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# Synthesis, Structure of $Me_6[14]N_4diene\cdot(ClO_4)_2$ and the Cyclic Voltammetry Measurement of its Copper(II) Complex

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The $Me_6[14]N_4diene\cdot(ClO_4)_2$ (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene·$2ClO_4$) has been synthesized and determined by X-ray diffraction. The crystal is orthorhombic, space group P2(1)/c with unit cell parameters: a = 14.9753(6)Å, b = 9.2169(4)Å, c = 16.4902(9)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2276.07(18)Å$^3$, Z = 8, Dc = 1.411 g/cm$^3$, $\mu = 0.334$ mm$^{-1}$, T = 293(2) K, Mr = 241.69, F(000) = 1032, R = 0.0626 and wR = 0.1745. The cyclic voltammograms of its copper(II) complex has been investigated.

**Key Words: Tetraaza-macrocycle, Crystal structure, Cyclic voltammetry.**

## INTRODUCTION

The research of macrocycle compounds is in a period of remarkable growth for their special structure and characters[1-8]. Now we report the synthesis, crystal structure of $Me_6[14]N_4diene\cdot(ClO_4)_2$ and the cyclic voltammetry character of its copper(II) complex.

## EXPERIMENTAL

IR spectra were recorded on Nexus-870 spectrophotometer. Elemental analysis were performed on Elementar Vario ELZ(III) analyzer. Cyclic voltammograms were tested by LK 2005 Electrochemical workstations. The crystal structure was determined by Siemens SMART CCD area-detector diffractometer.

The $Me_6[14]N_4diene\cdot(ClO_4)_2$ was prepared by mixed acetone and diamine. It was dissolved in methanol, keep the clear solution at room temperature for 1 week, colourless single crystals were obtained by slow evaporation.

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The cyclic voltammograms of its copper(II) complex (0.05 mol/L), which was prepared by mixed $Cu(ClO_4)_2 \cdot 6H_2O$ and $Me_6[14]N_4$diene$\cdot(ClO_4)_2$ in methanol, was dissolved in water. We used GC as the work pole, Pt as assistant pole, SCE as reference electrode. The range of voltage was from -0.2V to 1.0V.

## RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are listed in Table-1. The selected bond lengths and bond angles are listed in Table-2. Fig. 1 shows the molecular structure of the compound. Fig. 2 shows the packing arrangement of the unit cell of the compound. Fig. 3 shows the cyclic voltammograms of its copper(II) complex. The IR spectrum (KBr, $\nu_{max}$, $cm^{-1}$): (N-H) 3210, ($ClO_4^-$) 1090, 627, (C=N) 1642. The elemental analysis for $Me_6[14]N_4$ diene$\cdot(ClO_4)_2$: Calcd. (%) C, 50.1; H, 9.4; N, 14.6. Found: (%) C, 50.1; H, 9.1; N, 14.4.

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

| Atom | X | Y | Z | U(eq) |
|---|---|---|---|---|
| N(1) | 4033(1) | 982(2) | 855(1) | 26(1) |
| C(1) | 4154(2) | 55(3) | 2231(1) | 43(1) |
| Cl | 1419(1) | 1512(1) | 668(1) | 44(1) |
| O(1) | 1655(3) | 2953(3) | 538(3) | 121(1) |

TABLE-2
BOND LENGTHS (Å) AND ANGLES (º)

| Bond | Length | Angle | (º) |
|---|---|---|---|
| N(1)-C(8) | 1.492(3) | C(8)-N(1)-C(3) | 116.49(16) |
| C(1)-C(3) | 1.527(3) | N(1)-C(3)-C(2) | 109.52(18) |
| Cl-O(1) | 1.391(3) | O(1)-Cl-O(2) | 112.90(2) |

A single crystal (0.50 mm × 0.35 mm × 0.13 mm) was selected for crystallographic data collection at 293(2)K and structure determinated with graphite-monochromatic $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å). A total of 16162 reflections were collected in the range of $2.72° \leq \theta \leq 27.48°$, of which 2595 reflections were unique with $R_{int} = 0.0200$. The final full-matrix least-squares refinement including 136 variable parameters for 2595 reflec-tions with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of R = 0.0626 and wR = 0.1745, where $w = 1/[\sigma^2(F_0^2) + (0.00902P)^2 + 1.8191P]$ and $P = (F_0^2 + 2FC^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.516 and -0.644 e/$Å^3$ (CCDC No. 646128), respectively.

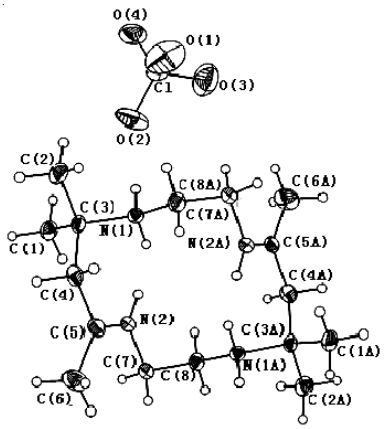


Fig. 1. Molecular strucutre

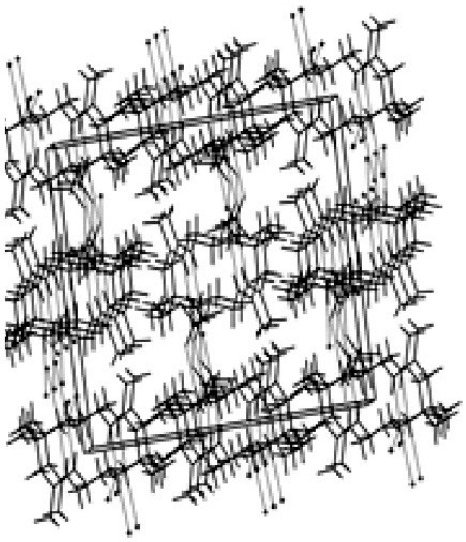

Fig. 2. Molecular packing arrangement

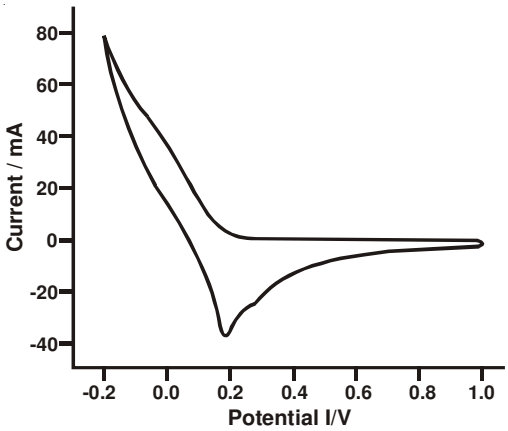


Fig. 3. Cyclic voltammograms of copper(II) complex

**Cyclic voltammograms of its copper(II) complex:** Fig. 3 showing, there was only one oxidation apex at 0.18 with the scan rate of 0.05v/s, but there was no deoxidize apex, so the electrolyse course was irreversible. It is interesting to find that the title compound has potential effect in redox process by comparing with the hydrate copper ($E^0 = 0.159$).

## Conclusion

$M_6[14]N_4$ diene·$(ClO_4)_2$ has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. The cyclic voltammograms of its copper(II) complex has been tested. The studies of more characteristics about it are in progress.

## ACKNOWLEDGEMENT

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