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Crystal and Molecular Structure of μ-Benzidine-bis(2,2′,2″-triaminotriethylamine)dicopper(II) Nitrate

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The structure of $[Cu_2(tren)_2(BZD)](NO_3)_4$, where tren is 2,2′,2″-triaminotriethylamine and BZD is benzidine (i.e., 4,4′-diaminobiphenyl), has been determined using a combination of direct and heavy-atom methods in conjunction with least-squares refinement with data measured on a four-circle X-ray diffractometer. The compound crystallizes in the monoclinic space group $P2_1/c$ with eight formula weights in a cell having the dimensions $a = 29.799$ (4) Å, $b = 13.960$ (2) Å, $c = 18.732$ (3) Å, $\beta = 106.49$ (1)°, and $V = 7471.9$ Å^3. The observed and calculated densities are 1.52 and 1.51 g cm^{-3}, respectively. The structure was refined using data collected with Cu Kα [8154 observed reflections with $I > 2\sigma(I)$] and Mo Kα [4420 observed reflections with $I \geq 2\sigma(I)$] radiation. The final refinement with Mo Kα radiation data gave conventional discrepancy factors of $R = 0.066$ and $R_w = 0.085$. Discrete $[Cu_2(tren)_2(BZD)]^{4+}$ and NO_3^- ions are found in the salt. There are two crystallographically different $[Cu_2(tren)_2(BZD)]^{4+}$ species (identified as binuclear complexes A and B) and eight nitrate anions in the asymmetric unit. The Cu–Cu distances within each of the binuclear cations are 12.273 (2) and 12.083 (2) Å for A and B, respectively. Each of the two different binuclear cations consists of two distorted [the trigonal angles vary from 104.6 (4) to 141.2 (4)°] trigonal-bipyramidal copper(II) ions with tetradentate tren ligands bridged by a benzidine molecule. The benzidine bridge in either of the binuclear cations of A and B is nonplanar with dihedral angles of 14.3 and 22.5°, respectively, between the phenyl rings. The C–C bond between the rings is appropriate for a single bond with an average length of 1.52 ± 0.03 Å. The BZD bridges are aromatic as indicated by a mean C–C bond distance of 1.388 ± 0.004 Å with a variation from 1.35 (2) to 1.42 (2) Å. The C–N bond distances of the two different BZD bridges range from 1.428 (13) to 1.457 (13) Å.

Introduction

Relatively few examples have been reported of transition-metal complexes containing para-substituted aromatic diamine ligands. Diamines such as *p*-phenylenediamine (PPD) or benzidine (BZD) potentially may serve as bridging ligands in binuclear complexes. However, complexes with PPD[2-5] and BZD[4-8] have been indicated on the basis of various physical measurements to possess polymeric structures. An air-sensitive monomeric complex with PPD has been reported[9] with ruthenium(II), which upon exposure to air reverts to a *p*-benzoquinonediimine complex stabilized apparently by the π-back-bonding ability of ruthenium(II). The redox behavior of PPD has made it a useful substrate to gauge the enzymatic activity of various copper proteins, in particular, laccase[10] and ceruloplasmin.[10-12]

Since aromatic diamines may coordinate to two different metal centers, it was thought that these bridging ligands would provide an extended superexchange pathway of phenyl or biphenyl moieties over which a magnetic exchange interaction might be propagated. With this in mind, complexes of the form $[Cu_2(tren)_2(DA)](Y)_4$ were prepared, where tren is 2,2′,2″-triaminotriethylamine, DA represents aromatic diamines such as PPD, BZD, or various derivatives, and Y^- can be NO_3^-, ClO_4^-, or PF_6^-. The magnetic properties of this series of complexes have been presented in a previous paper.[13] In order to establish the binuclear nature of these complexes, a single-crystal X-ray diffraction analysis was undertaken on the complex $[Cu_2(tren)_2(BZD)](NO_3)_4$. A preliminary account[14] of the structural and magnetic properties of these complexes has appeared. This paper reports the complete results of the X-ray crystallographic study.

Experimental Section

A sample of $[Cu_2(tren)_2(BZD)](NO_3)_4$ was prepared by mixing ca. 1.2 g (5 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ with ca. 0.75 g (5 mmol) of tren (Ames Laboratories, Inc.) in 95% ethanol, filtering the resulting mixture, and then adding a 95% ethanol solution of ca. 0.46 g (2.5 mmol) of BZD (Sigma). A microcrystalline dark green solid formed immediately and was washed with ether and dried in a vacuum desiccator over P_4O_{10}. Crystals were grown by slow evaporation of a 95% ethanol solution. Anal. Calcd for $[Cu_2(tren)_2(BZD)](NO_3)_4$, $C_{24}H_{48}N_{14}O_{12}Cu_2$: C, 33.84; H, 5.68; N, 23.02; Cu, 14.92. Found: C, 33.58; H, 5.62; N, 22.97; Cu, 14.89.

Table I. Experimental Data for the X-Ray Diffraction Study of $[Cu_2(tren)_2(BZD)](NO_3)_4$

Crystal Parameters

$a = 29.799$ (4) Å	space group $P2_1/c$
$b = 13.960$ (2) Å	$Z = 8$
$c = 18.732$ (3) Å	mol wt 851.83
$\beta = 106.49$ (1)°	$\rho_{calcd} = 1.51$ g cm^{-3}
$V = 7471.9$ Å^3	$\rho_{obsd} = 1.52$ g cm^{-3} (flotation in chloroform-bromoform)

Data Collection Parameters

	I	II
crystal size, mm	0.5 × 0.3 × 0.3	0.3 × 0.2 × 0.2
radiation	Cu Kα, $\bar{\lambda}$ 1.541 78 Å	Mo Kα, $\bar{\lambda}$ 0.710 69 Å
maximum 2θ, deg	130	40
scan mode	θ:2θ	ω
reflections measd	$+h, +k, \pm l$	$+h, +k, \pm l$
base width, deg	2.4	1.2
variable scan speed, deg min^{-1}	2–10	2–29.3
background/scan time	0.25	1.0
unique reflections	12286	6949
obsd reflections ($2\sigma(I)$)	8170	4420
no. standards monitored/50 reflections	3	2
absorption coeff, cm^{-1}	20.9	12.6

Crystal Measurements. Preliminary precession photographs showed systematic absences for $0k0$, $k = 2n + 1$, and for $h0l$, $l = 2n + 1$, which established the space group as $P2_1/c$. The final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator, and the results are given in Table I along with the details of the data collection.

Several of the dark green rectangular prisms were examined on the diffractometer before a crystal suitable for data collection was found. Some of the larger crystals have a tendency to be twinned along the a^* and c^* axes, but the crystals chosen for data collection showed *no* twinning problems. Two sets of data (designated I and II) were collected, first using Cu Kα radiation (I) and then MoKα (II).[15] The standard reflections monitored during data collection showed no signs of crystal deterioration. The data sets were corrected

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Table II. Final Positional Parameters[a] for $[Cu_2(tren)_2(BZD)](NO_3)_4$ Including Hydrogen Atoms[b]

atom	x	y	z	atom	x	y	z
Cu(1)	0.69079 (5)	0.23752 (10)	0.27725 (7)	N(28)	0.3128 (4)	0.0666 (7)	0.2967 (6)
Cu(2)	0.41362 (5)	0.30196 (10)	−0.34614 (7)	O(22)	0.3410 (3)	0.0448 (6)	0.2640 (4)
Cu(3)	0.19274 (5)	0.22364 (10)	0.26940 (7)	O(23)	0.2852 (3)	0.0083 (6)	0.3089 (6)
Cu(4)	−0.09160 (5)	0.24927 (11)	−0.33604 (7)	O(24)	0.3116 (4)	0.1456 (7)	0.3229 (7)
N(1)	0.6960 (3)	0.1774 (7)	0.3794 (5)	H(1)(C(1))	0.73625	0.24351	0.47280
N(2)	0.6939 (3)	0.3648 (7)	0.3317 (5)	H(2)	0.67708	0.25158	0.46003
N(3)	0.6212 (3)	0.1872 (7)	0.2515 (5)	H(3)(C(2))	0.73791	0.37106	0.43525
N(4)	0.7382 (4)	0.1370 (7)	0.2690 (6)	H(4)	0.67969	0.38234	0.42959
N(5)	0.6914 (3)	0.3005 (6)	0.1792 (5)	H(5)(N(2))	0.72045	0.40783	0.32186
N(6)	0.4245 (3)	0.3198 (7)	−0.4492 (5)	H(6)	0.66170	0.40049	0.31324
N(7)	0.3643 (3)	0.4046 (6)	−0.3810 (4)	H(7)(C(3))	0.65261	0.10998	0.42929
N(8)	0.4836 (3)	0.3559 (7)	−0.3078 (5)	H(8)	0.66909	0.06226	0.35620
N(9)	0.4189 (3)	0.1578 (6)	−0.3651 (5)	H(9)(C(4))	0.60074	0.22620	0.34354
N(10)	0.3994 (3)	0.2875 (6)	−0.2468 (4)	H(10)	0.58335	0.11371	0.31020
N(11)	0.1977 (3)	0.2862 (7)	0.3700 (4)	H(11)(N(3))	0.59823	0.24055	0.22297
N(12)	0.1220 (3)	0.2722 (7)	0.2415 (5)	H(12)	0.61759	0.12573	0.21799
N(13)	0.2431 (3)	0.3204 (7)	0.2637 (5)	H(13)(C(5))	0.73494	0.06190	0.43487
N(14)	0.1960 (4)	0.0968 (7)	0.3270 (6)	H(14)	0.76801	0.15552	0.41866
N(15)	0.1936 (3)	0.1596 (7)	0.1722 (4)	H(15)(C(6))	0.71481	0.01535	0.30915
N(16)	−0.0851 (4)	0.2474 (9)	−0.4416 (5)	H(16)	0.77434	0.03086	0.33791
N(17)	−0.0201 (3)	0.1955 (7)	−0.3073 (5)	H(17)(N(4))	0.72718	0.10403	0.21650
N(18)	−0.1390 (4)	0.1414 (8)	−0.3709 (5)	H(18)	0.77091	0.16947	0.27566
N(19)	−0.0850 (4)	0.3929 (8)	−0.3445 (6)	H(19)(N(5))	0.71730	0.26591	0.16047
N(20)	−0.1033 (3)	0.2552 (6)	−0.2343 (5)	H(20)	0.70069	0.37259	0.19062
C(1)	0.7037 (6)	0.2558 (11)	0.4337 (7)	H(21)(C(8))	0.66203	0.16247	0.08225
C(2)	0.7042 (8)	0.3442 (12)	0.4101 (8)	H(22)(C(9))	0.59056	0.15631	−0.01994
C(3)	0.6539 (4)	0.1218 (10)	0.3746 (7)	H(23)(C(11))	0.55555	0.43099	0.03907
C(4)	0.6107 (4)	0.1638 (10)	0.3207 (8)	H(24)(C(12))	0.62362	0.43113	0.14548
C(5)	0.7379 (4)	0.1141 (9)	0.3961 (7)	H(25)(C(14))	0.50775	0.44007	−0.06113
C(6)	0.7419 (5)	0.0657 (10)	0.3269 (7)	H(26)(C(15))	0.43776	0.43541	−0.16623
C(7)	0.6491 (4)	0.2988 (8)	0.1192 (5)	H(27)(C(17))	0.45442	0.14190	−0.18959
C(8)	0.6388 (4)	0.2207 (8)	0.0730 (6)	H(28)(C(18))	0.52531	0.14411	−0.08960
C(9)	0.5979 (4)	0.2174 (8)	0.0141 (6)	H(29)(C(19))	0.37559	0.36916	−0.54098
C(10)	0.5661 (4)	0.2950 (8)	−0.0006 (6)	H(30)	0.41031	0.45582	−0.48780
C(11)	0.5779 (4)	0.3713 (8)	0.0482 (6)	H(31)(C(20))	0.32553	0.38188	−0.48949
C(12)	0.6176 (4)	0.3732 (9)	0.1083 (7)	H(32)	0.34948	0.49415	−0.47190
C(13)	0.5229 (4)	0.2931 (7)	−0.0646 (5)	H(33)(N(7))	0.33316	0.38251	−0.37018
C(14)	0.4969 (4)	0.3748 (7)	−0.0884 (6)	H(34)	0.37600	0.46852	−0.35223
C(15)	0.4564 (4)	0.3718 (8)	−0.1484 (6)	H(35)(C(21))	0.47006	0.40754	−0.47823
C(16)	0.4403 (3)	0.2875 (7)	−0.1846 (5)	H(36)	0.49033	0.29398	−0.45285
C(17)	0.4659 (4)	0.2068 (8)	−0.1621 (6)	H(37)(C(22))	0.49638	0.46128	−0.37345
C(18)	0.5062 (4)	0.2078 (7)	−0.1046 (6)	H(38)	0.53258	0.36365	−0.36332
C(19)	0.3907 (8)	0.3937 (16)	−0.4864 (9)	H(39)(N(8))	0.48467	0.41437	−0.27203
C(20)	0.3555 (4)	0.4207 (9)	−0.4611 (7)	H(40)	0.50608	0.30184	−0.27915
C(21)	0.4718 (6)	0.3521 (13)	−0.4396 (9)	H(41)(C(23))	0.44158	0.21787	−0.51451
C(22)	0.4979 (5)	0.3862 (12)	−0.3714 (8)	H(42)	0.38321	0.22422	−0.52006
C(23)	0.4173 (6)	0.2250 (11)	−0.4837 (7)	H(43)(C(24))	0.45440	0.11264	−0.43544
C(24)	0.4217 (6)	0.1436 (10)	−0.4391 (8)	H(44)	0.39499	0.09584	−0.46575
C(25)	0.1564 (4)	0.3480 (9)	0.3628 (6)	H(45)(N(9))	0.44906	0.13027	−0.32702
C(26)	0.1118 (4)	0.3021 (9)	0.3102 (7)	H(46)	0.38924	0.12234	−0.35847
C(27)	0.2406 (5)	0.3427 (11)	0.3900 (7)	H(47)(N(10))	0.38157	0.22251	−0.24710
C(28)	0.2464 (5)	0.3914 (10)	0.3230 (8)	H(48)	0.37785	0.34464	−0.24067
C(29)	0.1998 (6)	0.2127 (11)	0.4243 (7)	H(49)(C(25))	0.16225	0.41468	0.34119
C(30)	0.2128 (7)	0.1218 (12)	0.4065 (8)	H(50)	0.15133	0.35761	0.41561
C(31)	0.1514 (4)	0.1706 (7)	0.1123 (5)	H(51)(C(26))	0.08452	0.35241	0.29765
C(32)	0.1453 (3)	0.2521 (8)	0.0706 (6)	H(52)	0.10198	0.24228	0.33614
C(33)	0.1038 (4)	0.2683 (8)	0.0133 (6)	H(53)(N(12))	0.11755	0.33041	0.20464
C(34)	0.0676 (3)	0.1988 (8)	−0.0007 (5)	H(54)	0.09936	0.21645	0.21640
C(35)	0.0737 (4)	0.1178 (8)	0.0447 (6)	H(55)(C(27))	0.26932	0.29735	0.41208
C(36)	0.1154 (4)	0.1041 (8)	0.1019 (6)	H(56)	0.23872	0.39410	0.42997
C(37)	0.0222 (4)	0.2131 (7)	−0.0643 (5)	H(57)(C(28))	0.21999	0.44305	0.30483
C(38)	0.0088 (4)	0.3053 (8)	−0.0894 (6)	H(58)	0.27928	0.42493	0.33605
C(39)	−0.0333 (4)	0.3178 (8)	−0.1468 (6)	H(59)(N(13))	0.27535	0.28553	0.27170
C(40)	−0.0606 (3)	0.2395 (8)	−0.1742 (5)	H(60)	0.23370	0.35438	0.21151
C(41)	−0.0474 (4)	0.1503 (7)	−0.1487 (6)	H(61)(C(29))	0.16654	0.20707	0.43260
C(42)	−0.0053 (4)	0.1356 (8)	−0.0930 (6)	H(62)	0.22420	0.23427	0.47400
C(43)	−0.0411 (7)	0.1976 (21)	−0.4386 (11)	H(63)(C(30))	0.19933	0.07120	0.43654
C(44)	−0.0069 (5)	0.1809 (13)	−0.3733 (9)	H(64)	0.24947	0.11803	0.42292
C(45)	−0.1264 (6)	0.1891 (16)	−0.4869 (8)	H(65)(N(14))	0.16265	0.06528	0.31486
C(46)	−0.1449 (5)	0.1177 (13)	−0.4471 (8)	H(66)	0.21931	0.04923	0.31273
C(47)	−0.0880 (9)	0.3455 (14)	−0.4685 (10)	H(67)(N(15))	0.19950	0.08608	0.18235
C(48)	−0.0847 (6)	0.4167 (12)	−0.4204 (9)	H(68)	0.22129	0.18916	0.15510
N(21)	0.3660 (4)	0.4451 (7)	0.3019 (6)	H(69)(C(32))	0.17203	0.30371	0.08159
O(1)	0.3875 (5)	0.4577 (8)	0.2547 (6)	H(70)(C(33))	0.09965	0.33111	−0.01876
O(2)	0.3586 (4)	0.5124 (6)	0.3385 (5)	H(71)(C(35))	0.04688	0.06666	0.03600
O(3)	0.3518 (3)	0.3656 (7)	0.3090 (7)	H(72)(C(36))	0.11935	0.04389	0.13669

Table II (*Continued*)

atom	x	y	z	atom	x	y	z
N(22)	0.0467 (4)	0.0612 (7)	0.2635 (6)	H(73)(C(38))	0.02967	0.36452	−0.06626
O(4)	0.0417 (4)	0.1252 (7)	0.2185 (6)	H(74)(C(39))	−0.04356	0.38632	−0.16837
O(5)	0.0854 (3)	0.0430 (9)	0.3064 (7)	H(75)(C(41))	−0.06891	0.09156	−0.17076
O(6)	0.0115 (4)	0.0145 (7)	0.2608 (7)	H(76)(C(42))	0.00513	0.06627	−0.07363
N(23)	0.5440 (3)	0.3982 (7)	0.2520 (6)	H(77)(C(43))	−0.02511	0.23771	−0.47211
O(7)	0.5081 (3)	0.4475 (6)	0.2381 (5)	H(78)	−0.15070	0.13013	−0.46291
O(8)	0.5413 (3)	0.3248 (6)	0.2131 (5)	H(79)(C(44))	0.02130	0.22674	−0.37175
O(9)	0.5778 (3)	0.4204 (7)	0.3011 (5)	H(80)	0.00395	0.10939	−0.37378
N(24)	0.8123 (4)	0.3905 (7)	0.3142 (6)	H(81)(N(17))	0.00247	0.24557	−0.27337
O(10)	0.8377 (3)	0.4193 (6)	0.2775 (5)	H(82)	−0.01814	0.13033	−0.27851
O(11)	0.7917 (4)	0.4491 (7)	0.3414 (6)	H(83)(C(45))	−0.11588	0.15394	−0.52900
O(12)	0.8082 (4)	0.3072 (7)	0.3246 (7)	H(84)	−0.15358	0.23720	−0.51099
N(25)	0.8641 (4)	0.0127 (8)	0.3162 (9)	H(85)(C(46))	−0.12770	0.05256	−0.44928
O(13)	0.8932 (4)	−0.0036 (8)	0.2865 (7)	H(86)	−0.18082	0.10974	−0.47363
O(14)	0.8500 (6)	−0.0505 (9)	0.3464 (9)	H(87)(N(18))	−0.12726	0.08049	−0.33804
O(15)	0.8530 (5)	0.0857 (10)	0.3304 (11)	H(88)	−0.17139	0.16327	−0.36458
N(26)	0.7777 (4)	0.1593 (10)	0.1111 (6)	H(89)(C(47))	−0.12051	0.35274	−0.50881
O(16)	0.7424 (3)	0.1124 (8)	0.1061 (5)	H(90)	−0.06099	0.35477	−0.49355
O(17)	0.8087 (4)	0.1318 (12)	0.0935 (9)	H(91)(C(48))	−0.11302	0.46303	−0.44257
O(18)	0.7746 (4)	0.2434 (8)	0.1341 (7)	H(92)	−0.05321	0.45275	−0.41676
N(27)	0.2825 (3)	0.2957 (9)	0.1062 (5)	H(93)(N(19))	−0.11333	0.42733	−0.33233
O(19)	0.2532 (3)	0.3555 (7)	0.1065 (5)	H(94)	−0.05359	0.41570	−0.30678
O(20)	0.3133 (3)	0.3122 (9)	0.0745 (6)	H(95)(N(20))	−0.12781	0.20224	−0.23159
O(21)	0.2800 (4)	0.2153 (8)	0.1318 (6)	H(96)	−0.11684	0.32301	−0.22756

[a] Standard deviations of the least significant figures are given in parentheses and are given in this fashion in succeeding tables. [b] The hydrogen atom positions were calculated with fixed bond lengths of 1.05 Å and assigned isotropic thermal parameters of 9.5 Å^2. The hydrogen atoms are bonded to the carbon or nitrogen atom in parentheses or the atom immediately above it.

for Lorentz and polarization effects but not for absorption.[16] The maximum and minimum transmission factors were estimated to be 0.53–0.35 for the Cu Kα data set and 0.78–0.69 for the Mo Kα data set.

Solution and Refinement of the Structure. The structure was initially solved using the Cu Kα data set. The four copper atom positions were found using the direct-methods program MULTAN of Germain, Main, Woolfson,[15,17] and these proved to fit the heavy-atom vectors of the Patterson map. From a series of five Fourier maps, 36 additional atoms were located. At this point the R factor was 0.45, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum_w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. From a Fourier difference map, ten more atom positions were located. Two cycles of block refinements of positional and isotropic thermal parameters reduced the R factor to 0.37. Another four cycles of structure factor calculations followed by a difference Fourier map yielded a total of 84 of the 104 nonhydrogen atoms. The methylene carbons C(1), C(2), C(19), C(20), C(29), C(30), and C(43)–C(48) were among the last to be found; their positions were not as pronounced in the difference maps. Evidence for static disorder about these positions could not be found. The mean positions of highest electron density were refined for these atoms. With all 104 nonhydrogen atoms included, five cycles of block refinements of the positional and isotropic thermal parameters yielded $R = 0.181$ and $R_w = 0.227$. The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \{[\sigma(|F_o|)]^2 + [p|F_o|]^2\}^{-1}$, $\sigma(|F_o|) = \sigma(I)/2|F_o|Lp$, p is the "ignorance" factor set equal to 0.06, and Lp is the Lorentz–polarization factor. With all nonhydrogen atoms having anisotropic thermal parameters, ten cycles of block refinements reduced the discrepancy indices to the values $R = 0.13$ and $R_w = 0.18$. A difference map at this point gave reasonable positions for 12 of the 96 missing hydrogen atoms. Still no evidence for any static disorder about the methylene carbon atoms with shortened bond lengths could be found. The positions of all 96 hydrogen atoms were calculated with fixed bond lengths of 1.05 Å and included in the model. The same isotropic thermal parameter, $B = 9.5$ Å^2, was assigned to all of the hydrogen atoms. None of the hydrogen atom parameters was allowed to vary in any of the subsequent refinements.

After we accounted for all 200 atoms, 10 more cycles of block refinements of 937 variables on 8154 observed reflections[18] gave final values for the Cu Kα data of $R = 0.11$ and $R_w = 0.16$ with ERF = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 2.17$, where m is the number of observations and n is the number of variables. The scattering factor tables for neutral atoms were taken from the analytical expression used in ref 19a. A final difference map showed 20 peaks above the electron density corresponding to 60% of a hydrogen atom. Eighteen of these peaks were located within 1.1 Å of the four Cu atoms and ranged in height from 1.0 to 0.7 e/Å^3 of a hydrogen atom. The remaining two, corresponding to 1.3 and 0.9 e/Å^3 of a hydrogen atom, were not located near any other atoms and were considered as resulting from the fact that the absorption correction was not included.

A second data set was collected on a smaller crystal (see Table I) with Mo Kα radiation to circumvent problems due to absorption encountered with the Cu Kα data. With the results of data set I as starting parameters for this refinement, the structure was block refined[15] to final discrepancy factors of $R = 0.066$, $R_w = 0.085$, and ERF = 1.52. A difference map showed three peaks above 33% of a hydrogen atom, with electron density corresponding to 82, 66, and 42% of a hydrogen atom. The highest peak is 2.8 Å from O(11) and O(17). The second highest is 2.9 Å from O(20) and 3.2 Å from C(3) and O(23). The last peak is located 3 Å from O(14). The second data set shows an overall improvement in the observed bond lengths and angles but there are still highly anisotropic thermal parameters and some shortened bonds, particularly the C–C methylene bonds. An application of Hamilton's R-factor ratio test showed that the model employing the Mo data set is better than the model with the Cu data set at the 99.5% significance level. All tabulated crystal coordinate data are obtained from refinement of data set II.

The effects of anomalous dispersion were included in the calculated structure factors using the real and imaginary dispersion corrections of Cromer and Liberman.[19] A compilation of the final values of $|F_o|$ and $|F_c|$ for the 6949 reflections collected with Mo Kα radiation is available.[20]

Results and Discussion

The final positional and anisotropic thermal parameters for $[Cu_2(tren)_2(BZD)](NO_3)_4$ are presented in Tables II and III, respectively. The interatomic distances and bond angles for the structure are given in Table IV.

Description of the Molecular Structure. The structure consists of five-coordinate copper atoms bridged by a BZD molecule comprising a binuclear $[Cu_2(tren)_2(BZD)]^{4+}$ cation and nitrate anions. Two binuclear cations, identified as binuclear complexes A and B, together with eight nitrate anions form the crystallographic asymmetric unit. The atom-labeling scheme and geometry of the two independent binuclear cations are depicted in Figure 1 along with the bond distances about each Cu atom and within the BZD bridge. Stereoscopic views of these binuclear cations are available in the supplementary material.

The Cu–Cu distances within each of the binuclear cations are 12.273 (2) and 12.083 (2) Å, for molecules A and B,

Table III. Anisotropic Thermal Parameters (B_{ij} in Å^2) for $[Cu_2(tren)_2(BZD)](NO_3)_4$[a]

atom	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	14.8 (2)	71.1 (10)	29.1 (5)	3.0 (4)	3.5 (3)	−3.6 (6)
Cu(2)	15.9 (2)	68.0 (10)	27.5 (5)	4.6 (4)	6.7 (3)	−0.2 (6)
Cu(3)	14.0 (2)	76.3 (11)	30.0 (5)	−0.9 (4)	4.9 (3)	0.0 (6)
Cu(4)	13.8 (2)	97.2 (12)	31.3 (6)	−5.5 (4)	5.6 (3)	8.0 (6)
N(1)	21 (2)	81 (8)	30 (4)	6 (4)	2 (2)	−1 (4)
N(2)	23 (2)	82 (8)	48 (4)	−6 (3)	11 (2)	−7 (5)
N(3)	13 (1)	91 (7)	35 (4)	−5 (3)	5 (2)	2 (4)
N(4)	26 (2)	96 (8)	60 (5)	25 (3)	22 (3)	29 (5)
N(5)	19 (2)	66 (7)	31 (4)	2 (3)	3 (2)	0 (4)
N(6)	28 (2)	93 (8)	29 (4)	12 (3)	15 (2)	0 (4)
N(7)	18 (2)	86 (7)	28 (4)	10 (3)	6 (2)	5 (4)
N(8)	15 (2)	82 (7)	40 (4)	−3 (3)	11 (2)	5 (4)
N(9)	24 (2)	64 (7)	48 (4)	2 (3)	17 (2)	−6 (4)
N(10)	17 (2)	67 (7)	28 (3)	−3 (3)	7 (2)	−1 (4)
N(11)	16 (2)	85 (8)	27 (3)	0 (3)	2 (2)	4 (4)
N(12)	17 (2)	92 (8)	31 (4)	−3 (3)	7 (2)	−6 (4)
N(13)	18 (2)	93 (8)	56 (5)	−6 (3)	11 (2)	−29 (5)
N(14)	30 (2)	71 (8)	57 (5)	0 (3)	22 (3)	3 (5)
N(15)	12 (1)	96 (8)	27 (3)	0 (3)	0 (2)	−2 (4)
N(16)	25 (2)	167 (12)	35 (4)	−16 (4)	8 (2)	−2 (6)
N(17)	16 (2)	104 (8)	43 (4)	2 (3)	7 (2)	3 (5)
N(18)	26 (2)	121 (9)	35 (4)	−20 (4)	6 (2)	7 (5)
N(19)	23 (2)	115 (10)	62 (6)	−4 (4)	10 (3)	28 (6)
N(20)	15 (2)	86 (7)	30 (4)	0 (3)	8 (2)	5 (4)
C(1)	57 (5)	124 (14)	30 (5)	1 (6)	7 (4)	−5 (7)
C(2)	84 (7)	121 (14)	35 (6)	−15 (8)	30 (5)	−11 (8)
C(3)	22 (3)	128 (14)	48 (6)	3 (4)	12 (3)	20 (7)
C(4)	18 (2)	115 (12)	66 (7)	6 (4)	15 (3)	6 (7)
C(5)	17 (2)	115 (12)	44 (6)	−3 (4)	−8 (3)	33 (6)
C(6)	24 (3)	111 (12)	64 (7)	17 (5)	17 (4)	17 (7)
C(7)	17 (2)	63 (8)	26 (4)	−6 (3)	8 (2)	−18 (5)
C(8)	16 (2)	80 (9)	33 (5)	8 (3)	3 (2)	0 (5)
C(9)	15 (2)	57 (8)	45 (5)	5 (3)	6 (3)	−5 (5)
C(10)	20 (2)	56 (8)	29 (4)	−3 (3)	11 (2)	2 (5)
C(11)	20 (2)	71 (9)	43 (5)	7 (4)	0 (3)	−16 (6)
C(12)	22 (2)	82 (10)	46 (6)	6 (4)	0 (3)	−17 (6)
C(13)	15 (2)	49 (7)	28 (4)	3 (3)	6 (2)	7 (4)
C(14)	17 (2)	54 (8)	32 (4)	2 (3)	6 (2)	6 (5)
C(15)	17 (2)	60 (8)	42 (5)	0 (3)	9 (3)	9 (5)
C(16)	15 (2)	55 (8)	26 (4)	0 (3)	6 (2)	4 (4)
C(17)	13 (2)	66 (8)	34 (5)	3 (3)	2 (2)	7 (5)
C(18)	19 (2)	45 (7)	37 (5)	3 (3)	5 (2)	0 (5)
C(19)	68 (6)	306 (27)	64 (8)	106 (11)	39 (6)	106 (12)
C(20)	15 (2)	90 (10)	61 (6)	17 (4)	10 (3)	4 (6)
C(21)	52 (5)	196 (19)	81 (9)	−63 (8)	46 (5)	−27 (10)
C(22)	20 (3)	177 (17)	69 (8)	13 (5)	7 (4)	22 (9)
C(23)	48 (4)	148 (15)	37 (6)	−17 (6)	24 (4)	−40 (7)
C(24)	43 (4)	75 (10)	60 (7)	12 (5)	13 (4)	−4 (7)
C(25)	16 (2)	97 (10)	41 (5)	−2 (4)	8 (3)	4 (6)
C(26)	16 (2)	97 (10)	60 (6)	−2 (4)	13 (3)	−7 (7)
C(27)	22 (3)	146 (14)	53 (6)	−7 (5)	5 (3)	−41 (8)
C(28)	29 (3)	109 (12)	84 (8)	−31 (5)	27 (4)	−44 (8)
C(29)	44 (4)	138 (14)	33 (5)	21 (6)	14 (4)	−2 (7)
C(30)	62 (5)	155 (16)	38 (6)	−3 (7)	21 (5)	24 (8)
C(31)	21 (2)	49 (8)	26 (4)	2 (3)	10 (2)	−6 (4)
C(32)	10 (2)	88 (9)	38 (5)	−6 (3)	3 (2)	−5 (5)
C(33)	15 (2)	75 (9)	42 (5)	−9 (3)	14 (3)	−9 (5)
C(34)	12 (2)	80 (9)	29 (4)	6 (3)	5 (2)	−8 (5)
C(35)	19 (2)	52 (8)	39 (5)	−2 (3)	4 (3)	11 (5)
C(36)	20 (2)	71 (9)	36 (5)	3 (4)	2 (3)	−1 (5)
C(37)	14 (2)	57 (8)	34 (4)	3 (3)	14 (2)	2 (5)
C(38)	18 (2)	77 (9)	29 (4)	5 (3)	3 (2)	0 (5)
C(39)	15 (2)	83 (9)	45 (5)	4 (3)	12 (3)	9 (6)
C(40)	13 (2)	80 (9)	25 (4)	3 (3)	4 (2)	1 (5)
C(41)	18 (2)	54 (8)	32 (4)	5 (3)	10 (2)	−4 (5)
C(42)	17 (2)	60 (8)	35 (4)	−5 (3)	4 (2)	0 (5)
C(43)	46 (5)	469 (40)	83 (10)	36 (12)	41 (6)	−37 (18)
C(44)	32 (3)	174 (17)	75 (8)	14 (6)	23 (4)	0 (10)
C(45)	30 (3)	306 (26)	40 (6)	−20 (8)	2 (4)	−25 (11)
C(46)	32 (4)	195 (18)	60 (7)	−26 (6)	14 (4)	−9 (9)
C(47)	90 (8)	170 (20)	69 (9)	−32 (10)	39 (7)	8 (11)
C(48)	35 (4)	142 (15)	104 (10)	6 (6)	26 (5)	69 (10)
N(21)	25 (2)	85 (8)	60 (5)	19 (3)	4 (3)	−4 (5)
O(1)	59 (3)	167 (11)	96 (6)	53 (5)	51 (4)	56 (7)
O(2)	50 (3)	71 (7)	76 (5)	−4 (3)	27 (3)	−11 (5)
O(3)	26 (2)	84 (8)	172 (9)	1 (3)	19 (3)	−47 (7)

Table III (*Continued*)

atom	B_{11} [b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(22)	27 (2)	50 (7)	83 (6)	−1 (3)	23 (3)	−13 (5)
O(4)	35 (2)	105 (8)	109 (7)	2 (3)	30 (3)	29 (6)
O(5)	23 (2)	164 (11)	127 (8)	15 (4)	−5 (3)	6 (7)
O(6)	34 (2)	87 (8)	150 (8)	−7 (3)	35 (4)	−12 (6)
N(23)	17 (2)	78 (8)	72 (5)	2 (3)	15 (3)	14 (5)
O(7)	26 (2)	75 (7)	93 (5)	−4 (3)	17 (3)	7 (5)
O(8)	27 (2)	97 (8)	81 (5)	0 (3)	16 (3)	−25 (5)
O(9)	18 (2)	139 (9)	83 (5)	−11 (3)	1 (2)	−9 (5)
N(24)	23 (2)	78 (8)	64 (5)	−4 (3)	11 (3)	−19 (5)
O(10)	24 (2)	103 (7)	63 (4)	6 (3)	18 (2)	−6 (4)
O(11)	37 (2)	112 (9)	127 (7)	−7 (4)	43 (4)	−39 (6)
O(12)	53 (3)	82 (8)	155 (9)	−5 (4)	47 (4)	7 (7)
N(25)	31 (3)	96 (10)	170 (11)	−16 (4)	41 (4)	−72 (9)
O(13)	47 (3)	142 (10)	149 (9)	−26 (5)	46 (4)	−67 (8)
O(14)	77 (5)	134 (12)	229 (14)	14 (6)	84 (7)	76 (11)
O(15)	44 (3)	150 (12)	320 (18)	−26 (5)	74 (7)	−37 (12)
N(26)	17 (2)	224 (15)	65 (6)	24 (4)	23 (3)	27 (7)
O(16)	25 (2)	188 (11)	72 (5)	19 (4)	21 (3)	35 (6)
O(17)	24 (2)	367 (21)	173 (10)	28 (6)	45 (4)	−19 (12)
O(18)	34 (2)	183 (12)	111 (7)	13 (4)	34 (3)	−8 (7)
N(27)	18 (2)	169 (11)	41 (4)	−3 (4)	9 (2)	−15 (6)
O(19)	23 (2)	146 (9)	64 (4)	−6 (3)	11 (2)	−27 (5)
O(20)	27 (2)	218 (13)	85 (6)	−11 (4)	22 (3)	0 (7)
O(21)	31 (2)	148 (10)	103 (6)	0 (4)	27 (3)	18 (6)
N(28)	25 (2)	76 (8)	72 (6)	−8 (3)	16 (3)	13 (5)
O(22)	24 (2)	103 (7)	57 (4)	−6 (3)	18 (2)	6 (4)
O(23)	31 (2)	79 (7)	141 (7)	6 (3)	43 (3)	13 (6)
O(24)	45 (3)	104 (8)	123 (7)	−8 (4)	38 (4)	−10 (6)

[a] Anisotropic thermal parameters are $\times 10^4$. [b] The form of the anisotropic thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}hl + 2B_{23}kl)]$.

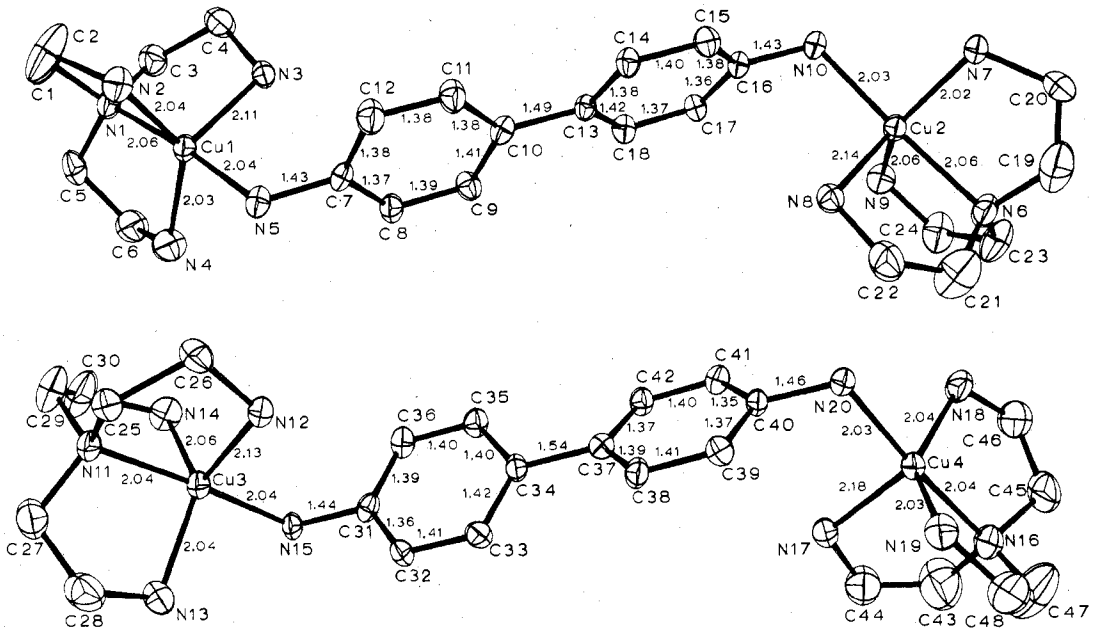

Figure 1. ORTEP plotting of the molecular structure of the two binuclear cations of molecules A and B in $[Cu_2(tren)_2(BZD)](NO_3)_4$ excluding the hydrogen atoms. Vibrational ellipsoids are drawn at the 50% probability level and bond distances given are to the nearest 0.01 Å.

respectively. The local Cu environments are all distorted trigonal bipyramids. The tertiary nitrogen of the tren ligand occupies one apical site with the remaining tren nitrogens disposed about the equatorial positions of the trigonal bipyramid. A nitrogen atom from the BZD bridge occupies the other apical position about the Cu atom. As can be seen from Figure 1, only minor variations in the Cu–ligand bond distances are observed when comparing similar bonds for the four Cu atoms. The four bond lengths from the Cu atoms to the tertiary nitrogen atoms have a weighted mean[21] 2.051 ± 0.005 Å with a range of 2.041 (10)–2.063 (9) Å. In a series of outer-sphere dimers of the form $[Cu_2(tren)_2X_2](BPh_4)_2$, where $X^- = CN^-$,[22] Cl^-,[23] NCO^-,[23] or NCS^-,[23] the Cu atom coordination geometry is also trigonal bipyramidal, and it has been noted in these complexes that the bond to the tertiary nitrogen is always the shortest distance among the Cu–N(tren) bonds. However, this trend is not followed for any of the copper ions in $[Cu_2(tren)_2(BZD)](NO_3)_4$ and the discrepancy could be due to different packing effects on the tren ligand from the NO_3^- and BPh_4^- counterions. The weighted mean[21] Cu–N(BZD) distance is 2.036 ± 0.002 Å when both binuclear molecules are included and the distance varies from 2.033 (8) to 2.044 (8) Å. A trend which emerges from the bond distances about all four Cu atoms shows that the two axial and

Table IV. Principal Interatomic Distances (Å) and Angles (deg) for $[Cu_2(tren)_2(BZD)](NO_3)_4$

Distances within $[Cu_2(tren)_2(BZD)]^{4+}$

Cu(1)-Cu(2)	12.273 (2)	N(1)-C(1)	1.47 (2)	N(16)-C(45)	1.52 (2)	C(19)-C(20)	1.32 (3)
Cu(3)-Cu(4)	12.083 (2)	N(1)-C(3)	1.46 (2)	N(16)-C(47)	1.45 (2)	C(21)-C(22)	1.38 (2)
Cu(1)-N(1)	2.055 (9)	N(1)-C(5)	1.49 (2)	N(17)-C(44)	1.42 (2)	C(23)-C(24)	1.39 (2)
Cu(1)-N(2)	2.038 (10)	N(2)-C(2)	1.44 (2)	N(18)-C(46)	1.43 (2)	C(25)-C(26)	1.55 (2)
Cu(1)-N(3)	2.110 (9)	N(3)-C(4)	1.45 (2)	N(19)-C(48)	1.46 (2)	C(27)-C(28)	1.48 (2)
Cu(1)-N(4)	2.028 (11)	N(4)-C(6)	1.45 (2)	N(20)-C(40)	1.457 (13)	C(29)-C(30)	1.39 (2)
Cu(1)-N(5)	2.042 (8)	N(5)-C(7)	1.432 (13)	C(1)-C(2)	1.31 (2)	C(31)-C(32)	1.36 (2)
Cu(2)-N(6)	2.063 (9)	N(6)-C(19)	1.47 (2)	C(3)-C(4)	1.51 (2)	C(31)-C(36)	1.39 (2)
Cu(2)-N(7)	2.023 (9)	N(6)-C(21)	1.44 (2)	C(5)-C(6)	1.50 (2)	C(32)-C(33)	1.41 (2)
Cu(2)-N(8)	2.140 (9)	N(6)-C(23)	1.46 (2)	C(7)-C(8)	1.37 (2)	C(33)-C(34)	1.42 (2)
Cu(2)-N(9)	2.057 (9)	N(7)-C(20)	1.47 (2)	C(7)-C(12)	1.38 (2)	C(34)-C(35)	1.40 (2)
Cu(2)-N(10)	2.033 (8)	N(8)-C(22)	1.44 (2)	C(8)-C(9)	1.39 (2)	C(34)-C(37)	1.54 (2)
Cu(3)-N(11)	2.044 (8)	N(9)-C(24)	1.43 (2)	C(9)-C(10)	1.41 (2)	C(35)-C(36)	1.40 (2)
Cu(3)-N(12)	2.133 (10)	N(10)-C(16)	1.428 (13)	C(10)-C(11)	1.38 (2)	C(37)-C(38)	1.39 (2)
Cu(3)-N(13)	2.044 (10)	N(11)-C(25)	1.48 (2)	C(10)-C(13)	1.49 (2)	C(37)-C(42)	1.37 (2)
Cu(3)-N(14)	2.061 (10)	N(11)-C(27)	1.46 (2)	C(11)-C(12)	1.38 (2)	C(38)-C(39)	1.41 (2)
Cu(3)-N(15)	2.036 (8)	N(11)-C(29)	1.43 (2)	C(13)-C(14)	1.38 (2)	C(39)-C(40)	1.37 (2)
Cu(4)-N(16)	2.041 (10)	N(12)-C(26)	1.46 (2)	C(13)-C(18)	1.418 (14)	C(40)-C(41)	1.35 (2)
Cu(4)-N(17)	2.177 (10)	N(13)-C(28)	1.47 (2)	C(14)-C(15)	1.40 (2)	C(41)-C(42)	1.40 (2)
Cu(4)-N(18)	2.041 (11)	N(14)-C(30)	1.47 (2)	C(15)-C(16)	1.38 (2)	C(43)-C(44)	1.37 (3)
Cu(4)-N(19)	2.026 (11)	N(15)-C(31)	1.436 (13)	C(16)-C(17)	1.36 (2)	C(45)-C(46)	1.44 (3)
Cu(4)-N(20)	2.032 (8)	N(16)-C(43)	1.47 (3)	C(17)-C(18)	1.37 (2)	C(47)-C(48)	1.33 (3)

Angles within $[Cu_2(tren)_2(BZD)]^{4+}$

N(1)-Cu(1)-N(2)	84.8 (4)	N(17)-Cu(4)-N(20)	101.4 (4)	C(43)-N(16)-Cu(4)	107.4 (11)	C(22)-C(21)-N(6)	120 (2)
N(1)-Cu(1)-N(3)	83.5 (4)	N(18)-Cu(4)-N(19)	141.2 (4)	C(45)-N(16)-C(47)	110.6 (13)	N(8)-C(22)-C(21)	116.5 (14)
N(1)-Cu(1)-N(4)	85.3 (4)	N(18)-Cu(4)-N(20)	92.4 (4)	C(45)-N(16)-Cu(4)	105.3 (9)	C(24)-C(23)-N(6)	119.7 (13)
N(1)-Cu(1)-N(5)	175.1 (4)	N(19)-Cu(4)-N(20)	94.5 (4)	C(47)-N(16)-Cu(4)	108.1 (11)	N(9)-C(24)-C(23)	116.6 (13)
N(2)-Cu(1)-N(3)	107.9 (4)	C(1)-N(1)-C(3)	113.8 (10)	C(44)-N(16)-Cu(4)	109.2 (9)	C(26)-C(25)-N(11)	110.9 (9)
N(2)-Cu(1)-N(4)	135.0 (4)	C(1)-N(1)-C(5)	109.9 (10)	C(46)-N(18)-Cu(4)	111.6 (9)	N(12)-C(26)-C(25)	108.9 (10)
N(2)-Cu(1)-N(5)	93.7 (4)	C(1)-N(1)-Cu(1)	107.2 (8)	C(48)-N(19)-Cu(4)	109.1 (9)	C(28)-C(27)-N(11)	109.6 (11)
N(3)-Cu(1)-N(4)	114.3 (4)	C(3)-N(1)-C(5)	110.7 (9)	C(40)-N(20)-Cu(4)	111.9 (6)	N(13)-C(28)-C(27)	109.4 (11)
N(3)-Cu(1)-N(5)	101.4 (4)	C(3)-N(1)-Cu(1)	108.9 (7)	C(2)-C(1)-N(1)	118.9 (14)	C(30)-C(29)-N(11)	116.3 (13)
N(4)-Cu(1)-N(5)	92.5 (4)	C(5)-N(1)-Cu(1)	106.1 (7)	N(2)-C(2)-C(1)	121 (2)	N(14)-C(30)-C(29)	114.8 (14)
N(6)-Cu(2)-N(7)	84.6 (4)	C(2)-N(2)-Cu(1)	107.6 (9)	C(4)-C(3)-N(1)	113.0 (11)	C(32)-C(31)-C(36)	120.4 (10)
N(6)-Cu(2)-N(8)	82.8 (4)	C(4)-N(3)-Cu(1)	108.5 (7)	N(3)-C(4)-C(3)	108.9 (11)	C(32)-C(31)-N(15)	118.7 (9)
N(6)-Cu(2)-N(9)	85.2 (4)	C(6)-N(4)-Cu(1)	108.9 (8)	C(6)-C(5)-N(1)	110.7 (10)	C(36)-C(31)-N(15)	120.6 (9)
N(6)-Cu(2)-N(10)	176.9 (4)	C(7)-N(5)-Cu(1)	117.9 (7)	N(4)-C(6)-C(5)	109.3 (11)	C(33)-C(32)-C(31)	121.1 (10)
N(7)-Cu(2)-N(8)	114.1 (4)	C(19)-N(6)-C(21)	110.7 (12)	C(8)-C(7)-C(12)	119.0 (10)	C(34)-C(33)-C(32)	119.3 (10)
N(7)-Cu(2)-N(9)	136.1 (4)	C(19)-N(6)-C(23)	115.5 (12)	C(8)-C(7)-N(5)	119.8 (10)	C(35)-C(34)-C(37)	120.6 (9)
N(7)-Cu(2)-N(10)	92.5 (4)	C(19)-N(6)-Cu(2)	105.0 (10)	C(12)-C(7)-N(5)	121.1 (10)	C(35)-C(34)-C(33)	118.8 (10)
N(8)-Cu(2)-N(9)	106.7 (4)	C(21)-N(6)-C(23)	110.8 (11)	C(9)-C(8)-C(7)	121.0 (10)	C(37)-C(34)-C(33)	120.7 (9)
N(8)-Cu(2)-N(10)	99.5 (4)	C(21)-N(6)-Cu(2)	109.3 (9)	C(10)-C(9)-C(8)	121.1 (10)	C(36)-C(35)-C(34)	120.6 (10)
N(9)-Cu(2)-N(10)	96.1 (4)	C(23)-N(6)-Cu(2)	105.2 (8)	C(11)-C(10)-C(13)	123.0 (10)	C(31)-C(36)-C(35)	119.8 (10)
N(11)-Cu(3)-N(12)	84.1 (4)	C(20)-N(7)-Cu(2)	110.0 (7)	C(11)-C(10)-C(9)	115.6 (10)	C(38)-C(37)-C(42)	121.2 (10)
N(11)-Cu(3)-N(13)	84.5 (4)	C(22)-N(8)-Cu(2)	108.3 (8)	C(13)-C(10)-C(9)	121.4 (10)	C(38)-C(37)-C(34)	119.0 (9)
N(11)-Cu(3)-N(14)	84.5 (4)	C(24)-N(9)-Cu(2)	109.4 (8)	C(12)-C(11)-C(10)	123.4 (11)	C(42)-C(37)-C(34)	119.8 (9)
N(11)-Cu(3)-N(15)	175.3 (4)	C(16)-N(10)-Cu(2)	113.3 (8)	C(7)-C(12)-C(11)	119.8 (11)	C(39)-C(38)-C(37)	118.5 (10)
N(12)-Cu(3)-N(13)	117.8 (4)	C(25)-N(11)-O(27)	110.8 (9)	C(14)-C(13)-C(18)	116.3 (9)	C(40)-C(39)-C(38)	119.5 (10)
N(12)-Cu(3)-N(14)	107.3 (4)	C(25)-N(11)-C(29)	110.6 (10)	C(14)-C(13)-C(10)	121.5 (9)	C(41)-C(40)-N(20)	120.9 (9)
N(12)-Cu(3)-N(15)	100.5 (4)	C(25)-N(11)-Cu(3)	109.0 (7)	C(18)-C(13)-C(10)	122.1 (9)	C(41)-C(40)-C(39)	121.3 (10)
N(13)-Cu(3)-N(14)	132.0 (4)	C(27)-N(11)-C(29)	110.2 (10)	C(15)-C(14)-C(13)	120.9 (10)	N(20)-C(40)-C(39)	117.7 (9)
N(13)-Cu(3)-N(15)	92.7 (4)	C(27)-N(11)-Cu(3)	107.2 (7)	C(16)-C(15)-C(14)	121.5 (10)	C(42)-C(41)-C(40)	120.4 (10)
N(14)-Cu(3)-N(15)	94.6 (4)	C(29)-N(11)-Cu(3)	109.0 (8)	C(17)-C(16)-N(10)	121.8 (9)	C(37)-C(42)-C(41)	119.1 (10)
N(16)-Cu(4)-N(17)	83.1 (4)	C(26)-N(12)-Cu(3)	108.2 (7)	C(17)-C(16)-C(15)	118.1 (10)	C(44)-C(43)-N(16)	123 (2)
N(16)-Cu(4)-N(18)	85.9 (4)	C(28)-N(13)-Cu(3)	107.4 (8)	N(10)-C(16)-C(15)	120.0 (9)	N(17)-C(44)-C(43)	116 (2)
N(16)-Cu(4)-N(19)	84.2 (4)	C(30)-N(14)-Cu(3)	106.2 (9)	C(18)-C(17)-C(16)	121.7 (10)	C(46)-C(45)-N(16)	116.8 (14)
N(16)-Cu(4)-N(20)	175.4 (4)	C(31)-N(15)-Cu(3)	114.9 (6)	C(13)-C(18)-C(17)	121.5 (10)	N(18)-C(46)-C(45)	113.5 (14)
N(17)-Cu(4)-N(18)	111.4 (4)	C(43)-N(16)-C(45)	110.0 (14)	C(20)-C(19)-N(6)	122 (2)	C(48)-C(47)-N(16)	119 (2)
N(17)-Cu(4)-N(19)	104.6 (4)	C(43)-N(16)-C(47)	115 (2)	N(7)-C(20)-C(19)	113.2 (13)	N(19)-C(48)-C(47)	118 (2)

Distances within the Nitrate Anions

N(21)-O(1)	1.24 (2)	N(23)-O(7)	1.237 (14)	N(25)-O(13)	1.18 (2)	N(27)-O(19)	1.21 (2)
N(21)-O(2)	1.220 (14)	N(23)-O(8)	1.245 (13)	N(25)-O(14)	1.19 (2)	N(27)-O(20)	1.25 (2)
N(21)-O(3)	1.210 (14)	N(23)-O(9)	1.197 (14)	N(25)-O(15)	1.13 (2)	N(27)-O(21)	1.23 (2)
N(22)-O(4)	1.209 (14)	N(24)-O(10)	1.226 (14)	N(26)-O(16)	1.22 (2)	N(28)-O(22)	1.211 (14)
N(22)-O(5)	1.23 (2)	N(24)-O(11)	1.22 (2)	N(26)-O(17)	1.13 (2)	N(28)-O(23)	1.22 (2)
N(22)-O(6)	1.22 (2)	N(24)-O(12)	1.192 (14)	N(26)-O(18)	1.26 (2)	N(28)-O(24)	1.21 (2)

Angles within the Nitrate Anions

O(1)-N(21)-O(2)	120.3 (11)	O(7)-N(23)-O(8)	115.2 (10)	O(13)-N(25)-O(14)	119 (2)	O(19)-N(27)-O(20)	120.3 (11)
O(1)-N(21)-O(3)	118.4 (12)	O(7)-N(23)-O(9)	120.4 (10)	O(13)-N(25)-O(15)	126 (2)	O(19)-N(27)-O(21)	120.2 (11)
O(2)-N(21)-O(3)	121.3 (11)	O(8)-N(23)-O(9)	124.4 (11)	O(14)-N(25)-O(15)	113 (2)	O(20)-N(27)-O(21)	119.2 (11)
O(4)-N(22)-O(5)	120.9 (11)	O(10)-N(24)-O(11)	118.7 (11)	O(16)-N(26)-O(17)	123.6 (14)	O(22)-N(28)-O(23)	121.8 (11)
O(4)-N(22)-O(6)	115.5 (11)	O(10)-N(24)-O(12)	121.3 (11)	O(16)-N(26)-O(18)	112.3 (12)	O(22)-N(28)-O(24)	122.6 (11)
O(5)-N(22)-O(6)	123.5 (11)	O(11)-N(24)-O(12)	120.0 (12)	O(17)-N(26)-O(18)	124.0 (14)	O(23)-N(28)-O(24)	115.5 (11)

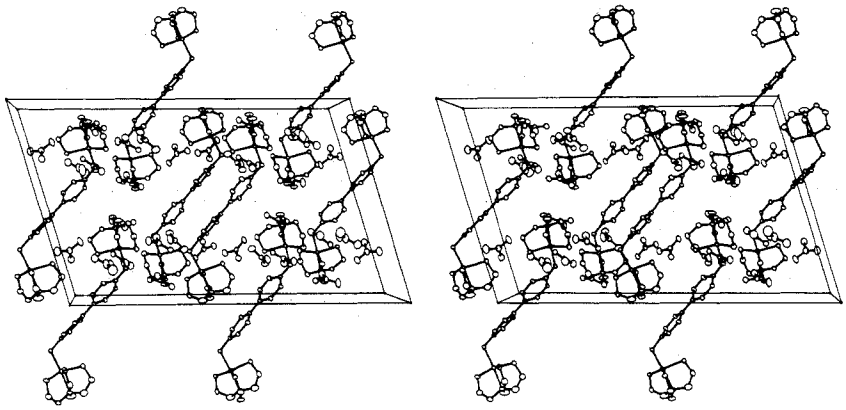

Figure 2. Stereoscopic view of the molecular packing in the unit cell of $[Cu_2(tren)_2(BZD)](NO_3)_4$ omitting the hydrogen atoms. The view is down the *b* axis with the *a* axis horizontal and the *c* axis approximately vertical.

two equatorial bonds are all about equal and average[21] 2.042 ± 0.003 Å in length with minimum and maximum values of 2.023 (9) and 2.063 (9) Å, respectively, while one longer bond completes the trigonal bipyramid in an equatorial position with a weighted mean Cu–N(tren) distance of 2.138 ± 0.014 Å with a range of 2.110 (9)–2.117 (10) Å. Finally, all four Cu atoms are displaced out of the trigonal plane formed by the three tren nitrogen atoms toward the BZD nitrogen atom by an average of 0.199 (1) Å. The trigonal and other selected least-squares planes for the structure are presented in Table V.[20]

The distorted nature of the trigonal-bipyramidal coordination in $[Cu_2(tren)_2(BZD)](NO_3)_4$ becomes evident from an examination of the N–Cu–N bond angles. The trigonal angles average[21] to 119 ± 4° but vary from 104.6 (4) to 141.2 (4)°. Among other structurally characterized molecules involving the $Cu(tren)^{2+}$ moiety,[22-24] the range in the trigonal angles is from ca. 112 to 130°. The greater variation in $[Cu_2(tren)_2(BZD)](NO_3)_4$ may be due to the packing forces or hydrogen-bonding interactions (vide infra) between the equatorial tren nitrogens and the oxygen atoms from the nitrate anions. The trigonal axis formed by N(tertiary)–Cu–N(BZD) is nearly linear and only ranges from 175.1 (4) to 176.9 (4)° for the four Cu atoms. The bonding of the sp^3-hybridized BZD nitrogen atoms is close to the expected tetrahedral angle with all C(BZD)–N(BZD)–Cu angles slightly larger than 109.5° and in the range of 111.9 (6)–117.9 (7)°.

The tren ligand shows shortened methylene C–C distances which are probably artifacts stemming from their very anisotropic thermal motion. Consequently, the mean[21] C–C distance in the tren ligand is 1.42 ± 0.02 Å with a range of 1.31 (2)–1.55 (2) Å. The average[21] C–N(tertiary) and C–N(tren) distances of 1.47 ± 0.01 and 1.45 ± 0.01 Å, respectively, closely follow the expected[25] C–N single-bond distance of 1.47 Å.

All four phenyl rings of the two BZD molecules are planar (see Table V[20]) with a dihedral angle between the phenyl rings of 14.3 and 22.5° for molecules A and B, respectively. The C–C bonds connecting the phenyl rings in the two molecules are 1.49 (2) and 1.54 (2) Å which are quite typical for other structurally characterized compounds containing the BZD unit.[26-33] The phenyl rings have a mean[21] C–C distance of 1.388 ± 0.004 Å. Consequently, the bond distances in the BZD bridges are appropriate for aromatic rings with no tendency toward a quinonoid character which has been associated with an ionic ground state in some charge-transfer complexes with diamine molecules.[34]

When the amino group of the aromatic diamine becomes protonated, the C–N bond length has been found to increase. For example, structural studies involving the BZD[27-33] or PPD[34,35] molecules show an average[21] C–N bond distance of 1.402 ± 0.005 Å, whereas protonated molecules such as BZD·$HClO_4$[26] or PPD·2HCl[36] have been found to have C–N bond lengths of 1.48 and 1.490 (13) Å, respectively. The two BZD molecules in the asymmetric unit of $[Cu_2(tren)_2(BZD)](NO_3)_4$ show C–N bond distances in the range of 1.428 (13)–1.457 (13) Å.

As can be seen in Table V,[20] the nitrate anions are planar with no deviations from the best planes greater than 0.03 (2) Å except N(25) which is displaced 0.06 (1) Å from the least-squares plane. The N–O distances of the nitrate ions show a weighted mean value[21] of 1.213 ± 0.006 Å, but this bond length varies from 1.13 (2) to 1.26 (2) Å when all eight independent nitrate groups in the asymmetric unit are considered. The O–N–O angles average[21] to 119.8 ± 0.7° (the range is 113 (2)–126 (2)°) which is close to the 120° angle expected for a trigonal geometry.

Molecular Packing. The two crystallographically independent binuclear molecules are related to each other by a translation of *almost* ($^1/_2$, 0, 0). The contents of the unit cell can be seen in the stereoscopic drawing of Figure 2. The view is down the *b* axis in the *ac* plane with the long *a* axis in the horizontal direction. The $[Cu_2(tren)_2(BZD)]^{4+}$ cations appear to have the $Cu(tren)^{2+}$ moieties located in the upper and lower portions of the unit cell (Figure 4) with the NO_3^- anions occurring in channels about each $Cu(tren)^{2+}$ unit. The relatively small nitrate counterions lead to *inter*molecular Cu–Cu distances as short as 7.376 (2) Å, whereas the intramolecular Cu–Cu distances within each binuclear cation average to about 12.2 Å. A compilation of the Cu–Cu distances within the asymmetric unit and neighboring units which are less than 15 Å appears in Table VI.[20] The shortest nitrate oxygen-to-copper contact is 3.33 (2) Å (Table VII[20] gives all O–Cu distances less than 4.4 Å) and hence, no coordination to the copper atoms from the nitrate oxygen atoms is evident. However, the nitrate oxygen atoms participate in hydrogen bonding (vide infra) to the coordinated amino groups. The network of intervening nitrate anions between the binuclear cations is summarized in Table VIII[20].

All nitrate oxygen atoms in the asymmetric unit participate in hydrogen-bonding interactions with the amino groups on the tren and BZD ligands. A total of eight contact distances less than 3.0 Å for the amino nitrogens and the nitrate oxygens can be found between independent molecules, and these distances are collected in Table IX[20] along with distances and angles for the hydrogen bond. None of the N···O distances is less than 2.9 Å[37] and these distances are all close to the upper limit of reported N···O hydrogen bond lengths of 2.99–3.01 Å.[38]

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Supplementary Material Available: Stereoscopic views of the two binuclear cations, Tables V (least-squares planes), VI (Cu–Cu distances within the asymmetric unit), VII (O–Cu distances less than 4.4 Å), VIII (network of nitrates between binuclear cations), and IX (possible hydrogen-bond distances and angles), final values of F_o and F_c for $[Cu_2(tren)_2(BZD)](NO_3)_4$ with unobserved reflections marked with asterisks (44 pages). Ordering information is given on any current masthead page.

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Crystal Structure of a Closo Six-Vertex Metalloboron Cluster, 1,2-$(\eta^5$-$C_5H_5)_2Co_2B_4H_6$, with Hydrogen Atoms Bridging Co_2B Triangular Faces

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A single-crystal X-ray diffraction investigation of the title compound established the structure as an octahedral Co_2B_4 cage with the metal atoms occupying adjacent vertices and each cobalt coordinated to an η^5-cyclopentadienyl ring, in agreement with the geometry originally proposed from ^{11}B and ^1H NMR data. Two crystallographically equivalent hydrogen atoms occupy face-bridging positions approximately over the centers of the two Co_2B triangular faces, in a manner very similar to face bridging of trimetallic faces in metal-cluster compounds. This structure represents the first instance in which face-bridging hydrogen atoms on an M_2N face (where M and N are metal and nonmetal atoms, respectively) have been located and refined and is the second example of a face-bridging hydrogen on a closo polyhedral boron cage (after CB_5H_7) to be precisely located. The Co–Co bond distance is 2.557 (1) Å, the longest such distance thus far known in a cobalt–boron cage compound; the unusual length is attributed to the presence of bridging hydrogen atoms on both sides of the Co–Co vector, which are thought to produce a lowering of the Co–Co bond order. The implications of these findings with respect to other closo metalloboranes and metallocarboranes containing "extra" hydrogen atoms are discussed. Crystal data: M_r = 297.4; space group $P2_1/m$; a = 7.601 (5), b = 9.060 (4), c = 9.793 (5) Å; β = 108.07 (5)°; V = 641 (1) Å^3; μ(Mo Kα) = 26.5 cm^{-1}; ρ(calcd) = 1.544 g cm^{-3} for Z = 2. The structure was refined by full-matrix least-squares methods to a final R value of 0.039 for the 994 reflections for which $F_o^2 > 3\sigma(F_o^2)$.

Introduction

An extensive series of air-stable, crystalline cobaltaboranes, several of which are structurally unique, is formed in the reaction of $CoCl_2$, $B_5H_8^-$, and $C_5H_5^-$ in cold tetrahydrofuran (THF). The isolation and characterization of a number of these compounds have been described elsewhere,[1] and X-ray structure determinations on 2-$(\eta^5$-$C_5H_5)CoB_4H_8$,[2] $(\eta^5$-$C_5H_5)CoB_9H_{13}$,[3] $(\eta^5$-$C_5H_5)_3Co_3B_3H_5$,[4] $(\eta^5$-$C_5H_5)_3Co_3B_4H_4$,[4]

