

CO₂ Fixation by Copper(II) Complexes of a Terpyridinophane Aza Receptor

Enrique García-España,^{*,†} Pablo Gaviña,[†] Julio Latorre,[‡] Conxa Soriano,[†] and Begoña Verdejo[†]

Instituto de Ciencia Molecular, Departamentos de Química Inorgánica y Orgánica, and Instituto de Materiales de la Universidad de Valencia, Departamento de Química Inorgánica, Universidad de Valencia, C/ Dr. Moliner 50, 46100, Burjassot (Valencia), Spain

Received November 13, 2003; E-mail: enrique.garcia-es@uv.es

Very often, biological processes are assisted by amino groups that fix or react with a given compound. A paramount example of such chemistry comes from the enzyme *rubisco*, which participates in the fixation of CO₂ by green plants through the formation of a carbamate moiety by reaction of CO₂ and a lysine assisted by Mg²⁺ or Mn²⁺ ions.¹ The elusive carbamate moiety is further stabilized by formation of a hydrogen-bond network with other amino acid residues.

In past years, some of us have concentrated on the study of the coordination chemistry of [1+1] aza cyclophane molecules containing different aromatic spacers and donor atoms.² The goal was to generate coordinatively unsaturated metal sites, which could bind different substrates through the formation of ternary complexes occupying the vacant positions in the coordination sphere or by removing the labile ancillary ligands that would be completing the coordination spheres of the metal ions.

Following these ideas, we had recently incorporated in our [1+1] cyclophane ligands the polyamine 4,7,10-triazatridecane-1,13-diamine connected through methylene groups to a 2,6-pyridine spacer.³ We wanted to achieve the coordination of one metal ion even if the polyamine chain had several protonated nitrogen donors. However, in the case of this macrocycle, its size and flexibility permit the involvement of all of the nitrogen atoms in the coordination to the metal. To block the metal ion at one side of the molecule and leave free the other one to lodge additional substrates, we have now replaced 2,6-pyridine by 2,2':6',2''-terpyridine as spacer to give ligand **L** (Scheme 1).

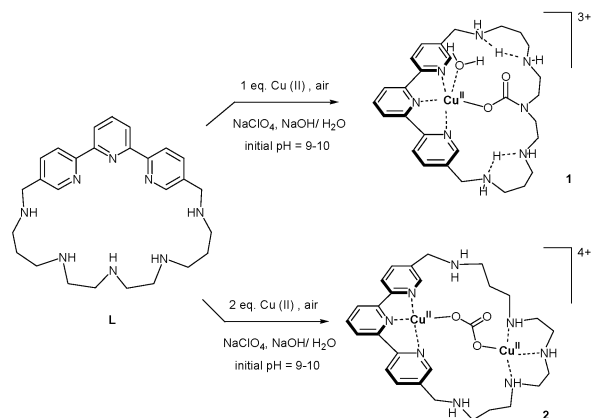
Indeed, terpyridine has been used as a ligand by itself and as a building block of a variety of supramolecular metal assemblies due to its capacity for fitting three corners of a polyhedron.⁴ Also, in a few cases, terpyridine has been used as an integral part of azacyclophane structures.⁵

Preliminary potentiometric studies on the coordination ability toward Cu²⁺ of **L** at variable pH show the formation of mononuclear species of [Cu(H₃L)]^{(2+x)+} stoichiometries with *x* ranging from 3 to 0 and the dinuclear hydroxylated species [Cu₂L(OH)]³⁺ and [Cu₂L(OH)₂]²⁺. For M:L molar ratios of 2:1, the dinuclear hydroxylated species prevail in solution over pH 7 (see Supporting Information).

Slow evaporation in an open vessel of aqueous solutions containing Cu(ClO₄)₂ and **L** in molar ratios of 1:1 with an initial pH of 9 yielded crystals suitable for X-ray diffraction of [Cu(H₂L)(H₂O)(carb)](ClO₄)₃·2H₂O (carb = carbamate) (**1**).⁶

The structure of **1** consists of three perchlorate anions and of the trivalent cation [Cu(H₂L)(H₂O)(carb)]³⁺ in which the metal ion has a square-pyramidal geometry: The base of the pyramid is constituted by the three pyridinic nitrogens (Cu–N(1) = 1.95(1) Å, Cu–N(2) = 2.02(1) Å, Cu–N(3) = 2.03(1) Å) and one oxygen

Scheme 1



atom of the carbamate group (Cu–O(1B) = 1.90(1) Å). The distorted axial position is occupied by a water molecule (Cu–O(100) = 2.275(8) Å) (Figure 1). The carbamate group is generated in situ by reaction of atmospheric CO₂ with the central amino group of the aliphatic chain without the need of bubbling CO₂ into the solution. The distances in this moiety are as follows: C–O(1b) = 1.30(2) Å, C–O(1a) = 1.20(2) Å, and C–N = 1.40(2) Å. All of the angles are close to 120°. The carbamate unit is further stabilized in the complex by intramolecular hydrogen bonding of the noncoordinated oxygen atom with the coordinated water molecule (O(1a)–O(20) = 2.82 Å) and with one of the amino groups adjacent to the central position O(1a)–N(7) = 2.83 Å. It is difficult to establish the protonated nitrogens in the polyamine chain. However, it seems logical that they can be any one of those connected by the propylene chains. Moreover, the formation of a hydrogen bond between the noncoordinated carbonyl of carbamate and one of the adjacent nitrogens to the bound amino group strongly suggests that this nitrogen is a firm candidate to be protonated.

As far as we know, this is the first reported structure of an abiotic system in which a carbamylation produced by atmospheric CO₂

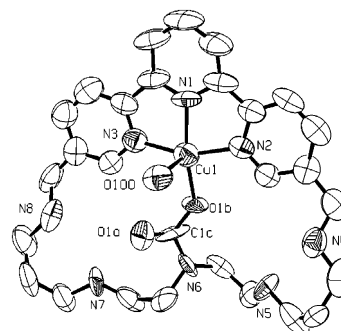


Figure 1. ORTEP drawing of the cation [Cu(H₂L)(H₂O)(carb)]³⁺ (carb = carbamate). Thermal ellipsoids are drawn at the 50% probability level.

[†] Instituto de Ciencia Molecular.

[‡] Instituto de Materiales de la Universidad de Valencia.

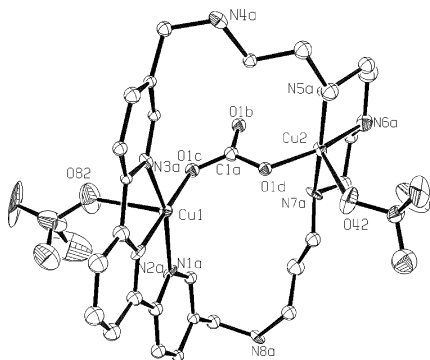


Figure 2. ORTEP drawing of one of the $[\text{Cu}_2(\text{H}_2\text{L})(\text{CO}_3)(\text{ClO}_4)_2]^{2+}$ subunits present in the asymmetric unit of **2**. Thermal ellipsoids are drawn at the 30% probability level.

and assisted by a complexed metal ion and by the presence of amino groups in the environment is produced within a macrocyclic structure.⁷ Interestingly enough, Cu^{2+} complexes of ligands containing the same polyamine bridge but pyridine or phenanthroline spacers did not show such a behavior.³ Therefore, these results suggest that carbamate stabilization needs a binding group able to fix spatially the divalent metal ion that assists the process as a Lewis acid and an environment which, at the same time, can acquire positive charge and form a hydrogen-bond network involving the elusive carbamate moiety.

This situation denotes the great avidity that these complexes have for taking up atmospheric CO_2 . Indeed, crystals of formula $[\text{Cu}_2(\text{H}_2\text{L})(\text{CO}_3)](\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ (**2**) were obtained when slowly evaporating in an open vessel aqueous solutions containing $\text{Cu}(\text{ClO}_4)_2$ and **L** in molar ratios of 2:1 with an initial pH of 9 (Figure 2).⁸ In this case, the crystal structure consists of two almost equivalent dinuclear $[\text{Cu}_2(\text{H}_2\text{L})(\text{CO}_3)]^{4+}$ cations, perchlorate anions, and water molecules.

The Cu^{2+} bound at the pyridine site presents strongly distorted square-planar coordination geometry. The metal ion is bound at the equatorial plane to the three pyridine nitrogens and to one oxygen of the bridging carbonate group. It is interesting to remark that the shorter bond distances correspond to the nitrogen of the central pyridine ring ($\text{Cu}(1)-\text{N}(2\text{A}) = 1.93(1) \text{ \AA}$) and to the oxygen atom of the carbonate bridging ligand ($\text{Cu}(1)-\text{O}(1\text{C}) = 1.91(1) \text{ \AA}$). The axial position is occupied by the oxygen atom of a perchlorate anion. The second metal ion, which is bound at the polyamine site, presents also a square-pyramidal geometry. The equatorial plane is formed by the three central nitrogens of the polyamine bridge, N(7A), N(6A), and N(5A), and by an oxygen atom of carbonate, O(1D). The distorted axial position is occupied by an oxygen atom of a perchlorate anion. The squares of the two coordination sites are placed in planes with different elevations which are interconnected by the carbonate anion that acts as a η^1 : η^1 bridging ligand. The angles in the carbonate units are close to 120° , and the distances are as follows: $\text{C}(1\text{a})-\text{O}(1\text{b}) = 1.26(2) \text{ \AA}$, $\text{C}(1\text{a})-\text{O}(1\text{a}) = 1.28(2) \text{ \AA}$, and $\text{C}(1\text{a})-\text{O}(1\text{d}) = 1.33(2) \text{ \AA}$. This coordination mode of carbonate has precedent, for instance, in the way in which carbonate is coordinated in anhydrous copper carbonate or in the way in which it was found in a binuclear complex of a porphyrin-type ligand.⁹ The noncoordinated nitrogens N4a and N8a should both be protonated. Thereby, in the case of

the dinuclear complex, the assistance for the binding of CO_2 comes from the second metal ion, and CO_2 is fixed as a bridging carbonate ligand between the metal ions.¹⁰

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Supporting Information Available: Description of the synthesis and characterization of **L**. Table of protonation constants of **L** and stability constants for the formation of Cu^{2+} complexes of **L**. CIF files for structures **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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