Acta Cryst. (1979). B35, 172–174

One Example of Disulphide as Bridging Ligand in μ-Disulphido-bis[η-(n-butylcyclopentadienyl)dichloromolybdenum]

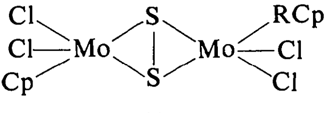
By Bernard Meunier and Keith Prout

Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, England

(*Received* 24 *June* 1978; *accepted* 28 *September* 1978)

Abstract. $Mo_2(C_9H_{13})_2Cl_4S_2.\frac{1}{2}CH_2Cl_2$, $C_{18}H_{26}Cl_4Mo_2S_2.\frac{1}{2}CH_2Cl_2$, $M_r = 682{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}058$ (2), $b = 12{\cdot}516$ (5), $c = 13{\cdot}250$ (4) Å, $\alpha = 86{\cdot}60$ (3), $\beta = 80{\cdot}97$ (2), $\gamma = 77{\cdot}46$ (2)°, $U = 1288$ Å^3, $Z = 2$, $D_c = 1{\cdot}75$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å), $\mu = 1{\cdot}60$ mm^{-1}. The two Mo atoms and the two S atoms form the corners of a distorted tetrahedron with a S–S bond length of 2·019 (3) and a Mo–Mo distance of 2·937 (1) Å.

Introduction. Few examples of disulphide, S_2^{2-}, as a bridging ligand between two transition metals have been observed (Vergamini & Kubas, 1976; Küllmer, Röttinger & Vahrenkamp, 1977). It has been suggested that this rather unusual sulphur ligand may occur in some ferredoxins (Kubas, Spiro & Terzis, 1973; Terzis & Rivest, 1973). A new disulphide complex has been prepared by Dr M. L. H. Green and Mr M. Bunker during their investigation of molybdenum–sulphur chemistry (Green & Bunker, 1978). We report here the structure of this complex (I) which is one of the few examples of a disulphide ligand bridging two Mo atoms.*



(I)

RCp = n-butylcyclopentadienyl

The crystals were supplied by Dr M. L. H. Green and Mr M. Bunker. A small black needle (size 0·2 × 0·2 × 1·1 mm) was sealed under nitrogen in a glass capillary tube and mounted on a Nonius CAD-4F diffractometer. Unit-cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflexions. The intensities of reflexions with $\theta < 28°$ were measured by an $\omega/2\theta$ scan, with a variable scan rate and an ω scan angle of $(1{\cdot}20 + 0{\cdot}35 \tan\theta)°$. Mo $K\alpha$ radiation from a graphite monochromator was used. Lorentz and polarization corrections were applied to the 4723 reflexions with $I > 3\sigma(I)$ which were used in subsequent calculations. No correction was made for absorption. The structure was solved by Patterson and Fourier techniques and refined by a least-squares method with a 'large-block' approximation. In the later stages of the refinement a difference synthesis revealed four peaks which were interpreted as disordered dichloromethane solvent molecules in holes in the crystal structure. The H atoms were positioned geometrically and included in the structure factor calculations, their location being adjusted after each cycle. After three cycles of refinement with unit weights, each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r(X)$ where n is the number of coefficients, A_r, for a Chebyshev series, T_r is the polynomial function and X is $|F_o|/|F_o(\max.)|$. Three coefficients, A_r, were used with values 12·5, 17·4 and 6·5 (Rollett, 1965). The refinement converged at $R = 0{\cdot}052$ ($R_w = 0{\cdot}060$). Calculations were performed on the Oxford University ICL 1906A and the London University CDC 7600 with the Oxford *CRYSTALS* package (Carruthers, 1975). The final positional parameters are given in Table 1.* Table 2 lists some interatomic distances and interbond angles with their standard deviations calculated from the variance–covariance matrix.

Discussion. The crystal structure consists of dimeric $[(n\text{-BuCp})MoCl_2S]_2$ units, one of which is illustrated by Fig. 1, in general positions in the unit cell.

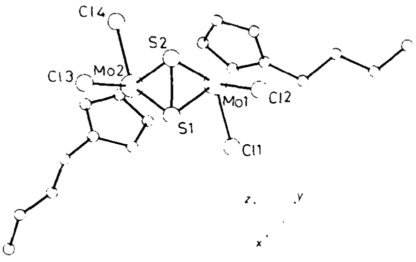


Fig. 1. Disulphide as a bridging ligand in $[Mo_2(n\text{-BuCp})_2Cl_4S_2]$.

---

* The first example has just been published (Müller, Nolte & Krebs, 1978).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33928 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/79/010172-03$01.00

The two Mo atoms and the two S atoms form the corners of a distorted tetrahedron. The S—S bond length (2·019 Å) is similar to the distances previously described for that ligand (Vergamini & Kubas, 1976; Dirand, Ricard & Weiss, 1975).

Table 1. *Fractional atomic coordinates with estimated standard deviations in parentheses*

	x	*y*	*z*
Mo(1)	0·12976 (6)	0·70806 (5)	0·12723 (4)
Mo(2)	0·29207 (6)	0·58919 (4)	0·29631 (4)
Cl(1)	0·2205 (2)	0·5761 (2)	−0·0073 (1)
Cl(2)	0·2110 (3)	0·8463 (2)	0·0060 (2)
Cl(3)	0·5237 (2)	0·6212 (2)	0·3796 (1)
Cl(4)	0·0939 (3)	0·6616 (2)	0·4430 (1)
S(1)	0·4316 (2)	0·6690 (2)	0·1465 (1)
S(2)	0·2753 (2)	0·7796 (1)	0·2427 (1)
C(1)	−0·1413 (8)	0·7450 (7)	0·0756 (6)
C(2)	−0·1266 (8)	0·6499 (7)	0·1400 (6)
C(3)	−0·1111 (8)	0·6774 (8)	0·2398 (6)
C(4)	−0·1134 (8)	0·7913 (7)	0·2375 (6)
C(5)	−0·137 (1)	0·8313 (7)	0·1400 (7)
C(6)	−0·172 (1)	0·7532 (9)	−0·0337 (7)
C(7)	−0·301 (1)	0·8544 (7)	−0·0580 (6)
C(8)	−0·354 (1)	0·8541 (8)	−0·1624 (7)
C(9)	−0·468 (1)	0·9613 (7)	−0·1903 (7)
C(10)	0·4521 (9)	0·4075 (6)	0·2979 (5)
C(11)	0·3859 (9)	0·4293 (5)	0·2030 (5)
C(12)	0·2047 (9)	0·4501 (5)	0·2239 (5)
C(13)	0·1562 (9)	0·4439 (6)	0·3307 (6)
C(14)	0·309 (1)	0·4181 (6)	0·3760 (5)
C(15)	0·636 (1)	0·3671 (7)	0·3104 (7)
C(16)	0·691 (1)	0·2466 (7)	0·2877 (7)
C(17)	0·872 (1)	0·1965 (8)	0·3079 (8)
C(18)	0·922 (2)	0·0759 (9)	0·282 (1)
C(19)*	0·267 (3)	−0·023 (2)	0·459 (2)
C(20)*	0·437 (4)	0·045 (2)	0·496 (2)
Cl(5)*	0·254 (1)	0·1151 (7)	0·4782 (7)
Cl(6)*	0·469 (2)	−0·083 (1)	0·476 (1)
H(21)	−0·1272	0·5748	0·1183
H(31)	−0·1005	0·6262	0·3004
H(41)	−0·1006	0·8346	0·2958
H(51)	−0·1486	0·9100	0·1178
H(61)	−0·0601	0·7539	−0·0786
H(62)	−0·2151	0·6875	−0·0483
H(71)	−0·2484	0·9195	−0·0550
H(72)	−0·4052	0·8604	−0·0052
H(81)	−0·2488	0·8394	−0·2146
H(82)	−0·4191	0·7944	−0·1628
H(91)	−0·4991	0·9564	−0·2597
H(92)	−0·4039	1·0216	−0·1908
H(93)	−0·5742	0·9766	−0·1390
H(111)	0·4555	0·4297	0·1337
H(121)	0·1246	0·4666	0·1719
H(131)	0·0359	0·4554	0·3678
H(141)	0·3147	0·4090	0·4510
H(151)	0·6506	0·3785	0·3822
H(152)	0·7085	0·4089	0·2621
H(161)	0·6099	0·2069	0·3314
H(162)	0·6852	0·2371	0·2140
H(171)	0·8784	0·2037	0·3819
H(172)	0·9541	0·2365	0·2652
H(181)	1·0413	0·0448	0·2856
H(182)	0·8403	0·0354	0·3242
H(183)	0·9160	0·0681	0·2076

* Disordered dichloromethane occupancy numbers: C(19) = 0·25, C(20) = 0·25, Cl(5) = 0·50, Cl(6) = 0·50.

Assuming complete delocalization of electrons between the Mo atoms and the S atoms, the four Mo—S distances can be expected to be equal. In fact, these Mo—S bond lengths are divided in two groups: 2·387 (2), 2·399 (2) Å and 2·426 (2), 2·427 (2) Å, so that each Mo atom forms with each S atom one short and one longer Mo—S bond. This is consistent with each S atom acting as a 2e donor to one Mo atom and a 1e donor to the other, so that each Mo acquires 3e from the disulphido ligand. The Mo—S bonds *trans* to the cyclopentadienyl ring (known to be a strong electron donor) have the longer bond lengths.

The torsion angle about the S(1)—S(2) bond for the Mo(1)—S(1) and Mo(2)—S(2) bonds (84·3°) is similar to those of organometallic disulphides (mean value: 90°) (Hordvik, 1966; Rahman, Safe & Taylor, 1970).

This conformation around the S—S bond and the disulphido ligand acting as a 3e donor towards each Mo atom together necessitate a relatively short distance between the two Mo atoms. This distance (2·937 Å) should not be considered as a direct bonding interaction Mo—Mo, but is only required by geometrical constraint of the disulphido ligand. Accordingly each Mo atom has a 16-electron configuration.

Many bridged Mo—Mo single-bond distances in neutral complexes are in the range 2·50–2·90 Å (Stieffel, 1977), but we have to keep in mind the fact that the metal—metal distance is not an absolute criterion for metal—metal bonding (for a recent review on the subject, see Vahrenkamp, 1978).

Both cyclopentadienyl rings are planar within experimental error and the C—C bond distances are in the range 1·38–1·42 Å (mean value: 1·41 Å) for the Mo(1) ring and 1·41–1·43 Å (mean value: 1·42 Å) for the Mo(2) ring.

The electron density in a hole in the crystal structure, detected by Watkin's (1972) method, has been inter-

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°)

Mo(1)···Mo(2)	2·937 (1)	S(1)—S(2)	2·019 (3)
Mo(1)—S(1)	2·426 (2)	Mo(2)—S(1)	2·399 (2)
Mo(1)—S(2)	2·387 (2)	Mo(2)—S(2)	2·427 (2)
Mo(1)—Cl(1)	2·420 (2)	Mo(2)—Cl(3)	2·425 (2)
Mo(1)—Cl(2)	2·415 (2)	Mo(2)—Cl(4)	2·400 (2)
Mo(1)—S(1)—Mo(2)	74·98 (5)	Mo(1)—S(2)—Mo(2)	75·17 (5)
S(1)—Mo(1)—S(2)	49·60 (7)	S(1)—Mo(2)—S(2)	49·46 (7)
Mo(1)—S(1)—S(2)	64·20 (7)	Mo(2)—S(1)—S(2)	66·00 (7)
Mo(1)—S(2)—S(1)	66·20 (7)	Mo(2)—S(2)—S(1)	64·54 (7)
Cl(1)—Mo(1)—Cl(2)	88·71 (8)	Cl(3)—Mo(2)—Cl(4)	88·48 (7)
Cl(1)—Mo(1)—S(1)	84·56 (6)	Cl(3)—Mo(2)—S(1)	85·63 (6)
Cl(1)—Mo(1)—S(2)	134·16 (7)	Cl(3)—Mo(2)—S(2)	82·40 (6)
Cl(2)—Mo(1)—S(1)	83·48 (7)	Cl(4)—Mo(2)—S(1)	134·38 (7)
Cl(2)—Mo(1)—S(2)	86·43 (7)	Cl(4)—Mo(2)—S(2)	84·91 (7)

preted as a dichloromethane molecule with a partial occupancy on two disordered sites.

We thank Dr P. Thomas for collecting the data. One of us (BM) thanks the Royal Society and the CNRS for support.

References

Carruthers, J. R. (1975). *CRYSTALS User Manual.* Oxford Univ. Computing Laboratory.

Dirand, J., Ricard, L. & Weiss, R. (1975). *Inorg. Nucl. Chem. Lett.* **11**, 661–664.

Green, M. L. H. & Bunker, M. (1978). Unpublished results.

Hordvik, A. (1966). *Acta Chem. Scand.* **20**, 1885–1891.

Kubas, G. J., Spiro, T. G. & Terzis, A. (1973). *J. Am. Chem. Soc.* **95**, 273–274.

Küllmer, V., Röttinger, E. & Vahrenkamp, H. (1977). *J. Chem. Soc. Chem. Commun.* pp. 782–783.

Müller, A., Nolte, W. O. & Krebs, B. (1978). *Angew. Chem. Int. Ed. Engl.* **17**, 279.

Rahman, R., Safe, S. & Taylor, A. (1970). *Q. Rev. Chem. Soc.* **24**, 208–237.

Rollett, J. S. (1965). *Computing Methods in Crystallography*, p. 40. Oxford: Pergamon Press.

Stieffel, E. I. (1977). *Prog. Inorg. Chem.* **22**, 1–223.

Terzis, A. & Rivest, R. (1973). *Inorg. Chem.* **12**, 2132–2136.

Vahrenkamp, H. (1978). *Angew. Chem. Int. Ed. Engl.* **17**, 379–392.

Vergamini, P. J. & Kubas, G. J. (1976). *Prog. Inorg. Chem.* **21**, 261–282.

Watkin, D. J. (1972). *Acta Cryst.* A**28**, 33–35.

Acta Cryst. (1979). B**35**, 174–177

Dimeric Chlorobis(triphenylphosphine)silver*

By Anders Cassel†

Division of Inorganic Chemistry 1, *Chemical Center, University of Lund, PO Box* 740, *S*-220 07 *Lund* 7, *Sweden*

(*Received* 21 *June* 1978; *accepted* 16 *October* 1978)

Abstract. $[Ag(C_{36}H_{30}P_2)Cl]_2$, triclinic, $P\bar{1}$, $a = 10{\cdot}308\,(5)$, $b = 12{\cdot}608\,(4)$, $c = 13{\cdot}893\,(6)$ Å, $\alpha = 113{\cdot}36\,(4)$, $\beta = 110{\cdot}29\,(3)$, $\gamma = 75{\cdot}02\,(3)°$, $V = 1539$ Å^3, $Z = 1$, $D_c = 1{\cdot}44$, $D_o = 1{\cdot}45$ Mg m^{-3}. Two Ag atoms are joined through a double Cl bridge. To each Ag are also coordinated two P atoms from two triphenylphosphine molecules. The coordination polyhedron around Ag is a distorted tetrahedron. The crystal structure is thus built up from discrete dimeric molecules.

Introduction. Prismatic crystals of the title compound were obtained on the slow cooling to room temperature of a warm CH_3CN solution of $AgNO_3$, $(C_2H_5)_4NCl$ and $P(C_6H_5)_3$; the molar ratio was 1:1:2. A single crystal defined by the six planes (001), (00$\bar{1}$), (10$\bar{1}$), ($\bar{1}$01), (110) and ($\bar{1}\bar{1}$0) was selected. The distances between parallel planes were 0·07, 0·08 and 0·08 mm.

The intensity measurements were carried out on a computer-controlled four-circle diffractometer (CAD-4) equipped with a graphite monochromator and using Cu $K\alpha$ radiation. The ω–2θ scan technique, with a scan interval of $\Delta\omega = (0{\cdot}60 + 0{\cdot}40 \tan\theta)°$, was employed. The background was measured for one quarter of the scan time at each end of the peak-scan interval. 6181 reflections were recorded in the range $5° < \theta < 50°$, and 4821 with $I > 2\sigma(I)$ were used in the subsequent calculations. The standard deviation $\sigma(I)$ is based on counting statistics. The intensities of three standard reflections measured regularly were used to scale the intensities of the other reflections. The intensity decrease was linear with respect to exposure time and the total decrease was 17·6%. Corrections were made for Lorentz, polarization and absorption effects [μ(Cu $K\alpha$) = 7·32 mm^{-1}]. No corrections for anomalous dispersion or secondary extinction were made.

The positions of Ag, Cl, P and C were determined using the Patterson function, successive electron density syntheses and least-squares refinements. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Ag, Cl and P were refined anisotropically and C isotropically. The H atoms were not included. In the final difference synthesis no peaks larger than 1·8 e Å^{-3} were found. Two peaks of 1·8 and 1·6 e Å^{-3} are residuals from the electron density of silver. Apart from these no peaks larger than 1·1 e Å^{-3} were found. The quantity minimized was $\sum w_i(|F_o| - |F_c|)^2$ giving $R = \sum||F_o| -$

---

* Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands. VIII.

† Present address: Inorganic Chemistry, Division of Mineral Processing, University of Luleå, S-951 87 Luleå, Sweden.

0567-7408/79/010174-04$01.00