Crystal structure of (tris(2-aminoethyl)amine-*N*,*N*′,*N*″)-(nicotinate-*N*)copper(II) tetrafluoroborate hydrate, $[Cu(C_6H_{18}N_4)(C_6H_4NO_2)][BF_4] \cdot H_2O$

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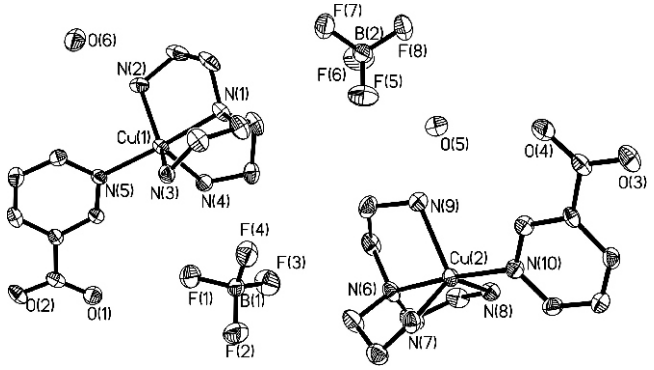

Abstract

$C_{24}H_{48}B_2Cu_2F_8N_{10}O_6$, orthorhombic, $Pca2_1$ (no. 29), a = 15.1807(2) Å, b = 8.4114(1) Å, c = 28.6983(4) Å, V = 3664.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.079, T = 296 K.

Source of material

A methanol solution (25 ml) of tris(2-aminoethyl)amine (tren, 0.073 g, 0.5 mmol) was added to a stirred methanol solution (30 ml) containing $Cu(C_5NH_4COO)_2 \cdot 2H_2O$ (0.173 g, 0.5 mmol) with the formation of a blue solution. After half an hour, $NaBF_4$ (0.055 g, 0.5 mmol) in methanol solution (20 ml) was added dropwise. The mixture was refluxed for 2 h and then filtered. The filtrate was left for slow evaporation at room temperature. Blue block-shaped crystals were formed after two weeks (0.302 g, yield 70 %). The Flack parameter of 0.04(1) confirms the absolute structure.

Elemental analysis — found: C, 33.36 %; H, 5.53 %; N, 15.88 %. calculated for $C_{12}H_{24}BCuF_4N_{10}O_6$: C, 33.00 %;H, 5.54 %; N, 16.04 %.

Discussion

Transition metal complexes of tris(2-aminoethyl)amine have been extensively investigated due to their rich structural chemistry and potential applications in biological systems and optical materials. Reactions of tris(2-aminoethyl)amine with copper(II) salts give out half-open, butterfly-shaped, nest-shaped complexes [1-4].

The asymmetric unit of the title crystal structure consists of two $[Cu(tren)(nic)]^+$ cations, two BF_4^- anions and two water molecules. The cations are crystallographically independent but chemically very similar with slight difference in bond distances and bond angles, identified as Cu1 and Cu2. The Cu atoms are both coordinated by four N atoms of tren and the N atom of nicotinate in distorted trigonal bipyramidal manner with an Addison parameter of 0.69 for Cu1 and 0.67 for Cu2 [5]. This is comparable to the other reported Cu(II) complexes [Cu(tren)(4-Apy)]$(ClO_4)_2$ and [Cu(tren)(CN)]ClO_4 [1,3]. The equatorial planes of Cu1 and Cu2 are defined by three primary amine nitrogen atoms (N2, N3 and N4 for Cu1 and N7, N8 and N9 for Cu2) of tren and the axial positions are occupied by the tertiary amine (N1 for Cu1 , N6 for Cu2) and the pyridine nitrogen atoms (N5, N10). The Cu1 lies 0.204 Å away from the equatorial plane toward N5 while Cu2 lies 0.218 Å away from the equatorial plane toward N10. The equatorial bond distances are d(Cu1—N2) = 2.045(2) Å, d(Cu1—N3) = 2.044(3) Å, and d(Cu1—N4) = 2.175(2) Å [d(Cu2—N7) = 2.050(3) Å, d(Cu2—N8) = 2.042(2) Å, and d(Cu2—N9) = 2.182(3) Å]; the axial bond distances are d(Cu1—N1) = 2.049(3) Å and d(Cu1—N5) = 2.018(3) Å, which are very close to those of Cu2 [d(Cu2—N6) = 2.049(3) Å and d(Cu2—N10) = 2.012(3) Å]. The equatorial bond angles are ∠N3–Cu1–N4 = 110.9(1)°, ∠N4–Cu1–N2 = 112.02(9)° and ∠N2–Cu1–N3 = 134.1(1)° which are also very close to those of Cu2 (∠N9–Cu2–N7 = 108.6(1)°), ∠N8–Cu2–N9 = 113.2(1)°, ∠N7–Cu2–N8 = 134.8(1)°). The bond angles of the tertiary amine with the three primary amine N atoms are in the range of 83.4(1) - 85.0(1)° for Cu1 and 83.2(1) - 84.3(1)° for Cu2. The striking feature of the complex is that nicotinate coordinates to Cu(II) via the pyridine N atom, not by the carboxylate O atom as found in reported complexes [6].

Table 1. Data collection and handling.

Crystal:	blue block, size 0.18 × 0.24 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	12.53 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX II CCD, φ/ω
$2\theta_{max}$:	55.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	30328, 6794
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5460
$N(param)_{refined}$:	470
Program:	SHELXTL [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*a*	0.9384	0.8214	0.6500	0.074
H(1B)	4*a*	0.9730	0.6473	0.6576	0.074
H(2A)	4*a*	0.8968	0.7125	0.7234	0.071
H(2B)	4*a*	0.8163	0.7750	0.6943	0.071
H(3A)	4*a*	0.6101	0.5587	0.7172	0.066
H(3B)	4*a*	0.6662	0.6904	0.6920	0.066

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4A)	4*a*	0.7500	0.5987	0.7531	0.070
H(4B)	4*a*	0.7347	0.4212	0.7382	0.070
H(5A)	4*a*	0.9069	0.1737	0.7027	0.064
H(5B)	4*a*	0.8068	0.2181	0.7089	0.064
H(6A)	4*a*	0.8912	0.4122	0.7457	0.071
H(6B)	4*a*	0.9456	0.4407	0.6999	0.071
H(7)	4*a*	0.7178	0.6788	0.5510	0.055
H(8)	4*a*	0.6735	0.6516	0.4758	0.058
H(9)	4*a*	0.6697	0.4043	0.4420	0.055
H(11)	4*a*	0.7636	0.2236	0.5599	0.046
H(13A)	4*a*	0.4009	-0.0744	0.8172	0.070
H(13B)	4*a*	0.4546	-0.2038	0.8448	0.070
H(14A)	4*a*	0.5269	0.0551	0.7957	0.076
H(14B)	4*a*	0.5417	-0.1251	0.7838	0.076
H(15A)	4*a*	0.7274	-0.3344	0.8902	0.065
H(15B)	4*a*	0.7620	-0.1611	0.8808	0.065
H(16A)	4*a*	0.6859	-0.2362	0.8156	0.074
H(16B)	4*a*	0.6050	-0.2919	0.8456	0.074
H(17A)	4*a*	0.6985	0.3078	0.8314	0.069
H(17B)	4*a*	0.5989	0.2640	0.8232	0.069
H(18A)	4*a*	0.6849	0.0652	0.7913	0.068

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(18B)	4*a*	0.7356	0.0437	0.8385	0.068
H(19)	4*a*	0.5053	-0.1834	0.9852	0.053
H(20)	4*a*	0.4588	-0.1513	1.0600	0.058
H(21)	4*a*	0.4581	0.0961	1.0933	0.052
H(24)	4*a*	0.5507	0.2721	0.9740	0.049
H(3C)	4*a*	0.6258	0.5088	0.6308	0.049
H(7C)	4*a*	0.4001	-0.0256	0.9000	0.049
H(2C)	4*a*	0.8412	0.7492	0.6001	0.049
H(4C)	4*a*	0.9030	0.2758	0.6313	0.049
H(4D)	4*a*	0.8234	0.1725	0.6370	0.049
H(7B)	4*a*	0.4321	0.1233	0.8741	0.049
H(3D)	4*a*	0.6412	0.3833	0.6581	0.049
H(9D)	4*a*	0.6837	0.2209	0.9058	0.049
H(9C)	4*a*	0.6177	0.3180	0.9046	0.049
H(2D)	4*a*	0.9190	0.6194	0.5892	0.049
H(8C)	4*a*	0.7037	-0.1231	0.9487	0.049
H(6C)	4*a*	0.7316	1.0156	0.6035	0.049
H(6D)	4*a*	0.7743	0.9547	0.5619	0.049
H(8D)	4*a*	0.6344	-0.2476	0.9387	0.049
H(5C)	4*a*	0.5503	0.5092	0.9727	0.049
H(5D)	4*a*	0.5093	0.4960	0.9238	0.049

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	4*a*	0.78610(2)	0.48490(3)	0.62964(2)	0.0359(2)	0.0377(2)	0.0331(3)	-0.0010(1)	-0.0050(2)	-0.0063(2)
F(1)	4*a*	0.6356(1)	0.1151(2)	0.64357(8)	0.094(2)	0.078(1)	0.049(2)	-0.010(1)	0.008(1)	-0.002(1)
O(1)	4*a*	0.7395(2)	0.0052(2)	0.5021(1)	0.082(2)	0.043(1)	0.050(2)	0.001(1)	-0.001(2)	-0.008(1)
N(1)	4*a*	0.8226(2)	0.5352(3)	0.6968(1)	0.036(2)	0.059(2)	0.039(2)	0.005(1)	-0.007(1)	-0.016(1)
C(1)	4*a*	0.9204(2)	0.7114(4)	0.6535(2)	0.053(2)	0.054(2)	0.078(4)	-0.013(2)	-0.015(2)	-0.018(2)
B(1)	4*a*	0.6197(2)	0.0587(5)	0.6890(2)	0.044(2)	0.044(2)	0.047(3)	0.003(2)	-0.005(2)	0.005(2)
Cu(2)	4*a*	0.57385(2)	0.00563(4)	0.90611(2)	0.0362(2)	0.0383(2)	0.0294(2)	0.0028(1)	0.0044(2)	-0.0036(2)
F(2)	4*a*	0.5487(2)	-0.0383(3)	0.6880(1)	0.073(2)	0.086(2)	0.099(2)	-0.026(1)	-0.008(2)	0.020(2)
O(2)	4*a*	0.6947(2)	0.1096(3)	0.43433(9)	0.057(2)	0.073(2)	0.039(2)	-0.006(1)	-0.006(1)	-0.021(1)
N(2)	4*a*	0.8733(2)	0.6598(3)	0.6117(1)	0.038(1)	0.038(1)	0.057(2)	-0.005(1)	-0.001(1)	-0.004(1)
C(2)	4*a*	0.8624(2)	0.6952(4)	0.6954(1)	0.058(2)	0.065(2)	0.054(3)	0.005(2)	-0.017(2)	-0.031(2)
B(2)	4*a*	0.9086(3)	0.5675(5)	0.8415(2)	0.060(3)	0.053(2)	0.056(4)	0.000(2)	-0.006(2)	-0.004(3)
F(3)	4*a*	0.6915(2)	-0.0197(3)	0.7054(1)	0.075(2)	0.079(2)	0.115(3)	0.025(1)	-0.029(2)	0.003(1)
O(3)	4*a*	0.4820(1)	0.3907(3)	1.09884(9)	0.057(2)	0.075(2)	0.038(2)	0.008(1)	0.011(1)	-0.022(1)
N(3)	4*a*	0.6610(2)	0.4845(3)	0.6560(1)	0.037(2)	0.050(2)	0.040(2)	0.000(1)	-0.009(1)	0.006(1)
C(3)	4*a*	0.6631(2)	0.5779(5)	0.6992(1)	0.043(2)	0.067(2)	0.054(3)	0.012(2)	0.004(2)	-0.011(2)
F(4)	4*a*	0.6046(2)	0.1907(2)	0.71637(9)	0.113(2)	0.064(1)	0.056(2)	0.016(1)	0.004(1)	-0.007(1)
O(4)	4*a*	0.5269(2)	0.4924(2)	1.0320(1)	0.079(2)	0.047(1)	0.049(2)	-0.002(1)	-0.005(2)	-0.010(1)
N(4)	4*a*	0.8518(2)	0.2599(3)	0.6434(1)	0.049(2)	0.041(1)	0.048(2)	0.004(1)	-0.005(2)	-0.001(1)
C(4)	4*a*	0.7427(3)	0.5286(5)	0.7266(2)	0.047(2)	0.084(3)	0.044(3)	0.012(2)	0.000(2)	-0.015(2)
F(5)	4*a*	0.8405(2)	0.4683(3)	0.8391(1)	0.075(2)	0.086(2)	0.123(3)	-0.026(1)	-0.004(2)	-0.016(2)
O(5)	4*a*	0.5516(2)	0.5516(3)	0.9410(1)	0.099(2)	0.052(1)	0.056(2)	-0.024(1)	-0.006(2)	0.003(2)
N(5)	4*a*	0.7466(2)	0.4537(3)	0.5631(1)	0.042(1)	0.037(1)	0.033(2)	-0.004(1)	-0.003(1)	-0.006(1)
C(5)	4*a*	0.8619(2)	0.2509(4)	0.6946(1)	0.056(2)	0.060(2)	0.044(3)	0.015(2)	-0.005(2)	0.006(2)
F(6)	4*a*	0.9830(2)	0.4998(3)	0.8244(1)	0.072(2)	0.086(2)	0.132(3)	0.015(1)	0.021(2)	-0.019(1)
O(6)	4*a*	0.7670(2)	0.9428(3)	0.5928(1)	0.106(2)	0.047(1)	0.053(2)	0.015(2)	0.004(2)	-0.004(1)
N(6)	4*a*	0.6131(2)	-0.0524(4)	0.8400(1)	0.037(2)	0.068(2)	0.030(2)	-0.002(1)	0.004(1)	-0.010(2)
C(6)	4*a*	0.8878(2)	0.4134(5)	0.7119(2)	0.048(2)	0.083(3)	0.046(2)	0.019(2)	-0.012(2)	-0.013(2)
F(7)	4*a*	0.8898(2)	0.7060(3)	0.81670(8)	0.137(2)	0.068(2)	0.059(2)	0.008(1)	-0.010(2)	0.009(1)
N(7)	4*a*	0.4498(2)	0.0069(3)	0.8778(1)	0.036(1)	0.060(2)	0.035(2)	0.001(1)	0.006(1)	0.005(1)
C(7)	4*a*	0.7184(2)	0.5784(4)	0.5375(1)	0.056(2)	0.035(2)	0.047(3)	-0.000(2)	-0.005(2)	-0.000(2)
F(8)	4*a*	0.9222(2)	0.6156(3)	0.88699(8)	0.103(2)	0.091(2)	0.050(2)	0.002(1)	-0.016(1)	0.003(1)
N(8)	4*a*	0.6604(2)	-0.1676(3)	0.9259(1)	0.045(2)	0.037(1)	0.046(2)	0.004(1)	-0.001(1)	-0.003(1)
C(8)	4*a*	0.6910(2)	0.5627(4)	0.4926(2)	0.051(2)	0.051(2)	0.045(3)	0.008(2)	-0.006(2)	0.007(2)
N(9)	4*a*	0.6377(2)	0.2314(3)	0.8899(1)	0.049(2)	0.046(1)	0.046(2)	-0.004(1)	0.001(2)	0.004(1)
C(9)	4*a*	0.6894(2)	0.4162(4)	0.4725(1)	0.037(2)	0.066(2)	0.034(2)	0.003(2)	-0.004(2)	-0.001(2)
N(10)	4*a*	0.5327(2)	0.0416(3)	0.9719(1)	0.046(2)	0.037(1)	0.035(2)	0.004(1)	0.006(1)	-0.004(1)
C(10)	4*a*	0.7171(2)	0.2854(3)	0.4975(1)	0.034(2)	0.044(2)	0.033(2)	-0.002(1)	-0.002(2)	-0.001(2)
C(11)	4*a*	0.7449(2)	0.3109(3)	0.5426(1)	0.042(2)	0.037(2)	0.036(2)	-0.003(1)	-0.004(2)	-0.005(2)
C(12)	4*a*	0.7164(2)	0.1184(4)	0.4766(1)	0.038(2)	0.053(2)	0.043(3)	-0.009(2)	0.003(2)	-0.013(2)
C(13)	4*a*	0.4530(2)	-0.0924(5)	0.8361(1)	0.047(2)	0.076(3)	0.052(3)	-0.011(2)	-0.004(2)	-0.002(2)
C(14)	4*a*	0.5338(2)	-0.0500(6)	0.8091(2)	0.049(2)	0.094(3)	0.046(3)	-0.010(2)	-0.005(2)	-0.014(2)
C(15)	4*a*	0.7095(2)	-0.2250(4)	0.8853(1)	0.043(2)	0.052(2)	0.069(3)	0.009(1)	0.005(2)	-0.014(2)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(16)	4*a*	0.6517(2)	-0.2137(4)	0.8434(2)	0.054(2)	0.072(2)	0.059(3)	0.006(2)	0.016(2)	-0.032(2)
C(17)	4*a*	0.6524(2)	0.2327(4)	0.8393(1)	0.047(2)	0.074(2)	0.051(3)	-0.011(2)	0.004(2)	0.020(2)
C(18)	4*a*	0.6788(2)	0.0689(5)	0.8250(1)	0.041(2)	0.096(3)	0.032(2)	-0.010(2)	0.014(2)	-0.009(2)
C(19)	4*a*	0.5052(2)	-0.0820(4)	0.9982(1)	0.048(2)	0.036(2)	0.048(3)	-0.004(2)	0.001(2)	-0.002(2)
C(20)	4*a*	0.4774(2)	-0.0635(4)	1.0429(2)	0.052(2)	0.051(2)	0.041(3)	-0.008(2)	0.006(2)	0.006(2)
C(21)	4*a*	0.4768(2)	0.0832(4)	1.0627(1)	0.046(2)	0.055(2)	0.029(2)	-0.003(2)	0.006(2)	-0.003(2)
C(22)	4*a*	0.5042(2)	0.2139(3)	1.0369(1)	0.035(2)	0.044(2)	0.026(2)	0.007(1)	-0.001(2)	-0.009(1)
C(23)	4*a*	0.5032(2)	0.3804(4)	1.0573(1)	0.034(2)	0.055(2)	0.036(2)	0.001(2)	-0.004(2)	-0.012(2)
C(24)	4*a*	0.5318(2)	0.1859(3)	0.9917(1)	0.042(2)	0.039(2)	0.040(2)	0.004(1)	0.004(2)	-0.002(2)

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