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Crystal structure of bis(tetraphenylphosphonium) distibiumheptadecasulfide, $[P(C_6H_5)_4]_2Sb_2S_{17.25}$

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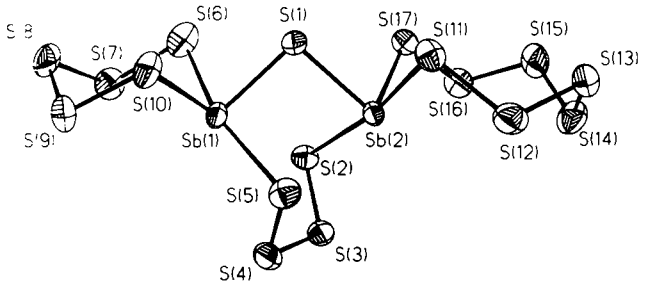

Fig. 1. The Sb_2S_{17} cluster.

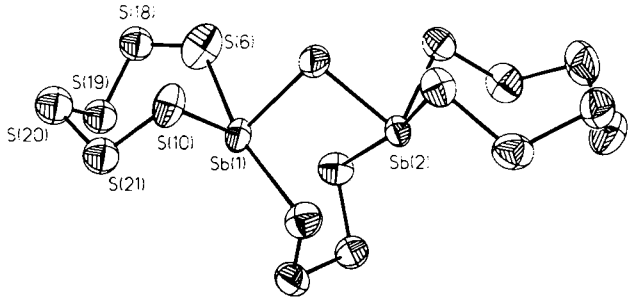

Fig. 2. The Sb_2S_{17} cluster shown with the S_6^{2-} ligand that partially replaces S_5^{2-}.

Source of material: Single crystals of $[(C_6H_5P)4]2Sb2S17$ were obtained in a hydrothermal reaction of elemental antimony and sulfur with tetraphenylphosphoniumbromide (molar ratio = 1:8:1) in a 0.2m aqueous ammonia solution within 9 days together with other thioantimonate species.

The hydrothermal treatment of the elements in the presence of tetraphenylphosphonium in an aqueous ammonia solution yielded $[P(C_6H_5)4]2Sb2S17$ which comprises the $Sb_2S_{17}^{2-}$ anion. Two Sb centers are bridged via a single S atom and a S_4 unit. Two additional S_5 and S_7 chelating ligands both adopting chair conformation complete the coordination spheres around the Sb centers (see Fig. 1., selected distances and angles: Sb(1)–S(1) 2.446(2) Å, Sb(2)–S(1) 2.452(2) Å, Sb(1)–S(5) 2.745(2) Å, Sb(2)–S(2) 2.776(2) Å, Sb(2)–S(11) 2.604(2) Å, Sb(2)–S(17) 2.531(2) Å, S(10)–Sb(1)–S(6) 91.85(7)°, S(11)–Sb(2)–S(17) 91.95(6)°, S(6)–Sb(1)–S(5) 167.14(7)°, S(11)–Sb(2)–S(2) 116.17(5)°). A very similar cluster $Sb_2S_{15}^{2-}$ which holds two chelating S_5^{2-} ligands was reported recently being prepared in strong donor solvents (see ref. 1). A partial substitution of the S_5 ligands by S_6 groups (see Fig. 2) with a fraction of 25% leads to an empirical formula of $[P(C_6H_5)4]2Sb2S17.25$ for the title compound. It is interesting to note that this replacement with a nearly identical proportion of 27% S_6 ligands was also reported for $Sb_2S_{15}^{2-}$. The conformation of the SbS_6 ring however is rather twisted than resembling cyclo-S_7 as reported for $Sb_2S_{15}^{2-}$. The most pronounced difference between $Sb_2S_{17}^{2-}$ and $Sb_2S_{15}^{2-}$ is an increased angle at the single bridging sulfur atom of 101.0° compared to 95.1° in the title compound. In addition, the Sb–S distances to the S_4 ligand (2.667 Å compared to 2.776 Å / 2.745 Å) are somewhat shorter. Thus the intercluster Sb–Sb distance in Sb_2S_{17} is reduced to 3.614 Å from 3.752 Å in Sb_2S_{15}.

$C_{48}H_{40}P_2S_{17.25}Sb_2$, monoclinic, $C1c1$ (No. 9), a =10.762(1) Å, b =32.384(2) Å, c =16.834(1) Å, β =91.058(6)°, V =5865.9 Å^3, Z =4, $R(F)$ =0.023, $R_w(F^2)$ =0.054.

Table 1. Parameters used for the X-ray data collection

Crystal:	yellow block, size 0.1 x 0.2 x 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.24 cm^{-1}
Diffractometer:	STOE AED II
Scan mode:	2θ
$T_{measurement}$:	293 K
$2\theta_{max}$:	50°
N(hkl)$_{unique}$:	5501
Criterion for I_o:	$I_o > 2\,\sigma(I_o)$
N($param$)$_{refined}$:	638
Programs:	SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å^2)

Atom	Site	Occ.	x	y	z	U_{iso}
S(18)	4a	0.25	0.1979(8)	0.5450(2)	0.5344(4)	0.069(2)
S(19)	4a	0.25	0.0467(8)	0.5169(3)	0.4941(5)	0.066(2)
S(20)	4a	0.25	0.964(1)	0.5562(4)	0.4131(7)	0.073(3)
S(21)	4a	0.25	0.814(2)	0.5748(6)	0.466(1)	0.062(4)
H(2)	4a		0.2301(6)	0.6329(2)	0.1767(3)	0.060
H(3)	4a		0.0852(7)	0.5977(2)	0.2491(4)	0.077
H(4)	4a		0.1043(8)	0.5275(3)	0.2687(4)	0.091
H(5)	4a		0.2634(9)	0.4920(2)	0.2126(4)	0.091
H(6)	4a		0.4067(7)	0.5255(2)	0.1371(4)	0.078
H(12)	4a		0.3051(7)	0.6729(2)	0.0051(4)	0.080
H(13)	4a		0.2849(8)	0.7426(2)	0.0235(5)	0.100
H(14)	4a		0.3949(7)	0.7760(2)	0.1218(4)	0.079
H(15)	4a		0.5325(7)	0.7396(2)	0.2004(4)	0.078
H(16)	4a		0.5504(6)	0.6687(2)	0.1861(3)	0.060
H(22)	4a		0.5755(7)	0.5927(2)	0.2248(4)	0.081
H(23)	4a		0.7701(8)	0.5667(2)	0.2570(5)	0.096
H(24)	4a		0.8971(8)	0.5430(2)	0.1574(6)	0.101
H(25)	4a		0.8378(7)	0.5510(2)	0.0272(6)	0.094
H(26)	4a		0.6473(6)	0.5788(2)	–0.0063(4)	0.071
H(32)	4a		0.2612(5)	0.5540(2)	1.0074(3)	0.056

Table 2. (Continued)

Atom	Site	Occ.	x	y	z	U_{iso}
H(33)	4*a*		0.2008(7)	0.5401(2)	0.8777(4)	0.080
H(34)	4*a*		0.2963(8)	0.5737(2)	0.7757(4)	0.087
H(35)	4*a*		0.4535(8)	0.6187(2)	0.8001(4)	0.089
H(36)	4*a*		0.5169(7)	0.6332(2)	0.9294(3)	0.071
H(42)	4*a*		0.3639(7)	0.5908(2)	0.3550(4)	0.077
H(43)	4*a*		0.4152(8)	0.5218(2)	0.3487(4)	0.089
H(44)	4*a*		0.5208(7)	0.4912(2)	0.4536(5)	0.084
H(45)	4*a*		0.5777(7)	0.5286(2)	0.5631(4)	0.081
H(46)	4*a*		0.5295(6)	0.5984(2)	0.5705(4)	0.063
H(52)	4*a*		0.6091(7)	0.6891(2)	0.5645(4)	0.075
H(53)	4*a*		0.6198(9)	0.7105(2)	0.6954(5)	0.100
H(54)	4*a*		0.447(1)	0.7087(2)	0.7720(4)	0.100

Table 2. (Continued)

Atom	Site	Occ.	x	y	z	U_{iso}
H(55)	4*a*		0.2611(9)	0.6866(3)	0.7186(5)	0.110
H(56)	4*a*		0.2482(8)	0.6665(2)	0.5863(4)	0.084
H(62)	4*a*		0.5068(6)	0.7391(2)	0.4349(3)	0.059
H(63)	4*a*		0.6612(6)	0.7684(2)	0.3599(4)	0.072
H(64)	4*a*		0.7979(6)	0.7281(2)	0.2931(4)	0.077
H(65)	4*a*		0.7833(6)	0.6574(2)	0.2987(4)	0.074
H(66)	4*a*		0.6299(5)	0.6266(2)	0.3720(3)	0.058
H(72)	4*a*		0.3731(5)	0.6963(2)	0.3147(3)	0.048
H(73)	4*a*		0.1987(5)	0.7112(2)	0.2391(3)	0.053
H(74)	4*a*		0.0056(6)	0.6935(2)	0.2832(4)	0.064
H(75)	4*a*		−0.0139(6)	0.6618(2)	0.4049(4)	0.080
H(76)	4*a*		0.1609(6)	0.6429(2)	0.4779(4)	0.074

Table 3. Final atomic coordinates and displacement parameters (in $Å^2$)

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	4*a*		0.90527(3)	0.58053(1)	0.65199(2)	0.0691(3)	0.0426(2)	0.0365(2)	0.0033(2)	0.0093(2)	−0.0003(2)
Sb(2)	4*a*		0.86952(3)	0.62786(1)	0.84463(2)	0.0562(2)	0.0376(2)	0.0378(2)	−0.0006(2)	−0.0003(2)	−0.0034(2)
S(1)	4*a*		0.9773(2)	0.64286(5)	0.7208(1)	0.091(1)	0.0489(8)	0.0531(9)	−0.0176(9)	0.0188(9)	−0.0015(7)
S(2)	4*a*		0.9364(2)	0.54584(5)	0.8236(1)	0.065(1)	0.0439(8)	0.076(1)	0.0056(8)	−0.0018(9)	0.0091(8)
S(3)	4*a*		0.7606(2)	0.52646(5)	0.8492(1)	0.083(1)	0.058(1)	0.0562(9)	−0.0140(9)	0.0059(9)	0.0119(8)
S(4)	4*a*		0.6571(2)	0.53537(6)	0.7462(1)	0.081(1)	0.068(1)	0.063(1)	−0.022(1)	−0.0023(9)	−0.0025(8)
S(5)	4*a*		0.6804(2)	0.59680(6)	0.7196(1)	0.063(1)	0.069(1)	0.0585(9)	0.0004(9)	−0.0014(8)	0.0122(8)
S(6)	4*a*		0.1410(2)	0.57628(7)	0.6117(1)	0.083(2)	0.099(2)	0.090(1)	0.035(1)	0.013(1)	0.016(1)
S(7)	4*a*	0.75	0.0958(3)	0.52752(8)	0.5280(2)	0.101(2)	0.056(2)	0.095(2)	0.023(2)	0.022(2)	−0.010(2)
S(8)	4*a*	0.75	0.0251(5)	0.5579(1)	0.4290(2)	0.128(3)	0.075(2)	0.060(2)	−0.006(2)	0.044(2)	−0.020(1)
S(9)	4*a*	0.75	0.8427(6)	0.5718(2)	0.4536(3)	0.110(4)	0.098(3)	0.045(2)	−0.018(3)	−0.004(2)	−0.013(2)
S(10)	4*a*		0.8501(2)	0.62319(5)	0.53009(9)	0.082(1)	0.068(1)	0.0447(8)	0.016(1)	0.0084(8)	0.0081(7)
S(11)	4*a*		0.8017(2)	0.70457(5)	0.8272(1)	0.066(1)	0.0454(8)	0.0583(9)	0.0081(8)	−0.0056(8)	0.0017(7)
S(12)	4*a*		0.6698(2)	0.70722(6)	0.9120(1)	0.053(1)	0.058(1)	0.092(1)	0.0001(9)	0.0036(9)	−0.0040(9)
S(13)	4*a*		0.7428(2)	0.73413(6)	0.0126(1)	0.096(1)	0.058(1)	0.076(1)	−0.005(1)	0.024(1)	−0.0150(9)
S(14)	4*a*		0.8028(2)	0.68913(7)	0.0904(1)	0.099(2)	0.106(2)	0.062(1)	−0.001(1)	0.021(1)	0.003(1)
S(15)	4*a*		0.9927(2)	0.68556(8)	0.0851(1)	0.100(2)	0.119(2)	0.062(1)	−0.008(1)	−0.018(1)	−0.026(1)
S(16)	4*a*		0.0409(2)	0.63322(6)	0.0235(1)	0.087(1)	0.082(1)	0.062(1)	0.005(1)	−0.022(1)	0.0132(9)
S(17)	4*a*		0.0742(2)	0.64870(5)	0.9094(1)	0.058(1)	0.059(1)	0.066(1)	0.0013(8)	−0.0071(8)	−0.0013(8)
P(1)	4*a*		0.4383(1)	0.60807(4)	0.08231(8)	0.0473(9)	0.0379(7)	0.0397(7)	−0.0035(7)	−0.0007(6)	−0.0010(6)
C(1)	4*a*		0.3326(6)	0.5832(2)	0.1489(3)	0.065(4)	0.048(3)	0.030(3)	−0.009(3)	−0.002(3)	0.001(2)
C(2)	4*a*		0.2368(6)	0.6044(2)	0.1831(3)	0.062(4)	0.048(4)	0.039(3)	−0.004(3)	0.001(3)	−0.006(3)
C(3)	4*a*		0.1511(7)	0.5835(2)	0.2269(4)	0.062(4)	0.083(5)	0.049(4)	−0.011(4)	0.013(3)	−0.003(3)
C(4)	4*a*		0.1620(8)	0.5415(3)	0.2382(4)	0.099(6)	0.079(5)	0.051(4)	−0.036(5)	0.002(4)	−0.001(4)
C(5)	4*a*		0.2569(9)	0.5204(2)	0.2048(4)	0.125(7)	0.045(4)	0.057(4)	−0.023(4)	0.006(4)	0.010(3)
C(6)	4*a*		0.3424(7)	0.5402(2)	0.1601(4)	0.094(5)	0.048(4)	0.054(4)	−0.001(4)	0.019(4)	0.006(3)
C(11)	4*a*		0.4302(5)	0.6632(2)	0.0935(3)	0.039(3)	0.043(3)	0.046(3)	−0.009(3)	−0.002(2)	0.001(2)
C(12)	4*a*		0.3508(7)	0.6859(2)	0.0452(4)	0.075(5)	0.051(4)	0.073(4)	−0.006(4)	−0.024(4)	−0.003(3)
C(13)	4*a*		0.3390(8)	0.7276(2)	0.0563(5)	0.103(6)	0.059(4)	0.087(5)	0.021(4)	−0.031(5)	−0.005(4)
C(14)	4*a*		0.4048(7)	0.7477(2)	0.1145(4)	0.078(5)	0.045(3)	0.075(4)	0.002(4)	0.008(4)	−0.010(3)
C(15)	4*a*		0.4853(7)	0.7260(2)	0.1617(4)	0.079(5)	0.057(4)	0.058(4)	−0.008(4)	−0.010(4)	−0.014(3)
C(16)	4*a*		0.4972(6)	0.6835(2)	0.1525(3)	0.059(4)	0.046(3)	0.044(3)	−0.007(3)	−0.004(3)	−0.004(3)
C(21)	4*a*		0.5906(6)	0.5887(2)	0.1061(4)	0.049(4)	0.039(3)	0.057(4)	−0.007(3)	−0.004(3)	−0.005(3)
C(22)	4*a*		0.6284(7)	0.5846(2)	0.1847(4)	0.076(5)	0.065(4)	0.060(4)	0.006(4)	−0.015(4)	−0.001(3)
C(23)	4*a*		0.7441(8)	0.5685(2)	0.2041(5)	0.092(6)	0.064(4)	0.083(5)	0.007(4)	−0.042(5)	0.003(4)
C(24)	4*a*		0.8208(8)	0.5550(2)	0.1446(6)	0.071(5)	0.065(5)	0.115(7)	0.005(4)	−0.021(5)	−0.017(5)
C(25)	4*a*		0.7847(7)	0.5594(2)	0.0671(6)	0.053(5)	0.064(5)	0.117(7)	0.004(4)	0.008(4)	−0.020(4)
C(26)	4*a*		0.6707(6)	0.5760(2)	0.0469(4)	0.049(4)	0.064(4)	0.064(4)	0.001(3)	0.001(3)	−0.013(3)
C(31)	4*a*		0.3926(5)	0.5955(2)	0.9813(3)	0.045(3)	0.041(3)	0.039(3)	−0.001(3)	0.002(2)	0.001(2)
C(32)	4*a*		0.2998(5)	0.5674(2)	0.9657(3)	0.050(4)	0.044(3)	0.046(3)	0.005(3)	0.000(3)	−0.003(2)
C(33)	4*a*		0.2638(7)	0.5591(2)	0.8885(4)	0.067(5)	0.066(4)	0.066(4)	0.001(4)	−0.014(4)	−0.020(4)
C(34)	4*a*		0.3215(8)	0.5789(2)	0.8279(4)	0.107(6)	0.059(4)	0.049(4)	0.020(4)	−0.019(4)	−0.017(3)
C(35)	4*a*		0.4145(8)	0.6059(2)	0.8423(4)	0.105(6)	0.074(5)	0.043(4)	0.016(5)	0.009(4)	0.009(3)
C(36)	4*a*		0.4524(7)	0.6147(2)	0.9194(3)	0.067(4)	0.063(4)	0.048(3)	−0.006(4)	0.007(3)	0.001(3)
P(2)	4*a*		0.4238(1)	0.65670(4)	0.46181(8)	0.0429(8)	0.0360(7)	0.0402(7)	−0.0002(6)	−0.0100(6)	0.0006(6)
C(41)	4*a*		0.4450(5)	0.6016(2)	0.4634(3)	0.051(4)	0.037(3)	0.043(3)	−0.002(3)	−0.003(3)	0.005(2)
C(42)	4*a*		0.4081(7)	0.5784(2)	0.3966(4)	0.086(5)	0.050(4)	0.054(4)	−0.008(4)	−0.023(3)	−0.002(3)
C(43)	4*a*		0.4377(8)	0.5373(2)	0.3932(4)	0.103(6)	0.045(4)	0.073(4)	−0.008(4)	−0.013(4)	−0.008(3)
C(44)	4*a*		0.5011(7)	0.5192(2)	0.4560(5)	0.082(5)	0.029(3)	0.099(6)	0.004(3)	0.010(4)	0.005(3)

Table 3. (Continued)

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(45)	4*a*		0.5352(7)	0.5414(2)	0.5212(4)	0.074(5)	0.051(4)	0.078(5)	0.005(4)	–0.014(4)	0.010(4)
C(46)	4*a*		0.5068(6)	0.5831(2)	0.5257(4)	0.063(4)	0.042(3)	0.052(3)	–0.001(3)	–0.015(3)	0.005(3)
C(51)	4*a*		0.4260(6)	0.6758(2)	0.5623(3)	0.058(4)	0.033(3)	0.039(3)	0.006(3)	–0.011(3)	–0.002(2)
C(52)	4*a*		0.5381(7)	0.6888(2)	0.5951(4)	0.069(4)	0.067(4)	0.051(3)	–0.013(4)	–0.016(3)	–0.007(3)
C(53)	4*a*		0.5446(9)	0.7013(2)	0.6737(5)	0.105(7)	0.069(5)	0.075(5)	–0.006(5)	–0.046(5)	–0.005(4)
C(54)	4*a*		0.442(1)	0.7004(2)	0.7191(4)	0.133(8)	0.072(5)	0.045(4)	0.025(5)	–0.029(5)	–0.020(4)
C(55)	4*a*		0.3314(9)	0.6874(3)	0.6874(5)	0.112(8)	0.114(7)	0.050(4)	0.007(6)	0.008(5)	–0.021(4)
C(56)	4*a*		0.3240(8)	0.6752(2)	0.6080(4)	0.077(5)	0.081(5)	0.053(4)	–0.006(4)	–0.006(4)	–0.016(3)
C(61)	4*a*		0.5531(5)	0.6795(2)	0.4107(3)	0.041(3)	0.038(3)	0.046(3)	–0.005(3)	–0.013(3)	0.005(2)
C(62)	4*a*		0.5620(6)	0.7225(2)	0.4075(3)	0.043(3)	0.043(3)	0.061(4)	–0.001(3)	0.000(3)	–0.004(3)
C(63)	4*a*		0.6544(6)	0.7398(2)	0.3628(4)	0.055(4)	0.040(3)	0.085(5)	–0.010(3)	–0.004(4)	0.003(3)
C(64)	4*a*		0.7359(6)	0.7158(2)	0.3228(4)	0.052(4)	0.066(4)	0.076(4)	–0.002(3)	0.010(3)	0.008(4)
C(65)	4*a*		0.7272(6)	0.6736(2)	0.3262(4)	0.045(4)	0.062(4)	0.076(4)	0.007(3)	–0.002(3)	–0.003(3)
C(66)	4*a*		0.6359(5)	0.6553(2)	0.3699(3)	0.037(3)	0.044(3)	0.064(4)	0.000(3)	–0.004(3)	0.002(3)
C(71)	4*a*		0.2843(5)	0.6691(2)	0.4056(3)	0.036(3)	0.044(3)	0.040(3)	–0.001(2)	–0.006(2)	0.000(2)
C(72)	4*a*		0.2950(5)	0.6890(2)	0.3329(3)	0.037(3)	0.045(3)	0.038(3)	–0.007(3)	0.002(2)	0.001(2)
C(73)	4*a*		0.1908(5)	0.6980(2)	0.2877(3)	0.046(4)	0.041(3)	0.044(3)	–0.002(3)	–0.004(3)	0.006(2)
C(74)	4*a*		0.0760(6)	0.6875(2)	0.3140(4)	0.041(4)	0.061(4)	0.058(4)	0.001(3)	–0.014(3)	0.009(3)
C(75)	4*a*		0.0647(6)	0.6680(2)	0.3861(4)	0.040(4)	0.097(5)	0.064(4)	–0.009(4)	0.001(3)	0.015(4)
C(76)	4*a*		0.1689(6)	0.6577(2)	0.4308(4)	0.052(4)	0.089(5)	0.044(3)	–0.011(4)	–0.005(3)	0.028(3)

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