Synthesis and Characterization of a Tripyrrane−Copper(II) Complex

Jonathan L. Sessler,* Andreas Gebauer, Vladimír Král, and Vincent Lynch

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Received June 7, 1996

To date, the study of linear oligopyrroles, systems containing several pyrrolic moieties linked by methylene or methene fragments, has been largely focused on the chemistry of naturally occurring bile pigments.[1] These pigments, which contain four pyrrolic fragments arranged in a linear fashion, have so far been used to stabilize complexes of Fe(II), Co(II), Mn(II), and Cu(II).[2] Bilirubin and related materials are thus emerging as biogenic ligands of considerable interest. However, the very success of these tetrapyrrolic chelands serves to raise an obvious question as to whether linear polypyrrolic systems containing a greater or lesser number of pyrroles might not also be employable as metal-complexing agents. In this communication we describe the synthesis of a Cu(II) complex (**2**) derived from an oxidized tripyrrane ligand.

Tripyrranes (e.g., **1**)[3] are one of the better studied oligopyrroles. They have been used extensively as building blocks in the synthesis of porphyrins[4] and expanded porphyrins,[5] including sapphyrin,[6] pentaphyrin,[7] hexaphyrin,[8] and texaphyrin.[9] When incorporated into the latter macrocycles, the tripyrranes and their 4-electron-oxidized congeners, the tripyrrodimethenes, display a rich metal-binding chemistry. However, it remains an open question at present whether these nonnatural "bile pigment analogues" can themselves act as ligands absent any kind of macrocyclic effect. It is known, however that dipyrromethenes can function in this regard.[10]

To test the above possibility we sought to prepare a representative tripyrrane−metal complex. After considerable experimentation, we found that exposure of the dibenzyl tripyrrane ester **1** to copper(II) acetate hydrate under oxidizing conditions (acetonitrile, trace triethylamine, reflux) leads to an apparent reaction (Scheme 1). Subjecting the resulting product(s) to successive column chromatographic purifications (silica gel, dichloromethane/1% methanol eluent) was found to give rise to only one blue-green fraction. After removal of solvent, this fraction gave a green solid that proved paramagnetic as judged by NMR spectroscopy. Mass spectrometric analysis of this product revealed a M^+ peak that was 14 mass units heavier than expected for a copper(II) tripyrrodimethene complex. This led us to consider the possibility that water or some other simple fragment was incorporated into the tripyrrane fragment during the course of metal complexation. However, these data did not tell us how or where this putative fragment was "inserted".

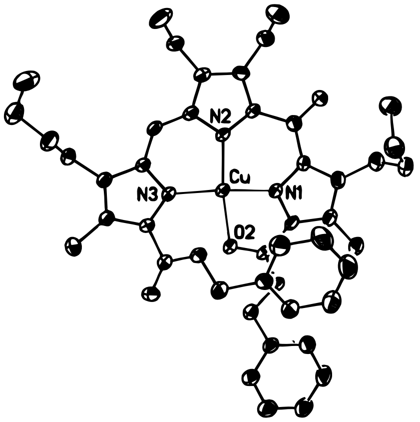


Figure 1. View of complex **2**, $C_{42}H_{45}N_3O_7Cu\cdot0.5\ CHCl_3$, showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level. Hydrogen atoms have been omitted for clarity.

Fortunately, the above complex proved stable as a dichloromethane solution when either stored at room temperature in the presence of air for several months or exposed briefly to aqueous solutions of pH 2−14.[11] It thus proved possible to crystallize it from chloroform/pentane. This, in turn, made it possible to resolve the "mystery" *via* X-ray diffraction analysis.

The X-ray crystal structure of the tripyrrane−Cu(II) complex (**2**) is shown in Figure 1.[12] It reveals that, in the course of metal chelation, the tripyrrane ligand is oxidized at one of the two bridging methylene positions to form a bridging methene and at the other to form an exocyclic keto group. This surprising oxidation process converts the starting tripyrrane into a species with two acidic protons. It thus generates a ligand that is able to coordinate Cu(II) in the form of an overall neutral complex.

As revealed by the X-ray structure, the coordination environment of the Cu(II) center in **2** is a distorted square plane. The

---

(1) Falk, H. *The Chemistry of Linear Oligopyrroles and Bile Pigments*; Springer Verlag: Vienna, 1989.

(2) (a) Balch, A. L.; Mazzanti, M.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 9114−9122. (b) Balch, A. L.; Mazzanti, M.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 12206−12207.

(3) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394−4397.

(4) (a) Boudif, A.; Momenteau, M. *J. Chem. Soc. Chem. Commun.* **1994**, 2069−2070. (b) Nguyen, L. T.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1996**, *61*, 998−1003. (c) Sessler, J. L.; Genge, J. W.; Sansom, P. I.; Urbach, A. *Synlett* **1996**, *2*, 187−188. (d) Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1246−1247. (e) Lin, Y.; Lash, T. D. *Tetrahedron Lett.* **1995**, *36*, 9441−9444.

(5) (a) Dolphin, D., *The Porphyrins Vols. I and IIB,* Academic Press, New York, 1978. (b) Sessler, J. L.; Burrell, A. *Top. Curr. Chem.* **1991**, *161*, 178−273.

(6) (a) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin I* **1972**, 2111−2116. (b) Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *103*, 6429−6436. (c) Sessler, J. L.; Cyr, M.; Burrell, A. K. *Tetrahedron* **1992**, *48*, 9661−9672 and references therein.

(7) (a) Rexhausen, H.; Gossauer, A. *J. Chem. Soc., Chem. Commun.* **1983**, 275. (b) Gossauer, A. *Chimia* **1983**, *37*, 341−342. (c) Gossauer, A. *Chimia* **1984**, *38*, 45−46.

(8) Gossauer, A. *Bull. Soc. Chim. Belg.* **1983**, *92*, 793−795.

(9) (a) Sessler, J. L.; Mody, T. D.; Hemmi, G. W.; Lynch, V. *Inorg. Chem.* **1993**, *32*, 3175−3187. (b) Sessler, J. L.; Hemmi, G. H.; Mody, T. D.; Murai, T.; Burrell, A.; Young, S. W. *Acc. Chem. Res.* **1994**, *27*, 43−50.

(10) For examples see: (a) Corwin, A. H.; Sydow, V. L. *J. Am. Chem. Soc.* **1953**, *75*, 4484−4486. (b)Murakami, Y.; Sakata, K. *Inorg. Chim. Acta* **1968**, *2*, 273−279. (c) Fritschi, H.; Leutenegger, U.; Siegmann, K.; Pfaltz, A.; Keller, W.; Kratky, C. *Helv. Chim. Acta* **1988**, *71*, 1541−1552.

(11) The stability of complex **2** was determined kinetically by monitoring the change in the Q-band absorbance at 608 nm as a function of pH using a Beckmann DU-7 spectrophotometer. This was done by exposing complex **2**, dissolved in dichloromethane, to aqueous solutions of a given pH between 1 and 14.

(12) Crystal data and details of the data collection and structure refinement are given in the Supporting Information.

(13) (a) Hathaway, B. J. *Essays Chem.* **1971**, *2*, 61−92. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley Intersience: New York, 1980; p 813.

S0020-1669(96)00678-7 CCC: $12.00

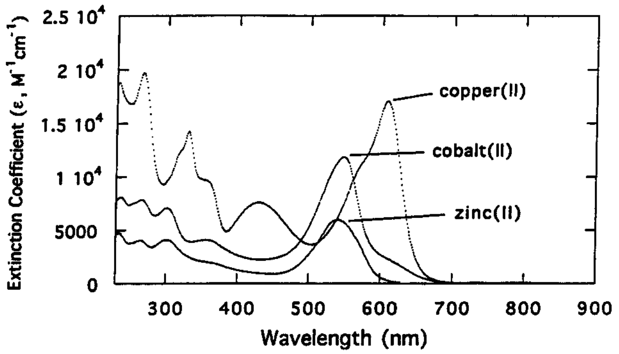
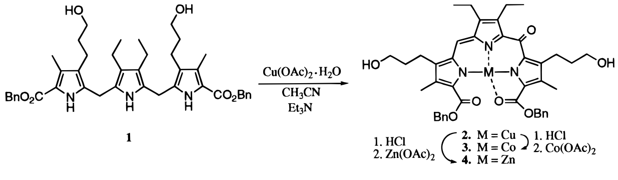
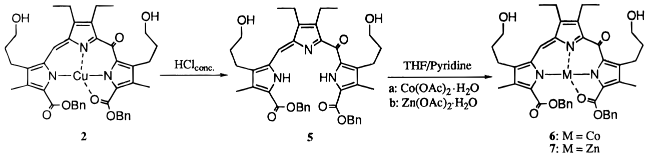


Figure 2. UV/vis spectra of the Cu(II)−, Co(II)−, and Zn(II)−tripyrrane complexes **2**, **3**, and **4** in dichloromethane.

Scheme 1



Scheme 2



copper atom is bound covalently to N1 and N3 at bond lengths of 1.878(5) and 1.909(5) Å, respectively, while N2 (Cu−N2 1.938(6) Å) and O2 (Cu−O2 2.156(5) Å) of the α-ester functionality are used to fill the coordination sphere of the copper atom. The angles involving N1, N2, N3, and Cu (N1−Cu−N3 173.8(2)°, N1−Cu−N2 90.3(2)°, N2−Cu−N3 94.2(2)°) resemble, with only small deviations, those expected for a square planar complex.[13] The angles involving O2, Cu, and N1−N3 (N1−Cu−O2 79.4(2)°, N2−Cu−O2 157.4(2)°, N3−Cu−O2 97.8(2)°), on the other hand, are distorted substantially from those expected for a metal bound in an idealized square planar ligand environment. This deviation is presumably a reflection of the steric requirements of the α-ester; this group must be bent into the main chelation plane in order to interact with the copper atom.

To explore whether such tripyrrane species can also act as ligands for other metal cations, two additional metal complexes were prepared. This was done by first demetalating the copper complex **2** with concentrated HCl and then treating the reaction mixture with either cobalt acetate or zinc acetate. The resulting complexes (**3** and **4**) were purified by chromatography and characterized by mass spectrometry and UV/vis spectroscopy.

Figure 2 shows an overlay of the UV/vis spectra of the cobalt−, copper−, and zinc−tripyrrane complexes **2**, **3**, and **4**. Both the cobalt− and zinc−oxotripyrromethene complexes display similar spectra, with the major difference being the higher extinction coefficients of the cobalt(II) species. The copper(II) complex, on the other hand, displays a markedly different spectrum. It shows a greater molar absorptivity and a stronger Q-type band. This latter is red-shifted (to about 608 nm) as compared to the corresponding bands of the cobalt and zinc complexes ($\lambda_{\max} \approx 540$ nm).

The electrochemical properties of the copper(II) complex **2** were probed using cyclic voltammetry.[14] When the complex is scanned between +400 and −1000 mV, a reversible Cu(II)/Cu(I) wave ($E_{1/2} = 480$ mV vs Ag/AgCl) is observed (Supporting Information). On the other hand, when the cyclovoltammogram is recorded between +2 and −2 V, a second reduction wave is observed (Supporting Information) that is tentatively assigned to a ligand-centered reduction process. Under these scanning conditions, the Cu(II)/Cu(I) couple becomes irreversible. This leads us to propose that once the ligand is reduced, some irreversible, presumably dissociative, process takes place such that the copper(I) cannot be oxidized back to copper(II).

The EPR spectrum of the copper(II)−tripyrrane complex **2** at 115 K was also recorded (Supporting Information).[15] From these measurements, an $A_{\|}$ value of about 150 G was determined for complex **2**. While the observed signals are very broad (making an exact determination of $A_{\|}$ difficult at this temperature), the fact that the $A_{\|}$ value for **2** is on the low side of what is generally seen for normal Cu(II) complexes (for which $A_{\|}$ values of 140−200 G are generally recorded[16]) leads us to suggest a degree of interaction between the copper(II) ion center and the tripyrrane ligand. Such a putative delocalization is consistent with what is observed by other spectroscopic means (*vide supra*). However, simple geometry-based explanations for this low value (i.e., distortion from pure square planarity) are also possible.

The present results serve to illustrate that "bile pigment analogues" containing but three pyrroles can be used as acyclic ligands for copper(II) and, seemingly, other transition metal cations. On this basis, we are inclined to propose that a wide range of oligopyrrolic species, including those containing five and six pyrrolic subunits,[17] could be used to support the formation of interesting metal complexes.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 9122161) to J.L.S.

Supporting Information Available: Text giving synthetic and X-ray experimental procedures, tables of crystallographic data, atomic thermal parameters, fractional coordinates, and bond lengths and angles for the tripyrrane−Cu(II) complex **2**, an EPR spectrum of complex **2**, cyclovoltammograms of complex **2** scanned between +0.4 and −1 V and between +2 and −2 V, and additional structural diagrams of **2** (24 pages). Ordering information is given on any current masthead page.

IC9606789

---

(14) Cyclic voltammetry was carried out at room temperature (25 ± 2 °C) under dry argon using a Bioanalytic Systems Inc. (BAS) CV-50W Version 2 MF 9093 voltammetric analyzer. Dry acetonitrile was the solvent, 0.1 M $[CH_3(CH_2)_3]_4NPF_6$ the electrolyte, a platinum disk the working electrode (1.6 mm diameter), and a platinum wire the auxiliary electrode. A Ag/AgCl couple, separated from the bulk solution by means of a porous Vycor plug, was used as the reference electrode.

(15) Recorded on a Bruker ESP 300 EPR spectrometer interfaced to an IBM ESP 1600 computer.

(16) Solomon, E. I.; Lowery, M. D. In *The Chemistry of the Copper and Zinc Triads*, Welch, A. J., Chapman, S. K., Eds.; Royal Society of Chemistry: London, 1993; see also references therein.

(17) Sessler, J. L.; Weghorn, S. J.; Lynch, V.; Fransson, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1289−1290.