Crystal Data and Nuclear Quadrupole Resonance Spectra of Tetra-arsenic Triselenide

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Tetra-arsenic triselenide, As_4Se_3, has been synthesized and isolated in two polymorphs of which α-As_4Se_3 is isostructural with α-As_4S_3. It is orthorhombic, space group *Pnma*, with $Z = 4$, in a unit cell of dimensions $a = 9.46(2)$, $b = 7.97(2)$, $c = 10.47(2)$ Å. The ^{75}As n.q.r. spectrum at 77 K shows three resonances with intensities 1 : 2 : 1 at 60.78 and 61.07 MHz due to the basal As and at 68.97 due to the apical As of the As_4Se_3 molecule. The polymorph β-As_4Se_3 is monoclinic, space group *C2/c* or *Cc*, with $Z = 16$ in a unit cell of dimensions $a = 25.62(5)$, $b = 6.52(2)$, $c = 23.01(5)$ Å, $\beta = 126.6 \pm 0.5°$. Its n.q.r. spectrum at 77 K shows a number of incompletely resolved lines between 57.5 and 61.0 MHz and between 69.5 and 71.5 MHz, associated with basal and apical As atoms of the As_4Se_3 molecule.

FOR the arsenic–sulphur system the structures of two polymorphs of As_4S_3,[1,2] two polymorphs of As_4S_4,[3,4] and of As_4S_5 [5] and As_2S_3 [6] have been determined in studies using *X*-ray diffraction, and the molecule As_4S_6 has been characterized in the gas phase by electron diffraction.[7] For the arsenic–selenium system the structures of As_4Se_4 [8,9] and As_2Se_3 [10] have been determined and the existence of As_4Se_3 in the gas phase has been inferred from mass-spectrometric data.[9]

We now report the isolation of the compound As_4Se_3 in the solid state in two crystal polymorphs and give the unit-cell dimensions of these and their ^{75}As n.q.r. spectra.

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We compare the n.q.r. spectra of As_4Se_3 with spectra reported for As_2Se_3,[11] As_4Se_4,[11] As_2S_3,[12] As_4S_4,[13,14] and As_4S_3.[15]

EXPERIMENTAL AND RESULTS

Purified arsenic and selenium powders were melted together in an evacuated silica ampoule to give a glass of stoicheiometry As_4Se_3. This glass was powdered and annealed at 220 °C for several days in an ampoule of length 150 mm and internal diameter 10 mm. The ampoule was then placed in a temperature gradient of 60—140 °C end-to-end for 4 weeks, when a mixture (*ca.* 30 mg) of very fine dark red crystals and larger lighter-coloured crystals had sublimed to the cold end of the ampoule. Enough sample was obtained for study by n.q.r. spectroscopy by repeating the experiment with 25 ampoules each containing 20 mg of As_4Se_3 glass. The annealing was continued until the samples had completely sublimed. A total yield of *ca.* 60 mg of the larger crystals was separated from the product by hand-picking under a microscope. Several crystals were mounted on an optical goniometer and they were found to be orthorhombic holosymmetric class *mmm*, with axial ratio $a : b : c = 1.187 : 1 : 1.314$. The forms represented were pinacoids {100}, {010}, and {001}, domes {011}, {101}, and {102}, and bipyramids {212}. This polymorph we call the α form: its crystal morphology and axial ratio suggest that it is isostructural with α-dimorphite, As_4S_3. Weissenberg single-crystal *X*-ray diffraction photographs of the *h*0*l* and 0*kl* layers of α-As_4Se_3 were compared visually with photographs of the same layers of α-As_4S_3 and the crystals were found to be indeed isostructural.

One of the smaller crystals, which we call the β form, was also examined by taking Weissenberg single-crystal *X*-ray diffraction photographs.

Crystal Data.—As_4Se_3, α form, $M = 536.52$, Orthorhombic, $a = 9.46(2)$, $b = 7.91(2)$, $c = 10.41(2)$ Å, $U = 789.4$ Å^3, $Z = 4$, $D_c = 4.51$, $F(000) = 936$. Space group *Pnma* from systematic absences: 0*kl* for $k + l$ odd, *hk*0 for *h* odd. These absences are compatible with space group *Pnma* or $Pn2_1a$,[16] but the former is indicated by the similarity of the structure to α-As_4S_3.

As_4Se_3, β form, $M = 536.52$, Monoclinic, $a = 25.62(5)$, $b = 6.52(2)$, $c = 23.01(5)$ Å, $\beta = 123.6 \pm 0.4°$, $U = 3\,202$ Å^3, $Z = 16$, $D_c = 4.45$. Space group $C2/c$ or Cc from systematic absences: *hkl* for $h + k$ odd, *h*0*l* for *l* odd.[16]

The ^{75}As n.q.r. spectra of the two types of crystal were recorded with a Zeeman-modulated noise-controlled super-regenerative oscillator spectrometer of standard design. For the sample (60 mg) of hand-picked crystals of α-As_4Se_3, three sharp well resolved peaks were observed with an intensity ratio 1 : 2 : 1. For the sample of the β form, two groups of resonances were observed. These resonances were less intense but broader than the resonances found for α-As_4Se_3. The peaks were stronger and more readily resolved at 77 than at 295 K and in Table 2 we have listed four resonances that could be resolved between 69.5 and 71.5 MHz and eight resonances between 57.5 and 61.0 MHz.

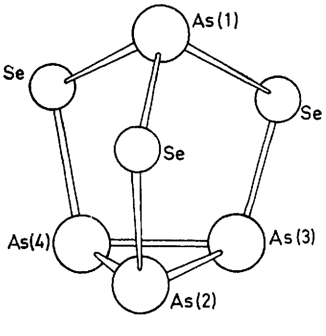
DISCUSSION

From their crystal morphology, unit-cell parameters (Table 1), and Weissenberg single-crystal *X*-ray diffraction photographs there is no doubt that α-As_4Se_3 is isostructural with α-As_4S_3. The crystals of α-As_4Se_3 thus consist of molecules (Figure) of C_{3v} symmetry, made up of four arsenic atoms in a triangular-pyramidal arrangement with selenium bridges along the adjacent apical edges. In the crystal the apical arsenic atom, As(1), and one of the three basal arsenic atoms, As(2), lie on the mirror plane in special positions 4(c) of the space group *Pnma*,[16] while the other two basal arsenic atoms, As(3) and As(4), are in symmetry-related general positions 8(d). This explains the three n.q.r. lines in intensity ratio 1 : 2 : 1. The peak at 61.07 MHz (at 77 K) is assigned to the equivalent atoms As(3) and

TABLE 1

Unit-cell parameters for As_4S_3 and As_4Se_3

	α-As_4Se_3	α-As_4S_3	β-As_4Se_3	β-As_4S_3
Space group	*Pnma*	*Pnma*	$C2/c$ or Cc	*Pnma*
a/Å	9.46	9.12	25.62	11.21
b/Å	7.97	7.99	6.52	9.90
c/Å	10.47	10.10	23.01	6.58
β/°			123.6	



The As_4Se_3 molecule

TABLE 2

Arsenic-75 n.q.r. frequencies (MHz) in As_4Se_3, with relative intensities in parentheses

	Form	
T/K	β	α
295	56.83	59.53 (5)
	57.45	60.04 (10)
	58.88	
	68.67	68.05 (5)
	69.26	
77	57.55 (9)	
	57.85 (5)	
	58.60 (2)	
	58.90 (3)	60.78 (5)
	59.38 (2)	61.07 (10)
	59.95 (3)	
	60.50 (4)	
	60.90 (4)	
	69.69 (3)	
	70.15 (5)	
	70.40 (4)	68.97 (5)
	71.40 (10)	

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As(4), that at 60.78 MHz to the other basal arsenic atom As(2), and that at 68.97 MHz to the apical arsenic atom As(1).

TABLE 3

N.q.r. frequencies at 77 K for arsenic sulphides and selenides

Compound		Frequency/MHz	Ref.
α-As_4S_3	Basal As	64.87, 65.94	15
	Apical As	79.56	
β-As_4S_3	Basal As	65.42, 67.16	15
	Apical As	79.65	
α-As_4Se_3	Basal As	60.78, 61.07	This work
	Apical As	68.97	
α-As_4S_4		89.27, 91.48, 92.09, 92.98	13
β-As_4S_4		89.84, 90.54	14
As_4Se_4		79.79, 81.63, 82.08, 82.38	11
As_2S_3		70.38, 72.78	12
As_2Se_3		56.07, 60.25	11

In Table 3 are listed the ^{75}As n.q.r. frequencies for a number of sulphides and selenides of arsenic. The comparatively small change contributed by crystal packing to the n.q.r. frequencies in these molecular crystals is apparent. Each of the crystals of α-As_4S_3, β-As_4S_3, α-As_4S_4, β-As_4S_4, and As_4Se_4 contains similarly bonded arsenic atoms that are crystallographically non-equivalent, because the point-group symmetry of the isolated molecule is lowered on incorporation in the crystal. This lifting of degeneracy of the isolated molecule gives rise to a splitting in frequency of up to 3.5 MHz. Our assignment of frequencies in α-As_4Se_3 is in accord with this observation.

The constitution and structure of the β crystals which we isolated are not as well characterized. The method of preparation, unit-cell parameters, and particularly the n.q.r. spectrum indicate that these crystals are a polymorphic form of As_4Se_3. The n.q.r. frequency differences between similarly bonded arsenic atoms in the polymorphic forms of As_4S_3 or of As_4S_4 are quite small (Table 3) and, by analogy, we would not expect marked differences between polymorphic forms of As_4Se_3. The groups of n.q.r. signals observed at 77 K for β-As_4Se_3 lying between 57.5 and 61.0 MHz and between 69.5 and 71.5 MHz are assigned to basal and apical arsenic atoms of the As_4Se_3 molecule respectively. We have already noted that the systematic absences of reflections of *X*-rays from β-As_4Se_3 are compatible with space groups *Cc* or *C2/c*. If the crystals are of space group *Cc* then all the atoms will be in general positions 4(a) and there will be four molecules of As_4Se_3 in the asymmetric unit of the unit cell, giving rise to 16 distinct ^{75}As n.q.r. frequencies: four from apical and 12 from basal arsenic atoms. If the crystal is centrosymmetric, space group *C2/c*, the atoms will be in eight-fold general positions and eight n.q.r. frequencies are predicted, two from apical and six from basal arsenics.

The assignments for the β form of As_4Se_3 at 77 K represent the minimum number of frequencies that we were able to resolve due to the sideband overlap obtained with a super-regenerative oscillator, but are sufficient to exclude the centrosymmetric space group *C2/c*. We observed the four apical arsenic frequencies expected for *Cc*, and certainly cannot exclude the possibility that four additional resonances would be separable in the range 57—62 MHz with a sufficiently sensitive regenerative (single-frequency) oscillator which would give a total of 12 basal arsenic resonances as needed for a consistent assignment to space group *Cc*.

From Table 3 we observe that, for the molecular lattices of As_4Se_3 and As_4Se_4 and for the layer lattice of As_2Se_3, the ^{75}As n.q.r. frequencies are appreciably lower in each case than for the similarly bonded arsenic atoms in the isostructural sulphur compounds. The fractional change in frequency between the selenide and the corresponding sulphide increases from 7% for an arsenic atom bonded to one chalcogen and two arsenic atoms to 19% for an arsenic atom bonded to three chalcogen atoms.

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