the Zn–N bond is a "single covalent" bond. It is also consistent with the photoelectron spectrum, which shows that the two electron pairs on the N atoms are at least approximately degenerate.[6]

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Registry No. $[(Me_3Si)_2N]_2Zn$, 3999-27-7.

Supplementary Material Available: Tables of the leveled total intensities, final backgrounds, and averaged molecular intensities (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

A ^{77}Se and ^{125}Te NMR Study of the $Te_2Se_6^{2+}$ Cation: Magnetic Inequivalence of Heavy Nuclei

Michael J. Collins and Ronald J. Gillespie*

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Selenium-77 NMR spectra were observed by us by continuous-wave methods as early as 1965.[1] In recent years developments in FT NMR spectroscopy and the availability of high-field instruments have led to a very considerable increase in studies of the NMR spectra of relatively insensitive nuclei such as ^{77}Se and ^{125}Te. Results obtained with these two nuclei have been reviewed in two recent monographs.[2,3] We have been engaged in a study of polyatomic cations of group 6 and have recently used ^{77}Se and ^{125}Te NMR spectroscopy to obtain structural information on some of these species.[4–10] (^{77}Se: spin $^1/_2$, 7.50% natural abundance, 6.9×10^{-3} relative sensitivity to ^1H. ^{125}Te: spin $^1/_2$, 7.00% natural abundance, 3.2×10^{-2} relative sensitivity to ^1H.) The present note is concerned with the $Te_2Se_6^{2+}$ cation.

The solid-state structure of the $Te_2Se_6^{2+}$ cation has recently been determined[11] in the compound $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$. The structure of this cation can be derived from a cube with the two tellurium atoms at opposite corners (Figure 1). In this structure both tellurium atoms are chemically equivalent, as are the six selenium atoms. The solid-state structure of the isovalent Se_8^{2+} cation is quite different from that of $Te_2Se_6^{2+}$. It is an eight-membered ring in the exo–endo conformation with a long transannular bond.[12] The ^{77}Se NMR spectrum of this species in SO_2 or 100% H_2SO_4 solution is consistent with this same structure.[13] The aim of the present work was to record the ^{77}Se and ^{125}Te NMR spectra of the $Te_2Se_6^{2+}$ cation to determine if the solid-state structure is retained in solution and to determine the chemical shifts and coupling constants in this species.

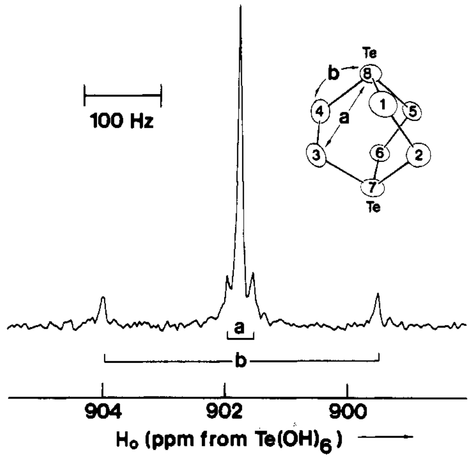

Figure 1. ^{125}Te NMR spectrum of $Te_2Se_6^{2+}$, natural abundance, showing the main resonance with two doublets corresponding to $J(^{77}Se–^{125}Te) = 355$ Hz and $^2J(^{77}Se–^{125}Te) = 32$ Hz; 148 000 scans (13.5 h), 3.0 Hz/data point. A line broadening of 1 Hz was applied to the exponential smoothing of the free-induction decay.

Experimental Section

Materials. Elemental selenium and tellurium (Koch-Light Laboratories Ltd.) were dried overnight at 24 °C on a vacuum line. Tellurium enriched to 77.3% ^{125}Te was obtained by reduction of the enriched dioxide[14] (Techsnabexport, Moscow). $(Te_2Se_8)(AsF_6)_2(SO_2)$ and $(Te_2Se_8)(AsF_6)_2$ were prepared as previously described.[5,11] Arsenic pentafluoride and arsenic trifluoride were prepared from the elements on a Monel vacuum line. AsF_5 was stored in a Monel cylinder; AsF_3 in a nickel pot over sodium fluoride. A sample of 100% H_2SO_4 was prepared by combining 96% H_2SO_4 and 30% oleum (Fisher Scientific Co.) until a maximum freezing point was obtained.

Sample 1. A sample of 200 mg of $(Te_2Se_8)(AsF_6)_2(SO_2)$ was transferred in a drybox into a 10-mm o.d. precision glass NMR tube (Wilmad) joined to $^1/_4$-in. o.d. standard wall tubing. The sample tube was attached to a vacuum line by means of a Teflon valve, and 5 g of AsF_3 was distilled into the tube at −196 °C before flame sealing.

Sample 2. Te (26.8 mg, 0.210 mmol, 77.3% ^{125}Te) and Se (87.2 mg, 1.10 mmol) were combined with AsF_5 (52 mg, 0.31 mmol) and AsF_3 (5 g) in a small glass vessel equipped with a magnetic stirring bar. The reaction mixture was stirred for 16 h. The resulting deep brown solution was then filtered through a glass frit into a 10-mm NMR tube and the tube was then flame sealed.

Nuclear Magnetic Resonance Spectroscopy. ^{77}Se NMR spectra were obtained with a Bruker WH-400 multinuclear spectrometer at 76.42 MHz in 16K of memory with a spectral width of 50 kHz (6.1 Hz/data point; pulse repetition time 0.16 s) and a pulse width of 40 μs. ^{125}Te NMR spectra were obtained with a Bruker WM-250 multinuclear spectrometer at 78.97 MHz in 16K of memory with spectral widths of 20–25 kHz (2.4–3.0 Hz/data point; pulse repetition time 0.41–0.33 s) and a pulse width of 20 μs. Samples were run unlocked (field drift <1 Hz/h) and referenced externally to saturated aqueous H_2SeO_3 and $Te(OH)_6$ at 25 °C. Spectra were simulated and summed with a Nicolet 1180 computer in the program NTCFT and plotted with a Zeta Plotter 100.

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Table I. ^{77}Se and ^{125}Te NMR Parameters for the $Te_2Se_6^{2+}$ Cation in AsF_3

	δ^b		J/Hz		
sample^a	^{77}Se	^{125}Te	J-(Se-Te)	^2J-(Se-Te)	^3J-(Te-Te)
1	−719.2	901.7	355^c 354^d	32^c	
2	−717.7	901.9	355^c	31^c	120

^{a} See Experimental Section. ^{b} Referenced with respect to external saturated aqueous H_2SeO_3 and $Te(OH)_6$. Conversions to chemical shifts (ppm) with respect to neat Me_2Se and Me_2Te are given by $\delta(Me_2Se) = \delta(H_2SeO_3) + 1302.6$ and $\delta(Me_2Te) = \delta(Te(OH)_6) + 710.9$. All measurements at the ambient temperature, approximately 25 °C. ^{c} Obtained from ^{125}Te spectrum. ^{d} Obtained from ^{77}Se spectrum.

Table II. Total Satellite Intensities for Coupling to 1, 2, and 3 Natural-Abundance ^{77}Se (7.50%) and ^{125}Te (7.00%) Nuclei

		intensity			
nucleus	no.	uncoupled	doublet	triplet	%^{a}
^{77}Se	1	92.50	7.50		8.1
	2	85.56	13.88	0.56	16.2
	3	79.14	19.25	1.56	24.1
^{125}Te	1	93.00	7.00		7.5
	2	86.49	13.02	0.49	15.0
	3	80.44	18.16	1.37	22.4

^{a} Total intensity of doublet relative to central line (uncoupled peak plus contribution from triplet).

Results and Discussion

$(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$ is the only known salt of the $Te_2Se_6^{2+}$ cation.[11] Numerous resonances are observed in the ^{77}Se NMR spectrum of a 100% H_2SO_4 solution of this compound, the intensities of which vary with time. A single resonance at −732 ppm grew and then diminished in intensity in a manner not mimicked by any of the other resonances, indicating that the species producing this resonance has only one selenium environment. A similar peak at −732 ppm is also observed in the spectra of solutions of $(Te_2Se_8)(AsF_6)_2$ in 100% H_2SO_4. It cannot be attributed to $Te_2Se_8^{2+}$ and is therefore assigned to $Te_2Se_6^{2+}$ produced by decomposition of $Te_2Se_8^{2+}$ since $Te_2Se_6^{2+}$ has only one selenium environment in the solid-state structure. Since $(Te_2Se_6)(Te_2Se_8)(AsF_6)_4(SO_2)_2$ is difficult to prepare while salts of the $Te_2Se_8^{2+}$ cation can be routinely prepared,[5,11] subsequent investigations of the $Te_2Se_6^{2+}$ cation were made on solutions of $Te_2Se_8^{2+}$ salts. Moreover, since AsF_3 solutions of $(Te_2Se_8)(AsF_6)_2(SO_2)$ produce a decomposition peak similar to that observed for the 100% H_2SO_4 solution (Table I), but with considerable reduction in line width and a corresponding increase in the signal-to-noise ratio, solutions in AsF_3 rather than H_2SO_4 were studied.

The resonance assigned to $Te_2Se_6^{2+}$ from the ^{125}Te NMR spectrum of natural-abundance $(Te_2Se_8)(AsF_6)_2(SO_2)$ dissolved in AsF_3 displays two clearly resolved doublets about the central, uncoupled peak (Figure 1). The total intensity of the outer satellite peaks ($J = 355 \pm 6$ Hz) is 22% relative to the central line, while the inner satellites ($J = 32 \pm 6$ Hz) appear to be of a comparable magnitude but are not as well resolved. This intensity is consistent with coupling of Te to three equivalent, naturally abundant ^{77}Se nuclei (Table II). The coupling constants indicate that one set of three Se atoms is directly bonded to Te, while the second set is more remote. This is consistent with the solid-state structure of $Te_2Se_6^{2+}$.

In the ^{77}Se spectrum of this same sample a resonance is observed with a satellite doublet of 7% intensity relative to the central line and a coupling of 354 ± 12 Hz (Table I). The 32-Hz coupling is not resolved. The doublet intensity indicates coupling to one naturally abundant ^{125}Te nucleus (Table II) and is again consistent with the solid-state structure.

When the concentration of ^{125}Te in the sample is enriched to 77.3% a large number of satellite peaks appear in the ^{125}Te spectrum in addition to those observed in the natural-abundance spectrum (Figure 2). These peaks are too intense to result from ^{77}Se–^{125}Te coupling, and since the two tellurium atoms in the structure are chemically equivalent, the additional lines in the spectrum must result from magnetic inequivalence. The most important satellite pattern for natural-abundance Se and 77.3% enrichment in ^{125}Te is an AA′X spectrum (ABX

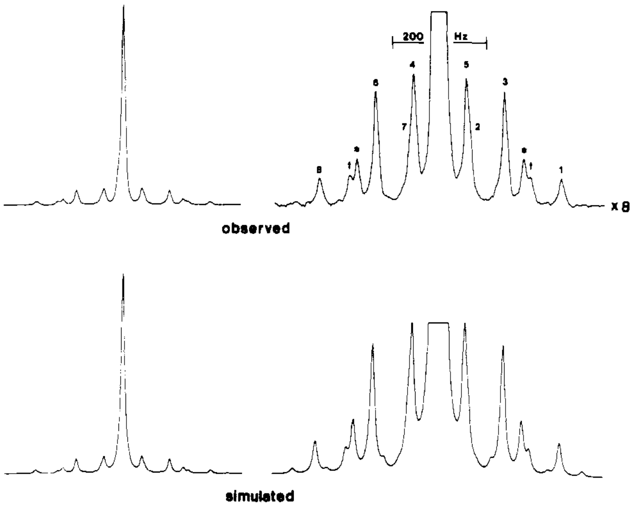

Figure 2. Observed and simulated ^{125}Te NMR spectra of $Te_2Se_6^{2+}$, 77.3% enriched in ^{125}Te, showing the main resonance and the AA′ region of the AA′X (1–8), AX (*), and AA′XX′ (†) coupling patterns. The observed spectrum was accumulated in 116 000 scans (13 h), 2.4 Hz/data point. A line broadening of 2 Hz was applied to the exponential smoothing of the free-induction decay.

Table III. Isotopic Distribution in $Te_2Se_6^{2+}$

		Se		Te				NMR-active %	
spin 1/2 nuclei^a	coupling pattern	1/2	0	1/2	0	M^b	%^{c}	^{77}Se	^{125}Te
none		0	6	0	2	1	3.23		
1	X	1	5	0	2	6	1.57	4.20	
1, 2	X_2(I)	2	4	0	2	3	0.06	0.17	
1, 3	X_2(II)	2	4	0	2	6	0.13	0.35	
1, 4	X_2(III)	2	4	0	2	6	0.13	0.35	
7	A	0	6	1	1	2	21.98		23.17
7, 8	A_2	0	6	2	0	1	37.43		39.46
1, 8	AX(I)	1	5	1	1	6	5.35	14.32	5.64
1, 7	AX(II)	1	5	1	1	6	5.35	14.32	5.64
1, 7, 8	AA′X	1	5	2	0	6	18.21	48.74	19.20
1, 2, 7	AXX′(I)	2	4	1	1	6	0.43	1.15	0.45
1, 3, 7	AXX′(II)	2	4	1	1	12	0.87	2.33	0.92
1, 4, 8	AX_2(I)	2	4	1	1	6	0.43	1.15	0.45
1, 4, 7	AX_2(II)	2	4	1	1	6	0.43	1.15	0.45
1, 3, 7, 8	AA′XX′(I)	2	4	2	0	6	1.48	3.96	1.56
1, 2, 7, 8	AA′XX′(II)	2	4	2	0	3	0.74	1.98	0.78
1, 4, 7, 8	$AA'X_2$	2	4	2	0	6	1.48	3.96	1.56
total							99.30	98.13	99.28

^{a} See Figure 1. ^{b} Multiplicity. ^{c} Percentage of isotopic isomer for 7.50% ^{77}Se, 77.3% ^{125}Te.

Table IV. AA′X Assignments in $Te_2Se_6^{2+}$, AA′ Region (Figure 2)

	position/Hz^a			position/Hz^a	
line	obsd^b	simulated	line	obsd^b	simulated
1	−256	−257	5	−54	−56
2	−63^c	−64	6	138	137
3	−136	−137	7	66^c	64
4	57	56	8	258	257

^{a} Relative to uncoupled line as zero. ^{b} Data point resolution is 2.4 Hz/point. ^{c} Estimated from other line positions.

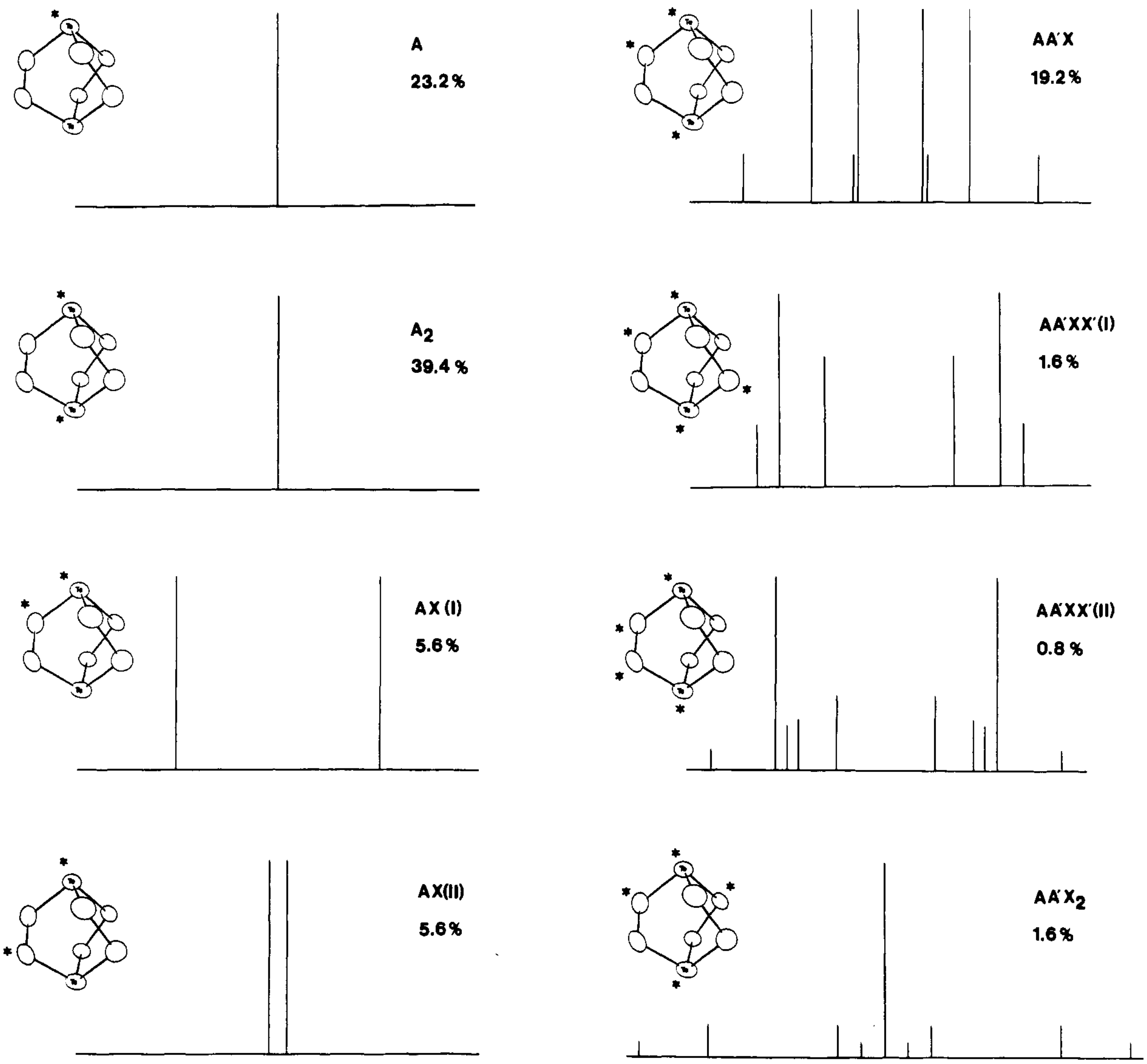

Figure 3. Components used to simulate the ^{125}Te NMR spectrum of $Te_2Se_6^{2+}$, 77.3% enriched in ^{125}Te.

with $\delta_A = \delta_B$) arising from both Te atoms and one Se atom (Table III). This has eight lines in the AA′ (^{125}Te) region and six lines in the X (^{77}Se) region.[15] Six of the eight AA′ lines can be clearly observed in the spectrum with the remaining two as shoulders on the two AA′ lines closest to the central, uncoupled line (Figure 2). By the use of previously established methods,[15,16] the two ^{77}Se–^{125}Te couplings and the ^{125}Te–^{125}Te coupling (Table I) can be extracted from the line separations in the AA′X multiplet (Table IV). The former two agree with those observed in the natural-abundance ^{125}Te spectrum.

Using the values of these coupling constants and the probabilities of the isotopic distribution for 7.50% ^{77}Se and 77.3% enrichment in ^{125}Te (Table III) and assuming the solid-state structure of two Te atoms joined by three, two-atom Se chains, we simulated and summed a series of spectra (Figures 2 and 3). The AA′XX′ patterns require estimates of the ^{77}Se–^{77}Se couplings. The 3-bond ^{77}Se–^{77}Se coupling in AA′XX′(I) was set to zero and the directly bonded coupling in AA′XX′(II) set to 100 Hz. The mean directly bonded coupling in Se_8^{2+} is 108 Hz.[13] Since the two strongest peaks in these patterns are insensitive to the magnitude of this coupling (compare AA′XX′(I) and AA′XX′(II) in Figure 3) and the species producing these patterns are of very low probability (Table III), these estimates do not produce any significant error. The AA′X$_2$ pattern is independent of the ^{77}Se–^{77}Se coupling constant. The resulting simulation (including a line width of 12 Hz) fits the observed spectrum extremely well with all of the

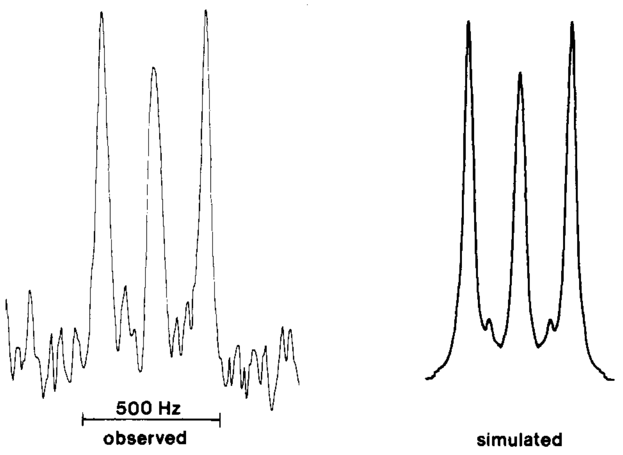

Figure 4. Observed and simulated ^{77}Se NMR spectra of $Te_2Se_6^{2+}$, 77.3% enriched in ^{125}Te, natural-abundance ^{77}Se. The observed spectrum was accumulated in 48 000 scans (2 h), 6.1 Hz/data point. A line broadening of 12 Hz was applied to the exponential smoothing of the free-induction decay.

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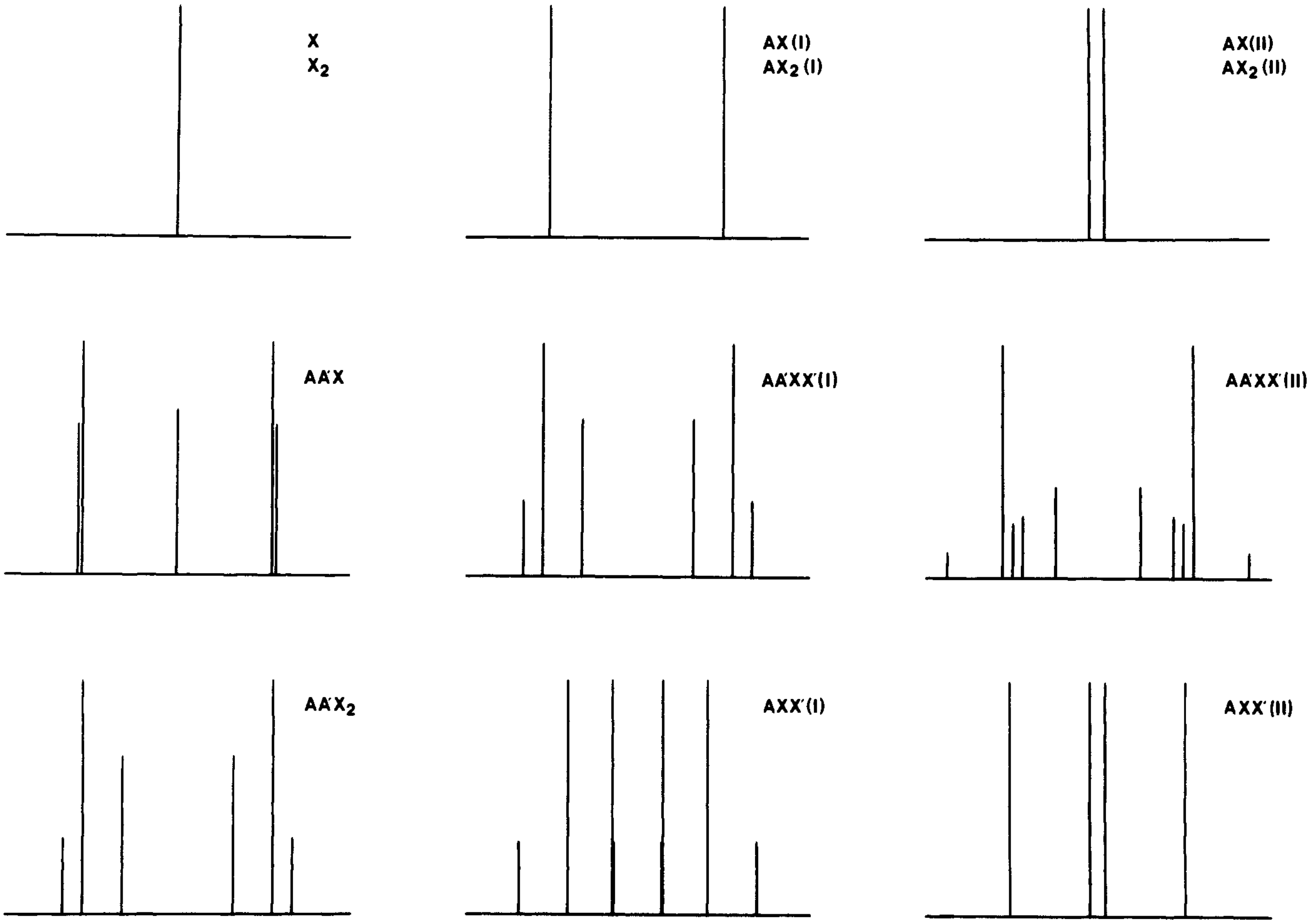

Figure 5. Components used to simulate the ^{77}Se NMR spectrum of $Te_2Se_6^{2+}$, 77.3% enriched in ^{125}Te, natural-abundance ^{77}Se.

observed satellites accounted for. AA′X and AA′XX′ systems have been reported, for example, in the ^{1}H spectrum of 2-furfurol[17] and the ^{19}F spectrum of 1,2-dichloro-3,4,5,6-tetrafluorobenzene,[18] but to our knowledge this is the first report of such inequivalence involving heavy nuclei.

The ^{77}Se NMR spectrum of this same sample complements the above analysis (Figure 4). The simulated spectrum incorporates the X portions of the coupling patterns described above as well as X, X_2, AXX′, and AX_2 components (Table III). The individual components used in the simulation are displayed in Figure 5. The signal-to-noise ratio in the observed spectrum is not good enough to determine any ^{77}Se–^{77}Se couplings, and the estimates used in the ^{125}Te simulation are retained here. The simulated ^{77}Se spectrum matches the observed spectrum when a line width of 30 Hz is used in the simulation.

Conclusions

The results of this ^{77}Se and ^{125}Te NMR investigation of the $Te_2Se_6^{2+}$ cation are consistent with retention in solution of the solid-state arrangement of two tellurium atoms joined by three, two-atom selenium chains. An important feature of the solid-state structure is the large Te–Se–Se–Te dihedral angle of 69°. The resulting interchain Se–Se distances are significantly shorter than twice the van der Waals radius of Se. These may therefore be weak bonding interactions.[11] Similar short interchain distances are observed in the $Te_2Se_8^{2+}$ cation[11] and the isostructural Se_{10}^{2+} cation.[8] Vicinal ^{1}H–^{1}H couplings in HCCH fragments are dependent upon the H–C–C–H dihedral angle.[19] The observed ^{125}Te–^{125}Te coupling for $Te_2Se_6^{2+}$ could, in principle, be of significance in deducing the Te–Se–Se–Te dihedral angle in solution, but since no other ^{125}Te–^{125}Te couplings have been reported for similar geometries, no correlation between the coupling constant and the dihedral angle can be established at present.

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Registry No. $Te_2Se_6^{2+}$, 98046-91-4; ^{77}Se, 14681-72-2; ^{125}Te, 14390-73-9; AsF_3, 7784-35-2.

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Contribution from the Chemical Physics Group,
Tata Institute of Fundamental Research,
Colaba, Bombay 400 005, India

Proton NMR Studies on Six-Coordinated "High-Spin" Iron(III) Porphyrins

D. V. Behere, R. Birdy, and S. Mitra*

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High-spin ferric ion in heme proteins generally occurs as six-coordinated while the corresponding iron(III) porphyrins are often five-coordinated. In order to find better synthetic models for the heme proteins, there has recently been con-

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