

Appendix 6

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Acta Cryst. (1999). C55, 000–000**A Novel Copper Salt of 18-membered Macrocyclic with *N,N'*-diacetate**YIN-HAN ZHANG,^a SUCHADA CHANTRAPROMMA,^b S. SHANMUGA SUNDARA RAJ,^c HOONG-KUN FUN,^c YU-PENG TIAN,^d FU-XIN XIE^d AND ZU-YAO CHEN^a^a*Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, P.R.China,* ^b*Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand,* ^c*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,* and ^d*Department of Chemistry, Anhui University, Hefei, Anhui 230039, P.R.China. E-mail: suchada@ratree.psu.ac.th***Abstract**

The centrosymmetric 18-membered title molecule has half molecule in the asymmetric unit and the other half is related by the mirror plane. The C—S *endo* cyclic distance is 1.701 (4) Å. The C—H... π interaction helps in packing apart from N—H...O and weak C—H...O interactions.

Comment

Selective complexation of macrocyclic ligands with specific metal ions is an important and rapidly expanding of research (Van Veggel, 1994). Zhang and Adam have investigated complexing properties of macrocyclic ligands with N-substituted by acetate acid (Zhang, Tian, Xie & Chen, 1998, Adam, Leong, Lindoy & Hendry, 1988). In this paper, a novel copper salt of 18 membered macrocycle with *N,N'*-diacetate structure is reported.

Scheme I

The centrosymmetric title compound has half molecule in the asymmetric unit and the other half of the molecule is related by a mirror plane passing through Cu1, C14 and S1 with no cavity inside. The results of the room temperature structure determination agrees with the reported values. The C—S *endo* cyclic bond distance 1.701 (4) Å is comparable with the related macrocyclic compounds. The C—O distance of the carbonyl group [C12—O2=1.212 (5); C12—O3=1.272 (5) Å] shows that it is partially double bonded and ionised. It is quite interesting to note that the Cu is in ionised state (2⁺) and the ligand is in zwitterinonic rather than 2⁻ state by the protonation of the N atom N1. The Cu ion is at a distance of 3.724 (4) Å from C11 3.733 (4) Å from C13. Though there are enough dentating centres, the macrocycle could not accommodate the Cu²⁺ ion inside which is due to the lack of cavity inside the macrocycle.

The torsion angle C1—C2—C3—O1 (151.5(6)°) fixes the orientation of the phenyl ring from the thiopene moiety. In the N—C—C—C—N chain the conformation is *anti-gauche-anti-anti*. The whole molecule is almost planar and the methyl acetate groups are perpendicular to the

plane.

The thiophene moiety is highly disordered and exists in planar conformation. The two conformers are in crossed position. The value of dihedral angle $[61.0(2)^\circ]$ between the planar phenyl ring and the methyl acetate group indicates a larger folding of the ligand. The analysis of the structure using *PLATON* (*Spec*, 1990) shows there is no solvent accessible areas in the structure. The packing of the molecules is stabilized by the intra- and inter molecular weak C—H \cdots O hydrogen bondings and the C—H \cdots π interaction. The H3A atom involves in this π bond interaction with the Cg of the phenyl ring (1 -x,-y,1-z). The molecule runs parallel to the c-axis as a chain formed by the intra- and inter molecular N—H \cdots O and C—H \cdots O hydrogen bonding.

Experimental

A Novel Copper Salt of 18-membered Macrocyclic with *N,N'*-diacetate acid(I) was synthesized according to method previously report (Xu, 1990). Copper nitrate (0.6 mmol) was added to a solution of the ligand in 30 ml dry ethanol and refluxed 5 min at room temperature. A green solid was obtained and washed with ethanol. Single crystals of the copper salt suitable for X-ray diffraction were obtained by recrystallization in methanol at room temperature.

Crystal data

$C_{27}H_{28}CuN_2O_6S$

$M_r = 572.11$

Orthorhombic

Pbcm

$a = 10.9776(1) \text{ \AA}$

$b = 14.0734(2) \text{ \AA}$

$c = 17.3262(2) \text{ \AA}$

$V = 2676.76(5) \text{ \AA}^3$

$Z = 4$

$D_x = 1.420 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8033 reflections

$\theta = 1.17\text{--}38.61^\circ$

$\mu = 0.938 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Slab

$0.40 \times 0.36 \times 0.16 \text{ mm}$

Green

Data collection

Siemens SMART CCD area detector diffractometer

ω scan

Absorption correction:

empirical SADABS (Sheldrick, 1996)

$T_{\min} = 0.657, T_{\max} = 0.884$

9400 measured reflections

2423 independent reflections

1962 reflections with

$>2\sigma(I)$

$R_{\text{int}} = 0.0316$

$\theta_{\max} = 25.00^\circ$

$h = -11 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -20 \rightarrow 19$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0591$ $wR(F^2) = 0.1947$ $S = 1.131$

2450 reflections

194 parameters

H atoms treated by a mixture of independent
and constrained refinement

$$w=1/[\sigma^2(F_o^2) + (0.1181P)^2 + 2.4866P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.000$$

$$\Delta\rho_{\max} = 0.933 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.454 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from *International Tables*
for Crystallography (Vol. C)Table 1. Selected geometric parameters (\AA , $^\circ$)

S1A—C2	1.701 (4)	O2—C12	1.213 (5)
O1—C4	1.364 (5)	O3—C12	1.269 (5)
O1—C3	1.433 (5)		

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N1...O2	1.00 (5)	2.22 (5)	2.757 (5)	112 (3)
N1—H1N1...O2 ⁱ	1.00 (5)	2.00 (5)	2.875 (5)	144 (4)
C8—H8A...O2 ⁱ	0.9295	2.5909	3.391 (6)	144.51
C10—H10A...O1	0.9698	2.3229	2.763 (5)	106.75

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30s covered 0.3° in ω . The crystal-to-detector distance was 3 cm and the detector swing angle was -40°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible.

Data collection: SMART (Siemens, 1996a). Cell refinement: SAINT (Siemens, 1996b). Data reduction: SAINT. Program(s) used to solve structure: *SHELXTL* (Siemens, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 1990) and *PARST* (Nardelli, 1995)'. .

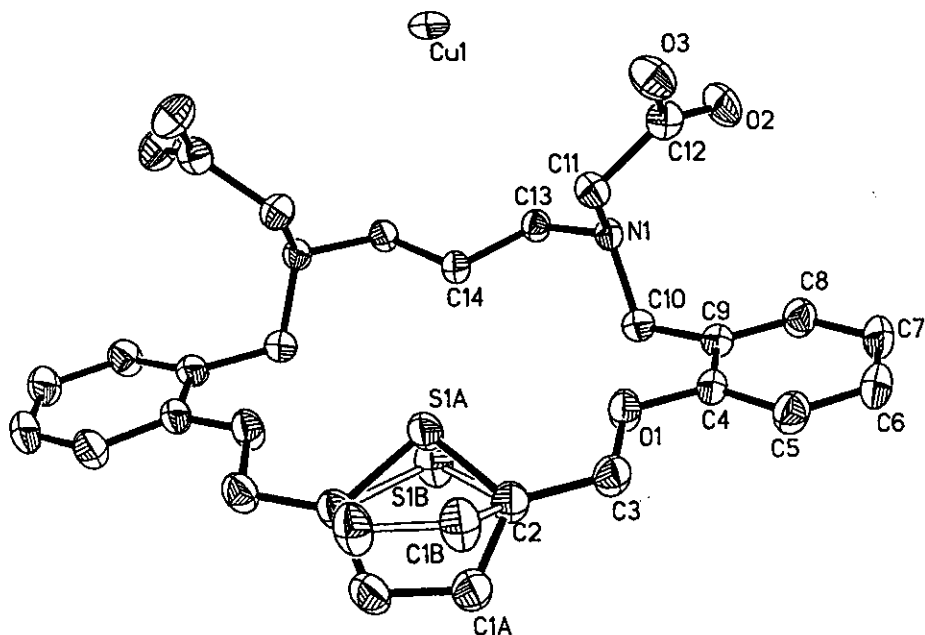
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: PRINTCIF). Services for accessing these data are described at the back of the journal.

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Fig. 1. The structure of title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.



Supplementary data

The tables of data shown below are not normally printed in *Acta Cryst. Section C* but the data will be available electronically *via* the online contents pages at

<http://www.iucr.org/journals/acta/tocs/actac/actac.html>

Specific tables may be included in the printed manuscript at the discretion of the Co-editor. If you wish to include any of the following tables in your paper, please state which tables are required in the `_publ_contact_letter` field of the CIF. In the case of tables of atomic coordinates, please state whether you wish the coordinates of any H atoms to be included.

Table S1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j a_i a_j.$$

	Occupancy	x	y	z	U_{eq}
Cu1	1	0.01481 (6)	0.19150 (5)	0.7500	0.0488 (3)
S1A	0.779 (17)	0.4947 (4)	-0.0984 (6)	0.7500	0.0684 (14)
C1A	0.779 (17)	0.6828 (6)	-0.1887 (7)	0.7092 (4)	0.074 (3)
H1AA	0.779 (17)	0.7421	-0.2187	0.6795	0.088
C2	1	0.5865 (4)	-0.1401 (3)	0.6786 (2)	0.0531 (10)
S1B	0.221 (17)	0.4805 (4)	-0.1461 (19)	0.7500	0.063 (4)
C1B	0.221 (17)	0.6933 (14)	-0.107 (2)	0.7087 (12)	0.067 (9)
H1BA	0.221 (17)	0.7587	-0.0863	0.6789	0.080
O1	1	0.4291 (3)	-0.1181 (2)	0.58766 (16)	0.0568 (8)
O2	1	0.0876 (3)	0.0939 (3)	0.49399 (19)	0.0691 (9)
O3	1	0.2328 (3)	0.1841 (2)	0.5447 (2)	0.0662 (9)
N1	1	0.1114 (3)	-0.0441 (2)	0.60597 (17)	0.0421 (7)
C3	1	0.5581 (4)	-0.1298 (3)	0.5954 (2)	0.0546 (11)
H3A	1	0.6002	-0.0750	0.5744	0.066
H3B	1	0.5846	-0.1859	0.5675	0.066
C4	1	0.3802 (4)	-0.1214 (3)	0.5153 (2)	0.0471 (9)
C5	1	0.4494 (4)	-0.1223 (3)	0.4477 (3)	0.0582 (11)
H5A	1	0.5340	-0.1209	0.4505	0.070
C6	1	0.3929 (5)	-0.1254 (4)	0.3772 (3)	0.0650 (13)
H6A	1	0.4395	-0.1264	0.3324	0.078
C7	1	0.2673 (5)	-0.1272 (4)	0.3721 (3)	0.0671 (13)
H7A	1	0.2293	-0.1279	0.3241	0.081
C8	1	0.1992 (4)	-0.1279 (3)	0.4389 (2)	0.0574 (11)
H8A	1	0.1147	-0.1305	0.4353	0.069
C9	1	0.2534 (4)	-0.1247 (3)	0.5117 (2)	0.0476 (9)
C10	1	0.1783 (4)	-0.1342 (3)	0.5840 (2)	0.0492 (9)
H10A	1	0.2314	-0.1524	0.6263	0.059
H10B	1	0.1193	-0.1847	0.5768	0.059
C11	1	0.1900 (4)	0.0443 (3)	0.6096 (2)	0.0504 (10)
H11A	1	0.2752	0.0260	0.6091	0.060
H11B	1	0.1743	0.0776	0.6576	0.060
C12	1	0.1651 (4)	0.1111 (3)	0.5419 (2)	0.0504 (10)
C13	1	0.0366 (4)	-0.0578 (3)	0.6782 (2)	0.0428 (9)
H13A	1	-0.0159	-0.1126	0.6715	0.051
H13B	1	-0.0151	-0.0026	0.6856	0.051
C14	1	0.1144 (5)	-0.0720 (4)	0.7500	0.0421 (12)
H14A	1	0.1812	-0.0268	0.7500	0.051
H14B	1	0.1485	-0.1356	0.7500	0.051
H1N1	1	0.052 (4)	-0.032 (3)	0.567 (2)	0.041 (10)

Table S2. Anisotropic displacement parameters (\AA^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	0.0441 (5)	0.0354 (4)	0.0669 (5)	0.0064 (3)	0.000	0.000
S1A	0.0592 (17)	0.106 (4)	0.0404 (13)	0.0408 (17)	0.000	0.000

C1A	0.064 (4)	0.105 (8)	0.052 (3)	0.036 (4)	0.004 (3)	-0.007 (4)
C2	0.037 (2)	0.074 (3)	0.048 (2)	0.0050 (19)	0.0004 (17)	-0.005 (2)
S1B	0.030 (4)	0.109 (12)	0.052 (5)	-0.008 (4)	0.000	0.000
C1B	0.044 (11)	0.10 (3)	0.054 (12)	-0.004 (12)	0.006 (9)	-0.001 (13)
O1	0.0442 (16)	0.089 (2)	0.0369 (14)	0.0108 (15)	-0.0004 (12)	-0.0043 (14)
O2	0.066 (2)	0.082 (2)	0.0597 (19)	0.0031 (17)	-0.0249 (16)	0.0108 (17)
O3	0.061 (2)	0.062 (2)	0.076 (2)	-0.0115 (15)	-0.0085 (17)	0.0199 (16)
N1	0.0444 (17)	0.0481 (18)	0.0337 (16)	0.0022 (14)	-0.0044 (13)	-0.0018 (13)
C3	0.042 (2)	0.074 (3)	0.047 (2)	0.007 (2)	0.0059 (18)	-0.003 (2)
C4	0.052 (2)	0.054 (2)	0.035 (2)	0.0046 (18)	0.0010 (16)	-0.0035 (16)
C5	0.053 (2)	0.073 (3)	0.048 (2)	0.003 (2)	0.0099 (19)	-0.004 (2)
C6	0.076 (3)	0.081 (3)	0.038 (2)	0.006 (3)	0.009 (2)	-0.004 (2)
C7	0.084 (4)	0.081 (3)	0.036 (2)	0.005 (3)	-0.007 (2)	-0.007 (2)
C8	0.052 (3)	0.073 (3)	0.047 (2)	0.006 (2)	-0.0085 (19)	-0.009 (2)
C9	0.049 (2)	0.051 (2)	0.043 (2)	0.0070 (17)	-0.0012 (17)	-0.0023 (16)
C10	0.052 (2)	0.048 (2)	0.047 (2)	0.0071 (18)	0.0018 (18)	0.0013 (17)
C11	0.054 (2)	0.052 (2)	0.045 (2)	-0.0013 (19)	-0.0039 (17)	0.0023 (17)
C12	0.040 (2)	0.060 (3)	0.051 (2)	-0.0011 (18)	0.0019 (18)	-0.0013 (19)
C13	0.0383 (19)	0.053 (2)	0.037 (2)	0.0025 (16)	0.0003 (15)	-0.0021 (16)
C14	0.042 (3)	0.050 (3)	0.034 (3)	-0.002 (2)	0.000	0.000

Table S3. Geometric parameters (\AA , $^\circ$)

S1A—C2	1.701 (4)	N1—C13	1.509 (5)
S1A—C2 ⁱ	1.701 (4)	N1—C10	1.514 (5)
C1A—C2	1.367 (7)	N1—C11	1.515 (5)
C1A—C1A ⁱ	1.415 (13)	C4—C9	1.394 (6)
C2—C1B	1.367 (7)	C4—C5	1.397 (6)
C2—C3	1.480 (6)	C5—C6	1.370 (7)
C2—S1B	1.701 (4)	C6—C7	1.381 (8)
S1B—C2 ⁱ	1.701 (4)	C7—C8	1.378 (7)
C1B—C1B ⁱ	1.43 (4)	C8—C9	1.396 (6)
O1—C4	1.364 (5)	C9—C10	1.506 (6)
O1—C3	1.433 (5)	C11—C12	1.527 (6)
O2—C12	1.213 (5)	C13—C14	1.523 (5)
O3—C12	1.269 (5)	C14—C13 ⁱ	1.523 (5)
C2—S1A—C2 ⁱ	93.4 (3)	O1—C3—C2	108.1 (3)
C2—C1A—C1A ⁱ	112.8 (3)	O1—C4—C9	115.8 (3)
C1B—C2—C1A	50.2 (13)	O1—C4—C5	123.8 (4)
C1B—C2—C3	121.3 (11)	C9—C4—C5	120.3 (4)
C1A—C2—C3	126.1 (4)	C6—C5—C4	120.1 (4)
C1B—C2—S1B	109.0 (10)	C5—C6—C7	120.6 (4)
C1A—C2—S1B	102.8 (6)	C8—C7—C6	119.2 (4)
C3—C2—S1B	124.7 (3)	C7—C8—C9	121.8 (4)
C1B—C2—S1A	96.4 (10)	C4—C9—C8	117.9 (4)
C1A—C2—S1A	110.4 (4)	C4—C9—C10	120.8 (4)
C3—C2—S1A	123.3 (3)	C8—C9—C10	121.1 (4)
S1B—C2—S1A	23.4 (7)	C9—C10—N1	113.6 (3)
C2—S1B—C2 ⁱ	93.4 (3)	N1—C11—C12	111.8 (3)
C2—C1B—C1B ⁱ	112.5 (9)	O2—C12—O3	126.8 (4)
C4—O1—C3	118.2 (3)	O2—C12—C11	121.9 (4)
C13—N1—C10	111.4 (3)	O3—C12—C11	111.3 (4)
C13—N1—C11	112.4 (3)	N1—C13—C14	112.9 (3)
C10—N1—C11	115.0 (3)	C13—C14—C13 ⁱ	109.6 (4)

Symmetry codes: (i) $x, y, \frac{3}{2} - z$.