the S_2CNC_2 portions of the dipropyldithiocarbamato ligand are very similar to those of the analogous diethyldithiocarbamato complex (Sit *et al.*, 1989). The bond distances and angles in the trispyrazolyl-hydroborate ligand, *L*, are normal (Cleland *et al.*, 1987).

References

Bray, R. C. (1980). *Adv. Enzymol. Relat. Areas Mol. Biol.* **51**, 107–165.
Cleland, W. E. Jr, Barnhart, K. M., Yamanouchi, K., Collison, D., Mabbs, F. E., Ortega, R. B. & Enemark, J. H. (1987). *Inorg. Chem.* **26**, 1017–1025.
Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.
Mayer, J. M. (1988). *Inorg. Chem.* **27**, 3899–3903.
Nugent, W. A. & Mayer, J. M. (1988). *Metal–Ligand Multiple Bonds*, New York: Wiley–Interscience.
Sit, F., Collison, D., Mabbs, F. E. & Cleland, W. E. Jr (1989). In preparation.
Spence, J. T. (1983). *Coord. Chem. Rev.* **48**, 59–82.
Spiro, T. G. (1985). Editor. *Molybdenum Enzymes.* New York: Wiley–Interscience.
Young, C. G., Roberts, S. A., Ortega, R. B. & Enemark, J. H. (1987). *J. Am. Chem. Soc.* **109**, 2938–2946.

Structure of Tetraphenylarsonium Heptanitrosyl-tri-μ_3-seleno-tetraferrate(1−)

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Abstract. $C_{24}H_{20}As^+.[Fe_4Se_3(NO)_7]^-$, $M_r = 1053.67$, triclinic, $P\bar{1}$, $a = 13.122$ (9), $b = 13.936$ (9), $c = 9.908$ (8) Å, $\alpha = 99.30$ (6), $\beta = 97.04$ (6), $\gamma = 71.94$ (5)°, $V = 1694.9$ Å³, $Z = 2$, $D_x = 2.065$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 58.87$ cm⁻¹, $F(000) = 1016$, $T = 295$ K, $R = 0.047$ for 5101 observations. The structure consists of isolated Ph_4As^+ cations and $[Fe_4Se_3(NO)_7]^-$ anions which exhibit approximate C_{3v} symmetry.

Introduction. It has been deduced from nuclear-magnetic-resonance spectroscopy (Butler, Glidewell, Hyde & McGinnis, 1985) that the iron–selenium–nitrosyl anion $[Fe_4Se_3(NO)_7]^-$ (Butler, Glidewell, Hyde, McGinnis & Seymour, 1983) has a structure, in solution, which is similar to that established by X-ray methods for the sulfur analogue $[Fe_4S_3(NO)_7]^-$ (Johansson & Lipscomb, 1958; Chu & Dahl, 1977). Structure analysis not only confirms

definitively the structure inferred from spectroscopy, but allows metrical comparison between $[Fe_4Se_3(NO)_7]^-$ and $[Fe_4S_3(NO)_7]^-$.

Experimental. Small black block crystals grown from methanol. Accurate cell dimensions and crystal orientation matrix determined on a Nicolet *P*3 diffractometer by least-squares refinement using the setting angles of 20 reflections in the range $15 \le \theta \le 18°$. Crystal dimensions $0.24 \times 0.40 \times 0.40$ mm; intensities of reflections with indices $h-17$ to $+17$, $k-18$ to $+18$, $l0$ to $+12$ with $2 \le 2\theta \le 55°$; ω–2θ scans, 2θ scan width $(2.40$–$2.75)°$, graphite-monochromated Mo $K\alpha$ radiation. 7830 reflections measured, 7828 unique, 5101 with $F \ge 4\sigma(F)$ labelled observed and used in structure solution and refinement. No intensity change was detected in two standard reflections measured after every 200 reflections. Data corrected for Lorentz and polarization effects and for absorption effects using a ψ-scan technique on the diffractometer (maximum and mini-

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mum values of transmission factors, 0·078 and 0·183 respectively). Space group $P1$ or $P\bar{1}$; $P\bar{1}$ chosen and confirmed by the successful refinement. The structure was solved by direct methods: the initial E map provided coordinates of eight heavy atoms, subsequently identified as one As, three Se and four Fe atoms. The remaining non-H atoms were found from difference syntheses. The asymmetric unit comprises one cation and one anion. Refinement, minimizing $\Sigma w||F_o| - |F_c||^2$, by full-matrix least-squares calculations, with anisotropic thermal parameters: in the final cycles of refinement, H atoms were included as riding atoms with C—H 1·08 Å, and a common isotropic temperature factor. The final cycles of refinement included 416 variable parameters, $R = 0·047$, $wR = 0·058$, $w = 1·3123/[\sigma^2(F_o) + 0·001308(F_o)^2]$. Max. shift/e.s.d. = 0·014 (excluding oscillatory U_H). The largest features on the final difference map were +0·60 and −0·62 e Å^{-3}. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–147). All calculations were performed on a Prime 6350 computer using *SHELX76* (Sheldrick, 1976) and *SHELXS86* (Sheldrick, 1985). Atomic parameters and details of the anion geometry are given in Tables 1* and 2. Fig. 1 shows the anion, with the atom-numbering scheme.

Discussion. The structure analysis shows that the compound consists of isolated Ph_4As^+ cations, and $[Fe_4Se_3(NO)_7]^-$ anions which exhibit approximate C_{3v} $(3m)$ symmetry (Fig. 1), although no symmetry is imposed by the space group. The analysis confirms that the structure of the cluster anion is that deduced from spectroscopic measurements (Butler, Glidewell, Hyde & McGinnis, 1985).

The anion contains a flattened tetrahedron of four Fe atoms: the apical Fe atom, Fe(1), carries a single nitrosyl ligand while each of the basal Fe atoms Fe(2), Fe(3) and Fe(4) carry two nitrosyl ligands. The $(C_{3v}$ averaged) distances Fe(apical)—Fe(basal) and Fe(basal)—Fe'(basal) are 2·784 Å [range 2·764 (1)–2·789 (1) Å] and 3·689 Å [range 3·617 (1)–3·768 (1) Å], respectively. Each of the three equivalent triangular faces which include the apical Fe atom is capped by an Se atom with average Fe(apical)—Se and Fe(basal)—Se distances of 2·330 Å [range 2·322 (1)–2·338 (1) Å] and 2·377 Å [range 2·373 (1)–2·388 (1) Å], respectively. In the analogous iron–sulfur cluster anion $[Fe_4S_3(NO)_7]^-$, the averaged values of the two types of iron—iron

Table 1. *Coordinates* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

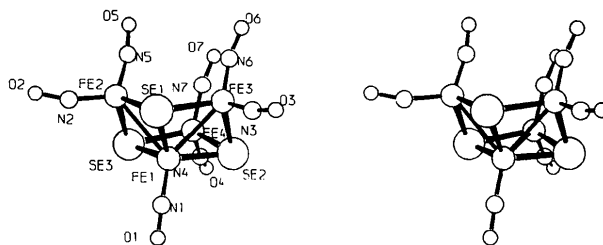|	x	y	z	$U_{eq}(\text{Å}^2)$
Se1	5622 (1)	8339 (1)	−160 (1)	41 (1)
Se2	3461 (1)	7123 (1)	−1700 (1)	44 (1)
Se3	4150 (1)	7391 (1)	2150 (1)	43 (1)
Fe1	4847 (1)	7066 (1)	13 (1)	36 (1)
Fe2	4886 (1)	8720 (1)	2000 (1)	40 (1)
Fe3	4121 (1)	8523 (1)	−1803 (1)	42 (1)
Fe4	2684 (1)	7690 (1)	443 (1)	39 (1)
N1	5711 (5)	5913 (4)	−202 (6)	52 (2)
N2	5932 (5)	8658 (5)	3179 (6)	57 (2)
N3	4657 (5)	8301 (5)	−3298 (6)	62 (2)
N4	1972 (4)	6924 (4)	663 (6)	44 (1)
N5	3890 (5)	9800 (5)	2127 (6)	53 (2)
N6	3167 (5)	9619 (4)	−1536 (6)	48 (1)
N7	1990 (5)	8907 (4)	407 (6)	51 (2)
O1	6285 (5)	5088 (4)	−382 (8)	97 (2)
O2	6522 (5)	8848 (5)	4080 (6)	87 (2)
O3	4923 (7)	8324 (6)	−4363 (7)	112 (3)
O4	1323 (5)	6568 (4)	849 (6)	68 (2)
O5	3285 (5)	10579 (5)	2444 (8)	93 (2)
O6	2506 (5)	10406 (4)	−1656 (6)	77 (2)
O7	1314 (5)	9678 (4)	312 (7)	82 (2)
As	9347 (1)	3078 (1)	5351 (1)	37 (1)
C11	10218 (5)	3574 (5)	6817 (6)	39 (1)
C12	11249 (5)	2931 (5)	7213 (7)	49 (2)
C13	11853 (6)	3317 (7)	8286 (8)	65 (2)
C14	11463 (6)	4305 (6)	8916 (8)	60 (2)
C15	10473 (6)	4915 (5)	8497 (7)	52 (2)
C16	9843 (5)	4548 (5)	7461 (6)	41 (2)
C21	8012 (5)	4130 (5)	5120 (7)	41 (2)
C22	7850 (6)	4719 (5)	4067 (8)	52 (2)
C23	6897 (7)	5492 (6)	3964 (9)	67 (3)
C24	6133 (6)	5680 (5)	4890 (10)	73 (3)
C25	6315 (6)	5089 (7)	5921 (9)	74 (3)
C26	7258 (6)	4289 (6)	6029 (8)	59 (2)
C31	10114 (5)	2771 (4)	3736 (6)	38 (1)
C32	11083 (5)	3001 (5)	3767 (8)	52 (2)
C33	11640 (6)	2734 (5)	2605 (9)	59 (2)
C34	11260 (7)	2248 (6)	1405 (9)	63 (2)
C35	9717 (5)	2294 (5)	2526 (7)	47 (2)
C36	10290 (6)	2028 (5)	1395 (8)	59 (2)
C41	9047 (5)	1886 (4)	5715 (6)	37 (1)
C42	8149 (6)	1642 (5)	5057 (7)	52 (2)
C43	7947 (6)	776 (6)	5269 (8)	62 (2)
C44	8631 (6)	147 (5)	6150 (8)	58 (2)
C45	9517 (6)	395 (5)	6821 (8)	59 (2)
C46	9732 (6)	1257 (5)	6622 (7)	51 (2)

Fig. 1. Stereoview of the anion $[Fe_4Se_3(NO)_7]^-$ showing the atom-numbering scheme.

distance are 2·700 Å [range 2·683 (2)–2·708 (2) Å] and 3·570 Å [range 3·519 (2)–3·628 (2) Å], respectively (Chu & Dahl, 1977), significantly shorter than those found here. Hence the dimensions of the Fe$_4$ core appear to be significantly influenced by the size of the capping atoms, although the shape of the Fe$_4$ cage is identical in $[Fe_4S_3(NO)_7]^-$ and in $[Fe_4Se_3(NO)_7]^-$; the ratio of the averages for the two types of iron—iron distance is 1·322 Å in $[Fe_4S_3(NO)_7]^-$ and 1·325 Å in $[Fe_4Se_3(NO)_7]^-$.

Table 2. *Interatomic distances (Å) and angles (°)*

Fe1—Se1	2·338 (1)	Fe2—Se1	2·369 (1)
Fe3—Se1	2·373 (1)	Fe1—Se2	2·322 (1)
Fe3—Se2	2·388 (1)	Fe4—Se2	2·379 (1)
Fe1—Se3	2·331 (1)	Fe2—Se3	2·372 (1)
Fe4—Se3	2·380 (1)	Fe2—Fe1	2·789 (1)
Fe3—Fe1	2·798 (1)	Fe4—Fe1	2·764 (1)
N1—Fe1	1·653 (5)	N2—Fe2	1·679 (6)
N5—Fe2	1·658 (5)	N3—Fe3	1·660 (7)
N6—Fe3	1·654 (5)	N4—Fe4	1·674 (7)
N7—Fe4	1·662 (5)	O1—N1	1·162 (7)
O2—N2	1·161 (9)	O3—N3	1·159 (10)
O4—N4	1·155 (10)	O5—N5	1·151 (8)
O6—N6	1·182 (7)	O7—N7	1·172 (7)
C11—As	1·911 (6)	C21—As	1·920 (5)
C31—As	1·914 (6)	C41—As	1·919 (7)
C12—C11	1·421 (8)	C16—C11	1·369 (8)
C13—C12	1·386 (11)	C14—C13	1·382 (11)
C15—C14	1·371 (10)	C16—C15	1·372 (10)
C22—C21	1·386 (11)	C26—C21	1·363 (10)
C23—C22	1·380 (9)	C24—C23	1·379 (13)
C25—C24	1·367 (14)	C26—C25	1·391 (10)
C32—C31	1·400 (11)	C35—C31	1·397 (9)
C33—C32	1·377 (12)	C34—C33	1·387 (11)
C36—C34	1·397 (13)	C36—C35	1·363 (11)
C42—C41	1·384 (10)	C46—C41	1·397 (9)
C43—C42	1·365 (12)	C44—C43	1·380 (11)
C45—C44	1·377 (12)	C46—C45	1·364 (12)

Fe2—Se1—Fe1	72·64 (3)	Fe3—Se1—Fe1	72·87 (3)
Fe3—Se1—Fe2	105·21 (3)	Fe3—Se2—Fe1	72·87 (3)
Fe4—Se2—Fe1	72·00 (4)	Fe4—Se2—Fe3	98·69 (4)
Fe2—Se3—Fe1	72·74 (3)	Fe4—Se3—Fe1	71·83 (3)
Fe4—Se3—Fe2	101·59 (4)	Se2—Fe1—Se1	108·60 (4)
Se3—Fe1—Se1	108·48 (4)	Se3—Fe1—Se2	109·33 (3)
Fe2—Fe1—Se1	54·19 (3)	Fe2—Fe1—Se2	122·66 (3)
Fe2—Fe1—Se3	54·30 (3)	Fe3—Fe1—Se1	54·13 (3)
Fe3—Fe1—Se2	54·65 (3)	Fe3—Fe1—Se3	119·86 (4)
Fe3—Fe1—Fe2	84·81 (4)	Fe4—Fe1—Se1	116·80 (4)
Fe4—Fe1—Se2	54·95 (4)	Fe4—Fe1—Se3	54·91 (3)
Fe4—Fe1—Fe2	83·07 (3)	Fe4—Fe1—Fe3	81·12 (3)
N1—Fe1—Se1	112·5 (2)	N1—Fe1—Se2	107·4 (2)
N1—Fe1—Se3	110·5 (2)	N1—Fe1—Fe2	130·0 (2)
N1—Fe1—Fe3	129·6 (2)	N1—Fe1—Fe4	130·7 (2)
Se3—Fe2—Se1	106·11 (4)	Fe1—Fe2—Se1	53·16 (3)
Fe1—Fe2—Se3	52·96 (3)	N2—Fe2—Se1	105·9 (2)
N2—Fe2—Se3	108·9 (3)	N2—Fe2—Fe1	120·9 (2)
N5—Fe2—Se1	112·3 (2)	N5—Fe2—Se3	107·2 (2)
N5—Fe2—Fe1	123·1 (2)	N5—Fe2—N2	115·9 (3)
Se2—Fe3—Se1	105·29 (4)	Fe1—Fe3—Se1	53·00 (4)
Fe1—Fe3—Se2	52·47 (3)	N3—Fe3—Se1	104·0 (2)
N3—Fe3—Se2	106·5 (3)	N3—Fe3—Fe1	119·4 (2)
N6—Fe3—Se1	114·0 (2)	N6—Fe3—Se2	111·1 (2)
N6—Fe3—Fe1	125·5 (2)	N6—Fe3—N3	115·1 (3)
Se3—Fe4—Se2	105·81 (4)	Fe1—Fe4—Se2	53·04 (3)
Fe1—Fe4—Se3	53·26 (3)	N4—Fe4—Se2	108·9 (2)
N4—Fe4—Se3	105·3 (2)	N4—Fe4—Fe1	125·3 (2)
N7—Fe4—Se2	106·0 (2)	N7—Fe4—Se3	114·8 (2)
N7—Fe4—Fe1	119·0 (2)	N7—Fe4—N4	115·6 (3)
O1—N1—Fe1	177·2 (6)	O2—N2—Fe2	164·2 (6)
O3—N3—Fe3	167·7 (6)	O4—N4—Fe4	166·9 (5)
O5—N5—Fe2	167·8 (6)	O6—N6—Fe3	164·7 (6)
O7—N7—Fe4	165·2 (6)	C21—As—C11	108·3 (2)
C31—As—C11	107·2 (3)	C31—As—C21	110·5 (3)
C41—As—C11	112·1 (3)	C41—As—C21	108·8 (3)
C41—As—C31	110·0 (3)	C12—C11—As	119·5 (4)
C16—C11—As	119·4 (4)	C16—C11—C12	121·0 (6)
C13—C12—C11	117·8 (6)	C14—C13—C12	120·4 (6)
C15—C14—C13	120·6 (7)	C16—C15—C14	120·5 (6)
C15—C16—C11	119·7 (5)	C22—C21—As	119·7 (5)
C26—C21—As	118·4 (5)	C26—C21—C22	121·8 (6)
C23—C22—C21	118·1 (7)	C24—C23—C22	120·9 (8)
C25—C24—C23	119·8 (7)	C26—C25—C24	120·5 (8)
C25—C26—C21	118·8 (8)	C32—C31—As	120·4 (5)
C35—C31—As	119·9 (5)	C35—C31—C32	119·8 (6)
C33—C32—C31	119·1 (7)	C34—C33—C32	121·5 (8)
C36—C34—C33	118·4 (8)	C36—C35—C31	119·9 (7)
C35—C36—C34	121·2 (7)	C42—C41—As	119·5 (5)
C46—C41—As	120·6 (5)	C46—C41—C42	119·9 (7)
C43—C42—C41	120·0 (6)	C44—C43—C42	120·1 (8)
C45—C44—C43	119·9 (8)	C46—C45—C44	120·8 (7)
C45—C46—C41	119·2 (7)		

The apical Fe(1)—N—O fragment is almost linear, with a bond angle of 177·3 (6)°. The nitrosyl ligands on the basal Fe atoms can be divided into two groups: equatorial, in which the Fe—N—O direction is roughly perpendicular to the approximate three-fold axis of the anion, and axial, in which the Fe—N—O direction is roughly parallel to this axis. In the Fe(NO)$_2$ groups the Fe—N bond lengths for the equatorial nitrosyl ligand are just significantly longer than those for the axial ligands: within each Fe(NO)$_2$ the Fe—N—O fragments are slightly non-linear [mean Fe—N—O angle 166·0°; range 164·0 (6)–167·8 (6)°] and the non-linearity is such that the oxygens are tilted towards one another. This phenomenon has been observed in the related diiron complexes [Fe$_2$(SR)$_2$(NO)$_4$] [R = CH$_3$, C(CH$_3$)$_3$ and n-C$_5$H$_{11}$] (Glidewell, Harman, Hursthouse, Johnson & Motevalli, 1988) and [Fe$_2$(S$_2$O$_3$)$_2$(NO)$_4$]$^{2-}$ (Glidewell, Hursthouse, Lambert & Motevalli, 1989): the underlying basis for this Fe(NO)$_2$ fragment geometry has been discussed (Summerville & Hoffmann, 1976).

Calculations on the anion [Fe$_4$Se$_3$(NO)$_7$]$^-$ using the extended Hückel method (Hoffmann, 1963) show that the pattern of the molecular orbitals is very similar to that in [Fe$_4$S$_3$(NO)$_7$]$^-$ (Sung, Glidewell, Butler & Hoffmann, 1985): in particular the uppermost bonding levels are all concentrated in the Fe$_4$ cage.

References

BUTLER, A. R., GLIDEWELL, C., HYDE, A. R. & McGINNIS, J. (1985). *Inorg. Chem.* 24, 2931–2934.

BUTLER, A. R., GLIDEWELL, C., HYDE, A. R., McGINNIS, J. & SEYMOUR, J. E. (1983). *Polyhedron*, 2, 1045–1052.

CHU, C. T.-W. & DAHL, L. F. (1977). *Inorg. Chem.* 16, 3245–3251.

GLIDEWELL, C., HARMAN, M. E., HURSTHOUSE, M. B., JOHNSON, I. L. & MOTEVALLI, M. (1988). *J. Chem. Res. (S)*, pp. 212–213; (M), pp. 1676–1690.

GLIDEWELL, C., HURSTHOUSE, M. B., LAMBERT, R. J. & MOTEVALLI, M. (1989). *J. Chem. Soc. Dalton Trans.* pp. 2061–2064.

HOFFMANN, R. (1963). *J. Chem. Phys.* 39, 1397–1412.

JOHANSSON, G. & LIPSCOMB, W. N. (1958). *Acta Cryst.* 11, 594–598.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

SUMMERVILLE, R. H. & HOFFMANN, R. (1976). *J. Am. Chem. Soc.* 98, 7240–7254.

SUNG, S.-S., GLIDEWELL, C., BUTLER, A. R. & HOFFMANN, R. (1985). *Inorg. Chem.* 24, 3856–3859.