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Synthesis of a Novel Sandwich Copper Complex $[(TACN)_2Cu](ClO_4)_2 \cdot H_2O$

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A novel sandwiched copper(II) complex with the ligand 1,4,7-triazacyclononane has been synthesized and characterized by using X-ray diffraction analysis. The results indicate that its crystallographic structure is monoclinic, possessing parameters: P2(1)/c, a = 9.5896(3) Å, b = 13.5820(10) Å, c = 9.5850(3) Å, α = 90.00°, β = 119.3850(10)°, γ = 90.00°, v = 1087.79(5) Å^3, Z = 2, Dx = 1.627 mg cm^{-3}, R = 0.0560, ωR = 0.1548, F(000) = 550.

Key Words: Copper(II) complex, Triazacyclononane, Sandwich structure.

INTRODUCTION

Interests in the synthesis and complexation properties of compounds comprising linked 1,4,7-triazacyclononane (TACN) macrocycles and its derivates have expanded considerably over the last two decades[1–14]. Not only are they ideally suited to producing polynuclear complexes of high kinetic and thermodynamic stability whilst leaving two or three coordination sites available per metal centre for the attachment of additional ligands or bridge formations, but also in some cases the resulting complexes find application as models for metallobiosites[2, 4, 5], catalytic reagents[9] and in the study of magnetic interactions between metal centres[4, 6, 8, 10, 14]. Many catalytic reagents, such as Cp_2Fe, Cp_2Ti, have sandwich structure and the non-sandwich structure complex of $[(TACN)Cu](Cl_2)$ about its catalytic character is known[9]. It is clear that the catalytic characteristics of a substance are closely related to its crystallographic structure. Hence, synthesis of a substance with novel structures is of great significance. In this communication, the synthesis of copper complex $[(TACN)_2Cu](ClO_4)_2 \cdot H_2O$ with a novel structure is reported.

EXPERIMENTAL

1,4,7-triazacyclononane (TACN) was synthesized as described elsewhere[15]. $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared in our laboratory. All solvent were commercially available and of analytical grade. IR spectra were recorded on a Nicolet 170sx spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 240 analyzer.

To a 25 mL methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (371 mg, 1 mmol) was added a 5 mL methanol solution of TACN (2 mmol) with constant stirring. The

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mixture was refluxed for 1 h to obtain a clear blue solution and after standing at room temperature for three weeks, well-shaped blue single crystals were obtained by slow evaporation. Perchlorate salts of metal complexes with organic ligands are potentially explosive. The dilute solutions were handled with great caution and evaporated slowly at room temperature. IR (KBr, cm^{-1}): 3306 (vs), 2925, 1089 (vs). Anal. Calcd. for $[(TACN)_2Cu](ClO_4)_2 \cdot H_2O$: C, 27.02; H, 6.00; N, 15.76%; Found: C, 27.16; H, 5.87; N, 16.07%.

Crystal structure determination

A deep blue crystal having approximate dimensions of $1.40 \times 0.46 \times 0.16$ mm was selected and mounted on a glass fibre in a random orientation for X-ray diffraction study. Diffraction experiments were performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoKα radiation ($\lambda = 0.71073$) at temperature 293(2) K, ω scan technique $2.86° \leq \theta \leq 25.00°$. A total of 3370 reflections were collected, of which 1873 reflections were unique with $R_{int} = 0.0324$. Lp effects and empirical absorption were applied in data eorrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 142 variable parameters for 1873 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R = \Sigma (| |F_0| - |F_c| |)/\Sigma |F_0| = 0.0560 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.1548 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.00984P)^2 + 1.7425P]$ and $P = (F_0^2 + 2F_c^2)/3$.

The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.795 and –0.887e/ $Å^3$, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters obtained are given in Table-1. The selected bond lengths and bond angles are listed in Table-2.

The molecular structure of $[(TACN)_2Cu](ClO_4)_2 \cdot H_2O$ is shown in Fig. 1, with hydrogen atoms, a molecular H_2O and anion ClO_4 being omitted.

In the compound, the title complex is the sandwich structure. Cu is located between two ligands (TACN) and coordinated by six N from two ligands (TACN). The Cu atom is in a slightly distorted octahedral geometry. This configuration is consistent with the coordination character of the ligand TACN, *i.e.*, two nitrogen atoms (N1(A) and N2(A)) are located in the plane CuN(2)N(2A)N(1)N(1A) (which are formed by the nitrogen atoms combined with the Cu atom and the two other coordination atoms); while the other nitrogen atom N3(A) is at the axis nearly normal to the plane. That can be proved by the following data: The mean deviation of the CuN(2)N(2A)N(1)N(1A) plane is *ca.* 0.0000 Å. The bond length of N(3)-Cu, [or N(3A)-Cu] (2.269(4) (Å)) are longer than the bond length of N(2)-Cu [or N(2A)-Cu] (2.129(4) (Å)) and N(1)-Cu [or N(1A)-Cu] (2.075(3) (Å)).

TABLE-1
NON-HYDROGEN ATOMIC COORDINATES ($\times 10^4$)
AND THERMAL PARAMETERS ($\times 10^3$ Å^2)

Atom	X	Y	Z	U(EQ)
CU	5000	5000	5000	27(1)
N(1)	3418(4)	5467(3)	5755(4)	42(1)
N(2)	2894(5)	4347(3)	3125(5)	48(1)
N(3)	3966(5)	6337(3)	3396(4)	47(1)
C(1)	1841(6)	4969(3)	4840(7)	49(1)
C(2)	1954(6)	4084(4)	3916(7)	55(1)
C(3)	2013(6)	5043(3)	1769(6)	46(1)
C(4)	3088(6)	5873(4)	1795(5)	50(1)
C(5)	2966(6)	6876(3)	3909(5)	46(1)
C(6)	3311(6)	6545(4)	5581(6)	50(1)
CL	7043(1)	8676(1)	6135(1)	45(1)
O(1)	6866(8)	9698(3)	6329(6)	93(2)
O(2)	8678(5)	8480(4)	6691(6)	86(1)
O(3)	6489(6)	8113(4)	7028(5)	79(1)
O(4)	6140(6)	8412(4)	4482(5)	76(1)
O(5)	9852(16)	7646(14)	4744(17)	127(5)

TABLE-2
THE SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Bond	Bond length	Angle	(°)	Angle	(°)
CU-N(1)	2.075(3)	N(1)-CU-N(1A)	180.000(1)	C(6)-N(1)-C(1)	113.0(4)
CU-N(1A)	2.075(3)	N(1)-CU-N(2)	82.45(15)	C(6)-N(1)-CU	106.7(3)
CU-N(2)	2.129(4)	N(1A)-CU-N(2)	97.55(15)	C(1)-N(1)-CU	111.2(3)
CU-N(2A)	2.129(4)	N(1)-CU-N(2A)	97.55(15)	C(2)-N(2)-C(3)	111.9(4)
CU-N(3)	2.269(4)	N(1A)-CU-N(2A)	82.45(15)	C(2)-N(2)-CU	103.4(3)
CU-N(3A)	2.269(4)	N(2)-CU-N(2A)	180.00	C(3)-N(2)-CU	111.7(3)
N(1)-C(1)	1.487(6)	N(1)-CU-N(3A)	99.18(14)	C(5)-N(3)-C(4)	115.2(4)
N(1)-C(6)	1.471(6)	N(1A)-CU-N(3A)	80.82(14)	C(5)-N(3)-CU	108.2(3)
N(2)-C(3)	1.478(7)	N(2)-CU-N(3A)	99.01(14)	C(4)-N(3)-CU	101.5(3)
N(2)-C(5)	1.490(6)	N(2A)-CU-N(3A)	80.99(14)	N(1)-C(2)-C(1)	111.0(4)
N(3)-C(5)	1.470(6)	N(1)-CU-N(3)	80.82(14)	N(2)-C(2)-C(1)	110.0(4)
N(3)-C(4)	1.481(6)	N(1A)-CU-N(3)	99.18(14)	N(2)-C(3)-C(4)	111.5(4)
		N(2)-CU-N(3)	80.99(14)	N(3)-C(3)-C(4)	111.6(4)
		N(2A)-CU-N(3)	99.01(14)	N(3)-C(5)-C(6)	111.2(4)
		N(3A)-CU-N(3)	180.00(1)	N(1)-C(6)-C(5)	112.1(4)

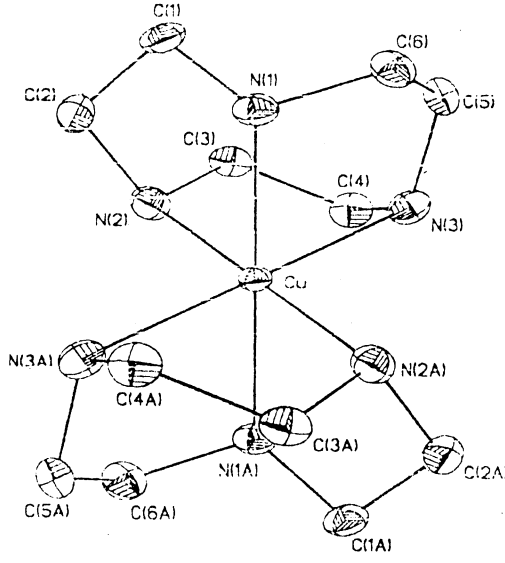

Fig. 1. The molecular structure of the title complex (omitted the water and the anion ClO_4^-)

Fig. 2 depicts the molecular packing in the unit cell, indicating that the adjacent molecules are linked to others by classical hydrogen bonds which connected the hydrogen atom of water to the oxygen atom of anion ClO_4 and slightly nonclassical hydrogen bonds, connecting the oxygen atom to the hydrogen atom of methylene of the macrocycle. They are revealed by the distance of 2.846 Å between oxygen atom

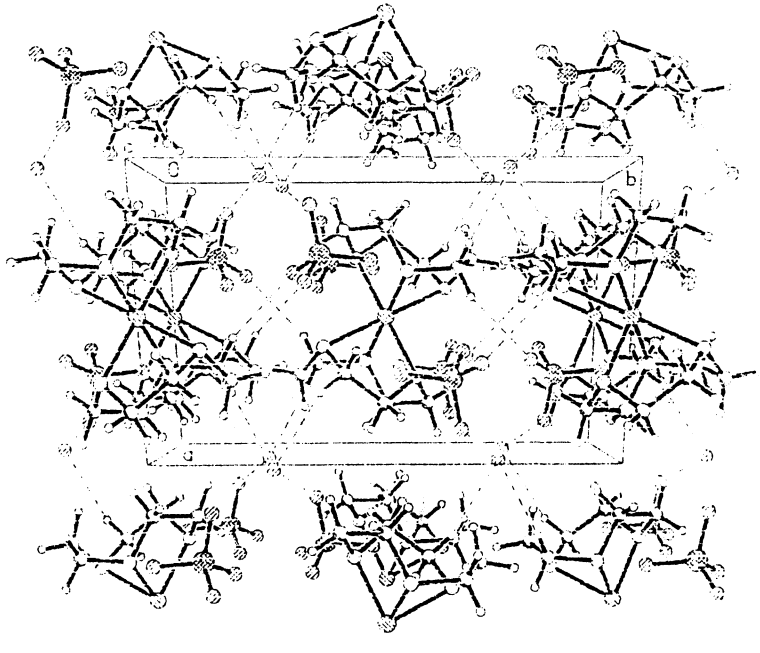

Fig 2. Molecular packing arrangement in the unit cell

of water and adjacent oxygen atom of anion or the distance of 3.406 between oxygen atom and adjacent hydrogen atom of macrocycle.

Conclusion

A sandwich structure copper complex with the ligand 1,4,7-triazacyclononane has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The studies of the catalytic characteristics about this complex are in progress.

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