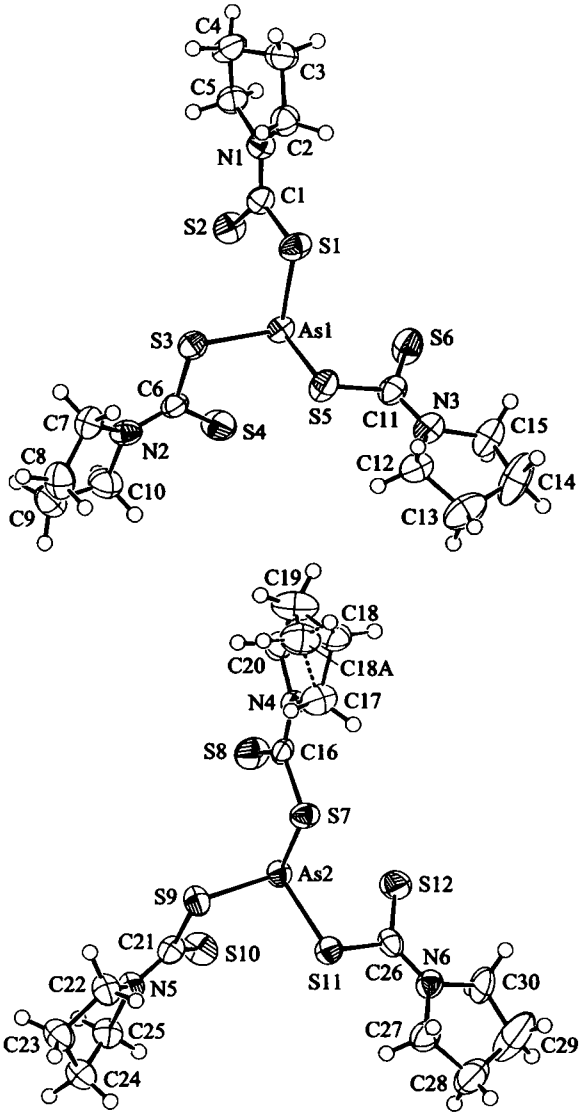
Crystal structure of tris(pyrrolinedithiocarbamato)arsenic(III), $As[S_2CN(CH_2)_4]_3$

Y. Liu[I] and E. R. T. Tiekink*[,II]

[I] National University of Singapore Department of Chemistry Singapore 117543
[II] Griffith University, School of Science, Nathan, Queensland 4111, Australia

Received April 18, 2005, accepted and available on-line May 4, 2005; CCDC no. 1267/1533



Abstract

$C_{15}H_{24}AsN_3S_6$, monoclinic, $P12_1/c1$ (no. 14),
$a = 18.8003(8)$ Å, $b = 12.8757(6)$ Å, $c = 18.3032(8)$ Å,
$\beta = 97.416(1)°$, $V = 4393.6$ Å^3, $Z = 8$,
$R_{gt}(F) = 0.068$, $wR_{ref}(F^2) = 0.153$, $T = 223$ K.

Source of material

The title compound was prepared as colorless crystals (m.p. 520-521 K) in accord with the literature procedure [1].

* Correspondence author (e-mail: etiekink@deakin.edu.au)

Experimental details

The H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation. High thermal motion was noted for the pyrroline residues and in the case of the C17–C20 ring, two positions were resolved for the C18 atom. From refinement, these were ascribed 50 % site occupancy factors each.

Discussion

Two similar molecules comprise the asymmetric unit of the crystal structure of $As[(S_2CN(CH_2)_4)]_3$. The As atom in each exists in a pyramidal environment, being coordinated by three S atoms, derived from three monodentate dithiocarbamate ligands. The lone pair of electrons on As occupies a position in the region occupied by pendent S atoms; the molecules have approximate threefold symmetry. The range of d(As—S), 2.312(2) Å to 2.336(2) Å, is clearly much shorter than d(As···S) of 2.867(2) Å to 2.960(2) A, underscoring the asymmetry in the As to S interactions. The overall geometry reported here basically reflects those found in the R = Me [2] (CH_2Cl_2 solvate), Et [3], n-Bu [4], CH_2Ph [4], and CH_2CH_2OH [5] structures as well as in the mixed species with R = Me and R' = CH_2CH_2OH [6]. The homogeneity in these structures contrasts that observed in their antimony(III) homologues [7].

Table 1. Data collection and handling.

Crystal:	colorless plate, size 0.05 x 0.36 x 0.57 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	21.23 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	25406, 7741
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6422
$N(param)_{refined}$:	461
Programs:	DIRDIF92 [8], SHELXL-97 [9], ORTEP-II [10]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(2A)	4e		0.1551	0.1047	0.3469	0.048
H(2B)	4e		0.2309	0.0547	0.3371	0.048
H(3A)	4e		0.2049	–0.0445	0.4314	0.054
H(3B)	4e		0.1205	–0.0350	0.4073	0.054
H(4A)	4e		0.1416	–0.1983	0.3651	0.055
H(4B)	4e		0.2177	–0.1660	0.3426	0.055

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(5A)	4e		0.1531	−0.1526	0.2308	0.051
H(5B)	4e		0.0812	−0.1248	0.2643	0.051
H(7A)	4e		0.3695	0.0876	−0.0340	0.045
H(7B)	4e		0.3706	0.2027	−0.0010	0.045
H(8A)	4e		0.3974	0.2753	−0.1084	0.056
H(8B)	4e		0.4416	0.1694	−0.1082	0.056
H(9A)	4e		0.3524	0.0894	−0.1857	0.056
H(9B)	4e		0.3519	0.2037	−0.2195	0.056
H(10A)	4e		0.2528	0.2499	−0.1703	0.057
H(10B)	4e		0.2370	0.1282	−0.1765	0.057
H(12A)	4e		0.1793	0.6180	0.1368	0.049
H(12B)	4e		0.1745	0.5847	0.0523	0.049
H(13A)	4e		0.1413	0.7693	0.0846	0.081
H(13B)	4e		0.0984	0.7136	0.0146	0.081
H(14A)	4e		0.0073	0.7563	0.0783	0.087
H(14B)	4e		0.0542	0.7354	0.1560	0.087
H(15A)	4e		−0.0028	0.5808	0.1459	0.060
H(15B)	4e		−0.0147	0.5855	0.0580	0.060
H(17A)	4e		0.3923	−0.0652	0.0770	0.056
H(17B)	4e		0.4606	−0.1067	0.1300	0.056
H(18A)	4e	0.5	0.3357	−0.1809	0.1414	0.059
H(18B)	4e	0.5	0.3937	−0.1707	0.2124	0.059

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(18C)	4e	0.5	0.3023	−0.0821	0.0928	0.064
H(18D)	4e	0.5	0.3318	−0.1827	0.1380	0.064
H(19A)	4e		0.3070	−0.0830	0.2501	0.078
H(19B)	4e		0.2771	−0.0442	0.1692	0.078
H(20A)	4e		0.3350	0.1003	0.2029	0.046
H(20B)	4e		0.3862	0.0438	0.2671	0.046
H(22A)	4e		0.5005	0.4084	−0.1161	0.044
H(22B)	4e		0.5731	0.3576	−0.1357	0.044
H(23A)	4e		0.5647	0.4881	−0.2195	0.052
H(23B)	4e		0.5224	0.5618	−0.1698	0.052
H(24A)	4e		0.6732	0.5203	−0.1491	0.049
H(24B)	4e		0.6361	0.6318	−0.1501	0.049
H(25A)	4e		0.6776	0.5470	−0.0259	0.043
H(25B)	4e		0.6044	0.6111	−0.0353	0.043
H(27A)	4e		0.8301	0.1450	0.0421	0.049
H(27B)	4e		0.8228	0.0216	0.0433	0.049
H(28A)	4e		0.9431	0.0259	0.0644	0.073
H(28B)	4e		0.9441	0.1410	0.0967	0.073
H(29A)	4e		0.9270	−0.0460	0.1719	0.115
H(29B)	4e		0.9690	0.0551	0.2031	0.115
H(30A)	4e		0.8724	0.1262	0.2368	0.059
H(30B)	4e		0.8438	0.0094	0.2356	0.059

Table 3. 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}
As(1)	4e		0.13434(3)	0.21402(5)	0.08420(3)	0.0348(4)	0.0288(3)	0.0344(4)	0.0020(3)	0.0026(3)	0.0027(3)
As(2)	4e		0.59660(3)	0.22116(5)	0.12306(3)	0.0305(3)	0.0286(3)	0.0291(3)	−0.0003(3)	0.0017(3)	0.0006(2)
S(1)	4e		0.1674(1)	0.1812(1)	0.20814(9)	0.054(1)	0.0261(8)	0.0349(9)	−0.0048(8)	−0.0001(8)	−0.0013(6)
S(2)	4e		0.11102(9)	−0.0018(1)	0.11875(9)	0.046(1)	0.0363(9)	0.0379(9)	−0.0041(8)	−0.0011(8)	−0.0052(7)
S(3)	4e		0.24944(9)	0.1720(1)	0.06142(9)	0.0341(9)	0.0426(9)	0.0341(9)	0.0083(8)	0.0002(7)	0.0056(7)
S(4)	4e		0.14415(9)	0.2144(2)	−0.0708(1)	0.0322(9)	0.068(1)	0.043(1)	0.0079(9)	0.0001(8)	0.0156(9)
S(5)	4e		0.17543(9)	0.3843(1)	0.1009(1)	0.0317(9)	0.0310(8)	0.059(1)	0.0011(7)	0.0055(8)	0.0022(7)
S(6)	4e		0.02045(9)	0.3611(1)	0.1136(1)	0.034(1)	0.0384(9)	0.070(1)	−0.0013(8)	0.0093(9)	−0.0020(8)
S(7)	4e		0.53195(9)	0.0684(1)	0.09929(9)	0.0353(9)	0.0316(8)	0.0387(9)	−0.0004(7)	0.0127(7)	−0.0037(7)
S(8)	4e		0.4725(1)	0.2138(1)	0.2023(1)	0.051(1)	0.0340(9)	0.061(1)	0.0025(8)	0.0202(9)	−0.0113(8)
S(9)	4e		0.54319(9)	0.2825(1)	0.00939(9)	0.0351(9)	0.0294(8)	0.0367(9)	−0.0054(7)	−0.0057(7)	0.0039(6)
S(10)	4e		0.6355(1)	0.4393(1)	0.09620(9)	0.050(1)	0.046(1)	0.0323(9)	−0.0126(9)	−0.0033(8)	−0.0057(7)
S(11)	4e		0.68890(8)	0.1521(1)	0.06396(8)	0.0306(8)	0.0400(9)	0.0267(8)	0.0003(7)	0.0001(6)	−0.0007(6)
S(12)	4e		0.70947(9)	0.1313(1)	0.22751(9)	0.039(1)	0.059(1)	0.0320(9)	−0.0004(9)	0.0040(7)	0.0070(8)
N(1)	4e		0.1491(3)	−0.0016(4)	0.2632(3)	0.032(3)	0.030(3)	0.033(3)	−0.004(2)	0.004(2)	−0.001(2)
N(2)	4e		0.2814(3)	0.1727(4)	−0.0740(3)	0.032(3)	0.039(3)	0.032(3)	−0.001(2)	−0.003(2)	0.008(2)
N(3)	4e		0.0867(3)	0.5403(4)	0.0999(3)	0.035(3)	0.031(3)	0.042(3)	−0.002(2)	−0.005(2)	−0.003(2)
N(4)	4e		0.4199(3)	0.0277(4)	0.1663(3)	0.029(3)	0.031(3)	0.029(3)	0.006(2)	0.005(2)	0.001(2)
N(5)	4e		0.5889(3)	0.4542(4)	−0.0461(3)	0.030(3)	0.028(3)	0.031(3)	−0.004(2)	−0.003(2)	0.000(2)
N(6)	4e		0.8087(3)	0.0892(4)	0.1410(3)	0.028(3)	0.035(3)	0.036(3)	−0.001(2)	−0.002(2)	0.000(2)
C(1)	4e		0.1424(3)	0.0499(4)	0.2019(3)	0.029(3)	0.028(3)	0.038(4)	−0.002(3)	0.003(3)	0.000(3)
C(2)	4e		0.1796(4)	0.0405(5)	0.3358(3)	0.045(4)	0.036(4)	0.038(4)	0.003(3)	0.004(3)	−0.003(3)
C(3)	4e		0.1670(4)	−0.0439(5)	0.3893(4)	0.039(4)	0.052(4)	0.044(4)	0.002(3)	0.008(3)	0.014(3)
C(4)	4e		0.1683(4)	−0.1427(5)	0.3443(4)	0.038(4)	0.035(4)	0.065(5)	0.001(3)	0.006(3)	0.018(3)
C(5)	4e		0.1331(4)	−0.1129(5)	0.2690(4)	0.049(4)	0.028(3)	0.053(4)	−0.003(3)	0.018(3)	0.006(3)
C(6)	4e		0.2282(3)	0.1858(4)	−0.0339(3)	0.035(4)	0.028(3)	0.031(3)	0.005(3)	0.001(3)	0.005(2)
C(7)	4e		0.3575(3)	0.1605(5)	−0.0453(4)	0.029(3)	0.037(3)	0.044(4)	0.001(3)	−0.002(3)	−0.005(3)
C(8)	4e		0.3935(4)	0.1994(6)	−0.1092(4)	0.034(4)	0.047(4)	0.062(5)	−0.006(3)	0.011(3)	−0.009(3)
C(9)	4e		0.3446(4)	0.1631(6)	−0.1758(4)	0.052(5)	0.046(4)	0.045(4)	−0.008(4)	0.017(3)	−0.005(3)
C(10)	4e		0.2708(4)	0.1810(6)	−0.1545(4)	0.052(5)	0.056(4)	0.033(4)	0.003(4)	0.004(3)	0.005(3)
C(11)	4e		0.0895(3)	0.4385(5)	0.1040(3)	0.037(4)	0.034(3)	0.034(3)	0.005(3)	−0.003(3)	0.000(3)
C(12)	4e		0.1470(4)	0.6103(5)	0.0906(4)	0.048(4)	0.034(3)	0.037(4)	−0.003(3)	−0.004(3)	−0.001(3)
C(13)	4e		0.1104(5)	0.7102(5)	0.0682(5)	0.084(7)	0.031(4)	0.084(6)	−0.007(4)	−0.003(5)	0.005(4)
C(14)	4e		0.0439(4)	0.7112(6)	0.1049(6)	0.047(5)	0.036(4)	0.127(8)	0.006(4)	−0.020(5)	−0.024(4)
C(15)	4e		0.0195(4)	0.5989(5)	0.1021(4)	0.043(4)	0.036(4)	0.066(5)	0.008(3)	−0.008(4)	−0.005(3)
C(16)	4e		0.4681(3)	0.0997(5)	0.1587(3)	0.026(3)	0.034(3)	0.029(3)	0.011(3)	0.006(3)	0.003(2)
C(17)	4e		0.4138(4)	−0.0727(5)	0.1284(4)	0.045(4)	0.041(4)	0.056(4)	−0.006(3)	0.013(3)	−0.012(3)
C(18)	4e	0.5	0.3653(9)	−0.132(1)	0.173(1)	0.04(1)	0.038(9)	0.07(1)	−0.009(8)	0.013(9)	0.006(8)
C(18A)	4e	0.5	0.336(1)	−0.107(1)	0.135(1)	0.06(1)	0.05(1)	0.05(1)	−0.013(9)	0.016(8)	−0.009(8)
C(19)	4e		0.3208(5)	−0.0576(7)	0.2034(5)	0.063(5)	0.075(6)	0.062(5)	−0.026(5)	0.024(4)	−0.008(4)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(20)	4e		0.3645(3)	0.0385(5)	0.2156(3)	0.036(4)	0.047(4)	0.033(3)	0.007(3)	0.006(3)	0.002(3)
C(21)	4e		0.5903(3)	0.4014(4)	0.0149(3)	0.027(3)	0.029(3)	0.036(3)	−0.002(3)	0.000(3)	−0.006(3)
C(22)	4e		0.5515(4)	0.4210(5)	−0.1187(3)	0.040(4)	0.031(3)	0.038(4)	−0.006(3)	−0.005(3)	0.001(3)
C(23)	4e		0.5618(4)	0.5118(5)	−0.1691(4)	0.044(4)	0.044(4)	0.040(4)	−0.010(3)	−0.006(3)	0.008(3)
C(24)	4e		0.6323(4)	0.5592(5)	−0.1349(3)	0.046(4)	0.036(4)	0.041(4)	−0.004(3)	0.006(3)	0.004(3)
C(25)	4e		0.6294(3)	0.5513(5)	−0.0532(3)	0.036(4)	0.026(3)	0.044(4)	−0.009(3)	−0.001(3)	−0.004(3)
C(26)	4e		0.7433(3)	0.1187(4)	0.1467(3)	0.035(4)	0.026(3)	0.034(3)	−0.005(3)	−0.002(3)	0.005(2)
C(27)	4e		0.8408(3)	0.0825(5)	0.0721(4)	0.038(4)	0.037(4)	0.049(4)	0.004(3)	0.008(3)	−0.004(3)
C(28)	4e		0.9207(4)	0.0731(7)	0.0967(5)	0.037(4)	0.070(5)	0.077(6)	0.009(4)	0.008(4)	0.000(4)
C(29)	4e		0.9254(5)	0.030(1)	0.1733(5)	0.051(6)	0.16(1)	0.071(7)	0.048(7)	−0.005(5)	−0.018(7)
C(30)	4e		0.8616(4)	0.0646(6)	0.2059(4)	0.032(4)	0.058(5)	0.053(4)	0.010(4)	−0.012(3)	0.010(4)

Acknowledgment. The Queensland Government is thanked for the award of a Smart Returns Fellowship (ERTT).

References

1. Manoussakis, G. E.; Tsipis, C. A.: Preparation and study of some arsenic and antimony tris(dithiocarbamates). J. Inorg. Nucl. Chem. **35** (1973) 743-750.
2. Chen, D.; Lai, C. S.; Tiekink, E. R. T.: Tris(*N,N*-dimethyldithiocarbamato)arsenic(III) dichloromethane solvate. Appl. Organomet. Chem. **17** (2003) 813-814.
3. Raston, C. L.; White, A. H.: Crystal structures of tris(diethyldithiocarbamato)rhodium(III) and -arsenic(III). J. Chem. Soc., Dalton Trans. (1975) 2425-2429.
4. Wenclawiak, B. W.; Uttich, S.; Deiseroth, H. J.; Schmitz, D.: Studies on bulky residual group substituted arsenic(III) dithiocarbamate structures. Inorg. Chim. Acta **348** (2003) 1-7.
5. Venkatachalam, V.; Ramalingam, K.; Casellato, U.; Graziani, R.: Structural and electronic effects of alkyl substituents on the main group dithiocarbamato complexes: crystal and molecular structures of tris(*N,N'*-iminodiethanoldithiocarbamato)metal(III) complexes (*M* = As, Sb and Bi) and cyclic voltammetric studies on substituted dithiocarbamates. Polyhedron **16** (1997) 1211-1221.
6. Venkatachalam, V.; Ramalingam, K.; Mak, T. C. W.; Luo, B.-S.: Synthesis and structure of tris(*N*-methylaminoethanoldithiocarbamato)arsenic(III). J. Chem. Crystallogr. **26** (1996) 467-470.
7. Liu, Y.; Tiekink, E. R. T.: Supramolecular associations in binary antimony(III) dithiocarbamates: influence of ligand steric bulk, influence on coordination geometry, and competition with hydrogen-bonding. CrystEngComm **7** (2005) 20-27.
8. Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; García-Granda, S.; Smits, J. M. M.; Smykalla, C.: The DIRDIF program system. Crystallography Laboratory, University of Nijmegen, The Netherlands 1992.
9. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
10. Johnson, C. K.: ORTEP-II. A Fortran Thermal-Ellipsoid Plot Program. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA 1976.