A Dimeric Tetranuclear Copper(II) Compound Assembled through Pentacoordinating Carbonate Anions

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Keywords: Macrocycle / Pyrazole / N-Heterocycle / Carbonate / Copper

The 22-membered macrocycle, spanning four endocyclic pyrazole groups, viz. 1,4,9,14,17,22,27,28,29,30-decaaza-5,13,18,26-tetramethylpentacyclo[24.2.1.1^{4,7}.1^{11,14}.1^{17,20}]-triacontane-5,7(28),11(29),12,18,20(30),24(27),25-octaene (**22Pz**), rendered the tetranuclear compound $[Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4$. The copper(II) ions are in distorted octahedral N_3O_3 environments. All four pyrazole groups of each macrocycle participate in the coordination of the copper(II) ions. The cationic part of this compound is in fact a dimer of two macrocyclic ligands, each containing two copper(II) ions bridged by two carbonate ions in the highly unusual pentacoordinating fashion.

Introduction

In the course of our investigations towards model compounds[1-4] for type-3 site copper proteins, like the important dioxygen processing enzymes hemocyanin and tyrosinase,[5-7] the macrocyclic ligand 9,22-di(pyridin-2-ylmethyl)-1,4,9,14,17,22,27,28,29,30-decaaza-5,13,18,26-tetramethylpentacyclo[24.2.1.1^{4,7}.1^{11,14}.1^{17,20}]triacontane-5,7(28),11(29),12,18,20(30),24(27),25-octaene (**MePy22Pz**) which contains four endocyclic pyrazole groups and two exocyclic pyridine groups, has been synthesised in an eleven-step procedure.[8,9] Several dinuclear coordination compounds have been prepared with this macrocyclic ligand, notably some copper(I) complexes which were found to bind one equivalent of dioxygen between the two copper ions as an O_2^{2-} anion in an end-on *trans*-μ-1,2-peroxo fashion inside the 22-membered cavity.[10] This appeared to be the first example of a dinuclear copper complex capable of binding dioxygen at room temperature in a protic solvent.

While processing a solution of this ligand with a copper(II) salt and sodium carbonate, with the objective to obtain a carbonate-bridged dinuclear copper(II) compound, the pendent pyridine arms were hydrolysed and a unique tetranuclear copper(II) compound resulted in which the carbonate groups indeed bridge the copper ions, but in an uncommon pentacoordinating fashion. The present paper reports the structure of this unusual carbonate-bridged tetranuclear copper compound.

Results and Discussion

Synthetic Aspects

The tetranuclear copper(II) compound $[Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4$ has been obtained by treating a solution of MePy22Pz and copper(II) perchlorate in methanol/water with a solution of sodium carbonate in water. During this process hydrolysation at the tertiairy nitrogen of the macrocycle resulted in the loss of the pendent pyridine groups and the formation of the "bare" 22-membered macrocycle **22Pz**. Vapor diffusion with diethylether resulted in the growth of single crystals of the coordination compound suitable for X-ray diffraction. The ligand field spectrum of this compound shows an asymmetric band at 16500 cm^{-1} in compliance with the distorted N_3O_3 environments of the copper(II) ions (vide supra). NMR spectra of the compound in solution could not be obtained due to linebroadening paramagnetism.

Description of the Structure

A PLUTON[11] plot of the cationic part is given in Figure 1. The asymmetric unit comprises half a molecule $[Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4$, the other half of the molecule is generated through a center of symmetry.

Firstly it is to be remarked that the ligand in this tetranuclear compound is a derivative of the macrocycle MePy22Pz,[8-10] viz. 1,4,9,14,17,22,27,28,29,30-decaaza-5,13,18,26-tetramethylpentacyclo[24.2.1.1^{4,7}.1^{11,14}.1^{17,20}]triacontane-5,7(28),11(29),12,18,20(30),24(27),25-octaene (**22Pz**) as during the synthesis of the coordination compound the pyridine groups and spacers were lost through hydrolysis. Also, all pyrazole groups are involved in the coordination of the copper ions, which appeared not to be the

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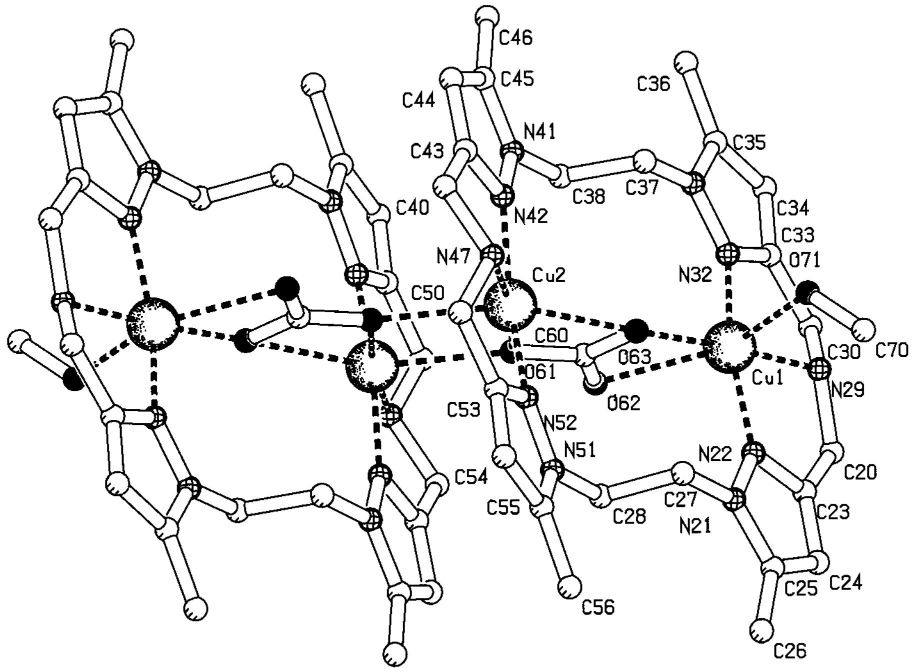

Figure 1. A PLUTON[11] projection of $[Cu_4(22Pz)_2(CO_3)_2(MeOH)_2]^{4+}$; hydrogen atoms are omitted for clarity

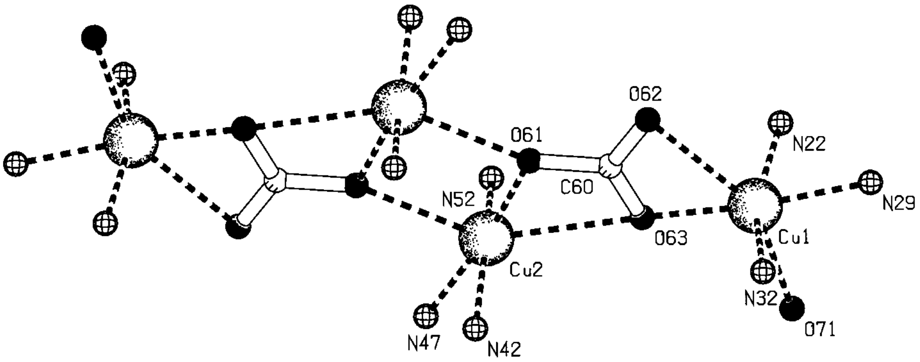

Figure 2. A PLUTON[11] projection of the coordination environments of the four copper(II) ions in the tetranuclear dimeric cation, showing the pentacoordination of the carbonate ions

case with the parent ligand MePy22Pz.[12] The most remarkable feature, however, is the penta-coordination mode of the carbonate ions (see Figure 2) with regular copper to oxygen bonds of 1.934(5) and 1.905(5) Å between respectively Cu(1) and O(63) and between Cu(2) and O(61), while the Cu(1) to O(62), the Cu(2) to O(61)a, and the Cu(2) to O(63) distances of respectively 2.589(8), 2.453(6), and 2.668(5) Å are regarded as *semi*-bonding distances (see Table 1).

O(62) binds to Cu(1), O(63) bridges between Cu(1) and Cu(2) in the same macrocyclic ring, while O(61) bridges between Cu(2) and Cu(1) in different macrocyclic rings. So, the two carbonate ions are bridging both intramolecularly and intermolecularly, thereby effecting that the tetranuclear cation is in fact a dimer of two dinuclear parts, viz. $[\{Cu_2(22Pz)(CO_3)(MeOH)\}^{2+}]_2$. Multiple bridging of carbonate groups in coordination compounds is not a rare phenomenon,[13,14] but only one compound has been reported so far,[13] viz. a trinuclear nickel compound,[15] in which the carbonate ion also bridges in a pentacoordinating fashion, in this case with five regular nickel to oxygen bonding distances (varying between 2.14 and 2.22 Å).

The coordination geometries of both copper ions are roughly the same. Each copper(II) ion is in a distorted, more or less elongated, octahedral N_3O_3 environment, with N(22), N(29), N(32), and O(63) equatorial and O(71) and O(62) axial for Cu(1) and with N(42), N(47), N(52), and O(61) equatorial and O(63) and O(61)a axial for Cu(2). The largest distortion from regular octahedral symmetry is of course caused by the didentate carbonate oxygens, imposing O−Cu−O angles of about 55° (see Table 1 and Figure 2).

The three-bond ligand bites contribute also to the deviation from regular octahedral symmetry. The two copper ions in the same macrocyclic ring, viz. Cu(1) and Cu(2), are at a distance of 4.601(2) Å, a distance suitable for the binding of a small molecule like dioxygen in a bridging fashion between the two copper ions. Two of the copper ions in different macrocyclic rings, viz. Cu(2) and Cu(2)a, are even

Table 1. Selected bond lengths [Å] and angles [deg] for $[\mathrm{Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4}$

Cu(1)−N(32) 1.979(7)	Cu(2)−N(52) 2.004(7)
Cu(1)−N(29) 2.039(7)	Cu(2)−O(61) 1.905(5)
Cu(1)−N(22) 2.000(7)	Cu(2)−N(42) 2.006(7)
Cu(1)−O(63) 1.934(5)	Cu(2)−N(47) 2.007(7)
Cu(1)−O(71) 2.294(5)	Cu(2)−O(61)a 2.453(6)
Cu(1)−O(62) 2.589(8)	Cu(2)−O(63) 2.668(5)
Cu(1)−Cu(2) 4.601(2)	Cu(2)−Cu(2)a 3.240(2)
O(63)−Cu(1)−N(29) 173.0(3)	O(61)−Cu(2)−N(47) 171.9(3)
O(63)−Cu(1)−O(71) 94.8(2)	O(61)−Cu(2)−N(52) 100.3(3)
O(63)−Cu(1)−N(32) 99.0(3)	O(61)−Cu(2)−N(42) 98.2(3)
O(63)−Cu(1)−N(22) 99.0(3)	O(61)−Cu(2)−O(61)a 84.8(2)
O(71)−Cu(1)−N(32) 93.3(3)	N(42)−Cu(2)−N(47) 80.7(3)
O(71)−Cu(1)−N(29) 92.2(3)	N(42)−Cu(2)−N(52) 161.0(3)
O(71)−Cu(1)−N(22) 93.0(3)	N(42)−Cu(2)−O(61)a 90.6(3)
N(22)−Cu(1)−N(32) 160.4(3)	N(47)−Cu(2)−N(52) 81.6(3)
N(22)−Cu(1)−N(29) 80.8(3)	N(47)−Cu(2)−O(61)a 87.3(3)
N(29)−Cu(1)−N(32) 80.4(3)	N(52)−Cu(2)−O(61)a 95.4(3)
O(62)−Cu(1)−O(63) 56.9(2)	O(63)−Cu(2)−O(61) 55.0(2)
O(62)−Cu(1)−O(71) 151.5(2)	O(63)−Cu(2)−N(42) 93.6(2)
O(62)−Cu(1)−N(22) 93.9(3)	O(63)−Cu(2)−N(47) 132.9(3)
O(62)−Cu(1)−N(29) 116.2(3)	O(63)−Cu(2)−N(52) 93.4(2)
O(62)−Cu(1)−N(32) 89.2(3)	O(63)−Cu(2)−O(61)a 139.7(2)

a = $1-x$, $-y$, $-z$.

on a smaller distance [3.240(2) Å] of course resulting from the bridging of O(61) (see Figure 2).

Experimental Section

Synthesis of $[\mathrm{Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4}$: To a solution of 25.0 mg of 9,22-di(pyridin-2-ylmethyl)-1,4,9,14,17,22,27,28,29,30-decaaza-5,13,18,26-tetramethylpentacyclo-$[24.2.1.1^{4,7}.1^{11,14}.1^{17,20}]$triacontane-5,7(28),11(29),12,18,20(30),24(27),25-octaene (**MePy22Pz**)[9][12] (38.8 mmol) in 5 mL of MeOH and 1 mL of H_2O, two equivalents (1.3 mL) of a solution of $\mathrm{Cu(ClO_4)_2 \cdot 6\ H_2O}$ in MeOH (59 mmol) were added. A clear green solution was obtained after gentle warming and subsequent filtration. Addition of one equivalent Na_2CO_3 (77.6 mmolar solution in H_2O) invoked a blue colorisation for only a few seconds. After filtration a clear green solution was obtained. Vapour diffusion with Et_2O at 298 K resulted after three weeks in light-blue crystals, suitable for X-ray diffraction, of $[\mathrm{Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4}$, with **22Pz** being 1,4,9,14,17,22,27,28,29,30-decaaza-5,13,18,26-tetramethylpentacyclo$[24.2.1.1^{4,7}.1^{11,14}.1^{17,20}]$triacontane-5,7(28),11(29),12,18,20(30),24(27),25-octaene.

Materials and Methods: FT-IR spectra were recorded on a Perkin Elmer paragon 1000 FT-IR spectrometer as KBr disks (4000−400 cm^{-1}). Ligand field spectra were registered on a Perkin Elmer lambda 900 UV/Vis/NIR spectrometer.

X-ray Structure Analysis of $[\mathrm{Cu_4(22Pz)_2(CO_3)_2(MeOH)_2](ClO_4)_4(MeOH)_4}$: $C_{51}H_{84}Cl_4Cu_4N_{20}O_{30}$, M = 1901.39, light-blue prismatic crystal (0.12 × 0.37 × 0.37 mm), Enraf-Nonius CAD4T diffractometer with rotating anode, $\lambda(\text{Mo-}K\alpha) = 0.71073$ Å, T = 290 K, monoclinic, $P2_1/c$, a = 12.419(3), b = 23.058(4), c = 14.743(4) Å, $\beta = 109.98(2)°$, $V = 3968(2)$ Å^3, Z = 2, D_c = 1.592 gcm^{-3}, $\mu(\text{Mo-}K\alpha) = 12.8\ cm^{-1}$, $F(000)$ = 1956, θ max = 26.5°, h, k, l range = −14/14, −27/27, 0/17, a total of 15281 reflections, of which 7462 unique, with R_{int} = 0.139 (poor crystal quality) and 3263 observed [$I>2\sigma(I)$], R = 0.087 (wR 0.23, S 0.89), ρ min/max = −0.47/1.05 e/Å^3, n(pars) = 561, correction for Lorentz and polarization, no absorption correction. Structure solved with automated Patterson techniques (DIRDIF/PATT[16]), refined on F^2, full-matrix least-squares (SHELXL-97.[17,18]) All non-hydrogen atoms refined with anisotropic displacement parameters, hydrogen atoms introduced on calculated positions and refined riding on their carrier atoms. The disordered perchlorate anions were isotropically refined with the oxygens on partly occupied positions, as were the non-hydrogens of the lattice solvent molecules without calculated hydrogens. Geometric calculations and molecular graphics were performed with PLATON.[11] Table 1 contains selected bond lengths and angles.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103045. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors are indebted to the EU for a grant as Host Institute in the EU Programme Human Capital and Mobility (1994−1997). Use of the services and facilities of the Dutch National NWO/SURF Expertise Center CAOS/CAMM, under grant numbers SON 326-052 and STW NCH99.1751, is gratefully acknowledged.

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Received September 25, 1998
[I98332]