Inorg. Chem. **1996,** *35,* 1091−1092

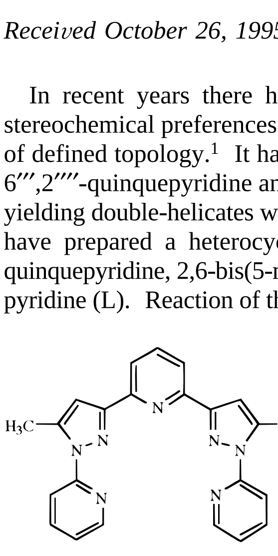
A Trinuclear Double-Helical Metal Complex of a Quinquepyridine Analog

Anthony T. Baker,*,† Donald C. Craig,‡ and Gordon Dong†

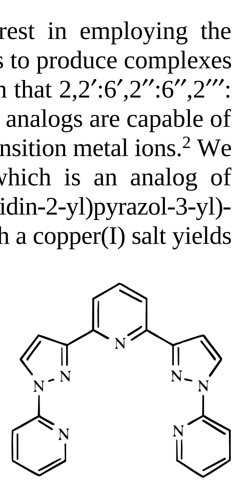
Department of Chemistry, University of Technology, Sydney, Broadway, NSW 2007, Australia, and School of Chemistry,
University of New South Wales, Sydney, NSW 2052, Australia

Received October 26, 1995

In recent years there has been interest in employing the stereochemical preferences of metal ions to produce complexes of defined topology.[1] It has been shown that 2,2′:6′,2′′:6′′,2′′′:6′′′,2′′′′-quinquepyridine and substituted analogs are capable of yielding double-helicates with certain transition metal ions.[2] We have prepared a heterocyclic ligand which is an analog of quinquepyridine, 2,6-bis(5-methyl-1-(pyridin-2-yl)pyrazol-3-yl)pyridine (L). Reaction of this ligand with a copper(I) salt yields a trinuclear double-helical complex. To date, no trinuclear double-helicate has been structurally characterized.



L



L′

We recently reported the structure of a copper(II) complex of the unsubstituted analog of L, 2,6-bis(1-(pyridin-2-yl)pyrazol-3-yl)pyridine (L′),[3] in which each unit of the dimeric complex is dinuclear. In the copper(II) complex of L′, the ligand binds each metal center employing a pyridinylpyrazole fragment and remains essentially planar. We herein report the preparation, characterization, and structure of the trinuclear copper(I) double-helical complex of L.

The ligand, L, was prepared by reacting the dipotassium salt of 2,6-bis(5-methylpyrazol-3-yl)pyridine[4,5] (1 equiv) with 2-bromopyridine (2 equiv) in diglyme, a method analogous to that used to prepare 2,6-bis(pyrazol-1-yl)pyridine and substituted derivatives.[6] The complex, $[Cu_3L_2(CH_3CN)_2][PF_6]_3$, was prepared by reacting L (2 equiv) with tetrakis(acetonitrile)copper(I) hexafluorophosphate (3 equiv) in methanol. These stoichiometries were confirmed by microanalysis and X-ray diffractometry. In solution, however, the complex seems to be somewhat unstable. The fast atom bombardment (FAB) mass spectrum exhibits peaks at *m/z* 1265 $[Cu_3L_2(PF_6)_2{}^+]$, 1139 $[Cu_2L_2(CH_3CN)_2(PF_6)^+]$, 1057 $[Cu_2L_2(PF_6)^+]$, 994 $[Cu_2L_2(CH_3CN)_2{}^+]$, 912 $[Cu_2L_2{}^+]$, and 456 $[CuL^+]$ (base peak; 100%). Electrospray ionization mass spectroscopy (ES-MS) exhibits similar peaks at *m/z* 456 $[CuL^+]$, 849 $[CuL_2{}^+]$, and 1059 $[Cu_2L_2(PF_6)^+]$. The NMR spectrum of the complex is similar to that of the ligand (8 proton environments) with minor differences in chemical shifts. This result suggests that the ligand has bound symmetrically to the metal ion(s) and coordination-induced shifts have been observed. It is to be noted that the NMR spectrum of the structurally characterized complex cation should reveal 15 proton environments. The cyclic voltammogram of an acetonitrile solution of $[Cu_3L_2(MeCN)_2][PF_6]_3$ shows that there is one reversible oxidation at $+0.19$ V and one at -0.65 V (with respect to the ferrocene/ferrocenium couple at $+0.40$ V). The structure determination indicates that there are two unique copper(I) sites (2:1 population) in the solid state. In solution, the cyclic voltammogram shows the presence of two metal sites. On oxidation of one copper(I) ion to copper(II), the overall oxidation state and the coordination requirement change, as has been observed for complexes of sexipyridine.[7] These changes will change the geometry of the double-helicate, in terms of metal−metal distances and the interannular twisting between the heterocyclic rings. In the case of this complex cation $[Cu_3L_2(MeCN)_2]^{3+}$, it appears that the deformation is such that the three metal centers cannot be accommodated.[8] This result correlates with the indication from NMR that the complex is unstable in solution.

Crystals suitable for X-ray diffractometry were grown by diffusion of diethyl ether vapor into an acetonitrile solution of the complex. The cation[9] has three copper(I) centers, each of which has approximately tetrahedral stereochemistry. The central metal atom is located on a 2-fold axis, so the asymmetric unit contains half of the trinuclear cation (the superscript "a" indicates the equiv position $1 - x, y, {}^1/_2 - z$ throughout). The twelve donor atoms, for the three four-coordinate centers, are provided by two quinquedentate ligands and two monodentate acetonitrile molecules. A view of the cation and the labeling of the metal and donor atoms is given in Figure 1 (the complete labeling scheme is included in the Supporting Information). Each quinquedentate ligand is wrapped around the three metal centers, producing a double-helicate. The central copper atom is coordinated by two pyridinylpyrazole fragments, i.e. the third and fourth heterocycles of each of the quinquedentate ligands. The other copper atoms are coordinated by a pyridinylpyrazole fragment, the first and second heterocycles of the quinquedentate ligand; a pyridinyl ring (the fifth heterocycle of the "other" heterocyclic ligand); and the acetonitrile molecule.

---

† University of Technology, Sydney.

‡ University of New South Wales.

(1) Schneider, H.-J.; Dürr, H. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Verlag Chemie: Cambridge, U.K., 1991. Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 1991.

(2) (a) Constable, E. C. *Tetrahedron* **1992**, *48*, 10013. (b) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67. (c) Gheysen, K. A.; Potts, K. T.; Hurrell, H. C.; Abruña, H. D. *Inorg. Chem.* **1990**, *29*, 1589. (d) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruña, H. D.; Arana, C. R. *Inorg. Chem.* **1993**, *32*, 4422. (e) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruña, H. D.; Arana, C. *Inorg. Chem.* **1993**, *32*, 4436.

(3) Dong, G.; Baker, A. T.; Craig, D. C. *Inorg. Chim. Acta* **1995**, *231*, 241.

(4) Gal, M.; Tarrago, G.; Steel, P. J.; Marzin, C. *New J. Chem.* **1985**, *9*, 617.

(5) Lin, Y.; Lang, S. A. *J. Heterocycl. Chem.* **1977**, *14*, 345.

(6) Jameson, D. L.; Goldsby, K. A. *J. Org. Chem.* **1990**, *55*, 4992.

(7) Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1675.

(8) Potts, K. T.; Keshavarz-K, M.; Tham, F. S.; Abruña, H. D.; Arana, C. *Inorg. Chem.* **1993**, *32*, 4436.

(9) Crystal data for $[Cu_3(C_{23}H_{19}N_7)_2(CH_3CN)_2](PF_6)_3$: $M = 1494.5$, monoclinic, space group $C2/c$, $a = 15.330(7)$ Å, $b = 20.847(5)$ Å, $c = 19.100(9)$ Å, $\beta = 101.95(2)°$, $V = 5972(4)$ Å^3, $D_c = 1.66$ g cm^{-3}, $Z = 4$, $\mu_{Mo} = 12.45$ cm^{-1}; crystal size $0.09 \times 0.09 \times 0.26$ mm, $2\theta_{max} = 50°$, minimum and maximum transmission factors 0.74 and 0.89. The number of reflections considered observed was 2810 ($I > 3\sigma(I)$) out of 5232 unique data, with $R_{merge} = 0.029$ for 125 pairs of equiv $0kl$ reflections. Final residuals R, R_w were 0.063, 0.082 for the observed data.

0020-1669/96/1335-1091$12.00/0

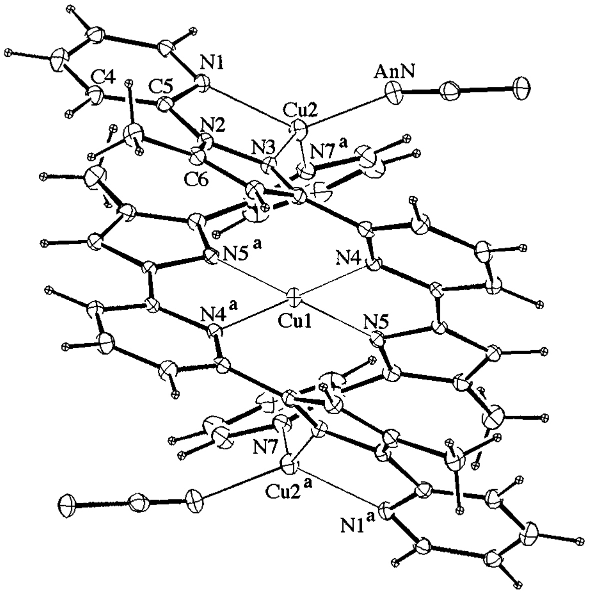


Figure 1. ORTEP representation (10% probability ellipsoids) of the complex trinuclear cation, showing a partial atom-labeling scheme. Selected distances (Å): Cu1−N4 2.099(7), Cu1−N5 1.992(7), Cu2−N1 2.090(7), Cu2−N3, 2.045(7), Cu2−AnN 1.996(9), Cu2−N7^a 2.060(7), Cu1⋯Cu2 3.216(1). Selected angles (deg): N4−Cu1−N5 78.9(3), N4−Cu1−N5^a 136.8(3), N4−Cu1−N4^a 105.4(4), N5−Cu1−N5^a 127.5(4), N1−Cu2−N3 77.8(3), N1−Cu2−AnN 130.4(3), N1−Cu2−N7^a 109.5(3), N3−Cu2−AnN 103.2(3), N3−Cu2−N7^a 136.8(3), AnN−Cu2−N7^a 102.7(3).

The Cu−N bond lengths are typical for copper(I) centers bound by nitrogen heterocycles.[10] The "bite angle" (N−Cu−N) for the pyridinylpyrazole didentate fragments are usual for relatively rigid didentate α-diimine ligands, and the values are very similar to the bite angles (79.6(3) and 79.5(2)°) found in the copper(II) complex of L′, the unsubstituted analog of L.[3] The narrow bite angle will cause a significant deviation from ideal tetrahedral geometry, and the coordination spheres at both copper centers in the asymmetric unit are flattened tetrahedra.

The structural type elucidated here has previously been predicted as a possibility for three tetrahedral metal centers coordinated by two quinquedentate ligands and two monodentate ligands.[11] The only minor difference is that, compared to the scheme previously proposed, the complex cation is of different symmetry. The structure reported here has a monodentate ligand "capping" each end of the double-helical complex rather than both being located at the same end of the complex.

In one of the double-helical dinuclear copper complexes of quinquepyridine that have been structurally characterized there is a six-coordinate copper(II) center coordinated by two terpyridine fragments [tpy + tpy] and a four-coordinate copper(I) center coordinated by two bipyridine fragments [bpy + bpy].[12] In that case, the different stereochemical requirements of the two metal centers are satisfied by the two quinquedentate ligands, indicating a satisfactory resolution of the potential conflict between ligand and metal atom demands. In another complex, containing two copper(II) atoms, one metal center is coordinated by two terpyridine fragments [tpy + tpy] and the other is five-coordinate with a monodentate acetato ligand supplementing the two bipyridine fragments.[12]

The individual heterocycles are planar, within experimental error, and the methyl groups are found to lie in the plane of the relevant pyrazolyl ring. The dihedral angles between the heterocycles, with the donor atom for the heterocycle listed in parentheses, are as follows: ring 1 (N1)−ring 2 (N3), 19.6(11)°; ring 2 (N3)−ring 3 (N4), 39.9(16)°; ring 3 (N4)−ring 4 (N5), 12.6(10)°; ring 4−ring 5 (N7), 45.6(18)°. Inspection of the relevant torsional angles confirms that the dihedral angles arise principally through a torsion about the interannular bond. The values for the torsional angles, calculated for the donor atoms and the atoms of the interannular bond and listed in the same order as the dihedral angles above, are −15.1(10), −38.7(11), −12.3(10), and −44.3(11)°. Sign can be disregarded, and it can be seen that the largest inconsistency between the dihedral angles and the torsional angles is found for ring 1−ring 2; otherwise the agreement is extremely good. The only significant "out-of-plane" angles associated with the interannular bonds are those of the N2−C5 bonds: 4.1(12) and 3.7(9)° out of the planes defined by the atoms C4, N1, and C5 and the atoms C6, N3, and N2, respectively. There is clearly loss of planarity between the first and second heterocycles through a torsion about the interannular bond (N2−C5) and arching perpendicular to this bond. The torsional angle N1−Cu2−Cu2^a−N7 is found to be 92.1(3)°, which means that this complex exhibits almost three-quarters of a turn of a double-helix.

A copper(I) complex of any quinquepyridine has not been structurally characterized. Potts et al.[2d] have also presented convincing evidence for the formation of a triple-helicate copper(I) complex of the substituted quinquepyridine 4′,4″-bis(methylthio)-2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine (mt-qpy): $[\mathrm{Cu^{I}_3(mt\text{-}qpy)_2}][\mathrm{PF_6}]_3$. Evidence for $[\mathrm{Cu^{II}(mt\text{-}qpy)}]_2[\mathrm{PF_6}]_4$ was also presented. From NMR studies it appears that dicopper complexes of substituted quinquepyridines are double-helical and stable in solution.

Acknowledgment. We thank the Australian Research Council Small Grants Scheme and the University of Technology, Sydney, Internal Research Grant Scheme for financial support. We also thank William Ha (AMBRI) for access to the NMR spectrometer and David Selby (AGAL) for access to the electrospray ionization mass spectrometer.

Supporting Information Available: Text giving details of the ligand synthesis and structure determination, a fully labeled diagram of the complex trinuclear cation, and listings of spectroscopic data for the ligand and thermal parameters, coordinates, and geometry for the complex (13 pages). Ordering information is given on any current masthead page.

IC951372P

---

(10) Melnik, M.; Macaskova, L.; Holloway, C. E. *Coord. Chem. Rev.* **1993**, *126*, 71.

(11) Potts, K. T.; Gheysen Raiford, K. A.; Keshavarz-K, M. *J. Am. Chem. Soc.* **1993**, *115*, 2793.

(12) Barley, M.; Constable, E. C.; Corr, S. A.; McQueen, R. C. S.; Nutkins, J. C.; Ward, M. D.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1988**, 2655.