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Key indicators

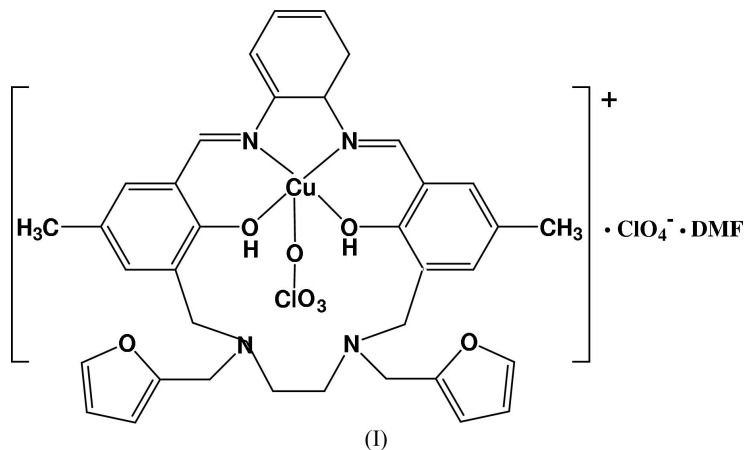
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.061
 wR factor = 0.140
Data-to-parameter ratio = 14.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(Perchlorato- κ O)[3,6,14,21-tetraaza-3,6-difuryl-27,28-dihydroxy-10,25-dimethyltetracyclo-[18.4.3.3^{8,12}.0^{15,20}]octacos-8,10,12(28),13,17,19,-21,23,25,27(1)-decaene- κ^4 N,N',O,O']copper(II) perchlorate dimethylformamide solvate**

In the title complex, $[\text{Cu}(\text{C}_{36}\text{H}_{36}\text{N}_4\text{O}_4)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{C}_3\text{H}_7\text{N}$, the coordination number of the Cu^{II} atom is 5 and the coordination configuration is best described as distorted tetragonal–pyramidal. There is a 13-membered macrocyclic ring in the molecule. One perchlorate anion and the dimethylformamide molecule do not participate in coordination. There are four intramolecular hydrogen bonds in the structure and these constrain the conformation of the macrocycle and enhance its stability.

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Comment

It is of interest to investigate metallic complexes with macrocyclic binucleating ligands containing different binding sites, in order to reproduce the behaviour of certain metallo-proteins (Coughlin *et al.*, 1984). In the course of our study in this field, we synthesized the title complex, (I).



In complex (I), the Cu^{II} atom lies at the centre of a quadrilateral, which consists of two phenolic O atoms and two imino N atoms (O1, O2, N1 and N2). The average Cu–O and Cu–N bond lengths are 1.922 (2) and 1.938 (2) Å, respectively. The Cu^{II} atom deviates from the Cu1/O1/O2/N1/N2 plane by 0.0459 (11) Å. A perchlorate anion coordinates to the Cu^{II} atom axially above this plane, with a Cu1–O5 bond length of 2.679 (2) Å, which is slightly longer than that of a reported perchlorate Cu–O distance [2.574 (2) Å; Li *et al.*, 1997]. Thus, the coordination number of the Cu^{II} atom is 5 and the coordination configuration is best described as distorted tetragonal–pyramidal.

There is a 13-membered macrocyclic ring in the complex, which includes one Cu atom, two O atoms, two N atoms and eight C atoms. A second perchlorate anion and a dimethyl-

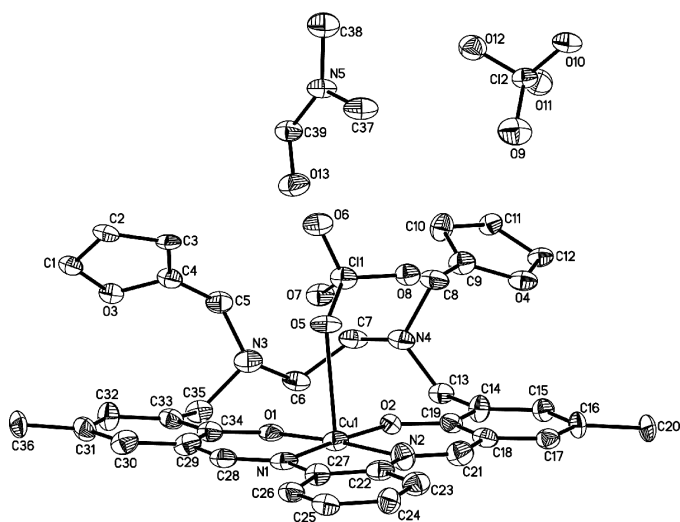


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted for clarity.

formamide molecule are present but do not participate in the coordination (Fig. 1).

There are four intramolecular hydrogen bonds in the structure of (I) (Table 1), which constrain the conformation of the macrocycle and enhance its stability.

Experimental

1,6-Bis(2-furyl)-2,5-bis(2-hydroxy-3-formyl-5-methylbenzyl)-2,5-diazahexane was synthesized according to our previously reported method (Sun *et al.*, 2001). To a suspension of 1,6-bis(2-furyl)-2,5-bis(2-hydroxy-3-formyl-5-methylbenzyl)-2,5-diazahexane (1 mmol) in ethanol (5 ml) was added dropwise an ethanol solution (5 ml) of $\text{Cu}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ (1 mmol), and the mixture was stirred until first it became clear and then a green powder appeared. 1,2-Phenylenediamine (1 mmol) was added to the mixture and stirring was continued for 30 h at 313 K. After filtration of the mixture, yellow microcrystals were obtained. Single crystals of (I) suitable for X-ray structure determination were formed by diffusion of diethyl ether into a dimethylformamide solution of the complex.

Crystal data

| | |
|--|---|
| $[\text{Cu}(\text{C}_{36}\text{H}_{36}\text{N}_4\text{O}_4)(\text{ClO}_4)](\text{ClO}_4) \cdot \text{C}_3\text{H}_7\text{N}$ | $D_x = 1.524 \text{ Mg m}^{-3}$ |
| $M_r = 924.22$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/n$ | Cell parameters from 1784 reflections |
| $a = 9.717$ (2) Å | $\theta = 2.0\text{--}25.5^\circ$ |
| $b = 27.863$ (3) Å | $\mu = 0.75 \text{ mm}^{-1}$ |
| $c = 14.902$ (5) Å | $T = 293$ (2) K |
| $\beta = 93.06$ (2)° | Prism, yellow |
| $V = 4028.9$ (16) Å ³ | $0.32 \times 0.26 \times 0.24 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEX CCD area-detector diffractometer | 7914 independent reflections |
| φ and ω scans | 6113 reflections with $I > 2\sigma(I)$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2000) | $R_{\text{int}} = 0.037$ |
| $T_{\text{min}} = 0.79$, $T_{\text{max}} = 0.84$ | $\theta_{\text{max}} = 26.0^\circ$ |
| 17 136 measured reflections | $h = -11 \rightarrow 11$ |
| | $k = -16 \rightarrow 34$ |
| | $l = -14 \rightarrow 18$ |

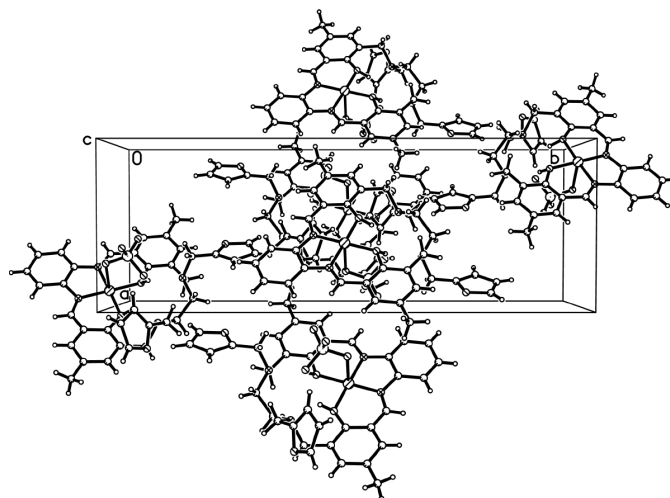


Figure 2
The crystal packing of (I), viewed down the c axis.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.140$
 $S = 1.09$
 7914 reflections
 543 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.9397P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.75 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

| $D\text{--}H \cdots A$ | $D\text{--}H$ | $H \cdots A$ | $D \cdots A$ | $D\text{--}H \cdots A$ |
|-----------------------------------|---------------|--------------|--------------|------------------------|
| $\text{O1--H1A} \cdots \text{N3}$ | 0.97 | 1.96 | 2.716 (4) | 133 |
| $\text{O1--H1A} \cdots \text{O7}$ | 0.97 | 2.39 | 3.221 (3) | 144 |
| $\text{O2--H2B} \cdots \text{N4}$ | 0.97 | 2.10 | 2.832 (4) | 131 |
| $\text{O2--H2B} \cdots \text{O7}$ | 0.97 | 2.36 | 3.230 (3) | 148 |

All H atoms were positioned geometrically and refined as riding, with C—H/O—H distances in the range 0.93–0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2$ to 1.5 times U_{eq} of the parent atom.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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References

- Bruker (2000). SMART, SAINT and SHELXTL, XPREF and XP. Bruker AXS Inc., Madison, Wisconsin, USA.
 Coughlin, P. K. & Lippard, S. J. (1984). *J. Am. Chem. Soc.* **106**, 2328–2336.
 Li, C., Kanehisa, N., Miyagi, Y., Nakao, Y., Takamizawa, S., Mori, W. & Kai, Y. (1997). *Bull. Chem. Soc. Jpn.* **70**, 2429–2436.
 Sun, G.-C., He, Z.-H., Li, Z.-J., Yuan, X.-D., Yang, Z.-J., Wang, G.-X., Wang, L.-F. & Liu, C.-R. (2001). *Molecules*, **6**, 1001–1005.