

Crystal Structure of Hexacyanoferrato(III)bis(μ -cyano){1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}copper(II) Hexacyanoferrato(III)- μ -cyano-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}cuprate(II) Tetradecahydrate

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The crystal structure of hexacyanoferrato(III)bis(μ -cyano){1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}copper(II) hexacyanoferrato(III)- μ -cyano-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}cuprate(II) tetradecahydrate consists of trinuclear cations and dinuclear anions whose copper atoms show square pyramidal and iron atoms octahedral coordination. The cations and anions are linked by hydrogen bonds involving 14 lattice water molecules in a network architecture. Crystals of the $C_{51}H_{82}Cu_3Fe_2N_{30}O_{17}$ belong to the triclinic $P\bar{1}$ space group [$a = 13.700(2)$, $b = 13.881(2)$, $c = 21.431(3)$ Å; $\alpha = 76.96(1)$, $\beta = 83.07(1)$, $\gamma = 74.70(1)^\circ$].

INTRODUCTION

The family of hexacyanometallate complexes represents a class of building-block reagents that are used in the synthesis of molecular-based magnets.¹ Of this family, the hexacyanoferrates have been most extensively documented. The other reactant assembled with this »Prussian blue« building block is invariably a transition metal complex that has either vacant or available coordination sites, as exemplified by the manganese-Schiff base complexes;² recently, lanthanum complexes have been used for this purpose.³ Following out interest in the chemistry of copper(II)-imidazole complexes,⁴ we have used the {1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]pro-

pan-2-ol}copper(II) dication⁵ to bind to the hexacyanoferrate(III) to afford the title compound, which was isolated as a hydrate.

EXPERIMENTAL

The Schiff-base, 1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol, was synthesized by the condensation of 1,3-diamino-2-propanol with 4-methylimidazolyl-5-aldehyde; the ligand was reacted with copper perchlorate to furnish {1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}copper diperchlorate.⁵ To the solution of the compound (1 mmol, 0.57 g) in methanol (10 mL), an aqueous solution of potassium ferricyanide hydrate (0.30 g, 1 mmol)

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was added dropwise. The green solution was filtered; prism-shaped crystals were separated from the solution when it was set aside.

The room-temperature diffraction measurements were performed on a Siemens R3m diffractometer,⁶ and the data were corrected for absorption effects by using a set of Ψ -scans.⁷ The structure was solved by direct methods and it was refined on F^2 (Ref. 8). The hydrogen atoms of the water molecules were not located; they were placed in cal-

TABLE I. Crystal data, data collection and refinement for $[(C_{13}H_{18}N_6O)_2Cu_2 \cdot Fe(CN)_6][(C_{13}H_{18}N_6O)Cu \cdot Fe(CN)_6] \cdot 14H_2O$

Crystal data	
Empirical formula	$C_{51}H_{82}Cu_3Fe_2N_{30}O_{17}$
M_r	1689.79
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell parameters ^(a)	
$a / \text{\AA}$	13.700(2)
$b / \text{\AA}$	13.881(2)
$c / \text{\AA}$	21.431(3)
$\alpha / ^\circ$	76.96(1)
$\beta / ^\circ$	83.07(1)
$\gamma / ^\circ$	74.70(1)
$V / \text{\AA}^3$	3821.6(9)
Z	2
$D_x / \text{Mg m}^{-3}$	1.468
Radiation	Mo-K α
μ / mm^{-1}	1.272
T / K	298
Crystal shape, colour	prism, green
Crystal size / mm	$0.38 \times 0.21 \times 0.14$
Data collection	
Diffractometer	Siemens R3m
Scan mode	ω
Absorption correction	empiric (Ψ scans)
Transmission; min., max.	0.644, 0.842
Reflections measured	12639
Independent reflections	12639
Reflections observed with $I > 2\sigma(I)$	9796
$\theta_{\text{max}} / ^\circ$	25
h, k, l limits	$-16 \rightarrow 16, -15 \rightarrow 16, 0 \rightarrow 25$
Refinement ^(b)	
$R [F^2 > 2\sigma(F^2)], wR (F^2)$	0.064, 0.192
Goodness-of-fit, S	1.06
Max. shift / error ratio, $(\Delta / \sigma)_{\text{max}}$	< 0.001
Residual electron density, $(\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}) / e \text{\AA}^{-3}$	1.10, -0.83
No. of parameters refined	937

^(a) Cell parameters from 25 reflections in θ range 7 to 15°.

^(b) Refinement on F^2 . Weighing scheme:

$$w = 1/[\sigma^2(F_o^2) + (0.1347P)^2 + 3.5987P] \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

H-atom parameters constrained.

culated positions by the HYDROGEN option⁹ in the WinGX suite.¹⁰ The structure was refined to $R = 0.064$. Crystallographic details are given in the Tables I and II. The structure is depicted as a 50 % probability ORTEP¹¹ in Figures 1a and 1b.

RESULTS AND DISCUSSION

The reaction of the {1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}copper(II) dication and the hexacyanoferrate(III) trianion affords the hexacyanoferrato(III)bis(μ -cyano){1,3-bis[(4-methyl-5-imidazol-1-

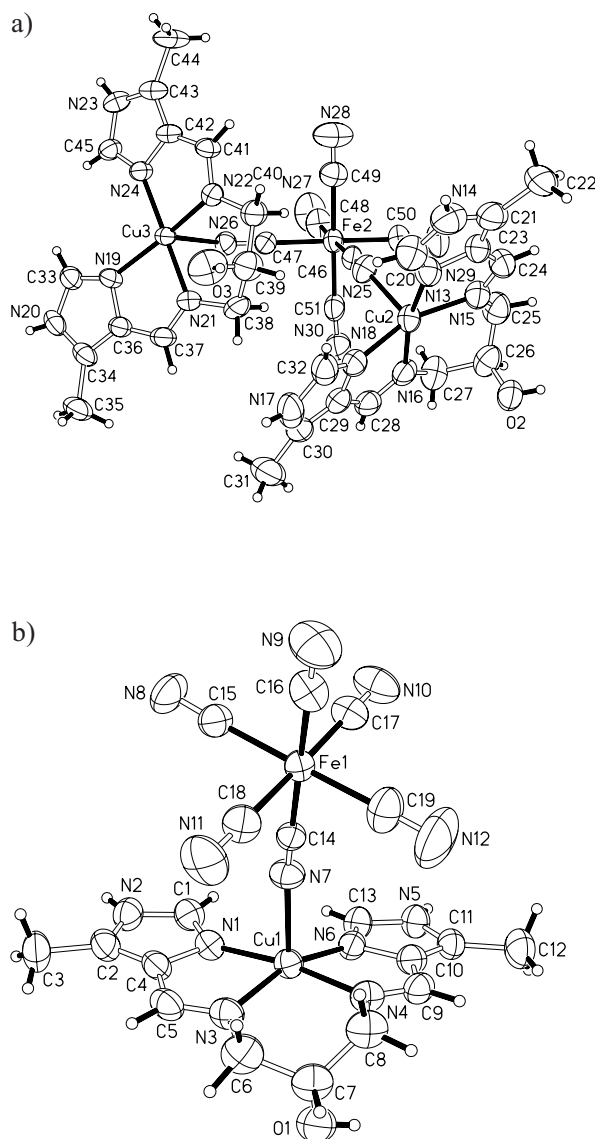


Figure 1. (a) ORTEP of the trinuclear hexacyanoferrato-bis(μ -cyano)-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}-copper cation and (b) ORTEP of the dinuclear hexacyanoferrato- μ -cyano-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}cuprate anion of hexacyanoferrato-bis(μ -cyano){1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}copper hexacyanoferrato- μ -cyano-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}cuprate tetradecahydrate.

TABLE II. Selected bond distances/Å and angles/°

Cation					
Cu2–N13	2.007(5)	N13–Cu2–N15	81.9(2)	N15–Cu2–N16	93.0(2)
Cu2–N15	2.009(5)	N13–Cu2–N16	166.7(2)	N15–Cu2–N25	96.2(2)
Cu2–N16	2.010(5)	N13–Cu2–N18	99.1(2)	N16–Cu2–N18	81.6(2)
Cu2–N18	2.000(5)	N13–Cu2–N25	102.5(2)	N16–Cu2–N25	90.2(2)
Cu2–N25	2.180(5)	N15–Cu2–N18	160.3(2)	N18–Cu2–N25	102.7(2)
Cu3–N19	2.003(4)	N19–Cu3–N21	82.0(2)	N21–Cu3–N24	172.6(2)
Cu3–N21	2.000(4)	N19–Cu3–N22	163.8(2)	N21–Cu3–N26	87.5(2)
Cu3–N22	2.022(4)	N19–Cu3–N24	100.4(2)	N22–Cu3–N24	82.4(2)
Cu3–N24	1.987(4)	N19–Cu3–N26	106.6(2)	N22–Cu3–N26	88.6(2)
Cu3–N26	2.310(5)	N21–Cu3–N22	93.3(2)	N24–Cu3–N26	98.4(2)
Fe2–C46	1.941(6)				
Fe2–C47	1.962(5)				
Fe2–C48	1.938(6)				
Fe2–C49	1.943(7)				
Fe2–C50	1.940(6)				
Fe2–C51	1.961(6)				
Anion					
Cu1–N1	2.017(4)	N1–Cu1–N3	82.2(2)	N3–Cu1–N6	160.9(2)
Cu1–N3	2.011(4)	N1–Cu1–N6	101.2(2)	N3–Cu1–N7	94.3(2)
Cu1–N4	2.000(4)	N1–Cu1–N7	96.0(2)	N4–Cu1–N6	81.7(2)
Cu1–N6	2.018(4)	N1–Cu1–N4	171.7(2)	N4–Cu1–N7	90.8(2)
Cu1–N7	2.211(4)	N3–Cu1–N4	92.5(2)	N6–Cu1–N7	104.0(2)
Fe1–C14	1.946(5)				
Fe1–C15	1.947(6)				
Fe1–C16	1.953(5)				
Fe1–C17	1.943(5)				
Fe1–C18	1.934(6)				
Fe1–C19	1.931(6)				

yl)ethylideneamino]propan-2-ol}copper(II) hexacyanoferrato(III)- μ -cyano-{1,3-bis[(4-methyl-5-imidazol-1-yl)ethylideneamino]propan-2-ol}cuprate(II) ion pair (Figure 1), which crystallizes with 14 water molecules. The cation and the anion are held by extensive hydrogen bonding interactions that involve the 14 water molecules to furnish a three-dimensional network structure. The cation is made up of two $(C_{13}H_{18}N_6O)Cu$ entities linked through the $-CN$ unit of $[Fe(CN)_6]^{3-}$ to form a trinuclear species (Figure 1a). The copper atom shows square-pyramidal coordination, and the copper-nitrogen bond lengths in the basal plane are approximately 2.00 Å, which compares well with typical distances found in the imidazole-containing complexes of copper. The bond distances fall into a fairly narrow range (1.980(3) to 1.999(3) Å).^{4,5} The apical copper-nitrogen (CN) bonds are somewhat longer; one is significantly longer than the other (2.310(5), 2.180(5) Å), which suggests that the coordination of one $(C_{13}H_{18}N_6O)Cu$ entity decreases the Lewis acidity of the central $[Fe(CN)_6]^{3-}$ entity. The negatively-charged counter-

ion consists of the 1/1 adduct, $(C_{13}H_{18}N_6O)Cu-Fe(CN)_6$, whose copper atom also shows square-pyramidal coordination. The copper-nitrogen (CN) distance (2.211(4) Å) is intermediate between the two corresponding lengths in the cation. In the cation, the Cu2 atom is 89.7 % displaced along the Berry pseudorotation pathway; the displacement parallels the 0.282(2) Å distance between the atom and the basal plane of the square pyramid. The Cu3 atom is 85.1 % displaced along this pathway, and its displacement from the corresponding basal plane is 0.200(2) Å. There are no important contacts that could raise the coordination number beyond five for both atoms.

Copper hexacyanoferrates that have been crystallographically characterized are limited to bis[tris(2-aminoethyl)aminecopper] hexacyanoferrate(II), which crystallizes with 12 water molecules,¹² hexakis[tris(2-pyridylmethyl)aminecopper hexacyanoferrate(II)] octaperchlorate, which crystallizes with 3 water molecules¹³ and tris(diethylenetriaminecopper) bis[hexacyanoferrate(III)] hexahydrate,¹⁴ and a 1,4,8,11-tetraazacyclotetradecane

hexacyanoferrate(III) complex that incorporates potassium, from the starting reagent, in the crystal structure.¹⁵ The bis[tris(2-aminoethyl)aminecopper] hexacyanoferrate(II) packs as a centrosymmetric molecular unit. The tris(diethylenetriaminecopper) bis[hexacyanoferrate(III)] exists as $[(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2\text{Cu})_2 \cdot \text{Fe}(\text{CN})_6]^{+}$ $[(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2\text{Cu} \cdot \text{H}_2\text{O}) \cdot \text{Fe}(\text{CN})_6]^{-}$. The diethylenetriamine ligand binds to the copper atom through three nitrogen atoms, and this feature allows the cyanide bridges to furnish a chain motif. The apical position of the square pyramid around the copper atom in the anion is occupied by a coordinated water molecule.

Supplementary Materials. – The crystallographic-information-file has been deposited with the Cambridge Crystallographic Database Centre as CCDC 170172. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EK, UK; fax: +441223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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SAŽETAK

Kristalna struktura heksacianoferato(III)bis(μ -cyano){1,3-bis-[(4-metil-5-imidazol-1-il)etilidenamino]propan-2-ol} bakrova(II) heksacianoferato(III)- μ -cyano-{(1,3-bis[4-metil-5-imidazol-1-il)-etilidenamino]propan-2-ol}kuprata(II) tetradekahidrata

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Kristalna struktura heksacianoferato(III)bis(μ -cyano){1,3-bis[(4-metil-5-imidazol-1-il)etilidenamino]propan-2-ol}bakrova(II) heksacianoferato(III)- μ -cyano-{1,3-bis[4-metil-5-imidazol-1-il)etilidenamino]propan-2-ol}kuprata(II) tetradekahidrata sastoji se od trinuklearnih kationa i dinuklearnih aniona čiji bakrovi atomi pokazuju kvadratno-piramidnu, a atomi željeza oktaedarsku koordinaciju. Kationi i anioni povezani su vodikovim vezama koje uključuju i 14 molekula vode prisutnih u rešetki. Kristali $\text{C}_{51}\text{H}_{82}\text{Cu}_3\text{Fe}_2\text{N}_{30}\text{O}_{17}$ pripadaju triklinskoj prostornoj grupi $P\bar{1}$ [$a = 13,700(2)$, $b = 13,88(2)$, $c = 21,431(3)$ Å; $\alpha = 76,96(1)$, $\beta = 83,07(1)$, $\gamma = 74,70(1)^\circ$].