Inorg. Chem. **2006**, *45*, 8826–8828

Inorganic Chemistry
Communication

Copper Complex of an Iminodioxabicyclo[3.3.1]nonane Pendant Ligand: The First Example of Iminodioxocin Bridgehead Nitrogen Coordination

Debashree Mandal,† A-Qing Wu,‡ Guo-Cong Guo,‡ and Debashis Ray*,†

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India, and Fujian Institute of Research on the Structure of Matter, CAS, China

Received May 15, 2006

The pentadentate N_4O amine–imine–naphthol ligand (HL^D) containing rigid 8,16-imino-8*H*,16*H*-dinaphtho[2,1-*b*:2,1-*f*][1,5]dioxocin is formed preferentially, under visible light irradiation conditions, instead of the product H_3L, expected from imidazolidine ring formation. A strained chelate bite enforces the first bridgehead nitrogen coordination to a copper(II) ion from the bicyclic iminodioxocin part of the ligand as shown by X-ray crystallography.

Ligands bearing rigid bulky groups with potential donor sites can impose strained coordination geometries around metal ions upon binding. Like Tröger's base (A), both epoxydioxocin (B) and iminodioxocin (C) have rigid concave shapes (Figure 1) and if incorporated within a multidentate ligand backbone are expected to give novel bridgehead oxygen or nitrogen coordination compounds. However, in the field of coordination chemistry, no iminodioxocin-based ligand system has been reported to date. The synthesis of sterically constrained ligands is of primary importance in coordination chemistry. The variation of the electronic and steric properties of the donor groups has a significant effect on the structure and reactivity of the resulting complexes. The anhydro dimer of *o*-hydroxybenzaldehyde (D), 6*H*,12*H*-6,12-epoxybenzo[*b*,*f*][1,5]dioxocin (E), is prepared by the addition of a dehydrating agent with a catalytic amount of acid present,[1] while the corresponding *o*-hydroxynaphthaldehyde-based analogue is also known (Scheme 1).[2] The same reaction in the presence of ammonium acetate in ethanol gives the imino derivative.[3] Thus, steric constraint and conformational rigidity within a multidentate ligand system can be achieved, for example, through iminodioxocin formation on a linear tetramine. Earlier we showed that heterocyclic N−C−N bridging ligands can be obtained from imidazolidine ring formation reactions occurring at the central ethylenediamine segment of the tetramine backbone of multidentate ligands.[4,5] In the reaction of the proligand H_2L with *o*-hydroxybenzaldehyde or *o*-hydroxynaphthaldehyde, a competition occurs between the formation of the imidazolidine ring[4−8] and the iminodioxocin ring (Scheme 2).[2,3,9] The characteristic head-to-tail trioxabicyclo[3.3.1]nonane[10] bis-acetal nucleus is present in preussomerins,[11,12] a family of fungal metabolites, and shows biological activity. In the present Communication, we report the first synthesis of an iminodioxabicyclo[3.3.1]nonane, which represents a fragment of the carbon skeleton of the preussomerin-type natural products,[12] in the form of the pentadentate ligand, HL^D ([(2-{2′-[2″-(2,6-dioxa-3,7-dinaphtha-9-azabicyclo[3.3.1]non-9-yl)ethylamino](ethylamino}ethylamino)methyl]-5-naphth-2-ol). HL^D is capable of coordinating a metal through the

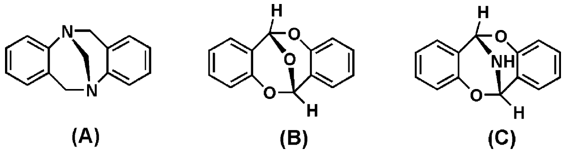
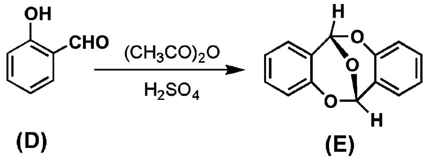


Figure 1. Structural formulas of Tröger's base (A), epoxydioxocin (B), and iminodioxocin (C).

Scheme 1



---

* To whom correspondence should be addressed. E-mail: dray@chem.iitkgp.ernet.in.

† Indian Institute of Technology.

‡ Fujian Institute of Research on the Structure of Matter.

(1) Kulkarni, V. S.; Hosangadi, B. D. *Synth. Commun.* **1986**, *16*, 191.

(2) Bachet, P. B.; Guidi-Morosini, C. B. *Acta Crystallogr., Sect. C* **1986**, *C42*, 1630.

(3) Refat, H. M.; Fadda, A. A.; Lu, Y.; Blehl, E. R. *Heterocycles* **1996**, *43*, 977.

(4) Mukhopadhay, U.; Falvello, L. R.; Ray, D. *Eur. J. Inorg. Chem.* **2001**, 2823.

(5) Bera, M.; Wong, W. T.; Aromí, G.; Ray, D. *Eur. J. Inorg. Chem.* **2005**, 2526.

(6) Boca, M.; Baran, P.; Boca, R.; Fuess, H.; Kickelbick, G.; Linert, W.; Renz, F.; Svoboda, I. *Inorg. Chem.* **2000**, *39*, 3205.

(7) Nanda, P. K.; Mandal, D.; Ray, D. *Polyhedron* **2006**, *25*, 702.

(8) Nanda, P. K.; Aromí, G.; Ray, D. *Inorg. Chem.* **2006**, *45*, 3143.

(9) Jones, P. R.; Gelinas, R. M. *J. Org. Chem.* **1981**, *46*, 195.

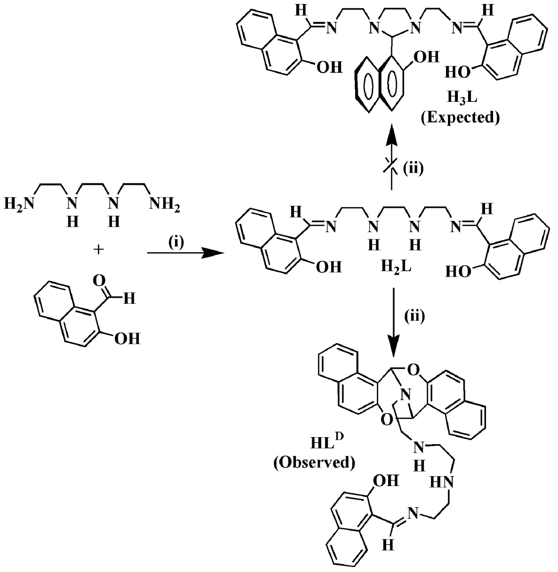
(10) Vonwiller, S. C. *J. Org. Chem.* **1997**, *62*, 1155.

(11) Quesada, E.; Stockley, M.; Ragot, J. P.; Prime, M. E.; Whitwood, A. C.; Taylor, R. J. K. *Org. Biomol. Chem.* **2004**, *2*, 2483.

(12) Ragot, J. P.; Prime, M. E.; Archibald, S. J.; Taylor, R. J. K. *Org. Lett.* **2000**, *2*, 1613.

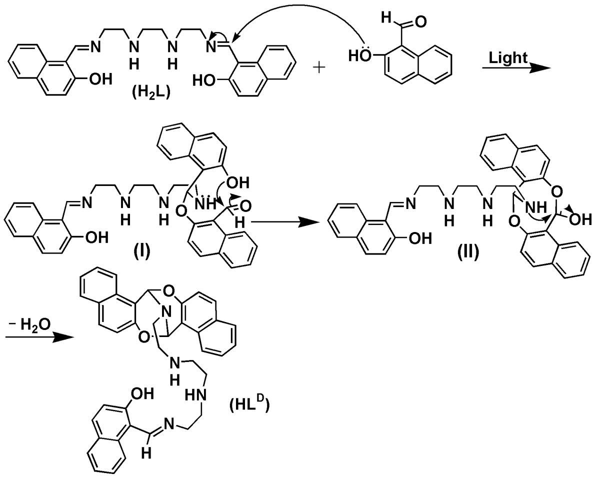
10.1021/ic060833b CCC: $33.50

Scheme 2. Synthesis[a] of HL^D



[a] (i) MeOH, stirring, rt. (ii) 1 equiv of 2-hydroxynapthaldehyde, MeOH, stirring, rt.

Scheme 3



iminodioxocin bridgehead nitrogen. The novel pentadentate N_4O ligand is formed preferentially, instead of H_3L (2-(2′-hydroxy-5,6-naphthyl)-1,3-bis[4-(2′-hydroxy-5,6-naphthyl)-3-azabut-3-enyl]-1,3-imidazolidine) when the hexadentate proligand H_2L reacts with 2-hydroxynaphthaldehyde in MeOH under visible light at room temperature (Scheme SI in the Supporting Information). A tentative mechanism of the formation of HL^D is given in Scheme 3. First, the Schiff base proligand H_2L reacts with one molecule of *o*-hydroxynaphthaldehyde, giving adduct **I**, to which follows the nucleophilic attack of naphthanol on the imine carbon at one end, which then cyclizes to an eight-membered dioxocin ring bearing an imine alcohol (**II**). The imine alcohol finally undergoes an intramolecular cyclization reaction, producing a red-brown gummy product identified as HL^D. The solid proligand H_2L is, in turn, isolated as a yellow solid (mp 110 °C) from the reaction of 2 mol of 2-hydroxynaphthaldehyde with 1 mol of triethylenetetramine. The expected imidazolidine ring formation reaction producing hitherto unknown H_3L was not observed (Scheme 2). On the other hand, it has been previously reported that irradiation with visible light leads, in absence of any dehydrating agent and catalyst, to a facile iminodioxocin condensation reaction.[12,13] The reaction in MeOH of $Cu(ClO_4)_2{\cdot}6H_2O$ with HL^D in the presence of NEt_3, using a 1:1:1 molar ratio, at 30 °C yields small brownish-green crystals upon slow evaporation. Alternatively, the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with 2-hydroxynaphthaldehyde, H_2L, and NEt_3 in a 1:1:1:1 molar ratio in MeOH gives the compound $[CuL^D]ClO_4$ in 60% yield. Elemental analysis, solution electrical conductivity in dimethylformamide, and room-temperature magnetic susceptibility values are consistent with the formula $[CuL^D]ClO_4$. The strong unsplit band $\nu(ClO_4^-)$ at around 1091 cm^{-1} is observed in Fourier transform IR due to the ν_3 mode of a perchlorate anion in T_d symmetry, suggesting no coordination of the perchlorate ion to the metal center.[14]

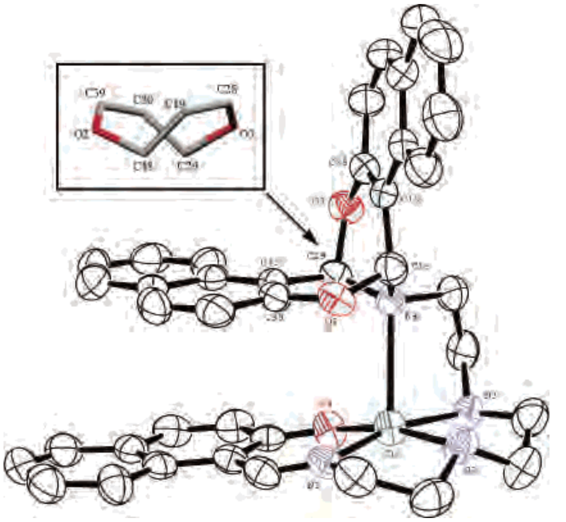


Figure 2. ORTEP view of the $[Cu^{II}L^D]^+$ cation with an atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The inset shows the conformation of the eight-membered dioxocin ring responsible for a rigid backbone of two fused naphthyl rings with a dihedral angle of 96.84°. Selected bond lengths (Å) and angles (deg): Cu1−O1, 1.8992(14); Cu1−N1, 1.9318(14); Cu1−N2, 2.0317(17); Cu1−N3, 2.0412(13); Cu1−N4, 2.589(13); O1−Cu1−N1, 93.12(6); N1−Cu1−N2, 84.63(6); N2−Cu1−N3, 84.94(6); N3−Cu1−O1, 95.27(6); N3−Cu1−N4, 77.83(2); N1−Cu1−N4, 113.93(8). Symmetry codes: (i) $-x, y + {}^1/_2, -z + {}^1/_2$; (ii) $-x, -y, -z$; (iii) $x, -y + {}^1/_2, z + {}^1/_2$.

Caution! *Perchlorate-containing salts are potentially explosive and should be handled in very small quantities.* The formation of the complex was confirmed by single X-ray crystal structure analysis, as well as the preferential formation of the iminodioxocin ring instead of the imidazolidine ring.[15] A labeled ORTEP view of the complex cation of $[CuL^D]ClO_4$ is shown in Figure 2. The complex consists of a cationic unit $[CuL^D]^+$ and one uncoordinated perchlorate anion. The

---

(13) Adams, R.; Fogler, M. F.; Kreger, C. W. *J. Am. Chem. Soc.* **1922**, *44*, 1126.

(14) Paital, A. R.; Nanda, P. K.; Das, S.; Aromi, G.; Ray, D. *Inorg. Chem.* **2006**, *45*, 505.

(15) Crystallographic data were collected at 293(2) K on a Rigaku Mercury CCD diffractometer with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Crystal data for compound **1** (CCDC 600364): $C_{39}H_{35}ClCuN_4O_7$, MW = 770.341, $T = 293(2)$ K, $\lambda = 0.710\ 73$ Å, monoclinic, $P21/c$, $Z = 4$, $a = 10.06520(10)$ Å, $b = 24.947(3)$ Å, $c = 14.107(3)$ Å, $\alpha = 90°$, $\beta = 107.049(10)°$, $\gamma = 90°$, $V = 3386.4(8)$ Å^3, 22 028 measured reflections, 5921 independent reflections ($R_{int} = 0.0642$), R1 = 0.0595, and wR2 = 0.1022.

terminal naphthol oxygen and three imine and amine nitrogens from the ligand form the square base around the copper ion. The coordination of the nitrogen atom from the 8,16-imino-6*H*,14*H*-dinaphtho[2,1-*b*:2,1-*f*]dioxocin moiety to the apical site of copper completes the square-pyramidal ON_4 coordination environment (τ parameter is 0.05).[16] Noncoordination of water or perchlorate oxygen also suggests, for the first time, the greater coordinating power of sterically crowded iminodioxocin nitrogen. X-ray crystallography thus confirms the incorporation of the C_2-symmetric iminodioxocin terminus, which displays fused naphthyl rings (dihedral angle 96.84°), into the ligand and the oblique apical coordination of copper(II) to the bicyclic iminodioxocin part of the ligand. The $O-Cu-N^{im}$, $N^{im}-Cu-N^{am}$, and $N^{am}-Cu-N^{am}$ basal bite angles within the square base are 93.12°, 84.63°, and 84.94°, respectively, whereas the $N^{am}-Cu-N^{imd}$ (im = imine, am = amine, and imd = iminodioxocin) basal–apical bite angle is 77.84°. This small bite angle is responsible for a ligand-enforced oblique apical coordination of the iminodioxocin nitrogen to the copper(II) ion. The acetal protons of the conformationally fixed bis-acetal nucleus of the iminodioxocin are both equatorial. The $Cu-N^{imd}$ distance is considerably longer than the Cu–N(apical pyridine) bond lengths of 2.17 Å in $[Cu(cyclops)(py)]ClO_4$[17] and of 2.12 and 2.13 Å in $[Cu_2(OAc)_4(py)_2]$[18] but shorter than the range of 2.6–2.8 Å observed for other known apical Cu–N[19] bonds. The perchlorate anions stay close to the heterobicyclic rings. The eight-membered imino-bridged dioxocin ring of the ligand adopts a twisted-boat conformation (Figure 2, inset), as judged from the eight torsion angles observed within this ring ($\tau_1-\tau_8$).[20] Presumably, the $\pi-\pi$ stacking of the naphthyl rings of the proligand H_2L controls the attachment of the third naphthyl ring to the latter, in the conformation observed in HL^D. The presence of a long tetramine tail is responsible for the –NR– bridgehead insertion in an opposite conformation to that obtained in the case of unsubstituted dinaphthoiminodioxocin.[3] The dinaphthoiminodioxocin part of the ligand exists in a folded conformation with a dihedral (folding) angle of 96.84° (Figure S6 in the Supporting Information), which is larger than that in the unsubstituted iminodioxocin molecule (92°).[3] The iminodioxocin nucleus imposes a steric restriction to both adjacent naphthyl rings locating this at an angle at about 96°, imparting a concave face to one end of the ligand. The stacking of horizontal iminodioxocin naphthyl and terminal imine naphthyl rings stabilizes the overall chair shape of the molecule with the copper chelate as the base, as shown in Figure 3a. This interaction is responsible for the opening of the dioxocin folding and the corresponding widening of the folding angle. The stacked molecule may intercalate other planar rings between both naphthyl rings. A closer examination of the stacking reveals that the shortest interaromatic $C_{ar}-C_{ar}$ distance is 3.664 Å (Figure S8 in the Supporting Information). The copper atom is 0.186 Å above the ON_3 coordination square base. The molecules also pack efficiently in three dimensions (Figure 3b).

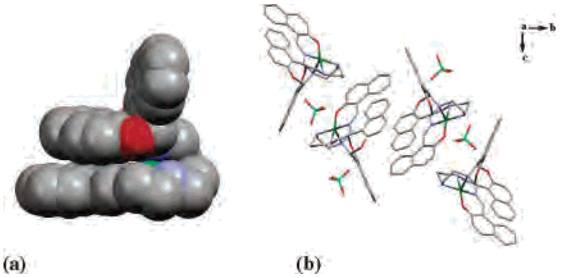


Figure 3. (a) Space-filling diagram of $[Cu^{II}L^{D}]^+$ along the *a* axis showing the naphthyl $\pi-\pi$ stacking within the complex. (b) Packing diagram of $[Cu^{II}L^{D}]^+$ along the *a* axis.

In conclusion, we have reported here the first ever example of any transition metal (copper) complex of a dinaphthoiminodioxocin-containing pentadentate ligand bound through the bridgehead nitrogen atom. The ligand forces the oblique apical coordination of the sterically fixed iminodioxocin bridgehead nitrogen and enforces an acute terminal N–Cu–N angle. The iminodioxabicyclo[3.3.1]nonane part of the ligand has four common carbon rings with the preussomerin family of natural products. Bridgehead imine coordination favors the $\pi-\pi$ interaction of the dioxocin with the terminal imine naphthyl rings. The potential of a weak and rare coordination mode of the bridgehead nitrogen of the new ligand containing the iminodioxocin ring may be exploited for the synthesis of other 3d metal ion complexes in unusual geometry.

Acknowledgment. D.M. acknowledges financial support from the Council of Scientific and Industrial Research, New Delhi, India, and G.-C.G. and A.-Q.W. acknowledge financial support from the Fujian Institute of Research on the Structure of Matter, CAS, China. We thank Dr. G. Aromí for his kind help.

Supporting Information Available: Detailed experimental procedures, IR spectra, and other characterizations of H_2L and **1**, crystallographic files in CIF format, tables of selected bond lengths and angles, Figures S1–S8, and Scheme SI. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060833B

---

(16) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
(17) Anderson, O. P.; Packard, A. B. *Inorg. Chem.* **1980**, *19*, 2123.
(18) Barclay, G. A.; Kennard, C. H. L. *J. Chem. Soc.* **1961**, 5244.
(19) Alam, M. A.; Nethaji, M.; Ray, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1940.
(20) Kataeva, O. N.; Litvinov, I. A.; Naumov, V. A.; Anonimova, I. V. *J. Mol. Struct.* **1995**, *344*, 95.