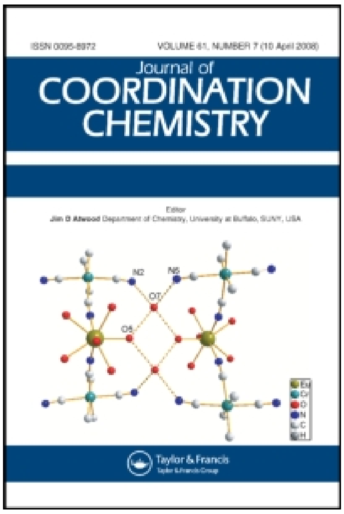

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ELECTROCHEMICAL GENERATION OF AN ASYMMETRIC COPPER MIXED VALENCE COMPLEX

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ELECTROCHEMICAL GENERATION OF AN ASYMMETRIC COPPER MIXED VALENCE COMPLEX

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Mixed-valence copper complexes have not been extensively studied in solution, probably due to their instability in this media. Nevertheless, the study of this type system acquires special relevance in relation to materials science (superconductors) and biochemistry (hemocyanin). The electrochemical feasibility of generating different mixed valence copper complexes has been reported recently.[1] In this paper we analyze the changes observed in the electronic spectra during the course of the electrolytic generation of a Cu(I)-Cu(II) complex from the fully reduced $[CuI(Br)(bpy)]_2$ precursor, (bpy = 2,2'bypiridine). The relevance of the results obtained in regard to hemocyanin is discussed.

KEYWORDS: copper, mixed valence, bimetallic, electrochemical, hemocyanin

EXPERIMENTAL

All solvents used (Merck, p.a.) were dried according to conventional techniques.[2] The CuBr needed to synthesize the precusor was obtained according to literature procedures.[3] The reagents 2,2'bipyridine (Merck, p.a.) and tetrabutylammonium tetrafluorborate (TBATFB, Aldrich 99%) were used as purchased. The precursor Cu(I)-Cu(I) complex was synthesized according to literature procedures.[4a] The corresponding mixed valence complex was obtained by controlled potential electrolysis at the first oxidation peak of the precursor, in an acetone (TBATFB 0.1M) solution, using a conventional three electrode cell. (Working electrode: reticulated vitreous carbon, counter electrode: platinum wire, reference electrode: Ag/AgCl electrode, adjusted to the SCE potential). The equipment used consisted of a Wenking EVI-80 Voltage Integrator and a Wenking HP-72 Potentiostate. The electronic absorption spectra were recorded with a Hewlett Packard 8452A diode array spectrophotometer, connected to a Vectra C5 computer. The solutions used were 1×10^{-3}M in acetone.(*)

RESULTS AND DISCUSSION

The crystal structure of $[CuI(Br)(bpy)]_2$ has been reported.[4c] It proves the dimeric

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(*) The use of other solvents was avoided because of insolubility of the precursor (dichloromethane) or dimer dissociation (acetonitrile and THF).

nature of the complex and the bridging properties of Br. The environment for both Cu(I) atoms corresponds to distorted tetrahedral, with a short Cu-Cu distance (2.86A°). Figure 1 shows a diagramatic sketch, adapted from reference 4c, of the local geometry around the Cu centers. The electronic spectrum of the brown solution obtained by dissolving the reduced precursor $[CuI(Br)(bpy)]_2$ in acetone shows a band at 442 nm and a shoulder at 540 nm, (Figure 2), assigned to MLCT transitions.[4a,b] The dimeric nature of the complex in acetone solution has been extensively discussed in the literature.[4a] By conductivity measurements we observed that it remains indefinitely as a dimer under inert atmosphere, while in the presence of air it slowly decomposes. In agreement with this observation, the corresponding cyclic voltammogram exhibits two oxidation processes.[1] Controlled potential electrolysis at the first oxidation peak (0.8V) shows, at first, the generation in solution of a light green complex with an absorption at 732 nm, (Figure 3a), as expected for tetrahedral Cu(II).[5] However, during the course of the electrolysis, the solution turns violet and a new band appears at 508 nm. There is also a blue shift of the 732 nm band. The spectrum recorded after the passage of one electron is illustrated in Figure 3b. The cyclic voltammogram of this violet electrolytic product does not exhibit the first oxidation peak (0.8V) shown by the reduced precursor. Controlled potential electrolysis at the second oxidation peak of the precusor (1.36V) results in the gradual disappearance of the band at 508 nm. After the overall passage of two electrons a green solution remains, in which the low energy band (with an enhanced intensity) is the only one that persists. A green solution

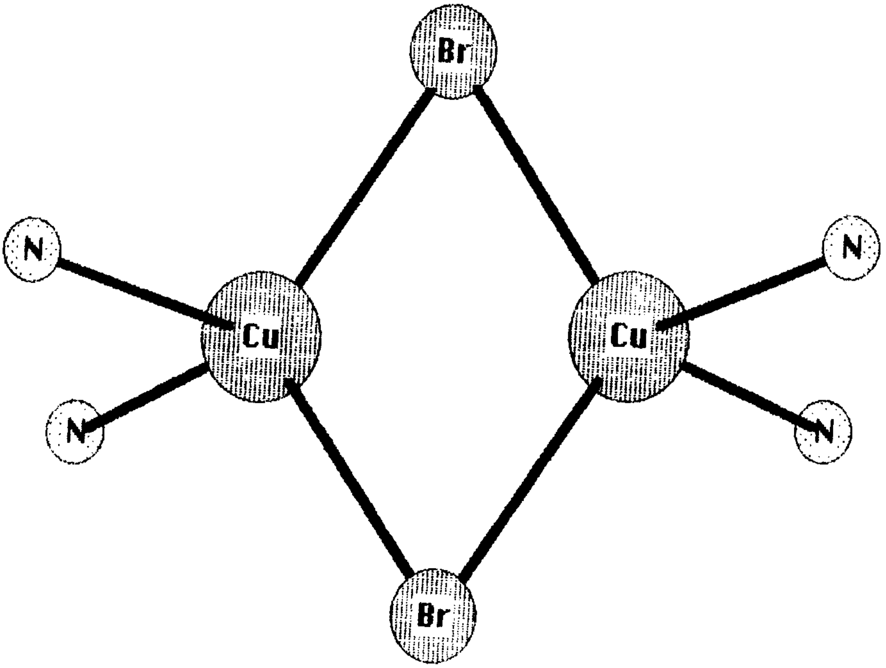

Figure 1 Diagramatic sketch, adapted from reference 4c, of the local geometry around the copper centers.

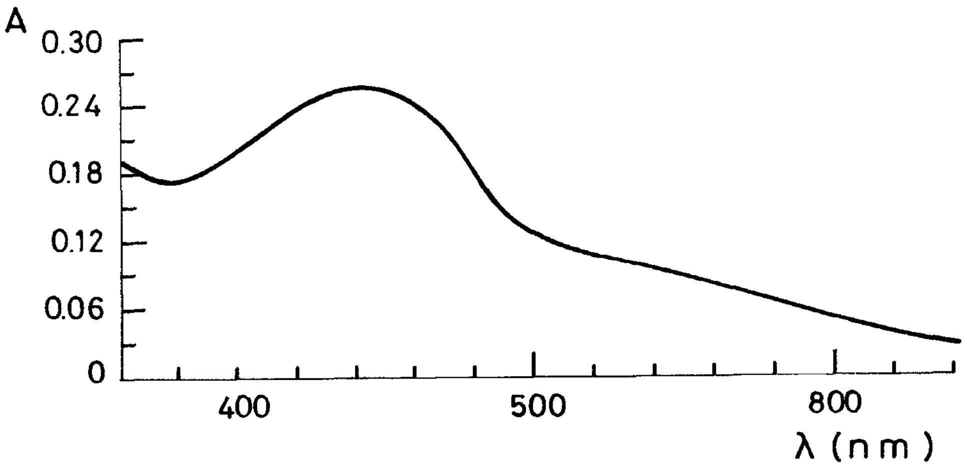

Figure 2 Electronic spectrum of the reduced precursor $[CuBrbpy]_2$ in acetone, $1 \times 10^{-4}M$.

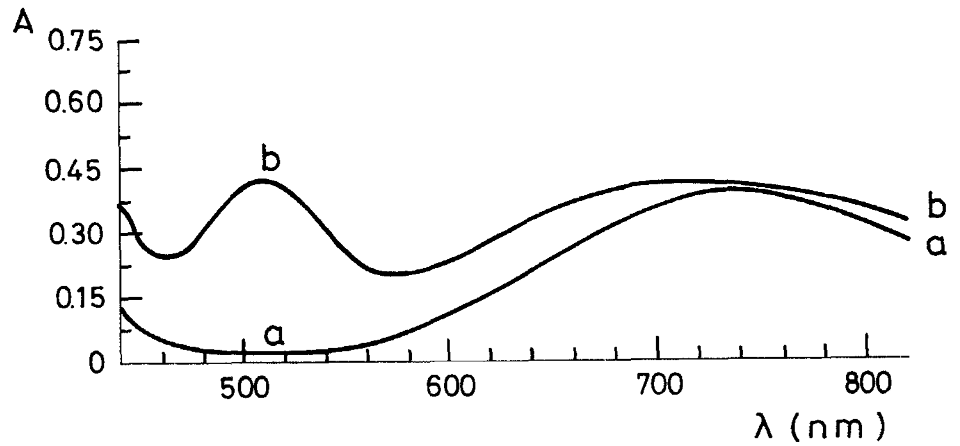

Figure 3 Electronic spectra of :

a) Product obtained at the beginning of the electrolysis at 0.8V. of the reduced precursor $[CuBrbpy]_2$ in acetone, $1 \times 10^{-3}M$.

b) Product obtained by the same electrolysis as in a) after the passage of one electron.

with the same spectrum is obtained by air oxidation of the violet electrolytic product.

On the basis of the observed behavior, and since the ligands experience no electrochemical reactions in the region analyzed.[4b] we assign both oxidations to copper centered processes:

$$[bpyCu(I)Br_2Cu(I)bpy] \longrightarrow [bpyCu(I)Br_2Cu(II)bpy]^+ + e^-$$

$$[bpyCu(I)Br_2Cu(II)bpy]^+ \longrightarrow [bpyCu(II)Br_2Cu(II)bpy]^{2+} + e^-$$

Therefore, the band observed at 508 nm is associated with the mixed valence species [bpyC(I)Br_2Cu(II)bpy]$^+$. A similar band has in fact been reported for several mixed valence complexes, with distinctly different ligands, and in different solvents.[1,6] Moreover, this same band has also been observed in half-met(*) derivatives of deoxygenated hemocyanin,[7a,b] and in some oxygenated models of this protein.[7c] Since this band is not observed in either the fully reduced precursor or in the fully oxidized electrolytic product, it can be attributed to the mixed valence species. Morover, the transition of 508 nm can be assigned to a high energy intervalence transfer band in the mixed valence complex. The unprecedented high energy of this intervalence transition is probably associated with the environment of the metal centers. Indeed, the change in electronic spectra *during the course* of the electrolysis at E = 0.8V could be indicative of a geometrical rearrangement around the copper center while it is undergoing oxidation. The species formed initially (Figure 3a) would be a symmetrical Type I (non-interacting) copper mixed valence complex, while the violet complex (Figure 3b) would reflect the rearrangement of Cu(II) to acquire a more appropriate geometry. This conformational change allows some interaction among the copper centers, thus generating a Type II copper mixed valence complex, consequently, an intervalence transfer band.[8] Moreover, a visible band at 510 nm with similar spectroscopic characteristics has been reported in the literature for a Cu mixed-valence complex with a comparable Cu-Cu distance.[6a] This transition was also assigned to an intervalence transfer band, based on the EPR spectrum of the complex in solution at room temperature, which showed a seven-line pattern, consistent with the interaction of the electron with both Cu centers.[6a] The high energy of these intervalence transfer bands would therefore reflect the different geometries around Cu(I) and Cu(II), ("heteronuclear" mixed valence complex) through the additional contribution, E_0, to the transition energy.[8] As mentioned above, the crystal structure of $[\mathrm{CuI(Br)(bpy)}]_2$ has been reported[4c] (see Figure 1) as well as other halogen-bridged Cu(I) analogues.[4a,9] These studies indicate that the CuX_2Cu plane is approximately perpendicular to the Cubpy plane, resulting in a distorted tetrahedral geometry around each Cu(I) centre. The geometry around the Cu center being oxidized would change during the course of the electrolysis tending to a more square planar distribution. This assumption is consistent[5] with the blue shift observed for the low energy band after the one-electron oxidation (Figure 3). A similar structural change as a consequence of a redox electrolytic process on a Cu complex has been reported.[10] It is important to mention that the description of the copper mixed valence species here obtained as "heteronuclear" or asymmetric is also supported by a compilation of X-ray crystal structure data for mixed valence copper complexes.[12] It can be seen that more than 95% of these complexes are asymmetric. Unfortunately, due to the high instability of the complex and the media from which it was obtained, it was not possible to obtain crystals in our case.

Interestingly, an asymmetric copper center has been postulated recently for hemocyanin.[13] Also a band at ~500 nm has been observed in half-met derivatives of deoxygenated hemocyanin[7a,b] and in oxygenated models of this protein.[7c] In both cases the assignment of the band has been to CT transitions related to

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(*) Half-met: semi-oxidized, *i.e.* Cu(I)-Cu(II) hemocyanin.

exogenous ligands (N_3^- and O_2, respectively). In the system described herein, the assignment of the band to a low energy Cu(I) - > bpy CT should not be dismissed. Nevertheless, the appearance of a similar band in a variety of different copper mixed-valence complexes[1,6,7,11] merits the search for a more general assignment, such as the one postulated in this paper. We believe that a knowledge of the origin of this band would aid our understanding of the relationship between structure and function in hemocyanin. Future work is aimed at this objective.

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References

1. B. Loeb in "NATO Advanced Research Workshop: Mixed Valency Chemistry; Applications in Physics, Chemistry and Biology", Aghia Pelaghia, Greece, June 1990.
2. A. Vogel "Practical Organic Chemistry", 3rd. Ed., Longman, 1967.
3. L.F. Andrieth, J.C. Bailar, W.C. Fernelius, W.C. Johnson, R.E. Kirk, *Inorg. Synth.*, **2**, (1946).
4. a) S. Kitagawa, M. Munakata, *Inorg. Chem*, **20**, 2261 (1981).
   b) S. Kitagawa, M. Munakata, N. Miyaji, *Bull. Chem. Soc. Jpn.*, **56**, 2258 (1983).
   c) B.W. Skelton, A.F. Waters, A.H. White, *Aust. J. Chem.*, **44**, 1207 (1991).
5. A.B.P. Lever, "Inorganic Electronic Spectroscopy", (Elsevier Science Publishers B.V., The Netherlands, 1984, Chapter 6.
6. a) I.G. Crivelli, C.G. Andrade, *Inorg. Chim. Acta*, **203**, 115 (1993).
   b) I. Delsahut, A.M. Haberland, E. Hunt, B. Loeb, in "Cuarto encuentro de Química Inorgánica", Valparaíso, Chile, January 1991.
7. a) E.I. Solomon, in "Copper Proteins", (Volume 3 of *Metal Ions in Biology Series*, Wiley Interscience, New York, 1981) 43.
   b) E.I. Solomon, M.J. Baldwin, M.D. Lowery, *Chem. Rev.*, **92**, 51 (1992)
   .c) K.D. Karlin, M.S. Haka, R.W. Cruse, G.J. Meyer, A. Farooq, Y. Gultneh, J.C. Hayes, J. Zubieta, *J. Am. Chem. Soc.*, **110**, 1196 (1988).
8. N.S. Hush, *Prog. Inorg. Chem*, **8**, 391 (1967).
9. a) P. Healy, C. Pakawatchai, A. White, *J. Chem. Soc. Dalton Transac.*, 2531 (1985).
   b) M.R. Churchill, G. Davies, M.A. El-Sayed, J.A. Fournier, J.P. Hutchinson, J.A. Zubieta, *Inorg. Chem.*, **23**, 783 (1984).
   c) R. Graziani, G. Bombieri, E. Forsellini, *J. Chem. Soc. A.*, 2331 (1971).
   d) L. Engelhardt, P. Healy, J. Kildea, A. White, *Aust. J. Chem.* **42**, 913 (1989)
10. A. Cinquantini, G. Opromolla, P. Zanello, *J. Chem. Soc. Dalton Transac.*, 3161 (1991).
11. a) T.N. Sorrell, V.A. Vankai, *Inorg. Chem.*, **29**, 1687 (1990).
    b) H.J. Schugar, C. Ou, J.A. Thich, J.A. Potenza, R.A. Lalancette, W. Furey Jr. *J. Am. Chem. Soc.*, **98**, 3047 (1976).
    c) C. Sigwart; P. Hemmerich, J.T. Spence, *Inorg. Chem.*, **7**, 2545 (1968).
12. M. Dunaj-Jurco, G. Ondrejovic, M. Melnik *Coord. Chem. Rev.*, **83**, 11 (1988).
13. a) M. Sarwar Nasir, K.D. Karlin, D. McGowty, J. Zubieta, *J. Am. Chem. Soc.*, **113**, 698 (1991) and references therein.
    b) A. Volbeda, W.G.J. Hol, *J. Mol. Biol.*, **209**, 249 (1989).