

Nearly Tetrahedral 1:2 Complexes of Copper(I), Copper(II), Nickel(II), Cobalt(II), and Zinc(II) with 2,2'-Bis(2-imidazolyl)biphenyl

Spencer Knapp,* Terence P. Keenan, Xiaohua Zhang, Ronald Fikar, Joseph A. Potenza,* and Harvey J. Schugar*

Department of Chemistry, Rutgers
The State University of New Jersey
New Brunswick, New Jersey 08903

Received October 28, 1986

We describe here several pseudotetrahedral complexes whose tetrakis(imidazolyl) ligand sets exhibit an unparalleled degree of geometric control. These chromophores are relevant models for native and derivatized superoxide dismutases with Cu(I, II), Ni(II), Co(II), or Zn(II) ions in pseudotetrahedral metal binding sites.¹⁻⁴ Construction of site analogues requires the use of ligand constraints to overcome the ligand field (LF) driven distortion of tetrahedral Ni(II) and Cu(II) imidazole complexes toward planarity^{5,6} and the preference of Cu(I) imidazole complexes for 2- or 3-coordination.^{7,8} Nonplanar Cu^{II}N₄ and Ni^{II}N₄ complexes of nonbiological N-donors have been reported with MN₂/MN'₂ dihedral angles (DA) up to 71.9° (ideal planar and tetrahedral limits are 0° and 90°, respectively).⁹⁻¹⁴ Bidentate aromatic N-donor ligands afford Cu^IN₄ complexes with larger DA's (70-80°),¹⁵⁻¹⁷ while the Cu(pyridine)₄⁺ cation shows 4 site symmetry (DA = 90°) and is nearly tetrahedral.¹⁸

Although electron transfer between dissimilar Cu(I) and Cu(II) sites may be reversible,^{19,20} the fastest rates should obtain when coordination changes are small, as with Cu(I) and Cu(II) plastocyanin.²¹ The search²²⁻²⁴ for a nearly tetrahedral Cu^I/Cu^{II}N₄

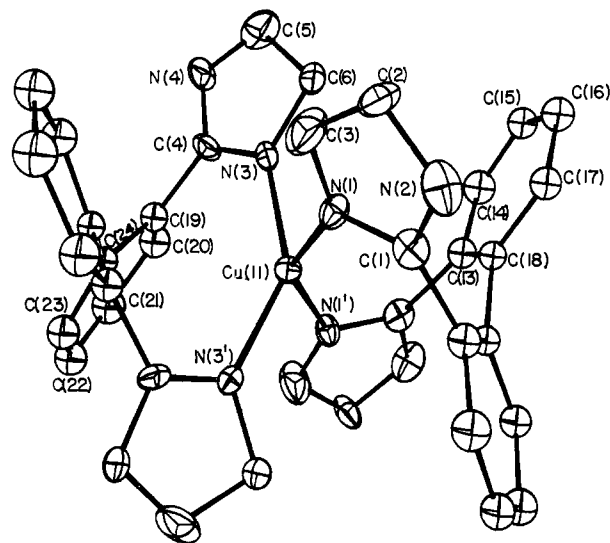


Figure 1. View of one of the two similar cations in Cu(1)₂·2ClO₄. H atoms have been omitted for clarity. Selected interatomic distances and angles: Cu-N(1), 1.953 (7) [1.980 (7)]; Cu-N(3), 1.961 (7) [1.949 (8)] Å; N(1)-Cu-N(1'), 140.3 (4)° [141.9 (4)°]; N(3)-Cu-N(3'), 142.5 (4)° [141.6 (5)°]; N(1)-Cu-N(3), 93.0 (3)° [93.6 (3)°]; N(1)-Cu-N(3'), 99.5 (3)° [98.7 (3)°]; N(1)-Cu-N(1')/N(3)-Cu-N(3'), 86.4 (2)° [89.1 (2)°]; N(1')-Cu-N(3)/N(1)-Cu-N(3'), 51.3 (2)° [51.1 (2)°]; N(1)-Cu-N(3)/N(1')-Cu-N(3'), 54.2 (2)° [53.4 (2)°]. Values for the second unique cation are in square brackets.

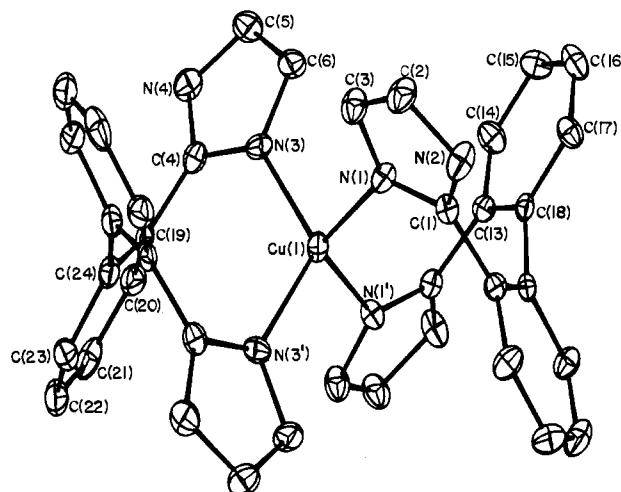


Figure 2. View of one of the two cations in Cu(1)₂·ClO₄. For clarity, H atoms have been omitted. Selected interatomic distances and angles: Cu-N(1), 2.022 (8) [2.031 (7)]; Cu-N(3), 2.037 (8) [2.052 (7)] Å; N(1)-Cu-N(1'), 119.5 (3)° [120.6 (3)°]; N(3)-Cu-N(3'), 121.6 (3)°; N(1)-Cu-N(3), 105.9 (3)° [104.4 (3)°]; N(1)-Cu-N(3'), 102.5 (3)° [107.5 (3)°]; N(1')-Cu-N(3'), [100.4 (3)°]; N(1)-Cu-N(1')/N(3)-Cu-N(3'), 87.9 (1)° [89.4 (1)°]; N(1')-Cu-N(3)/N(1)-Cu-N(3'), 78.9 (1)° [77.9 (1)°]; N(1)-Cu-N(3)/N(1')-Cu-N(3'), 76.8 (1)° [77.4 (1)°]. Values for the second cation are in square brackets.

redox pair containing the *same* ligands has now been resolved. This pair as well as the analogous Co(II), Zn(II), and the novel Ni(II)N₄ complexes are described here.

The bidentate bis(imidazole) donor ligand **1** was prepared in three steps from dimethyl diphenate.²⁵ Reaction with excess ethylenediamine at reflux²⁶ gave the crystalline bis[*N*-(2-aminoethyl)amide], which was cyclized and dehydrated by using

(1) Calabrese, L.; Cocco, D.; Morpurgo, L.; Mondovi, B.; Rotilio, G. *FEBS Lett.* **1975**, *59*, 29.

(2) Calabrese, L.; Cocco, D.; Morpurgo, L.; Mondovi, B.; Rotilio, G. *Eur. J. Biochem.* **1976**, *64*, 465.

(3) Pantoliano, M. W.; Valentine, J. S.; Nafe, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 6310.

(4) Ming, L.-J.; Valentine, J. S. *Abstracts of Papers, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; INOR 193.*

(5) Bernarducci, E.; Bharadwaj, P. K.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1983**, *105*, 3860.

(6) Lum, V.; Gray, H. B. *Isr. J. Chem.* **1981**, *21*, 23.

(7) (a) Sorrell, T. N.; Borovik, A. S. *J. Am. Chem. Soc.* **1986**, *108*, 2479.

(b) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013.

(8) Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2637.

(9) Johnson, J. E.; Beineke, T. A.; Jacobson, R. A. *J. Chem. Soc. A* **1971**, 1371.

(10) Baxter, C. E.; Rodig, O. R.; Schlutzer, R. K.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1918.

(11) Gouge, E. M.; Geldard, J. F.; Sinn, E. *Inorg. Chem.* **1980**, *19*, 3356.

(12) Patmore, D. J.; Rendle, D. F.; Storr, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 718.

(13) Davis, W. M.; Zask, A.; Nakanishi, K.; Lippard, S. J. *Inorg. Chem.* **1985**, *24*, 3737.

(14) Davis, W. M.; Roberts, M. M.; Zask, A.; Nakanishi, K.; Nozoe, T.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3864.

(15) Goodwin, K. V.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1986**, *25*, 2033.

(16) Burke, P. J.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1980**, *19*, 1211.

(17) Dobson, J. F.; Green, B. E.; Healy, P. C.; Kennard, C. H. L.; Pakawatchai, C.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 649 and references cited therein.

(18) Nilsson, K.; Oskarsson, A. *Acta Chem. Scand., Ser. A* **1982**, *36*, 605.

(19) Pulliam, E. J.; McMillin, D. R. *Inorg. Chem.* **1984**, *23*, 1172.

(20) Hartman, J.-A., R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202.

(21) Garret, T. P. J.; Clingeffer, D. J.; Guss, J. M.; Rogers, S. J.; Freeman, H. C. *J. Biol. Chem.* **1984**, *259*, 2822.

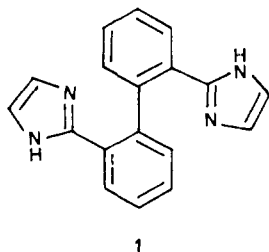
(22) Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, *21*, 1881.

(23) Bernarducci, E. E.; Bharadwaj, P. K.; Lalancette, R. A.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1983**, *22*, 3911.

(24) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1982**, *64*, L219.

(25) Underwood, H. W., Jr.; Kochmann, E. L. *J. Am. Chem. Soc.* **1924**, *46*, 2069.

(26) Hill, A. J.; Aspinall, S. R. *J. Am. Chem. Soc.* **1939**, *61*, 822.



1

p-toluenesulfonic acid at 200 °C. The resulting bis(imidazole) was oxidized with BaMnO₄ according to the procedure we developed for 2-substituted imidazoles,²⁷ and **1** was isolated as colorless crystals, mp 273–274 °C.²⁸ Complexes of **1** were prepared by treatment with 0.5 equiv of the M(II) perchlorate in ethanol. The green Cu(II) complex (1.7 μ_B) crystallized as the diperchlorate from acetone–ether. The dark-blue Ni(II) (3.7 μ_B), purple Co(II), (4.7 μ_B), and colorless Zn(II) complexes crystallized from ethanol–ether as isostructural diperchlorates having three lattice ethanol molecules per metal. The Cu(I) complex was obtained as the pale-yellow perchlorate by diffusing ether into a deoxygenated acetonitrile solution containing 1 equiv of **1** and 0.5 equiv of Cu(CH₃CN)₄·ClO₄.

From X-ray analysis, the metal ions were found to lie on twofold axes which either relate two molecules of **1** in the 2:1 complexes (Ni(II), Co(II), Zn(II), Cu(I)), or which bisect the biphenyl 1,1'-bond and relate halves of **1** [Cu(I), Cu(II), Figures 1 and 2].²⁹ Comparison of the figures shows the strong similarity of the Cu(I) and Cu(II) structures. Geometrical constraints within the nine-membered chelate rings cause the intraligand N(1)–M–N(1') angles to exceed 109°, flattening the otherwise tetrahedral MN₄ units. Additional LF effects result in larger angles for the Cu(II) [140.3 (4)°, 142.5 (4)°] and Ni(II) [130.2 (2)°] complexes compared with those for Co(II) [123.2 (2)°] and Cu(I) [119.5 (3)°, 121.6 (3)°]. The DA's between the intraligand N₂M units (e.g., N(1)–M–N(1')/N(3)–M–N(3'), Figure 1) are 86.4 (2)°, 87.2 (2)°; 87.9 (1)°, 89.4 (1)°; 89.3 (2)°; and 87.6 (1)° respectively for the Cu(II), Cu(I), Co(II), and Ni(II) complexes. Increasing *D*_{2d} flattening is reflected by the successive decrease in the interligand DA's observed for Cu(I) [76.8 (1)–78.9 (1)°], Co(II) [74.0 (2)°, 74.7 (2)°], Ni(II) [65.4 (2)°, 67.7 (2)°], and Cu(II) [51.1 (2)–54.2 (2)°]. The Cu(II)–N distances (Figure 1) are ca. 0.05 Å shorter than those generally observed for planar or tetragonal tetrakis(imidazole)copper(II) complexes⁵ but are typical for tetrahedrally distorted Cu(II) complexes having four sp² N-donors.^{10–12} The Cu(I)–N distances (Figure 2) are normal.^{15–18} The Co(II)–N distances [1.987 (4), 2.001 (6) Å] are the same as those [1.988 (3), 2.002 (3) Å] for the essentially tetrahedral (1,2-dimethylimidazole)₄Co·2ClO₄ complex.³⁰ The

Ni(II)–N distances [1.960 (5), 1.966 (6) Å] are similar to those of pseudotetrahedral Ni(II) tropocoronand complexes with DA's in the range 70.1–85.2°.¹⁴

Electronic spectra of the Cu(II) complex (mulls and solution) include a LF absorption at 660 nm (ε ~400) and the predicted³¹ π(imidazole) → Cu(II) LMCT absorption at 450 nm (ε ~600). The Cu(II)-doped Zn(II) complex exhibits axial EPR spectra (*g*_z = 2.32, *g*_⊥ = 2.06, *A*_{||}^{Cu} = 118 × 10⁻⁴ cm⁻¹) considerably different from those (*g*_{||} = 2.26, *g*_⊥ = 2.08, *A*_{||}^{Cu} = 178 × 10⁻⁴ cm⁻¹) of a planar tetrakis(phenylimidazole)copper(II) reference complex³² but similar to those³ for superoxide dismutase with Cu(II) doped into the Zn(II) site (*g*_z = 2.316, *g*_y = 2.118, *g*_x ≈ 2.01, *A*_z^{Cu} = 116 × 10⁻⁴ cm⁻¹). The Ni(II) complex exhibits LF absorptions at 770 (ε ~30), 640 (ε ~85), and 470 nm (ε ~140); the π(imidazole) → Ni(II) LMCT absorption appears at 350 nm (ε ~800). π(Imidazole) → Ni(II) LMCT at 335 and 355 nm has been reported for Ni(II)-substituted stellacyanin and azurin, respectively.⁶ The Co(II) complex exhibits LF absorptions at 590 (ε ~600) and 520 nm (ε ~470); the π(imidazole) → Co(II) LMCT absorption appears at 310 nm (ε ~900). The ligand **1** does not exhibit electronic absorptions at wavelengths longer than 300 nm.

Acknowledgment. This research was supported by the NSF (Grant CHE8417548), the David and Joanna Busch Foundation, and the NIH (Instrumentation Grant 1510 RRO 1486 O1A).

Supplementary Material Available: Full details for the synthesis of **1** and positional and thermal parameters for Cu(1)₂·2ClO₄, Cu(1)₂·ClO₄, Ni(1)₂·2ClO₄·3EtOH, and Co(1)·2ClO₄·3EtOH (26 pages). Ordering information is given on any current masthead page.

(32) Prochaska, H. J.; Schwindinger, W. F.; Schwartz, M.; Burk, M. J.; Bernarducci, E.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 3446.

Reactivity of Pentaammineosmium(II) with Benzene

W. D. Harman and H. Taube*

Department of Chemistry, Stanford University
Stanford, California 94305
Received October 30, 1986

Our continued interest in the reactivity of pentaammineosmium(II) with unsaturated ligands^{1,2} has prompted us to investigate its interaction with unsubstituted aromatic hydrocarbons. When Os(NH₃)₅(CF₃SO₃)₃³ is reduced by magnesium in the presence of excess benzene, a deep orange solution results.^{4a} The material isolated from this reaction was characterized as [Os(NH₃)₅(η²-benzene)](TFMS)₂ (**1**).^{5a} The ¹H NMR spectrum of **1** at room temperature shows resonances at 4.75 and 3.45 ppm,

(1) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227.

(2) Taube, H. *Pure Appl. Chem.* **1979**, *51*, 901–912.

(3) Lay, P.; Magnuson, R.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(4) (a) Preparation of **1**: 200 mg of Os(NH₃)₅(TFMS)₃ and 1.0 mL of benzene are dissolved in a cosolvent mixture of 1.5 mL of dimethylacetamide (DMA) and 20 mL of freshly distilled dimethoxyethane. Magnesium, 1.0 g, cleaned with iodine and washed with DMA, is added and the stirred solution becomes orange. After 50 min, the reduced solution is filtered and treated with 100 mL of CH₂Cl₂, precipitating the final product. (b) Preparation of **2**: 1, 100 mg, is suspended in ethyl acetate (EtOAc) for 24 h. The solution is filtered and the precipitate collected and washed with EtOAc and Et₂O. **2** is recrystallized by vapor diffusion of ether into acetone.

(5) (a) **1**: Anal. Calcd for C₈H₂₁Os₁S₂F₆O₆N₅: C, 14.75; H, 3.25; N, 10.75. Found: C, 14.75; H, 3.48; N, 10.57. IR (KBr) 3040, 2961, 1529, 1450, 988, 927 cm⁻¹ (plus CF₃SO₃⁻ and ammine absorptions); ¹H NMR (acetone-*d*₆, 20 °C) δ 6.45 (5.5 H, br), 4.75 (3 H, br), 3.45 (12 H, br), -87 °C: 7.25 (2 H, br), 6.55 (2 H, br), 5.22 (2 H, br). (b) **2**: Anal. Calcd for C₈H₃Os₁S₂F₂O₁₂N₁₀³⁺/4C₃H₆O: C, 11.76; H, 3.20; N, 10.94. Found: C, 11.60; H, 3.22; N, 11.04. IR (KBr) 3005, 2958 (m), 1464, 1156, 1047, 927 cm⁻¹ (plus SO₃CF₃⁻ and ammine absorptions); ¹H NMR (acetone-*d*₆) δ 6.53 (1.9 H, m), 4.63 (2.0, d), 4.33 (1.9, m), 4.90 (5.8, br), 3.65 (23, br); ¹³C NMR (acetone-*d*₆, proton decoupled) 127.6 (s), 53.1 (s), 49.6 (s), 123 (q) ppm (CF₃SO₃⁻).

(27) Hughey, J. L., IV; Knapp, S.; Schugar, H. J. *Synthesis* **1980**, 489.

(28) See the supplementary material for more information.

(29) Crystallography: Cu(1)₂·ClO₄, CuClO₄N₈C₃₆H₂₈, monoclinic, *C2/c*, *a* = 20.922 (7) Å, *b* = 20.603 (3) Å, *c* = 16.127 (3) Å, β = 90.36 (2)°, *Z* = 8; *d*_{obsd} = 1.40 (1), *d*_{calcd} = 1.406 g/cm³. The structure was solved (2252 reflections (*I* > 1σ(*I*)), Mo Kα radiation, 0.71073 Å, empirical absorption corrections) using the Enraf-Nonius SDP and refined to give *R*_{F(W_F)} = 0.070 (0.070) and a goodness of fit of 1.93. Cu(1)₂·2ClO₄, CuCl₂O₈N₈C₃₆H₂₈, orthorhombic, *Pbcn*, *a* = 17.581 (3) Å, *b* = 21.706 (2) Å, *c* = 19.154 (2) Å, *Z* = 8; *d*_{obsd} = 1.51 (1), *d*_{calcd} = 1.518 g/cm³, 2783 reflections (*I* > 1σ(*I*)), *R*_{F(W_F)} = 0.098 (0.095), and GOF = 2.24. Co(1)₂·2ClO₄·3EtOH, CoCl₂·O₁₁N₈C₄₂H₄₆, monoclinic, *C2/c*, *a* = 27.239 (4) Å, *b* = 13.041 (2) Å, *c* = 16.205 (2) Å, β = 125.39 (1)°, *Z* = 4; *d*_{obsd} = 1.41 (1), *d*_{calcd} = 1.371 g/cm³, 2019 reflections (*I* > 1σ(*I*)), *R*_{F(W_F)} = 0.070 (0.085), and GOF = 2.72. Ni(1)₂·2ClO₄·3EtOH, NiCl₂O₁₁N₈C₄₂H₄₆, monoclinic, *C2/c*, *a* = 26.842 (5) Å, *b* = 13.022 (2) Å, *c* = 16.406 (2) Å, β = 126.21 (1)°, *Z* = 4; *d*_{obsd} = 1.39 (1), *d*_{calcd} = 1.390 g/cm³, 2049 reflections (*I* > 3σ(*I*)), *R*_{F(W_F)} = 0.080 (0.085), and GOF = 2.25. The Co, Ni, and a nominally 3% Ni(II)-doped Zn(1)₂ complex (lattice constants *a* = 27.26 (1) Å, *b* = 13.021 (3) Å, *c* = 16.18 (1) Å, β = 125.44 (5)°) are isostructural. The perchlorate anions in all the complexes showed high thermal parameters and/or disorder, resulting in higher than normal *R* factors. Complete structural details will be presented elsewhere.

(30) Bernarducci, E.; Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr. Sect. C*, accepted for publication.

(31) Bernarducci, E.; Schwindinger, W. F.; Hughey, J. L., IV; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1686.