

| | | | | |
|-----------------------------|----------|----------|----------|---------|
| C2—H2A...O3A ⁱⁱⁱ | 0.92 (7) | 2.35 (7) | 3.01 (2) | 129 (5) |
| C2—H2B...O4B ^v | 0.98 (7) | 2.52 (8) | 3.35 (3) | 142 (5) |
| C3—H3A...O4A ⁱⁱⁱ | 0.94 (9) | 2.46 (9) | 3.12 (2) | 128 (6) |
| C5—H5B...O4A ^{iv} | 1.09 (7) | 2.38 (7) | 3.43 (3) | 162 (4) |
| C5—H5B...O3B ^{iv} | 1.09 (7) | 2.52 (6) | 3.23 (2) | 121 (4) |

| Compound (2) | | | | |
|-----------------------------|----------|----------|-----------|---------|
| N1—H1M...S2 ^{vi} | 0.81 (4) | 2.77 (4) | 3.505 (2) | 152 (3) |
| N4—H4M...S2 ^{vii} | 0.81 (3) | 2.60 (3) | 3.364 (3) | 158 (3) |
| N1—H1M...O4 ^{viii} | 0.81 (4) | 2.77 (4) | 3.269 (6) | 122 (3) |
| N2—H2M...O3 ^v | 0.80 (4) | 2.69 (4) | 3.245 (4) | 129 (4) |
| N2—H2M...O1 ^v | 0.80 (4) | 2.34 (4) | 3.101 (4) | 159 (4) |
| N3—H3M...O1 ^{vii} | 0.79 (4) | 2.33 (4) | 3.005 (5) | 145 (3) |
| N6—H6M...O2 | 0.84 (4) | 2.70 (4) | 3.258 (4) | 126 (3) |
| C2—H2C...O3 ^{viii} | 1.00 (6) | 2.62 (6) | 3.277 (6) | 124 (4) |
| C3—H3A...O2 ^{ix} | 0.87 (5) | 2.64 (6) | 3.330 (5) | 137 (4) |
| C6—H6C...O2 ^{vii} | 0.98 (5) | 2.57 (5) | 3.349 (6) | 137 (4) |

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, 1 + z$; (iii) $1 + x, y, z$; (iv) $-x, 2 - y, -z$; (v) $-x, 1 - y, 1 - z$; (vi) $1 - x, 2 - y, 1 - z$; (vii) $1 - x, 1 - y, 1 - z$; (viii) $x, 1 + y, z - 1$; (ix) $x, y, z - 1$.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93*. Geometrical calculations: *PARST* (Nardelli, 1983).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R & D No. 123-3417-2201. KS thanks Universiti Sains Malaysia for a Visiting Post Doctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1251). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bowmaker, G. A., Pakawatchai, C., Skelton, B. W., Thavornmyutikarn, P., Wattananakajana, Y. & White, A. H. (1994). *Aust. J. Chem.* **47**, 15–24.
- Girling, R. L. & Amma, E. L. (1971). *Inorg. Chem.* **10**, 335–340.
- Hanic, F. & Durcanska, E. (1969). *Inorg. Chim. Acta*, **3**, 293–298.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Okaya, Y. & Knobler, C. (1964). *Acta Cryst.* **17**, 928–930.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- Sheldrick, G. M. (1990). *SHELXTL/PC. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spofford, W. A. III & Amma, E. L. (1968). *J. Chem. Soc. Chem. Commun.* pp. 405–407.
- Spofford, W. A. III & Amma, E. L. (1970). *Acta Cryst.* **B26**, 1474–1483.
- Taylor, I. F., Weininger, M. S. & Amma, E. L. (1974). *Inorg. Chem.* **13**, 2835–2842.
- Vizzini, E. A. & Amma, E. L. (1966). *J. Am. Chem. Soc.* **88**, 2872–2873.
- Weininger, M. S., Hunt, G. W. & Amma, E. L. (1972). *J. Chem. Soc. Chem. Commun.* pp. 1140–1141.

Acta Cryst. (1996). **C52**, 1957–1959

(Acetonitrile)[*N,N*-bis(3-aminopropyl)-1,3-propanediamine-*N,N',N'',N'''*]copper(II) Diperchlorate

ANDREAS M. DITTLER-KLINGEMANN,^a F. EKKEHARDT HAHN,^a CHRIS ORVIG^b AND STEVEN J. RETTIG^b

^a*Freie Universität Berlin, Institut für Anorganische und Analytische Chemie, Fabockstrasse 34-36, D-14195 Berlin, Germany, and* ^b*University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1. E-mail: xtal@xray1.chem.ubc.ca*

(Received 3 June 1996; accepted 11 June 1996)

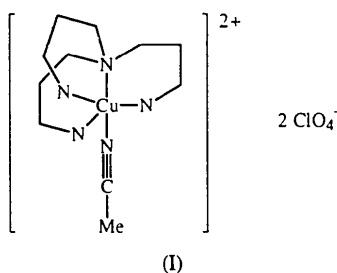
Abstract

The structure of the title compound, [Cu(C₂H₃N)(C₉H₂₄N₄)](ClO₄)₂, consists of (acetonitrile)[tris(3-aminopropyl)amine-*N,N',N'',N'''*]copper(II) cations and perchlorate anions linked by an extensive network of weak N—H...O and C—H...O hydrogen bonds. The Cu^{II} atom has a coordination geometry intermediate between tetragonal pyramidal (with one of the three primary amine N atoms occupying the apical coordination site) and trigonal bipyramidal (with the tertiary amine and acetonitrile N atoms in the axial positions). Main dimensions include Cu—N(amine) 2.035 (8)–2.121 (8) Å and Cu—N(acetonitrile) 2.099 (7) Å.

Comment

During our investigation of the various factors which affect the coordination geometry of Cu²⁺ ions with tripodal tetraamines (Dittler-Klingemann & Hahn, 1996), we became particularly interested in the importance of protonated complexes. These compounds have recently been shown to be the route between mono- and binuclear complexes (Dittler-Klingemann *et al.*, 1996). The reaction of Cu(OH)₂ with tris(3-amino-*n*-propyl)amine (trpn) and NH₄PF₆ under basic conditions yields a trigonal bipyramidal complex, [Cu(trpn)(NH₃)](PF₆)₂ (Dittler-Klingemann & Hahn, 1996). However, the reaction of trpn with Cu(NO₃)₂·3H₂O at neutral pH yields the binuclear square-pyramidal complex [Cu₂(trpn)₂(NO₃)₂](NO₃)₂ (Dittler-Klingemann *et al.*, 1996). Determination of the complex-formation constants in aqueous solution has shown that the predominant complex in the pH range 6 to 8 is [Cu(Htrpn)(H₂O)₂]³⁺, in which one arm of the amine ligand is protonated and uncoordinated (Dittler-Klingemann *et al.*, 1996). Changing the solvent from protic polar water to aprotic acetonitrile for the crystallization of [Cu(Htrpn)(H₂O)₂]³⁺ induces instead the crystallization of the title com-

pound, (I), in which the nonprotonated Cu^{II} complex has one acetonitrile molecule as a coligand, forming [Cu(trpn)(CH₃CN)](ClO₄)₂.



The more tetragonal pyramidal coordination geometry in the title compound differs significantly from the trigonal bipyramidal copper(II) complexes based on tris(2-aminoethyl)amine (tren), [Cu(Me₆tren)L]ⁿ⁺ (*n* = 1, 2) (Scott, Lee & Holm, 1994). The τ parameter (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984) for the [Cu(trpn)(CH₃CN)]²⁺ cation is 0.46, indicating a geometry intermediate between tetragonal pyramidal ($\tau = 0$) with the primary amino atom N(4) apical and trigonal bipyramidal ($\tau = 1$) with the tertiary amino and acetonitrile N atoms, N(1) and N(5), respectively, axial. For comparison, the τ values for the [Cu(Me₆tren)L]ⁿ⁺ complexes are all in the range 0.9–1.0. The variation of the Cu—N bond lengths is entirely consistent with this intermediate coordination geometry. All remaining geometrical features are as expected. The ionic species present are linked by weak N—H···O and C—H···O hydrogen bonds as summarized in Table 3.

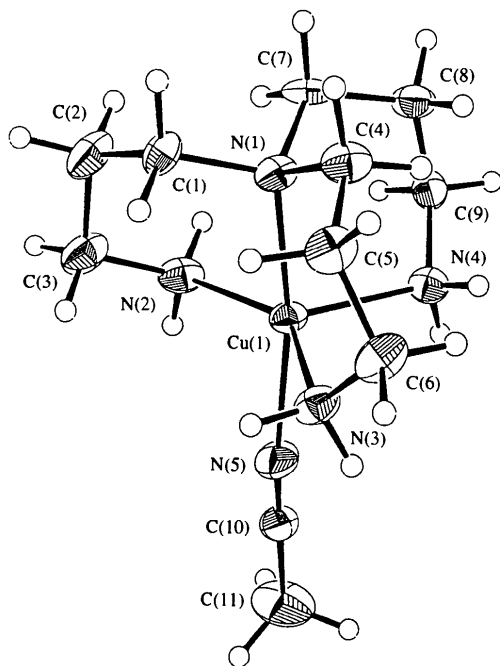


Fig. 1. Perspective view of the [Cu(trpn)(CH₃CN)]²⁺ cation; 33% probability displacement ellipsoids are shown for non-H atoms.

Experimental

The reaction of Cu(OH)₂ and the tris hydrogen perchlorate salt of trpn in aqueous solution yields the protonated [Cu(Htrpn)(H₂O)₂]³⁺ cation showing the expected UV/vis absorption of a square-pyramidal Cu²⁺ ion. This complex can be isolated as a powder; however, attempts to crystallize it from water failed. The solution of the complex in acetonitrile resulted an unchanged UV/vis spectrum and blue crystals were obtained after saturating the solution at 323 K and leaving overnight at room temperature. The change in solvent to an aprotic medium caused the disproportionation of [Cu(Htrpn)(H₂O)₂]³⁺ to [Cu(trpn)(CH₃CN)]²⁺, H₃trpn³⁺ and [Cu(CH₃CN)₅]²⁺.

Crystal data

[Cu(C₂H₃N)(C₉H₂₄N₄)](ClO₄)₂
M_r = 491.82
 Orthorhombic
*Pna*2₁
a = 11.815 (3) Å
b = 19.334 (2) Å
c = 8.839 (2) Å
V = 2019.1 (6) Å³
Z = 4
D_r = 1.618 Mg m⁻³
D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 7.7–11.9°

μ = 1.394 mm⁻¹

T = 294.2 K

Prism

0.40 × 0.22 × 0.22 mm

Blue

Data collection

Rigaku AFC-6S diffractometer

ω -2 θ scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

T_{min} = 0.915, *T_{max}* = 1.000

3343 measured reflections

3343 independent reflections

1127 observed reflections

[*I* > 3 σ (*I*)]

θ_{\max} = 30.0°

h = 0 → 16

k = 0 → 27

l = 0 → 12

3 standard reflections

monitored every 200

reflections

intensity decay: 1.26%

Refinement

Refinement on *F*

R = 0.0392

wR = 0.0339

S = 1.581

1127 reflections

243 parameters

H(C) and H(N) atoms

riding (C—H 0.98,

N—H 0.91 Å)

w = 1/ σ^2 (*F_o*)

(Δ/σ)_{max} = 0.0002

$\Delta\rho_{\max}$ = 0.32 e Å⁻³

$\Delta\rho_{\min}$ = -0.32 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* [1992,

Vol. C, Tables 4.2.6.8,

6.1.1.1 (C, Cl, Cu, N, O)

and 6.1.1.2 (H)]

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|-------|-------------|-------------|-------------|-----------------------|
| Cu(1) | 0.22391 (9) | 0.55731 (5) | 0.4340 | 0.0347 (3) |
| Cl(1) | 0.1793 (3) | 0.4124 (2) | -0.1227 (5) | 0.053 (1) |
| Cl(2) | 0.4899 (2) | 0.6365 (1) | -0.0742 (6) | 0.0501 (9) |
| O(1) | 0.0771 (8) | 0.4399 (6) | -0.170 (1) | 0.141 (5) |

| | | | | |
|-------|-------------|------------|-------------|-----------|
| O(2) | 0.181 (1) | 0.4004 (6) | 0.036 (1) | 0.119 (5) |
| O(3) | 0.2558 (8) | 0.4644 (6) | -0.161 (1) | 0.118 (4) |
| O(4) | 0.200 (1) | 0.3539 (5) | -0.193 (1) | 0.228 (7) |
| O(5) | 0.5683 (7) | 0.6076 (5) | -0.175 (1) | 0.083 (3) |
| O(6) | 0.4791 (9) | 0.5932 (5) | 0.054 (1) | 0.092 (4) |
| O(7) | 0.3822 (7) | 0.6441 (5) | -0.142 (1) | 0.105 (4) |
| O(8) | 0.5261 (7) | 0.7015 (4) | -0.027 (2) | 0.121 (5) |
| N(1) | 0.2452 (6) | 0.6623 (4) | 0.4047 (10) | 0.037 (3) |
| N(2) | 0.2492 (7) | 0.5430 (4) | 0.2084 (10) | 0.045 (3) |
| N(3) | 0.1016 (6) | 0.5655 (4) | 0.5968 (10) | 0.044 (3) |
| N(4) | 0.3802 (7) | 0.5435 (4) | 0.5480 (10) | 0.040 (3) |
| N(5) | 0.1840 (6) | 0.4515 (4) | 0.437 (2) | 0.053 (3) |
| C(1) | 0.1614 (9) | 0.6894 (6) | 0.289 (1) | 0.039 (4) |
| C(2) | 0.178 (1) | 0.6582 (6) | 0.134 (1) | 0.060 (4) |
| C(3) | 0.162 (1) | 0.5804 (6) | 0.121 (1) | 0.058 (4) |
| C(4) | 0.223 (1) | 0.7016 (6) | 0.550 (1) | 0.047 (4) |
| C(5) | 0.108 (1) | 0.6908 (7) | 0.628 (1) | 0.051 (4) |
| C(6) | 0.1043 (10) | 0.6233 (6) | 0.707 (1) | 0.052 (4) |
| C(7) | 0.3638 (9) | 0.6777 (5) | 0.354 (1) | 0.048 (4) |
| C(8) | 0.4582 (8) | 0.6534 (5) | 0.458 (2) | 0.048 (4) |
| C(9) | 0.4757 (8) | 0.5765 (5) | 0.470 (1) | 0.043 (4) |
| C(10) | 0.1836 (7) | 0.3938 (5) | 0.435 (2) | 0.047 (3) |
| C(11) | 0.1814 (9) | 0.3187 (5) | 0.435 (2) | 0.087 (4) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|-----------------|-----------|-----------------|-----------|
| Cu(1)—N(1) | 2.061 (7) | Cu(1)—N(4) | 2.121 (8) |
| Cu(1)—N(2) | 2.035 (8) | Cu(1)—N(5) | 2.099 (7) |
| Cu(1)—N(3) | 2.046 (8) | | |
| N(1)—Cu(1)—N(2) | 89.6 (3) | N(2)—Cu(1)—N(4) | 108.7 (3) |
| N(1)—Cu(1)—N(3) | 95.6 (3) | N(2)—Cu(1)—N(5) | 85.1 (5) |
| N(1)—Cu(1)—N(4) | 94.5 (3) | N(3)—Cu(1)—N(4) | 106.9 (3) |
| N(1)—Cu(1)—N(5) | 171.3 (4) | N(3)—Cu(1)—N(5) | 84.7 (4) |
| N(2)—Cu(1)—N(3) | 143.5 (3) | N(4)—Cu(1)—N(5) | 93.8 (3) |

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

| D—H...A | D—H | H...A | D...A | D—H...A |
|-----------------------------------|------|-------|----------|---------|
| N(2)—H(1)...O(6) | 0.91 | 2.30 | 3.19 (1) | 165 |
| N(2)—H(2)...O(2) | 0.91 | 2.42 | 3.25 (1) | 153 |
| N(3)—H(3)...O(1 ⁱ) | 0.91 | 2.33 | 3.16 (1) | 152 |
| N(3)—H(4)...O(1 ⁱⁱ) | 0.91 | 2.31 | 3.20 (1) | 165 |
| N(4)—H(5)...O(7 ⁱⁱ) | 0.91 | 2.49 | 3.36 (1) | 162 |
| N(4)—H(6)...O(6 ⁱⁱⁱ) | 0.91 | 2.30 | 3.12 (1) | 150 |
| C(3)—H(12)...O(1 ⁱ) | 0.98 | 2.45 | 3.40 (2) | 161 |
| C(4)—H(13)...O(7 ⁱⁱⁱ) | 0.98 | 2.54 | 3.49 (2) | 163 |
| C(7)—H(19)...O(6) | 0.98 | 2.48 | 3.40 (1) | 157 |
| C(11)—H(27)...O(8 ^{iv}) | 0.98 | 2.53 | 3.36 (1) | 142 |

Symmetry codes: (i) $-x, 1-y, \frac{1}{2}+z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$.

The polarity (for the crystal used for data collection) was determined by a parallel refinement of the mirror image. The residuals were slightly higher for the opposite polarity: $R = 0.0396$ and $wR = 0.0340$. One of the perchlorate ions shows marked anisotropy consistent with some possible unresolved disorder; this is not uncommon in structures with such small, almost spherical, anions.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

We thank the Natural Sciences and Engineering Research Council of Canada, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie for financial support; FEH and CO acknowledge NATO for a Collaborative Research grant (CRG 930121).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Dittler-Klingemann, A. M. & Hahn, F. E. (1996). *Inorg. Chem.* **35**, 1996–1999.
- Dittler-Klingemann, A. M., Orvig, C., Hahn, F. E., Thaler, F., Hubbard, C. D., van Eldik, R., Schindler, S. & Fabian, I. (1996). *Inorg. Chem.* Submitted.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1992). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Scott, M. J., Lee, S. C. & Holm, R. H. (1994). *Inorg. Chem.* **33**, 4651–4662.

Acta Cryst. (1996). **C52**, 1959–1961

Bis(2-hydroxybenzoato-*O,O'*)dimethyltin

TUSHAR S. BASU BAUL† AND EDWARD R. T. TIEKINK

Department of Chemistry, The University of Adelaide, South Australia 5005, Australia. E-mail: etiekink@chemistry.adelaide.edu.au

(Received 5 February 1996; accepted 18 April 1996)

Abstract

The Sn atom in $[\text{Sn}(\text{C}_7\text{H}_5\text{O}_3)_2(\text{CH}_3)_2]$ is in a skew trapezoidal bipyramidal geometry with two types of Sn—O bond distances of approximately 2.1 and 2.5 Å. The methyl substituents lie over the weaker Sn...O interactions. The weakly bonded O atoms are involved in intramolecular hydrogen-bonding contacts with the hydroxyl groups. In addition, there is a close intermolecular contact between one of the weakly associated O atoms and a symmetry-related hydroxyl group.

† Permanent address: Chemical Laboratory, Regional Sophisticated Instrumentation Centre, North-Eastern Hill University, Bijnai Complex, Shillong 793 003, India.