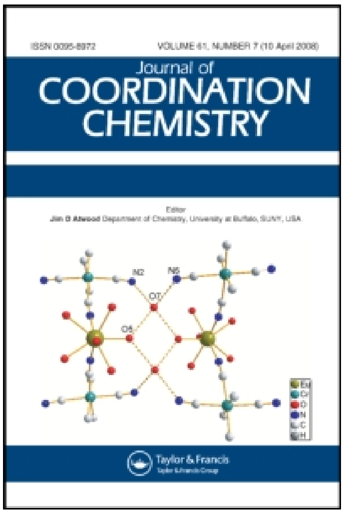

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Syntheses, crystal structures, and properties of two Cd–Fe heterobimetallic compounds with bridging *en* and *dien* ligands

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From the system Cd(II)–L–$[Fe(CN)_6]^{4-}$, complexes $[\{Cd(en)\}_2\{Fe(CN)_6\}]$ (**1**) and $[\{Cd(H_2O)(dien)\}_2\{Fe(CN)_6\}]\cdot 4H_2O$ (**2**) were prepared and characterized. The same products were also isolated from mother liquors containing $[Fe(CN)_6]^{3-}$ in which Fe(III) was reduced to Fe(II) upon irradiation. By the combination of IR and Mössbauer spectroscopy, the presence of the low-spin state ($S=0$) for Fe(II) was corroborated in both **1** and **2**. The Cd(II) and Fe(II) in both complexes are linked by bridging cyano ligands forming a 3-D crystal structure of **1** and a 1-D ribbon-like structural motif in **2**. The bidentate *en* in **1** links two pentacoordinated Cd(II), while in **2** the *dien* ligand exhibits a rare chelating-bridging bonding mode completing the hexacoordination of Cd(II) and enhancing the dimensionality of the formed structure to 2-D. Fe(II) in both structures exhibits octahedral coordination by cyano bridging in **1** whereas in **2** two cyano ligands are terminal. Water of crystallization and the coordinated water in **2** are involved in hydrogen bonds. Dehydration in **2** is a one-step process with a minimum on the DTA curve at 92°C.

Keywords: Cadmium; Hexacyanoferrate; Synthesis; Crystal structure; Mössbauer spectroscopy

1. Introduction

The bridging ability of cyanide makes it suitable for the formation of polymeric structures with various dimensionalities (D) [1]. Previously, these materials were mainly studied due to their ability to form various types of mineral mimetic and host–guest systems, especially Hofmann-type clathrates and their analogs. In these materials, Cd(II) was used as the cation of the host framework [2]. Cyano-bridged frameworks often have a porous character, which renders them suitable for the separation of small

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molecules, absorption, and ion exchange [3]. For example, selected hexacyanoferrates were used in removing cesium from radioactive waste waters [4], or, more recently, the ability of dehydrated variants of $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb) and Prussian Blue analogs $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) to adsorb hydrogen was demonstrated [5]. The use of porous hexacyanometallates as materials for molecular electronics and compounds with potential catalytic activity was suggested, too [6]. Nevertheless, at present, cyanocomplexes are of primary interest as models for magnetism. Prussian blue and its analogs have long-range magnetic ordering [7], cobalt hexacyanoferrates exhibit photo-induced magnetism [8], and some Prussian blue analogs show spin glass behavior [9].

As a part of our wider study on syntheses, crystal structures, and properties of cyanocomplexes [1d, 10], we are also interested in hexacyanoferrates of various cations, which are also coordinated by chelating *N*-donor ligands in order to lower the connectivity of the cationic building block [11]. In this study, Cd(II) was chosen because it is known that this central atom enables a chelating as well as bridging bonding of 2(3)*N*-donor ligands [12]. Here we report the results of syntheses, spectroscopic and structural characterizations of $[\{Cd(en)\}_2\{Fe(CN)_6\}]$ and $[\{Cd(H_2O)(dien)\}_2\{Fe(CN)_6\}] \cdot 4H_2O$, which were isolated from the aqueous systems Cd(II)–L–$[Fe(CN)_6]^{3/4-}$ (L = *en*, *dien*).

2. Experimental

2.1. *Materials*

Cadmium(II) chloride penta-hemihydrate ($CdCl_2 \cdot 2.5H_2O$, Lachema), potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$, Merck), potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6] \cdot 3H_2O$, Merck), tetraethylammonium bromide ($(CH_3CH_2)_4NBr$, Merck), 1,2-diaminoethane ($C_2H_8N_2$, Aldrich), and 1,4,7-triazaheptane ($C_4N_3H_{13}$, Aldrich) in analytical grade were used as received.

2.2. *Synthesis and characterization*

2.2.1. $[\{Cd(en)\}_2\{Fe(CN)_6\}]$ (1). This product was prepared by two different procedures, a direct synthesis starting from the solution of $K_4[Fe(CN)_6]$ (section 2.2.1.1), and, unexpectedly, nevertheless reproducibly, from the solution of $K_3[Fe(CN)_6]$ (section 2.2.1.2).

2.2.1.1. *Synthesis of* **1A**. 0.18 cm^3 of 1,2-diaminoethane (3 mmol) and 5 cm^3 of a 0.1 mol aqueous solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.5 mmol) were successively, slowly, added to 10 cm^3 of a 0.1 mol aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1 mmol) acidified with one drop of concentrated hydrochloric acid (inhibition of hydrolysis). The colorless solution was filtered and left aside for crystallization. Colorless needles were formed overnight from the mother liquor. The formed crystals were filtered off, washed with a small portion of water, and dried in air. Yield: 40%.

2.2.1.2. *Synthesis of* **1B**. Crystals of better quality were formed unexpectedly for X-ray structure analyses by an alternative procedure: 0.3 cm^3 of 1,2-diaminoethane (5 mmol), 10 cm^3 of a 0.1 mol solution of [Et_4N]Br (1 mmol) and 10 cm^3 of a 0.1 mol aqueous solution of $K_3[Fe(CN)_6]$ (1 mmol) were successively, slowly, added to 10 cm^3 of a 0.1 mol aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1 mmol) acidified with one drop of concentrated hydrochloric acid (inhibition of hydrolysis). The resulting yellow solution was filtered and left aside for crystallization in sunlight. Within 24 h the mother liquor discolored and subsequently small colorless parallelepipeds suitable for X-ray analysis were obtained. The formed crystals were filtered off, washed with a small portion of water, and dried in air. Yield: 55%. Anal. for $C_{10}H_{16}Cd_2Fe_1N_{10}$ ($M = 556.98\ g\ mol^{-1}$); C 21.6 (Calcd 21.7); H 2.9 (3.0); N 25.1 (25.3); Cd 40.4 (41.0); Fe 10.1 (10.8)%. IR (vs = very strong, m = medium, w = weak, in cm^{-1}): $\nu(NH_2)$ 3324 m, 3272 m; $\nu(CH_2)$ 2972 w; ν(CN) 2056 vs; $\delta(NH_2)$ 1589 m; $\delta(CH_2)$ 1448 m; 1248 w; 1123 w; 1052 w; 967 m; 779 w; δ(Fe–CN) 589 w; ν(Fe–C) 419 m.

2.2.2. $[\{Cd(H_2O)(dien)\}_2\{Fe(CN)_6\}] \cdot 4H_2O$ (2).

0.33 cm^3 of 1,4,7-triazaheptane (*dien*, 3 mmol) and 5 cm^3 of a 0.1 M solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.5 mmol) were successively, slowly, added to 10 cm^3 of a 0.1 mol aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1 mmol). The obtained transparent solution was left for crystallization at room temperature. Colorless prismatic crystals formed after 1–3 days were filtered off, washed with a small amount of water, and dried in air (synthesis procedure of **2A**). Yield: 50%.

Crystals suitable for X-ray structure analyses were obtained by addition of 0.33 cm^3 of *dien* (3 mmol) and 10 cm^3 of 0.1 mol solution of $K_3[Fe(CN)_6]$ (1 mmol) to the mixture formed of 10 cm^3 of a 0.1 mol solution of [Et_4N]Br (1 mmol) and 10 cm^3 of a 0.1 mol aqueous solution of $CdCl_2 \cdot 2.5H_2O$ (1 mmol) (synthetic procedure **2B**). The resulting yellow solution was left aside for crystallization in sunlight. Within 24 h colorless crystals appeared in the discolored solution; they were collected by filtration, washed with water, and dried in air. Yield: 35%. Anal. for $C_7H_{19}CdFe_{0.5}N_6O_3$ ($M_r = 375.61\ g\ mol^{-1}$); C 22.4 (Calcd · 22.4); H 5.1 (5.1); N 22.4 (22.3); Cd 29.9 (30.3); Fe 7.4 (7.2)%. IR: ν(OH) 3564 bm; $\nu(NH_2)$ 3363 m, 3226 m, 3149 m; $\nu(CH_2)$ 2989 w, 2864 w; ν(CN) 2060 vs, 2043 s; $\delta(NH_2)$ 1595 m; $\delta(CH_2)$ 1495 m, 1250 w, 1140 m, 1096 m, 937 m, 880 w; δ(Fe–CN) 591 w, 439 w; ν(Fe–C) 414 m, 205 w.

2.3. *X-ray crystal structure determinations*

Diffraction data were collected at 193(2) K on a Stoe IPDS II area detector system equipped with a graphite monochromator using Mo-Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using 11728 (**1**) and 4247 (**2**) reflections. For the integration of data of **2**, which crystallized as a (1 0 0) reflection twin, the "Twin integration" option of the Stoe X-Area 1.28c program was used [13]. No instrument or crystal instability during data collections was observed. A numerical absorption correction (Gaussian type), based on the indexed crystal faces, was applied in both cases. The structures were solved by direct methods using SHELXTL5 [14] and refined against F^2 data using full-matrix least squares. For twinned structure **2**, the structure was solved using a data set integrated with the orientation matrix of individual 1 only.

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

	1	**2**
Empirical formula	$C_{10}H_{16}Cd_2FeN_{10}$	$C_{14}H_{38}Cd_2Fe_1N_{12}O_6$
Formula weight	556.98	751.22
Temperature (K)	153(2)	193(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
Unit cell dimensions (Å, °)		
a	13.8850(13)	7.7510(9)
b	11.5213(9)	7.9050(11)
c	9.7506(8)	23.169(2)
β		107.948(8)
Volume (Å^3), *Z*	1559.8(2), 4	1350.5(3), 2
Calculated density (mg m^{-3})	2.372	1.847
Absorption coefficient (mm^{-1})	3.634	2.142
F(000)	1072	752
Crystal size (mm^3)	$0.13 \times 0.08 \times 0.05$	$0.15 \times 0.10 \times 0.10$
θ range for data collection (°)	2.93–29.22	2.74–29.00
Limiting indices	$-18 \le h \le 19$; $-15 \le k \le 15$; $-13 \le l \le 13$	$-10 \le h \le 10$; $0 \le k \le 10$; $0 \le l \le 31$
Reflections collected/unique	14009/2106 [*R*(int) = 0.0287]	3516/3516 [twin corr.]
Completeness to $\theta = 29.22$ (%)	99.4	98.1
Absorption correction	Numerical	Numerical
Max. and min. transmission	0.862 and 0. 676	0.814 and 0.739
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2 after twin treatment
Data/restraints/parameters	2106/0/107	3516/6/194
Goodness-of-fit on F^2	1.043	1.051
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0232$, $wR_2 = 0.0431$	$R_1 = 0.0493$, $wR_2 = 0.1428$
R indices (all data)	$R_1 = 0.0404$, $wR_2 = 0.0467$	$R_1 = 0.0531$, $wR_2 = 0.1453$
Largest difference peak and hole (e Å^{-3})	0.416 and −0.387	2.554 and −1.151

Then, twin refinement (HKLF 5 option of SHELXL) with all data was performed. As in this mode the merging of equivalent reflections is switched off, leading to unrealistic standard uncertainties, for the final cycles the contributions of structure factors of individual 2 were subtracted according to the refined twin ratio. Then, "normal" refinement using merged data could be performed. Due to the twinning with the strong overlap of reflections of the two twin domains, the quality of results is reduced for **2**. Non-H atoms were treated anisotropically. Hydrogens in both structures were obtained from difference Fourier maps but included "riding" on idealized positions with isotropic displacement parameters taken as 1.2 times the U_{eq} value of the corresponding bonding partner. The crystal and experimental data for both compounds are displayed in table 1 and selected geometric parameters are gathered in table 2. Possible hydrogen bonds (HBs) were calculated using the program PARST [15] and are displayed in table 3. The figures were drawn with DIAMOND [16].

2.4. *Physical methods*

Elemental analyses (C, H, and N) were measured on a Perkin Elmer CHN 2400 Elemental Analyzer. Metal contents were estimated on a Varian Spectr AA–30

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

1		**2**	
Cd–N1	2.303(2)	Cd–N2	2.250(4)
Cd–N2	2.262(2)	Cd–N3	2.306(5)
Cd–N3	2.279(2)	Cd–N4	2.320(4)
Cd–N4	2.364(2)	Cd–N5	2.369(4)
Cd–N5^{i}	2.298(2)	Cd–N6	2.339(5)
Fe–C1	1.931(2)	Cd–O3	2.614(4)
Fe–C2^{ii}	1.907(2)	Fe1–C1	1.922(5)
Fe–C3^{ii}	1.925(2)	Fe1–C2	1.910(5)
C4–N4–Cd	117.8(2)	Fe1–C3^{ix}	1.920(5)
C1–N1–Cd	159.8(2)	C2–N2–Cd	145.9(4)
C2^{iii}–N2–Cd	146.9(2)	N2–Cd–N3	101.68(17)
		N2–Cd—N6	162.85(17)
		N4–Cd–N5	171.54(15)
		N6–Cd–N5	76.51(15)
		N4–C4–C7^{x}–N5^{x}	172.710(6)

Symmetry transformations used to generate equivalent atoms: $^{i}1/2-x, -1/2-y, z$; $^{ii}-x, -y, 2-z$; $^{iii}1/2+x, y, 3/2-z$; $^{ix}-1+x, y, z$; $^{x}x, -1+y, z$.

Table 3. Possible hydrogen bonds for **2** (Å, °).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O3–H103···O1^{xii}	0.85(2)	1.90(3)	2.723(6)	161(7)
O3–H203···O2^{xvi}	0.85(2)	1.99(3)	2.788(6)	156(7)
O3–H203···N6	0.85(2)	2.61(6)	3.140(6)	121(6)
N6–H6A···O1	0.79(8)	2.31(8)	3.038(7)	152(7)
N6–H6B···O2^{xvi}	0.90(8)	2.29(7)	3.075(7)	145(6)
O2–H101···O3^{xvii}	0.86(2)	1.96(3)	2.798(6)	165(10)
O2–H202···N1^{xviii}	0.85(2)	2.10(6)	2.821(7)	141(8)
O1–H101···N3	0.85(2)	2.53(8)	3.132(7)	129(8)
O2–H201···N1^{xix}	0.85(2)	2.10(5)	2.882(7)	152(9)

Notes: Symmetry transformations used to generate equivalent atoms: $^{xii}-1+x, y, z$; $^{xvi}1-x, -1/2+y, 1/2-z$; $^{xvii}1+x, y, z$; $^{xviii}-x, 1-y, -z$; $^{xix}-x, -y, -z$.

spectrometer after the mineralization of the samples in aqua regia. Infrared spectra were recorded on a Bruker IFS88 Spectrometer using KBr pellets (4000–400 cm^{-1}) or in a nujol suspension (600–200 cm^{-1}). Electronic spectra were taken on a Specord 250 Spectrometer (300–600 nm) in an aqueous solution. Mössbauer spectra were obtained on a constant acceleration spectrometer with a source of ^{57}Co in a rhodium matrix. Calibration was made with a metallic iron foil at room temperature. The least-squares program MOSFIN [17] was used to fit the Mössbauer parameters and to determine their standard deviations of statistical origin (given in parentheses). TG and DTA curves were taken on an Exstar 6200 (Seiko Instruments) thermal analyzer from 25°C to 250°C with a heating rate of 2.5°C min^{-1} in nitrogen using Pt crucibles. The weight of the sample was 63.176 mg for **2**. Powder diffraction measurements of polycrystalline **1** and **2** were measured on Philips X'Pert using Mo-Kα radiation. The theoretical diagrams of both complexes were calculated using the programs X'Pert Plus and Powder Cell [18].

3. Results and discussion

3.1. *Preparation and identification*

From the system Cd(II), *en*, $[Fe(CN)_6]^{4-}$ (section 2.2.1.1) we isolated $[\{Cd(en)\}_2\{Fe(CN)_6\}]$ (**1**) which was further characterized by chemical analysis and spectroscopic methods. During our study of the system $[Et_4N]^+$, Cd(II), *en*, $[Fe(CN)_6]^{3-}$, the same complex (**1**) was formed if the mother liquor was irradiated by sunlight (section 2.2.1.2). $[Et_4N]Br$ was added to the mother liquor to balance the different charges of Cd^{2+} and $[Fe(CN)_6]^{3-}$ anion. The possibility of reduction of a solution containing $[Fe(CN)_6]^{3-}$ yielding $[Fe(CN)_6]^{4-}$ upon irradiation was indicated by Rader *et al*. [19]. In order to obtain a better insight on the synthesis procedures, we measured the electronic spectra of the mother liquors used for the syntheses as well as of the aqueous solutions containing $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, respectively (figure 1).

Aqueous solution containing $[Fe(CN)_6]^{3-}$ displays an absorption in the visible region with a maximum centered at 423 nm (spectrum a) which can be attributed to a CT band (reported at 425 nm) [20]. From the same figure it can be seen that the solution containing the $[Fe(CN)_6]^{4-}$ anion does not produce an absorption peak in this region (spectrum b). Spectrum c corresponds to the mother liquor used for the direct synthesis of **1A** (section 2.2.1.1), corroborating the presence of $[Fe(CN)_6]^{4-}$. The spectra d and e arise from the mother liquors used for the synthesis of **1B**, one kept in dark (d) and the second kept in dark and warm (40°C) (spectrum e); these spectra confirm the presence of $[Fe(CN)_6]^{3-}$ and do not suggest significant reduction. Spectrum f taken from the

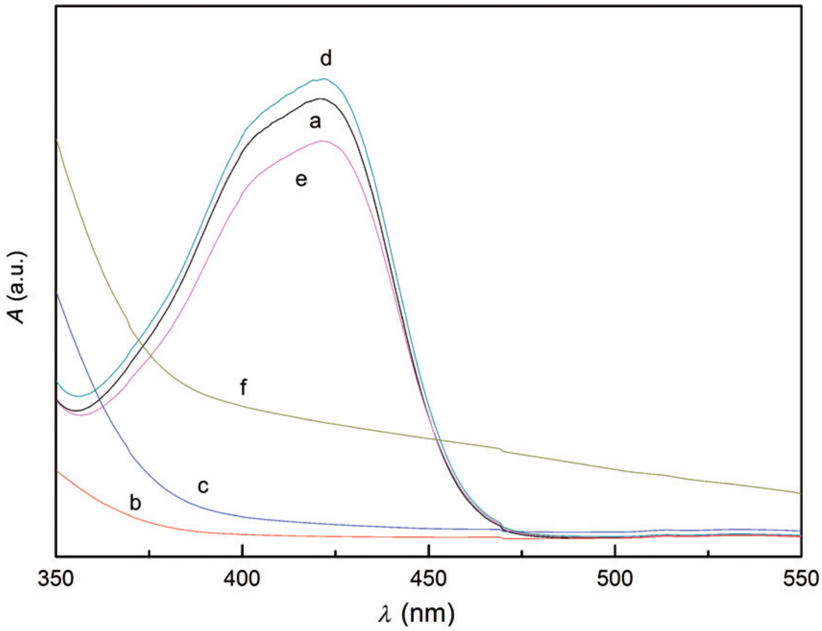

Figure 1. Electronic spectra of: (a) aqueous solution of $[Fe(CN)_6]^{3-}$; (b) aqueous solution of $[Fe(CN)_6]^{4-}$; (c) mother liquor used in procedure **1A**; (d) mother liquor used in procedure **1B**, kept in dark; (e) mother liquor used in procedure **1B**, kept in dark and warm (40°C); (f) mother liquor used in procedure **1B**, irradiated by sunlight. All spectra were taken 24 h after mixing the initial solutions.

mother liquor used for the synthesis of **1B** and irradiated by sunlight indicates that reduction leading to the formation of $[Fe(CN)_6]^{4-}$ occurred during the crystallization process. These results support our assumption that during the synthesis of **1B** the reduction of $[Fe(CN)_6]^{3-}$ anions occurs.

Our previous synthesis experiments with Cd(II), *en*, $[Fe(CN)_6]^{3-}$, when the formed mother liquors were kept in the dark, led to the formation of three complexes: $(Et_4N)\{[Cd(en)]_4[Fe(CN)_6]_3\}$ (**3**) [21], $(Et_4N)[Cd(en)_2Fe(CN)_6] \cdot 4H_2O$ (**4**) [22], and $[\{Cd(en)\}_3\{Fe(CN)_6\}_2] \cdot 4H_2O$ (**5**) [23]. Complex **3** was crystallized at room temperature from the same mother liquor used in the synthesis of **1B**. From the same mother liquor left for crystallization at lower temperature (11–13°C), we separated a few crystals of **4** only once [22]. Finally, replacing $[Et_4N]^+$ by the more voluminous $[Pr_4N]^+$ and $[Bu_4N]^+$ organic cations, respectively, and keeping the same crystallization conditions as in the case of **3**, led to the formation of **5** exhibiting a polymeric structure which did not incorporate the voluminous organic cations.

From Cd(II), *dien*, $[Fe(CN)_6]^{4-}$ it was possible to isolate $[\{Cd(H_2O)(dien)\}_2\{Fe(CN)_6\}] \cdot 4H_2O$ (**2**) (synthesis of **2A**), but the formed crystals were of bad quality. X-ray quality crystals were formed from the solution containing $[Fe(CN)_6]^{3-}$ as the initial reactant, which was left for crystallization in a sunny place (synthesis of **2B**). The last remark concerning the synthesis experiments is that the synthesis procedures leading to **2** were insensitive to the Cd : *dien* molar ratios within the range from 1 : 1 to 1 : 6.

The homogeneity of the microcrystalline powder of both the compounds was confirmed by the measurement of XRPD. The calculated diffraction patterns are in good agreement with the experimental ones (Supplementary material).

3.2. *Spectroscopic characterization*

The most characteristic absorption bands in the infrared spectra of both **1** and **2** are those arising from ν(CN). The IR spectrum of $K_4[Fe(CN)_6] \cdot 3H_2O$ displays one absorption band at $2044\,cm^{-1}$ [24]. In the IR spectrum of **1**, one absorption occurs at $2056\,cm^{-1}$, while in the IR spectrum of **2**, two absorptions at 2060 and $2043\,cm^{-1}$ were observed. The observed positions of these bands indicate the presence of bridging cyano ligands in **1** and both bridging and terminal cyano ligands in **2**. These assignments were confirmed by the results of X-ray structure analyses of both the complexes.

Mössbauer spectra of both the compounds were measured at room temperature (Supplementary material). Both spectra exhibit one narrow singlet with the Γ values of $0.302(4)\,mm\,s^{-1}$ for **1** and $0.278(3)\,mm\,s^{-1}$ for **2**. The corresponding values of isomer shifts (δ) are $-0.083(1)\,mm\,s^{-1}$ (**1**) and $-0.096(1)\,mm\,s^{-1}$ (**2**). These parameters are characteristic for a t_{2g}^6, low spin, configuration of Fe(II), e.g., in $CdK_2[Fe(CN)_6] \cdot xH_2O$ and in $Mn_2[Fe(CN)_6] \cdot 8H_2O$ similar values of δ ($-0.097\,mm\,s^{-1}$ and $-0.076\,mm\,s^{-1}$, respectively) were observed [25].

3.3. *Crystal structure*

In the structure of **1,** the Cd(II) is pentacoordinate by five nitrogens, two from two bridging *en* ligands, and three from bridging cyano. On the basis of the τ value

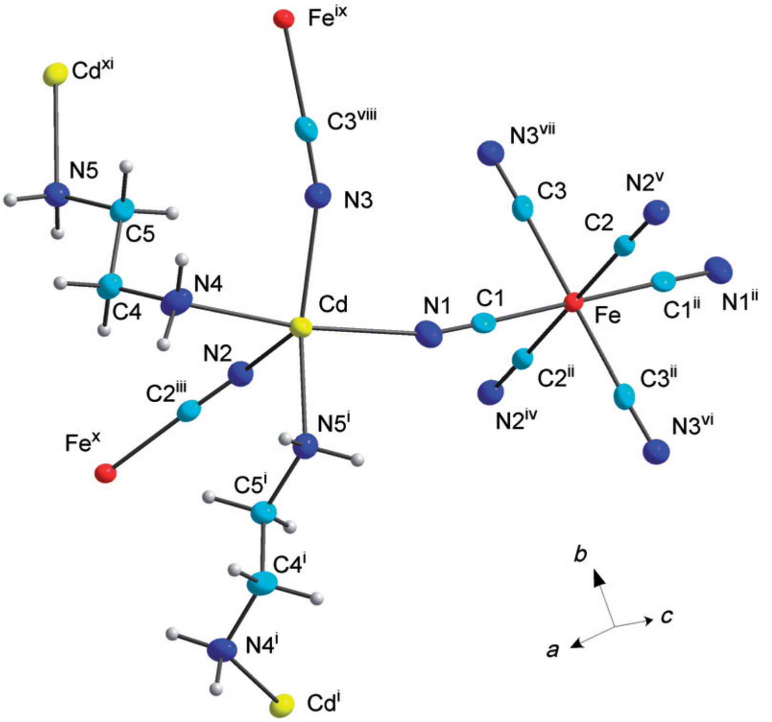

Figure 2. A view of the coordination modes of Cd and Fe in **1** along with atom numbering scheme. The ellipsoids are drawn at 70% probability. Symmetry codes: $^{i}1/2-x, -1/2-y, z$; $^{ii}-x, -y, 2-z$; $^{iii}1/2+x, y, 3/2-z$; $^{iv}1/2-x, -y, 1/2+z$; $^{v}-1/2+x, y, 3/2-z$; $^{vi}-x, -1/2+y, 3/2-z$; $^{vii}x, 1/2-y, 1/2+z$; $^{viii}x, 1/2-y, -1/2+z$; $^{ix}-x, 1/2+y, 3/2-z$; $^{x}1/2-x, -y, -1/2+z$; $^{xi}1/2-x, 1/2+y, z$.

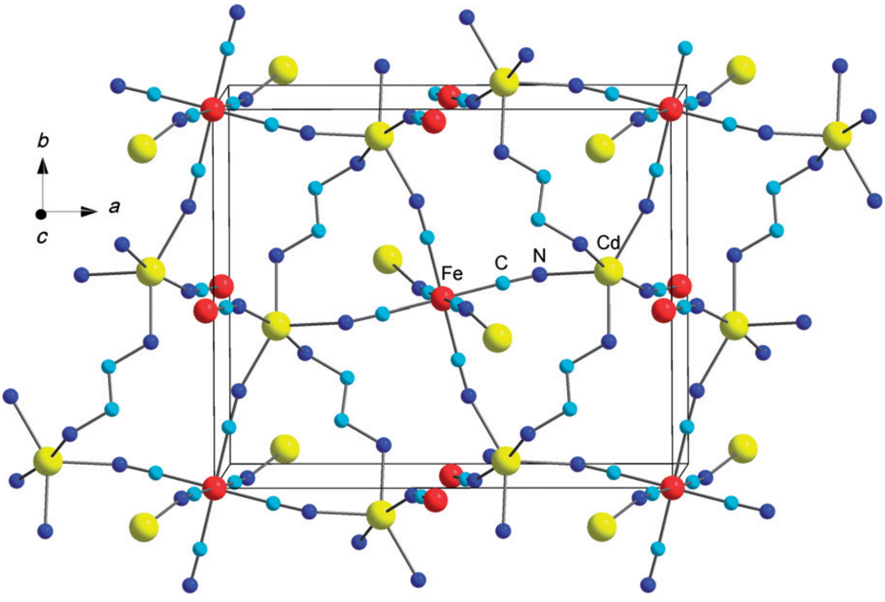

Figure 3. Projection of the crystal structure of **1** along the [0 0 1] direction. The hydrogens have been omitted for clarity.

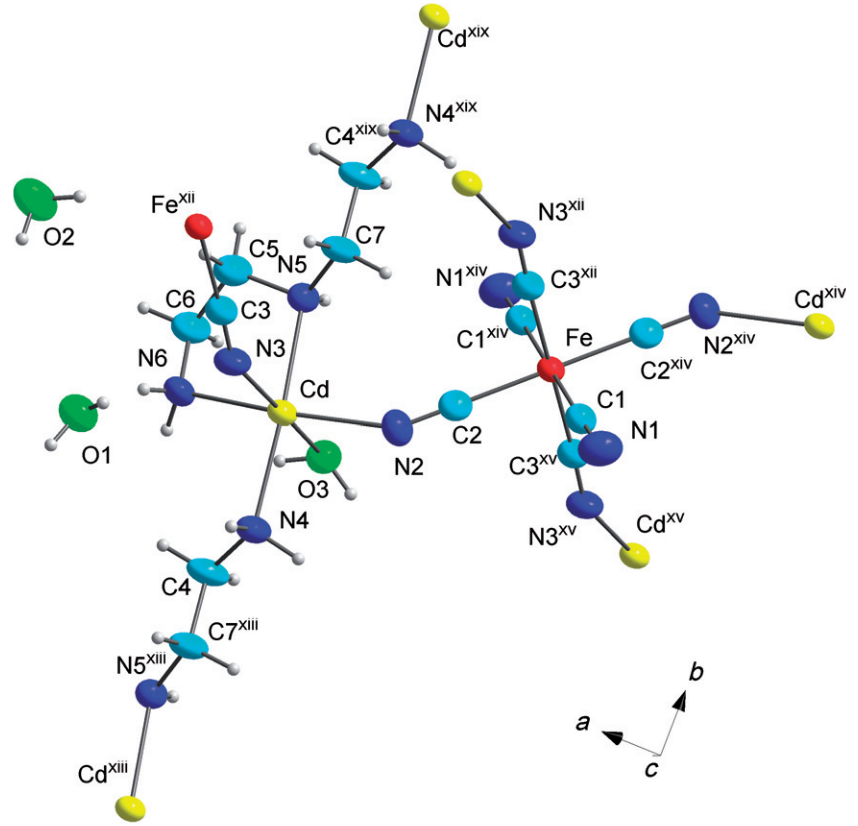

Figure 4. A part of the crystal structure of **2** with atom numbering scheme. Displacement ellipsoids were drawn at 50% probability. Symmetry codes: $^{xii}-x+1, y, z$; $^{xiii}x, -1+y, z$; $^{xiv}-1-x, 1-y, -z$; $^{xv}-1+x, y, z$; $^{xix}x, y+1, z$.

($\tau = 43.6\%$) defined by Addison *et al.* [26], the coordination polyhedron around the Cd(II) atom can be described as an intermediate between tetragonal pyramidal and trigonal bipyramidal (figure 2). Pentacoordination of Cd(II) is not very common but has been observed, e.g., in $[Cd_2(en)_4(\mu\text{-}en)]^{4+}$ [27]. Only a few compounds with bridging *en* linking two Cd(II) atoms have been structurally characterized, e.g., $[Cd(en)(debt)_2] \cdot 2H_2O$ (*debt* = diethylbarbiturate) or a clathrate $[Cd_2(en)_2(\mu_2\text{-}en)Ni_2(CN)_2(\mu_2\text{-}CN)_6] \cdot 4C_6H_5OH$ [28, 29]. The Fe(II) lies in the center of symmetry (4b) and is coordinated by six carbons from bridging cyanide in a slightly compressed octahedron (figure 2, table 2). The geometric parameters associated with the anion are similar to those for $[Cd\{tet\}]_2[Fe(CN)_6] \cdot 3H_2O$ and $[Ni(dien)_2]_2[Fe(CN)_6] \cdot 4H_2O$ [30].

The Fe(II) and Cd(II) (atomic ratio 1 : 2) in **1** are linked by bridging μ_2-CN yielding a 3-D structure (figure 3). The bridging *en* ligands which link the neighboring Cd (figure 2) do not enhance the dimensionality of the structure, as the corresponding Cd atoms are already bridged by a –NC–Fe–CN– unit. An analogous scaffold-like 3-D structure with connectivity of the building entities (3 *vs.* 6) and coordination numbers of the respective central atoms (5 and 6 for Cu(II) and Fe(III), respectively) was found in the cationic part of the structure of $[\{Cu(chda)\}_6\{Fe(CN)_6\}_3][Fe(CN)_6] \cdot 12H_2O$

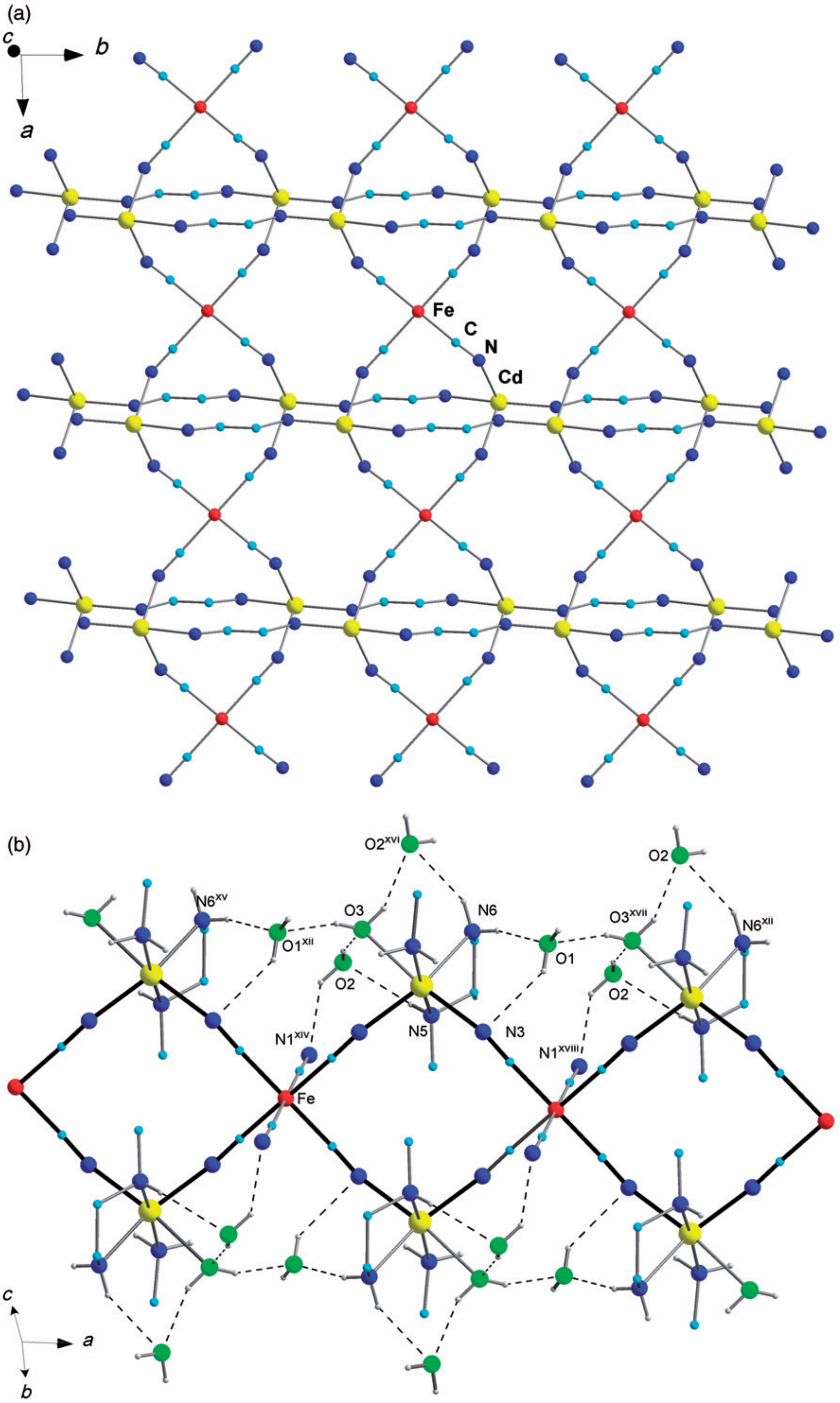

Figure 5. (a). A view on the structure of **2** displaying the linking of 2,4 ribbon-like structural motifs *via* bridging *dien* into layers. Atoms not participating in the propagation of the structure were omitted for the sake of clarity. (b). A 2,4-ribbon-like structural motif and the system of hydrogen bonds in **2**. The hydrogens not connected to hydrogen bonds have been omitted for clarity. Symmetry codes: $^{\text{xii}}-x+1, y, z$; $^{\text{xiv}}-1-x, 1-y, -z$; $^{\text{xv}}-1+x, y, z$; $^{\text{xvi}}1-x, -1/2+y, 1/2-z$; $^{\text{xvii}}1+x, y, z$; $^{\text{xviii}}-x, 1-y, -z$.

(*chda* = *cis*-cyclohexane-1,2-diamine). The difference is represented by the bonding mode of the amine ligand *chda* which in the Cu–Fe complex is a chelate [31].

In the crystal structure of **2** the Cd(II) is coordinated as a distorted octahedron CdN_5O. Two coordination sites are occupied by the *N*-bonded bridging cyano groups and one by water. The remaining three coordination sites are occupied by two crystallographically independent *dien* molecules in the ratio of 2 : 1, which means that the *dien* ligand is tridentate linking to two Cd(II) atoms; to one Cd(II) it is a chelate and to the other Cd(II) it is coordinated by nitrogen from the remaining ethylamine arm (figure 4). The N–C–C–N conformations of the chelate part of *dien* are *gauche* to facilitate the bonding of the N-sites to the metal ions, and both conformations (δ and λ) are present in the structure. In contrast, the bridging $N4–C4–C7^{xiii}–N5^{xiii}$ (xiii: $x, y-1, z$) moiety in **2** is in the *anti* conformation (table 2). A similar chelate-bridging mode of the coordination of *dien* is rare but was observed, e.g., in $[(\mu_2\text{-}dien)Hg_2(dien)_2](ClO_4)_4$ [32]. Nevertheless, the present structure represents the first example of such coordination of *dien* in a Cd(II) complex. The geometric parameters associated with the cationic part of the structure are similar to those found in other Cd-dien compounds, e.g., in $[Cd(dien)_2](NO_3)_2$ [33–35]. The Fe(II) in **2** is octahedrally coordinated by six carbons, two from terminal cyanoligands, while the remaining four are from bridging cyanoligands. The Fe–C bond lengths are similar to those found in trinuclear $[\{Cu(tren)_2\}_2Fe(CN)_6] \cdot 12H_2O$ (*tren* = (tris(2-aminoethyl)amine-N,N′,N″,N‴) [36].

The presence of bridging cyanide linking Cd(II) and Fe(II) (atomic ratio 2 : 1) forms a 2,4-ribbon structural motif (2 and 4 denote the respective connectivities of the cationic and anionic building blocks), which propagates along the *a* axis (figure 5a). The same 2,4-ribbon structural motif was found in $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [37]. Neighboring ribbons are linked in the [0 1 0] direction by a bridging *dien* yielding a covalently bound 2-D structure (figure 5a). There are two crystallographically independent water molecules in **2** per formula unit. These are connected to the aqua ligand by O–H $\cdots$ O hydrogen bonds and to *dien* by N–H $\cdots$ O. Hydrogen bonds O–H $\cdots$ N(C) are also present (figure 5b, table 3).

Because **2** contains coordinated water and water of crystallization, dehydration was checked by thermal analysis. The TG and DTA curves are displayed in the "Supplementary material". Dehydration starts at 53°C. The DTA curve indicates that dehydration is a single-step endothermic process with a minimum temperature of 92°C. The observed weight loss (14.2%) up to 100°C corresponds well to the removal of six water molecules from the formula unit (Calcd 14.4%).

4. Conclusion

Two new heterobimetallic Cd-Fe coordination compounds, $[\{Cd(en)\}_2\{Fe(CN)_6\}]$ (**1**) and $[\{Cd(H_2O)(dien)\}_2\{Fe(CN)_6\}] \cdot 4H_2O$ (**2**), have been prepared from the systems Cd(II), L, $[Fe(CN)_6]^{4-}$ and characterized by chemical analyses, IR, and Mössbauer spectroscopy. The same products were also isolated from Cd(II), L, $[Fe(CN)_6]^{3-}$ after irradiation by sunlight. Polymeric character of both crystal structures, 3-D in **1** and 2-D in **2**, are the consequence of the bridging character of the cyano ligands as well as the presence of bridging *en* in **1** and bridging-chelating character of tridentate *dien* in **2**.

Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 716353 and 716354. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

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