

Structure of a Copper(I) Complex of a Tripodal Schiff-Base Ligand, {Tris[4-(2-thienyl)-3-aza-3-butenyl]amine}copper(I) Triiodide Chloroform Solvate

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(Received 9 February 1990; accepted 22 March 1990)

Abstract. $\{[(SC_4H_3)CHNCH_2CH_2]_3NCu\}[I_3].CHCl_3$, $[Cu(C_{21}H_{24}N_4S_3)]I_3.CHCl_3$, $M_r = 992.27$, monoclinic, $C2/c$, $a = 31.869$ (11), $b = 11.425$ (2), $c = 18.215$ (4) Å, $\beta = 96.56$ (2)°, $V = 6589$ (5) Å³, $Z = 8$, $D_x = 2.00$ g cm⁻³, $F(000) = 3776$, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 39.0$ cm⁻¹, $R = 0.027$ for 5020 observed reflections at 294 K. The copper(I) geometry is trigonal pyramidal, with coordination occurring from the apical tertiary amine N atom and the three azomethine N atoms of the tripodal Schiff-base ligand but not from the three thiophene moieties. Principal bond lengths and angles are Cu—N(ap.) 2.275 (3), Cu—N(eq.) 2.004 (3) Å (av.) and N(ap.)—Cu—N(eq.) 82.5 (1)° (av.), N(eq.)—Cu—N(eq.) 118.3 (1)° (av.); the Cu···S contacts are 3.162 (1), 3.268 (1) and 3.383 (1) Å.

Introduction. A previous molecular structure analysis of tris[4-(2-thienyl)-3-aza-3-butenyl]amine, (S₃tren), revealed its potential as a heptadentate tripodal ligand (Alyea, Liu, Li, Xu & You, 1989). As part of metal complexation studies of this new Schiff-base ligand derived from tris(2-aminoethyl)amine (tren), we have reacted S₃tren with copper(II) salts (Alyea, Li, Xu & You, 1990). When excess NaI is added to a solution containing copper(II) acetate and S₃tren, and the solution exposed to air for several days, reduction occurs to give the Cu^I title complex, whose X-ray structural analysis is now reported.

Experimental. A ruby coloured multifaceted crystal having approximate dimensions 0.26 × 0.52 × 0.59 mm was selected from several similar crystals grown from a chloroform solution. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range 12 < θ < 14°. Intensities of reflections with indices h 0 to 40, k 0 to 14, l -23 to 23, with 2 < 2 θ < 52° measured; ω -2 θ scans, ω scan width (0.60 + 0.35tan θ)°; graphite-monochromatized

Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 6570 reflections measured, 6454 unique (R_{int} 0.018) and the 5020 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement. Data corrected for Lorentz, polarization and absorption effects (max. and min. transmission coefficients 0.41, 0.20). Space group $C2/c$ or Cc determined from the systematic absences (hkl absent if $h + k = 2n + 1$; $h0l$ absent if $l = 2n + 1$) and $C2/c$ chosen and confirmed by successful refinement. The structure was solved by the Patterson heavy-atom method using *SHELXS86* (Sheldrick, 1986) and subsequent difference syntheses. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement a difference map showed that there was chloroform of solvation trapped in the crystal lattice; there is one chloroform per molecule of the complex. In the final rounds of calculations H atoms were positioned on geometrical grounds (C—H 0.95 Å) and included in the structure factor calculations with an overall B_{iso} of 5.0 Å². The final cycle of refinement included 326 variable parameters, $R = 0.027$, $wR = 0.044$, goodness-of-fit 1.71, $w = 1/[\sigma^2(F_o) + 0.025(F_o)^2]$. Max. shift/e.s.d. in final cycle 0.01; density in final difference map ± 0.65 e Å⁻³ in the vicinity of the triiodide anion; there were no chemically significant features. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a *PDP11/73* computer using *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983). Atomic coordinates† and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *ORTEPII* (Johnson, 1976).

† Lists of structure factors, anisotropic thermal parameters, least-squares planes, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53153 (59 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Positional and thermal parameters and their e.s.d.'s

	x	y	z	B(Å ²)
Cu	0.63429 (1)	0.97382 (4)	0.48258 (3)	3.190 (9)
S(1)	0.54986 (4)	1.1262 (1)	0.42317 (7)	4.50 (2)
S(2)	0.57597 (4)	1.0297 (1)	0.60743 (7)	4.59 (2)
S(3)	0.55280 (4)	0.7988 (1)	0.45719 (8)	5.72 (3)
N(4)	0.7048 (1)	0.9647 (3)	0.4735 (2)	3.38 (7)
N(1)	0.6458 (1)	1.1460 (3)	0.4888 (2)	3.26 (6)
N(2)	0.6502 (1)	0.8707 (3)	0.5707 (2)	3.39 (7)
N(3)	0.6309 (1)	0.9004 (3)	0.3823 (2)	3.45 (7)
C(11)	0.7188 (1)	1.0873 (4)	0.4777 (3)	3.91 (9)
C(12)	0.6904 (1)	1.1589 (3)	0.5209 (3)	3.96 (9)
C(13)	0.6266 (1)	1.2375 (3)	0.4652 (2)	3.68 (8)
C(14)	0.5839 (1)	1.2430 (3)	0.4301 (2)	3.69 (8)
C(15)	0.5652 (2)	1.3386 (4)	0.3962 (4)	6.1 (1)
C(16)	0.5230 (2)	1.3177 (5)	0.3656 (4)	6.6 (1)
C(17)	0.5117 (1)	1.2085 (5)	0.3763 (3)	5.5 (1)
C(21)	0.7213 (1)	0.8929 (4)	0.5373 (2)	3.55 (8)
C(22)	0.6879 (1)	0.8065 (3)	0.5558 (2)	3.67 (8)
C(23)	0.6373 (1)	0.8579 (3)	0.6335 (2)	3.73 (8)
C(24)	0.6032 (1)	0.9221 (4)	0.6591 (2)	3.59 (8)
C(25)	0.5883 (1)	0.9091 (4)	0.7277 (2)	4.25 (9)
C(26)	0.5558 (2)	0.9907 (5)	0.7368 (3)	4.8 (1)
C(27)	0.5460 (2)	1.0593 (4)	0.6761 (3)	5.1 (1)
C(31)	0.7072 (1)	0.9087 (4)	0.4009 (3)	4.07 (9)
C(32)	0.6682 (1)	0.9356 (4)	0.3486 (3)	4.08 (9)
C(33)	0.6067 (1)	0.8236 (4)	0.3475 (2)	3.97 (9)
C(34)	0.5702 (1)	0.7721 (4)	0.3733 (3)	4.09 (9)
C(35)	0.5446 (2)	0.6899 (4)	0.3348 (3)	5.4 (1)
C(36)	0.5113 (2)	0.6501 (4)	0.3747 (4)	6.1 (1)
C(37)	0.5119 (2)	0.7016 (5)	0.4404 (3)	6.1 (1)
I(1)	0.24620 (1)	0.16719 (4)	0.24032 (2)	6.353 (8)
I(2)	0.29255 (1)	0.35207 (2)	0.18078 (2)	3.931 (6)
I(3)	0.33820 (1)	0.54905 (2)	0.11865 (2)	4.367 (6)
C	0.6297 (2)	0.4688 (4)	0.6650 (3)	5.3 (1)
Cl(1)	0.61026 (5)	0.3267 (1)	0.65267 (9)	6.73 (3)
Cl(2)	0.65074 (7)	0.5148 (2)	0.5865 (1)	10.52 (5)
Cl(3)	0.59007 (6)	0.5628 (2)	0.6903 (1)	9.15 (5)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

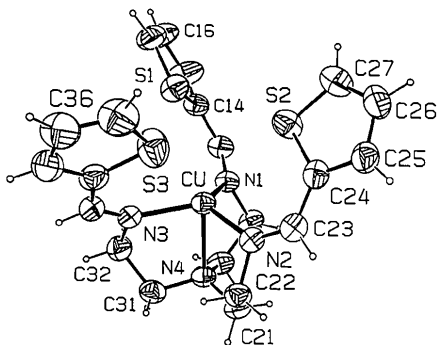


Fig. 1. A general view of the cation with our numbering scheme. Ellipsoids are at the 50% level.

Discussion. The Cu^I geometry in the [(SC₄H₃)CHNCH₂CH₂]₃NCu⁺ cation is distorted trigonal pyramidal, with coordination occurring from the four N donor atoms. The Cu—N(eq.) distances to the N atoms N1, N2, N3 are 2.002 (3), 2.009 (3) and 2.002 (3) Å, respectively, with the N(1)—Cu—N(2), N(2)—Cu—N(3) and N(1)—Cu—N(3) angles being 120.2 (1), 117.8 (1) and 117.0 (1)°, respectively. The Cu atom sits 0.2620 (5) Å above the plane of the equatorial azomethine N atoms, while the apical tertiary amine atom (N4) lies 2.014 (3) Å below the

Table 2. Bond lengths (Å) and bond angles (°)

Cu	N(4)	2.275 (3)	C(13)	C(14)	1.438 (5)		
Cu	N(1)	2.002 (3)	C(14)	C(15)	1.359 (6)		
Cu	N(2)	2.009 (3)	C(15)	C(16)	1.414 (7)		
Cu	N(3)	2.002 (3)	C(16)	C(17)	1.319 (8)		
S(1)	C(14)	1.715 (4)	C(21)	C(22)	1.520 (6)		
S(1)	C(17)	1.689 (5)	C(23)	C(24)	1.433 (6)		
S(2)	C(24)	1.722 (4)	C(24)	C(25)	1.393 (6)		
S(2)	C(27)	1.694 (6)	C(25)	C(26)	1.419 (7)		
S(3)	C(34)	1.712 (5)	C(26)	C(27)	1.362 (7)		
S(3)	C(37)	1.713 (5)	C(31)	C(32)	1.510 (6)		
N(4)	C(11)	1.469 (5)	C(33)	C(34)	1.431 (6)		
N(4)	C(21)	1.469 (5)	C(34)	C(35)	1.380 (6)		
N(4)	C(31)	1.479 (6)	C(35)	C(36)	1.426 (8)		
N(1)	C(12)	1.482 (5)	C(36)	C(37)	1.331 (9)		
N(1)	C(13)	1.262 (5)	I(1)	I(2)	2.8610 (5)		
N(2)	C(22)	1.459 (5)	I(2)	I(3)	2.9729 (4)		
N(2)	C(23)	1.266 (6)	C	Cl(1)	1.744 (5)		
N(3)	C(32)	1.455 (6)	C	Cl(2)	1.728 (6)		
N(3)	C(33)	1.286 (5)	C	Cl(3)	1.759 (6)		
C(11)	C(12)	1.506 (6)					
N(4)	Cu	N(1)	82.7 (1)	S(1)	C(14)	C(15)	110.5 (3)
N(4)	Cu	N(2)	82.5 (1)	C(13)	C(14)	C(15)	125.6 (4)
N(4)	Cu	N(3)	82.3 (1)	C(14)	C(15)	C(16)	113.0 (4)
N(1)	Cu	N(2)	120.2 (1)	C(15)	C(16)	C(17)	111.4 (5)
N(1)	Cu	N(3)	117.0 (1)	S(1)	C(17)	C(16)	114.0 (4)
N(2)	Cu	N(3)	117.8 (1)	N(4)	C(21)	C(22)	109.9 (3)
C(14)	S(1)	C(17)	91.0 (2)	N(2)	C(22)	C(21)	109.2 (3)
C(24)	S(2)	C(27)	91.7 (3)	N(2)	C(23)	C(24)	124.8 (4)
C(34)	S(3)	C(37)	92.4 (3)	S(2)	C(24)	C(23)	122.7 (3)
Cu	N(4)	C(11)	104.4 (2)	S(2)	C(24)	C(25)	111.4 (3)
Cu	N(4)	C(21)	103.7 (2)	C(23)	C(24)	C(25)	125.9 (4)
Cu	N(4)	C(31)	103.7 (2)	C(24)	C(25)	C(26)	111.3 (4)
Cl(1)	N(4)	C(21)	114.4 (3)	C(25)	C(26)	C(27)	112.7 (4)
Cl(1)	N(4)	C(31)	114.3 (3)	S(2)	C(27)	C(26)	112.8 (4)
C(21)	N(4)	C(31)	114.5 (3)	N(4)	C(31)	C(32)	110.7 (4)
Cu	N(1)	C(12)	106.4 (2)	N(3)	C(32)	C(31)	109.4 (4)
Cu	N(1)	C(13)	135.7 (3)	N(3)	C(33)	C(34)	125.7 (4)
C(12)	N(1)	C(13)	117.2 (3)	S(3)	C(34)	C(33)	125.3 (3)
Cu	N(2)	C(22)	106.5 (3)	S(3)	C(34)	C(35)	110.0 (4)
Cu	N(2)	C(23)	135.3 (3)	C(33)	C(34)	C(35)	124.7 (5)
C(22)	N(2)	C(23)	117.9 (3)	C(34)	C(35)	C(36)	112.9 (5)
Cu	N(3)	C(32)	107.9 (2)	C(35)	C(36)	C(37)	112.4 (5)
Cu	N(3)	C(33)	134.6 (3)	S(3)	C(37)	C(36)	112.3 (4)
C(32)	N(3)	C(33)	116.9 (4)	I(1)	I(2)	I(3)	178.13 (1)
N(4)	C(11)	C(12)	110.3 (3)	Cl(1)	C	Cl(2)	110.0 (3)
N(1)	C(12)	C(11)	110.3 (3)	Cl(1)	C	Cl(3)	110.3 (3)
N(1)	C(13)	C(14)	125.8 (4)	Cl(2)	C	Cl(3)	112.9 (3)
S(1)	C(14)	C(13)	123.9 (3)				

plane. The Cu—N4 distance is 2.275 (3) Å and the N4—Cu—N(1), N4—Cu—N(2) and N4—Cu—N(3) angles are 82.7 (1), 82.5 (1) and 82.3 (1)°, respectively. These structural parameters are similar to those reported for the [Cu(pmas)]⁺ cation, where pmas is the tripodal ligand N(CH₂py)(CH₂CH₂SR)₂: Cu—N(ap.) 2.158 (8), Cu—N(py.) = 2.035 (10) Å, and Cu is 0.077 Å from the equatorial plane (Zubieta, Karlin & Hayes, 1983). The coordination geometry adheres closely, as expected, to that recently found for the Cu^I complex of the related tripodal ligand, tris[4-phenyl-3-aza-3-butenyl]amine, (Ph₃tren) (Alyea, Ferguson, Jennings & Xu, 1990). Principle dimensions for [(C₆H₅)CHNCH₂CH₂]₃NCu⁺ were Cu—N(ap.) 2.232 (2) Å, Cu—N(eq.) 2.019 (2), 2.006 (2) and 2.004 (2) Å, and N(ap.)—Cu—N(eq.) 83.7 (1) to 84.6 (1)°.

The thiophene moieties do not coordinate to the Cu atom and the Cu...S distances of 3.283 (1), 3.162 (1) and 3.268 (1) Å are close to the sum of the van der Waals radii (3.2 Å) (Bondi, 1964). In the free S₃tren molecule (Alyea *et al.*, 1989), the dihedral

angles between the plane of the three S atoms and the plane of each thiophene ring are 91.4, 88.7 and 93.7°, respectively, as compared with 123.4, 124.4 and 119.7° in the complex. Bond distances and angles within the thiophene group of the title species, e.g. C—S 1.689 (5)–1.722 (4) Å, C—S—C 91.0 (2)–92.4 (3)°, are similar to those in the free S₃tren molecule.

The I₃ anion has I—I bond distances of 2.8610 (5) and 2.9729 (4) Å; the mean I—I distance in six I₃⁻ ions is 2.9717 (11) Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The I—I—I angle is 178.13 (1)°. The chloroform solvate possesses no unusual features.

We thank NSERC Canada for Operating and Infrastructure Grants (ECA and GF), and for a CIDA Award (ZX).

Acta Cryst. (1990). C46, 2349–2351

Structure of *trans*-Dibromobis(5,7-dimethyl-8*H*-[1,2,4]triazolo[1,5-*a*]pyrimidine)-palladium(II) Methanol Solvate

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(Received 17 January 1990; accepted 19 April 1990)

Abstract. [PdBr₂(C₇H₈N₄)₂].CH₃OH, *M*_r = 594.58, triclinic, *P* $\bar{1}$, *a* = 9.153 (4), *b* = 8.858 (5), *c* = 8.317 (3) Å, α = 123.54 (3), β = 92.25 (3), γ = 109.31 (3)°, *V* = 508.9 Å³, *Z* = 1, *D*_x = 1.94, *D*_m = 1.93 Mg m⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 4.811 mm⁻¹, *F*(000) = 288.0, *T* = 293 K, *R* = 0.035 for 1474 unique reflections [*I* > 2 σ (*I*)]. The two triazolopyrimidine ligands are coordinated to palladium *via* N(3) at a distance of 2.015 (4) Å; the bromides are *trans* coordinated at a distance of 2.4196 (7) Å, which is in the range expected for this type of complex.

Introduction. Square-planar palladium and platinum compounds are of interest in inorganic and organometallic chemistry. For example, the antitumour activity of *cis*-Pt(NH₃)₂Cl₂ and related compounds has been studied extensively. It is observed that the platinum ion binds preferentially *via* N(7) of the guanine base in DNA (Reedijk, Fichtinger-Schepman, van Oosterom & van der Putte, 1987).

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Triazolopyrimidines are of interest because of their use as models for naturally occurring purines. Recently a systematic study concerning the coordination compounds of dimethyltriazolopyrimidine (dmtp) has been started in our laboratory (Favre, Haasnoot & Reedijk, 1986; Biangini-Cingi, Manotti-Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983; Dillen, Lenstra, Haasnoot & Reedijk, 1983). Previous crystal structure determinations of metal compounds containing dmtp ligands have revealed that binding occurs only *via* N(3) of the ligand. We now investigate whether the same nitrogen atom coordinates to palladium, and compare this system with previously reported, related palladium compounds.

Experimental. Yellow crystals of [PdBr₂(C₇H₈N₄)₂].CH₃OH were obtained after refluxing PdBr₂ and dmtp (1:4) in methanol (60 mL) for 3 h. A rod-shaped single crystal was selected for the crystal structure determination. Experimental data for the compound are shown in Table 1. Analysis: Calculated for C₁₅H₂₀Br₂N₈OPd: C 30.30, H 3.39, N 18.85, O 2.69%; found C 30.56, H 3.34, N 18.80, © 1990 International Union of Crystallography

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