

Trigonal Planar Copper(I) Complex: Synthesis, Structure, and Spectra of a Redox Pair of Novel Copper(II/I) Complexes of Tridentate Bis(benzimidazol-2'-yl) Ligand Framework as Models for Electron-Transfer Copper Proteins[†]

Ramalingam Balamurugan and Mallayan Palaniandavar*

Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India

R. Srinivasa Gopalan

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India

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The copper(II) and copper(I) complexes of the chelating ligands 2,6-bis(benzimidazol-2'-ylthiomethyl)pyridine (bbtmp) and *N,N*-bis(benzimidazol-2'-ylthioethyl)methylamine (bbtma) have been isolated and characterized by electronic and EPR spectra. The molecular structures of a redox pair of Cu(II/I) complexes, viz., [Cu(bbtmp)-(NO₃)]NO₃, **1**, and [Cu(bbtmp)]NO₃, **2**, and of [Cu(bbtmp)Cl], **3**, have been determined by single-crystal X-ray crystallography. The cation of the green complex [Cu(bbtmp)(NO₃)]NO₃ possesses an almost perfectly square planar coordination geometry in which the corners are occupied by the pyridine and two benzimidazole nitrogen atoms of the bbtmp ligand and an oxygen atom of the nitrate ion. The light-yellow complex [Cu(bbtmp)]NO₃ contains copper(I) with trigonal planar coordination geometry constituted by the pyridine and two benzimidazole nitrogen atoms of the bbtmp ligand. In the yellow chloride complex [Cu(bbtmp)Cl] the asymmetric unit consists of two complex molecules that are crystallographically independent. The coordination geometry of copper(I) in these molecules, in contrast to the nitrate, is tetrahedral, with pyridine and two benzimidazole nitrogen atoms of bbtmp ligand and the chloride ion occupying the apexes. The above coordination structures are unusual in that the thioether sulfurs are not engaged in coordination and the presence of two seven-membered chelate rings facilitates strong coordination of the benzimidazole nitrogens and discourage any distortion in Cu(II) coordination geometry. The solid-state coordination geometries are retained even in solution, as revealed by electronic, EPR, and ¹H NMR spectra. The electrochemical behavior of the present and other similar CuN₃ complexes has been examined, and the thermodynamic aspects of the electrode process are correlated to the stereochemical reorganizations accompanying the redox changes. The influence of coordinated pyridine and amine nitrogen atoms on the spectral and electrochemical properties has been discussed.

Introduction

The active site coordination geometries of type I copper proteins are unusual and consist of a trigonally disposed His₂-Cys ligand complement with a strong, highly covalent Cu–S(cys) interaction that primarily determines both the trigonal geometry around copper(II) and their unique spectral and redox properties.^{1–4} They vary depending on the additional protein ligands coordinated to copper; thus, the coordination of methionine as an additional ligand leads to the generation of an unusual trigonal pyramidal active site geometry in plastocyanin, which can be approximated as a distorted tetrahedron,⁵ whereas

that of methionine and glutamic acid leads to a trigonal bipyramidal geometry in azurin, and the reduced copper(I) form in both of them has a distorted tetrahedral geometry.⁶ In contrast, there is no additional ligand for fungal laccase,⁷ ceruloplasmin,^{8,9}

[†] Dedicated to Professor C. N. R. Rao, FRS on the occasion of his 65th birthday.

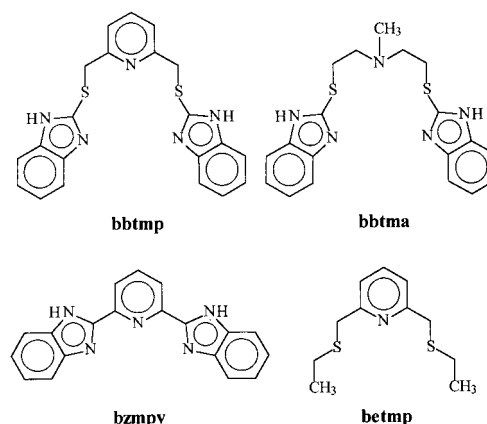
* To whom correspondence should be addressed. E-mail: palani@bdu.ernet.in.

- (1) (a) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, 278, 319. (b) Adman, E. T.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, 123, 35. (c) Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, 102, 168.
- (2) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, 92, 521.
- (3) (a) Solomon, E. I.; Lowery, M. D. *Science*, **1993**, 259, 1575. (b) Guckert, J. A.; Lowery, M. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1995**, 117, 2817. (c) LaCroix, L. B.; Shadle, S. E.; Wang, Y.; Averill, B. A.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1996**, 118, 7755. (d) Solomon, E. I.; Penfield, K. W.; Gewirth, A. A.; Lowery, M. D.; Shadle, S. E.; Guckert, J. A.; LaCroix, L. B. *Inorg. Chim. Acta* **1996**, 243, 67.
- (4) (a) Pierloot, K.; De Kerpel, J. O. A.; Ryde, U.; Roos, B. O. *J. Am. Chem. Soc.* **1997**, 119, 218. (b) Olsson, M. H. M.; Ryde, U.; Roos, B. O.; Pierloot, K. *J. Biol. Inorg. Chem.* **1998**, 3, 109.
- (5) Guss, J. M.; Freeman, H. C. *J. Mol. Biol.* **1983**, 169, 521. (b) Norris, G. E.; Anderson, B. F.; Baker, E. N. *J. Am. Chem. Soc.* **1986**, 108, 2784.
- (6) Guss, J. M.; Harrowell, P. R.; Murata, M.; Norris, V. A. Freeman, H. C. *J. Mol. Biol.* **1986**, 192, 361.
- (7) Ducros, V.; Brzozowski, A. M.; Wilson, K. S.; Brown, S. H.; Ostergaard, P.; Schneider, P.; Yaver, D. S.; Pedersen, A. H.; Davis, G. J. *Nature Struct. Biol.* **1998**, 5, 310.
- (8) Zaitseva, I.; Zaisev, V.; Card, G.; Moshkov, K.; Bax, B.; Ralph, A.; Lindley, P. J. *Biol. Inorg. Chem.* **1996**, 1, 15.
- (9) Machonkin, T. E.; Zhang, H. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *Biochemistry* **1998**, 37, 9570.

and certain azurin mutants¹⁰ to produce a three-coordinated trigonal planar copper site, and possibly the copper(I) active site in ceruloplasmin^{8,9} also possesses a trigonal planar geometry. The close resemblance between the Cu(II) and Cu(I) geometries^{5,6,11} in these proteins markedly facilitates the change of redox state of copper and accounts for a small reorganization energy accompanying redox¹² and hence for the high rate of electron transfer by the proteins. This is in sharp contrast to the differing geometries, viz., square-based and tetrahedral adopted by normal Cu(II) and Cu(I) complexes, respectively, which means that their interconversion is accompanied by large structural changes. However, it has been shown¹³ that in low molecular weight complexes the coordination geometry imposed by the ligand primarily controls the Cu^{II}/Cu^I redox couple^{14,15} entirely due to the effect of ligand geometry and donor atom strength on the stability of the copper(II) complex with little or no effect on the stability of the copper(I) complex.

To understand the nature of the Cu^{II}/Cu^I redox process, which underlies the function of copper proteins, and hence elucidate the structure–electron transfer relationships of proteins, it is necessary to examine the structure and chemical consequences of copper in different oxidation states but occupying similar coordination geometries constituted by biomimetic donor atoms. Several Cu(II)¹⁶ and Cu(I)^{17–19} complexes containing pyridine/benzimidazole and thioether donors have been synthesized as models for the redox-active sites in the proteins, and their structures and spectral and redox behavior have been investigated. Though copper complexes of several N₂S₃,^{20,21} N₂S₂,^{16,21–25} and N₂S_{2.26 ligands containing unsaturated nitrogens have been well-documented, those of NS₂ type of ligands have not elicited}

Chart 1



much interest, and only recently a few complexes of ligands like 2,6-bis(ethylthiomethyl)pyridine (betmp, Chart 1) are known.²⁷ Such ligands are of interest in making models for type I copper proteins as a low-pH form of plastocyanin, with one of the two histidine imidazoles in the type I active sites being protonated and containing a site with a planar CuNS₂ chromophore.⁹ We describe here the syntheses and crystal structures of copper(II) and copper(I) complexes of the NS₂ ligand 2,6-bis(benzimidazol-2'-ylthiomethyl)pyridine (bbtmp, Chart 1). To evaluate the role of the pyridine nitrogen coordination in these complexes, the copper complexes of *N,N*-bis(benzimidazol-2'-ylthioethyl)methylamine (bbtma) have been also prepared and investigated. The strategies behind the selection of such ligands are that (i) they would force on copper(II) only monomeric trigonal bipyramidal or square pyramidal stereochemistry, (ii) the chelating nature of the ligand will facilitate the weak thioether sulfur donor to bind to copper(II), (iii) they are interesting ambidentate ligands because, in addition to the basic NS₂ donor set, they contain two additional benzimidazole donors, and (iv) the incorporation of two bulky benzimidazole moieties, apart from mimicking the imidazole function in proteins, will cause steric crowding on copper, which may help to induce unusual coordination geometries and hence interesting spectral and redox properties; however, though it may not be an approximation to the protein environment, geometries and properties closer to the proteins may be generated. In fact, when two benzimidazole moieties are incorporated as in Cu(II) complexes of bis(benzimidazolyl)diamine/dithia ligands, tetrahedral distortion (CuN₄)²⁸ or trigonal bipyramidal geometry (CuN₂S₂)²⁵ is imposed on Cu(II). We have now found that the copper(I) chloride complex of bbtmp is tetrahedral. However, the crystal structure of the Cu(I) nitrate complex of the same ligand contains, interestingly, a trigonal planar geometry²⁹ for

- (10) Karlsson, B. G.; Nordling, M.; Pascher, T.; Tsai, L. C.; Sjölin, L.; Lundberg, L. G. *Protein Eng.* **1991**, *4*, 343.
- (11) (a) Shepard, W. E. B.; Anderson, B. F.; Lewandoski, D. A.; Norris, G. E.; Baker, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 7817. (b) Dodd, F. E.; Abraham, Z. H. L.; Eady, R. R.; Hasnain, S. *Acta Crystallogr.* **2000**, *D56*, 690.
- (12) Zanello, P. *Comments Inorg. Chem.* **1988**, *8*, 45.
- (13) Ambundo, E. A.; Deydier, M. V.; Grall, A. J.; Agüera-Vega, N.; Dressel, L. T.; Cooper, T. H.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4233.
- (14) McMaster, J.; Beddoes, R. L.; Collison, D.; Eardley, D. R.; Helliwell, M.; Garner, C. D. *Chem. Eur. J.* **1996**, *2*, 685. (b) Muller, E.; Bernardinelli, G.; Reedijk, J. *Inorg. Chem.* **1996**, *35*, 1952. (c) Goodwin, J. A.; Wilson, L. J.; Stanbury, D. M.; Scott, R. A. *Inorg. Chem.* **1989**, *28*, 42.
- (15) Knapp, S.; Keenan, T. P.; Zhang, X.; Fikar, R.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1990**, *112*, 3452.
- (16) (a) Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 357. (b) Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2637. (c) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (17) Sorrell, T. N.; Malachowski, M. R. *Inorg. Chem.* **1983**, *22*, 1883.
- (18) Malachowski, M. R.; Adams, M.; Elia, N.; Rheingold, A. L.; Kelly, R. S. *J. Chem. Soc., Dalton Trans.* **1999**, 2177.
- (19) Thompson, A. M. W. C.; Blandford, I.; Redfearn, H.; Jeffery, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1997**, 2661. (b) Casella, L. *Inorg. Chem.* **1984**, *23*, 2781.
- (20) (a) Adhikary, B.; Lucas, C. R. *Inorg. Chem.* **1994**, *33*, 1376. (b) Kanters, R. P. F.; Yu, R.; Addison, A. W. *Inorg. Chem. Acta* **1992**, *196*, 97. (c) Addison, A. W.; Palaniandavar, M. *Abstracts of Papers*, 188th American Chemical Society National Meeting, Washington, DC, 1984; INOR-068.
- (21) Usha, S.; Palaniandavar, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2277.
- (22) Nanda, K. K.; Addison, A. W.; Butcher, R. J.; McDevitt, M. R.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1997**, *36*, 134.
- (23) Haanstra, W. G.; Cabral, M. F.; Cabral, J. de O.; Driessen, W. L.; Reedijk, J. *Inorg. Chem.* **1992**, *31*, 3150. (b) Haanstra, W. G.; Driessen, W. L.; de Graaff, R. A. G.; Reedijk, J.; Wang, Y. F.; Stam, C. H. *Inorg. Chem. Acta* **1991**, *186*, 215. (c) Rietmeijer, F. J.; Birker, P. J. M. W. L.; Gorter, S.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1191. (d) Birker, P. J. M. W. L.; Godefroi, E. K.; Helder, J.; Reedijk, J. *J. Am. Chem. Soc.* **1982**, *104*, 7556.

- (24) (a) Hormann, E.; Riesen, P. C.; Neuburger, M.; Zehnder, M.; Kaden, T. A. *Helv. Chim. Acta* **1996**, *79*, 235. (b) Balakrishnan, K. P.; Riesen, A.; Zuberbühler, A. D.; Kaden, T. A. *Acta Crystallogr.* **1990**, *C46*, 1236. (c) Comba, P.; Lawrance, G. A.; Rossignoli, M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 773. (d) Westerby, B. C.; Juntunen, K. L.; Leggett, G. H.; Pett, V. B.; Koenigbauer, M. J.; Purgett, M. D.; Taschner, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 2109.
- (25) Vaidyanathan, M.; Balamurugan, R.; Usha, S.; Palaniandavar, M. Unpublished results.
- (26) (a) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 3645. (b) Lockhart, J. C.; Clegg, W.; Hill, M. N. S.; Rushon, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3541.
- (27) Escrich, L.; Sanz, M.; Casabo, J.; Teixidor, F.; Molins, E.; Miravittles, C. *J. Chem. Soc., Dalton Trans.* **1989**, 1739.
- (28) Pandiyan, T.; Palaniandavar, M.; Lakshminarayanan, M.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1992**, 3377.

the CuN_3 chromophore, which is uncommon. Further, in both the Cu(II) and Cu(I) nitrate complexes of the same bbtmp ligand, copper is found coordinated, unexpectedly, through benzimidazole nitrogens rather than the sulfur atoms, despite forming otherwise less favorable seven-membered chelate rings. This is very interesting because only a few copper complexes have been structurally characterized in two oxidation states^{22,30} with precisely the same ligand.^{13,15,31–35} A structural comparison of such a redox pair of complexes constituted by biologically relevant donors would enable us to gain a better understanding of the interplay of stereochemistry and oxidation state. Also, the present study focuses on the spectral and electrochemical behavior and the structural reorganization occurring in the Cu(II) and Cu(I) complexes during electron transfer.

Experimental Section

Materials. Copper(II) chloride dihydrate, copper(II) nitrate trihydrate, *N*-methyldiethanolamine (Sisco, India), 2,6-pyridinedimethanol, 2-mercaptobenzimidazole (Aldrich), tetrabutylammonium bromide (G. F. Smith), and sodium perchlorate (Loba, India) were used without further purification. Thionyl chloride (Ranbaxy, India) was purified by fractional distillation. Tetrabutylammonium perchlorate was prepared by the addition of sodium perchlorate to a hot ethanol solution of tetrabutylammonium bromide. The product was recrystallized from aqueous ethanol and was tested for the absence of bromide.

Syntheses of Ligands. The ligand 2,6-bis(benzimidazol-2'-ylthio-methyl)pyridine³⁶ (bbtmp) and 2,6-bis(benzimidazol-2'-yl)pyridine³⁷ (bzmpy) were synthesized as reported earlier.

***N,N*-Bis(benzimidazol-2'-ylthioethyl)methylamine (bbtma).** *N*-methyldiethanolamine (5.96 g, 0.05 mol) was suspended in dichloromethane (50 mL), and an excess of thionyl chloride (23.79 g, 2.0 mol) was added dropwise with constant stirring at 0 °C. The reaction

mixture was refluxed for an hour and then cooled. The excess thionyl chloride was removed by adding a small amount of methanol, and the hydrochloride formed was collected and dried over CaCl_2 in a vacuum. The ligand bbtma was prepared by employing the procedure adopted for bbtmp. Sodium hydroxide (0.80 g, 20 mmol) and 2-mercaptobenzimidazole (3.00 g, 20 mmol) were combined in ethanol (50 mL), and the solute was stirred for 30 min under nitrogen. An ethanol (30 mL) solution of bis(chloroethyl)-*N*-methylamine hydrochloride (1.93 g, 10 mmol) was added to this solution, and the resulting solution was stirred for an hour and then refluxed for an hour. The pH of the resulting mixture was adjusted to 9 with sodium hydroxide. The volume of ethanol was reduced by rotary evaporation, and 100 mL of water was added. The white product (2.58 g, 67.27%) obtained was recrystallized from methanol. ¹H NMR (dimethyl sulfoxide-*d*₆; δ , ppm): 2.34 (s, 3H, N-CH_3), 2.81 (t, 4H, N-CH_2 -), 3.43 (t, 4H, S-CH_2 -), 7.08 (m, 8H, Ar H). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_5\text{S}_2$: C, 59.50; H, 5.52; N, 18.26. Found: C, 59.92; H, 5.83; N, 18.68.

[Cu(bbtmp)(NO₃)](NO₃), 1, and [Cu(bbtmp)](NO₃), 2. A methanolic solution (20 mL) of cupric nitrate (0.22 g, 1 mmol) was added to a solution of bbtmp (0.40 g, 1 mmol) in methanol with constant stirring. The green solution was filtered and kept for slow evaporation. The green crystals formed were found to be suitable for X-ray diffraction. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_7\text{S}_2\text{CuO}_6$: C, 42.67; H, 2.90; N, 16.59. Found: C, 42.48; H, 2.69; N, 16.76. A light-yellow crystalline solid of [Cu(bbtmp)](NO₃) was also formed along with the green crystals when the solution was kept for a few more days. The light-yellow crystals were separated manually. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_6\text{S}_2\text{CuO}_3$: C, 47.67; H, 3.24; N, 15.88. Found: C, 47.86; H, 3.09; N, 15.72.

[Cu(bbtmp)Cl], 3. To a methanolic solution (20 mL) of bbtmp (0.40 g, 1 mmol) copper(II) chloride dihydrate (0.17 g, 1 mmol) in methanol was added slowly with constant stirring. The resultant solution was filtered and kept for slow evaporation. The yellow crystals obtained were found to be suitable for X-ray diffraction. Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_5\text{S}_2\text{CuCl}$: C, 50.19; H, 3.41; N, 13.94. Found: C, 50.31; H, 3.29; N, 13.72.

[Cu(bbtma)(NO₃)](NO₃), 4. The ligand bbtma (0.37 g, 1 mmol) was dissolved in methanol (20 mL), and to this a methanolic solution of cupric nitrate (0.22 g, 1 mmol) was added slowly. The volume of green solution was reduced by rotary evaporation and then cooled. The complex formed was filtered and dried under vacuum. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_5\text{S}_2\text{CuO}_6$: C, 39.96; H, 3.71; N, 17.17. Found: C, 39.78; H, 3.58; N, 17.02.

[Cu(bbtma)(H₂O)](BF₄)₂, 5. A methanolic solution (20 mL) of copper(II) tetrafluoroborate (0.24 g, 1 mmol) was added to bbtma (0.37 g, 1 mmol) in methanol slowly. The solution was kept for slow evaporation. The green complex formed was filtered off and dried. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_5\text{S}_2\text{CuB}_2\text{F}_8\text{O}_1$: C, 35.73; H, 3.63; N, 10.97. Found: C, 36.12; H, 3.94; N, 11.15.

[Cu(bbtma)Cl]Cl, 6. To a methanolic solution (20 mL) of bbtma (0.37 g, 1 mmol), copper(II) chloride dihydrate (0.17 g, 1 mmol) in methanol was added slowly with constant stirring. The yellow complex formed was filtered off and dried. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_5\text{S}_2\text{CuCl}_2$: C, 44.06; H, 4.09; N, 13.52. Found: C, 44.43; H, 4.45; N, 13.23.

[Cu(bzmpy)(CH₃CN)](ClO₄)₂, 7. The complex was prepared as reported earlier.³⁸

Physical Measurements. Elemental analysis were performed at CDRI, Lucknow. The reflectance and solution spectra were recorded on a Hitachi U-3410 double-beam UV-vis-NIR spectrophotometer. EPR spectra were recorded on a JEOL JES-TE 100 X-band spectrometer, the field being calibrated with diphenylpicrylhydrazyl (dpph). The values of g_{\parallel} and A_{\parallel} were measured at 77 K. Nuclear magnetic resonance spectra were obtained at room temperature on a Bruker (400 MHz) spectrometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed using a three-electrode cell configuration. A platinum sphere, a platinum plate, and Ag(s)/AgNO_3 were used as working, auxiliary, and reference electrodes, respectively. The platinum sphere electrode was sonicated for 2 min in dilute nitric acid, dilute

- (29) (a) Bowmaker, G. A.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2825. (b) Haitko, D. A. *J. Coord. Chem.* **1984**, 13, 119. (c) Karlin, K. D.; Gulteh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, 23, 519. (d) Ainscough, E. W.; Brodie, A. M.; Brown, K. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1042. (e) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, 19, 2993. (f) Weininger, M. S.; Hunt, G. W.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1140.
- (30) Dagdigian, J. V.; McKee, V.; Reed, C. A. *Inorg. Chem.* **1982**, 21, 2781.
- (31) Karlin, K. D.; Dahlstrom, P. L.; Stanford, M. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1979**, 465. (b) Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kinsey, R. A.; Kutchan, T. M.; Mottel, E. A. *Inorg. Chem.* **1979**, 18, 299.
- (32) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 906.
- (33) Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I. M. W.-Y.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, 107, 2399. (b) Diaddario, L. L.; Dockal, E. R., Jr.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1985**, 24, 356. (c) Glass, R. S.; Steffen, L. K.; Swanson, D. D.; Wilson, G. S.; Gelder, R. D.; Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1993**, 207, 241. (d) Salhi, C. A.; Yu, Q.; Heeg, M. J.; Villeneuve, N. M.; Juntunen, K. L.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, 34, 6053. (e) Krylova, K.; Kulatilleke, C. P.; Heeg, M. J.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, 38, 4322.
- (34) Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, 21, 1881. (b) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, 108, 1202. (c) Goodwin, J. A.; Stanbury, D. M.; Wilson, L. J.; Eigenbrot, C. W.; Scheidt, W. B. *J. Am. Chem. Soc.* **1987**, 109, 2979. (d) Munakata, M.; Kitagawa, S.; Asahara, A.; Masuda, H. *Bull. Chem. Soc. Jpn.* **1987**, 60, 1927.
- (35) Sanaullah; Kano, K.; Glass, R. S.; Wilson, G. S. *J. Am. Chem. Soc.* **1993**, 115, 592. (b) Flanagan, S.; Dong, J.; Haller, K.; Wang, S.; Scheidt, W. R.; Scott, R. A.; Webb, T. R.; Stanbury, D. M.; Wilson, L. J. *J. Am. Chem. Soc.* **1997**, 119, 8857. (c) Kuchiyama, Y.; Kobayashi, N.; Takagi, H. D. *Inorg. Chim. Acta* **1998**, 277, 31.
- (36) (a) Wahlgren, C. G.; Addison, A. W. *J. Heterocycl. Chem.* **1989**, 26, 541. (b) Baker, W.; Buggle, K. M.; McOmie, J. F.; Watkins, D. A. *M. J. Chem. Soc.* **1958**, 3594.
- (37) Addison, A. W.; Burke, P. J. *J. Heterocycl. Chem.* **1981**, 18, 803.

- (38) 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.

Table 1. Crystal Data and Structure Refinement Details for **1–3**

	1	2	3
empirical formula	Cu ₁ C ₂₁ H ₁₇ N ₇ S ₂ O ₆	Cu ₁ C ₂₁ H ₁₇ N ₆ S ₂ O ₃	Cu ₂ C ₄₂ H ₃₄ N ₁₀ S ₄ Cl ₂
fw	591.08	529.07	1005.01
cryst syst	monoclinic	orthorhombic	triclinic
space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1
<i>a</i> , Å	9.2339(5)	8.7099(2)	8.4268(14)
<i>b</i> , Å	14.2902(8)	10.9708(2)	13.525(2)
<i>c</i> , Å	9.3986(5)	22.1656(3)	18.850(4)
α, deg	90.000	90.000	99.030(2)
β, deg	108.808(2)	90.000	99.650(2)
γ, deg	90.000	90.000	89.872(14)
<i>V</i> , Å ³	1173.96(11)	2118.02(7)	2114.6(6)
<i>Z</i>	4	4	2
λ, Å	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Cu Kα, 1.5418
<i>D</i> _{calcd} , g cm ^{−3}	1.672	1.659	1.578
GOF on <i>F</i> ²	0.992	1.081	1.036
total no. reflns measd	4967 (<i>R</i> _{int} = 0.0469)	8819 (<i>R</i> _{int} = 0.0341)	8026 (<i>R</i> _{int} = 0.0803)
unique reflns with <i>I</i> > 2.00 σ(<i>I</i>)	3156	3030	7478
<i>R</i> ^a	0.040	0.029	0.058
<i>R</i> _w ^b	0.099	0.083	0.155

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = \{ \sum w[(F_o^2 - F_c^2)^2 / \sum w[(F_o^2)^2]]^{1/2}.$$

hydrazine hydrate, and doubly distilled water to remove the impurities. The temperature of the electrochemical cell was maintained at 25 ± 0.2 °C by a cryocirculator (HAAKE D8 G). The solutions were deoxygenated by bubbling research grade nitrogen, and an atmosphere of nitrogen was maintained over the solution during measurements. The *E*_{1/2} values were observed under identical conditions for various scan rates. The instruments utilized included an EG&G PAR 273 potentiostat/galvanostat and an IBM PS2 computer along with EG&G M270 software to carry out the experiments and to acquire the data.

Data Collection and Structure Refinement. High-quality crystals suitable for X-ray diffraction were chosen after careful examination under an optical microscope. For compound **3** preliminary cell dimensions and the crystal system were determined, the data were collected at room temperature on a four-circle Enraf-Nonious CAD4 X-ray diffractometer, and graphite monochromatized Cu Kα was used. The intensities of the reflections were corrected for Lorentz and polarization effects. For the crystals of **1** and **2** X-ray diffraction intensities were measured by ω scans using a Siemens three-circle diffractometer attached to a CCD area detector and a graphite monochromator for the Mo Kα radiation (50 kV, 40 mA). The unit cell parameters and the orientation matrix of the crystal were initially determined using ~ 60 reflections from 25 frames collected over a small ω scan of 7.5° sliced at 0.3° interval. A hemisphere of reciprocal space was then collected using SMART software³⁹ with the 2θ setting at 28°. Data reduction was performed using the SAINT program,³⁹ and the orientation matrix along with the detector and cell parameters were refined for every 40 frames on all the measured reflections. An empirical absorption correction based on symmetry-equivalent reflections was applied using the SADABS program⁴⁰ taking the merged reflection file obtained from SAINT as the input. The correct Laue group of the crystal was chosen (2/*m* for compound **2** and *mmm* for compound **3**) for the absorption correction. The *R*_{int} values before and after the absorption corrections were 0.0517 and 0.0537 for **2** and 0.0820 and 0.0437 for **3**. All the structures were solved by direct methods using the SHELXS-97 program⁴¹ and refined by a full-matrix least-squares method on *F*² using SHELXL-93 program.⁴² The position of the hydrogen atoms were located from Fourier difference maps and fixed. The non-hydrogens were refined anisotropically. Crystal data and additional details of the data collection and refinement of the structure are presented in Table 1.

Results and Discussion

Synthesis. Our initial aim had been to prepare NS₂ tridentate chelating ligands to incorporate NS₂ coordination elements on the copper atom. The present benzimidazole ligands are interesting in their own right to force the resultant metal complexes into specific desired geometries and also offer an opportunity to study the contribution of coordinated benzimidazole moieties to the Cu^{II}/Cu^I redox potential. The judicious choice of ligands, which force the metal ions into unusual geometries or which stabilize both oxidation states, are of interest in designing models in bioinorganic chemistry.^{30,31,43}

The ¹H NMR spectra of bbtma in DMSO-*d*₆ solutions indicated a five-proton environment, and the assignments were made as in Experimental Section. The eight protons of the two benzimidazole rings show a multiplet, indicating that the two halves of the ligand are equivalent in solution. All the complexes were readily isolated in good yields by the reaction of the ligands with 1 equiv of the corresponding copper salts. Treatment of bbtmp with copper(II) chloride in methanol led to no immediate change in color of the solution. From these solutions X-ray quality yellow crystals of [Cu(bbtmp)Cl] were isolated, signifying reduction of copper(II) to copper(I). These complexes are air-stable indefinitely. Their formulations as copper(I) species was made by an analytical method and ¹H NMR and electronic spectra and confirmed for [Cu(bbtmp)Cl] by X-ray crystallography. On the other hand, the mixing of copper(II) nitrate/tetrafluoroborate solution with bbtmp and bbtma solutions in methanol did not lead to any bleaching of the green color; however, from these solutions copper(II) and copper(I) complexes of bbtmp were isolated, as evidenced by elemental analysis and spectra and by X-ray crystallography of [Cu(bbtmp)(NO₃)]NO₃ and [Cu(bbtmp)]NO₃. Spontaneous reduction of copper(II), which occurs upon complexation with bbtmp in the presence of soft Cl[−] ions, suggests that the sterically demanding benzimidazole-containing ligands have the ability to destabilize¹³ the Cu(II) state by inducing distortions on the coordination environment; however, the presence of harder NO₃[−] ion tends to stabilize Cu(II). Addison and co-workers²² have also observed such autoreduction of copper(II) with N₂S₂ ligand systems, which is proposed to occur through the copper-catalyzed oxidation of solvent or via ligand involvement.

(39) Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

(40) Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, Germany, 1993.

(41) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Determination*; Universität Göttingen: Göttingen, Germany, 1997.

(42) Sheldrick, G. M. *SHELXL-93, Program for Crystal Structure Determination*; Universität Göttingen: Göttingen, Germany, 1993.

(43) Sorrell, T. N. *Tetrahedron* **1989**, 45, 3.

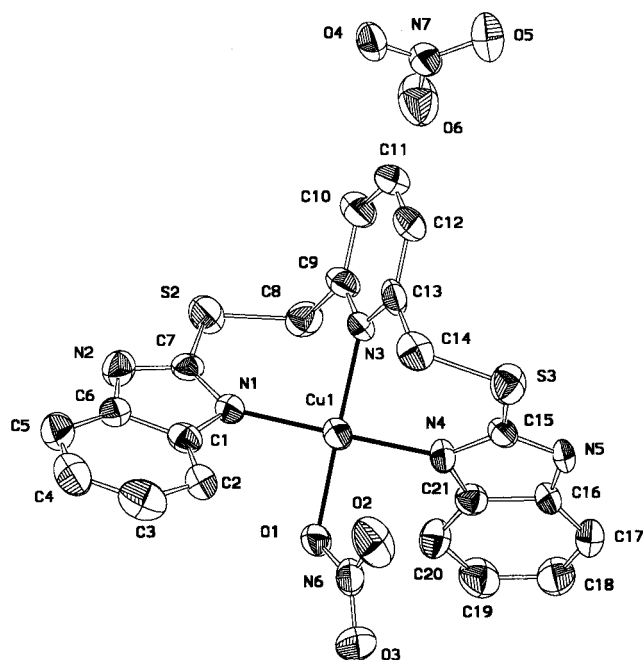


Figure 1. ZORTEP drawing of $[\text{Cu}(\text{bbtm})(\text{NO}_3)]\text{NO}_3$ showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

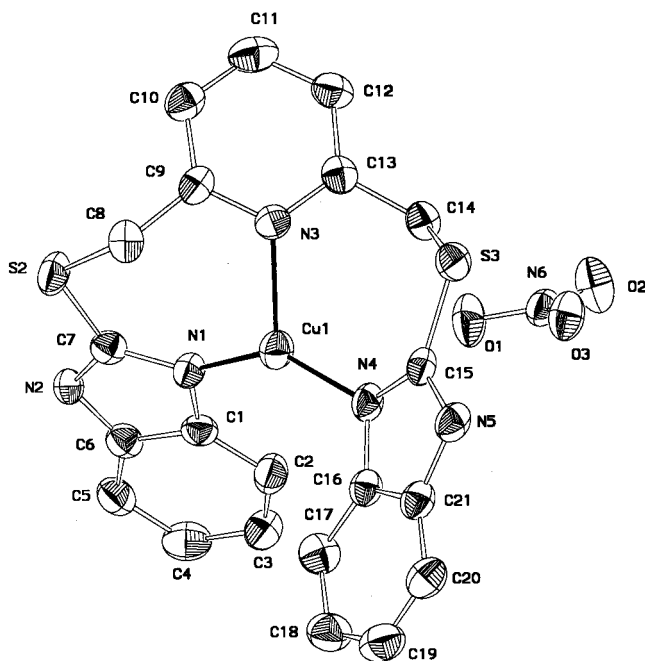


Figure 2. ZORTEP drawing of $[\text{Cu}(\text{bbtm})]\text{NO}_3$ showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

Structures of the Complexes. Description of the Structures of $[\text{Cu}(\text{bbtm})(\text{NO}_3)]\text{NO}_3$, **1, $[\text{Cu}(\text{bbtm})]\text{NO}_3$, **2**, and $[\text{Cu}(\text{bbtm})\text{Cl}]$, **3**.** The ZORTEP⁴⁴ views of complexes **1**–**3** are depicted in Figures 1–3, along with the atom numbering scheme. The relevant bond length and bond angle information is given in Table 2. The structure of **1** consists of a discrete complex cation and a nitrate anion. In the cation the tridentate bbtm ligand is coordinated to copper(II) through the pyridine

and benzimidazole nitrogen atoms and the nitrate(O1) ion is coordinated monodentately. The coordination geometry of the cation may be best described as square planar with the three nitrogen atoms and the oxygen atom occupying the corners. The present $\text{Cu}-\text{N}_{\text{bzim}}$ and $\text{Cu}-\text{N}_{\text{py}}$ distances fall within the ranges 1.94–2.06^{16,38} and 2.00–2.11 Å,^{27,38} respectively, observed for basal $\text{Cu}(\text{II})-\text{N}_{\text{bzim/py}}$ bonds. Though shorter bond distances are expected for the present complex with lower coordination number, longer distances are observed obviously because of strong coordination by NO_3^- , which tends to decrease the charge on copper(II). Similarly, the relatively long $\text{Cu}-\text{N}_{\text{im}}$ bonds (~ 2.02 Å) observed for four-coordinate $\text{Cu}(\text{II})$ proteins like plastocyanin^{5,6} may be ascribed to the highly covalent and hence short $\text{Cu}-\text{S}_{\text{cys}}$ bond [2.10(2) Å for azurin]⁴⁵ formed by the cysteinate anion. Further, the bond angles $\text{N1}-\text{Cu}-\text{N3}$ (89.60°) and $\text{N3}-\text{Cu}-\text{N4}$ (89.0°) deviate only slightly from the ideal 90° for regular square planar geometry and the dihedral angle (θ) between $\text{Cu}-\text{N1}-\text{O1}$ and $\text{Cu}-\text{N3}-\text{N4}$ planes is found to be only 2.46° , suggesting that copper(II) is located in a geometry much closer to square planar. In fact, the copper(II) ion lies only 0.02 Å above the N_3O least-squares plane.

The structure of **2** consists of discrete monomeric units composed of a cationic copper complex and a nitrate anion. The coordination geometry around copper(I) in the cation is distorted trigonal planar with the pyridine and benzimidazole nitrogen atoms of bbtm ligand occupying the corners. The observed $\text{Cu}(\text{I})-\text{N}_{\text{bzim/py}}$ bond distances fall within the ranges expected [$\text{Cu}(\text{I})-\text{N}_{\text{bzim}}$, 1.90–1.93 Å;³⁰ $\text{Cu}(\text{I})-\text{N}_{\text{py}}$, 2.03–2.42 Å³¹]. The terminal benzimidazole rather than the middle pyridine nitrogen is coordinated strongly [$\text{Cu}-\text{N}_{\text{py}}$, 2.082(3); $\text{Cu}-\text{N}_{\text{bzim}}$, 1.921(3), 1.912(3) Å]; this trend is interestingly different from that observed for the corresponding copper(II) complex **1**. It appears that the pyridine nitrogen atom is unable to closely approach Cu(I) located in the trigonal plane because of ligand constraint. The copper is located 0.031 Å below the N_3 ($\text{N1}-\text{N3}-\text{N4}$) plane, indicating that it is almost coplanar with the donor atoms. Thus, the sum of the bond angles of $\text{N1}-\text{Cu}-\text{N3}$ (106.96°), $\text{N4}-\text{Cu}-\text{N3}$ (109.93°), and $\text{N4}-\text{Cu}-\text{N1}$ (143.03°) around copper(I) is equal to 360° within experimental error.

The asymmetric unit cell of compound **3** consists of two crystallographically independent molecules of the complex. Both molecules have essentially identical coordination geometries, but the corresponding bond lengths and bond angles are slightly different. The geometry around copper(I) in each molecule is described as distorted tetrahedral. The benzimidazole [$\text{Cu}-\text{N1}$, 2.008(4); $\text{Cu}-\text{N4}$, 1.996(4) Å] rather than pyridine [$\text{Cu}-\text{N3}$, 2.123(4) Å] nitrogen is strongly coordinated to copper; this is similar to that observed for **2**, confirming the role of ligand constraints in preventing efficient coordination of pyridine nitrogen to Cu(I) in this geometry. The $\text{N1}-\text{Cu}-\text{Cl}$ bond angle [$109.5(12)^\circ$] is very close to that expected for a regular tetrahedral geometry; however, the geometry is distorted from regular tetrahedral [$\text{N4}-\text{Cu}-\text{N3}$, $115.4(2)$; $\text{N1}-\text{Cu}-\text{N3}$, $93.6(2)^\circ$] due to the presence of ligand constraints. The dihedral angle (θ) between $\text{Cu}-\text{N1}-\text{N4}$ and $\text{Cu}-\text{N3}-\text{Cl}$ planes, which is a measure of closeness of fit to a tetrahedron, is 78.66° . This value of θ falls within the range 65 – 87° observed^{17,31} for $\text{Cu}(\text{I})$ complexes of tetradentate chelating ligands, confirming the presence of severely distorted tetrahedral geometry. The $\text{Cu}(\text{I})$ ion lies 0.58 Å above the plane formed by three N atoms of the ligand, indicating the compression of an ideal tetrahedron to pseudotetrahedral geometry along the C_3 axis connecting Cu and Cl atoms.

(44) Zsolnai, L. ZORTEP, an interactive ORTEP program; University of Heidelberg: Heidelberg, Germany, 1996.

(45) Baker, E. N. *J. Mol. Biol.* **1988**, 203, 1071.

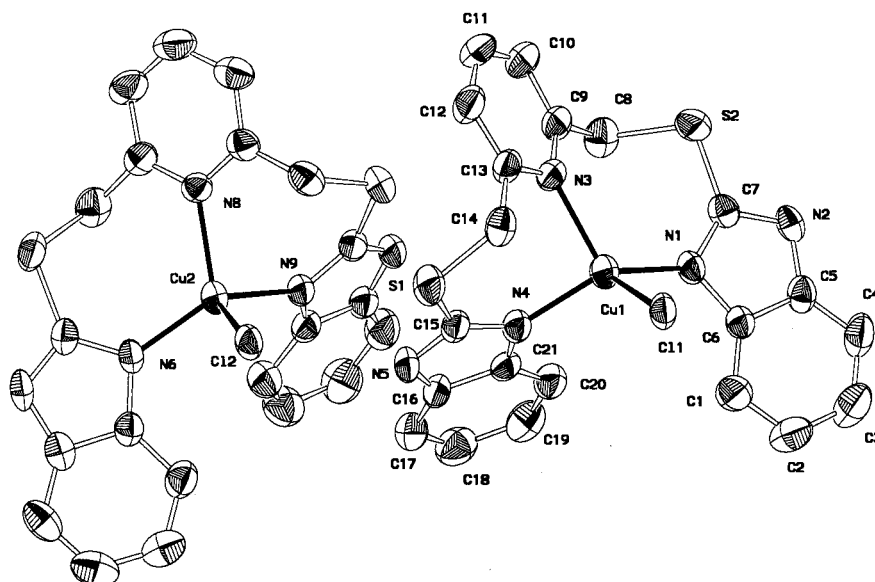


Figure 3. ORTEP drawing of $[\text{Cu}(\text{bbtmp})\text{Cl}]$ showing the atom numbering scheme and the thermal motion ellipsoids (50% probability level) for the non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **1–3**

compd	bond lengths		bond angles		torsion angles	
1	Cu(1)–N(1)	2.011(5)	N(1)–Cu(1)–N(3)	89.6(2)	N(1)–Cu(1)–N(3)–C(9)	–68.55(0.62)
	Cu(1)–N(3)	1.997(5)	N(1)–Cu(1)–N(4)	177.1(3)	Cu(1)–N(3)–C(9)–C(8)	0.38(0.91)
	Cu(1)–N(4)	1.999(5)	N(3)–Cu(1)–N(4)	89.0(2)	S(2)–C(8)–C(9)–N(3)	93.32(0.74)
	Cu(1)–O(1)	1.966(4)	O(1)–Cu(1)–N(1)	91.6(2)	C(7)–S(2)–C(8)–C(9)	–65.45(0.60)
			O(1)–Cu(1)–N(3)	178.8(2)	C(8)–S(2)–C(7)–N(1)	–7.29(0.75)
			O(1)–Cu(1)–N(4)	89.8(2)	Cu(1)–N(1)–C(7)–S(2)	–2.10(1.00)
					N(3)–Cu(1)–N(1)–C(7)	56.50(0.63)
2	Cu(1)–N(1)	1.921(3)	N(1)–Cu(1)–N(3)	106.96(12)	N(1)–Cu(1)–N(3)–C(9)	32.44(0.28)
	Cu(1)–N(3)	2.082(3)	N(4)–Cu(1)–N(3)	109.93(12)	Cu(1)–N(3)–C(9)–C(8)	34.18(0.37)
	Cu(1)–N(4)	1.912(3)	N(4)–Cu(1)–N(1)	143.03(13)	N(3)–C(9)–C(8)–S(2)	–110.62(0.30)
					C(7)–S(2)–C(8)–C(9)	73.17(0.29)
					C(8)–S(2)–C(7)–N(1)	–5.94(0.37)
					Cu(1)–N(1)–C(7)–S(2)	9.48(0.53)
					N(3)–Cu(1)–N(1)–C(7)	–44.62(0.35)
3	Cu(1)–N(1)	2.008(4)	N(4)–Cu(1)–N(1)	131.4(2)	N(3)–Cu(1)–N(1)–C(7)	10.24(0.46)
	Cu(1)–N(3)	2.123(4)	N(4)–Cu(1)–N(3)	93.7(2)	Cu(1)–N(1)–C(7)–S(2)	–16.68(0.66)
	Cu(1)–N(4)	1.996(4)	N(1)–Cu(1)–N(3)	115.4(2)	C(8)–S(2)–C(7)–N(1)	–29.74(0.50)
	Cu(1)–Cl(1)	2.547(2)	N(4)–Cu(1)–Cl(1)	109.53(12)	C(7)–S(2)–C(8)–C(9)	105.11(0.39)
	Cu(2)–N(6)	1.986(4)	N(1)–Cu(1)–Cl(1)	95.55(12)	S(2)–C(8)–C(9)–N(3)	–81.70(0.53)
	Cu(2)–N(8)	2.125(4)	N(3)–Cu(1)–Cl(1)	111.39(12)	Cu(1)–N(3)–C(9)–C(8)	0.62(0.60)
	Cu(2)–N(9)	2.026(4)	N(6)–Cu(2)–N(9)	132.2(2)	N(1)–Cu(1)–N(3)–C(9)	27.11(0.42)
	Cu(2)–Cl(2)	2.562(2)	N(6)–Cu(2)–N(8)	115.4(2)		
			N(9)–Cu(2)–N(8)	94.5(2)		
			N(6)–Cu(2)–Cl(2)	95.19(12)		
			N(9)–Cu(2)–Cl(2)	109.04(12)		
			N(8)–Cu(2)–Cl(2)	110.06(11)		

As evident from the torsion angles (Table 2), the seven-membered chelate ring formed by Cu, N(3), and N(1) and the intermediate C(7), S(2), C(8), and C(9) atoms in **1** has a relatively stable flattened boat conformation, which is between the two extreme idealized chair and boat conformations. On the reduction of copper(II) to copper(I) the chelate rings in **2** adopt the unstrained chair conformation in order to reduce the constraint around copper(I). On the other hand, they have the twisted boat conformation flattened at the S2–C7–N1 end in **3**. It appears that the ease of conformational changes in the seven-membered chelate rings, which is more flexible than five- and six-membered rings, facilitates the copper to assume three different geometries within the same ligand framework. Thus, the strain-free seven-membered chelate rings facilitate benzimidazole and pyridine nitrogen lone pair orbitals to be properly oriented toward the $d_{x^2-y^2}$ orbital of Cu(II).

In all the complexes an interesting network of inter- and intramolecular hydrogen bonding appears to stabilize the lattice structures. Thus, one of the benzimidazole N–H groups of the complex molecule **1** is hydrogen-bonded to the uncoordinated nitrate ion of the same molecule while the other N–H group is hydrogen-bonded to the coordinated nitrate ion of the other molecule. One of the benzimidazole N–H groups of **2** is involved in bifurcated hydrogen bonding with two oxygen atoms of the uncoordinated nitrate ion, while the other N–H group is hydrogen-bonded to the oxygen atom of the nitrate ion of another molecule. The coordinated chloride ion in **3** is engaged in bifurcated hydrogen bonding with two benzimidazole N–H groups on two other complex molecules.

Comparison of Structures. The most unusual feature of the structures **1–3** is that the thioether sulfurs are not coordinated to copper. This is in contrast to the coordination of thioethers

in the Cu(II) complex²⁷ of the analogous NS₂ ligand betmp (Chart 1). Obviously, the steric bulk and the negative inductive effect⁴⁶ of the adjoining benzimidazole groups in **1–3** would discourage the coordination of thioether sulfur, which frequently exhibits reluctance¹⁸ to bind to Cu(II). Ligands containing two sterically demanding benzimidazole moieties have been found^{20,22,23} to discourage strictly square planar coordination around copper(II). But the incorporation of two strain-free seven-membered chelate rings involving the coordinated benzimidazole nitrogen atoms as in **1** and in other CuN₄ complexes^{47–49} favors the idealized square planar geometry around copper(II); however, for similar CuN₄ complexes containing chelate rings with more than seven members, a quite distorted square planar geometry is observed.^{48,49} Also, an increase in ligand flexibility by increasing the bridging chain length is believed to progressively destabilize the copper(II) state, but it facilitates the copper(I) state to adopt the pseudotetrahedral geometry suitable for it.^{21,50} All these observations imply that in the presence of large chelate rings the nature and type of donor atoms and ligand geometry determine the nature of distorted geometry around copper(II). This is relevant to the distorted geometries found in type I copper proteins, which are imposed by the type and orientation of the donor atoms in the presence of large chelate rings provided by the proteins. Thus, Solomon³ and Ryde⁴ attribute the unusual geometries of type I copper sites to strong Cu–S(cys) bond and not to the protein matrix itself.

The novel trigonal planar (TP) geometry of Cu(I) in **2**, though preferred by three-coordinated (sp² hybrids) d¹⁰ complexes, is rare, and only a few such examples are now known.²⁹ The importance of the bulky benzimidazole moieties in imposing this geometry is illustrated by the observation of a similar but T-shaped three-coordinate geometry³⁰ for [Cu(bbes)]⁺ [bbes = 1,5-bis(benzimidazol-2-yl)-3-thiapentane]. Further, the bbtmp ligand is ideally suited for assuming the preferred extreme geometries of both Cu(I) and Cu(II), viz., trigonal planar/tetrahedral and square planar, respectively, and hence, **1** and **2** constitute a *redox pair* suitable for structural comparison. The Cu–N_{bzim} distance decreases in passing from Cu(II) in **1** to Cu(I) in **2** because of the uncompensated positive charge on the Cu(I) cation as well as the decrease in coordination number from 4 (square planar) to 3 (trigonal planar), with the Cu(I) geometry involving less repulsion among donor atoms. However, the Cu–N_{py} distance increases, as expected of the decrease in formal positive charge. Further, the poor π -back-bonding from Cu(I) to pyridine donor, because of ligand constraint, does not offset the expected increase in σ -bond length on going from a d⁹ to a d¹⁰ configuration of copper. Interestingly, a similar trend has been observed for plastocyanin⁵¹ on reducing Cu(II) to Cu(I); the Cu–N_{im} bond distance decreases from 2.02 to 2.00 Å, which should be due to the decrease in coordination number from 4 (pH 7) to 3 (pH 4), as observed in the present model compounds.

Interestingly, both Cu–N_{py} and Cu–N_{bzim} distances in **3** are higher than those in **2** because of an increase in coordination number rather than a decrease in formal positive charge on **2** by chloride ion coordination to give **3**. Further, a comparison of the structures of **1** and **3** reveals that in passing from Cu(II) to Cu(I) the Cu–N_{bzim} distances remain constant but the Cu–N_{py} bond undergoes elongation as expected of the decrease in formal positive charge on copper, keeping constant the ligand constraint as well as the coordination number of both the oxidation states at 4. Thus, the changes in geometries of the present low molecular weight complexes on electron transfer are considerable and do not parallel those of type I proteins where changes in bond angles upon reduction of Cu(II) to Cu(I) are of a minimal nature.

Spectral Properties. The copper(II) complexes **1**, **4**, **5**, and **6** exhibit a broad band in the visible region both in the solid state and in DMF/DMSO solutions (Table 3). The relatively low $\bar{\nu}_{\max}$ values (13100–14700 cm^{−1}) of this feature and the very low intensities (ϵ , 25–90 M^{−1} cm^{−1}) in solution are consistent with the almost square planar geometry found in the solid state, the tridentate nature of the ligands, and anion⁵² or oxygen⁵³ (solvent) coordination (CuN₃O chromophore). The cryogenic solution EPR spectra of all the complexes are axial [$g_{\parallel} > g_{\perp} > 2.0$, $G^{54} = (g_{\parallel} - 2)/(g_{\perp} - 2) = 3.2\text{--}4.3$], suggesting the presence of a d_{x²−y²} ground state for Cu(II) located in square planar geometries. The spectrum of **1** is consistent with the presence of two species;⁵⁵ the minor species (B) is typical of the solvated cupric species [Cu(bbtmp)(DMSO)]²⁺ formed from **1**, and the major species (A) corresponds to undissociated nitrate complex with both the g_{\parallel} and A_{\parallel} values (Table 3) lying in the range for CuN₃O chromophores.^{54,56} Thus, the intensity of the signal for the major species increased on adding NaNO₃, and the addition of excess pyridine to **1** in DMSO solution generates only one species consistent with the formation of [Cu(bbtmp)(py)]²⁺ (g_{\parallel} , 2.253; A_{\parallel} , 178; $g_{\parallel}/A_{\parallel}$, 127 cm; Figure 4). Further, the g_{\parallel} and A_{\parallel} values of most of the present complexes lie in the region for the CuN₃O chromophore in the g_{\parallel} vs A_{\parallel} plot.⁵⁶ In contrast to **1**, complexes **4–6** possess a higher g_{\parallel} and appreciably lower A_{\parallel} values ($g_{\parallel}/A_{\parallel}$ quotient, 142–160 cm; for Cu(II) complexes with perfectly square planar geometry, the $g_{\parallel}/A_{\parallel}$ quotient^{21,56} ranges from 105 to 135 cm). This reflects the steric demand of the N–Me group, which would change⁵⁷ the orientation of the nitrogen lone pair orbital toward the copper orbital, leading to a distorted CuN₃O square planar geometry.⁵⁸

To understand whether the solid-state structures of the copper(I) complexes are retained in solution or not, the ¹H NMR spectra of the ligand bbtmp as well as its complexes **2** and **3** were recorded in DMSO-*d*₆ solution (Table 4). The spectrum

- (46) Aronne, L.; Dunn, B. C.; Vyvyan, J. R.; Souvignier, C. W.; Mayer, M. J.; Howard, T. A.; Salhi, C. A.; Goldie, S. N.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 357. (b) Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1997**, *36*, 3253.
- (47) van Albada, G. A.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; Reedijk, J. *Inorg. Chim. Acta* **1999**, *290*, 105.
- (48) van Albada, G. A.; Smeets, W. J. J.; Spek, A. L.; Reedijk, J. *Inorg. Chim. Acta* **1999**, *288*, 220.
- (49) Matthews, C. J.; Clegg, W.; Elsegood, M. R. J.; Leese, T. A.; Thorp, D.; Thornton, P.; Lockhart, J. C. *J. Chem. Soc., Dalton Trans.* **1996**, 1531.
- (50) Nikles, D. E.; Powers, M. J.; Urbach, F. L. *Inorg. Chem.* **1983**, *22*, 3210.
- (51) Freeman, H. C. *Coord. Chem.—Invited Lect. Int. Conf.*, 21st **1980**, 29.
- (52) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. G.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 533.
- (53) (a) West, D. X.; Palaniandavar, M. *Inorg. Chim. Acta* **1983**, *71*, 61. (b) West, D. X.; Palaniandavar, M. *Inorg. Chim. Acta* **1983**, *76*, L149. (c) West, D. X.; Palaniandavar, M. *Inorg. Chim. Acta* **1983**, *77*, L97.
- (54) (a) Vaidyanathan, M.; Viswanathan, R.; Palaniandavar, M.; Balasubramanian, T.; Prabhakaran, P.; Muthiah, T. P. *Inorg. Chem.* **1998**, *37*, 6418. (b) Addison, A. W. In *Copper Coordination Chemistry: Bio-chemical and Inorganic Perspectives*; Karlin, K. D.; Zubieta, J., Eds.; Adenine Press: Guilderland, New York, 1983; p 109.
- (55) The species cannot be [Cu(DMSO)₄]²⁺ with a CuO₄ chromophore because Cu(ClO₄)₂ in DMSO is found to have the g_{\parallel} and A_{\parallel} values of 2.39 and 137×10^{-4} cm^{−1}, respectively.
- (56) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600.
- (57) Pandiyan, T.; Palaniandavar, M.; Lakshminarayanan, M.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1995**, 455.
- (58) Nishida, Y.; Takahashi, K. *J. Chem. Soc., Dalton Trans.* **1988**, 691.

Table 3. Electronic and EPR Spectral Data of the Complexes

complex	electronic spectra ^a $\bar{\nu}_{\max} \times 10^3 \text{ cm}^{-1} (\epsilon, \text{M}^{-1} \text{cm}^{-1})$			EPR spectra ^b	
	solid	solution		solid	frozen solution
		DMF	DMSO		
[Cu(bbtmmp)(NO ₃)](NO ₃), 1	15.1 19.2	14.7 (31) 34.1 (17 705) 34.8 (17 440)	14.3 (40)	g_{\parallel} 2.233 g_{\perp} 2.067	g_{\parallel} 2.278 (A) ^c g_{\perp} 2.076 A_{\parallel} 180
1 + NaNO ₃		12.8 (45)	12.3 (64)		g_{\parallel} 2.277 (A) ^c g_{\perp} 2.084 A_{\parallel} 171
1 + pyridine		14.9 (68)	13.4 (57)		g_{\parallel} 2.253 g_{\perp} 2.060 A_{\parallel} 178
[Cu(bbtmmp)](NO ₃), 2		34.1 (18 805) 34.8 (17 650)			
[Cu(bbtmmp)Cl], 3		34.0 (21 590) 34.7 (20 980)			
[Cu(bbtma)(NO ₃)](NO ₃), 4	14.5	13.4 (38) 35.9 (22 188) 39.1 (14 850)	12.8 (31)	g_{\parallel} 2.289 g_{\perp} 2.117 A_{\parallel} 156	g_{\parallel} 2.316 g_{\perp} 2.073 A_{\parallel} 163
4 + NaNO ₃		14.9 (67)	13.4 (46)		
4 + pyridine		13.0 (43)	12.3 (42)		
[Cu(bbtma)(H ₂ O)](BF ₄) ₂ , 5	15.2	13.9 (25) 35.9 (22 310) 39.1 (13 870)		g_{\parallel} 2.266 g_{\perp} 2.121 A_{\parallel} 163	g_{\parallel} 2.332 g_{\perp} 2.078 A_{\parallel} 146
[Cu(bbtma)Cl]Cl, 6	14.1	13.1 (89) 35.9 (22 078) 39.1 (14 820)		g_{av} 2.093	g_{\parallel} 2.289 g_{\perp} 2.090 A_{\parallel} 150

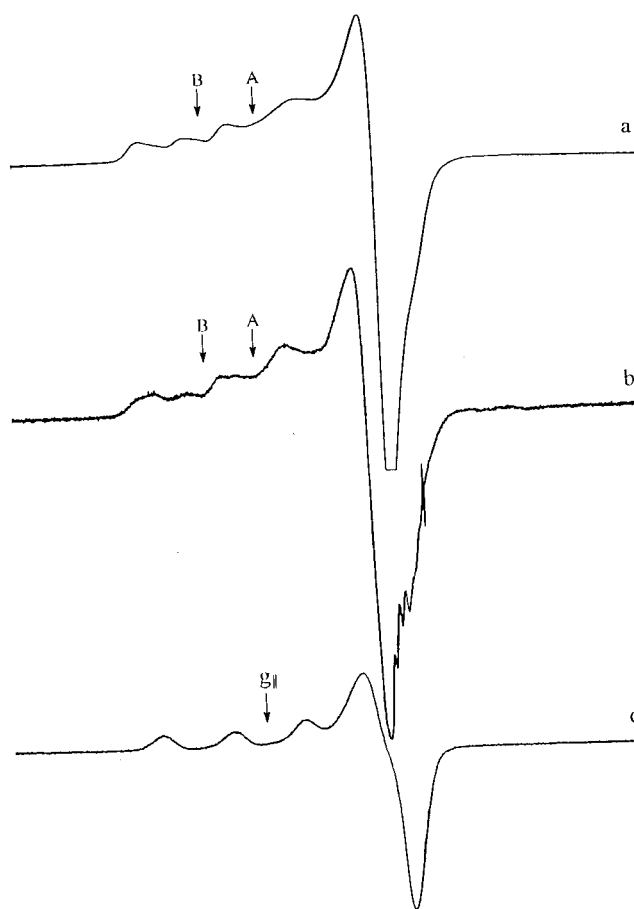
^a Concentration 2×10^{-3} for ligand field and 2×10^{-5} M for ligand-based transitions. ^b A_{\parallel} in 10^{-4} cm^{-1} . ^c Minor species B [Cu(bbtmmp)(DMSO)]²⁺ (g_{\parallel} , 2.358; A_{\parallel} , 130) is present.

Table 4. ¹H NMR Chemical Shifts^a (δ) for bbtmmp Ligand and Diamagnetic Complexes **2** and **3** ($\Delta\delta$ in Parentheses) in DMSO-*d*₆

compound	chemical shift, δ^a ($\Delta\delta$) ^b			
	Py-H	bzim-H	CH ₂ S-H	
bbtmmp	7.72(t)	7.43(d)	7.12(m)	4.68(s)
[Cu(bbtmmp)]NO ₃ , 2	8.05(t)	7.67(d)	7.59(s)	4.99(s)
	(0.33)	(0.25)	(0.47)	(0.31)
[Cu(bbtmmp)Cl], 3	7.94(s)	7.64(s)	7.17(s)	4.90(s)
	(0.22)	(0.21)	(0.05)	(0.22)

^a δ in ppm referenced to TMS internal standard. ^b $\Delta\delta$ ($\delta_c - \delta_L$) is the chemical shift change upon complexation.

of bbtmmp shows an AB₂ spin pattern with a triplet and a doublet for pyridine protons. The observation of a singlet for methylene and a multiplet for the benzimidazole protons indicates the equivalence of the two halves of the ligand, implying a plane of symmetry bisecting the pyridine moiety perpendicular to the plane of the ligand or a rapid equilibration of two nonequivalent sites relative to the NMR time scale. The complexes **2** and **3** show spectral patterns similar to the patterns of the ligand; however, downfield shifts^{59,60} were observed for all the proton signals, suggesting the stability of the complex species and meridional tridentate coordination of bbtmmp in solution as in the solid state. The H₆ pyridine signal is shifted ($\Delta\delta$, 0.330) downfield more than the H₅ pyridine signal ($\Delta\delta$, 0.245) because of electromeric effects. The multiplet of the benzimidazole moiety and the singlet signal of the methylene protons also undergo downfield shifts for both **2** and **3**. The observation of only two singlet signals instead of two triplets and two doublets for the phenylene group in the benzimidazole region, with line shapes typical of exchange at a moderately fast rate on the NMR time scale is consistent with the suggestion that the benzimid-

**Figure 4.** EPR spectra of **1** before (a) and after the addition of NaNO₃ (b) and slight excess of pyridine (c) in DMSO/CH₂Cl₂ (8:1 v/v) glass at 77 K.

(59) Piguet, C.; Bernardinelli, G.; Williams, A. F. *Inorg. Chem.* **1989**, 28, 2920.

(60) Abramovitch, R. A.; Davis, J. B. *J. Chem. Soc. B* **1966**, 1137.

Table 5. Electrochemical Data^a for the Copper Complexes at 25 ± 2 °C

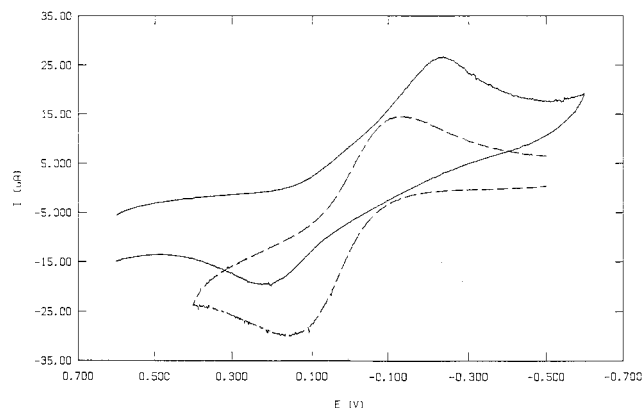
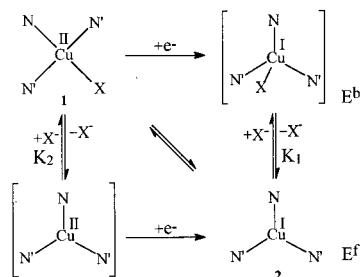
compound	E_{pc} , V	E_{pa} , V	ΔE_p , mV	ΔE_p° , ^b mV	$E_{1/2}$, V		i_{pa}/i_{pc}	$10^6 D$, cm ² s ⁻¹
					CV	DPV ^c		
[Cu(bbtm)(NO ₃)]NO ₃ , 1	-0.236	0.216				-0.158		3.9
[Cu(bbtm)](NO ₃), 2	-0.250	0.248				0.056		1.2
[Cu(bbtm)Cl], 3	-0.140	0.152	292	210	0.006	0.028	1.0 ^d	2.3
[Cu(bbtma)(NO ₃)]NO ₃ , 4	-0.296	-0.018	278	225	-0.157	-0.149	1.6 ^e	2.2
[Cu(bbtma)(H ₂ O)](BF ₄) ₂ , 5	-0.298	0.044	342	275	-0.127	-0.141	1.4 ^e	1.2
[Cu(bbtma)Cl]Cl, 6	-0.154	0.092	246	208	-0.031	-0.035	1.1	3.1
[Cu(bzmpy)(CH ₃ CN)](ClO ₄) ₂ , 7	-0.578					-0.315		2.7

^a Measured vs nonaqueous Ag/Ag⁺ reference electrode. Add 544 mV [300 mV, Ag/Ag⁺ to SCE + 244 mV, SCE to SHE] to convert to standard hydrogen electrode (SHE). Fc/Fc⁺ couple, $E_{1/2}$: 0.039 V (CV); 0.042 (DPV). ΔE_p° , 94 mV. Scan rate, 50 mV s⁻¹. Supporting electrolyte, tetra-*N*-butylammonium perchlorate (0.1 mol.dm⁻³). Complex concentration, 1 mmol dm⁻³. ^b ΔE_p° extrapolated to zero scan rate. ^c Differential pulse voltammetry. Scan rate, 1 mV s⁻¹; pulse height, 50 mV. ^d Value of i_{pc}/i_{pa} . ^e Decreases toward unity with an increase in scan rate.

azole sidearms undergo rapid decomplexation from copper(I). The pyridine nucleus, which remains complexed, is strongly affected by the positive charge localized on copper(I), and this illustrates the higher downfield shift for the pyridine protons. The two benzimidazole singlets observed for **2** merge into a broad singlet for **3**, suggesting that the Cu–Cl coordination would facilitate rapid exchange of coordinated benzimidazole sidearms. Further, the downfield shift of all the proton signals in **3**, which are lower than those in **2**, is obviously due to a decrease in the formal charge on Cu(I) by chloride coordination. This is in line with the trends in bond lengths observed in the X-ray structures of **2** and **3**. Thus, the ¹H NMR spectral study reveals that no structural change occurs for **2** and **3** on dissolution and that the subtle effect of change in oxidation state on coordination number and bond length holds good in solution also.

Electrochemical Behavior of Complexes. Cyclic and differential pulse voltammograms of all the complexes (Table 5) have been obtained in DMF solution. For the chloride complexes **3** and **6** complete regeneration of the original complex, following oxidation and reduction, respectively, is observed (the ratio of the peak currents is ~1.0; Table 5), suggesting chemically reversible Cu^{II}/Cu^I one-electron transfer. However, the value of the limiting peak-to-peak separation (ΔE_p° , ~210 mV, Table 5), which is much higher than that for the Fc/Fc⁺ couple (94 mV) under identical conditions, suggests that the heterogeneous electron-transfer process in these complexes is hardly reversible^{61,62} (ΔE_p , ~60 mV for reversible one-electron redox process) and is accompanied by considerable stereochemical reorganization.³² In contrast to **3** and **6** the i_{pa}/i_{pc} values for **4** and **5** are far from unity but approaches unity with an increase in scan rate, implying that the copper(II) form of the complexes is weakly adsorbed⁶¹ on the platinum electrode. Further, their higher ΔE_p° values (225, 275 mV) suggest that the complexes undergo larger structural reorganization on electron transfer.

The redox behavior of **1** is interestingly different from that of **3** (Figure 5), suggesting that the nitrate anion is coordinated to Cu(II) but not to Cu(I) even in solution (cf. above ¹H NMR studies), thereby making the reduction of the square planar [Cu(bbtm)(NO₃)]⁺, **1**, more difficult to occur than the reduction of [Cu(bbtm)Cl]⁺, the latter being the species generated by the electrochemical oxidation of the [Cu(bbtm)Cl], **3**, species, which is obviously more facile than that of [Cu(bbtm)]⁺. Thus, the redox behavior of **1** corresponds to the redox of two related species: three-coordinated [Cu(bbtm)]^{+/2+} species, reduced at more positive $E_{1/2}$ values, and the four-coordinated [Cu-

**Figure 5.** Cyclic voltammograms (CV) of 0.001 M complex **1** (—) and **3** (---) in DMF at 25 °C at 0.05 V s⁻¹ scan rate.**Scheme 1**

(bbtm)(NO₃)]^{+/2+} species (Scheme 1). This accounts for the large separation of the two responses observed for **1** and **2**. Similar schemes have been demonstrated^{35,63} to exist for Cu(II/I) complex systems. The relative stabilities of nitrate-bound and free forms in solution was calculated from the redox potentials using the general formula⁶⁴

$$E^b - E^f = 0.059 \log(K_1/K_2)$$

and assuming $K \gg 1$, where E^b (-0.158 V) and E^f (0.056 V) are the redox potentials of nitrate-bound and free forms, respectively, and K_1 and K_2 are the equilibrium constants, respectively, for Cu(I) and Cu(II) species to bind to X⁻. The

(61) Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

(62) Brown, E. R.; Large, R. F. In *Techniques of Chemistry: Physical Methods of Chemistry*; Weissberger, A., Rossiter, B., Eds.; Wiley: New York, 1971; Vol. 1, Part IIA, p 475.

(63) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012. (b) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 10411. (c) Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 3957. (d) Villeneuve, N. M.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1997**, *36*, 4475.

(64) (a) Sivagnanam, U.; Palaniandavar, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1992**, *341*, 197. (b) Ohsawa, Y.; Shimazaki, M.; Aoyagui, S. *J. Electroanal. Chem.* **1980**, *114*, 235.

very low K_1/K_2 value calculated (2.36×10^{-4}) is consistent with the isolation of nitrate-coordinated Cu(II) rather than the Cu(I) form.

The pyridine-based bbtmp complexes display $E_{1/2}$ values higher than the values of bbtma complexes. The ligand bbtmp destabilizes¹³ copper(II) more than bbtma through π -interaction⁵⁰ involving the pyridine moiety; also, the bbtma ligand tends to stabilize copper(II) because of the electron-releasing NMe group. Complex **4** displays a redox potential more negative than **6**, which is expected of the coordination of the harder nitrate anion. The bbtma complexes **4–6** show redox potentials less negative than the 1:1 copper(II) complexes of bis(benzimidazol-2'-ylmethyl)methylamine.⁵⁷ This reveals that the seven-membered chelate rings of bbtmp and bbtma ligands are suitable for destabilizing Cu(II) relative to Cu(I). Further, the irreversible Cu^{II}/Cu^I redox process of **7** is observed at potentials more negative than those of both **1** and **4** because of enhanced rigidity of the bzmpy ligand.

Conclusion

We have described here the structures of 1:1 monomeric copper(II) and copper(I) complexes of a common ligand (bbtmp) containing potentially more biologically relevant benzimidazolyl, pyridyl, and thioether donors. The Cu(II) nitrate complex with CuN₃O chromophore is almost square planar, while the copper(I) nitrate complex with CuN₃ chromophore assumes a novel, essentially trigonal planar geometry that, though not unusual, is rare. The Cu(I) structure, though it does not contain a thiolate donor, approximates the active-site geometries in type I copper protein sites, particularly the trigonal planar geometry in fungal laccase⁷ and ceruloplasmin^{8,9} sites. Interestingly, the copper(I) chloride complex with CuN₃Cl chromophore possesses a distorted tetrahedral structure. The bulky benzimidazolyl moieties fail to impose any steric constraint on copper(II) but allow both copper(II) and copper(I) ions to manifest their intrinsic structural preferences within the same ligand framework, facilitated by the strain-free seven-membered chelate ring systems. However, interestingly, they prevent the thioether sulfurs from coordination to copper(II) as well as copper(I), which normally tend to raise the Cu^{II}/Cu^I redox potential by destabilizing copper(II).⁶⁵ Thus, the present low molecular weight copper(I) complex achieves the uncommon trigonal geometry in a totally different manner than do the proteins.

A comparison of the present Cu(II) and Cu(I) structures reveals the significance of a change in oxidation state and the concomitant change in coordination number. The bond distances observed for Cu(II) and Cu(I) complexes with no ligand constraints throw light on the importance of the Cu–S(cys) bond in copper proteins and also help us to illustrate the range of bond lengths observed for the active sites of copper proteins with an unconstrained protein environment. Interestingly, the three-coordinate oxidized form of the present Cu(I) complex is very unstable within the time scale of the voltammetric experiment. In this regard it is noted that a three-coordinate Cu(II) complex with a trigonal planar structure but involving a different donor atom set has been recently reported.⁶⁶ Thus, the present ligand system promises to be a suitable biomimetic ligand on which new ligand systems may be designed to enforce on Cu(II) a Cu(I)-like trigonal or tetrahedral-like coordination geometry and hence achieve a fully reversible Cu^{II}/Cu^I redox couple with a positive redox potential.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic thermal parameters, atomic coordinates of hydrogen atoms and hydrogen-bonding interactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0003372

- (65) (a) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257. (b) Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4322. (c) Augustin, M. A.; Yandell, J. K.; Addison, A. W.; Karlin, K. D. *Inorg. Chim. Acta* **1981**, *55*, L35. (d) Nikles, D. E.; Powers, M. J.; Urbach, F. L. *Inorg. Chim. Acta* **1979**, *37*, L499.
- (66) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270.