Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Chloro(nitrato)[1,4,7-tris(4-vinyl)benzyl-1,4,7-triazacyclononane]copper(II)

**Jeffrey R. Deschamps,[a]* Christopher M. Hartshorn,[b] Alok Singh[c] and Eddie L. Chang[c]†**

[a]Laboratory for the Structure of Matter, Code 6030, Naval Research Laboratory, Washington, DC 20375, USA, [b]Geo-Centers, Inc., 10903 Indian Head Hwy., Ft. Washington, MD, USA, and [c]Center for Bio/Molecular Science and Engineering, Code 6930, Naval Research Laboratory, Washington, DC 20375-5348, USA

† Corresponding author; e-mail elc@cbmse.nrl.navy.mil.

Correspondence e-mail: deschamps@nrl.navy.mil

Received 26 June 2002
Accepted 2 July 2002
Online 12 July 2002

**Key indicators**

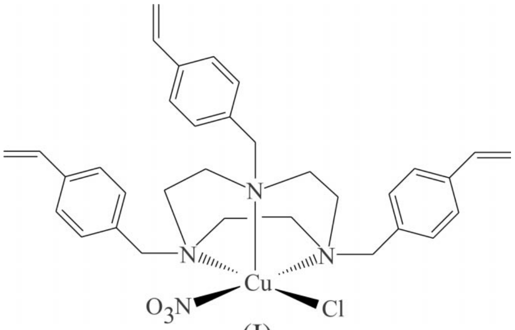
Single-crystal X-ray study
$T$ = 93 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.023
$wR$ factor = 0.064
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[CuCl(NO_3)(C_{33}H_{39}N_3)]$ or Cu([9]-ane(Nvbz)$_3$NO$_3$Cl, is the polymerizable form of a potent metal-chelator complex that catalyses the hydrolysis of phosphate esters. The coordination geometry around the Cu atom is square pyramidal. The structure has a similar conformation to the parent catalyst Cu([9]aneN$_3$)Cl$_2$, showing that the extensive functionalization does not significantly distort the metal-complex geometry.

## Comment

The hydrolysis of phosphate esters in nature is often facilitated by metalloenzymes. The catalytic processes involved are, in general, rapid and highly selective. Numerous phosphate mono-, di-, and triesterases have been isolated and their structure and reactivity investigated in order to elucidate the features contributing to the hydrolytic ability of these enzymes (Wilcox, 1996). Of particular environmental interest are triesterases that accelerate the rate of degradation of highly toxic phosphate triesters (Donarski *et al.*, 1989; Caldwell & Raushel, 1990; Benning *et al.*, 1995; LeJeune *et al.*, 1997; Hong & Raushel, 1999).



(I)

Given the environmental significance of triester hydrolysis, there have been numerous attempts to design easily recoverable heterogeneous catalysts that can also rapidly hydrolyse these toxic substances (Dannenberg & Pehkonen, 1998; Menger & Tsuno, 1989; Srivatsan & Verma, 2000; Srivatsan & Verma, 2001). We are exploring the utility of heterogeneous catalytic systems for the hydrolysis of phosphate esters, using insoluble polymeric materials as a scaffold for incorporation of potent homogeneous catalytic systems (Hartshorn *et al.*, 2001).

Recent research, especially by Burstyn and co-workers, on homogeneous catalysis of phosphoesters has shown that the 1,4,7-triazacyclononane–Cu$^{2+}$ (Cu[9]aneN$_3$) complex is very efficient in hydrolyzing selected phosphate diesters (Hegg & Burstyn, 1996; Hegg *et al.*, 1999). The process of making

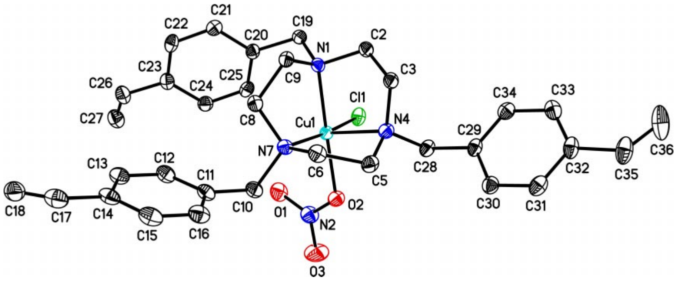


**Figure 1**
The structure of (I). Displacement ellipsoids are shown at the 50% probability level.

inhomogeneous, catalytically active forms of this system, however, requires the attachment of a polymerizable group to the cyclononane. This functionalization may adversely affect the ability of the Cu[9]ane$N_3$ complex to hydrolyse phosphate esters.

We report here the crystal structure of a copper complex of a 1,4,7-triazacyclononane ([9]ane$N_3$) ligand that contains three polymerizable 4-vinylbenzyl substituents, Cu([9]-ane(Nvbz)$_3$)$NO_3$Cl, (I), and compare it with a previously reported crystal structure of Cu([9]ane$N_3$)$Cl_2$ (Schwindinger *et al.*, 1980). Correlation between coordination geometry of the catalyst and reaction rates for phosphate ester hydrolysis has previously been reported, although the reasons for this behavior were not fully elucidated (Hegg *et al.*, 1999)

The structure of (I) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The nitrate ion acts as a monodentate ligand, and the Cu1—O2 and Cu1···O1 distances are 1.984 (2) and 2.815 (2) Å, respectively. This complex and Cu([9]ane$N_3$)$Cl_2$ have quite similar structures. Both are square pyramidal, with $\tau = 0.04$ and 0.02, respectively, where $\tau$ is a measure of the difference between two opposite 'basal' angles divided by 60; a perfect square pyramid has a $\tau$ value of 0.00. Likewise, the geometry of the respective $CuN_3$ fragments is also quite similar. The different electronegativity of the $NO_3^-$ ligand compared to $Cl^-$ skews the bond distances in (I), but the average Cu—N bond distances, 2.13 and 2.12 Å, are similar. The sum of the three N—Cu—N angles is increased slightly to 253°, compared with 249°, and the O2—Cu1—Cl1 angle is 90.74 (5)°, compared with the Cl—Cu—Cl angle of 94.23 (5)° in the previously reported complex (Schwindinger *et al.*, 1980). Interestingly, such changes in bond angles correlated to increased rates of reactivity with bis(4-nitrophenyl)phosphate for a series of cyclic polyamine complexes (Hegg *et al.*, 1999), but in the present case these bonding changes may also be an artifact of the $N_3$ClO donor set as opposed to $N_3Cl_2$.

## Experimental

All reagents and solvents were purchased from commercial sources and used as received. [9]ane$N_3$ (504 mg, 3.9 mmol) was dissolved in $CH_2Cl_2$ (20 ml) and stirred under argon. To this, 4-vinylbenzyl chloride (5.9 mmol) dissolved in $CH_2Cl_2$ (30 ml) was added dropwise. The mixture was stirred for 4 h, over which time a small amount of white precipitate (found by $^1$H NMR to be [9]ane$N_3$, which presumably precipitated out as a hydrochloride salt) formed in the yellow solution. Upon filtering, the solvent was removed under reduced pressure to give a yellow oil. The residue was loaded on to a silica column and eluted using chloroform/methanol (92:8 *v*:*v*). The second fraction was 1,4,7-tris(4-vinyl)benzyl-1,4,7-triazacyclononane (129 mg). The eluent was slowly adjusted to 85:15 chloroform/methanol, to complete the elution of the [9]ane(Nvbz)$_3$. To prepare the title compound (I), $Cu(NO_3)_2\cdot 2.5H_2O$ (0.1 mmol) and [9]-ane(Nvbz)$_3$ (0.1 mmol) were mixed in methanol (10 ml). The resulting green solution was allowed to slowly evaporate, yielding green crystals of (I) suitable for analysis by single-crystal X-ray diffraction.

*Crystal data*

[CuCl($NO_3$)($C_{33}H_{39}N_3$)]
$M_r = 638.67$
Monoclinic, *Cc*
$a = 9.7764$ (10) Å
$b = 28.491$ (3) Å
$c = 11.2790$ (12) Å
$\beta = 102.437$ (2)°
$V = 3068.0$ (6) Å$^3$
$Z = 4$
$D_x = 1.383$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 5031 reflections
$\theta = 4.7$–56.5°
$\mu = 0.84$ mm$^{-1}$
$T = 93$ (2) K
Prism, blue
0.35 × 0.20 × 0.10 mm

*Data collection*

Bruker SMART 1000 CCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: by integration (*XPREP*; Bruker, 1997)
$T_{\min} = 0.68$, $T_{\max} = 0.87$
10947 measured reflections
5597 independent reflections
5414 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 28.3°$
$h = -12 \rightarrow 13$
$k = -36 \rightarrow 37$
$l = -14 \rightarrow 14$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.064$
$S = 0.88$
5597 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 1.7291P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.22$ e Å$^{-3}$
Absolute structure: (Flack, 1983), 1798 Friedel pairs
Flack parameter = 0.011 (6)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—O2 | 1.9837 (15) | Cu1—N4 | 2.2232 (17) |
| Cu1—N1 | 2.0428 (17) | Cu1—Cl1 | 2.2892 (6) |
| Cu1—N7 | 2.1111 (17) | | |
| O2—Cu1—N1 | 174.25 (7) | N7—Cu1—N4 | 83.90 (6) |
| O2—Cu1—N7 | 91.42 (7) | O2—Cu1—Cl1 | 90.74 (5) |
| N1—Cu1—N7 | 84.70 (7) | N1—Cu1—Cl1 | 93.69 (5) |
| O2—Cu1—N4 | 90.96 (6) | N7—Cu1—Cl1 | 171.91 (5) |
| N1—Cu1—N4 | 84.43 (6) | N4—Cu1—Cl1 | 103.86 (5) |

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *XPREP* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

This research was supported in part by the Office of Naval Research (ONR) and the Naval Research Laboratory (NRL).

*Acta Cryst.* (2002). E**58**, m396–m398 Jeffrey R. Deschamps *et al.* • [CuCl($NO_3$)($C_{33}H_{39}N_3$)] **m397**

## References

Benning, M. M., Kuo, J. M., Raushel, F. M. & Holden, H. M. (1995). *Biochemistry*, **34**, 7973–7978.

Bruker (1997). *XPREP*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SMART*. Version 5.059. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SAINT* (Version 6.02A) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Caldwell, S. R. & Raushel, F. M. (1990). *Mechanism of Enzymatic Phosphotriester Hydrolysis in Chemical Aspects of Enzyme Biotechnology*, edited by T. O. Baldwin, pp. 41–52. New York, Plenum Press.

Dannenberg, A. & Pehkonen, S. O. (1998). *J. Agric. Food. Chem.* **46**, 325–334.

Donarski, W. J., Dumas, D. P., Heitmeyer, D. P., Lewis, V. E. & Raushel, F. M. (1989). *Biochemistry*, **28**, 4650–4655.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hartshorn, C. M., Singh, A. & Chang, E. L. (2001). **Journal?** Submitted.

Hegg, E. L. & Burstyn, J. N. (1996). *Inorg. Chem.* **35**, 7474–7481.

Hegg, E. L., Mortimore, S. H., Cheung, C. L., Huyett, J. E., Powell, D. R. & Burstyn, J. N. (1999). *Inorg. Chem.* **38**, 2961–2968.

Hong, S. B. & Raushel, F. M. (1999). *Biochemistry*, **38**, 1159–1165.

LeJeune, K. E., Mesiano, A. J., Bower, S. B., Grimsley, J. K., Wild, J. R. & Russell, A. J. (1997). *Biotechnol. Bioeng.* **54**, 105–114.

Menger, F. M. & Tsuno, T. (1989). *J. Am. Chem. Soc.* **111**, 4903–4907.

Schwindinger, W. F., Fawcett, T. G., Lalancette, R. A., Schugar, H. J. & Potenza, J. A. (1980). *Inorg. Chem.* **19**, 1379–1381.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Srivatsan, S. G. & Verma, S. (2000). *Chem. Commun.* pp. 515–516.

Srivatsan, S. G. & Verma, S. (2001). *Chem. Eur. J.* **7**, 828–833.

Wilcox, D. E. (1996). *Chem. Rev.* **96**, 2435–2458.

**m398** Jeffrey R. Deschamps *et al.* • [CuCl(NO$_3$)(C$_{33}$H$_{39}$N$_3$)] *Acta Cryst.* (2002). E**58**, m396–m398