Inorganica Chimica Acta, 37 (1979) L509–L510
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

New Copper(II) Dimers Bridged by the Imidazolato Ligand

HUGO M. J. HENDRIKS and JAN REEDIJK*

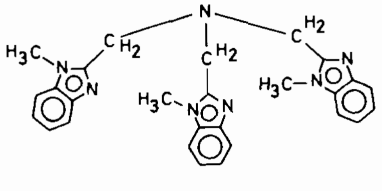
Department of Chemistry, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands

Received July 2, 1979

Several metalloproteins have been reported to contain imidazole ligands coordinated to the metal ions. These imidazole ligands usually originate from the histidine side chains of the protein [1–4].

In recent years considerable evidence has been presented for the occurrence of a ligand bridge between two nearby metal ions in the protein. Examples are laccase, hemocyanin, hemerythrine, cytochrome-c-oxidase and superoxide dismutase [4–8]. In the latter two cases evidence has been presented for the imidazolate ion as the bridging ligand between the two metal ions [7, 8]. This concerns the unit Cu–Iz–Zn in bovine superoxide dismutase, and the Fe–Iz–Cu unit in cytochrome-c-oxidase (Iz stands for the N–N bridging imidazolato group).

Very recently, Lippard, Hendrickson and coworkers [9–12] have reported interesting model compounds containing the unit Cu–Iz–Cu. Although this unit is relatively unstable with respect to dissociation and protonation of the Iz^- ligand, stabilisation appeared to be possibly by either including the two Cu(II) ions in a binucleating cryptate, or the imidazolato group in a binucleating chelate [9, 10]. Moderate stabilisation of the Cu–Iz–Cu unit is also possible by using tetradentrate amine ligands (tren), and even by tridentate amines and heterocyclic bidentate chelates like bipy [11, 12]. So far no systems have been reported in which the non-bridging ligands are also imidazoles. We here present evidence for a group of stable dimers containing the unit Cu–Iz–Cu, in which the other ligands around Cu(II) are provided by a tetradentate imidazole chelate. The chelate stabilising this dimeric unit is tris(2(N-methyl)-benzimidazolylmethyl)amine.



MNTB

This ligand (abbreviated MNTB) is easily prepared by methylation of tris(2-benzimidazolyl)-methylamine [13], (NTB), using CH_3I and potassium [14].

Treatment of a solution of 2 mmol of $Cu(ClO_4)_2 \cdot (H_2O)_6$ in MeOH with an equivalent amount of MNTB in hot methanol initially results in a yellow-green precipitate. Under vigorous stirring 1 mmol of sodium imidazolate (NaIz) in H_2O is added, upon which the green colour intensifies. After stirring for about 15 minutes the precipitate is isolated by filtration, washed with MeOH and diethyl ether and finally dried *in vacuo* at 60 °C.

In an alternative preparation a 2:1 mixture of MNTB and NaIz in 90% aqueous MeOH is slowly added to a MeOH solution of $Cu(ClO_4)_2(H_2O)_6$. Upon cooling of the deep green solution, crystals are obtained which are isolated as described above. Similar products have been obtained for the corresponding tetrafluoroborate and for the nitrate. All products have been characterized by elemental analyses (Cu, C, H, N) and agree with the general formula $[Cu_2(Iz)(MNTB)_2(anion)_3$ (anion = ClO_4, BF_4 or NO_3).

Ligand-field spectra of all three products are very similar in showing a maximum at 11.0 kK with a shoulder at the high-energy side. Such a band-shape is in agreement with Cu(II) in a trigonal bipyramidal geometry and suggests a chromophore $[CuN_5]$ [15].

Direct evidence for a dimeric structure comes from the EPR powder spectra of the compounds. Both X-band and Q-band spectra show distinct $\Delta m = 2$ transitions in the g = 4 region. The spectral data in the whole region can be analysed as Cu(II) dimers [16], yielding g = 2.15(2), D ≈ 0.09(1) cm^{-1}. In addition, low-temperature magnetic susceptibility measurements (down to 4 K) indicate a considerable magnetic interaction between the Cu(II) pairs. Analysing the observed χ *vs* T curve using the well-known Bleany–Bowers expression [9–12, 16] yields g = 2.15(5), J = –30(4) cm^{-1}. This value of J falls in the range observed for other Iz-bridged dimers. Previous work of Lippard and Hendrickson [9–12] has shown that –J can vary between 25 and 90 cm^{-1} in case of square-pyramidal coordinated copper, depending upon the position of the Iz ring with respect to the equatorial ligand plane. In case of trigonal-bipyramidal coordination with Iz-bridging ligand in the axial position values for –J between 25 and 50 cm^{-1} have been observed. Our present compounds are believed to belong to this category.

Present research is devoted to the isolation of single crystals suitable for X-ray diffraction and to substitution of the bridging Iz ligand by other azoles.

---

*Author to whom all correspondence should be addressed.

Acknowledgements

The authors are indebted to Drs. J. A. C. van Ooijen and P. J. van der Put for assistance with the ESR and magnetic susceptibility measurements.

References

1 R. J. Sundberg and R. B. Martin, *Chem. Rev., 74,* 471 (1974).

2 J. A. Fee, *Struct. Bonding (Berlin), 23,* 1 (1975).

3 G. I. Eichorn, Ed., 'Inorganic Biochemistry', Elsevier, New York, 1973.

4 R. E. Stenkamp, L. C. Sieker and L. H. Jensen, *Proc. Natl. Acad. Sci. (USA), 73,* 349 (1976).

5 D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon and H. B. Gray, *Proc. Natl. Acad. Sci. (USA), 75,* 3019 (1978).

6 R. S. Himmelwright, N. C. Eickman and E. I. Solomon, *J. Am. Chem. Soc., 101.* 1576 (1979).

7 M. F. Tweedle, L. J. Wilson, L. Garcia-Iniguez, G. T. Babcock and G. Palmer, *J. Biol. Chem., 253,* 8065 (1978).

8 K. M. Beem, D. C. Richardson and K. V. Rajagopalan, *Biochemistry, 16,* 1930 (1977).

9 C. L. O. Young, J. C. Dewan, H. R. Lilienthal and S. J. Lippard, *J. Am. Chem. Soc., 100,* 7291 (1978).

10 P. K. Coughlin, J. C. Dewan, S. J. Lippard, E. Watanabe and J. M. Lehn, *J. Am. Chem. Soc., 101,* 265 (1979).

11 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem., 17,* 2622 (1978).

12 M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem., 18,* 141 (1979).

13 L. K. Thompson, B. S. Ramaswamy and E. A. Seymour, *Can. J. Chem., 55,* 878 (1977).

14 S. Trofimekno, *J. Am. Chem. Soc., 92,* 5118 (1970).

15 R. C. Slade, A. A. G. Tomlinson, B. J. Hathaway and D. E. Billing, *J. Chem. Soc. A,* 61 (1968).

16 J. Reedijk, D. Knetsch and B. Nieuwenhuijse, *Inorg. Chim. Acta, 5,* 568 (1971).