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^{77}Se Nuclear Magnetic Resonance Study of Se_8^{2+} and Se_{10}^{2+}: Examples of Rigid and Fluxional Species. Disproportionation of Se_{10}^{2+} at Low Temperatures

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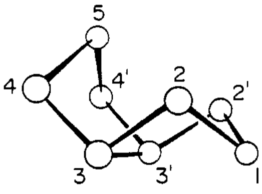
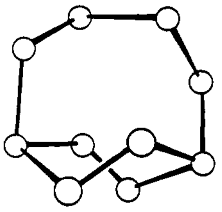
Selenium-77 NMR studies have been performed on natural-abundance and 92.4% ^{77}Se-enriched samples of $Se_8(AsF_6)_2$ and $Se_{10}(AsF_6)_2$ in SO_2 and 100% H_2SO_4. The Se_8^{2+} species was found to be rigid in solution at all temperatures from −70 °C to room temperature, although there was some evidence for slow exchange at higher temperatures. All chemical shifts have been assigned while the ^{77}Se–^{77}Se coupling constants have been evaluated by using a computer fitting procedure; no unique assignment of coupling constants is obtainable, and all possible sets are given. Some correlation of chemical shift with the net positive charge for each environment is noted. The Se_{10}^{2+} species appears to undergo structural isomerism in SO_2 solution at ambient temperatures to give two forms, α- and β-Se_{10}^{2+}, one of which disproportionates below ca. 273 K to give Se_8^{2+} and a second, higher nuclearity species. This is tentatively identified (empirical formulation) as Se_{17}^{2+} or, less likely, Se_{18}^{2+} on the basis of integrated intensity measurements.

Introduction

Our earlier success in identifying and assigning the solution structures of the $Te_{4-n}Se_n^{2+}$ (n = 0–4), $Te_2Se_4^{2+}$, $Te_3Se_3^{2+}$, Te_6^{4+}, and $Te_2Se_6^{2+}$ polyatomic cations by high-resolution ^{77}Se and ^{125}Te pulse FT-NMR spectroscopy[2,3] has led us to investigate the solution structures of the homopolyatomic selenium cations, Se_8^{2+} and Se_{10}^{2+}. X-ray crystal structures[4–7] of these species have shown that the former has an eight-membered ring with an exo–endo conformation and a long cross-ring bond (structure I) while the latter has a bicyclo[4.2.2]decane geometry (structure II). It has been reported that there is considerable difference between the solution-state and solid-state electronic spectra of the Se_{10}^{2+} species.[6] This suggests that the solid-state structure is not retained in solution.



I



II

This paper reports a ^{77}Se (I = $^1/_2$, 7.58% natural abundance) NMR spectroscopic study of Se_8^{2+} in SO_2 and 100% H_2SO_4 solution and Se_{10}^{2+} in SO_2 solution.

Results and Discussion

Se_8^{2+} Cation. The Se_8^{2+} ring possesses an exo–endo conformation in $Se_8^{2+}(AlCl_4^-)_2$ and $(Se_8^{2+})(Te_6^{4+})(AsF_6^-)_6{\cdot}SO_2$,[4,5] the structural parameters also indicating that there is a long transannular bond linking the two Se(3) sites (structure I). The observed ^{77}Se NMR spectra are completely consistent with a rigid Se_8^{2+} cation in SO_2 and 100% H_2SO_4 solution. Selenium-77 spectra of both natural-abundance (7.58% ^{77}Se) and 92.4% ^{77}Se-enriched samples in the above solvents display five distinct selenium environments of integrated intensity ratio 2:2:1:2:1 (A:M:V:Y:Z, see Figure 1) at room temperature. There is no mirror plane in the cation in either of the reported crystal structures, and the slight deviations from C_s symmetry probably result from packing considerations in the solid state. Partially resolved fine structure was also observed for the ^{77}Se-enriched Se_8^{2+} samples under the conditions given above. The splittings are, however, well resolved below ca. −30 °C in SO_2, suggesting that a very slow exchange process is responsible for the broadening at room temperature. The ^{77}Se NMR spectra of natural-abundance and 92.4% ^{77}Se-enriched Se_8^{2+} in SO_2 at −70 °C are shown in Figures 1 and 2a, respectively. In the natural-abundance spectrum, the five unique environments also exhibit a number of different satellite peaks. The spin–spin coupling, chemical shift, and integrated intensity data listed in Table I along with assignments were measured from a ^{77}Se natural-abundance Se_8^{2+} sample at 203 K in SO_2.

Table I. Chemical Shifts (δ) and Coupling Constants (J) for the Se_8^{2+} Cation in SO_2[a,b]

environment	designation[c]	integration[d]	δ,[e] ppm	J,[f] Hz
1	V	0.8	−106.1	64, 41
2 (2′)	M	2.1	219.3	152, 65, 35 (35?)
3 (3′)	A	1.9	668.0	248, 153, 84
4 (4′)	Y	2.0	−231.2	247, 86, 37 (37?)
5	Z	1.2	−256.3	all <40

[a] Natural-abundance ^{77}Se. [b] Measurements recorded at −70 °C. [c] Designation from Figure 1. [d] Integration scaled to a total of eight atoms. [e] Referenced with respect to external saturated aqueous H_2SeO_3 at 24 °C (δ(Me_2Se) = δ(H_2SeO_3) + 1302.6). [f] Estimated error, ± 5 Hz.

Table II. Isotopic Distribution in 92.4% ^{77}Se-Enriched Se_8^{2+}

no. of spin-$^1/_2$ nuclei	coupling patterns	probability (P)	multiplicity (S)	percentage (100PS)
8	AA′MM′VYY′Z	0.5313	1	53.13
7	AA′MM′VYY′, AA′MM′VYZ, etc.	0.0437	8	34.96
6	AA′MM′VY, AA′MVYY′, etc.	0.0036	28	10.08
				tot 98.17

The spectrum of the 92.4% ^{77}Se-enriched sample results from the superposition of subspectra of species of different isotopic distribution. The isotopic distributions for species containing eight, seven, and six spin-$^1/_2$ nuclei are given in Table II. Thus, it may be noted that the most abundant isotopic species ($^{77}Se_8^{2+}$) contributes only 53.1% to the observed spectrum, with the eight $^{77}Se_7Se^{2+}$ species contributing another 35.0%.

From the natural-abundance spectrum it was possible to observe six (possibly seven) of the 16 possible coupling constants (all

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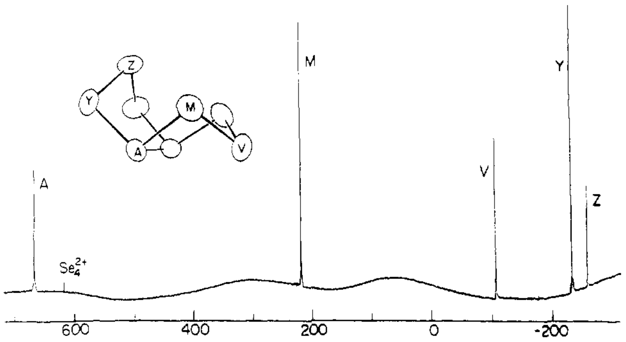

Figure 1. Natural-abundance ^{77}Se NMR spectrum of Se_8^{2+} in SO_2 at -70 °C.

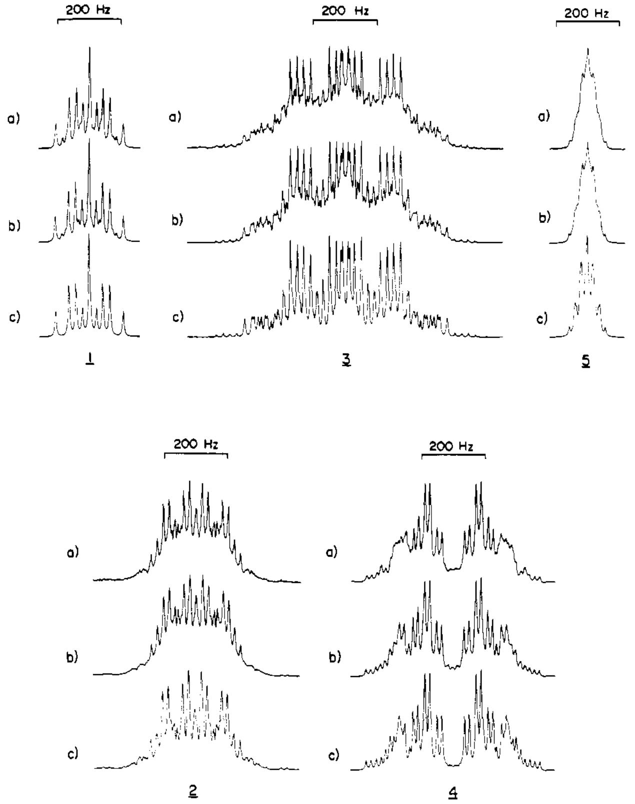

Figure 2. ^{77}Se NMR spectra of the five environments (Structure I) of 92.4% ^{77}Se-enriched Se_8^{2+} showing (a) the experimentally observed profiles, (b) the simulated sum of the contributions from $^{77}Se_8^{2+}$ and $^{77}Se_7Se^{2+}$ (multiplicity of 8), and (c) the simulated profile of only the $^{77}Se_8^{2+}$ contribution. In the simulated spectra line widths were 6 Hz for environments 1, 2, 4, and 5, and 5 Hz for environment 3. All spectra are drawn to the same vertical and horizontal (frequency) scales.

Table III. ^{77}Se–^{77}Se Spin–Spin Coupling Constants for Se_8^{2+} [a]

atoms (*X*, *Y*)	*J*(*X*–*Y*), Hz	atoms (*X*, *Y*)	*J*(*X*–*Y*), Hz
1, 2 (1, 2′)	±64.2 (1)	2, 4′ (2′, 4)	46.8 (3)
1, 3 (1, 3′)	±42.2 (1)	2, 5 (2′, 5)	±18.4 (1)
1, 4 (1, 4′)	0	3, 3′	±78.9 (2)
1, 5	0	3, 4 (3′, 4′)	247.6 (1)
2, 2′	±91.3 (3)	3, 4′ (3′, 4)	86.8 (1)
2, 3 (2′, 3′)	152.7 (1)	3, 5 (3′, 5)	±22.6 (1)
2, 3′ (2′, 3)	29.4 (2)	4, 4′	±25.6 (3)
2, 4 (2′, 4′)	28.1 (2)	4, 5 (4′, 5)	±15.5 (1)

[a] For signs of coupling constants *J*(2–3), *J*(2–3′), *J*(2–4), *J*(2–4′), *J*(3–4), and *J*(3–4′), see set 1(i) in Table IV.

greater than ca. 35 Hz), providing some idea of the connectivity relationships between the five selenium environments. Recourse to the spectrum of the ^{77}Se-enriched sample confirmed these coupling constants and provided values for all of those remaining except for the cross-ring coupling constants *J*(2–2′), *J*(3–3′), and *J*(4–4′). It was also evident that *J*(2–3) and *J*(2–3′) were of opposite sign, as were *J*(3–4) and J(3–4′). With the 13 known values (*J*(1–4) and *J*(1–5) are actually zero) and a likely assignment of coupling constants, estimates could be made for the three missing couplings by simulation and matching to the observed profiles. Spectra for $^{77}Se_8^{2+}$ were simulated by using the computer program NUMARIT.[8] At this stage the "X-approximation" was used except for environments 4 and 5, although the effect on the profiles of environments 2 and 3 is quite minor (environment 1 is not affected). During this investigation it was found that the calculated profiles were invarient to (a) the signs of the couplings involving the unique atoms 1 and 5, (b) the signs of the cross-ring couplings *J*(2–2′), *J*(3–3′), and *J*(4–4′), and (c) certain combinations of sign and/or rearrangement of the coupling constants *J*(2–3), *J*(2–3′), *J*(2–4), *J*(2–4′), *J*(3–4), and *J*(3–4′), that is, those couplings involving the atoms where magnetic inequivalence can arise, and (d) that *J*(2–4) and *J*(2–4′) had to be of the same sign (both + *or* –). After one combination subject to the above criteria was chosen and after the appropriate transition assignments were made, the chemical shifts and coupling constants for $^{77}Se_8^{2+}$ were iterated to fit the experimental data. The root-mean-square error for 202 assigned, *unique* (i.e. non-degenerate) transitions was 0.72 Hz, with the greatest difference between an observed and calculated frequency being 2.56 Hz. The data are given in Table III, and it may be noted that the largest calculated error for the individual coupling constants is 0.3 Hz. However, the actual error is probably somewhat higher as the data point resolution was ca. 1 Hz, and moreover, the actual contribution of $^{77}Se_8^{2+}$ to the observed spectrum is only 53.1% (Table II). The 32 possible combinations of sign and allocations of coupling constant involving selenium environments 2–4 are given in Table IV. All of these lead to the same profile. For the original combination of iterated coupling constants (set 1–4, combination i, Table IV, with all other coupling constants positive in sign) and chemical shift data, the individual eight-spin ($^{77}Se_8^{2+}$) and seven-spin ($^{77}Se_7Se^{2+}$; multiplicty of 8) and subspectra were simulated by using the program PANIC[9] and summed according to their probabilities. The resulting spectra are shown in Figure 2b, while the original $^{77}Se_8^{2+}$ simulation is given in Figure 2c. The simulated environments in Figure 2b account for 88.1% of the observed spectrum, so that the differences with the observed profiles, Figure 2a, arise from the chosen allocation (set) of coupling constants (important for the eight $^{77}Se_7Se^{2+}$ contributions), from the missing 11.9% of ^{77}Se (present as $^{77}Se_6Se_2^{2+}$, etc.), and from errors arising from the original fitting of $^{77}Se_8^{2+}$ (53.1%) to the observed profile itself (100%).

With the evaluations of the coupling constants it is now possible to make some comment regarding assignment of the observed signals to particular selenium environments. That is, when structure I is compared with the Se_8^{2+} cation in Figure 1, whether (a) *A* = 3, *M* = 2, *V* = 1, *Y* = 4, and *Z* = 5, as shown, is correct or the alternative assignment (b) *A* = 3, *M* = 4, *V* = 5, *Y* = 2, and *Z* = 1 is possible. In assignment a the "three-bond" coupling *J*(1–4) = 0 Hz and *J*(2–5) = ±18.4 Hz, while assignment b would require *J*(2–5) = 0 Hz and *J*(1–4) = ±18.4 Hz. The relevant interatomic distances in Se_8^{2+} are given in Table V. We note that Se(2/2′)–Se(5) (average 3.781 Å) is considerably shorter than Se(1)–Se(4/4′) (average 5.244 Å) and is thus more likely to account for the observed coupling of ±18.4 Hz, especially when it is noted that there is no coupling between the unique atoms Se(1) and Se(5) themselves, i.e. *J*(1–5) = 0 Hz, which are actually closer

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(9) The individual selenium environment spectra for $^{77}Se_8^{2+}$ and the eight possible $^{77}Se_7Se^{2+}$ species were simulated in four groups with 1, 2 (2′), and 3 (3′) calculated separately and 4 (4′) and 5 together by using a spectral width of 2008 Hz and 4K of memory in each case, allowing a data point resolution of 0.76 Hz.

Table IV. Signs and Allocation Sets for Couplings (Hz) Involving Magnetic Inequivalence in Se_8^{2+}

coupling const	coupling const set[a]							
	1–4	5–8	9–12	13–16	17–20	21–24	25–28	29–32
J(2–3)	152.7	152.7	29.4	29.4	152.7	152.7	29.4	29.4
J(2–3′)	29.4	29.4	152.7	152.7	29.4	29.4	152.7	152.7
J(2–4)	+28.1	−46.8	+46.8	−28.1	+46.8	−28.1	+28.1	−46.8
J(2–4′)	+46.8	−28.1	+28.1	−46.8	+28.1	−46.8	+46.8	−28.1
J(3–4)	247.6	247.6	247.6	247.6	86.8	86.8	86.8	86.8
J(3–4′)	86.8	86.8	86.8	86.8	247.6	247.6	247.6	247.6

[a] Each group of four has the following sign combinations for J(2–3), J(2–3′), J(3–4), and J(3–4′): (i) +, −, +, −; (ii) +, −, −, +; (iii) −, +, +, −; (iv) −, +, −, +.

Table V. Interatomic Distances for Se_8^{2+} in $Se_8^{2+}(AlCl_4^-)_2$ and $(Se_8^{2+})(Te_6^{4+})(AsF_6^-)_6{\cdot}SO_2$

atoms[a]	interatomic dist, Å	
	$Se_8^{2+}(AlCl_4^-)_2$[b,d]	$(Se_8^{2+})(Te_6^{4+})(AsF_6^-)_6{\cdot}SO_2$[c,e]
1-2, 1-2′	2.313, 2.334	2.311, 2.288
2-3, 2′-3′	2.313, 2.304	2.297, 2.293
3-4, 3′-4′	2.355, 2.328	2.310, 2.327
4-5, 4′-5	2.310, 2.287	2.314, 2.310
2-2′	3.279	3.253
3-3′	2.842	2.905
4-4′	3.344	3.345
1-3, 1-3′	3.431, 3.410	3.393, 3.358
1-4, 1-4′	5.246, 5.290	5.219, 5.222
1-5	5.023	5.011
2-3′, 2′-3	3.800, 3.853	3.851, 3.819
2-4, 2′-4′	3.545, 3.640	3.588, 3.601
2-4′, 2′-4	4.895, 4.874	4.909, 4.845
2-5, 2′-5	3.803, 3.746	3.829, 3.746
3-4′, 3′-4	3.853, 3.885	3.860, 3.908
3-5, 3′-5	3.547, 3.466	3.520, 3.524

[a] Atom arrangement according to structure I. [b] Reference 4. [c] Reference 5. [d] Error ±0.010 Å. [e] Error ±0.004 Å.

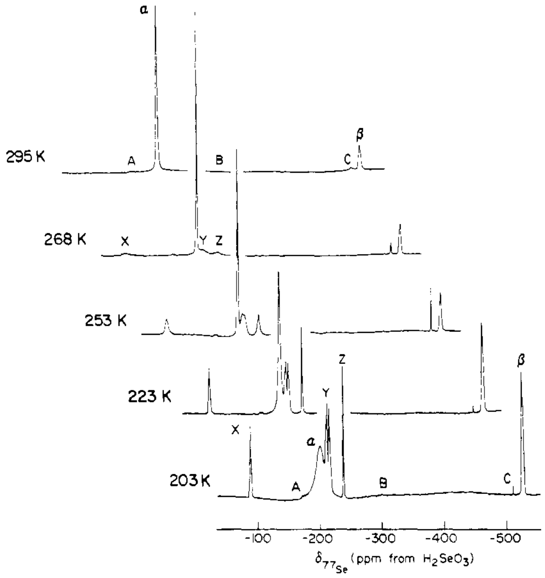

Figure 3. Series of ^{77}Se spectra showing the temperature dependence and disproportionation of Se_{10}^{2+} (92.4% ^{77}Se enriched) over the range 295–203 K. α and β are major resonances, and A–C are minor ones; see text. X, Y, and Z correspond to three of the five resonances attributable to environments 1, 4 and 5 (structure I) of Se_8^{2+}, formed at low temperatures. The spectra are not drawn to the same vertical scale.

(average 5.017 Å) than Se(1)–Se(4/4′). While our assignment is most likely correct, one possible way to check this would be to measure T_1 values for each of the five environments and relate these to the distances of each site to the center of mass of the molecule.

The large range of chemical shifts observed for Se_8^{2+} (924 ppm) suggests that paramagnetic contributions, using Ramsey's notation,[10] are dominant. We note, however, that there appears to be some correlation of chemical shift with the net atomic charge for each environment. The atomic charges were recently calculated by using a semiempirical INDO-type SCF method, giving the following results: Se(1) (structure I), +0.251; Se(2,2′), +0.141; Se(3,3′), +0.442; Se(4,4′), +0.209; Se(5), +0.164.[11] The predicted ordering of selenium environments based on net positive charge is therefore 3 > 1 > 4 > 5 > 2, with 3 being to high frequency (most deshielded). In passing, we note that Se_4^{2+} (net charge/Se = +0.5) has almost the same chemical shift (δ = +624, Figure 1) as Se(3), with a similar net charge (+0.442). The observed order is actually 3 > 2 > 1 > 4 > 5, with environment 2 having moved to higher frequency, implying less shielding, hence a greater positive charge than calculated. It is interesting, therefore, that the cross-ring coupling J(2-2′) (91.3 Hz) has a greater absolute value than J(3–3′) (78.9 Hz) when in fact Se(3)–Se(3′) is considerably shorter than Se(2)–Se(2′) (Table V). Of course, all three cross-ring distances (2–2′, 3–3′, and 4–4′) are considerably shorter than the sum of the van der Waals radii (4.0 Å[12]), indicating some interaction across the ring. Indeed, a plethora of resonance structures have been invoked in a valence bond discussion of both Se_8^{2+} and S_8^{2+} species.[11,13] Interestingly, the INDO treatment indicates negligible interaction energies across Se(2)–Se(2′) and Se(4)–Se(4′) compared to Se(3)–Se(3′) *based on the solid-state geometry*. In solution, however, if chemical shift is a direct indicator of net positive charge, then there may be a slightly stronger interaction and hence shorter distance across Se(2)–Se(2′) compared to Se(3)–Se(3′) than observed in the solid state.

In view of the 32 possible combinations of coupling constant among selenium environments 2–4, an in-depth discussion and attempted correlation with the observed interatomic distances would not be useful. We do note that directly bonded atoms could have spin–spin couplings varying from (absolute values) 247.6 to 15.5 Hz, while two- and three-bond couplings could vary from 247.6 to 18.4 Hz. Notably, the small value for ^1J(4–5) of 15.5 Hz is anomalous compared to ^1J(1–2), 64.2 Hz, although their signs are unknown. Also, with the single exception of J(2–4′), no couplings are observed between atoms that are further apart than the sum of the van der Waals radii. Some values in related species are available for comparison with the above values, namely the one-bond couplings in Se_3S^{2+} (336 Hz),[14] Se_3Te^{2+} (188 Hz),[2] and $Te_2Se_4^{2+}$ (92 Hz)[2] and the two- and three-bond couplings in $Te_2Se_4^{2+}$ (13 and 39 Hz) and $Te_3Se_3^{2+}$ (17.4 Hz).[2]

Se_{10}^{2+} Cation. In the solid state the Se_{10}^{2+} cation has a cage-like bicyclo[4.2.2]decane geometry (structure II). Natural-abundance and 92.4% ^{77}Se-enriched spectra of solutions of $Se_{10}(AsF_6)_2$ in SO_2 exhibit two major resonances at −200.0 (α) and −528.4 ppm (β) in SO_2 at 295 K, with an integrated intensity ratio for α:β of 3.87:1. No evidence of fine structure is apparent. Three minor resonances at −158, −297 (very weak), and −514 ppm (A–C, respectively) are also observed in the spectrum of the enriched

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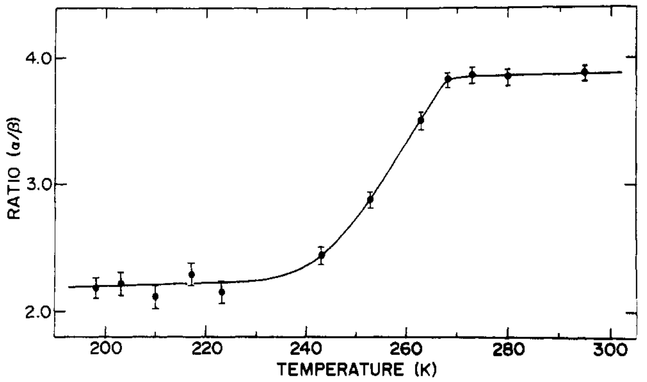

Figure 4. Plot of the ratio of the integrated intensities of $\alpha:\beta$ from 295 to 198 K.

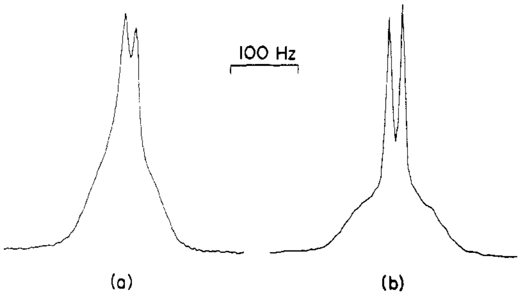

Figure 5. ^{77}Se NMR spectra (selenium enriched to 92.4% in ^{77}Se) of the α resonance (see text) showing the magnetic field dependence of the profile: (a) 47.77 MHz at 263 K, 3.1 Hz/data point (line broadening of 0 Hz); (b) 17.19 MHz at 252 K, 4.4 Hz/data point (line broadening of 2 Hz).

sample, with that at −158 ppm exhibiting evidence of fine structure ($J \approx 160$ Hz). On cooling, however, a number of interesting phenomena are observed. A series of spectra depicting this behavior is given in Figure 3. Below about 273 K, $\mathrm{Se_8}^{2+}$ appears in the spectrum (in fact it may be present at room temperature, but in unobservable amounts) and progressively increases in concentration concomitant with a decrease in the integrated intensity ratio of α to β. The latter data are shown in Figure 4. It is interesting to note that in the presence of $\mathrm{Se_{10}}^{2+}$, fine structure is not observed for the $\mathrm{Se_8}^{2+}$ environments until 253–223 K in these equilibrium mixtures, whereas spin–spin couplings are well resolved for pure $\mathrm{Se_8}^{2+}$ samples at or near room temperature. Thus, it appears the equilibria involved in $\mathrm{Se_8}^{2+}$ formation may also serve to promote intermolecular chemical exchange among the various species and their ^{77}Se environments. The $\alpha:\beta$ ratio reaches an approximately constant value of ca. 2.25 below 230 K, close to the freezing point of the solution. Over this temperature range, the profile of the α resonance in a 92.4% ^{77}Se-enriched sample undergoes a remarkable change. At 295 K it appears as a symmetric peak, $w_{1/2} = 110$ Hz, which on cooling narrows significantly. Below ca. 280 K it splits into a "doublet" having a separation of 17.5 Hz. This is best observed between 273 and 253 K. However, even at 273 K it is apparent that the profile is not a pure doublet, as evidenced by the appearance of broad shoulders at the base (Figure 5). On further cooling, the doublet feature disappears (below ca. 240 K) and the α resonance once again appears as a symmetric peak, broadening significantly below ca. 215 K. The β resonance exhibits an essentially unchanged line shape and width ($w_{1/2} = 150$ Hz) at all temperatures. The minor resonances A and B exhibit little change, except to become progressively more prominent as the temperature decreases. Peak C, however, sharpens considerably, reaching a maximum *height* in relation to the β resonance at ca. 250 K and then decreasing as the temperature is lowered. In terms of integrated intensity it remains fairly constant with respect to the β resonance (ca. 13%) despite the relative line width narrowing and increase in height, only decreasing in integrated intensity relative to β below 250 K as the relative height decreases. All of the above observations, both for the major and minor resonances, are reversible with temperature. Minor resonances A and B do not appear to be related to the $\mathrm{Se_{10}}^{2+}$ or $\mathrm{Se_8}^{2+}$ signals, while C may be attributed to a species that undergoes reaction or exchange with α or β below ca. 250 K. However, as its integrated intensity is only 2.7% (at >250 K) of that of the combined integrated intensities of α and β, we assume its presence does not affect the following interpretation.

A number of models may be considered to explain the above observations. Intramolecular exchange of $\mathrm{Se_{10}}^{2+}$ to give two environments (ratio 4:1) can be ruled out since the $\alpha:\beta$ ratio changes markedly with temperature and the drastic α line shape variation is not mimicked by the β resonance. Disproportionation of $\mathrm{Se_{10}}^{2+}$ into two species, $\mathrm{Se}_m{}^{n+}$ and $\mathrm{Se}_p{}^{q+}$ may occur, with one of these undergoing further disproportionation on cooling to give $\mathrm{Se_8}^{2+}$ and a fourth species. However, such a large number of previously unobserved selenium polyatomic cations seems rather unlikely (also, see below). Alternatively, $\mathrm{Se_{10}}^{2+}$ may exist in two forms in $\mathrm{SO_2}$ solution at room temperature, α-$\mathrm{Se_{10}}^{2+}$ (α resonance) and β-$\mathrm{Se_{10}}^{2+}$ (β resonance). Presumably, each of the $\mathrm{Se_{10}}^{2+}$ isomers undergoes intramolecular exchange to account for the observed singlets. The existence of two isomeric forms is not unprecedented, as demonstrated by the eight-atom heterochalcogen cations themselves, where $\mathrm{Te_2Se_6}^{2+}$ is known to have a different structure to that of $\mathrm{Se_8}^{2+}$ or $\mathrm{S_8}^{2+}$.[4,5,13,15] Analogies also exist in borane chemistry, where *closo*-$\mathrm{B_8H_8}^{2-}$ exists in one form (dodecahedron, D_{2d}) in the solid state, and two different forms (square antiprism, D_{4d}; bicapped trigonal prism, C_{2v}) in solution, the two forms *coexisting* in certain nonpolar solvents.[16-18] At lower temperatures, α-$\mathrm{Se_{10}}^{2+}$ disproportionates into $\mathrm{Se_8}^{2+}$ and another species. Assuming a +2 charge for the latter species ("$\mathrm{Se}_n{}^{2+}$"), a common feature of the polychalcogen cations (species with odd charges, e.g. $\mathrm{Se}_n{}^{+}$, would be paramagnetic), the equations are as follows:

n even ($n = 8 + 2x$)

$$x\mathrm{Se_{10}}^{2+} \rightleftharpoons (x-1)\mathrm{Se_8}^{2+} + \mathrm{Se}_{(8+2x)}{}^{2+} \qquad (1)$$

n odd ($n = 8 + x$)

$$x\mathrm{Se_{10}}^{2+} \rightleftharpoons (x-2)\mathrm{Se_8}^{2+} + 2\mathrm{Se}_{(8+x)}{}^{2+} \qquad (2)$$

The chemical shift of $\mathrm{Se}_n{}^{2+}$ would appear to be almost identical with that of α-$\mathrm{Se_{10}}^{2+}$, its precursor.[19] Indeed, the spectral ranges on either side of the α and β resonances have been examined for over 50 000 Hz at low temperatures (203 K), with no evidence of any other selenium-containing species. The overlapping of two separate signals therefore accounts for the change in profile of the α resonance with temperature.[20] It may also be seen from Figure 5 that skewing of the doublet from the broad, overlapping resonance is different at 47.77 and 17.19 MHz, indicating that the chemical shifts of α-$\mathrm{Se_{10}}^{2+}$ and $\mathrm{Se}_n{}^{2+}$ are very slightly different. As the temperature is lowered below ca. 250 K, $\mathrm{Se}_n{}^{2+}$ becomes a significant contributor to the α resonance. If α-$\mathrm{Se_{10}}^{2+}$ is in equilibrium with β-$\mathrm{Se_{10}}^{2+}$, then the intensity of the β resonance

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(19) The assumption that the chemical shift of $\mathrm{Se}_n{}^{2+}$ ($n > 10$) is almost identical with that of α-$\mathrm{Se_{10}}^{2+}$ would seem inconsistent with the observed trend of weighted average chemical shifts of various selenium polycations ($\mathrm{Se_4}^{2+}$, $\mathrm{Se_8}^{2+}$, and α- and β-$\mathrm{Se_{10}}^{2+}$) with average charge per selenium. However, in related systems, for example, the tellurium polycations, the chemical shift for $\mathrm{Te_6}^{4+}$ indicates that the ^{125}Te environment is considerably more shielded than the trend implied by the ^{125}Te signals of $\mathrm{Te}_n\mathrm{Se}_{4-n}{}^{2+}$ (n = 1–4).[2]

(20) The small splitting, 17.5 Hz, observed for α-$\mathrm{Se_{10}}^{2+}$ is unquestionably a coupling as the ^{77}Se NMR of a natural abundance sample shows only a singlet over the same temperature range, ruling out the possibility of structural inequivalence of environments as intramolecular exchange slows. The splitting is actually better seen at lower magnetic field strength, as shown in Figure 5b, and must stem from magnetic inequivalence. The enhanced resolution at lower external field strength is presumably a shielding anisotropy effect.

should also decrease somewhat with decreasing temperature. We note an observed difference in the ratio of $(Se_8^{2+} + \alpha):\beta$ at low temperatures (ca. 5.9:1) compared to the $\alpha:\beta$ ratio at ambient temperatures (3.9:1). Indeed, the appearance of substantially more selenium at lower temperatures (relative to the "yardstick" β resonance) is another problem with the Se_m^{n+}/Se_p^{q+} model discussed above. Now, in the low-temperature region (<223 K) where the $\alpha:\beta$ ratio is fairly constant (Figure 4), it is possible to calculate a value for the ratio of $(Se_8^{2+}):(Se_n^{2+}$ + residual α-$Se_{10}^{2+})$. The data are as follows (temperature and ratio): 223 K, 1.75; 217 K, 1.53; 210 K, 1.67; 203 K, 1.68; 198 K, 1.74. These data yield an average value of 1.67(6):1. Assuming that the residual α-Se_{10}^{2+} contributing to the α-resonance is negligible, a not insignificant assumption if α- and β-Se_{10}^{2+} are in equilibrium, knowing that β-Se_{10}^{2+} exists in this low-temperature region, it is now possible to return to eq 1 and 2 and match the observed ratio to calculated ones. The best agreement is for Se_{17}^{2+}, for which the ratio is 1.65:1. For Se_{18}^{2+} and Se_{19}^{2+} the calculated ratios are 1.78 and 1.90:1, respectively. However, if either of these species were Se_n^{2+}, substantial amounts of α-Se_{10}^{2+} would have to be present at low temperatures (up to 25% of the α-resonance for Se_{19}^{2+}) and would presumably be observable. It is probable then that Se_n^{2+} has the (empirical) formulation Se_{17}^{2+} or, less likely, Se_{18}^{2+} although Se_{19}^{2+} cannot be excluded on the basis of the assumptions used.[21] Interestingly, related studies of selenium cations in molten $NaAlCl_4$[22,23] have indicated the presence of Se_4^{2+}, Se_8^{2+}, Se_{12}^{2+}, and a species designated as Se_{16}^{2+}. The ions Se_4^{2+}, Se_8^{2+}, and Se_{10}^{2+} but not Se_{12}^{2+} have been observed in anhydrous SO_2, H_2SO_4, or HSO_3F. In the molten-salt work Se_{16}^{2+} could just have legitimately been formulated as Se_{17}^{2+} on the basis of the observed numbers, but the former was favored on the basis of the *then* considered existence of S_{16}^{2+}, which subsequently has been shown to be S_{19}^{2+}.[24] Of course, there may not necessarily be a one-to-one correspondence between species in such different solvent systems, as shown by Se_{10}^{2+} and Se_{12}^{2+}, but it is gratifying to note the presence of a high nuclearity species in the molten-salt work corresponding to that observed in this study, with a very similar formulation.

Experimental Section

Materials. Elemental selenium ("Baker Analyzed", J. T. Baker Chemical Co.), selenium enriched to 92.4 (7)% (Techsnabexport, Moscow), and AsF_5 (Ozark Mahoning Co.) were used as supplied. Anhydrous sulfur dioxide (Matheson of Canada) was stored over P_4O_{10} for at least 24 h before use. Sulfuric acid (100%) was prepared by adding 30% oleum to commercial sulfuric acid (95.5%) until the freezing point reached a maximum.

Preparations. The cations Se_8^{2+} and Se_{10}^{2+} were prepared as their AsF_6^- salts, as described previously,[6,25] by oxidizing selenium powder (natural abundance or 92.4% ^{77}Se enriched) with AsF_5 in SO_2 solvent according to eq 3 and 4. A slight excess (ca. 5%) of AsF_5 in eq 3 and

$$8Se + 3AsF_2 \xrightarrow[25\ °C]{SO_2} Se_8^{2+}(AsF_6^-)_2 + AsF_3 \tag{3}$$

$$10Se + 3AsF_5 \xrightarrow[25\ °C]{SO_2} Se_{10}^{2+}(AsF_6^-)_2 + AsF_3 \tag{4}$$

of selenium in eq 4 were used to ensure that no Se_{10}^{2+} or Se_8^{2+}, respectively, were present. The reduction product, AsF_3, and SO_2 solvent were removed under vacuum to give solid products, which were redissolved in the appropriate solvent, SO_2 or 100% H_2SO_4. Samples were contained in 10 mm o.d. precision glass NMR tubes (Wilmad), which were attached to the reaction tubes and flame sealed after transfer of the reconstituted solutions.

NMR Spectroscopy. Selenium-77 NMR spectra were obtained on a Bruker WM-250 spectrometer at 47.77 MHz. For the enriched samples of Se_8^{2+}, the free induction decays were accumulated in 16K of memory over spectral widths of 8065 Hz (0.98 Hz/data point, with a line-broadening parameter of 1 Hz in the exponential multiplication of the free induction decay) using a pulse width of 30 μs. From 6000 to 15000 scans were collected for each environment with a pulse repetition time of 1.02 s. Natural-abundance spectra were recorded using 32 K of memory over spectral widths of 50000 Hz (3.05 Hz/data point, line broadening of 1–3 Hz, pulse repetition time 0.33 s) with a pulse width of 30 μs, in 90000-125000 scans. For enriched Se_{10}^{2+}, the free induction decays were accumulated in 16 K of memory over a spectral width of 50000 Hz (6.1 Hz/data point, line broadening of 6 Hz, pulse repetition time 0.16 s) with a pulse width of 30 μs, in 5000–25000 scans. Natural-abundance spectra were accumulated by using the same parameters. Some enriched Se_{10}^{2+} spectra were also run at a lower magnetic field, 17.19 MHz, on a Bruker WH-90 spectrometer. Free induction decays were accumulated in 16K of memory over a spectral width of 25000 Hz (4.4 Hz/data point, line broadening of 2 Hz, pulse repetition time 0.23 sec) by using a pulse width of 17 μs, in 60000–80000 scans. All samples were allowed to equilibrate for 0.25–0.5 h at each temperature before the spectra were recorded. Samples were run unlocked on the WM-250 (field drift < 1 Hz/h) but were ^{2}H locked to an external D_2O sample in the WH-90 probe head. Spectra were referenced externally to saturated aqueous H_2SeO_3 at 24 °C ($\delta(Me_2Se) = \delta(H_2SeO_3) + 1302.6$).

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[21] n cannot be less than 17 as the observed ratio of $(Se_8^{2+}):(Se_n^{2+}$ + residual α-$Se_{10}^{2+})$ is 1.67 (6):1 and is already greater than that predicted for Se_{16}^{2+} (1.50:1) based on no contribution of α-Se_{10}^{2+} to the α resonance.

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