Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Harrison, P. G. (1994). *Dictionary of Organometallic Compounds*, pp. 4111–4235. London: Chapman & Hall.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Lefferts, J. L., Molloy, K. C., Hossain, M. B., van der Helm, D. & Zuckerman, J. J. (1982). *J. Organomet. Chem.* **240**, 349–361.
Ng, S. W. (1996). *Acta Cryst.* C**51**, 2292–2293.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC*. Version 4.1. 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.
Sisido, K., Takeda, Y. & Kinugawa, Z. (1961). *J. Am. Chem. Soc.* **83**, 538–541.
Smith, P. J. (1981). *J. Organomet. Chem. Libr.* **12**, 97–147.
Tse, J. S., Lee, F. L. & Gabe, E. J. (1986). *Acta Cryst.* C**42**, 1876–1878.

Acta Cryst. (1997). C**53**, 58–60

Bis{μ-chloro-[2(3*H*)-benzothiazolethione](triphenylphosphine)copper(I)} Dihydrate

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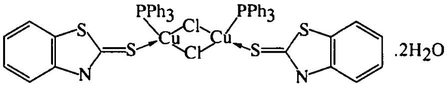
Abstract

The chloro-bridged dimeric structure of the title compound, bis[benzothiazole-2(3*H*)-thione]-1κ*S*;2κ*S*-di-μ-chloro-1:2κ^4*Cl*-bis(triphenylphosphine)-1κ*P*;2κ*P*-di-copper(I) dihydrate, [$Cu_2Cl_2(C_7H_5NS_2)_2(Ph_3P)_2$].$2H_2O$, is reported. The molecule is centrosymmetric with a Cu···Cu distance of 3.400 (2) Å and two Cu—μ-Cl distances of 2.396 (2) and 2.516 (2) Å. The heterocyclic ligand benzothiazole-2(3*H*)-thione acts as a monodentate ligand coordinating to copper through the S atom, with a Cu—S distance of 2.304 (3) Å. A hydrogen bond between the μ-Cl and heterocyclic N atom is also found, with a Cl···N distance of 3.134 (6) Å and a Cl···H—N angle of 162.4°.

Comment

The coordination chemistry of heterocyclic thiones, especially with copper, continues to draw attention (Raper, 1985). The known structures of the complexes are almost all monomers or S-bridged dimers (Raper, 1994). Some examples with halogen-bridged dimers are [Cu_2(merhod)$_4Cl_2$] (Moers, Beurskens, Noordik & Smits, 1986), [Cu_2(pu6tH)$_2Cl_4$] (Dubler & Gyr, 1988) and [Cu_2(mepu6tH)$_2Cl_4$] (Sletten & Apeland, 1975). As for benzothiazole-2(3*H*)-thione (bztztH), there are some reports of Cu$^{\rm I}$ complexes, such as [Cu(bztztH){(bztz)$_2S_3$}]ClO_4.$2CHCl_3$ (Jeannin, Jeannin & Lavigne, 1979) and [{Cu(bztzt)(dppe)}$_2$(μ-dppe)] (dppe = diphenylphosphinoethane) (Ainscough, Baker, Bingham, Brodie & Smith, 1989). The title compound, (I), is the first example of a halogen-bridged binuclear complex of this ligand.



(I)

The Cu atom adopts a tetrahedral coordination and the $CuCl_2Cu$ nucleus is almost planar and nearly forms a square. The Cu···Cu distance is 3.400 (2) Å, which is shorter than the distance of 3.501 (1) Å found in [Cu_2(pu6tH)$_2Cl_4$] (Dubler & Gyr, 1988) and longer than the distance of 2.906 (1) found in [Cu_2(merhod)$_4Cl_2$] (Moers *et al.*, 1986). The Cl1—Cu1 and Cl1$^{\rm i}$—Cu1 distances are 2.516 (2) and 2.396 (2) Å, respectively [symmetry code: (i) $1-x$, $-y$, $-z$]. The difference here is larger than is the case in [Cu_2(pu6tH)$_2Cl_4$], in which the two Cu—μ-Cl distances are 2.465 (1) and 2.493 (1) Å.

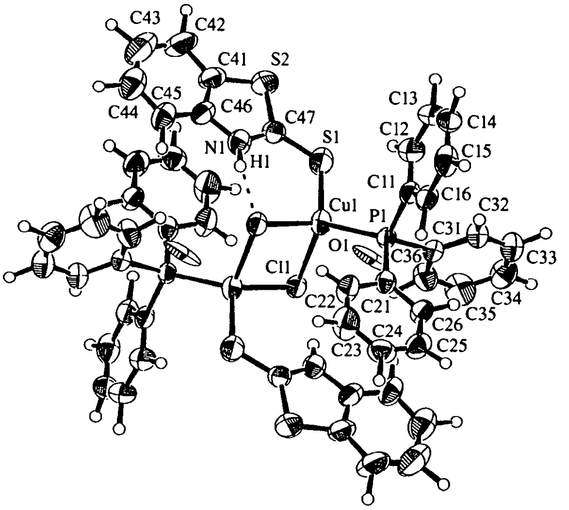


Fig. 1. A view of the title complex (*ORTEP*II; Johnson, 1976) with displacement ellipsoids shown at the 40% probability level. The intramolecular hydrogen bond is shown as a dashed line.

The heterocyclic ligand benzothiazole-2(3*H*)-thione acts as a monodentate ligand, the terminal S atom coordinating to the Cu atom. The heterocyclic N and S atoms are not coordinated to the Cu atom. The Cu—S distance of 2.304 (3) Å is comparable to that found in both [{Cu(bztzt)(dppe)}$_2$(μ-dppe)] (Ainscough *et al.*, 1989) and [Cu(bztztH){(bztz)$_2$S$_3$}]ClO$_4$.2CHCl$_3$ (Jeannin *et al.*, 1979). Unexpectedly, a hydrogen bond exists between the μ-Cl and heterocyclic N atoms. The Cl···N$^{\rm i}$ distance is 3.134 (6) Å and the Cl···H—N$^{\rm i}$ angle is 162.4°. This is unusual among the transition metal complexes of heterocyclic ligands. Although there are many examples of terminal Cl atoms forming hydrogen bonds (Ferral, Fava, Pelizzi & Tarasconi, 1985), no examples of bridging Cl atoms forming hydrogen bonds have been reported.

Experimental

The title compound was prepared by the reaction of equimolecular amounts of CuPPh$_3$Cl and benzothiazole-2(3*H*)-thione in CH$_2$Cl$_2$. Single crystals were obtained by slow evaporation of the solvent.

Crystal data

[Cu$_2$Cl$_2$(C$_7$H$_5$NS$_2$)$_2$-(C$_{18}$H$_{15}$P)$_2$].2H$_2$O
M_r = 1093.10
Monoclinic
$P2_1/n$
a = 17.133 (3) Å
b = 13.714 (1) Å
c = 10.776 (1) Å
β = 98.60 (1)°
V = 2503.6 (5) Å^3
Z = 2
D_x = 1.450 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 31.1–32.4°
μ = 4.516 mm^{-1}
T = 292.7 K
Prismatic
0.45 × 0.36 × 0.34 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{\rm min}$ = 0.067, $T_{\rm max}$ = 0.215
3448 measured reflections
3272 independent reflections

2415 observed reflections [$I > 1.5\sigma(I)$]
$R_{\rm int}$ = 0.0232
$\theta_{\rm max}$ = 60.1°
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections monitored every 150 reflections
  intensity decay: none

Refinement

Refinement on *F*
R = 0.0650
wR = 0.0859
S = 1.658
2415 reflections
290 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00160|F_o|^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.0170

$\Delta\rho_{\rm max}$ = 1.40 e Å^{-3} (at 1.87 Å from O1)
$\Delta\rho_{\rm min}$ = −0.35 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.003 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.1 and 6.1.1.2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	0.44377 (7)	−0.09048 (7)	0.0484 (1)	0.0570 (4)
Cl1	0.5684 (1)	−0.0037 (1)	0.1408 (2)	0.0503 (5)
S1	0.3455 (2)	−0.0541 (2)	0.1655 (2)	0.0719 (8)
S2	0.2082 (2)	0.0799 (2)	0.1624 (2)	0.0761 (8)
P1	0.4699 (1)	−0.2493 (1)	0.0329 (2)	0.0436 (5)
O1	0.0423 (4)	−0.4201 (4)	−0.0342 (6)	0.093 (2)
N1	0.2994 (4)	0.0893 (4)	−0.0003 (6)	0.055 (2)
C11	0.3845 (5)	−0.3233 (4)	−0.0324 (6)	0.047 (2)
C12	0.3149 (6)	−0.3110 (6)	0.0219 (8)	0.067 (3)
C13	0.2502 (5)	−0.3698 (7)	−0.0160 (10)	0.076 (3)
C14	0.2522 (6)	−0.4381 (6)	−0.1094 (10)	0.073 (3)
C15	0.3182 (7)	−0.4484 (6)	−0.1628 (8)	0.071 (3)
C16	0.3865 (5)	−0.3922 (5)	−0.1250 (7)	0.058 (3)
C21	0.5437 (4)	−0.2786 (4)	−0.0669 (6)	0.047 (2)
C22	0.5470 (5)	−0.2224 (6)	−0.1726 (7)	0.067 (3)
C23	0.6019 (7)	−0.2425 (7)	−0.2516 (8)	0.087 (4)
C24	0.6544 (6)	−0.3181 (6)	−0.2252 (8)	0.069 (3)
C25	0.6528 (6)	−0.3717 (6)	−0.1229 (8)	0.067 (3)
C26	0.5987 (5)	−0.3548 (5)	−0.0412 (7)	0.055 (3)
C31	0.5055 (5)	−0.3132 (4)	0.1791 (6)	0.045 (2)
C32	0.4786 (5)	−0.4067 (5)	0.2064 (7)	0.057 (2)
C33	0.5095 (6)	−0.4524 (6)	0.3184 (8)	0.067 (3)
C34	0.5658 (6)	−0.4071 (7)	0.4023 (8)	0.079 (3)
C35	0.5925 (7)	−0.3146 (7)	0.3768 (8)	0.088 (4)
C36	0.5611 (6)	−0.2680 (6)	0.2667 (7)	0.068 (3)
C41	0.1898 (6)	0.1689 (6)	0.0460 (9)	0.069 (3)
C42	0.1291 (6)	0.2382 (8)	0.031 (1)	0.100 (4)
C43	0.1279 (8)	0.3010 (8)	−0.073 (1)	0.106 (5)
C44	0.1843 (7)	0.2957 (7)	−0.1538 (10)	0.086 (4)
C45	0.2444 (5)	0.2277 (5)	−0.1344 (8)	0.068 (3)
C46	0.2456 (5)	0.1649 (5)	−0.0353 (8)	0.058 (3)
C47	0.2895 (5)	0.0379 (5)	0.0993 (7)	0.056 (3)
H1	0.3349	0.0686	−0.0608	0.0887

Table 2. *Selected geometric parameters (Å, °)*

Cu1—Cu1$^{\rm i}$	3.400 (2)	S2—C41	1.745 (9)
Cu1—Cl1	2.516 (2)	S2—C47	1.738 (8)
Cu1—Cl1$^{\rm i}$	2.396 (2)	P1—C11	1.832 (8)
Cu1—S1	2.304 (3)	P1—C21	1.823 (7)
Cu1—P1	2.235 (2)	P1—C31	1.826 (6)
Cl1···N1$^{\rm i}$	3.134 (6)	N1—C46	1.402 (9)
Cl1···H1$^{\rm i}$	2.169	N1—C47	1.316 (9)
S1—C47	1.678 (8)	N1—H1	0.997
Cl1—Cu1—Cl1$^{\rm i}$	92.43 (7)	S1—Cu1—P1	115.04 (8)
Cl1—Cu1—S1	109.11 (9)	Cu1—Cl1—Cu1$^{\rm i}$	87.57 (7)
Cl1—Cu1—P1	108.83 (8)	Cu1$^{\rm i}$—Cl1—H1$^{\rm i}$	81.84
Cl1$^{\rm i}$—Cu1—S1	111.80 (8)	Cu1—S1—C47	110.4 (3)
Cl1$^{\rm i}$—Cu1—P1	117.02 (7)		

Symmetry code: (i) $1 - x, -y, -z$.

Data were collected using the ω–2θ scan technique, with a scan speed of 4.0° min^{-1} and a scan width of (1.10 + 0.30tanθ)° (in ω). ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.31°, with a take-off angle of 6.0°. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The H-atom coordinates were found unequivocally from difference Fourier calculations, except those of the water of crystallization. H atoms were included in calculations and not refined. A peak with $\Delta\rho$ = 1.40 e Å^{-3} at 1.87 Å from O1 was found in a difference Fourier calculation. Refinement of O atoms at O1 and this site with occupancy factors of 0.8 and 0.2, respectively, resulted in a high displacement parameter for this peak. It was ignored in the final calculations. All calculations were performed using the *TEXSAN* (Molecular Structure Corporation, 1995) program package.

Data collection: Rigaku/AFC diffractometer control software. Cell refinement: Rigaku/AFC diffractometer control software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ainscough, E. W., Baker, E. N., Bingham, G. A., Brodie, A. M. & Smith, C. A. (1989). *J. Chem. Soc. Dalton Trans*, pp. 2167–2171.
Dubler, E. & Gyr, E. (1988). *Inorg. Chem.* **27**, 1466–1473.
Ferral, M. B., Fava, G. G., Pelizzi, C. & Tarasconi, P. (1985). *Inorg. Chim. Acta*, **98**, L45–L52.
Jeannin, S., Jeannin, Y. & Lavigne, G. (1979). *Inorg. Chem.* **18**, 3528–3535.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Moers, F. G., Beurskens, P. T., Noordik, J. H. & Smits, J. M. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 107–113.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Raper, E. S. (1985). *Coord. Chem. Rev.* **61**, 115–184.
Raper, E. S. (1994). *Coord. Chem. Rev.* **129**, 91–156.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sletten, E. & Apeland, A. (1975). *Acta Cryst.* B**31**, 2019–2022.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

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Dichloro[*N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine]samarium(III) Perchlorate

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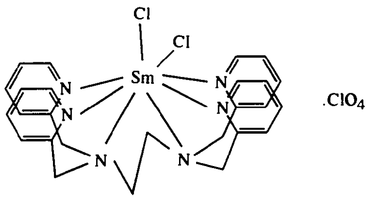
Abstract

The crystal structure of the title compound, $[SmCl_2\{C_2H_4N_2(CH_2C_5H_4N)_4\}]ClO_4$, at room temperature was solved and compared with the previously determined structure of $[Eu^{III}Cl_2(R\text{-tppn})]ClO_4$ [where *R*-tppn is *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-(*R*)-propylenediamine]. The Sm^{3+} ion is eight-coordinated through the six N atoms of the *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine ligand and two Cl^- ions. The coordination is best described as dodecahedral with some important distortions.

Comment

The europium(III) complex $[EuCl_2(R\text{-tppn})]ClO_4$ [*R*-tppn is *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-(*R*)-propylenediamine], (II), which was prepared as a chiral NMR-shift reagent for aqueous solution, has a unique asymmetrically distorted dodecahedral structure (Hazama, Umakoshi, Kabuto, Kabuto & Sasaki, 1996). In order to determine whether the structure is common to other lanthanide(III) ions, we decided to prepare other lanthanide(III) complexes of *R*-tppn and a related ligand, *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen). We report here the X-ray crystal structure of the samarium(III)–tpen complex, $[SmCl_2(tpen)]ClO_4$, (I).



(I)

The crystal structure of (I) (Fig. 1) consists of a monomeric complex cation and a perchlorate