C4—C5	1.387 (3)	C5′—C6′	1.413 (3)
C4—N9	1.384 (3)	C5′—N7′	1.385 (3)
C5—C6	1.412 (3)	C6′—N11′	1.323 (3)
C5—N7	1.392 (3)	N7′—C8′	1.337 (3)
C6—N11	1.332 (3)	N7′—C10′	1.460 (3)
N7—C8	1.335 (3)	C8′—N9′	1.326 (3)
Cl1—Zn—Cl2	109.75 (3)	N7—C8—N9	113.1 (2)
Cl1—Zn—Cl3	113.02 (3)	Zn—N9—C4	128.8 (1)
Cl1—Zn—N9	106.22 (6)	Zn—N9—C8	124.7 (1)
Cl2—Zn—Cl3	108.49 (3)	C4—N9—C8	105.5 (2)
Cl2—Zn—N9	112.24 (6)	C2′—N1′—C6′	119.7 (2)
Cl3—Zn—N9	107.15 (6)	N1′—C2′—N3′	126.0 (2)
C2—N1—C6	119.5 (2)	C2′—N3′—C4′	116.8 (2)
N1—C2—N3	129.0 (2)	N3′—C4′—C5′	120.8 (2)
C2—N3—C4	111.6 (2)	N3′—C4′—N9′	126.9 (2)
N3—C4—C5	125.1 (2)	C5′—C4′—N9′	112.3 (2)
N3—C4—N9	126.1 (2)	C4′—C5′—C6′	119.3 (2)
C5—C4—N9	108.8 (2)	C4′—C5′—N7′	104.1 (2)
C4—C5—C6	118.5 (2)	C6′—C5′—N7′	136.6 (2)
C4—C5—N7	106.0 (2)	N1′—C6′—C5′	117.4 (2)
C6—C5—N7	135.4 (2)	N1′—C6′—N11′	116.3 (2)
N1—C6—C5	116.3 (2)	C5′—C6′—N11′	126.3 (2)
N1—C6—N11	118.4 (2)	C5′—N7′—C8′	106.3 (2)
C5—C6—N11	125.2 (2)	C5′—N7′—C10′	128.8 (2)
C5—N7—C8	106.5 (2)	C8′—N7′—C10′	124.9 (2)
C5—N7—C10	128.6 (2)	N7′—C8′—N9′	114.0 (2)
C8—N7—C10	124.8 (2)	C4′—N9′—C8′	103.3 (2)

The title structure was solved using Patterson and Fourier techniques. The H atoms were observed in a difference map but placed at calculated positions using *BONDAT* (*Xtal*3.2; Hall, Flack & Stewart, 1992), except for those on the methyl groups, where one was positioned from the difference map and the others calculated from this. The positions of the H atoms on the water molecule were taken from the difference map. Refinement of an extinction correction parameter was attempted, but this did not give a physically realistic value for the parameter and was subsequently omitted.

Data reduction: *Xtal*3.2 *DIFDAT ADDREF ABSORB SORTRF*. Program(s) used to solve structure: *Xtal*3.2. Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

The authors thank Mr Don Craig of the University of New South Wales for collecting the data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2738–2740

Bis(pyridine-2-thione)-2κS;3κS-tetra-μ-sulfido-1:2$\kappa^4 S$;1:3$\kappa^4 S$-bis(triphenylphosphine)-2κP;3κP-dicoppermolybdenum Bis(dichloromethane) Solvate

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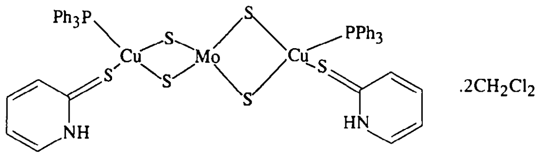
Abstract

The structure determination of $[Cu_2MoS_4(C_5H_5NS)_2(C_{18}H_{15}P)_2].2CH_2Cl_2$ is reported. The compound contains a linear $[CuS_2MoS_2Cu]$ cluster core, with each Cu atom having a distorted tetrahedral coordination involving two S atoms of a tetradentate MoS_4^{2-} moiety, one S atom of a pyridine-2-thione ligand and one P atom of a triphenylphosphine ligand.

Comment

Several linear clusters have been prepared over the past two decades, for example, $[MS_4M'_2(PPh_3)_3]$ (M = Mo, W; M' = Cu, Ag; Müller, Bögge & Schimanski, 1983) and the heterometallic trinuclear clusters $(Et_4N)[(PPh_3)_2AgS_2MS_2Cu(CN)]$ (M = Mo, W; Du, Zhu, Chen, Wu & Lu, 1992*a*,*b*). The title compound, (I), also has a linear $[CuS_2MoS_2Cu]$ core, but one in which both Cu atoms are tetrahedrally coordinated by mixed ligands.



(I)

The Mo atom in (I) has tetrahedral coordination, MoS_4^{2-}, and each Cu atom is coordinated by a distorted tetrahedron involving two S atoms of the tetradentate MoS_4^{2-} moiety, one S atom of C_5H_5NS and one P atom of PPh_3 (Fig. 1). The average Cu$\cdots$Mo, μ-S—Mo and μ-S—Cu distances of 2.7347 (7), 2.199 (2) and 2.298 (2) Å, respectively, are comparable with the corresponding values of 2.710 (3), 2.208 (5) and 2.267 (5) Å found in $[Cu_2MoS_4(PPh_3)_3].0.8CH_2Cl_2$. The Cu—S($C_5H_5NS$) bond length of 2.348 (2) Å is longer than that of 2.284 (2) Å in $[Cu_2(C_5H_5NS)_6]Cl_2$ (Constable & Raithby, 1987). The S—C bond length of 1.703 (6) Å in the C_5H_5NS ligand is fully in accord with the ligand existing as the thione tautomer (Mura, Olby & Robinson, 1985).

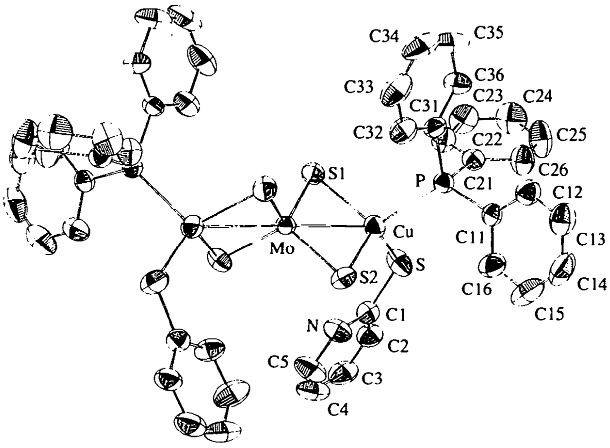


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title compound was synthesized by reaction of $[Cu_2MoS_4(PPh_3)_3].0.8CH_2Cl_2$ with excess C_5H_5NS in dichloromethane. Crystals suitable for analysis were obtained by allowing the filtrate to stand overnight after addition of 2-propanol.

Crystal data

$[Cu_2MoS_4(C_5H_5NS)_2(C_{18}H_{15}P)_2].2CH_2Cl_2$
$M_r = 1268.06$
Monoclinic
$C2/c$
$a = 32.027$ (7) Å
$b = 9.829$ (2) Å
$c = 17.420$ (6) Å
$\beta = 96.89$ (3)°
$V = 5444$ (3) Å^3
$Z = 4$
$D_x = 1.55$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–13°$
$\mu = 1.51$ mm^{-1}
$T = 293$ K
Block
0.35 × 0.25 × 0.18 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.67$, $T_{\max} = 0.76$
5249 measured reflections
5249 independent reflections

3213 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max} = 25°$
$h = -38 \rightarrow 38$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 300 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.045$
$wR = 0.051$
$S = 1.35$
3213 reflections
279 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.82$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo	0	0.32667 (7)	1/4	2.46 (1)
Cu	0.06893 (2)	0.32212 (7)	0.17134 (4)	3.26 (1)
Cl1	0.28411 (9)	0.3121 (3)	0.0973 (2)	10.53 (8)
Cl2	0.32025 (9)	0.5192 (4)	0.0096 (2)	11.57 (9)
S	0.08303 (5)	0.1908 (2)	0.06483 (9)	4.41 (4)
S1	0.00879 (5)	0.4514 (2)	0.14944 (9)	3.89 (3)
S2	0.05697 (5)	0.2005 (2)	0.27906 (9)	3.40 (3)
P	0.12501 (4)	0.4676 (2)	0.18098 (8)	2.70 (3)
N	0.0399 (2)	−0.0043 (5)	0.1245 (3)	4.0 (1)
C	0.3128 (3)	0.343 (1)	0.0206 (6)	10.0 (3)
C1	0.0591 (2)	0.0361 (6)	0.0642 (3)	3.3 (1)
C2	0.0565 (2)	−0.0528 (6)	0.0017 (4)	4.2 (1)
C3	0.0354 (2)	−0.1722 (7)	0.0024 (4)	4.9 (2)
C4	0.0165 (2)	−0.2094 (6)	0.0660 (4)	5.3 (2)
C5	0.0191 (2)	−0.1245 (7)	0.1276 (4)	5.5 (2)
C11	0.1728 (2)	0.4035 (6)	0.2354 (3)	2.9 (1)
C12	0.2043 (2)	0.4849 (6)	0.2723 (4)	3.9 (1)
C13	0.2390 (2)	0.4307 (7)	0.3148 (4)	4.9 (2)
C14	0.2431 (2)	0.2939 (8)	0.3216 (4)	5.9 (2)
C15	0.2130 (2)	0.2096 (7)	0.2855 (5)	6.1 (2)
C16	0.1778 (2)	0.2626 (6)	0.2424 (4)	4.3 (2)
C21	0.1400 (2)	0.5152 (6)	0.0870 (3)	3.0 (1)
C22	0.1081 (2)	0.5510 (6)	0.0304 (4)	4.1 (1)
C23	0.1171 (2)	0.5984 (7)	−0.0406 (4)	4.9 (2)
C24	0.1579 (2)	0.6086 (8)	−0.0557 (4)	5.8 (2)
C25	0.1896 (2)	0.5688 (9)	−0.0003 (4)	6.3 (2)
C26	0.1811 (2)	0.5219 (7)	0.0707 (3)	4.3 (1)
C31	0.1176 (2)	0.6323 (5)	0.2262 (3)	3.0 (1)
C32	0.0979 (2)	0.6312 (6)	0.2934 (4)	4.3 (1)
C33	0.0929 (2)	0.7504 (8)	0.3329 (4)	5.6 (2)
C34	0.1070 (2)	0.8708 (7)	0.3040 (4)	6.1 (2)
C35	0.1246 (3)	0.8740 (6)	0.2376 (4)	5.7 (2)
C36	0.1303 (2)	0.7548 (6)	0.1981 (4)	3.9 (1)

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

Mo···Cu	2.7347 (7)	Cu—S1	2.301 (2)
Mo—S1	2.184 (2)	Cu—S2	2.295 (2)
Mo—S2	2.214 (2)	Cu—P	2.286 (2)
Cu—S	2.348 (2)	S—C1	1.703 (6)
Cu···Mo···Cu^i	178.13 (3)	Mo···Cu—S1	50.51 (4)
Cu···Mo—S1	54.40 (4)	Mo···Cu—S2	51.32 (5)
Cu···Mo—S1^i	126.91 (5)	Mo···Cu—P	128.85 (5)
Cu···Mo—S2	54.04 (4)	S—Cu—S1	114.15 (6)
Cu···Mo—S2^i	124.68 (5)	S—Cu—S2	115.25 (6)
S1—Mo—S1^i	111.68 (6)	S—Cu—P	100.25 (6)
S1—Mo—S2	108.42 (6)	S1—Cu—S2	101.82 (6)
S1—Mo—S2^i	108.24 (5)	S1—Cu—P	107.54 (6)
S2—Mo—S2^i	111.87 (7)	S2—Cu—P	118.18 (6)
Mo···Cu—S	130.41 (5)	Cu—S—C1	111.5 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The title structure was refined by full-matrix least-squares techniques, with anisotropic displacement parameters for the non-H atoms, except for those of the dichloromethane solvent molecules. H atoms were placed in calculated positions which were not refined. The structure solution and refinement were carried out on a Compaq Prolinear 4/50 computer using the *MolEN* (Fair, 1990) program package, including *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1271). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aquatris(2,6-difluorobenzoato)praseodymium(III)

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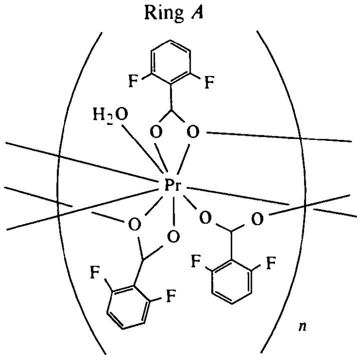
Abstract

The title compound, *catena*-poly[aquapraseodymium(III)-tris(μ-2,6-difluorobenzoato)-*O*:*O*′;*O*,*O*′:*O*;*O*,*O*′:*O*], $[Pr(C_7H_3F_2O_2)_3(H_2O)]$, is a single-strand polymer. The Pr atoms are ninefold coordinated by three bridging 2,6-difluorobenzoate ligands and one water molecule. The 2,6-difluorobenzoate ligands bind in two unique modes, with one ligand forming a common μ-*O*:*O*′ bridge and the other two forming less common μ-*O*,*O*′:*O* bridges. One of the F atoms of a benzoate ligand forms a three-center hydrogen bond.

Comment

In the title complex, (I), the 2,6-difluorobenzoate ions are arbitrarily called rings *A*, *B* and *C*.



(I)

Praseodymium(III), $[Xe]4f^2$, forms a nine-coordinate complex with three 2,6-difluorobenzoate ions and a water molecule (Fig. 1). The coordination sphere of the Pr atom is a square-face-capped trigonal prism; atoms O1*A*, O2*B*^{i} and O1*C*^{i} form the top triangle, and O1*C*, O1*W* and O1*A*^{ii} form the bottom triangle, with O1*B*, O2*A* and O2*C* as the caps [symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$] (Fig. 2). The Pr atom receives 14 electrons from nine ligand atoms (two electrons from each, except for two O1*C* atoms and two O1*A* atoms which donate one electron each due to the bridging represented in the scheme above).

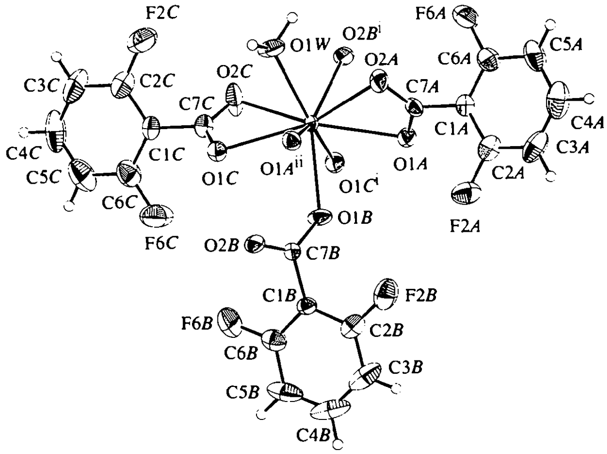


Fig. 1. The crystal structure of the asymmetric unit of the title polymer. Displacement ellipsoids are plotted at the 50% probability level.

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† Deceased (1994).