Notes

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Molecular Tweezer-Type Ligands.[1] A Trigonal-Bipyramidal Copper(II) [5.8.5] Complex: Synthesis and Single-Crystal X-ray Structure Determination

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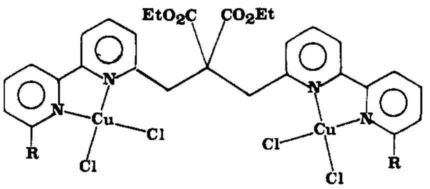
The variable geometries of copper(II) complexes possessing cation and anion distortions are well documented.[3] Thus, use of macrocyclic ligands to prepare dimeric copper(II) species[4,5] has led to increasing interest in the physical and chemical properties of the complexes. Due to our interest in dinuclear complexes, the quadridentate ligands **5** were devised in an attempt to isolate the dimeric copper(II) complexes **7** and subsequently to exchange halide ions with bridging ligands. The syntheses and complexation of open-chain planar quadridentate ligands have been shown to afford [5.5.5], [5.6.5], and [5.7.5] coordination; however, presence of "obstacle" groups such as pyridine 6-methyl substituent(s) prevented the formation of certain copper(II) complexes.[6] The juxtaposition of the terminal methyl groups was deemed responsible for the inability to prepare stable copper(II) complexes of these ligands.[6] Surprisingly, ligands **5** formed tweezer-type mononuclear [5.8.5] copper(II) complexes **6** with a distorted trigonal-bipyramidal geometry. The methyl groups in **6b** were considered to be spatially close as based on CPK models, but not sufficiently so as to retard complex formation.



7a (R=H)
7b (R=CH_3)

We herein report the synthesis of a novel tweezer-type ligand system, demonstrate its complexation with copper(II) chloride, and discuss the hindrance factors ("obstacle effect")[6] caused by the terminal 6-methyl substituent on a pyridine moiety.

Experimental Section[7]

A. Ligand Synthesis. 6-(Chloromethyl)-6′-methyl-2,2′-bipyridine (3) was prepared by a four-step procedure described in detail elsewhere;[8] mp 61–62 °C.

6-(Bromomethyl)-2,2′-bipyridine (1) was prepared from 6-methyl-2,2′-bipyridine[9] [bp 117–119 °C (0.1 mm); 2.04 g, 12 mmol] with *N*-bromosuccinimide (2.67 g, 15 mmol) and AIBN (10 mg) in benzene (200 mL). Chromatography (ThLC) eluting with $CHCl_3$–EtOH (9:1) afforded (79%) **1**, as white crystals:[10] 2.36 g; mp 68–69 °C; R_f 0.50; ^{1}H NMR δ 4.63 (s, py CH_2), 7.30 (ddd, py 5′-H, $J = 7.9, 4.9, 1.8$ Hz), 7.46 (d, py 5-H, $J = 7.9$ Hz), 7.81 (t, py 4,4′-H, $J = 7.9$ Hz), 8.33 (d, py 3-H, $J = 7.9$ Hz), 8.46 (d, py 3′-H, $J = 7.9$ Hz), 8.67 (dd, py 6′-H, $J = 4.9, 1.8$ Hz); IR (CsI) 1615, 1570, 1450 cm^{-1}; MS *m/e* 250 [M$^+$ (^{81}Br), 22], 169 (M$^+$ – Br, *100*). A second fraction was shown to be the 6-dibromomethyl derivative **2**, as an oil: 350 mg (9%); R_f 0.70; spectral data support the assignment.

General Procedure for the Synthesis of Substituted Malonate Ligands. A mixture of the appropriate halomethyl derivative, diethyl malonate, and anhydrous K_2CO_3 in purified[11] DMF (50 mL) was stirred at 25 °C for 20 h. The reaction mixture was filtered, concentrated in vacuo, and chromatographed (ThLC) by eluting with ether–petroleum ether (bp 30–60 °C) (2:3) to afford the desired bipyridine ligands.

6-[2″,2″-Bis(carbethoxy)ethyl]-2,2′-bipyridine (4a) was prepared (94%) from **1** (2.49 g, 10 mmol), diethyl malonate (4.0 g, 25 mmol), and K_2CO_3 (2.5 g): oil;[10] bp 127–128 °C (0.6 mm); R_f 0.35; ^{1}H NMR δ 1.22 (t, CH_3, $J = 7.3$ Hz), 3.52 (d, py CH_2, $J = 7.3$ Hz), 3.85 (t, $CH(CO_2Et)_2$, $J = 7.3$ Hz), 4.21 (m, CH_2CH_3), 7.20 (d, py 5-H, $J = 7.9$ Hz), 7.26 (dd, py 5′-H, $J = 7.9, 4.3$ Hz), 7.70 (t, py 4′-H, $J = 7.9$ Hz), 7.78 (t, py 4-H, $J = 7.9$ Hz), 8.27 (d, py 3-H, $J = 7.9$ Hz), 8.45 (d, py 3′-H, $J = 7.9$ Hz), 8.64 (d, py 6′-H, $J = 4.3$ Hz); IR (neat) 1730 (C=O), 1425, 1260 cm^{-1}; MS *m/e* 328 (M$^+$, 27), 209 (M$^+$ – $C_5H_{11}O_3$, *100*).

6-[2″,2″-Bis(carbethoxy)ethyl]-6′-methyl-2,2′-bipyridine (4b) was prepared (91%) from **3**[8] (mp 61–62 °C; 2.18 g, 10 mmol), diethyl malonate (4.0 g, 25 mmol), and K_2CO_3 (2.5 g): oil; bp 146–148 °C (1.3 mm); R_f 0.46; ^{1}H NMR δ 1.19 (t, CH_3, $J = 7.3$ Hz), 2.55 (s, py CH_3), 3.50 (d, py CH_2, $J = 7.3$ Hz), 4.19 (m, CH_2CH_3), 4.30 (t, $CH(CO_2Et)_2$, $J = 7.3$ Hz), 7.07, 7.14 (2d, py 5-H, $J = 7.3$ Hz), 7.62, 7.64 (2t, py 4-H, $J = 7.3$ Hz), 8.24, 8.28 (2d, py 3-H, $J = 7.3$ Hz); IR (neat) 1730 (C=O), 1435, 1260 cm^{-1}; MS *m/e* 342 (M$^+$, 25), 269 (M$^+$ – CO_2Et, *100*).

Bis(bipyridine) ligand 5a was prepared (79%) from **4a** (330 mg, 1 mmol), **1** (250 mg, 1 mmol), and K_2CO_3 (1 g): white crystals;[10] mp 130–131 °C; R_f 0.16; ^{1}H NMR δ 1.18 (t, CH_3, $J = 7.3$ Hz), 3.70 (s, py CH_2), 4.24 (q, CH_2CH_3, $J = 7.3$ Hz), 6.98 (d, py 5-H, $J = 7.9$ Hz), 7.29 (ddd, py 5′-H, $J = 7.9, 4.9, 1.2$ Hz), 7.66 (t, py 4-H, $J = 7.9$ Hz), 7.83 (ddd, py 4′-H, $J = 7.9, 7.9, 1.8$ Hz), 8.28 (d, py 3-H, $J = 7.9$ Hz), 8.40 (d, py 3′-H, $J = 7.9$ Hz), 8.66 (d, py 6′-H, $J = 4.9$ Hz); IR (CsI) 1710, 1445, 1420, 1265 cm^{-1}; MS *m/e* 496 (M$^+$, 1), 170 (M$^+$ – $C_{17}H_{18}N_2O_4$, *100*).

Bis(bipyridine) ligand 5b was prepared (66%) from **4b** (220 mg, 1 mmol), **3** (340 mg, 1 mmol), K_2CO_3 (1 g): colorless crystals;[10] mp 120–121 °C; R_f 0.39; ^{1}H NMR δ 1.17 (t, CH_3, $J = 7.3$ Hz), 2.61 (s, py CH_3), 3.70 (s, py CH_2), 4.24 (q, CH_2CH_3, $J = 7.3$ Hz), 6.96, 7.13 (2d, py 5,5′-H, $J = 7.3$ Hz), 7.62, 7.69 (2t, py 4,4′-H, $J = 7.3$ Hz), 8.20, 8.30 (2d, py 3,3′-H, $J = 7.3$ Hz); IR (CsI) 1720 (C=O), 1440, 1240 cm^{-1}; MS *m/e* 524 (M$^+$, 7), 451 (M$^+$ – CO_2Et, *100*).

B. Complex Formation. Preparation of the Copper(II) Complexes of 5. A mixture of anhydrous copper(II) chloride (27 mg, 0.2 mmol) and **5a** or **5b** (0.1 mmol) in a solution of MeOH (10 mL) and $CHCl_3$ (5 mL) was refluxed for 2 h. The solution was concentrated to 5 mL, affording, upon standing, green crystals, which were recrystallized from MeOH and dried at 50 °C in vacuo. The crystals for X-ray analysis were obtained from $CHCl_3$–MeOH (1:1).

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(1) Chemistry of Heterocyclic Compounds. 77. Previous related paper in this series: Newkome, G. R.; Kohli, D. K.; Fronczek, F. R. *J. Am. Chem. Soc.* **1982**, *104*, 994.

(2) On leave from the University of Delhi, Delhi, India, 1980–1982.

(3) Ray, N.; Mulett, L.; Sheahan, R.; Hathaway, B. J. *Inorg. Nucl. Chem. Lett.* **1979**, *14*, 305.

(4) Newkome, G. R.; Kohli, D. K.; Fronczek, F. R.; Hales, B. J.; Case, E. E.; Chiari, G. *J. Am. Chem. Soc.* **1980**, *102*, 7608.

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(9) Kauffmann, Th.; König, J.; Woltermann, A. *Chem. Ber.* **1976**, *109*, 3864.

(10) All new ligands possess elemental analyses within acceptable limits.

(11) DMF in light slowly releases HCN; therefore care must be taken to prevent photodecomposition.[12]

(12) (a) Newkome, G. R.; Robinson, J. M. *Tetrahedron Lett.* **1974**, 691. (b) Trisler, J. C.; Freasier, B. F.; Wu, S.-M. *Ibid.* **1974**, 687.

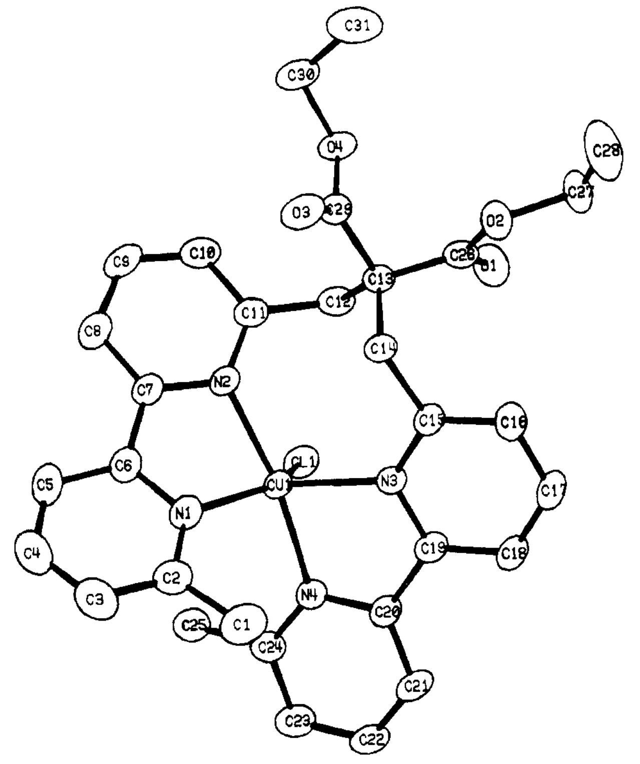


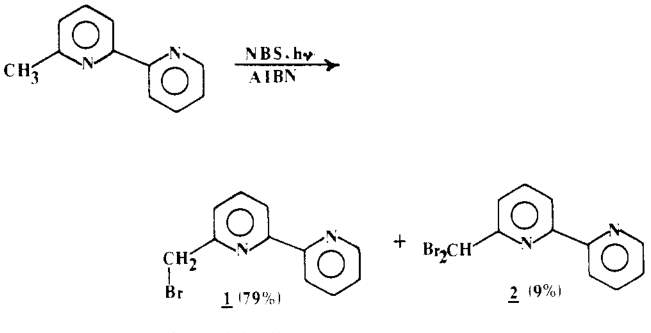
Figure 1. ORTEP drawing of chloro[1,3-bis(6″-methyl-2′,2″-bipyridyl)-2,2-bis(carbethoxy)propane]copper(II) (**6b**). Hydrogen atoms have been omitted for clarity.

Complex 6a was isolated (91%) as green crystals: 70 mg; mp 162–164 °C dec; IR (CsI) 1725, 1450, 1410, 1285, 1245 cm^{-1}. Anal. Calcd for $C_{29}H_{28}N_4O_4Cu_2Cl_4$: C, 45.50; H, 3.69; N, 7.32. Found: C, 45.35; H, 3.80; N, 7.55.

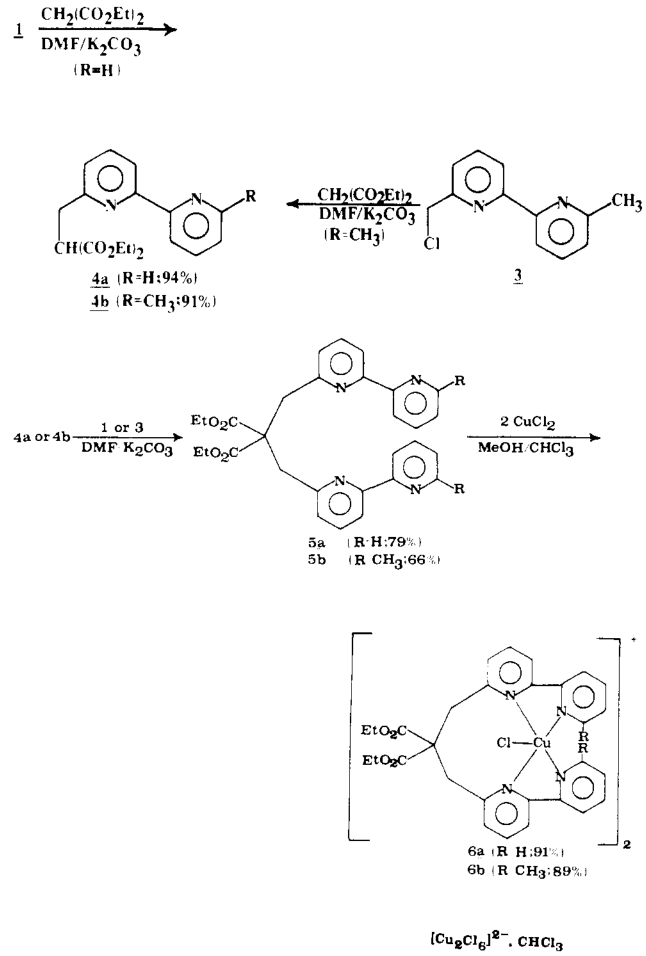
Complex 6b was isolated (89%) as green crystals: 70 mg; mp 233–234 °C dec; IR (CsI) 1715, 1465, 1445, 1255, 1245 cm^{-1}. Anal. Calcd for $C_{31}H_{32}N_4O_4Cu_2Cl_4$: C, 46.92; H, 4.06; N, 7.06. Found: C, 46.82; H, 3.96; N, 7.02.

Results and Discussion

A. Ligand Synthesis. 6-Methyl-2,2′-bipyridine[9] was brominated with *N*-bromosuccinimide to give **1** (79%), as the main product, along with the dibromo derivative **2**.



Treatment of **1** with diethyl malonate in the presence of anhydrous K_2CO_3 suspended in purified[11] *N*,*N*-dimethylformamide gave the monoalkylated product **4a** in high yield. Similar reaction of **3**[8] (prepared by the *N*-oxide rearrangement with acetic anhydride, hydrolysis, and treatment with thionyl chloride) with diethyl malonate produced **4b**. With use of the same alkaline conditions, **4a** and **4b** were subsequently condensed with **1** and **3**, respectively, to afford the desired tweezer-type ligands **5**, as crystalline solids. Each of the ligands was spectrally characterized and support the assigned structure.



B. Complex Formation. Ligands **5a** and **5b** were treated with 2 equiv of copper(II) chloride to give complexes that had compositions corresponding to **6a** and **6b**, respectively. So that the mode of complexation could be established, a single-crystal X-ray analysis was conducted on copper complex **6b**. These data would also afford precise insight into the steric hindrance (the obstacle effect) to normal modes of bonding caused by the methyl substituents.

C. Structure Description. The ligands **5a** and **5b** behave like a tweezer so that there is sufficient room for only one copper(II) ion between the two bipyridine units. Thus the complexes have a distorted trigonal-bipyramidal geometry, the five coordination sites being occupied by four nitrogens and a chlorine atom (Figure 1). The charge is balanced by $[Cu_2Cl_6]^{2-}$ anions (Figure 2). Table I contains the coordinates of non-hydrogen atoms, and the typical bond angles and distances in the coordination sphere are given in Table II.

The structure **6b** contains isolated [Cu(**5b**)Cl]$^+$ cations, the $[Cu_2Cl_6]^{2-}$ anion, and a disordered solvent region. The [Cu(**5b**)Cl]$^+$ is clearly five-coordinate, and the donor atoms N(1), N(3), and Cl(1) define an approximate trigonal plane about Cu(1), while N(2) and N(4) occupy the apices of the trigonal bipyramid. Distortions from ideal geometry are large (see Table II). In particular, the Cl(1)–Cu(1)–N(1) angle of 141.7° suggests a geometry intermediate between trigonal bipyramidal and square pyramidal. Some evidence for this is the significantly longer Cu(1)–N(3) distance (2.146 Å) relative to that of 2.095 Å for the Cu(1)–N(1) distance, suggestive of a distorted square-pyramidal stereochemistry in which N(1), N(2), Cl(1), and N(4) generate the distorted square. The CuN_4Cl unit is significantly more distorted than that of $[Cu(bpy)_2Cl]\cdot H_2O$, which has an almost regular set of trigonal-bipyramidal angles.[13]

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Table I. Coordinates of Non-Hydrogen Atoms

atom	*x*	*y*	*z*
Cu(1)	0.1600 (1)	0.20282 (6)	0.33930 (6)
Cu(2)	0.6092 (1)	0.58134 (8)	0.07946 (7)
Cl(1)	−0.0211 (2)	0.2434 (1)	0.4173 (1)
Cl(2)	0.5992 (3)	0.4249 (1)	0.0200 (2)
Cl(3)	0.5578 (3)	0.6718 (2)	0.1916 (1)
Cl(4)	0.8446 (3)	0.6237 (3)	0.1104 (3)
Cl(5)	0.0136 (4)	0.6045 (2)	0.3245 (2)
Cl(6)	0.2145 (5)	0.5180 (3)	0.4463 (3)
Cl(7)	0.2879 (4)	0.7234 (3)	0.4186 (2)
Cl(8)	0.108 (1)	0.4862 (9)	0.4214 (8)
Cl(9)	0.283 (2)	0.6723 (12)	0.3850 (11)
O(1)	−0.3548 (5)	0.0132 (4)	0.1603 (3)
O(2)	−0.2751 (5)	−0.0379 (3)	0.0317 (3)
O(3)	−0.0160 (5)	0.1560 (4)	−0.0207 (3)
O(4)	−0.2370 (5)	0.1809 (3)	−0.0086 (3)
N(1)	0.3661 (6)	0.2636 (4)	0.3033 (3)
N(2)	0.1087 (5)	0.2823 (4)	0.2352 (3)
N(3)	0.0800 (5)	0.0483 (3)	0.3000 (3)
N(4)	0.2301 (5)	0.1489 (4)	0.4562 (3)
C(1)	0.4961 (8)	0.1396 (6)	0.3497 (6)
C(2)	0.4950 (7)	0.2417 (5)	0.3266 (4)
C(3)	0.6242 (8)	0.3111 (7)	0.3246 (6)
C(4)	0.6209 (9)	0.4029 (7)	0.2979 (6)
C(5)	0.4922 (9)	0.4243 (5)	0.2686 (5)
C(6)	0.3632 (7)	0.3513 (5)	0.2702 (4)
C(7)	0.2197 (7)	0.3610 (4)	0.2284 (4)
C(8)	0.1998 (9)	0.4406 (5)	0.1806 (5)
C(9)	0.0610 (9)	0.4386 (5)	0.1379 (5)
C(10)	−0.0491 (8)	0.3575 (5)	0.1424 (5)
C(11)	−0.0239 (7)	0.2780 (4)	0.1903 (4)
C(12)	−0.1404 (6)	0.1865 (5)	0.1894 (4)
C(13)	−0.1319 (6)	0.1056 (4)	0.1146 (4)
C(14)	0.0031 (6)	0.0626 (4)	0.1370 (4)
C(15)	0.0040 (6)	0.0039 (4)	0.2214 (4)
C(16)	−0.0644 (7)	−0.0971 (5)	0.2128 (4)
C(17)	−0.0509 (8)	−0.1500 (5)	0.2900 (4)
C(18)	0.0311 (8)	−0.1061 (5)	0.3691 (4)
C(19)	0.0976 (7)	−0.0048 (4)	0.3741 (4)
C(20)	0.1885 (7)	0.0492 (4)	0.4576 (4)
C(21)	0.2318 (8)	0.0037 (5)	0.5354 (4)
C(22)	0.3130 (8)	0.0587 (5)	0.6100 (4)
C(23)	0.3538 (8)	0.1599 (5)	0.6089 (4)
C(24)	0.3067 (7)	0.2039 (5)	0.5311 (4)
C(25)	0.3423 (8)	0.3126 (5)	0.5298 (5)
C(26)	−0.2668 (7)	0.0239 (5)	0.1060 (4)
C(27)	−0.4033 (8)	−0.1215 (5)	0.0134 (5)
C(28)	−0.3924 (11)	−0.1717 (7)	−0.0737 (6)
C(29)	−0.1193 (7)	0.1496 (5)	0.0204 (4)
C(30)	−0.2379 (8)	0.2253 (6)	−0.0979 (5)
C(31)	−0.2968 (9)	0.1455 (8)	−0.1756 (5)
C(32)	0.1371 (11)	0.6173 (7)	0.4222 (7)

Table II. Distances (Å) and Angles (deg) in the Coordination Sphere

Cu(1)–Cl(1)	2.343 (1)	Cu(1)–N(3)	2.146 (3)
Cu(1)–N(1)	2.095 (4)	Cu(1)–N(4)	2.003 (3)
Cu(1)–N(2)	2.005 (3)		
Cl(1)–Cu(1)–N(1)	141.7 (1)	N(1)–Cu(1)–N(3)	114.2 (1)
Cl(1)–Cu(1)–N(2)	89.8 (1)	N(1)–Cu(1)–N(4)	96.0 (1)
Cl(1)–Cu(1)–N(3)	104.1 (1)	N(2)–Cu(1)–N(3)	110.6 (1)
Cl(1)–Cu(1)–N(4)	87.6 (1)	N(2)–Cu(1)–N(4)	168.9 (1)
N(1)–Cu(1)–N(2)	79.5 (1)	N(3)–Cu(1)–N(4)	80.5 (1)

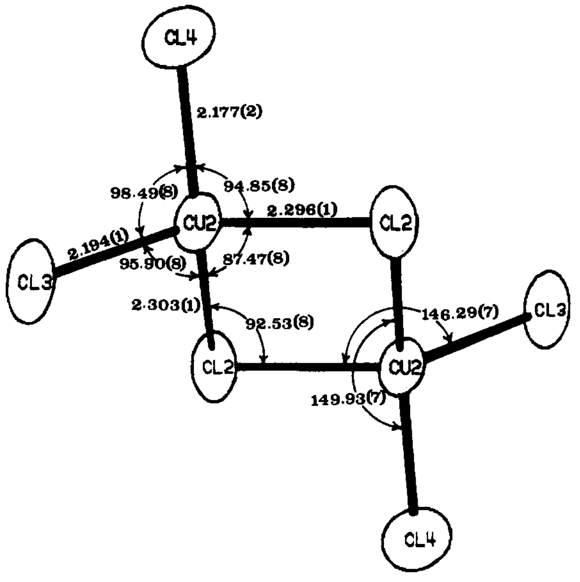

Figure 2. Distances and angles in the $[Cu_2Cl_6]^{2-}$ anion.

The pyridine rings are planar; the pairs of pyridine rings in each 2,2′-bipyridine moiety are inclined at angles of 14.3 and 9.5°. An unusual feature of this complex is the formation of a [5.8.5] chelate ring system. This central eight-membered chelate ring leads to a large angle [110.6 (1)°: N(2)–Cu(1)–N(3)] subtended by axial and equatorial donor atoms. Torsion angles within this mediocycle are listed in Table III.

Table III. Torsion Angles in the Eight-Membered Chelate Ring

atom 1	atom 2	atom 3	atom 4	angle, deg
C(11)	N(2)	Cu(1)	N(3)	55.3
N(2)	Cu(1)	N(3)	C(15)	−1.5
Cu(1)	N(3)	C(15)	C(14)	18.2
N(3)	C(15)	C(14)	C(13)	−98.8
C(15)	C(14)	C(13)	C(12)	66.8
C(14)	C(13)	C(12)	C(11)	68.6
C(13)	C(12)	C(11)	N(2)	−81.6
C(12)	C(11)	N(2)	Cu(1)	−23.7

Table IV. Summary of Crystal Structure Determination for Complex 6b

formula: $[CuClC_{31}H_{32}N_4O_4]_2[Cu_2Cl_4]\cdot 1.5CHCl_3\cdot 0.5CH_2Cl_2$
space group: triclinic, $P\bar{1}$
a: 9.570 (2) Å α: 92.66 (2)°
b: 14.017 (2) Å β: 96.81 (2)°
c: 14.567 (2) Å γ: 103.61 (2)°
Z: 1
diffractometer: Enraf-Nonius CAD-4, θ–2θ scans
radiation: Cu Kα; λ = 1.541 84 Å
refinement: full-matrix, weighted least squares; non-hydrogen atoms anisotropic
obsd data: 3643 [$F > 3\sigma(F)$]
R: 0.061

The $[Cu_2Cl_6]^{2-}$ anion has crystallographic C_i symmetry, and the coordination geometry of each Cu(II) center can be described as a flattened tetrahedron of approximately D_2 symmetry. Discrete $[Cu_2Cl_6]^{2-}$ ions with strictly four-coordinate copper are also present in the isomorphous salts $P(C_6H_5)_4CuCl_3$[14] and $As(C_6H_5)_4CuCl_3$.[15] The terminal Cu–Cl bonds in the present determination average 2.185 Å, slightly shorter than the Cu–Cl bonds found in $CuCl_4^{2-}$ ions. The bridging Cu–Cl bonds are longer (as is the case for $Cu_2Cl_6^{2-}$ dimers[14,15]) and average 2.300 Å. The two chlorine bridges are more symmetrical than the similar known dimers.[14,15] The dihedral angle between the Cu(2)–Cl(3)–Cl(4) plane and the Cu(2)–Cl(2)–Cl(2′) plane is 44.0° and is cation dependent; values of 50° for $[P(C_6H_5)_4CuCl_3]$[14] and 65.9° for $[As(C_6H_5)_4CuCl_3]$[15] have been reported.

Although the obstacle effect described by Goodwin and Lions[6] may play an important role in smaller more rigid

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(14) Textor, M.; Dubler, E.; Oswald, H. R. *Inorg. Chem.* **1974**, *13*, 1361.
(15) Willett, R. D.; Chow, C. *Acta Crystallogr., Sect. B* **1974**, *B30*, 207.

molecules or bipyridine complexes with transition metals which impose a square-planar or octahedral configuration,[16] the central mediocyclic ring affords sufficient flexibilty to permit the nitrogen atoms access to the metal ion and to permit adequate avoidance of the terminal methyl substituents. Removal of these methyl substituents will probably make only a minor contribution to the ability of **5a** to complex Cu(II) ions, as based on their minimal interaction in complex **6b**.

Contrary to the lack of terminal group participation herein demonstrated, in a series of palladium(II) complexes of pyridine- and pyrazine-based ligands, we have observed that the terminal methyl groups have a tremendous effect on the mode of complexation.[17] Further work is in progress to delineate the effect(s) of terminal substituents in complex formation.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work.

Registry No. **1**, 83478-63-1; **2**, 83478-64-2; **3**, 82740-64-5; **4a**, 83478-65-3; **4b**, 83478-66-4; **5a**, 83478-67-5; **5b**, 83478-68-6; **6a**, 83478-70-0; **6b**, 83478-73-3; 6-methyl-2,2′-bipyridine, 56100-22-2.

Supplementary Material Available: Details of data collection and refinement for complex **6b** and tables of anisotropic thermal parameters, coordinates of hydrogen atoms, bond distances, bond angles, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(16) Newkome, G. R.; Fronczek, F. R.; Gupta, V. K.; Puckett, W. E.; Pantaleo, D. C.; Kiefer, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 1782.

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Comments on the Formation of Bis(catecholato)borates. Potassium Bis(4-methylcatecholato)borate(III)

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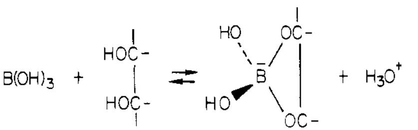
Boric acid, $B(OH)_3$, is capable of forming complexes with bidentate chelating ligands according to eq 1 and 2. Ligands that undergo this type of reaction include polyols,[2-5] 1,2-benzenediols,[2,3,6,7] and α-hydroxy carboxylic acids.[8,9] While the existence of bis complexes has been generally accepted for polyols and α-hydroxy carboxylic acids, there has been considerable discussion over the years as to whether bis complexes of catechol and substituted catechols exist in aqueous solution to any appreciable extent. Although salts of bis(catecholato)borates can be isolated from aqueous solution,[3,10] reactant concentrations are generally quite high. Much of our recent work in the area has concerned the mechanism of formation of 1:1 complexes.[11,12] In the course of those studies, the complexation of boric acid with catechol and substituted catechols was investigated. Our kinetic and thermodynamic study of such reactions supports the contention that in acidic solution in which reactant concentrations are ≤0.05 M only 1:1 complexes are formed. However, in the case of 4-methylcatechol, we have isolated a white solid from slightly basic aqueous solution. The salt is potassium bis(4-methylcatecholato)borate(III). The present paper concerns the characterization and properties of that salt and a discussion of equilibria in boric acid systems of this type.



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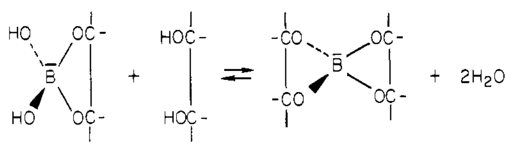

(2)

Experimental Section

Reactants were used as described previously.[12] The white solid reaction product was isolated from slightly basic aqueous solution ($\mu = 0.1$ M (KNO_3)) in the course of a pH titration. Elemental analysis is consistent with $K[(CH_3C_6H_3O_2)_2B]$. The salt melts at a temperature greater than 355 °C and is soluble in ethanol (with discoloration indicating ligand oxidation), THF, and $(CH_3)_2SO$. Infrared spectra were taken in KBr and Nujol on a Beckman 18A IR spectrometer; proton NMR spectra were taken in $(CD_3)_2SO$ on a Varian A-60.

Results

Although the vibrational spectra of complexes of this type have recently been analyzed,[5,9] only one spectral feature is of fundamental importance for our purposes. There is *no* O–H stretch in the infrared spectrum. Hence, there is no 1:1 complex present. The proton NMR spectrum is also consistent only with 1:2 complex formation. Two proton resonances occur, the peak integration showing the expected 1:1 ratio of aromatic to methyl protons with normal chemical shifts for such protons. Also of interest is the fact that the anion, $(CH_3C_6H_3O_2)_2B^-$, is stable in $(CH_3)_2SO$.

Discussion

The surprising aspect of the isolation of $K[(CH_3C_6H_3O_2)_2B]$ under our experimental conditions is that it precipitates from a solution in which the concentration of $(CH_3C_6H_3O_2)_2B^-$ must be very small. This result prompted an examination of the equilibria in boric acid systems. While such equilibria are conveniently studied by pH titration methods,[2-4,6,8,11,12] many other experimental techniques have been used. These include infrared[9] and Raman[5] spectroscopy, visible spectroscopy,[13] ^{13}C NMR,[14] ^{11}B NMR,[7] and ORD.[15]

The existence of equilibria as shown in eq 1 and 2 for α-hydroxy carboxylic acids has been generally accepted since the early work of Vermaas.[8] Extensive studies on borate/polyol complexes[2] have shown that these ligands also form complexes of both 1:1 and 1:2 stoichiometry. Equilibria involving catechol and substituted catechols have proved more problematic, with some authors[12-14] (ourselves included) finding only 1:1 complexes, some proposing both 1:1 and 1:2

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