References

Fun, H.-K., Sivakumar, K., Tian, Y.-P., Duan, C.-Y., Lu, Z.-L. & You, X.-Z. (1996). *Acta Cryst.* C52, 1143–1145.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Scovill, J. P., Klayman, D. L., Lambros, C., Childs, G. E. & Notsch, J. D. (1984). *J. Med. Chem.* 27, 87–91.

Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual.* 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.

Uechi, T. & Oniki, T. (1982). *Bull. Chem. Soc. Jpn*, 55, 971–974.

West, D. X., Liberta, A. E., Padhye, S. B., Chikate, R. C., Sonawane, P. B., Kumbhar, A. S. & Yerande, R. G. (1993). *Coord. Chem. Rev.* 123, 49–71.

Zhao, M. T., Samoc, M., Singh, B. P. & Prasad, P. N. (1989). *J. Phys. Chem.* 93, 7916–7920.

Acta Cryst. (1996). C52, 2153–2155

1,4-Dimethylpyridinium Bis(6,7-dihydro-5H-1,4-dithiepine-2,3-dithiolato-S,S')cuprate(III)

Hoong-Kun Fun,[a]* Kandasamy Sivakumar,[a]† Jing-Lin Zuo,[b] Fei You[b] and Xiao-Zeng You[b]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and* [b]*Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China. E-mail: hkfun@usm.my*

Abstract

In the title complex, $(C_7H_{10}N)[Cu(C_5H_6S_4)_2]$, the CuS_4 core adopts a square-planar geometry. Alternate columns of cations and anions form thick layers parallel to the *bc* plane. Weak $C—H\cdots Cu$ and $C—H\cdots S$ interactions help to link the cations and anions together.

Comment

Ever since the metal complexes of 4,5-dimercapto-1,3-dithiole-2-thionate (dmit) were first reported to exhibit high conductivities, a massive research effort has centred on the design and synthesis of similar complexes (Cassoux, Valade, Kobayashi, Kobayashi, Clark & Underhill, 1991). The multi-sulfur 1,2-dithiolene

complexes $[M(dddt)_2]^-$ (M = Cu, Ni; dddt = 6,7-dihydro-5H-1,4-dithiepine-2,3-dithiolate) have been synthesized and studied previously (Bereman & Lu, 1993; Yao, You, Li, Li & Yang, 1994). It is believed that molecular interactions through $S\cdots S$ contacts form effective electrical conduction pathways in these crystal phases. In addition, the introduction of various organic counter cations is of interest because of the possibilities of modifying the interactions between the anions (Cornelissen, Creyghton, de Graaff, Haasnoot & Reedijk, 1991). In order to investigate the effects of the cation on the crystal packing and properties, the title complex, (I), was prepared for comparison with $(Bu_4N)[Cu(dddt)_2]$ and $(Et_4N)[Cu(dddt)_2]$.

(I)
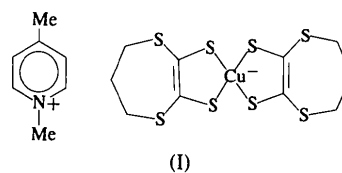
The crystal of (I) is built from exactly centrosymmetric cations and anions (Fig. 1). The former are disordered and there is an equal probability that the sites labelled C7 and N7 in Fig. 1 contain C or N atoms. The four S atoms surround the Cu atom yielding a square-planar environment, with nearly equal Cu—S bond lengths and S—Cu—S bond angles. In the five-membered ring containing the Cu atom, the average Cu—S, S—C and C=C bond lengths are 2.184 (1), 1.747 (3) and 1.339 (4) Å, respectively. The corresponding values in $(Bu_4N)[Cu(dddt)_2]$ are 2.181, 1.749 and 1.342 Å, and in $(Et_4N)[Cu(dddt)_2]$ are 2.182, 1.749 and 1.337 Å. The seven-membered ring (S3, C3–C5, S4, C2, C1) adopts a chair conformation. The anion as a whole has an extended linear conformation. The cation is planar and makes an angle of 69.4 (1)° with the plane of the anion.
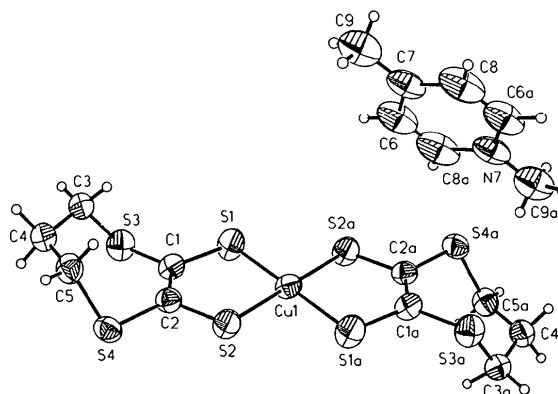

Fig. 1. A 50% probability displacement ellipsoid plot of the title compound with the atom-numbering scheme. The disorder of the C7/N7 site is not shown.

† On leave from the Department of Physics, Anna University, Madras 600 025, India.

The crystal consists of alternate layers of anions and cations. One such layer viewed down the a axis is shown in Fig. 2. These layers lie parallel to the bc plane and are stacked one above the other. There are no significant S$\cdots$S contacts, but other notable short contacts are H4$B\cdots$Cu^{i,ii} 3.09 (5), H9$C\cdots$S1^{iii} 2.88 (8) and H9$B\cdots$S2^{iv} 2.88 (7) Å; symmetry codes: (i) x, $1+y$, z; (ii) $1-x$, $1-y$, $1-z$; (iii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $z-\frac{1}{2}$; (iv) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$. While the Cu$\cdots$H contacts link the cations along the b axis into a chain, the S$\cdots$H contacts establish the interlayer connectivity.
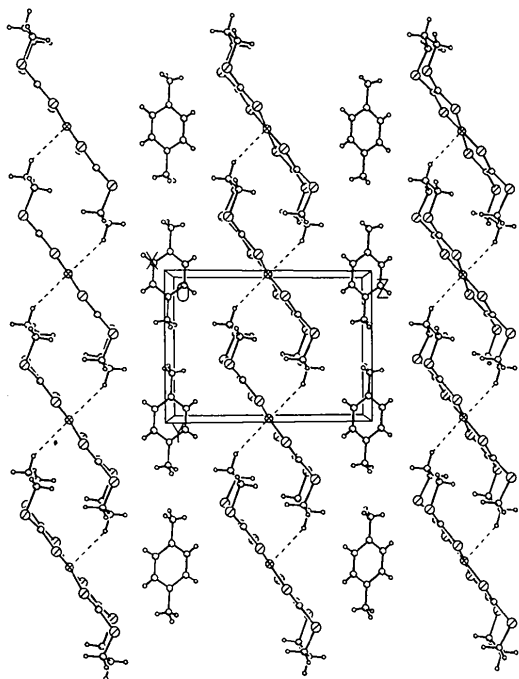

Fig. 2. One layer of cations and anions viewed down the a axis. Cu$\cdots$H contacts are shown as dashed lines.

Experimental

The title complex was synthesized according to the method of Zuo, Yao, Xu, You & Huang (1995). Single crystals were obtained from an acetonitrile solution by slow evaporation at room temperature.

Crystal data

$(C_7H_{10}N)[Cu(C_5H_6S_4)_2]$
$M_r = 560.38$
Monoclinic
$P2_1/n$
$a = 10.2145\,(7)$ Å
$b = 8.9516\,(6)$ Å
$c = 12.5214\,(8)$ Å
$\beta = 96.770\,(6)°$
$V = 1136.93\,(13)$ Å^3
$Z = 2$
$D_x = 1.637$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 8-25°$
$\mu = 1.700$ mm^{-1}
$T = 293\,(2)$ K
Polyhedron
$0.56 \times 0.42 \times 0.36$ mm
Black

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical via ψ scans ($XSCANS$; Siemens, 1994)
$T_{min} = 0.712$, $T_{max} = 0.916$
3419 measured reflections
2608 independent reflections
1978 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0279$
$\theta_{max} = 27.49°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 11$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R(F) = 0.0449$
$wR(F^2) = 0.1332$
$S = 0.957$
2608 reflections
168 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0939P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
Cu1	1/2	0	1/2	0.0430 (2)
S1	0.33603 (9)	0.13080 (11)	0.54866 (9)	0.0603 (3)
S2	0.64264 (8)	0.15386 (10)	0.58360 (8)	0.0522 (2)
S3	0.30553 (9)	0.38231 (12)	0.69581 (8)	0.0571 (3)
S4	0.63715 (8)	0.41095 (10)	0.72918 (7)	0.0478 (2)
C1	0.4135 (3)	0.2688 (4)	0.6325 (3)	0.0449 (7)
C2	0.5451 (3)	0.2793 (3)	0.6458 (2)	0.0414 (6)
C3	0.3335 (4)	0.5676 (4)	0.6443 (3)	0.0546 (9)
C4	0.4546 (4)	0.6486 (4)	0.6961 (3)	0.0541 (8)
C5	0.5852 (4)	0.5885 (4)	0.6690 (3)	0.0503 (8)
C6	0.4375 (4)	0.0755 (8)	0.0738 (3)	0.0719 (13)
C7/N7†	0.4860 (3)	0.1552 (6)	−0.0063 (2)	0.0621 (10)
C8	0.5488 (4)	0.0738 (8)	−0.0795 (3)	0.077 (2)
C9	0.4732 (5)	0.3168 (8)	−0.0125 (5)	0.0743 (13)

† This disordered site was assigned a scattering factor of $\frac{1}{2}$C + $\frac{1}{2}$N.

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

Cu1—S2	2.1808 (8)	S4—C2	1.769 (3)
Cu1—S1	2.1881 (10)	S4—C5	1.811 (4)
S1—C1	1.748 (3)	C1—C2	1.339 (4)
S2—C2	1.745 (3)	C3—C4	1.512 (5)
S3—C1	1.756 (3)	C4—C5	1.513 (6)
S3—C3	1.814 (4)		
S2—Cu1—S1	91.05 (3)	S1—C1—S3	114.6 (2)
C1—S1—Cu1	103.78 (11)	C1—C2—S2	121.1 (3)
C2—S2—Cu1	103.68 (11)	C1—C2—S4	125.2 (3)
C1—S3—C3	103.6 (2)	S2—C2—S4	113.6 (2)
C2—S4—C5	103.3 (2)	C4—C3—S3	116.2 (3)
C2—C1—S1	120.1 (3)	C3—C4—C5	115.5 (3)
C2—C1—S3	125.3 (3)	C4—C5—S4	116.2 (3)

The H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecu-

lar graphics: *SHELXTL/PC*. Geometrical calculations: *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1254). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bereman, R. D. & Lu, H. (1993). *Inorg. Chim. Acta*, **204**, 53–63.
Cassoux, P., Valade, L., Kobayashi, H., Kobayashi, A., Clark, R. A. & Underhill, A. E. (1991). *Coord. Chem. Rev.* **110**, 115–160.
Cornelissen, J. P., Creyghton, E. J., de Graaff, R. A. G., Haasnoot, J. G. & Reedijk, J. (1991). *Inorg. Chim. Acta*, **185**, 97–102.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
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.
Yao, T.-M., You, X.-Z., Li, C., Li, L.-F. & Yang, Q.-C. (1994). *Acta Cryst.* C50, 67–69.
Zuo, J.-L., Yao, T.-M., Xu, X.-X., You, X.-Z. & Huang, X.-Y. (1995). *Polyhedron*, **14**, 483–487.

trans-Dichlorotetrakis(pyridine-*N*)-molybdenum(III) Tribromide

ROK ROTAR, IVAN LEBAN AND JURIJ V. BRENČIČ

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, PO Box 537, 1001 Ljubljana, Slovenia. E-mail: ivan.leban@uni-lj.si

Abstract

In the title compound, *trans*-[$Mo^{III}Cl_2(C_5H_5N)_4$]Br_3, the Cl and pyridine N atoms define a slightly distorted octahedron around the Mo atom. Both cations and anions lie on twofold axes. Pyridine rings which are located *trans* with respect to one another are staggered. The tribromide ion, Br_3^-, is essentially linear.

Comment

It is known that pyridine can occupy up to three coordination positions around an Mo^{III} ion. Several examples of compounds such as [$NH_2(CH_3)_2$][$MoCl_5(py)$] (Brenčič, Leban, Modec & Carugo, 1995), *cis*-Rb[$MoCl_4(py)_2$].H_2O (Brenčič, Leban & Modec, 1994) and *mer*-$MoCl_3(py)_3$ (Brenčič, 1974) have been prepared and structurally characterized. *trans*-[$Mo^{III}Cl_2(py)_4$]Br_3, which was isolated from *trans,trans*-[$MoCl_2(py)_4$][$MoCl_4(py)_2$] (Brenčič, Golič, Leban, Rotar & Sieler, 1996) in the form of the tribromide, (1), is the first complex in which four pyridine ligands are coordinated to the same Mo^{III} atom. Pyridine rings which are *trans* with respect to one another but are not symmetry related are in a staggered conformation.

(1)
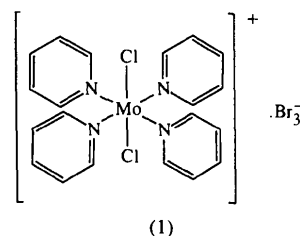
The acute interplanar angle between the N11, C12–C16 (ring I) and N21, C22–C26 (ring II) planes is 60.6 (3)°. The interplanar angles between two pyridine rings in a staggered conformation [ring I and ring II at $(-x, y, \frac{1}{2}-z)$] is 84.9 (2)°. The angle between ring I and ring I at $(-x, y, \frac{1}{2}-z)$ is 60.8 (2)°, and between ring II and ring II at $(-x, y, \frac{1}{2}-z)$ is 70.1 (2)°. The Mo—Cl bond length of 2.407 (2) Å is shorter than those found in corresponding anions, for example, in [$MoCl_4(py)_2$]$^-$ (Brenčič & Čeh, 1989), for steric reasons. The two Cl atoms in [$MoCl_2(py)_4$]$^+$ can approach the central Mo atom more closely than in [$MoCl_4(py)_2$]$^-$, where four Cl atoms occupy more space around the central Mo atom. The shortening of the Mo—Cl bond is also in agreement with the positive charge of the bulky cation.

Although the tribromide ion is symmetrical, it is not exactly linear. As was noted previously, large cations favour symmetrical tribromide ions (Atwood, Junk, May & Robinson, 1994). Almost identical cation geometry was found previously in the structures of *trans*-[$Ir^{III}Cl_2(py)_4$]Cl.$6H_2O$ (Gillard, Mitchell, Williams & Vagg, 1984), *trans*-[$Rh^{III}Cl_2(py)_4$][$H(ONO_2)_2$] (Dobinson, Mason & Russel, 1967) and *trans*-[$Ru^{III}Cl_2(py)_4$]-[$H(ONO_2)_2$] (Al-Zamil, Evans, Gillard, James, Jenkins, Lancashire & Williams, 1982). All the cations have a staggered conformation of the *trans* pyridine rings. It is noteworthy that *trans*-[$M^{III}Cl_2(py)_4$][$H(ONO_2)_2$], where M = Rh or Ru, crystallize in the same space group (*Pbcn*) as *trans*-[$Mo^{III}Cl_2(py)_4$]Br_3, with cations located on a twofold axis with the same relative positions of the atoms.