Crystal Structure of a New Heterotrinnuclear Complex, [Cu(C₂H₈N₂)₂][{HB(C₃H₃N₂)₃}Fe(CN)₃]₂

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The title compound, [Cu(C₂H₈N₂)₂][{HB(C₃H₃N₂)₃}Fe(CN)₃]₂, crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 34.924(2) Å, *b* = 7.923(2) Å, *c* = 13.546(2) Å, β = 96.201(3)°, *V* = 3726.3(11) Å³, *Z* = 4. The structure was refined to a final *R* value of 0.0622 for 4365 reflections (*I* > 2σ(*I*)). The copper atom is in a distorted octahedral environment: two cyano nitrogen atoms in *trans* positions and four nitrogen atoms from the ethylenediamine molecules. The intramolecular Fe(1)–Cu(1), Fe(2)–Cu(1) and Fe(1)–Fe(2) distances are 5.199, 5.211 and 10.410 Å, respectively.

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Recently, much interest has been focused on the study of cyanide-containing metal complexes because of their unique magnetic properties.^{1,2} Among these interesting research subjects, low-dimensional as well as polynuclear clusters have attracted special attention. The reason is that such systems can be used to investigate the intermetallic magnetic coupling quantitatively, whereas the lack of an appropriate model for high-dimensional systems creates a problem for quantitative magnetic analysis. In an effort to continue this remarkably

diverse chemistry, we choose the tailored cyanometalate precursor, (Bu₄N)[(Tp)Fe(CN)₃] (Tp = tris(pyrazolyl)hydroborate; Bu₄N⁺ = tetrabutylammonium cation), which consists of three CN[−] groups and the ligand of tris (pyrazolyl)hydroborate (Tp). This compound was also reported by Julve's group as

Table 1 Crystal and experimental data

Formula: C ₂₈ H ₃₆ B ₂ CuFe ₂ N ₂₂	
Formula weight: 877.65	
Crystal system: Monoclinic	
Space group: <i>P</i> 2 ₁ / <i>c</i>	<i>Z</i> = 4
<i>a</i> = 34.924(2) Å	
<i>b</i> = 7.923(2) Å	β = 96.201(3)°
<i>c</i> = 13.546(2) Å	
<i>V</i> = 3726.3(11) Å ³	
<i>D</i> _{calc} = 1.564 g/cm ³	
<i>F</i> (000) = 1796	
<i>T</i> = 293(2) K	
λ(Mo <i>K</i> _α) = 0.71073 Å	
θ _{max} = 26.00	
<i>R</i> = 0.0622	
<i>R</i> _w = 0.1461	
(Δρ) _{max} = 0.00	
(Δρ) _{max} = 0.938 e Å ^{−3}	
(Δρ) _{min} = −0.697 e Å ^{−3}	
No. of reflections measured = 19105	
No. of reflections used = 4365	
Goodness-of-fit = 1.086	
Measurement: Bruker Smart Apex CCD	
Program system: Smart, Saint, Shelxtl	
Structure determination: direct method	
Refinement: full-matrix	

Table 2 Selected atomic coordinates and equivalent isotropic thermal parameters *U*_{eq} (Å²) for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu1	0.2500(1)	0.5006(1)	0.6626(1)	0.037(1)
Fe1	0.1312(1)	0.2334(1)	0.4555(1)	0.036(1)
Fe2	0.3687(2)	0.7678(1)	0.8714(1)	0.034(1)
N1	0.0953(1)	0.1429(6)	0.5500(4)	0.043(1)
N2	0.0568(1)	0.1565(5)	0.5260(3)	0.039(1)
N3	0.0979(1)	0.4355(6)	0.4383(3)	0.036(1)
N4	0.0601(1)	0.4234(6)	0.4303(3)	0.040(1)
N5	0.0981(1)	0.1345(5)	0.3422(3)	0.037(1)
N6	0.0585(1)	0.1480(5)	0.3432(3)	0.039(1)
N7	0.1819(1)	0.4051(6)	0.6246(4)	0.041(1)
N8	0.1934(1)	0.3470(6)	0.3275(3)	0.043(1)
N9	0.1779(1)	−0.0960(6)	0.4821(4)	0.045(1)
N10	0.4024(1)	0.8669(5)	0.9859(3)	0.035(1)
N11	0.4410(1)	0.8464(5)	0.9891(3)	0.035(1)
N12	0.3999(1)	0.5576(6)	0.8857(3)	0.043(1)
N13	0.4396(1)	0.5747(6)	0.8997(3)	0.043(1)
N14	0.4048(1)	0.8580(6)	0.7817(3)	0.043(1)
N15	0.4441(1)	0.8442(6)	0.8094(4)	0.043(1)
N16	0.3187(1)	0.5882(6)	0.7063(4)	0.044(1)
N17	0.3221(1)	1.0926(6)	0.8479(3)	0.044(1)
N18	0.3052(1)	0.6509(6)	0.9961(3)	0.044(1)
N19	0.2624(1)	0.2616(5)	0.7020(3)	0.043(1)
N20	0.2631(1)	0.4276(5)	0.5263(3)	0.044(1)
N21	0.2378(1)	0.7402(5)	0.6230(3)	0.042(1)
N22	0.2374(1)	0.5702(5)	0.8023(3)	0.039(1)
C10	0.1627(2)	0.3390(7)	0.5618(4)	0.043(2)
C11	0.1688(2)	0.3069(7)	0.3689(4)	0.043(2)
C12	0.1608(2)	0.0301(7)	0.4714(4)	0.044(2)
C22	0.3369(2)	0.6625(7)	0.7639(4)	0.043(2)
C23	0.3389(2)	0.9684(7)	0.8544(4)	0.043(2)
C24	0.3305(2)	0.6884(7)	0.9516(4)	0.043(2)
C25	0.2263(2)	0.8386(7)	0.7076(4)	0.045(2)
C26	0.2172(2)	0.7314(7)	0.7901(4)	0.045(2)
C27	0.2728(2)	0.1728(7)	0.6215(4)	0.045(2)
C28	0.2755(2)	0.2614(7)	0.5260(4)	0.045(2)
B1	0.0423(2)	0.2482(8)	0.4253(5)	0.041(2)
B2	0.4567(2)	0.7568(8)	0.9044(5)	0.043(2)

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$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} (a_i^* a_j^*) (a_i a_j).$$

Table 3 Selected bond distances (Å) and angles (°)

Cu(1)-N(19)	2.002(4)	Fe(1)-C(10)	1.908(6)
Cu(1)-N(21)	2.005(4)	Fe(1)-C(12)	1.914(6)
Cu(1)-N(20)	2.034(4)	Fe(1)-C(11)	1.942(6)
Cu(1)-N(22)	2.064(4)	Fe(2)-C(23)	1.901(6)
Cu(1)-N(7)	2.494(4)	Fe(2)-C(24)	1.915(6)
Cu(1)-N(16)	2.507(5)	Fe(2)-C(22)	1.925(6)
C(10)-N(7)-Cu(1)	139.1(4)	N(19)-Cu(1)-N(21)	179.62(19)
C(22)-N(16)-Cu(1)	140.1(5)	N(19)-Cu(1)-N(20)	84.79(18)
N(7)-C(10)-Fe(1)	178.7(6)	N(21)-Cu(1)-N(20)	95.06(18)
N(8)-C(11)-Fe(1)	172.5(5)	N(19)-Cu(1)-N(22)	94.02(18)
N(9)-C(12)-Fe(1)	177.9(5)	N(21)-Cu(1)-N(22)	86.13(17)
N(16)-C(22)-Fe(2)	173.6(6)	N(20)-Cu(1)-N(22)	178.70(18)
N(17)-C(23)-Fe(2)	176.6(5)	N(19)-Cu(1)-N(7)	86.72(17)
N(18)-C(24)-Fe(2)	174.0(5)	N(21)-Cu(1)-N(7)	93.63(17)
N(20)-Cu(1)-N(7)	91.73(17)	N(22)-Cu(1)-N(7)	88.73(16)
N(19)-Cu(1)-N(16)	91.36(17)	N(21)-Cu(1)-N(16)	88.29(17)

Estimated standard deviations in the least-significant figure are given in parentheses.

Fig. 1 Chemical diagram.

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

tetraphenylphosphonium salt recently.³

A mixture of ethanol and water was gently layered on the top of a solution of $[\text{Cu}(\text{en})_3]\text{Cl}_2$ (en: ethylenediamine) in water. A solution of $(\text{Bu}_4\text{N})[(\text{Tp})\text{Fe}(\text{CN})_3]$ in ethanol was carefully added as a third layer. Crystals were obtained after one week, washed with ethanol, ether and dried in air. An orange crystal obtained in this way was chosen and its structure was determined by single-crystal X-ray diffraction. The crystal and experimental data are given in Table 1. The residual density maximum is $0.938 \text{ e}\text{\AA}^{-3}$, which is near Fe1 atom. All H atoms

were placed in calculated positions and included in the refinement in riding motion approximation with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the carrier atom. The final fractional atomic coordinates and equivalent isotropic thermal parameter for non-hydrogen atoms are given in Table 2. Selected bond distances and bond angles are listed in Table 3.

The structure consists of neutral trinuclear entities of formula $[\text{Cu}(\text{en})_2][(\text{Tp})\text{Fe}(\text{CN})_3]_2$ (Fig. 1). In this trinuclear complex, the $[(\text{Tp})\text{Fe}(\text{CN})_3]^-$ unit acts as a monodentate ligand through one of its three cyano groups toward a central $[\text{Cu}(\text{en})_2]^{2+}$ motif (Fig. 2). Each iron atom is coordinated by three Tp nitrogen atoms and three cyano carbon atoms, taking a C_{3v} symmetry. The Fe-C(cyano) bond length (1.901(6) – 1.942(6) Å) is in good agreement with those observed in the low-spin Fe^{3+} unit.^{3,4} The Fe-C-N angles for both terminal (172.5(5) – 177.9(5)°) and bridging (173.6(6) – 178.7(6)°) cyano groups depart somewhat from strict linearity. The copper atom is octahedrally coordinated through six nitrogen atoms. Four nitrogens from the ethylenediamine molecules form the equatorial plane. The average Cu-N(en) distance is 2.026 Å. Two cyano nitrogen atoms occupy the axial positions. The average Cu-N(cyano) bond distance is 2.501 Å, which is much longer than the average Cu-N(en) bond length (2.026 Å). The values of Cu(1)-N(7)-C(10) (139.1(4)°) and Cu(1)-N(16)-C(22) (140.1(5)°) depart clearly from 180°; the angles are similar to the corresponding values found in $[\text{Cu}(\text{dien})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ (dien = diethylenetriamine) (138.7 and 142°).⁵ Each trinuclear entity is linked to the two adjacent trinuclear entities through hydrogen bonds, with N(21)-H(21B)···N(9) and N(19)-H(19A)···N(17) distances of 2.975(7) and 3.025(7) Å, respectively.

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