

- DUCHAMP, D. J. (1964). *CRYM* crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KHAN, N. I., FACKLER, J. P. JR, KING, C., WANG, J. C. & WANG, S. (1989). *Inorg. Chem.* **27**, 1672–1673.
- KING, C., WANG, J. C., KHAN, N. I. & FACKLER, J. P. JR (1989). *Inorg. Chem.* **28**, 2145–2149.
- ORPEN, A. G., BRAMMER, L., ALLEN, F. H., KENNARD, O., WATSON, D. G. & TAYLOR, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- ÚSON, R., LAGUNA, A. & VICENTE, J. (1977). *J. Organomet. Chem.* **131**, 471–475.

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## Structure of $\beta$ -Mo<sub>2</sub>(SCN)<sub>4</sub>[(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane]<sub>2</sub> Nitromethane Solvate

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**Abstract.** Bis- $\mu$ -[(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane-*P,P'*]-bis[bis(thiocyanato)molybdenum](*Mo—Mo*) nitromethane solvate, [Mo<sub>2</sub>(SCN)<sub>4</sub>(C<sub>28</sub>H<sub>28</sub>P<sub>2</sub>)<sub>2</sub>].CH<sub>3</sub>NO<sub>2</sub>, *M<sub>r</sub>* = 1338.2, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2, *a* = 15.890 (3), *b* = 17.532 (3), *c* = 24.745 (3) Å, *V* = 6893 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.29 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 6.0$  cm<sup>-1</sup>, *F*(000) = 2736, *T* = 298 K, *R* = 0.067 for 3341 unique observed reflections. The asymmetric unit consists of two half molecules of the title complex, each residing on a twofold axis. The Mo—Mo quadruple bond [2.172 (3) and 2.154 (3) Å] is bridged by an *S,S*-dppb ligand, and each Mo atom is *N*-coordinated to two thiocyanate groups. The intraligand P—Mo—Mo—P torsion angles ( $\varphi$ ) are 25.8 (3) and 21.9 (3)°.

**Introduction.** Compounds of the structural type  $\beta$ -Mo<sub>2</sub>X<sub>4</sub>(PP)<sub>2</sub> have been intensively studied in the recent past (Agaskar, Cotton, Fraser, Manojlovic-Muir, Muir & Peacock, 1986). When the Mo<sub>2</sub>X<sub>4</sub>P<sub>4</sub> core is twisted about the Mo—Mo axis, an inherently dissymmetric Mo<sub>2</sub><sup>4+</sup> chromophore results (Peacock, 1987). In order to observe the optical activity of this chromophore, it is necessary to stabilize one conformer of the Mo<sub>2</sub>P<sub>2</sub>C<sub>2</sub> ring by using a chiral diphosphine such as (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane, (*S,S*-dppb). One of us has previously reported the structures of  $\beta$ -Mo<sub>2</sub>X<sub>4</sub>(*S,S*-dppb) (*X* = Cl, Br) (Agaskar *et al.*, 1986), and herein we detail the structure of the thiocyanate derivative.

**Experimental.** The title complex was synthesized as follows. (NH<sub>4</sub>)<sub>4</sub>[Mo<sub>2</sub>(SCN)<sub>8</sub>].6H<sub>2</sub>O (0.08 g) and a

slight excess of *S,S*-dppb (0.09 g) were refluxed in methanol (35 ml) under nitrogen atmosphere. The colour of the solution changed from green to yellow-brown during the course of the reaction. Removal of the methanol, followed by chromatography on alumina, using toluene as an eluant afforded a yellow band. The product was recrystallized from nitromethane. Analysis, calculated for C<sub>60</sub>H<sub>56</sub>Mo<sub>2</sub>N<sub>4</sub>P<sub>4</sub>S<sub>4</sub>: C 56.4, H 4.42, N 4.39%; found C 56.00, H 4.37, N 4.41%. A yellow-green prism, *ca* 0.5 × 0.4 × 0.15 mm, was mounted in a general position on a glass fibre; systematic absences: *h* = 2*n* + 1 in *h*00, *k* = 2*n* + 1 in 0*k*0; the reflections *l* = 2*n* + 1 in 00*l* were systematically weak; Enraf-Nonius CAD-4F diffractometer; graphite monochromator;  $\theta/2\theta$  scan mode; cell parameters refined by least-squares methods on basis of 25 independent  $\theta$  values, 11 <  $\theta$  < 13°; intensities measured to  $\theta = 25.0^\circ$  over *hkl* range 0 to 18, 0 to 20, 0 to 29; 402 and 042 measured every 2 h and showed a decay of *ca* 3% over data collection; 6990 data measured, 6935 independent data with 3341 having *I* > 2.0 $\sigma$ (*I*) considered observed and used in structure determination and refinement: *R*<sub>int</sub> = 0.034; corrected for decomposition, Lorentz-polarization effects and absorption (*DIFABS*; Walker & Stuart, 1983), max. and min. values of applied absorption correction 1.40 and 0.77; solved by direct methods (*MITHRIL*; Gilmore, 1984) for heavy atoms, and subsequent full-matrix least squares; anisotropic thermal parameters for all non-H atoms except aryl C atoms and solvent atoms; phenyl groups refined as rigid groups with idealized geometry, C—C 1.395, C—H 1.0 Å; aliphatic C—H atoms included at calculated positions, C—H 1.0 Å, fixed contributions to structure factors for all H atoms, with *U* =

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Table 1. Final positional parameters (fractional coordinates) and isotropic thermal parameters ( $\text{\AA}^2$ ) (equivalent isotropic parameters  $U_{\text{eq}}$  for anisotropic atoms), with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Mo(1)	0.03047 (12)	-0.05545 (9)	0.58150 (8)	0.033
Mo(2)	0.94131 (12)	-0.03074 (9)	0.08117 (8)	0.038
S(1)	0.0433 (7)	-0.1608 (5)	0.4032 (3)	0.122
S(2)	0.1279 (6)	-0.1400 (6)	0.7536 (3)	0.112
S(3)	0.8167 (7)	-0.0436 (7)	-0.0940 (3)	0.161
S(4)	0.8903 (9)	-0.1226 (6)	0.2617 (3)	0.151
P(1)	-0.0907 (4)	-0.1447 (3)	0.6055 (2)	0.040
P(2)	-0.1836 (4)	0.0248 (3)	0.5608 (2)	0.043
P(3)	0.8323 (5)	0.0726 (3)	0.0996 (3)	0.050
P(4)	1.0168 (4)	0.1687 (3)	0.0615 (2)	0.039
N(1)	0.0274 (13)	-0.0913 (10)	0.5043 (7)	0.049
N(2)	0.0715 (12)	-0.0807 (10)	0.6597 (8)	0.041
N(3)	0.8998 (11)	-0.0289 (10)	0.0023 (8)	0.046
N(4)	0.9233 (14)	-0.0682 (10)	0.1618 (7)	0.058
C(1)	0.0373 (17)	-0.1198 (12)	0.4657 (11)	0.058
C(2)	0.0936 (14)	-0.1078 (13)	0.6992 (10)	0.043
C(3)	0.8672 (17)	-0.0374 (15)	-0.0369 (9)	0.069
C(4)	0.908 (2)	-0.092 (1)	0.205 (1)	0.083
C(S1)	0.092 (3)	-0.300 (3)	0.224 (2)	0.05 (1)
C(S2)	0.658 (5)	-0.141 (3)	0.237 (2)	0.08 (2)
C(11)	-0.1973 (14)	-0.1357 (12)	0.5737 (11)	0.049
C(12)	-0.2369 (13)	-0.0585 (14)	0.5920 (9)	0.051
C(13)	-0.2507 (14)	-0.2031 (13)	0.5885 (12)	0.063
C(14)	-0.3338 (14)	-0.0576 (15)	0.5781 (13)	0.083
C(21)	0.8403 (14)	0.1721 (11)	0.0757 (9)	0.039
C(22)	0.9230 (14)	0.2113 (12)	0.0934 (8)	0.043
C(23)	0.7623 (13)	0.2173 (13)	0.0937 (10)	0.050
C(24)	0.9158 (14)	0.2969 (11)	0.0796 (12)	0.061
C(111)	-0.1098 (15)	-0.1553 (11)	0.6778 (5)	0.039 (6)
C(112)	-0.1349 (19)	-0.2242 (11)	0.7010 (7)	0.066 (8)
C(113)	-0.1528 (11)	-0.2278 (6)	0.7561 (7)	0.077 (9)
C(114)	-0.1456 (13)	-0.1626 (10)	0.7881 (5)	0.070 (8)
C(115)	-0.1205 (16)	-0.0937 (9)	0.7649 (7)	0.054 (7)
C(116)	-0.1026 (8)	-0.0901 (7)	0.7098 (6)	0.038 (6)
C(121)	-0.0492 (19)	-0.2358 (7)	0.5802 (13)	0.055 (6)
C(122)	-0.0666 (8)	-0.2594 (16)	0.5275 (13)	0.057 (7)
C(123)	-0.0272 (17)	-0.3240 (15)	0.5065 (5)	0.087 (9)
C(124)	0.0296 (16)	-0.3650 (7)	0.5381 (11)	0.086 (9)
C(125)	0.0471 (10)	-0.3414 (15)	0.5908 (10)	0.090 (9)
C(126)	0.008 (2)	-0.277 (1)	0.612 (1)	0.09 (1)
C(211)	-0.236 (2)	0.111 (1)	0.583 (1)	0.041 (6)
C(212)	-0.2230 (17)	0.1760 (10)	0.5522 (9)	0.063 (8)
C(213)	-0.2491 (8)	0.2470 (10)	0.5714 (8)	0.084 (9)
C(214)	-0.2880 (16)	0.2527 (7)	0.6218 (10)	0.09 (1)
C(215)	-0.3008 (13)	0.1874 (10)	0.6530 (7)	0.10 (1)
C(216)	-0.2746 (11)	0.1164 (10)	0.6338 (10)	0.084 (9)
C(221)	-0.2156 (17)	0.0162 (15)	0.4928 (5)	0.050 (6)
C(222)	-0.2938 (17)	0.0418 (7)	0.4747 (9)	0.070 (8)
C(223)	-0.3191 (8)	0.0273 (12)	0.4217 (10)	0.079 (8)
C(224)	-0.2663 (14)	-0.0128 (12)	0.3868 (5)	0.064 (8)
C(225)	-0.1881 (14)	-0.0384 (7)	0.4049 (10)	0.066 (7)
C(226)	-0.1628 (9)	-0.0239 (15)	0.4579 (10)	0.054 (6)
C(311)	0.808 (2)	0.082 (1)	0.172 (1)	0.064 (8)
C(312)	0.7271 (18)	0.0792 (18)	0.1941 (9)	0.11 (1)
C(313)	0.7151 (11)	0.0882 (11)	0.2496 (11)	0.071 (8)
C(314)	0.7842 (18)	0.0999 (11)	0.2834 (7)	0.09 (1)
C(315)	0.8652 (15)	0.1026 (16)	0.2617 (10)	0.11 (1)
C(316)	0.8771 (14)	0.0936 (9)	0.2062 (11)	0.09 (1)
C(321)	0.7396 (19)	0.0328 (21)	0.0654 (8)	0.071 (8)
C(322)	0.7060 (15)	0.0676 (10)	0.0195 (8)	0.077 (8)
C(323)	0.6396 (10)	0.0332 (17)	-0.0082 (10)	0.12 (1)
C(324)	0.6069 (16)	-0.0360 (18)	0.0100 (7)	0.11 (1)
C(325)	0.6405 (12)	-0.0708 (9)	0.0558 (9)	0.12 (1)
C(326)	0.7069 (13)	-0.0364 (21)	0.0835 (11)	0.10 (1)
C(411)	1.0078 (14)	0.1964 (13)	-0.0078 (5)	0.038 (5)
C(412)	1.0332 (17)	0.2682 (13)	-0.0258 (4)	0.051 (6)
C(413)	1.0261 (11)	0.2872 (7)	-0.0803 (6)	0.066 (7)
C(414)	0.9934 (12)	0.2344 (11)	-0.1169 (5)	0.076 (8)
C(415)	0.9679 (15)	0.1626 (11)	-0.0989 (5)	0.058 (7)
C(416)	0.9751 (9)	0.1436 (6)	-0.0443 (6)	0.043 (5)
C(421)	1.1085 (15)	0.2177 (15)	0.0855 (7)	0.044 (6)
C(422)	1.180 (2)	0.216 (1)	0.053 (1)	0.068 (8)
C(423)	1.2552 (14)	0.2484 (6)	0.0719 (9)	0.061 (7)
C(424)	1.2581 (13)	0.2821 (12)	0.1230 (7)	0.079 (9)
C(425)	1.1861 (18)	0.2836 (11)	0.1552 (7)	0.088 (9)
C(426)	1.1113 (12)	0.2514 (8)	0.1365 (9)	0.063 (7)
N(S1)	0.121 (4)	-0.334 (3)	0.271 (2)	0.16 (2)
O(S1)	0.049 (4)	-0.298 (4)	0.290 (2)	0.18 (2)
N(S2)	0.598 (5)	-0.121 (4)	0.237 (3)	0.15 (2)
O(S2)	0.150 (3)	-0.500 (3)	0.189 (2)	0.17 (2)
O(S3)	0.545 (3)	-0.102 (3)	0.269 (2)	0.13 (2)
O(S4)	0.540 (4)	-0.110 (3)	0.212 (2)	0.17 (2)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ), with *e.s.d.*'s in parentheses

Primed atoms are related to unprimed atoms by the symmetry operation  $-x, -y, z$ .

Mo(1)—Mo(1')	2.172 (3)	Mo(2)—Mo(2')	2.154 (3)
Mo(1)—P(1)	2.551 (7)	Mo(2)—P(3)	2.548 (7)
Mo(1)—P(2')	2.545 (7)	Mo(2)—P(4')	2.556 (6)
Mo(1)—N(1)	2.01 (2)	Mo(2)—Mo(3)	2.06 (2)
Mo(1)—N(2)	2.09 (2)	Mo(2)—N(4)	2.12 (2)
N(1)—C(1)	1.09 (4)	N(3)—C(3)	1.11 (4)
N(2)—C(2)	1.14 (4)	N(4)—C(4)	1.16 (3)
C(1)—S(1)	1.71 (3)	C(3)—S(3)	1.63 (3)
C(2)—S(2)	1.60 (3)	C(4)—S(4)	1.54 (3)
Mo(1')—Mo(1)—P(1)	102.3 (2)	Mo(2')—Mo(2)—P(3)	103.5 (2)
Mo(1')—Mo(1)—P(2')	103.7 (2)	Mo(2')—Mo(2)—P(4')	104.2 (2)
Mo(1')—Mo(1)—N(1)	105.6 (6)	Mo(2')—Mo(2)—N(3)	105.6 (6)
Mo(1')—Mo(1)—N(2)	109.2 (5)	Mo(2')—Mo(2)—N(4)	105.8 (6)
P(1)—Mo(1)—P(2')	153.9 (3)	P(3)—Mo(2)—O(4')	152.2 (3)
N(1)—Mo(1)—N(2)	145.2 (8)	N(3)—Mo(2)—N(4)	148.5 (8)
P(1)—Mo(1)—N(1)	90.6 (6)	P(3)—Mo(2)—N(3)	86.6 (6)
P(1)—Mo(1)—N(2)	83.7 (6)	P(3)—Mo(2)—N(4)	87.7 (6)
P(2')—Mo(1)—N(1)	84.1 (6)	P(4')—Mo(2)—N(3)	85.3 (6)
P(2')—Mo(1)—N(2)	86.1 (6)	P(4')—Mo(2)—N(4)	85.5 (5)

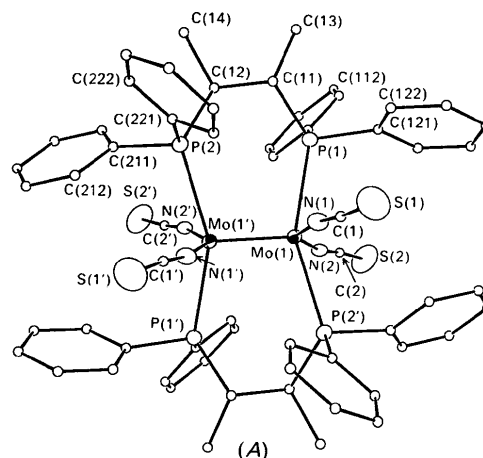


Fig. 1. Molecular structure and atomic labelling scheme for molecule (A). Thermal ellipsoids are shown at the 20% probability level, C atoms shown as spheres of arbitrary radius.

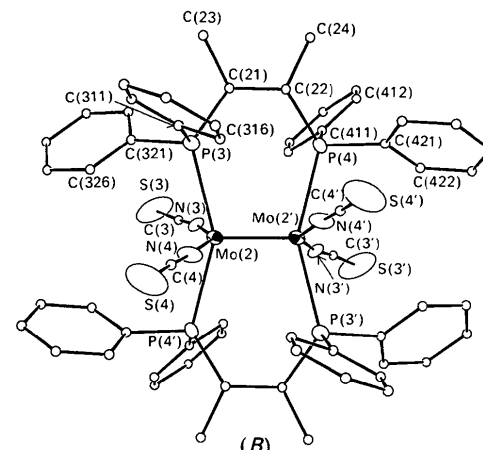


Fig. 2. Molecular structure and atomic labelling scheme for molecule (B). Thermal ellipsoids are shown at the 20% probability level, C atoms shown as spheres of arbitrary radius.

0.08 Å<sup>2</sup>;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o)]^{-1}$ ; max.  $\Delta/\sigma = 0.063$ , av. = 0.004;  $(\Delta\rho)_{\max} = 0.67$ ,  $(\Delta\rho)_{\min} = -0.50$  e Å<sup>-3</sup>;  $R = 0.067$ ,  $wR = 0.089$ ,  $S = 2.93$ ; expected *S* configuration at chiral C atoms confirmed by refinement on  $\eta$  parameter (Rodgers, 1981) [ $\eta = 1.14$  (36),  $(1 + \eta)/\sigma(\eta) = 5.4$ ]; a solvent molecule of nitromethane was disordered over two sites, with occupancies of each site set at 0.5; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–151) with corrections for anomalous scattering; calculations carried out on a MicroVAX 3600 computer using the Glasgow *GX* suite of programs (Mallinson & Muir, 1985).

**Discussion.** Final positional parameters are given in Table 1, with selected bond distances and angles in Table 2.\* The atomic labelling scheme and molecular structures of the two independent molecules, (*A*) and (*B*), are shown in Figs. 1 and 2. There are only relatively minor differences between the two crystal-

\* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positional parameters, and a complete listing of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54438 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lographically independent molecules. The Mo—Mo distances of 2.172 (3) and 2.154 (3) Å [(*A*) and (*B*) respectively] are similar, differing by only  $5\sigma$ , and fall within the range previously tabulated (Agaskar *et al.*, 1986). The torsion angle P—Mo—Mo—P ( $\varphi$ ) defines the degree of twist in the Mo<sub>2</sub> chromophore, and is 25.8 (3)° for (*A*) and 21.9 (3)° for (*B*). The nearly linear SCN ligands [range of angle N—C—S 174 (3)–178 (3)°] are *N*-coordinated to the Mo atoms, as found in [Mo<sub>2</sub>(SCN)<sub>6</sub>]<sup>4-</sup> (Bino, Cotton & Fanwick, 1979), Mo<sub>2</sub>(SCN)<sub>4</sub>(dppm)<sub>2</sub> (Abbott, Bose, Cotton, Hall & Sekutowski, 1978) and Mo<sub>2</sub>(SCN)<sub>4</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub> (Cotton & Matusz, 1989).

#### References

- ABBOTT, E. H., BOSE, K. S., COTTON, F. A., HALL, W. T. & SEKUTOWSKI, J. C. (1978). *Inorg. Chem.* **17**, 3240–3245.  
 AGASKAR, P. A., COTTON, F. A., FRASER, I. F., MANOJLOVIC-MUIR, L. J., MUIR, K. W. & PEACOCK, R. D. (1986). *Inorg. Chem.* **25**, 2511–2519.  
 BINO, A., COTTON, F. A. & FANWICK, P. E. (1979). *Inorg. Chem.* **18**, 3558–3561.  
 COTTON, F. A. & MATUSZ, M. (1989). *Inorg. Chim. Acta*, **157**, 223–225.  
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.  
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 PEACOCK, R. D. (1987). *Polyhedron*, **6**, 715–721.  
 RODGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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## Structure of Tetraspiro[1,3,5,7-tetraoxa-2,4,6,8-tetragermacyclooctane-2,1':4,1'':6,1''':8,1''''-tetrakisgerminane]

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**Abstract.** C<sub>20</sub>H<sub>40</sub>Ge<sub>4</sub>O<sub>4</sub>,  $M_r = 634.89$ , monoclinic, *C2/c*,  $a = 13.628$  (4),  $b = 22.562$  (3),  $c = 10.329$  (3) Å,  $\beta = 128.47$  (2)°,  $V = 2486$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.67$ ,  $D_x = 1.696$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 4.75$  mm<sup>-1</sup>,  $F(000) = 1280$ ,  $T = 142$  K,  $R = 0.037$  for 2515 unique reflections. The germacyclohexane rings adopt chair conformations in which the fold of the ring is smaller in the vicinity of and greater away

from the germanium atom. The tetraoxatetragermacyclooctane ring adopts a skewed-tub conformation.

**Introduction.** Germacyclohexane is a key compound in the stereochemistry of organogermanium compounds. In our previous study, NMR and molecular mechanics calculations revealed that the germacyclohexane ring adopts a chair conformation in