O3	1.5845 (3)	0.7708 (3)	0.6949 (4)	0.022 (2)
O4	1.6625 (4)	0.5724 (3)	0.9216 (5)	0.024 (2)
O5	1.3241 (5)	0.4764 (3)	0.9115 (5)	0.034 (2)
O7	0.8715 (4)	0.8013 (3)	0.9395 (5)	0.027 (2)
O8	1.0731 (5)	0.8805 (4)	1.1452 (7)	0.054 (4)
O*W*	0.8982 (6)	0.8758 (4)	0.5146 (6)	0.049 (4)
O*W'*	0.4567 (5)	0.8733 (4)	0.3662 (6)	0.042 (3)
C1	1.1539 (4)	0.7145 (5)	0.9363 (5)	0.023 (2)
C2	1.2984 (4)	0.7820 (4)	0.8290 (6)	0.023 (2)
C3	1.4467 (3)	0.7007 (5)	0.7764 (4)	0.018 (2)
C4	1.5150 (4)	0.6405 (3)	0.9720 (5)	0.019 (2)
C5	1.3752 (5)	0.5634 (3)	1.0646 (6)	0.022 (2)
C6	1.2223 (5)	0.6415 (4)	1.1178 (6)	0.027 (3)
C7	1.0242 (4)	0.8083 (4)	1.0133 (6)	0.027 (3)

Table 2. *Geometric parameters* (Å, °)

Cu—Cl	2.245 (1)	C5—C6	1.527 (5)
Cu—O3^i	2.010 (2)	C6—C1	1.511 (5)
Cu—O7	1.937 (3)	C1—C7	1.554 (5)
Cu—O1	2.021 (2)	O1—C1	1.447 (4)
Cu—O4^i	2.429 (3)	O3—C3	1.445 (4)
Cu—O*W*	2.370 (4)	O4—C4	1.427 (4)
C1—C2	1.542 (5)	O5—C5	1.436 (4)
C2—C3	1.519 (5)	O8—C7	1.226 (6)
C3—C4	1.512 (4)	O7—C7	1.265 (4)
C4—C5	1.530 (4)		
Cl—Cu—O7	173.7 (1)	O4^i—Cu—O*W*	159.1 (1)
O1—Cu—O3^i	164.8 (1)		
C1—C2—C3—C4	−56.7 (3)	O3—C3—C2—C1	−174.5 (4)
C2—C3—C4—C5	61.9 (3)	O3—C3—C4—O4	−56.5 (3)
C3—C4—C5—C6	−60.4 (3)	O3—C3—C4—C5	−179.3 (3)
C4—C5—C6—C1	54.3 (3)	O5—C5—C6—C1	−63.7 (3)
C5—C6—C1—C2	−49.7 (3)	O5—C5—C4—O4	−60.9 (3)
C6—C1—C2—C3	50.9 (3)	O5—C5—C4—C3	59.5 (3)
O1—C1—C6—C5	73.0 (3)	O1—C1—C2—C3	−73.7 (3)

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

As the product is air sensitive, the crystal was coated with vaseline oil and sealed in a Lindemann capillary. 12 H atoms out of the 15 present in the compound (HO1, HO5, H2*W* missing) were located from a Fourier map, introduced in fixed positions and attributed isotropic thermal factors equal to those of the bound atoms. The absolute configuration of the original product (1*R*,3*R*,4*R*,5*R*) has been checked by refinement (*R* was equal to 0.045 instead of 0.063 for the opposite enantiomer) and by comparison of 88 selected Bijvoet pairs $\pm h \pm k + l$ corresponding to $\Delta F_c > 1.5$ e using the anomalous dispersion of the Cu and Cl atoms.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond angles, least-squares-planes data and selected Bijvoet pairs have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71411 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1060]

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cis-$[IrCl(CO)(PPh_3)(\mu\text{-}P_4S_3)]_2.2CH_3C_6H_5$

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Abstract

The structure of *cis*-bis(μ-2,6,7-trithia-1,3,4,5-tetraphosphabicyclo[2.2.1]heptanato)-1κP^3,1:2$\kappa^2 P^5$;-2κP^3,1:2$\kappa^2 P^5$-bis[carbonylchloro(triphenylphosphine)-iridium] toluene solvate, *cis*-$[IrCl(CO)(PPh_3)(\mu\text{-}P_4S_3)]_2$.-$2CH_3C_6H_5$, has been determined by single-crystal X-ray diffraction. Each P_4S_3 ligand is bidentate, binding to the two Ir centers through oxidative addition and the cleavage of a basal P—P bond.

Comment

Tetraphosphorus trisulfide, P_4S_3, has exhibited interesting coordination chemistry with a variety of transition-metal complexes and is the subject of two review articles (di Vaira, Stoppioni & Peruzzini, 1990; di Vaira & Stoppioni, 1992). The complex *trans*-$[IrCl(CO)(PPh_3)(\mu\text{-}P_4S_3)]_2$, which exhibited a single carbonyl stretching band at 2055 cm^{-1} in its Nujol-mull infrared spectrum, was the reported product from the equimolar reaction between Vaska's complex, $[IrCl(CO)(PPh_3)_2]$, and P_4S_3 in benzene at 333 K; its X-ray crystal structure was determined (Ghilardi, Midollini & Orlandini, 1983).

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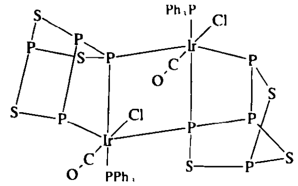
We report here that the use of excess P_4S_3 and a lower reaction temperature results in the isolation of the crystalline *cis* isomer (I). Toluene solutions of $[IrCl(CO)(PPh_3)_2]$ and P_4S_3 in molar ratios in excess of 1:2 were reacted at room temperature under an Ar atmosphere to produce a reddish brown solution. An olive-green powder, whose Nujol-mull infrared spectrum exhibited a single carbonyl stretching band at 2046.72 cm^{-1}, formed shortly after the complete addition of the P_4S_3 solution. Recrystallization attempts of this powder have been unsuccessful. After the precipitate was allowed to settle overnight in a refrigerator, the orange supernatant was separated, concentrated and stored in a freezer. Emerald-green crystals, which exhibited two carbonyl stretching bands at 2051.55 and 2044.79 cm^{-1}, formed after a few days. A crystallographic study showed that this compound is *cis*-$[IrCl(CO)(PPh_3)(\mu\text{-}P_4S_3)]_2.2CH_3C_6H_5$.



(I)

The two carbonyl bands in the infrared spectrum are consistent with the presence of single carbonyl ligands on each Ir center related to each other by C_2 symmetry. The two chloride ligands are also present in this spatial relationship. Conversely, the previously reported stereoisomer has its carbonyl ligands on each Ir center in a *trans* relationship to each other with C_i symmetry.

The symmetry differences between the *cis* and *trans* isomers are seen in the orientations of the two P_4S_3 ligands in each dimer. The angle between the planes P2, P3, P4 and $P2^i$, $P3^i$, $P4^i$ is 85.56° in the *cis* isomer and 0.0° in the *trans* isomer. In the *cis* isomer, the apex of each P_3 plane, represented by atoms P4 and $P4^i$, respectively, is in a *cis* orientation with respect to the Ir_2P_2 plane, thereby reflecting the twofold symmetry of the dimer. This contrasts with the *trans* orientation of the P_3 planes found in the *trans* isomer due to the presence of the inversion center.

The formation of this stereoisomer at a lower temperature demonstrates that the cleavage of one of the P—P bonds in the basal triangle of P_4S_3 is a facile process. Although excess P_4S_3 was used, the isolation of the crystalline product involving the basal P atoms rather than the apical one also demonstrates the favorable bonding mode between μ-P_4S_3 and the Ir center. The *cis* and *trans* Ir dimers represent the first crystallographically characterized stereoisomeric pair of transition-metal complexes containing a P_4S_3 ligand.

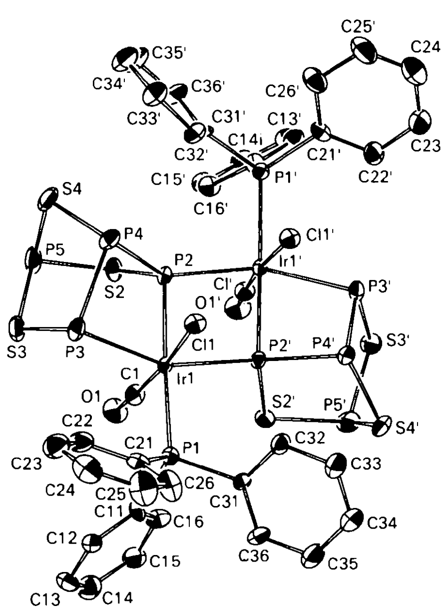


Fig. 1. *ORTEP* (Johnson, 1965) view of *cis*-$[IrCl(CO)(PPh_3)(\mu\text{-}P_4S_3)]_2$ with 25% probability ellipsoids.

Experimental

Crystal data

$[Ir_2Cl_2(P_4S_3)_2(C_{18}H_{15}P)_2\text{-}(CO)_2].2C_7H_8$
$M_r = 1660.4$
Monoclinic
$C2/c$
$a = 14.794\ (19)$ Å
$b = 18.377\ (15)$ Å
$c = 23.413\ (35)$ Å
$\beta = 97.63\ (11)°$
$V = 6309\ (13)$ Å^3
$Z = 4$

$D_x = 1.749$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 13 reflections
$\theta = 3.55\text{-}12.53°$
$\mu = 4.581$ mm^{-1}
$T = 293$ K
Plate
0.30 × 0.30 × 0.10 mm
Emerald green

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: empirical
$T_{min} = 0.49$, $T_{max} = 1.25$
6313 measured reflections
4062 independent reflections
2391 observed reflections $[I > 3\sigma(I)]$

$R_{int} = 0.036$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 20$
$l = -25 \rightarrow 25$
4 standard reflections monitored every 50 reflections
intensity variation: none

Refinement

Refinement on F
$R = 0.039$
$wR = 0.045$
2391 reflections
299 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.573$
$\Delta\rho_{max} = 0.90$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968)

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

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

	x	y	z	U_{eq}
Ir1	0.11542 (4)	0.14535 (3)	0.79473 (2)	0.028 (1)
P1	0.2755 (3)	0.1620 (2)	0.7806 (2)	0.035 (4)
P2	−0.0430 (3)	0.1389 (2)	0.8062 (1)	0.033 (4)
P3	0.1227 (3)	0.1692 (2)	0.8981 (2)	0.049 (4)
P4	−0.0239 (3)	0.2139 (3)	0.8840 (2)	0.048 (4)
P5	−0.0401 (4)	0.0492 (3)	0.9334 (2)	0.076 (6)
S2	−0.0821 (3)	0.0395 (2)	0.8428 (2)	0.049 (4)
S3	0.1013 (3)	0.0705 (3)	0.9441 (2)	0.064 (5)
S4	−0.0895 (3)	0.1570 (3)	0.9445 (2)	0.071 (5)
Cl1	0.1022 (3)	0.2759 (2)	0.7948 (2)	0.046 (4)
O1	0.1320 (9)	−0.0173 (6)	0.8105 (5)	0.067 (9)
C1	0.1270 (12)	0.0442 (8)	0.8029 (7)	0.046 (10)
C11	0.3420 (11)	0.0775 (7)	0.7913 (6)	0.040 (9)
C12	0.4188 (11)	0.0686 (10)	0.8332 (7)	0.055 (10)
C13	0.4633 (12)	0.0002 (11)	0.8408 (8)	0.063 (10)
C14	0.4295 (14)	−0.0587 (11)	0.8057 (9)	0.072 (11)
C15	0.3559 (13)	−0.0511 (11)	0.7626 (8)	0.066 (10)
C16	0.3097 (12)	0.0167 (8)	0.7558 (7)	0.052 (10)
C21	0.3423 (10)	0.2298 (7)	0.8266 (7)	0.041 (9)
C22	0.3412 (12)	0.2261 (10)	0.8882 (8)	0.065 (10)
C23	0.3921 (14)	0.2801 (12)	0.9224 (9)	0.079 (11)
C24	0.4405 (15)	0.3340 (11)	0.8975 (10)	0.083 (11)
C25	0.4409 (16)	0.3373 (11)	0.8392 (10)	0.092 (11)
C26	0.3922 (14)	0.2843 (10)	0.8016 (8)	0.073 (10)
C31	0.2909 (9)	0.1911 (8)	0.7072 (6)	0.036 (9)
C32	0.2393 (11)	0.2538 (9)	0.6850 (7)	0.052 (10)
C33	0.2601 (14)	0.2846 (11)	0.6314 (8)	0.070 (10)
C34	0.3230 (14)	0.2533 (12)	0.6008 (8)	0.080 (11)
C35	0.3723 (15)	0.1900 (12)	0.6231 (9)	0.084 (11)
C36	0.3564 (11)	0.1631 (10)	0.6768 (7)	0.061 (10)
C2	0.1715 (17)	0.3833 (13)	0.9280 (11)	0.043 (6)
C3	0.1177 (19)	0.3890 (14)	0.9724 (11)	0.049 (6)
C4	0.1157 (17)	0.4527 (11)	1.0046 (11)	0.049 (6)
C5	0.1704 (17)	0.5110 (9)	0.9926 (9)	0.042 (6)
C6	0.2105 (15)	0.5097 (11)	0.9419 (8)	0.033 (5)
C7	0.2109 (17)	0.4463 (10)	0.9091 (10)	0.038 (5)
C8	0.1733 (20)	0.5790 (11)	1.0281 (10)	0.053 (6)

Table 2. *Geometric parameters* (Å, °)

Ir1—P1	2.453 (4)	P1—C21	1.847 (14)
Ir1—P2	2.397 (4)	C21—C22	1.45 (2)
Ir1—P2^{i}	2.464 (3)	C22—C23	1.43 (3)
Ir1—P3	2.449 (4)	C23—C24	1.39 (3)
Ir1—Cl1	2.407 (4)	C24—C25	1.37 (3)
Ir1—C1	1.874 (15)	C25—C26	1.44 (3)
O1—C1	1.144 (16)	C21—C26	1.42 (2)
P2—P4	2.271 (6)	P1—C31	1.842 (14)
P3—P4	2.302 (7)	C31—C32	1.44 (2)
S2—P2	2.130 (5)	C32—C33	1.45 (2)
S3—P3	2.155 (6)	C33—C34	1.37 (3)
S4—P4	2.099 (6)	C34—C35	1.43 (3)
S2—P5	2.138 (6)	C35—C36	1.40 (2)
S3—P5	2.109 (7)	C31—C36	1.38 (2)
S4—P5	2.140 (9)	C2—C3	1.40 (4)
P1—C11	1.837 (14)	C3—C4	1.40 (3)
C11—C12	1.41 (2)	C4—C5	1.40 (3)
C12—C13	1.42 (2)	C5—C6	1.40 (3)
C13—C14	1.41 (3)	C6—C7	1.40 (3)
C14—C15	1.39 (3)	C2—C7	1.40 (3)
C15—C16	1.42 (2)	C5—C8	1.50 (3)
C11—C16	1.44 (2)		
Ir1···Ir1^{i}	3.762 (1)	S2···S3	3.406 (6)
Cl1···Cl1^{i}	3.444 (9)	S2···S4	3.228 (7)
P2···P3	3.091 (6)	S3···S4	3.241 (7)
P2···P2^{i}	3.070 (7)		
P2—Ir1—P1	175.5 (1)	S4—P5—S3	99.4 (3)
P3—Ir1—P1	101.2 (1)	P5—S2—P2	105.6 (3)
P2^{i}—Ir1—P1	100.4 (1)	P5—S3—P3	107.9 (3)
P2—Ir1—P2^{i}	78.3 (1)	P5—S4—P4	100.5 (3)
P3—Ir1—P2	79.3 (1)	P1—C11—C12	124 (1)
P3—Ir1—P2^{i}	155.9 (1)	P1—C11—C16	117 (1)
Cl1—Ir1—P1	87.5 (1)	C12—C11—C16	119 (1)
Cl1—Ir1—P2	88.2 (1)	C11—C12—C13	121 (2)
Cl1—Ir1—P2^{i}	91.3 (2)	C12—C13—C14	119 (2)
Cl1—Ir1—P3	79.3 (2)	C13—C14—C15	122 (2)
C1—Ir1—P1	93.5 (5)	C14—C15—C16	119 (2)
C1—Ir1—P2	91.0 (5)	C11—C16—C15	120 (2)
C1—Ir1—P2^{i}	94.2 (5)	P1—C21—C22	118 (1)
C1—Ir1—P3	94.9 (5)	P1—C21—C26	120 (1)
C1—Ir1—Cl1	174.1 (5)	C22—C21—C26	121 (2)
O1—C1—Ir1	177 (2)	C21—C22—C23	117 (2)
Ir1—P2—Ir1^{i}	101.4 (2)	C22—C23—C24	122 (2)
S2—P2—Ir1^{i}	108.6 (2)	C23—C24—C25	121 (2)
P4—P2—Ir1^{i}	137.0 (2)	C24—C25—C26	121 (2)
C11—P1—Ir1	112.7 (5)	C21—C26—C25	118 (2)
C21—P1—Ir1	117.2 (5)	P1—C31—C32	116 (1)
C21—P1—C11	104.8 (7)	P1—C31—C36	124 (1)
C31—P1—Ir1	113.8 (5)	C32—C31—C36	119 (1)
C31—P1—C11	104.0 (7)	C31—C32—C33	118 (2)
C31—P1—C21	102.9 (7)	C32—C33—C34	122 (2)
P4—P2—Ir1	92.3 (2)	C33—C34—C35	120 (2)
S2—P2—Ir1	114.2 (2)	C34—C35—C36	118 (2)
S2—P2—P4	102.1 (2)	C31—C36—C35	123 (2)
P4—P3—Ir1	90.2 (2)	C3—C2—C7	119 (2)
S3—P3—Ir1	110.6 (2)	C2—C3—C4	122 (3)
S3—P3—P4	100.0 (2)	C3—C4—C5	119 (2)
P3—P4—P2	85.1 (2)	C4—C5—C6	118.8 (9)
S4—P4—P2	102.7 (3)	C4—C5—C8	120.2 (4)
S4—P4—P3	103.7 (3)	C6—C5—C8	120.2 (4)
S3—P5—S2	106.6 (3)	C5—C6—C7	121 (2)
S4—P5—S2	98.0 (3)	C2—C7—C6	119 (2)

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

A suitable crystal was dipped in Paratone-N while in an Ar stream and sealed in a Lindemann capillary for the crystallographic study. The systematic absences indicated the probable space groups to be *Cc* or *C*2/*c*. Patterson maps, computed using *SHELXS*86 (Sheldrick, 1986), revealed possible Ir positions. Attempts to obtain a meaningful structural model in space group *Cc* failed since no complete ligand could be located. The successful solution and refinement of the crystal structure confirmed the choice of the centrosymmetric space group *C*2/*c*. Subsequent difference Fourier maps, computed using *SHELX*76 (Sheldrick, 1976), clearly revealed the ligands bound to the Ir center and the presence of a toluene solvent molecule. All full-matrix least-squares refinement cycles were performed using *SHELX*76. As a result of disorder, the C_{ring}—C_{ring} and C_{methyl}—C_{ring} bond distances were fixed at 1.395 and 1.499 Å, respectively. The toluene atoms, C2–C8, were refined isotropically. The non-H atoms of the Ir complex were refined anisotropically. H atoms were not included in the structural model. Geometrical calculations were performed using *SHELX*76, *XANADU* (Roberts & Sheldrick, 1975) and *PLANE* (Brändén & Lundgren, 1978). Data collection: *P*2$_1$ *Assembler Language Data Collection Programs* (Syntex, 1975). Data reduction: locally written program (Tipton, 1977). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71424 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1074]

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Copper Complex of 6,7-Dihydro-5*H*-1,4-dithiepine-2,3-dithiolate

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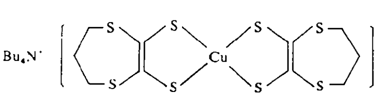
Abstract

A short C—S bond distance and a planar ligand structure indicate extensive delocalization of electron density in the anion of tetrabutylammonium bis(6,7-dihydro-5*H*-1,4-dithiepine-2,3-dithiolato)copper(III), $[\mathrm{N(C_4H_9)_4}][\mathrm{Cu(C_5H_6S_4)_2}]$. The central metal ion, formally $\mathrm{Cu^{III}}$, has an unusual oxidation state. The crystal has a layer-like structure formed by the anions, while the tetrabutylammonium cations intercalate between them.

Comment

Multi-sulfur 1,2-dithiolene complexes have attracted much attention from chemists because of their structural similarity to BEDT-TTF salts, which are molecular organic superconductors (Williams, Ferraro, Thorn, Carlson, Geiser, Wang, Kini & Whangbo, 1992). Some of these complexes, such as $[M(\mathrm{dddt})_2]^{n-}$ (Schultz, Wang, Soderholm, Shifter & Williams, 1987) and $[M(\mathrm{dmit})_2]^{n-}$ (Fan, Li, Ou & You, 1992), have been studied extensively. The title complex (1) is an analogue of $\mathrm{Bu_4N}[M(\mathrm{dddt})_2]$ but differs in the external ligand unit. An X-ray analysis was undertaken to investigate the importance of the ligand unit in determining molecular structure and crystal packing.



(1)

The dithiolate ligand of complex (1) was prepared as a dipotassium salt following a method described by Kato, Kobayashi & Sasaki (1986), but using nitrogen instead of argon. The salt (1.2 g) was dissolved in methanol and 0.21 g of $\mathrm{CuCl_2.2H_2O}$ in methanol was added dropwise. Stirring was continued for 1 h. Air was bubbled through the reaction mixture for 15 min. After filtration, 1.5 g of tetrabutylammonium bromide was added to the brown filtrate. The dark-brown precipitate was collected by filtration, washed with methanol and dried in air. The powder product was recrystallized in acetone by slow evaporation. Single crystals were obtained in 2 weeks. Analysis for $\mathrm{C_{26}H_{48}CuNS_8}$: calculated C 44.95, H 6.96, N 2.02%; found C 44.31, H 6.70, N 1.70%.

The four S atoms surround the Cu atom to yield a square-planar environment. The $\mathrm{CuS_4}$ core is distorted from D_{2h} symmetry by a twist angle of 6.10 (1)° in contrast with that of 29° in $\mathrm{Bu_4N[Cu(dddt)_2]}$. The ligand, with the exception of the external propene unit, is almost planar. The maximum displacement from the least-squares plane defined by S(1)—C(2)—S(3) is 0.076 (8) Å. It is apparent that this complex has better planarity than $\mathrm{Bu_4N[Cu(dddt)_2]}$ (Vance, Welch & Bereman, 1989). The average *M*—S (2.181 Å) and C=C (1.342 Å) bond distances are close to the corresponding values in $\mathrm{Bu_4N[Cu(dddt)_2]}$. The C—S bond distances in the dithiolene group vary from 1.743 (6) to 1.768 (6) Å and are intermediate between those of C=S and C—S. The shorter C—S bond length shows partial double-bond character. The C—S distances in the five-membered ring formed through coordination with the Cu atom are shorter than those in the periphery of the ligand. This may indicate slight electron delocalization in the coordination ring. The electron delocalization makes it difficult to assign an oxidation state to the central metal ion.

The external seven-membered rings adopt a chair conformation and the two propene groups have a *trans* orientation.