potential bridging ligands with another species possessing empty or available co-ordination sites.

Cyanometallate complexes [10–14] have been used extensively, they react with transition metal complexes to afford three-dimensional cyano-bridged metal complex assemblies with Prussian-Blue like structures. Hexacyanometallate ions $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Cr}, \text{etc.}$) act as effective building blocks to provide heterometallic assemblies exhibiting spontaneous magnetisation [15–17]. The many different bridging modes available enable formation of heterometallic assemblies of either discrete molecules or extended network structures. We have reported a 2-D polymeric compound with an exceptional 1,1 end-on cyanide bridge [18] and a discrete pentanuclear com-

plex $[(\text{CuL})_4\text{Fe}(\text{CN})_6] \cdot 16\text{H}_2\text{O}$ [$\text{L} = N,N\text{-dimethyl-}N'\text{-(}\alpha\text{-methylsalicylidene)ethane-1,2-di amine}$] [19].

Wei and coworkers had prepared both the discrete bimolecular complex $[\text{Ni}(\text{bipy})_3][\text{Fe}(\text{CN})_5(\text{NO})] \cdot 3\text{H}_2\text{O}$, (bipy = bipyridyl) and a one-dimensional polymeric complex $[(\text{en})_2\text{Ni}(\mu\text{-NC})_2\text{Fe}(\text{CN})_3(\text{NO})] \cdot \text{H}_2\text{O}$, (en = ethylenediamine) [20], in which two cyano groups serve as a bridge to the Ni(II) atom through nitrogen. The iron analogue of the discrete bimolecular bipy complex above has also been prepared [21], which crystallises as a tetrahydrate. Zinc has been used less frequently in cyano-bridged complexes. Most recently, a Zn porphyrin linked to $\text{Fe}(\text{C}_5\text{H}_5)(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)$ via a CN bridge [22] was found in the Cambridge Structural Database [23] in addition to several examples of $\text{Zn}(\text{en})_2$ bridged to iron and nickel [24] cyanide centres.

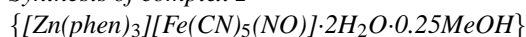
We have also synthesised two new cyano-bridged dinuclear complexes $[\text{Cu}(\text{dmen})_2\text{Fe}(\text{CN})_5(\text{NO})]$ and $[\text{Cu}(\text{dmpn})_2\text{Fe}(\text{CN})_5(\text{NO})]$ [25], (where dmen = 2-dimethylaminoethylamine and dmpn = 1-dimethylamino-2-propylamine). Very recently, we have reported a polymeric cyano- and aquo-bridged complex $\{[\text{Ba}_2(\text{phen})_4(\text{H}_2\text{O})_6\text{Fe}(\text{CN})_6] \cdot \text{Cl} \cdot 2(\text{phen}) \cdot 3\text{H}_2\text{O}\}_n$ [26], (where phen = 1,10-phenanthr-

oline) and a cyano-bridged trinuclear complex $[(\text{CuL})_2\text{Fe}(\text{CN})_6][\text{ClO}_4] \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ [27], (where $\text{L} = N,N'$ -bis(2-pyridylimine)propane-1,3-diamine). The crystal structure analysis reveals that the Ba_2Fe species [26], forms a zig-zag polymeric chain which is composed of alternating single cyano and double aquo bridges. In the copper complex [27], both copper(II) ions have a distorted square pyramidal geometry and are *trans* to each other, linked *via* cyanide bridges to the iron(III) centre.

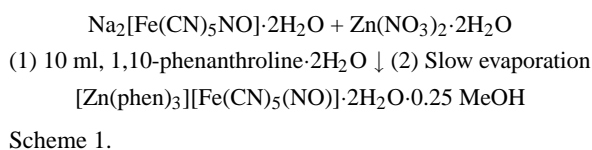
In this communication, we report on the bimolecular complexes $[\text{Zn}(\text{phen})_3][\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O} \cdot 0.25\text{MeOH}$, (**1**), ($\text{phen} = 1,10$ -phenanthroline) and a bimetallic cyano-bridged complex $[(\text{bipy})_2(\text{H}_2\text{O})\text{Zn}(\mu\text{-NC})\text{Fe}(\text{CN})_4(\text{NO})] \cdot 0.5\text{H}_2\text{O}$, (**2**), ($\text{bipy} = 2,2'$ -bipyridyl). Herein the results of crystallographic, IR and TGA studies are described.

Results and Discussion

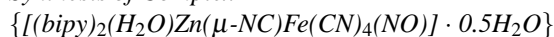
Synthesis of complex 1



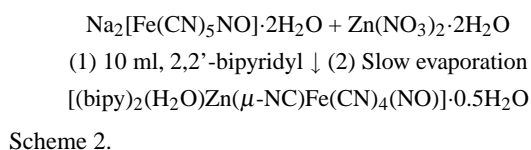
It was prepared by adding $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ to a stirred mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and 1,10-phenanthroline monohydrate (Scheme 1).



Synthesis of Complex 2



It was prepared following the same procedure as for **1**, by using 2,2'-bipyridyl instead of 1,10-phenanthroline monohydrate (Scheme 2).



IR spectra

The most useful aspects of the IR spectra of **1** and **2** concern the vibrational stretching frequencies of NO and CN groups. In the case of terminally bound NO, simple MO theory predicts that whilst M-N-O^+ will be linear, M-N-O may be bent. Therefore the formal

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

	1	2
Empirical formula	$\text{C}_{41.25}\text{H}_{29}\text{FeN}_{12}\text{O}_{3.25}\text{Zn}$	$\text{C}_{25}\text{H}_{19}\text{FeN}_{10}\text{O}_{2.50}\text{Zn}$
Formula weight	865.98	620.72
Temperature	160(2) K	160(2) K
<i>a</i> [Å]	10.022(1)	14.733(1)
<i>b</i> [Å]	19.539(3)	13.891(2)
<i>c</i> [Å]	19.701(2)	12.997(1)
β [°]	100.73(1)	97.82(1)
<i>V</i> [Å ³]	3790.4(8)	2635.2(5)
<i>Z</i>	4	4
Space group	$P2_1/n$	$P2_1/c$
Crystal size [mm]	$0.18 \times 0.52 \times 0.28$	$0.10 \times 0.32 \times 0.22$
μ [mm]	1.075	1.507
θ Range [°]	2.10–25.00	2.02–25.00
Refls collected	8365	5767
R Indices (all data)	$R_1 = 0.1453$ $wR_2 = 0.1715$	$R_1 = 0.0536$ $wR_2 = 0.0886$
Goof on F^2	1.104	0.923

oxidation state of the metal centre can be established by examining the IR spectra [20, 28]. The nitroprusside anion of $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ has a linear Fe-N-O angle and IR active NO stretching frequency of 1938 cm^{-1} , indicating an NO^+ complex of iron(II) with extensive π -bonding.

The IR spectrum of **1** showed a single absorption band at 2145 cm^{-1} which can be assigned to CN stretching, whereas two strong absorption bands at 2143 and 2164 cm^{-1} have been observed for complex **2**, which probably arose from the bridging CN and terminal CN stretching vibrations, respectively. Strong single peaks at 1912 for **1** and 1913 cm^{-1} for **2** were assigned to NO stretching. X-ray crystallographic studies confirmed that the NO ligand is linear in **1** and **2**. Another characteristic band appeared at 3206 cm^{-1} for complex **2** due to the zinc-bound water molecule.

TGA analysis

The thermogravimetric study showed that the thermal decomposition of **1** occurred in one step (Fig. 1). The mass loss in the temperature range 50 – 65 °C, corresponded to the release of two uncoordinated water molecules. Complex **2** is stable up to 55 °C. Beyond this temperature, the compound decomposed and most of the mass loss proceeded in two temperature ranges, 55 – 60 °C and 80 – 90 °C. The first step is the loss of half-equivalent uncoordinated water molecule, and the second, the release of one coordinated water molecule (Fig. 1). The difference in the temperature range is probably due to the differing number and coordination modes of solvent molecules in the lattice.

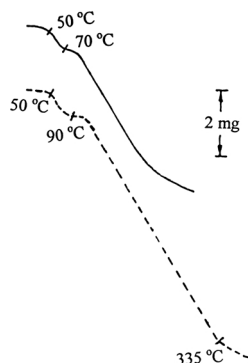


Fig. 1. TGA curves for complex **1** (—) (weight taken = 5.00 mg) and complex **2** (---) (weight taken = 14.20 mg). Heating rate is $10\text{ }^{\circ}\text{C min}^{-1}$ in each run.

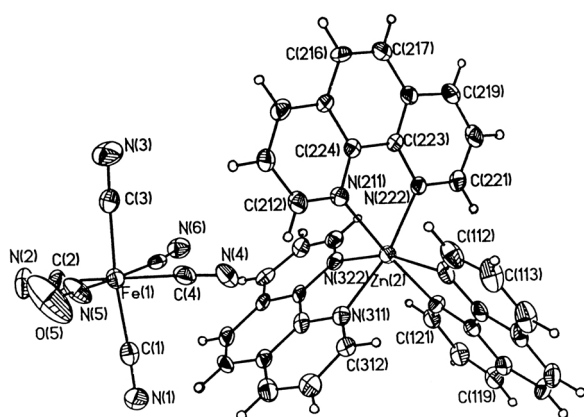


Fig. 2. A perspective view of **1** with atom numbering scheme. Displacements ellipsoids are drawn at the 50% probability level.

Crystal structure of **1**

A perspective view of **1** with the atom numbering scheme is shown in Fig. 2. Selected bond distances and angles are given in Table 2. As depicted in Fig. 2, **1** consists of discrete $[\text{Zn}(\text{phen})_3]^{2+}$ cations and $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ anions. The geometry of $[\text{Zn}(\text{phen})_3]^{2+}$ has approximate point-group symmetry D_3 . The structure of the iron analogue $[\text{Fe}(\text{phen})_3][\text{Fe}(\text{CN})_5(\text{NO})]\cdot\text{H}_2\text{O}$ is practically isostructural with **1** but was determined at room temperature [29]. Other tris(phenanthroline) complexes such as $[\text{Fe}(\text{phen})_3]^{2+}$ have been combined with $[\text{HgI}_3]^-$, $[\text{ClHgI}_3]^{2-}$ and Cl^- [30] and shown to give crystal lattices composed of tightly packed supramolecular interactions. Larger metals have given opportunity for expansion of the coordination sphere seen in a tetra(phenanthroline) lead complex with a

Table 2. Selected bond distances [\AA] and angles [$^{\circ}$] for **1**.

Fe(1)–N(5)	1.654(7)	Fe(1)–C(1)	1.937(8)
Fe(1)–C(2)	1.964(8)	Fe(1)–C(3)	1.932(8)
Fe(1)–C(4)	1.944(8)	Fe(1)–C(6)	1.953(8)
N(5)–O(5)	1.136(8)		
Zn(2)–N(111)	2.149(6)	Zn(2)–N(122)	2.198(5)
Zn(2)–N(211)	2.207(5)	Zn(2)–N(222)	2.122(6)
Zn(2)–N(311)	2.152(6)	Zn(2)–N(322)	2.161(6)
N(1)–C(1)–Fe(1)	176.1(7)	N(2)–C(2)–Fe(1)	179.6(9)
N(3)–C(3)–Fe(1)	177.7(7)	N(4)–C(4)–Fe(1)	177.2(7)
O(5)–N(5)–Fe(1)	179.2(7)	N(6)–C(6)–Fe(1)	174.1(6)
N(222)–Zn(2)–N(111)	95.3(2)	N(222)–Zn(2)–N(311)	167.0(2)
N(222)–Zn(2)–N(322)	99.0(2)	N(111)–Zn(2)–N(322)	162.4(2)
N(111)–Zn(2)–N(311)	90.4(2)	N(311)–Zn(2)–N(322)	77.9(2)

Table 3. Hydrogen bond distances [\AA] and angles [$^{\circ}$] for **1**.

D–H...A	$d(\text{D–H})$	$d(\text{H...A})$	$d(\text{D...A})$	$\angle(\text{DHA})$
O(1W)–H(12W)...N(4) ^{#2}	0.89(2)	1.96(3)	2.839(8)	169(9)
O(2W)–H(21W)...O(1W) ^{#3}	0.90(2)	1.95(3)	2.822(8)	165(9)

Symmetry transformations used to generate equivalent atoms:

^{#1} $-x+1, -y+1, -z+1$; ^{#2} $-x+3/2, y-1/2, -z+1/2$; ^{#3} $x, y, z+1$.

chlorate oxygen also bound to the lead centre [31]. A penta(phenanthroline) barium species has been reported more recently [32].

The geometry of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ is in good agreement with those of previous studies [20, 25]. The mean Fe–C, C–N and individual Fe–N, N–O bond distances in the $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ moiety are 1.946, 1.154 and 1.654, 1.135 \AA , respectively, and the Fe–N–O bond angle [$179.2(7)^{\circ}$] is linear.

In **1**, the nitrosyl oxygen O(5) makes the shortest hydrogen bond with the disordered methanol solvent molecule [C(1S), O(1S)], and cyanide atom N(4), *cis* to NO, forms a longer bond with one of the water molecules. The two water molecules [O(1W), O(2W)] in the lattice are also linked *via* hydrogen bonding (Table 3).

Crystal structure of **2**

A perspective view of bimetallic complex **2** with the atom numbering scheme is shown in Fig. 3. Selected bond distances and angles are given in Table 4. The metal complex in **2**, consists of a zinc bipyridyl centre linked to $\text{Fe}(\text{CN})_5(\text{NO})$ *via* a CN bridge. The cyanide bridge is *cis* to the water bound to the zinc centre [$90.12(10)^{\circ}$] and *trans* to a bipy N atom [$168.22(10)^{\circ}$]. The Zn(1)–N(29) bond length [$2.232(3)\text{ \AA}$] is significantly longer than the other Zn–N_{bipy} distances, as a result of the *trans* influence. The geometry around the Zn atom is distorted octahedral. The coordination ge-

Table 4. Selected bond distances [Å] and angles [°] for **2**.

Fe(1)-N(12)	1.660(3)	Fe(1)-C(16)	1.936(3)
Fe(1)-C(15)	1.939(3)	Fe(1)-C(13)	1.944(3)
Fe(1)-C(11)	1.950(3)	Fe(1)-C(14)	1.953(4)
N(12)-O(12)	1.145(4)		
Zn(1)-N(30)	2.123(2)	Zn(1)-N(20)	2.151(3)
Zn(1)-N(39)	2.161(3)	Zn(1)-N(29)	2.232(3)
O(12)-N(12)-Fe(1)	178.(3)	N(11)-C(11)-Fe(1)	178.3(3)
N(13)-C(13)-Fe(1)	177.6(3)	N(14)-C(14)-Fe(1)	177.4(3)
N(15)-C(15)-Fe(1)	178.1(3)	N(16)-C(16)-Fe(1)	175.2(3)
O(1)-Zn(1)-N(16)	90.12(10)		
N(16)-Zn(1)-N(30)	100.16(10)	N(16)-Zn(1)-N(20)	93.53(10)

Table 5. Hydrogen bond distances [Å] and angles [°] for **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(2)...N(13) ^{#1}	0.82(4)	1.98(4)	2.785(3)	167(4)
O(1)-H(1)...N(15) ^{#3}	0.82(4)	2.00(4)	2.796(4)	166(4)
O(1W)-H(1W)...N(11) ^{#4}	0.95(2)	2.10(5)	2.917(7)	143(7)
O(1W)-H(2W)...N(11) ^{#2}	0.96(2)	2.18(6)	2.976(7)	140(7)

Symmetry transformations used to generate equivalent atoms: ^{#1} -x, -y + 1, -z; ^{#2} -x + 1, -y, -z; ^{#3} x, -y - 1/2, z - 1/2; ^{#4} x - 1, y + 1, z.

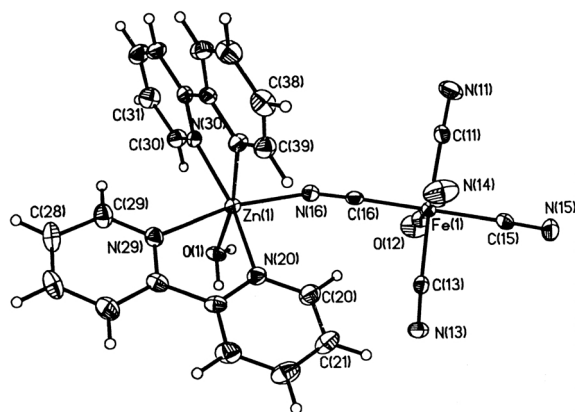


Fig. 3. A perspective view of **2** with atom numbering scheme. Displacements ellipsoids are drawn at the 50% probability level.

ometry about iron is almost regular octahedral with the greatest deviation from the ideal being found in the C(14)-Fe(1)-C(16) angle of 83.07(13)°. Recently, the structure of three six-coordinate Mn(bipy)₂ centres linked *via* CN bridges provided by W(CN)₆ was determined [33]. As in the case for **2**, the coordination of water completed the coordination sphere of the terminal Mn(bipy)₂ units.

The mean bond lengths of Fe-C, Fe-N, C-N and N-O in the [Fe(CN)₅(NO)]²⁻ moiety are in accordance with those in complex **1** with the nitrosyl angle, Fe-N-O, also being linear [178.3(3)°]. An important aspect of the crystal structure of **2**, is the presence of an infinite

two-dimensional hydrogen-bonded network (Table 5). The water molecules act as donors with the terminal cyano nitrogen atoms [N(13), N(15) and N(11)] being acceptors.

Experimental Section

Materials

All chemicals and solvents used were of reagent grade. 2,2'-Bipyridyl and 1,10-Phenanthroline monohydrate (Aldrich), Zn(NO₃)₂·2H₂O (Lancaster) and Na₂[Fe(CN)₅NO]·2H₂O (Loba Chemie, India) were obtained commercially and used as received.

Physical techniques

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 883-Infrared spectrometer as KBr pellets. Thermal investigations were carried out on a Shimadzu TGA-50 thermal analyser under a flow of nitrogen.

Synthesis of [Zn(phen)₃][Fe(CN)₅(NO)]·2H₂O·0.25MeOH (**1**)

Complex **1** was prepared by adding an aqueous solution (10 ml) of Na₂[Fe(CN)₅(NO)]·2H₂O (0.298 g, 1 mmol) to a stirred mixture of 15 ml aqueous solution of Zn(NO₃)₂·2H₂O (0.207 g, 1 mmol) and 10 ml methanolic solution of 1,10-phenanthroline monohydrate (0.395 g, 2 mmol). On slow evaporation of the solution, at 20 °C, the light orange coloured crystals appeared after 4–5 days. The crystals were washed with water and dried in air and used for X-ray analysis. Analysis for C_{41.25}H₃₁FeN₁₂O_{3.25}Zn: calcd. C 57.21, H 3.38, N 19.41, Zn 7.55; found C 57.50, H 3.53, N 19.39, Zn 7.58.

Synthesis of [(bipy)₂(H₂O)Zn(μ-NC)Fe(CN)₄(NO)]·0.5H₂O (**2**)

Complex **2** was prepared following the same procedure as for **1**, by using 2,2'-bipyridyl (0.312 g, 2 mmol) instead of phenanthroline. Light orange crystals suitable for X-ray diffraction were collected. Analysis for C₂₅H₁₉FeN₁₀O_{2.50}Zn: calcd. C 48.26, H 3.01, N 22.14, Zn 10.53; found C 48.33, H 3.06, N 22.25, Zn 10.58.

X-ray crystallography

Orange coloured crystals of **1** and **2** were obtained from slow evaporation of methanol solutions, covered in nujol and mounted with vacuum grease on glass fibres on a Bruker AXS P4 diffractometer. Data were collected with Mo-K_α radiation (0.7107 Å) at 160 K with an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data

were corrected for absorption by ψ scans. The structures were solved by direct and different Fourier methods and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters and phen and bipy hydrogen atoms were constrained to idealised geometries and refined with riding isotropic displacement parameters (1.2 times that of the bound C atom). The H atoms of both solvent water molecules in **1** were located in the difference Fourier map, their O–H distances restrained to 0.90(2) Å and refined with riding isotropic displacement parameters 1.5 times that of equivalent isotropic displacement parameter (U_{eq}) of the bound oxygen atom. The zinc-bound and solvent water H atoms in **2** were located in the difference Fourier map. The O–H and H···H distances in the solvent water were restrained to 0.95(2) and 1.50(2) Å, respectively. The displacement parameters of both sets of aqua H atoms were treated as riding on the oxygen atoms, being 1.2 times that of the U_{eq} of O(1) or O(1W). There is some disordered solvent in **1**, most likely CH₃OH whose atoms were assigned

0.25 occupancy on the basis of the atomic displacement parameters. H atoms were not included in the model of this solvent molecule. Crystallographic computing was performed using SHELXTL [34] programs. Further details are given in Table 1.

Supplementary data

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition numbers CCDC 187033 and 187034. e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>

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