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Dipicolylamine Complexes of Copper(II): Two Different Coordination Geometries in the Same Unit Cell of $Cu(Dipica)_2(BF_4)_2$

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Bright blue $Cu(Dipica)_2(BF_4)_2$ crystallizes in the monoclinic space group $P2_1/n$, with unit cell parameters $a = 23.406(6)$ Å, $b = 9.338(2)$ Å, $c = 25.573(7)$ Å, $\beta = 95.39(2)°$, and $Z = 8$. The structure was solved by conventional Patterson and Fourier methods. The R and R_w values for 5282 observed reflections were 7.06% and 9.10% respectively. Two structurally different complex cations are present in the same unit cell, one hexacoordinate and the other pentacoordinate. In the hexacoordinate cation, the two tridentate bis(2′-picolyl)amine ligands are *trans*-facially coordinated with two pyridine nitrogens and the two secondary amine nitrogens situated on four positions in a plane [$Cu-N_{pyr} = 2.189(6)$, 2.146(6) Å; $Cu-N_{sat} = 2.207(6)$, 2.201(5) Å]. The remaining two pyridine nitrogens constitute the axis [$Cu-N_{pyr} = 2.035(5)$, 2.038(5) Å] in an equatorially expanded pseudooctahedral geometry. The pentacoordinate cation possesses a square-pyramidal configuration, the two secondary nitrogens being mutually *cis*, with one Dipica equatorially tridentate [$Cu-N_{pyr} = 2.044(5)$, 2.027(5) Å, $Cu-N_{sat} = 1.995(5)$ Å]. The other Dipica functions as a bidentate ligand, with one of the pyridine nitrogens occupying the equator [$Cu-N_{pyr} = 1.986(5)$ Å] and the aliphatic nitrogen defining the axial copper position [$Cu-N_{sat} = 2.344(5)$ Å]. Its second pyridine is uncoordinated but hydrogen-bonded to the coordinated NH of the other ligand. Solution properties offer no clear distinction between the two cation stereochemistries. The ternary chelates $[Cu(Dipica)(Acac)]ClO_4$ and $[Cu(Dipica)(Bipy)](ClO_4)_2$ are also described.

Introduction

One of the consequences of the Jahn−Teller theorem in the stereochemistry of copper(II) has been termed the "plasticity effect",[2] as a result of which copper(II) forms compounds of coordination number 4−6 with many kinds of irregular coordination geometries. The geometry of the coordination polyhedron around copper(II) is also influenced by several subtle ligand factors, such as ligand constraints, steric hindrance and the ligands' donor atoms' strengths. Two closely related chelating imidazole−thioether ligands (bidhx, bhdhx) with an N_2S_2 donor set have been found[3] to impose two different Cu(II) coordination geometries, and in fact, the Cu−bidhx system forms both pseudooctahedral and trigonal bipyramidal chlorides. Further, two structural isomers have been encountered[4] for the pentacoordinate copper(II) complex of a bidentate imidazole−thioether ligand, each with the same counteranion.

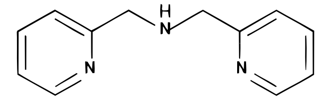

Figure 1. The ligand Dipica.

While the archetypical tridentate ligand dien (diethylenetriamine) is well-known to form meridionally coordinated octahedral complexes such as $Cu(dien)_2(NO_3)_2$[5] and $Cu(dien)_2Br_2\cdot H_2O$,[6] a few branched chain tridentate triaza ligands have been employed[7] to impose facial coordination. Their symmetry is intended to preclude geometric isomerism in the bis-complexes. Bis(azaarylalkyl)amines which have recently been observed to fold into the *cis*-facial configuration include bba (bis[benzimidazol-2′-ylmethyl]amine) in $Cu(bba)_2(ClO_4)_2\cdot 2H_2O$[8] and Dipica (dipicolylamine, bis(2′-picolyl)amine; Figure 1) in complexes of the type $M(Dipica)_2^{2+}$ [M = Fe(II),[9] Mn(II), Zn(II), or Cd(II)[10]]. In continuing our work[9,11] with Dipica, we give here details of a complex which reveals the ability of Dipica to coordinate facially as well as meridionally to copper(II). This paper describes details of our novel observation[12] of two different copper(II) coordination geometries for the Dipica

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(2) (a) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143 and references therein. (b) Hathaway, B. J. *Struct. Bonding (Berlin)* **1984**, *57*, 55.

(3) (a) Bouwman, E.; Bourik, A.; ten Hove, J. C.; Driessen, W. L.; Reedijk, J. *Inorg. Chim. Acta* **1988**, *150*, 125. (b) Bouwman, E.; Day, R.; Driessen, W. L.; Tram, W.; Krebs, B.; Wood, J. S.; Reedijk, J. *Inorg. Chem.* **1988**, *27*, 4614.

(4) Glass, R. S.; Sabahi, M.; Hojjatie, M.; Wilson, G. S. *Inorg. Chem.* **1987**, *26*, 2194.

(5) Stephens, F. *J. Chem. Soc. A* **1969**, 883.

(6) Hodgson, P. G.; Penfield, B. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1870.

(7) (a) Flückiger, J. R.; Schläpfer, C. W.; Couldwell, C. *Inorg. Chem.* **1980**, *19*, 2493. (b) Keene, F. R.; Snow, M. R.; Stephenson, P. J.; Tiekink, E. R. T. *Inorg. Chem.* **1988**, 27, 2040. (c) Henrick, K.; McPartlin, M.; Munjoma, S.; Owston, P. G.; Peters, R.; Sangokoya, S. A.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1982**, 225. (d) Ammeter, J. H.; Bürgi, H.-B.; Gamp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733. (e) Bernhardt, P. V.; Comba, P.; Mahu-Rickenbach, A.; Stebler, S.; Steiner, S.; Varnagy, K.; Zehnder, M. *Inorg. Chem.* **1992**, *31*, 4194.

(8) Palaniandavar, M.; Pandiyan, T.; Lakshiminarayanan, M.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1995**, 455.

(9) Butcher, R. J.; Addison, A. W. *Inorg. Chim. Acta* **1989**, *158*, 211.

(10) Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelson, K.; Nielsen, K. M.; Weihe, H. *Inorg. Chem.* **1992**, *31*, 4611.

(11) Addison, A. W.; Burman, S.; Wahlgren, C. G.; Rajan, O. A.; Rowe, T. M.; Sinn, E. *J. Chem. Soc. Dalton Trans.* **1987**, 2621.

(12) Addison, A. W.; Butcher, R. J.; Cain, M. R.; Palaniandavar, M.; Wahlgren, C. G. American Chemical Society, 22nd Mid-Atlantic Regional Meeting, 1988, No. 198.

(13) Holz, R. C.; Thompson, L. C. *Inorg. Chem.* **1993**, *32*, 5251. Following submission of this paper, reports appeared dealing with isomerism in crystals of hexacoordinate compounds of rhodium(III) and copper(II), respectively: Purcell, W.; Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Preston, H. *Inorg. Chim. Acta* **1995**, *234*, 153. Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Berens, H. W.; van der Linden, J. G. M.; Admiraal, G.; Beurskens, P. T.; Kooijman, H.; Spek, A. L.; Nolte, R. J. M. *Inorg. Chem.* **1995**, *34*, 4735.

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Table 1. Crystal Data for Cu(Dipica)$_2$(BF$_4$)$_2$

formula	$C_{24}H_{26}B_2CuF_8N_6$
molar mass	635.66
space group	$P2_1/n$ (monoclinic, No. 14)
a (Å)	23.406(6)
b (Å)	9.338(2)
c (Å)	25.573(7)
β (deg)	95.39(2)
V (Å^3)	5564.7(4.3)
Z	8
T	22 °C
λ (Å) Mo Kα	0.71073
ρ_{calcd} (Mg m^{-3})	1.517
μ (cm^{-1})	8.627
residuals[a]	
R	0.706
R_w	0.0910

[a] $R = \sum|(F_o - F_c)|/\sum F_o$; $R_w = \sum|(F_o - F_c)|w^{1/2}/\sum F_o w^{1/2}$; $w = (\sigma(F)^2 + p(F)^2)^{-1}$; $p = 0.07$.

ligand within the same unit cell. A similar phenomenon has been reported recently for a lanthanide chelate,[13] which exhibits two different octacoordinate isomers within the unit cell.

Experimental Section

Materials. All reagents for syntheses were used as received from Aldrich Chemical, Fisher Scientific, G. F. Smith, or Nepera (Dipica). For electrochemistry, tetrakis(*n*-hexyl)ammonium perchlorate (G. F. Smith) was recrystallized from aqueous ethanol, while methanol was distilled off magnesium turnings under N_2.

Bis(dipicolylamine)copper(II) Tetrafluoroborate, Cu(Dipica)$_2$(BF$_4$)$_2$. This was prepared by the addition of a methanolic solution (5 mL) of Cu(BF$_4$)$_2$·6H$_2$O (1 mmol) to a solution of Dipica (2.1 mmol) in methanol (10 mL) with stirring and subsequently keeping the solution aside for slow evaporation. The bright blue prisms of the tetrafluoroborate which deposited after a few days were suitable for X-ray diffraction. Anal. Calcd for $C_{24}H_{26}B_2CuF_8N_6$: C, 45.4; H, 4.12; N, 13.2. Found: C, 45.3; H, 4.14; N, 13.2.

(Dipicolylamine)(2,2′-bipyridyl)copper(II) Perchlorate, Cu(Dipica)(Bipy)(ClO$_4$)$_2$. To a warm, stirred solution of Dipica (1 mmol) in MeOH (10 mL) was added Cu(ClO$_4$)$_2$·6H$_2$O (1 mmol, in 5 mL of MeOH), followed by 2,2′-bipyridyl (1 mmol) in MeOH (10 mL). The finely divided bright blue crystals obtained were filtered off, washed with small amounts of methanol, and dried under vacuum over P_4O_{10}. Anal. Calcd for $C_{22}H_{21}Cl_2CuN_5O_8$: C, 42.8; H, 3.43; N, 11.3%. Found: C, 43.6; H, 3.57; N, 11.6.

(Dipicolylamine)(pentane-2,4-dionato)copper(II) Perchlorate, Cu(Dipica)(Acac)(ClO$_4$). A methanolic solution (5 mL) of Cu(ClO$_4$)$_2$·6H$_2$O (1 mmol) was added to a stirred solution of Dipica (1 mmol) and acetylacetone (1 mmol) in methanol (10 mL). Triethylamine (1

Table 2. Atomic Positional Parameters (with Standard Deviations): Hydrogens Excluded

atom	x/a	y/b	z/c	B (Å^2)[a]	atom	x/a	y/b	z/c	B (Å^2)[a]
Cu1	0.03407(5)	0.6299(1)	0.25102(4)	3.6(2)	C43a	0.2836(5)	0.512(1)	−0.1392(4)	6.4(3)
Cu2	0.24916(4)	0.7447(1)	0.00023(4)	3.34(2)	C43	0.4073(4)	0.533(1)	0.0380(4)	6.1(3)
N11	0.0886(3)	0.4641(7)	0.2398(3)	3.9(2)	C44	0.4481(4)	0.636(1)	0.0376(4)	6.3(3)
N11a	−0.0039(3)	0.7898(8)	0.2887(3)	4.4(2)	C44a	0.3049(5)	0.606(1)	−0.1737(4)	7.0(3)
N12	0.0257(3)	0.5280(8)	0.3185(3)	4.3(2)	C45a	0.3080(5)	0.745(1)	−0.1610(4)	6.4(3)
N21	0.0450(3)	0.7371(7)	0.1856(3)	3.7(2)	C45	0.4324(4)	0.777(1)	0.0289(4)	5.2(2)
N21a	−0.0840(3)	0.4094(8)	0.2852(3)	5.2(2)	C46	0.3755(4)	0.807(1)	0.0211(4)	5.1(2)
N22	−0.0407(3)	0.5382(7)	0.1932(2)	3.4(1)	C46a	0.2898(5)	0.789(1)	−0.1143(4)	5.9(3)
N31	0.2357(3)	0.7894(7)	0.0805(3)	4.9(2)	C47a	0.2409(5)	0.461(1)	−0.0551(4)	6.1(3)
N31a	0.1646(3)	0.7828(7)	−0.0217(3)	3.7(2)	C47	0.3021(4)	0.462(1)	0.0274(4)	6.0(3)
N32	0.2489(3)	0.9810(8)	−0.0016(3)	4.7(2)	B1	0.1007(6)	0.659(1)	0.5344(4)	5.4(3)
N41	0.3342(3)	0.7081(7)	0.0198(3)	3.7(2)	B2	0.1053(5)	0.325(1)	0.0431(5)	4.7(3)
N41a	0.2683(3)	0.6995(8)	−0.0803(3)	4.6(2)	B3	0.3345(6)	0.321(1)	0.1737(5)	5.9(3)
N42	0.2487(3)	0.5091(7)	−0.0005(3)	4.4(2)	B4	0.6545(6)	0.318(1)	0.3269(5)	6.3(3)
C12	0.0945(4)	0.372(1)	0.2803(3)	4.8(2)	F11	0.0915(3)	0.6653(7)	0.4813(3)	8.7(2)*
C12a	−0.0067(4)	0.767(1)	0.3400(3)	4.7(2)	F12	0.1570(3)	0.6224(7)	0.5487(3)	7.9(2)*
C13a	−0.0305(5)	0.867(1)	0.3708(4)	6.5(3)	F13	0.0921(3)	0.7923(7)	0.5554(3)	8.3(2)*
C13	0.1239(5)	0.245(1)	0.2774(4)	6.4(3)	F14	0.0658(3)	0.5607(8)	0.5533(3)	9.0(2)*
C14	0.1504(5)	0.218(1)	0.2322(5)	7.2(3)	F21	0.1012(4)	0.1883(9)	0.0565(3)	5.9(2)*
C14a	−0.0522(6)	0.991(1)	0.3550(5)	8.7(4)	F22	0.1606(3)	0.3732(8)	0.0593(3)	7.28(2)*
C15	0.1458(4)	0.312(1)	0.1914(4)	6.3(3)	F23	0.1112(5)	0.331(1)	−0.0110(5)	7.1(3)*
C15a	−0.0501(6)	1.013(1)	0.2976(5)	8.3(4)	F24	0.0713(4)	0.405(1)	0.0675(4)	6.8(2)*
C16	0.1145(4)	0.435(1)	0.1974(4)	4.8(2)	F25	0.427	0.748	0.420	5(1)*
C16a	−0.0259(5)	0.912(1)	0.2678(4)	5.9(3)	F26	0.0810(6)	0.339(1)	−0.0060(5)	8.2(3)*
C17a	0.0206(4)	0.631(1)	0.3612(3)	5.5(2)	F27	0.060	0.417	0.033	5.4(6)*
C17	0.0701(5)	0.418(1)	0.3292(4)	5.8(3)	F28	0.389	0.681	0.413	5(1)*
C22	0.0169(3)	0.6941(8)	0.1400(3)	3.4(2)	F29	0.159	0.325	0.028	6.1(7)*
C22a	−0.1034(4)	0.372(1)	0.2371(3)	4.6(2)	F31	0.3398(5)	0.242(1)	0.1284(4)	7.8(3)*
C23a	−0.1559(5)	0.314(1)	0.2266(4)	6.9(3)	F32	0.367	0.209	0.182	6.5(9)*
C23	0.0234(4)	0.763(1)	0.0932(3)	4.3(2)	F33	0.205	0.794	0.369	5.7(6)*
C24	0.0595(4)	0.881(1)	0.0925(3)	4.7(2)	F34	0.288	0.396	0.185	9.3(6)*
C24a	−0.1916(5)	0.300(1)	0.2673(5)	8.2(3)	F35	0.2775(6)	0.329(2)	0.1571(6)	9.2(4)*
C25a	−0.1723(5)	0.344(1)	0.3168(4)	7.1(3)	F36	0.117	0.904	0.314	8.0(6)*
C25	0.0872(4)	0.9259(9)	0.1390(4)	5.1(2)	F37	0.306	0.234	0.217	8.9(7)*
C26	0.0796(4)	0.8533(9)	0.1844(3)	4.8(2)	F38	0.3699(7)	0.429(2)	0.1553(7)	9.2(4)*
C26a	−0.1192(5)	0.397(1)	0.3228(4)	6.2(3)	F39	0.148	0.943	0.306	6.4(7)*
C27a	−0.0632(4)	0.3897(9)	0.1951(4)	5.1(2)	F41	0.8588(4)	0.750(1)	0.2201(4)	8.0(2)*
C27	−0.0196(4)	0.5629(9)	0.1410(3)	3.9(2)	F42	0.6018(4)	0.328(1)	0.3445(4)	8.0(6)*
C32	0.2432(4)	0.9270(9)	0.0945(4)	4.7(2)	F43	0.6657(5)	0.455(1)	0.3090(5)	9.1(3)*
C32a	0.1506(4)	0.9157(9)	−0.0369(3)	4.1(2)	F44	0.7972(5)	0.794(1)	0.1423(4)	8.8(3)*
C33a	0.0956(4)	0.951(1)	−0.0547(4)	5.2(2)	F45	0.872	0.753	0.132	8(6)*
C33	0.2433(4)	0.970(1)	0.1465(4)	5.8(3)	F46	0.697	0.414	0.335	8.5(7)*
C34	0.2370(5)	0.871(1)	0.1851(4)	6.7(3)	F47	0.827	0.713	0.138	8.6(8)*
C34a	0.0529(4)	0.848(1)	−0.0557(4)	5.5(3)	F48	0.617	0.448	0.326	10(1)*
C35	0.2271(5)	0.731(1)	0.1704(4)	6.6(3)	F49	0.836	0.710	0.212	8.1(5)*
C35a	0.0661(4)	0.712(1)	−0.0383(4)	4.5(2)	F210	0.135	0.445	0.076	7(1)*
C36	0.2274(5)	0.695(1)	0.1180(5)	6.4(3)	F211	0.076	0.475	0.074	6(1)*
C36a	0.1224(4)	0.6839(9)	−0.0221(3)	4.0(2)	F310	0.127	0.811	0.365	7(1)*
C37a	0.1984(4)	1.023(1)	−0.0352(5)	6.2(3)	F311	0.316	0.433	0.208	7.6(5)
C37	0.2511(5)	1.035(1)	0.0521(4)	6.6(3)	F312	0.3495(4)	0.220(1)	0.2112(4)	7.8(3)*
C42	0.3506(4)	0.573(1)	0.0281(3)	4.4(2)	F313	0.381	0.274	0.201	6.1(8)*
C42a	0.2659(4)	0.5605(9)	−0.0935(4)	4.3(2)					

[a] B-values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. An asterisk denotes a value for an isotropically refined atom.

Table 3. Selected Bond Distances and Angles in the $[Cu(Dipica)_2]^{2+}$ Cations[a]

Cu1−N11	2.044(5)	N32−C32	1.341(8)
Cu1−N11a	2.027(5)	N32−C36	1.328(10)
Cu1−N12	1.995(5)	N31a−C32a	1.332(8)
Cu1−N21	1.986(5)	N31a−C36a	1.352(8)
Cu1−N22	2.344(5)	N32−C37a	1.449(9)
Cu2−N31	2.146(6)	N32−C37	1.461(9)
Cu2−N31a	2.038(5)	N32−HN32	0.950(5)
Cu2−N32	2.207(6)	N41−C42	1.327(8)
Cu2−N41	2.035(5)	N41−C42a	1.342(8)
Cu2−N41a	2.189(6)	C32−C37	1.506(10)
Cu2−N42	2.201(5)	C32a−C37a	1.499(9)
N11−C12	1.345(8)	N42−C47a	1.461(9)
N11a−C12a	1.337(8)	N42−C47	1.448(9)
N12−C17a	1.470(8)	N42−HN42	0.976(5)
N12−C17	1.468(9)	C12−C17	1.486(10)
N12−HN12	0.864(5)	C12a−C17a	1.501(10)
N21−C22	1.346(7)	C22−C27	1.496(9)
N21a−C22a	1.318(8)	C22a−C27a	1.503(9)
N22−C27a	1.485(8)	C42−C47	1.539(10)
N22−C27	1.484(7)	C42a−C47a	1.507(10)
N22−HN22	0.913(5)		

N11−Cu1−N11a	158.80(2)	N32−Cu2−N42	178.30(2)
N11−Cu1−N12	82.80(2)	N41−Cu2−N41a	85.20(2)
N11−Cu1−N21	97.60(2)	N41−Cu2−N42	80.70(2)
N11−Cu1−N22	94.20(2)	N41a−Cu2−N42	78.50(2)
N11a−Cu1−N12	81.80(2)	Cu1−N12−C17a	110.60(4)
N11a−Cu1−N21	97.20(2)	Cu1−N12−C17	111.60(4)
N11a−Cu1−N22	103.60(2)	Cu1−N12−HN12	91.40(4)
N12−Cu1−N21	177.40(2)	C17a−N12−C17	115.10(6)
N12−Cu1−N22	104.10(2)	C17a−N12−HN12	115.50(6)
N21−Cu1−N22	78.50(2)	C17−N12−HN12	110.30(6)
N31−Cu2−N31a	90.10(2)	Cu1−N22−C27a	124.50(4)
N31−Cu2−N32	80.00(2)	Cu1−N22−C27	102.70(4)
N31−Cu2−N41	91.40(2)	Cu1−N22−HN22	110.10(4)
N31−Cu2−N41a	176.60(2)	C27a−N22−C27	108.90(5)
N31−Cu2−N42	101.60(2)	C27a−N22−HN22	104.60(5)
N31a−Cu2−N32	79.60(2)	C27−N22−HN22	104.50(5)
N31a−Cu2−N41	178.30(2)	Cu2−N32−C37	109.10(5)
N31a−Cu2−N41a	93.20(2)	Cu2−N32−HN32	110.60(4)
N31a−Cu2−N42	99.70(2)	C37a−N32−C37	114.60(6)
N32−Cu2−N41	100.00(2)	C37a−N32−HN32	117.70(6)
N32−Cu2−N41a	100.00(2)	C37−N32−HN32	98.00(6)

[a] Distances in Å, angles in deg, and standard deviation in last significant digit in parentheses.

mmol) was then added, and the blue precipitate eventually obtained was filtered off, washed with small amounts of methanol and dried under vacuum over P_4O_{10}. Anal. Calcd for $C_{17}H_{20}ClCuN_3O_6$: C, 44.3; H, 4.37; N, 9.11. Found: C, 44.3; H, 4.31; N, 9.13.

Physical Measurements. Elemental analyses were performed by Canadian Microanalytical Service (Vancouver, Canada). Solution electronic spectra were measured on a Perkin-Elmer 320 spectrophotometer and the diffuse reflectance spectra of the solids on a Perkin-Elmer 330 spectrophotometer equipped with an integrating sphere. EPR spectra were recorded on a Varian E12 spectrometer, the field being calibrated with DPPH. Electrochemistry was performed with a three-electrode cell controlled with a PAR-173 potentiostat, a PAR-176 *i/E* converter, and a PAR-175 wave form generator. Potentials in nonaqueous solution were measured with respect to the Ag^+(0.01 M), NEt_4ClO_4(0.1 M)/Ag electrode, and may be estimated with reference to the standard hydrogen electrode by the addition of *ca.* +545 mV.[14] Electrodes used for stationary electrode cyclic voltammetry and/or rotating disk polarography were a Beckman (rotating) platinum disk (rde) and a platinum bead.

Crystal Structure Determination. X-ray diffraction data were collected by standard methods with scans 1.2° above and below $K_{\alpha1}$ and $K_{\alpha2}$ of the graphite-monochromated Mo x-radiation. All nonequivalent reflection intensities for which $3.8° < 2\theta < 60°$ were collected. The intensities of four standard reflections monitored every 96 reflections showed no greater fluctuations than would be expected from Poisson statistics. The raw intensity data were corrected for Lorenz−polarization effects and absorption.[15] The structure was solved by conventional Patterson and Fourier methods. A three-dimensional Patterson synthesis was used to determine the heavy atom positions, which phased the data sufficiently well to permit the location of the remaining non-hydrogen atoms from difference Fourier synthesis. Values for scattering factors and anomalous dispersion terms (real and imaginary) were from standard sources.[16,17] Tests for extinction showed none significant. Full-matrix least squares refinement of the model was carried out as previously described.[18] Anisotropic temperature factors were introduced for all non-hydrogen atoms. All but one of the BF_4^- ions are quite disordered and were modeled by taking the top peaks from their difference Fourier maps based on the ordered components of the structure and then refining their multiplicities (constrained to 4) while their isotropic thermal parameters were refined under the constraint of equivalence. Further difference Fourier calculation enabled the location of the hydrogen atom positions, which were included in the refinement for four least-squares cycles and then held fixed. The model converged with an agreement factor (R_{int}) of 1.7%. A final Fourier difference map was featureless. Crystal data, positional parameters and molecular metrics are summarized in Tables 1−3, respectively.

Results and Discussion

Description of the Structure. The complex cation $Cu(Dipica)_2^{2+}$ exhibits two entirely different coordination structures in the same unit cell. The ORTEP projections of these two cations, showing also the atomic numbering scheme, are provided in Figures 2 and 3, and the structural dimensions are detailed in Table 3. In the hexacoordinate cations (Figure 2), the two tridentate Dipica ligands are *trans*-facially coordinated, in contrast to the meridional coordination in $Cu(dien)_2^{2+}$.[5,6] The equatorial plane is constituted by four pyridine nitrogens, while the axial positions are occupied by the two amino nitrogens at longer distances (2.20, 2.21 Å). The four coplanar pyridine nitrogens are also *trans*-paired, with two at 2.15 and 2.19 Å and the other two at *ca.* 2.04 Å. As only the last two distances are typical of nonelongated Cu−N linkages, the somewhat rhombic geometry gives the impression of an equatorially inflated or expanded octahedron, with the more “normal” shorter $Cu-N_{pyr}$’s on the axis. Each of the ligands form two five-membered chelate rings and thus pinches together the three Cu−N bonds to make the intrachelate NCuN angles 10° less than the 90° ideal. All four five-membered chelate rings are in the envelope conformation with the picolyl $-CH_2-$ carbon defining the apex of the “flap”. The hexacoordinate molecule has a pseudo-C_2 axis (bisecting N31CuN41). This coordination geometry is quite similar to that reported for $Fe(Dipica)_2(BF_4)_2$[9] which has a true C_2-axis. In both cations, BF_4^- ions are H-bonded to secondary amine nitrogens, and this is likely responsible for their reduced disorder.[19]

In contrast to this facially hexacoordinated structure, the pentacoordinate cation (Figure 3) contains one of the Dipica ligands meridionally coordinated about the equator within an essentially square-pyramidal geometry. Although this and the hexacoordinate cation in the unit cell are both of C_1 symmetry, this one is the more obviously asymmetric. Its second ligand is acting as a bidentate one, with its amino nitrogen defining the apex of the pyramid at 2.34 Å. The mutually *trans* Cu−

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(14) Addison, A. W.; Li, T. H.; Weiler, L. S. *Can. J. Chem.* **1977**, *55*, 766.

(15) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(16) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*, Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(18) (a) Storm, C. B.; Freeman, C. M.; Butcher, R. J.; Turner, A. H.; Rowan, N. S.; Johnson, F. O.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 678. (b) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335.

(19) We thank a reviewer for drawing our attention to this feature.

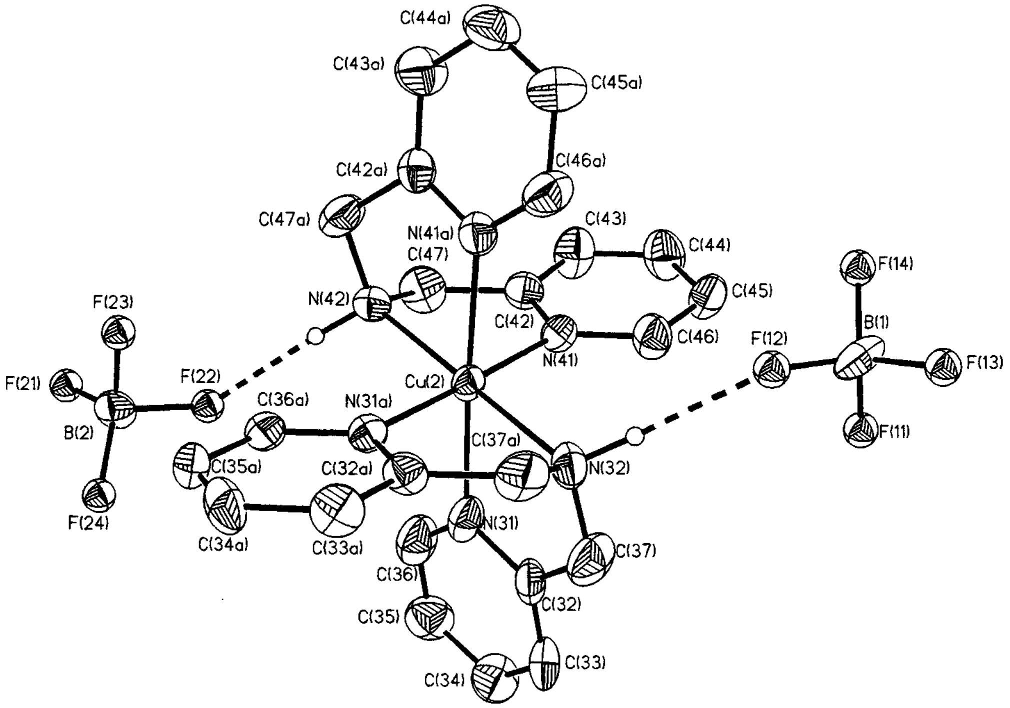

Figure 2. The hexacoordinate Cu(Dipica)$_2^{2+}$ ion. The halves of each ligand are designated by "*a*"-suffixed and nonsuffixed atom numbers, but are not symmetry-related. (C protons omitted for clarity of presentation.)

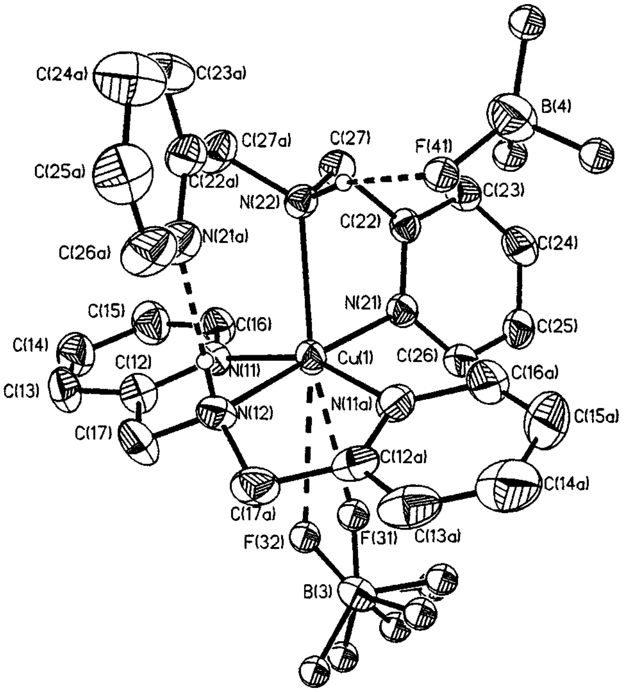

Figure 3. The pentacoordinate Cu(Dipica)$_2^{2+}$ ion. H[N12] is between N[21a] and N[12], which are separated by 2.85 Å. The second half of each ligand is designated by "*a*"-suffixed atom numbers (C protons omitted for clarity of presentation.)

N_{pyr} distances of the meridionally tridentate ligand are 2.04 and 2.03 Å, while its unique Cu−N_{sat} distance (1.995 Å) and the last Cu−N_{pyr} bond are both shorter. Cu−N_{sat} linkages like Cu−N22 are generally a little longer (2.01−2.10 Å) than CuN_{het} ones (1.98−2.03 Å,[20] as is also the case in Fe(Dipica)$_2^{2+}$.[9] The shorter Cu−N_{sat} bond in the present complex is a mechanical consequence of the simultaneous *trans*-coordination of the two pyridines. The NCuN angles are again consequently a little acute, and the geometry is noticeably distorted towards trigonal-bipyramidal, as shown by the trigonality index[21] $\tau = 0.38$. For the bidentate ligand the Cu−N_{sat} bond distance is 2.34 Å, consistent with its Jahn−Teller elongated situation, while across the copper atom from it, a BF_4^- alternates between two semicoordinate positions at 2.61 and 2.85 Å. Thus the Jahn−Teller conflict observed in the six-coordinate geometry is relieved in this five-coordinate structure, the energy increase due to breakage of one of the Cu−pyridine bonds being compensated by H-bond formation between the uncoordinated pyridine nitrogen and the hydrogen atom of the secondary amino nitrogen. In this regard, the structure is reminiscent of that observed for the perchlorate salt of bis[2,6-bis(*N*′-methylbenzimidazol-2′-yl)pyridine]copper(II),[22] in which one of the ligands is meridionally tridentate, while the second is bidentate, with its uncoordinated benzimidazole *π*-stacked against the first ligand.

Spectral Properties. The reflectance and solution spectra of all the complexes display two ligand field bands (15.9, 10.8 × 10^3 cm^{-1}), consistent with the square-based geometries revealed in the crystal structure. The EPR spectral patterns and parameters are also appropriate for planar or tetragonal CuN_4 chromophores, as constituted by four imidazole nitrogens[23] in compounds such as Cu(bba)$_2$(ClO$_4$)$_2$.[8] The EPR parameters (Table 4) are all quite similar to one another, as there is little distinction between *g*-values for oxygen *vs* aromatic nitrogen donors in tetragonal complexes,[24] and these spectra are bereft of N-shf structure. The ligand-field spectral feature around 19.8 × 10^3 cm^{-1} observed for the 1:2 Cu(II) complex of bis(imidazol-

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(20) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.

(21) The index *τ* is zero for a square pyramid, unity for a trigonal bipyramid: Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(22) Sanni, S. B.; Behm, H. J.; Beurskens, P. T.; van Albada, G. A.; Reedijk, J.; Lenstra, A. T. H.; Addison, A. W.; Palaniandavar, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1429.

(23) van Steenbergen, A. C.; Bouwman, E.; de Graaff, R. A. G.; Driessen, W. L.; Reedijk, J.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3175.

(24) Addison, A. W. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J. A., Eds.; Adenine Press: Guilderland, NY, 1983; p 109.

Table 4. Electronic Properties of the Complexes

parameter	$Cu(Dipica)_2(BF_4)_2$			$Cu(Dipica)(Bipy)(ClO_4)_2$			$Cu(Dipica)(Acac)(ClO_4)$		
medium	solid	MeOH	NM[a]	solid	MeOH		solid	MeOH	NM
ν [ϵ][b]	10.8	10.5 [70]	10.5 [110]	12.2	12.1		11.1 sh	10.8 sh	13.5 [96]
	15.9	14.9 [104]	14.3 [132]	16.6	14.8		14.7	14.3 [94]	
	22.7	21.1 [315]			25.0			25.6 [82]	
medium[a]	solid	alcohol	NM/Tol	solid	alcohol	NM/Tol	solid	alcohol	NM/Tol
g_0		2.122			2.121	2.121		2.128	2.127
A_0[c]		61			64	59		55	59
$g_{\parallel}$[d]	~2.25[e]	2.233	2.242	~2.18	2.222	2.222 2.175[f]	2.340	2.250	2.246
$A_{\parallel}$		187	181		202	196		178	175
$g_{\perp}$	2.070		2.08[h]	~2.06	2.07[h]	2.07[h]	2.077	2.07[h]	2.07[h]
$A_{\perp}$[h]		−2			−5	−10		−7	−1

[a] NM = nitromethane; alcohol = 9:1 v/v MeOH/EtOH; NM/Tol = 5:1 v/v NM/toluene; ambient temperature and 77 K. [b] Maxima in optical absorption from ca. 10^{-2} M solutions; ν (in 1000 cm^{-1} units, ϵ in M^{-1} cm^{-1}); sh = shoulder. [c] A values ±3, in units of 10^{-4} cm^{-1}. Their signs are relative, not absolute. [d] $g_{\parallel}$ ±0.003 from solutions at 77 K. For neat powders, estimates of $g_{\parallel}$ from poorly resolved low-field features at 77 K. [e] Ambient-temperature value. At 77 K, a line appears at $g = 2.35$. [f] Minor species. [g] Footnote deleted in proof. [h] Estimates *via* $3g_0 = g_{\parallel} + 2g_{\perp}$, $3A_0 = A_{\parallel} + 2A_{\perp}$ from ambient temperature fluid solution g_0 and A_0.

2′-ylmethyl) sulfide[25] with a similar equatorial N_4(imidazole) donor set illustrates the strong axial interaction by the amine nitrogens, compared to the weaker Cu−S(thioether) interaction. This is further evidenced by the estimated $A_{\perp}$ values, which are significantly reduced by the strong axial interactions in comparison to a square-planar N_4 donor set.[25]

Electrochemical Properties. The electrochemical behavior for $Cu(Dipica)_2(BF_4)_2$ and $Cu(Bipy)(Dipica)(ClO_4)_2$ at a Pt electrode in MeOH/THAP was characteristic of quasi-reversible Cu(II)/Cu(I) redox processes. $Cu(Dipica)_2^{2+}$ exhibited an $E_{1/2}$ of −0.49 V (i_{pa}/i_{pc} and ΔE_p were 0.98 and 120 mV respectively, at $v = 50$ mV s^{-1}), while the $Cu^I \rightarrow Cu^0$ reduction was observed at *ca.* −0.8 V at the RDE. The slightly more negative $Cu^{II} \rightarrow Cu^I$ potential than is observed for the corresponding bis(benzimidazol-2-ylmethyl)amine ($E_{1/2} = -0.41$ V [8]) is attributable to the higher basicity and lesser steric bulk of pyridine compared to benzimidazole. On the other hand, 2,2′-bipyridyl tends to stabilize copper(I) fairly effectively,[26] so this mixed-ligand complex yielded a more positive potential: $E_{p,a} = -0.305$ V, $E_{p,c} = -0.500$ V; a small additional anodic peak was observed at −0.05 V, suggesting some coordinative rearrangement in the Cu^I form.

Conclusion

The present structures provide a demonstration of the flexibility of copper ion to achieve different geometries and is the first report of two entirely different cationic copper complex coordination geometries in the same unit cell.

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Supporting Information Available: Figure S1, stereoview of unit cell contents, Table S1, positional parameters for H-atoms, Table S2, bond lengths, Table S3, bond angles, Table S4, *U*-values, Table S5, least-squares planes, and Table S6, crystallographic data (13 pages). Ordering information is given on any current masthead page.

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(25) Addison, A. W.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1984**, *23*, 1957.
(26) James, B. R.; Williams, R. J. P. *J. Chem. Soc.* **1961**, 2007.