Nuclear magnetic shielding tensors for the carbon, nitrogen, and selenium nuclei of selenocyanates — a combined experimental and theoretical approach

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Abstract: The principal components of the carbon, nitrogen, and selenium chemical shift (CS) tensors for several solid selenocyanate salts have been determined by NMR measurements on stationary or slow magic-angle-spinning powder samples. Within experimental error, all three CS tensors are axially symmetric, consistent with the expected linear geometry of these anions. The spans (W) of the carbon and selenium CS tensors for the selenocyanate anion (SeCN–) are approximately 300 and 800 ppm, respectively, much less than the corresponding values for carbon diselenide (CSe2). This difference is a consequence of the difference in the CS tensor components perpendicular to the C2 symmetry axes in these systems. Ab initio calculations show that the orbital symmetries of these compounds are a significant factor in the shielding. For CSe2, efficient mixing of the s and π orbitals results in a large paramagnetic contribution to the total shielding of the chemical shielding tensor components perpendicular to the molecular axis. Such mixing is less efficient for the SeCN–, resulting in a smaller paramagnetic contribution and hence in greater shielding in directions perpendicular to the molecular axis.

Key words: selenocyanates, solid-state NMR, carbon shielding tensors, nitrogen shielding tensors, selenium shielding tensors, ab initio calculations.

Résumé : À partir de mesures RMN sur des échantillons de poudre stationnaires ou à rotation lente à l’angle magique de plusieurs sélénocyanates solides, on en a déterminé les principaux composant des tenseurs des déplacements chimiques (DC) du carbone, de l’azote et du sélénium. Dans les limites des erreurs expérimentales, les trois tenseurs des DC sont axialement symétriques, ce qui est en accord avec la géométrie linéaire attendue pour ces anions. Les plages, W, des tenseurs du carbone et du sélénium pour l’anion sélénocyanate (SeCN–), sont approximativement de 300 et de 800 ppm respectivement, des valeurs beaucoup plus faible que les valeurs correspondantes observées dans le disélénure de carbone (CSe2). Cette différence est une conséquence de la différence dans les composants du tenseur DC qui sont perpendiculaire aux axes de symétrie C2 dans ces systèmes. Des calculs ab initio montrent que les symétries des orbitales de ces composés sont un facteur important dans le blindage. Pour le CSe2, une combinaison efficace des orbitales σ et π conduit à une contribution paramagnétique importante au blindage total des composantes du tenseur de blindage chimique perpendiculaires à l’axe moléculaire. Une telle combinaison est moins efficace pour le SeCN–; il en résulte que la contribution paramagnétique est plus faible et, en conséquence, que le blindage est plus grand dans les directions perpendiculaires à l’axe moléculaire.

Mots clés : sélénocyanates, RMN à l’état solide, tenseurs de blindage du carbone, tenseurs de blindage de l’azote, tenseurs de blindage du sélénium, calculs ab initio.

Introduction

The selenocyanate ligand (SeCN–) has been of considerable interest because of its ambidentate nature (1). That is, it may coordinate to a metal through the nitrogen, the selenium, or by various bridging modes. In the absence of diffraction data, NMR spectroscopy may provide the most reliable information concerning the coordination and structure of these ligands. A review by Duddeck provides an overview of the 77Se NMR literature including the results of several solution NMR studies of organic selenocyanate compounds (2). Carbon-13 and nitrogen-14 or -15 NMR results for selenocyanates have been discussed in several reviews (3, 4). The coordination of metal atoms with several selenocyanate anions has been investigated by solution NMR (5, 6). An analogous study of the thiocyanate anion in copper(I) complexes was conducted using solid-state 13C
NMR (7). In addition to providing insight into the coordination mode of the cation in these complexes, this study showed that conclusions about coordination to the metal drawn from solution NMR studies cannot always be extended to solids.

With four NMR-active nuclei, $^{13}$C, $^{14}$N, $^{15}$N, and $^{77}$Se, much information may be gained from solid-state NMR studies of SeCN$^-$; it is important to understand the shielding tensor of the uncoordinated ligand. Towards this end, we present the preliminary results of a solid-state 13C NMR study of a related compound, potassium cyanate. The interpretation of the observed magnetic shielding tensors is aided by high-level ab initio calculations.

Selenocyanate anions are thought to be linear; the selenocyanate ion of a copper complex which had been reported as bent (8) has recently been shown to be linear (9). Linear systems are ideal for a study of nuclear magnetic shielding since, in the absence of intermolecular effects, the orientation of the axially symmetric CS tensor is known exactly and the unique component of the CS tensor, along the $C_z$ symmetry axis, is dependent only on the diamagnetic term of the shielding (vide infra). The relative simplicity of these systems allows one to identify the specific molecular orbitals (MOs) responsible for the paramagnetic shielding.

Although carbon and nitrogen shielding tensors are available for most functional groups, corresponding data for selenium are not as widespread (10). The first comprehensive experimental study of selenium CS tensors was that of Collins et al. (11). A surprising feature of the selenocyanate ligands is that the spins of the carbon and selenium CS tensors are much smaller than those of CSe$_2$ (12). With high-level ab initio calculations on SeCN$^-$ and CSe$_2$, the MOs responsible for the different magnetic shielding in these closely related compounds were identified.

**Background theory**

It is convenient to discuss the nuclear magnetic shielding ($\sigma$) of nuclei in linear molecules or ions using Ramsey’s theory (13). In this model, the magnetic shielding is expressed as the sum of diamagnetic ($\sigma^d$) and paramagnetic ($\sigma^p$) components (14):

$$\sigma = \sigma^d + \sigma^p$$

where

$$\sigma^d = \frac{\mu_0}{4\pi} \frac{e^2}{2m} \sum_{\alpha} \frac{1}{E_n - E_0} \langle 0 | \sum_k \frac{I_{\alpha k}}{r_k^2} | n \rangle \langle n | I_{\alpha k} | 0 \rangle$$

and

$$\sigma^p = H_0 \sum_{\alpha \beta} \sum_{\alpha \beta} \frac{1}{E_n - E_0} \langle 0 | \sum_k \frac{I_{\alpha k}}{r_k^2} | n \rangle \langle n | \sum_k \frac{I_{\beta k}}{r_k^2} | 0 \rangle$$

In the above equations, $\mu_0$ is the permeability of free space, $e$ and $m$ are the electron charge and rest mass, respectively, while $|0\rangle$ and $|n\rangle$ represent ground and excited electronic states of the molecule with electronic energy $E_0$ and $E_n$, respectively. The position vector for electron $k$ is defined by $r_k$, and $I_{\alpha k}$ is the angular momentum operator. Equations 2 and 3 describe the shielding in the directions of the principal components of the chemical shielding tensor and are valid only if the nucleus of interest is chosen as the gauge origin. Expressions for the off-diagonal elements of the chemical shielding tensor and for different gauge origins have been derived (14, 15).

The contribution to shielding from $\sigma^d$ (eq. [2]) is always positive, leading to increased shielding relative to the bare nucleus. Because $\sigma^d$ depends only on the ground electronic state of the molecule, it can be calculated accurately at relatively low levels of theory and hence is expected to be essentially invariant to basis set size or to the effects of electron correlation. Gierke and Flygare (16) have shown that $\sigma^d$ may be approximated if the molecular structure is known. For example, the shielding for nucleus A in the $x$-direction may be approximated by:

$$\sigma^d_{ax} = \sigma^d_{av} \text{(free atom)} + \frac{\mu_0}{4\pi} \frac{e^2}{2m} \sum_{\alpha \beta} \frac{Z_B}{r_{AB}^3} \left( y_{\alpha \beta}^2 + z_{\alpha \beta}^2 \right)$$

where $\sigma^d_{av} \text{(free atom)}$ is the shielding for the “free” atom. The summation is carried out over all other atoms in the molecule, $Z_B$ is the atomic number of the atom being summed, $y_{\alpha \beta}$ and $z_{\alpha \beta}$ are the Cartesian coordinates of the atoms which are a distance $r_{AB}$ from the origin (the site of the observed nucleus). The remaining tensor components may be approximated by cyclic permutations of eq. [4]. In linear molecules, the component of the chemical shielding tensor along the $C_z$ axis is labelled $\sigma_z$, while the two components perpendicular to this axis are labelled $\sigma_{x,y}$. Since $\sigma_z = \sigma_{x,y}$ for the nuclei of linear molecules, it follows from eq. [4] that:

$$\sigma_z = \sigma_{x,y} = \sigma_{av} \text{(free atom)}$$

The paramagnetic term (eq. [3]) is a second-order electronic property which depends on the mixing of ground and excited electronic states of the molecule. These states correspond approximately to the occupied and unoccupied MOs (17). The paramagnetic term is usually negative and is inversely proportional to the difference in the electronic energy of the orbitals undergoing mixing. Contributions to $\sigma^p$ arise from induced electron motion in the plane perpendicular to the direction of the applied magnetic field such that charge appears to rotate (17). This can be understood by considering the action of the angular momentum operator in eq. [3]. For example, consider $I_x p_x$; the operator $I_x$ rotates $p_x$ by 90° about the $z$-axis. Thus, there is an effective mixing between $p_x$ and $p_y$. Mixing of MOs can only occur between occupied and unoccupied MOs with magnetic-dipole allowed symmetry. This is shown graphically in Fig. 1.
Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and dis-

will be discussed in terms of chemical shielding. The experimental data are related to those calculated by ab initio meth-

It is convenient to discuss the NMR line shape of static powder samples in terms of the span, \( \Omega = \sigma_{33} - \sigma_{11} = \delta_{11} - \delta_{33} \), and the skew, \( \kappa = (\sigma_{11} - \sigma_{33})/\Omega = 3(\delta_{32} - \delta_{33})/\Omega \). With a few exceptions (24), \( \sigma_{ii} > \sigma_{g} \) and \( \kappa = +1.0 \) for linear molecules with perfect axial symmetry.

**Experimental**

Ammonium selenocyanate (25) and tetramethylammonium selenocyanate (26) were prepared according to literature methods. Potassium cyanate and potassium selenocyanate were purchased from Aldrich and used without further purification.

Natural abundance \(^{13}\text{C}\), \(^{15}\text{N}\), and \(^{77}\text{Se}\) NMR spectra were obtained on Bruker MSL-200 and AMX-400 NMR spectrometers (\( B_0 = 4.7 \) and 9.4 T, respectively). Samples were packed into 7 and 4 mm o.d. zirconium oxide rotors. Cross polarization (CP) and high-power proton decoupling were employed in acquiring all NMR spectra, except for KSeCN, where spectra were acquired after a single pulse. Unless otherwise noted, recycle delays were 5 s. Carbon chemical shifts were referenced to tetramethylsilane by setting the high-frequency isotropic peak of solid adamantane to 38.56 ppm (27). Nitrogen chemical shifts were referenced to NH\(_4\)(293 K) by setting the NMR peak of the ammonium ion in solid \(^{15}\text{NH}_4\text{NO}_3\) to +23.8 ppm. The chemical shift for CH\(_3\)NO\(_2\) (27). Nitrogen chemical shifts were referenced to NH\(_4\)(293 K) by setting the NMR peak of the ammonium ion in solid \(^{15}\text{NH}_4\text{NO}_3\) to +23.8 ppm. The chemical shift for CH\(_3\)NO\(_2\) to +23.8 ppm. The chemical shift for CH\(_3\)NO\(_2\) to +23.8 ppm. The chemical shift for CH\(_3\)NO\(_2\) to +23.8 ppm.

NMR spectra of MAS samples were analyzed by the method of Herzfeld and Berger (29) using the program HBA. Spectra of stationary samples were analyzed with the program WSOILDS, which incorporates the POWDER algorithm of Alderman et al. (30). Both programs were developed in this laboratory and run on IBM compatible microprocessors.

Ab initio calculations of the carbon, nitrogen, and selenium chemical shielding tensors were performed with the Gaussian 98 suite of programs\(^2\) mounted on an IBM RS/6000 computer. The chemical shielding tensors for all compounds were calculated at the Hartree–Fock (HF) level of theory using the gauge-independent atomic orbitals (GIAO) method (31) with the 6–311+G* basis set. The basis-set dependence of these results was determined by calculating the chemical shielding tensors for CSe\(_2\) and SeCN\(^-\) with basis sets\(^3\) ranging from 3–21G to \( cc-pVQZ \) (32). The effects of electron correlation

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on these two compounds were investigated by calculating the chemical shielding tensors at the second-order Møller–Plesset (MP2) level of theory (33). The geometries used in these calculations are from a high-level ab initio geometry optimization of SeCN– (34), a neutron diffraction study of NH$_4$SCN (35), a microwave study of SeCO (36), and an IR study of CSe$_2$ (37). To facilitate comparison, experimental chemical shifts ($\delta$) were converted to chemical shielding ($\sigma$) according to $\sigma_{\text{exp}} = \delta_{\text{ref}} - \delta_{\text{exp}}$. The carbon shielding in TMS ($\delta_{\text{TMS}}$, 300 K) was taken to be 188.1 ppm (20), that for nitrogen in NH$_3$ ($\delta_{\text{NH}_3}$, 293 K) was taken to be 264.5 ppm (21) and that for the selenium in Se(CH$_3$)$_2$ ($\delta_{\text{Se(CH}_3)_2}$) was taken to be 1769 ppm (22). The latter value is an approximate non-relativistic value. That is, in deriving the absolute shielding scale for selenium, it was assumed that $\sigma_{\text{free Se atom}} = 2998$ ppm (38).

### Results and discussion

Observed chemical shift and spin–spin coupling data determined from stationary and MAS powder samples of solid selenocyanate salts investigated in this study are collected in Table 1. Included for comparison are data obtained from a previous $^{13}$C and $^{15}$N NMR study of ammonium thiocyanate (39).

#### Carbon-13 NMR spectra

The $^{13}$C NMR spectrum of an MAS sample of solid ammonium selenocyanate is shown in Fig. 2. The spinning sidebands of the experimental spectrum have been added to the isotropic peak to produce the spectrum expected at the high-spinning limit. The asymmetric doublets arise because the carbon is directly bonded to the quadrupolar $^{14}$N nucleus ($I = 1$, natural abundance = 99.64%). Although the isotropic $^{13}$C chemical shift can be accurately determined from the spectrum of an MAS sample, it is more difficult to extract the principal components of the carbon chemical shift tensors from spinning sidebands because the presence of the dipolar interaction with $^{14}$N nuclei must be considered (40).

The $^{13}$C NMR spectrum of a stationary powder sample of NH$_4$SeCN is shown in Fig. 3. As well as being perturbed by anisotropic shielding, the $^{13}$C NMR line shape is modified by the $^{14}$N, $^{13}$C dipolar interaction. The splittings at $\delta$ and $\delta_i$ are $R_{DD}$ and $2R_{DD}$, respectively (41). The $^{14}$N, $^{13}$C direct dipolar coupling constant ($R_{DD}$) is defined as

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**Table 1. Experimental carbon, nitrogen, and selenium chemical shift tensors for some solid cyanate salts.$^a$**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleus</th>
<th>$\delta_{\text{iso}}$</th>
<th>$\delta_{11}$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
<th>$\Omega$</th>
<th>$\kappa$</th>
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<tr>
<td>KOCN</td>
<td>$^{13}$C</td>
<td>130.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NH$_4$SCN$^e$</td>
<td>$^{13}$C</td>
<td>133.1</td>
<td>240</td>
<td>240</td>
<td>-81</td>
<td>321</td>
<td>1.00</td>
</tr>
<tr>
<td>NH$_4$SeCN</td>
<td>$^{13}$C</td>
<td>125.7$^f$</td>
<td>228</td>
<td>226</td>
<td>-77</td>
<td>305</td>
<td>0.99</td>
</tr>
<tr>
<td>NMe$_2$SeCN</td>
<td>$^{13}$C</td>
<td>119.1$^e$</td>
<td>215</td>
<td>212</td>
<td>-70</td>
<td>285</td>
<td>0.98</td>
</tr>
<tr>
<td>NH$_4$SCN$^e$</td>
<td>$^{15}$N</td>
<td>211.0</td>
<td>349</td>
<td>349</td>
<td>-66</td>
<td>415</td>
<td>1.00</td>
</tr>
<tr>
<td>NMe$_2$SeCN</td>
<td>$^{15}$N</td>
<td>255$^h$</td>
<td>401</td>
<td>401</td>
<td>-38</td>
<td>439</td>
<td>1.00</td>
</tr>
<tr>
<td>KSeCN</td>
<td>$^{77}$Se</td>
<td>-282.6$^i$</td>
<td>25</td>
<td>-23</td>
<td>-849</td>
<td>874</td>
<td>0.89</td>
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<tr>
<td>NH$_4$SeCN</td>
<td>$^{77}$Se</td>
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<td>26</td>
<td>-15</td>
<td>-778</td>
<td>804</td>
<td>0.9</td>
</tr>
<tr>
<td>NMe$_2$SeCN</td>
<td>$^{77}$Se</td>
<td>-299.4</td>
<td>-40</td>
<td>-40</td>
<td>-814</td>
<td>854</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^a$All chemical shift values are in ppm. Uncertainties are estimated to be less than 0.5 ppm for $\delta_{\text{iso}}$; those of the individual components are estimated to be on the order of 2–3% of the total span of the tensor.

$^b$$\delta_{\text{iso}}$ may not be exactly equal to the average of the individual tensor components since the values of the former were obtained from the isotropic peak of an MAS sample.

$^c$Span $\Omega = \delta_{11} - \delta_{33}$.

$^d$Skew $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.

$^e$Ref. 39.

$^f$From MAS spectra: $\chi(14N) = -2.6 \pm 0.3$ MHz; $^1J(14N, 13C) = 15 \pm 3$ Hz.

$^g$From MAS spectra: $\chi(14N) = -2.6 \pm 0.3$ MHz; $^1J(77Se, 13C) = 260 \pm 30$ Hz; methyl groups: $\delta_{\text{iso}} = 56.1$ ppm.

$^h$Tetramethylammonium: $\delta_{\text{iso}} = 47.3$ ppm.

$^i$Surface solvated: $-297.5$ ppm.

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Fig. 3. Experimental (top) and calculated (bottom) $^{13}$C NMR spectra of a stationary powder sample of NH$_4$SeCN at 4.7 T; 20549 transients were acquired. The splitting of the parallel and perpendicular components arise from the dipolar interaction with $^{14}$N.

\[ R_{DD} = \frac{\mu_0 h}{4\pi 2\pi} \gamma^{(13)C} \gamma^{(14)N} (\langle r_{CN}^3 \rangle) \]

where $\langle r_{CN} \rangle$ is the motionally averaged C—N bond length. The splittings due to $R_{DD}$ for crystallites oriented such that $\delta$ is parallel to $B_0$ are clearly seen at high frequency in Fig. 3; although it is not as well resolved, the effect of $R_{DD}$ on the spectra of crystallites oriented such that $\delta$ is parallel to $B_0$ are also observed at low frequency. From the fit of the NMR spectrum of a stationary powder sample, $R_{DD} = 1250 \pm 20$ Hz, corresponding to $r_{CN} = 1.205 \pm 0.007$ Å. This is significantly longer than the value of $r_{CN}$ determined from an early X-ray diffraction study of KSeCN (42), 1.117 Å, but is in agreement with the results of an ab initio study (34). In principle, the quadrupolar interaction with $^{14}$N should also be considered in the fit, but it has been shown (39–41) that this interaction has only minor effects on the positions of the critical frequencies in spectra of stationary samples acquired at the external magnetic fields used in this study. From the dipolar coupling, and assuming that the largest component of the $^{14}$N EFG tensor is along the C,N bond with an asymmetry of zero, analysis of the spectrum of an MAS sample (Fig. 2) yields $C_Q^{(14)N} = -2.6 \pm 0.3$ MHz. This value is in excellent agreement with the value reported for the NCS$^-$ anion, $|C_Q^{(14)N}| = 2.3$ MHz (43).

The $^{13}$C NMR spectrum of an MAS sample of NMe$_4$SeCN (not shown) contains some smaller peaks, attributed to $^{13}$C nuclei bonded to the $^{77}$Se nucleus (natural abundance = 7.58%, $I = 1/2$). The value of $J_{14N}^{(77)Se}$ is estimated to be $260 \pm 30$ Hz. These satellite peaks are not resolved in the spectrum of NH$_4$SeCN (Fig. 2), a consequence of the broader lines. The line shape of the asymmetric doublet in the $^{13}$C NMR spectrum of an MAS sample of NMe$_4$SeCN cannot be simulated as well as that of NH$_4$SeCN (Fig. 2); this may be caused by the onset of self-decoupling of the $^{14}$N (44). The $^{13}$C NMR spectrum of a stationary sample of NMe$_4$SeCN is dominated by the contribution from the four methyl groups, but the splittings due to $R_{DD}^{(14N, 13C)}$ in the high-frequency region of the spectrum are well resolved. With these features and with the isotropic chemical shift obtained from the spectra of MAS samples, analysis of the spectrum is possible, yielding the principal components of the carbon CS tensors summarized in Table 1. From the $^{14}$N, $^{13}$C dipolar splittings observed in the high-frequency region, $R_{DD} = 1180 \pm 30$ Hz, corresponding to $r_{CN} = 1.23 \pm 0.01$ Å. This value is slightly longer than the value of 1.205 Å obtained for NH$_4$SeCN. While the difference is only slightly greater than the experimental error, the longer value obtained for NMe$_4$SeCN is probably a consequence of greater librational motion of the selenocyanate anion of the latter salt. Note that motion of the N—C bond will result in partial averaging of $R_{DD}^{(14N, 13C)}$ and an apparent lengthening of $r_{CN}$.

For the $^{13}$C MAS NMR spectrum of KOCN, recycle delays in excess of one hour were used, but the signal-to-noise ratio was still very low, precluding any analysis for the compound at natural abundance. Hence only the isotropic chemical shift was determined. The value of $\delta_{iso}$, 130.2 ppm, is within experimental error of the value determined for KOCN dissolved in D$_2$O, 129.7 ppm (45).

**Nitrogen-15 NMR spectra**

The $^{15}$N MAS NMR spectrum of NMe$_4$SeCN (Fig. 4) consists of an intense peak at 47.3 ppm, due to NMe$_4^+$, and a weaker, spinning rate invariant peak at 255.0 ppm due to SeCN$^-$. The spinning sidebands of the latter peak were analyzed by the Herzfeld–Berger method to obtain the span of the nitrogen CS tensor, $\Omega = 439 \pm 10$ ppm. This value is within experimental error of the value obtained for NH$_4$SCN, 415 $\pm$ 15 ppm (39). The average nitrogen shielding for SeCN$^-$ in solid NMe$_4$SeCN is 44 ppm less than the value for SCN$^-$ of solid NH$_4$SCN. In aqueous solutions, the shielding of the nitrogen nuclei of SeCN$^-$ dissolved in D$_2$O (46) decreases by 30 ppm compared to that of the nitrogen nuclei of SCN$^-$ dissolved in H$_2$O (47).

**Selenium-77 NMR spectra**

Selenium-77 NMR spectra of MAS samples of NMe$_4$SeCN are shown in Fig. 5. The isotropic $^{77}$Se chemical shift is comparable to that of KSeCN measured in solution (6). The experimental spectra of the selenocyanates were simulated via a non-linear least-square implementation of the method of Herzfeld and Berger (29); the resulting data are summarized in Table 1. These simulations indicate large
anisotropies in the $^{77}$Se CS tensors, making the observation of spectra of stationary powder samples difficult. Non-axially symmetric CS tensors are not precluded by the linear SeCN$^-$ anion, since the positions of the cations in the crystal lattice may affect the shielding. For example, the crystal structure of KSeCN shows that the potassium atoms are not arranged symmetrically about the selenium (42). Chemical shift tensors determined from the analysis of spinning sideband intensities in spectra of slow-spinning MAS samples are subject to significant errors if the tensor is approximately axially symmetric (48). In light of the above and considering the errors associated with the experimental data, the values quoted in Table 1 do not conclusively determine the symmetry of the selenium CS tensor. In cases where cross-polarization was used to obtain the spectra, further artifacts could be introduced in the spinning sideband intensities from anisotropy in the cross-relaxation stage of the experiment (49). For example, clear differences were observed for NMe$_4$SeCN in regular CP experiments (Fig. 5, top) and experiments employing variable-amplitude cross-polarization (50) (see Fig. 5, middle). In the spectrum obtained with regular CP, the intensities of the spinning sidebands in the neighbourhood of the isotropic peak (indicated with an asterisk) are much stronger relative to the higher-order spinning sidebands about the position of $\delta_2$ and $\delta_3$, than are those obtained with VACP. The latter spectrum agrees much better with the calculated spectrum. This effect is probably due to the offset dependence of the Hartmann–Hahn matching condition (50). In spite of the possible errors and artifacts, it is clear that the selenium CS tensors do not deviate significantly from axial symmetry (the maximum deviation in $\kappa$ is estimated to be 10%). In the ensuing discussion, we will assume that the carbon, nitrogen, and selenium tensors are axially symmetric, consistent with our experimental data.

**Ab initio calculations**

*Carbon and nitrogen shielding tensors for SeCN$^-$ and related molecules*

The calculated carbon and nitrogen chemical shielding tensor components are listed in Tables 2 and 3, respectively.

For comparison, the chemical shift values of the experimental data have been converted to chemical shielding (see experimental section). While the observed spans for the carbon CS tensors of SCN$^-$ and SeCN$^-$ are similar (321 to 285 ppm), the span is significantly greater for SeCO (399 ppm) and CSe$_2$ (506 ppm). These experimental trends are reproduced by the highest level ab initio computations that we can presently apply to all three molecules, HF/6–311+G*. Likewise, ab initio calculations correctly predict a larger span for the nitrogen nucleus of the SeCN$^-$ anion than for that of the SCN$^-$ anion.

The calculated isotropic carbon chemical shielding for SeCN$^-$ plotted against basis set size is shown in Fig. 6 (top). This figure indicates that the calculated isotropic shielding is converging to a value which is approximately 15 ppm less than the experimental value. Similar results were obtained for the calculated shielding of the nitrogen of SeCN$^-$ (Table 3) and the carbon of CSe$_2$ (Table 2).

The calculated carbon chemical shielding tensor components parallel to the bond are invariant to basis set size or to
the effects of electron correlation, reflecting the fact that there is no paramagnetic contribution to this component of the chemical shielding tensor. However, the experimental values of \( \sigma_i \) are approximately 30 ppm less than the calculated values, perhaps a consequence of intermolecular effects. Calculations on a larger portion of the crystal lattice would be instructive but are not practical at this time given the computational requirements. In addition to intermolecular effects, vibrational effects are a factor, although these are expected to be fairly small for carbon and nitrogen (51). For example, Lounila et al. (52) calculated a vibrational correction of \( \sigma_{\text{iso}} = -2.4 \) ppm for the carbon of CSe₂. For molecules containing large atoms, relativistic effects (53) may become significant (\textit{vide infra}), even for the calculated shielding of neighbouring nuclei (54).

The chemical shielding tensors for the carbon and nitrogen nuclei of SeCN⁻ as well as that for the carbon of CSe₂ were calculated at the MP2 level (Tables 2 and 3). In all cases, the isotropic shielding values calculated at the MP2 level are significantly greater than the corresponding HF values, and are generally greater than the experimental values, reflecting the fact that the effects of electron correlation are not considered in HF calculations but are often overestimated by MP2 (55). A particularly large electron correlation effect is expected for the carbon of CSe₂ because of its multiple bonding (56). The large deshielding (57) and span (12) reported for the carbon of CSe₂ are in agreement with our calculations, as well as with those of an earlier computational study (52).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>( \sigma_{\text{iso}} )</th>
<th>( \sigma_i )</th>
<th>( \sigma_j )</th>
<th>( \Omega )</th>
</tr>
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<tbody>
<tr>
<td>OCN⁻</td>
<td>HF/6–311+G*</td>
<td>223.4</td>
<td>162</td>
<td>347</td>
<td>185</td>
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<tr>
<td>NH₄SCN</td>
<td>Exp</td>
<td>53.5</td>
<td>-85</td>
<td>331</td>
<td>416</td>
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<tr>
<td>SCN⁻</td>
<td>HF/6–311+G*</td>
<td>19.3</td>
<td>-144</td>
<td>346</td>
<td>490</td>
</tr>
<tr>
<td>NH₄SeCN</td>
<td>Exp</td>
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<td>-137</td>
<td>303</td>
<td>440</td>
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<tr>
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<td>-221</td>
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<td>566</td>
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<tr>
<td>CSe₂</td>
<td>MP2/6–311+G*</td>
<td>32.0</td>
<td>-125</td>
<td>346</td>
<td>471</td>
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</table>

See the footnotes to Table 1 for details on experimental data.

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From reference 39.
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Table 4. Selenium chemical shielding tensors for CSe$_2$, SeCO, and for some selenocyanate salts.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>$\sigma_{iso}$</th>
<th>$\sigma_i$</th>
<th>$\sigma_z$</th>
<th>$\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$SeCN</td>
<td>Exp</td>
<td>2025</td>
<td>1764</td>
<td>2547</td>
<td>783</td>
</tr>
<tr>
<td>NMe$_2$SeCN</td>
<td>Exp</td>
<td>2067</td>
<td>1809</td>
<td>2583</td>
<td>774</td>
</tr>
<tr>
<td>SeCN$^-$</td>
<td>HF/6–311+G*</td>
<td>2343</td>
<td>2009</td>
<td>3011</td>
<td>1002</td>
</tr>
<tr>
<td></td>
<td>MP2/6–311+G*</td>
<td>2443</td>
<td>2160</td>
<td>3010</td>
<td>850</td>
</tr>
<tr>
<td>SeCO</td>
<td>Exp$^b$</td>
<td>2347</td>
<td>2018</td>
<td>3006</td>
<td>988</td>
</tr>
<tr>
<td></td>
<td>Exp$^c$</td>
<td>2216</td>
<td>1887</td>
<td>2875</td>
<td>988</td>
</tr>
<tr>
<td></td>
<td>HF/6–311+G*</td>
<td>2327</td>
<td>1986</td>
<td>3008</td>
<td>1022</td>
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<tr>
<td>CSe$_2$</td>
<td>Exp$^d$</td>
<td>1438</td>
<td>701$^c$</td>
<td>2911</td>
<td>2210</td>
</tr>
<tr>
<td></td>
<td>HF/6–311+G*</td>
<td>1547</td>
<td>816</td>
<td>3009</td>
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<tr>
<td></td>
<td>MP2/6–311+G*</td>
<td>1816</td>
<td>1220</td>
<td>3007</td>
<td>1787</td>
</tr>
</tbody>
</table>

$^a$See the footnotes to Table 1 for details on the experimental data.
$^b$From reference 56(a), Vol. 25, p. 48.
$^c$The isotropic value is from a solution-state study (reference 57). The chemical shielding tensor components were calculated from this value and the experimental value of $\Omega$ (reference 56a, Vol. 25, p. 48) according to $\sigma = \sigma_{iso} - (1/3)\Omega$ and $\sigma_1 = \sigma_{iso} + (2/3)\Omega$.
$^d$Components of the chemical shielding tensor are calculated from the experimental values of $\sigma_{iso}$ (reference 57) and $\Omega$ (reference 12); see footnote c above.

A value of $\sigma_1 = 1068$ ppm, determined from a solid state NMR study at ~90°C, has also been reported (reference 63).

**Selenium chemical shielding tensors for SeCN$^-$ and related molecules**

The existence of an absolute shielding scale for selenium (22) combined with experimental data on simple molecules has prompted several theoretical groups to investigate selenium chemical shielding tensors. For example, the selenium shielding for CSe$_2$, has been calculated at the CHF (12), HF/IGLO (55), MP2/GIAO (55, 58), CCD (58), and DFT (59) levels of theory. Recently Lounila et al. reported the results of a detailed computational study of this molecule, which included DFT and CAS calculations (52). Such calculations are challenging, a consequence of the large chemical shielding range of selenium (60) and of the fact that selenium shielding is subject to relativistic effects (53). The progress of selenium shielding calculations has been reviewed recently (56).

The calculated selenium chemical shielding tensors are listed in Table 4. The calculated results are more dependent on basis set size than are those of carbon and nitrogen (Fig. 6), reflecting the greater chemical shift range of selenium compared to those of carbon (3) or nitrogen (61). Figure 6 shows that the calculated isotropic selenium chemical shielding for both SeCN$^-$ and CSe$_2$ are converging to values which are significantly shielded compared to experimental values. Ab initio calculations are performed on isolated molecules, which may result in significant discrepancies between calculated and experimental results, since selenium is known to be susceptible to medium effects. For example, the isotropic shielding for gaseous H$_2$Se is 126.6 ppm greater than that for the same molecule in its liquid phase, which in turn is shielded by 11.4 ppm compared to its value in the solid (62). For CSe$_2$, the gas-phase shielding is 74.7 ppm greater than that for the same molecule in its liquid phase (63).

An electron correlation effect of 100 ppm is predicted for SeCN$^-$, based on the results of calculations at the MP2 level. The effect is more significant for CSe$_2$: $\delta_{iso}$ calculated at the MP2 level is 269 ppm greater than the value calculated at the HF level (Table 4). Chesnut has noted that isotropic chemical shielding constants calculated at various orders of Møller–Plesset theory converge such that the infinite-order Møller–Plesset calculated shielding may be approximated by (64):

$$\sigma_{iso} = \frac{1}{3} \sigma_{HF} + \frac{2}{3} \sigma_{MP2}$$

Substituting our calculated values for CSe$_2$ (Table 4), we obtain a value of $\sigma_{iso} = 1726$ ppm, close to the value calculated with the CAS method, 1755.2 ppm (52).

In the absence of intermolecular effects $\sigma_1 = \sigma_{av}^d$ (free atom) (eq. [5]). Our calculated values of $\sigma_1$ (Table 4) are comparable to the non-relativistic value of $\sigma_{av}^d$ (free Se), 2998 ppm (38), reflecting the fact that first-order molecular properties can usually be calculated accurately. Experimental values of $\sigma_1$ for the selenocyanate salts are significantly smaller than the calculated values. This difference is attributed to intermolecular effects. A paramagnetic contribution to $\sigma_1$ in the selenocyanate salts arises from the fact that, with the neighbouring nuclei such as potassium in KSeCN, the selenium atoms are not in a perfectly linear environment and hence the assumption that $\sigma_1^s = 0$ is no longer strictly valid.

**A comparison of the selenium chemical shielding tensors for SeCN$^-$ and CSe$_2$**

One might expect the selenium chemical shielding tensors for Se=C=N$^-$ and Se=C=Se to be similar, but this is not the case (Table 4). Particularly surprising is the large difference in the spans — that of CSe$_2$ is almost three times greater than the spans of the selenocyanates. This is remarkable given that selenium is directly bonded to carbon in both cases. The difference cannot be attributed to the charge on SeCN$^-$, since the span of SeCO (65) is comparable to those of the selenocyanate salts. These large differences are reproduced qualitatively by the calculations. In particular, we note that agreement between the experimental and calculated spans of SeCO is very good. Since the experimental span of SeCO was determined from spin-rotation data (65), it is that of an isolated molecule and is thus ideal for comparison with calculated values. To a first approximation, the span of the chemical shielding tensor is invariant to the effects of

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relativity (52), and thus may be the best gauge of the accuracy of non-relativistic calculations.

The large difference in the spans of the selenium chemical shielding tensors for CSe\(_2\) and SeCN\(^-\) is a consequence of a large difference in their respective \(s_z\) values because \(s_z\) does not vary greatly amongst linear molecules. The contribution to the span from \(s_d\) can be estimated from eq. [4]. For SeCN\(^-\), \(s_{z||d} = 2998\) ppm and \(s_{z\perp d} = 3078\) ppm, giving a span in \(s_d\) of 80 ppm. Similarly, a span of 151 ppm is predicted for \(s_d\) of CSe\(_2\). These numbers are much smaller and opposite in sign to those observed for \(s_p\). Thus, to understand the large difference between the spans of CSe\(_2\) and SeCN\(^-\), one must consider \(s_z\).

One of the factors contributing to \(s_z\) is the number of MOs undergoing mixing, since eq. [3] is a summation. Figure 7 shows the energies for the highest occupied and lowest unoccupied MOs of SeCN\(^-\) and CSe\(_2\), calculated at the HF level using the cc-pVQZ basis set. Although the energy difference between the highest occupied and lowest unoccupied MOs is comparable for the two compounds, there are more low-lying unoccupied MOs for CSe\(_2\) than for SeCN\(^-\). However, we must also consider the symmetry of these MOs, since mixing will only occur between MOs with magnetic-dipole allowed symmetry. These are indicated with arrows in Fig. 7.

\[\text{MO 33 (or degenerate MO 38 or 39) for CSe}_2\text{, illustrating the magnetic-dipole allowed } \sigma_u \rightarrow \pi_u^* \text{ mixing for an applied magnetic field perpendicular to the page.}\]

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Figure 8 illustrates that MO 33 with \(\sigma_u\) symmetry can mix with degenerate MOs 38 or 39, with \(\pi_u^*\) symmetry. Because of the favourable symmetry, these MOs are expected to be a major factor in the deshielding observed in the direction perpendicular to the \(C_u\) axis of CSe\(_2\). In Fig. 9, MO 36 (or degenerate MO 37) of CSe\(_2\), with \(\pi_u\) symmetry, is shown along with MO 40, which has \(\sigma_u\) symmetry. Figures 8 and 9 illustrate the importance of symmetry in considering contributions to \(s_p\). Although MOs 36 and 37 are only separated by 0.46 hartrees from MO 40, compared to 0.57 hartrees separating MO 33 from MOs 38 and 39, the shape of the latter is much more favourable for mixing.

Figure 10 demonstrates why the selenium chemical shielding tensor for SeCN\(^-\) has a large span which nevertheless is much smaller than that for CSe\(_2\). The illustrated MOs, occupied \(\pi MO 23\) (or degenerate MO 24) and unoccupied \(\sigma_u MO 25\), have a relatively small difference in energy, 0.42 hartrees, but the symmetry of the MOs clearly is not as favourable for mixing here. Hence, these MOs are expected to be a significant factor in the deshielding perpendicular to the \(C_u\) axis of the anion, but the lower symmetry makes mixing much less favourable than in the case of CSe\(_2\).

In summary, the smaller span of the chemical shielding tensor of SeCN\(^-\) compared to that of CSe\(_2\) may be attributed to two factors. The selenocyanate anion has fewer low-lying unoccupied MOs which can mix with occupied MOs and contribute to \(s_p\), and the mixing of most of those MOs separated by a small energy difference are not magnetic-dipole allowed. The latter may be attributed to the lower symmetry
of SeCN\(^-\) (\(C_{\infty v}\)), compared to that of CSe\(_2\) (\(D_{2h}\)). This conclusion is supported by the observation that the chemical shielding tensor for SeCO, which also has \(C_{\infty v}\) symmetry, is comparable to that of SeCN\(^-\). Finally we note that, although we have not explicitly discussed the spans of the carbon shielding tensors for SeCN\(^-\) and CSe\(_2\) (Table 2), the different spans of these shielding tensors may also be explained as above. For example, the mixing of MOs 33 with MOs 38 and 39 of CSe\(_2\), which contributes to \(\sigma^p\) of the selenium chemical shielding tensor, will also be an important factor in the paramagnetic component of the carbon shielding perpendicular to the \(C_{\infty v}\) symmetry axis.

Conclusions

The carbon, nitrogen, and selenium chemical shift tensors for several solid selenocyanate salts have been characterized by NMR. Within experimental error, the chemical shift tensors are axially symmetric. A notable result of this study is the observation that the spans of the carbon and selenium CS tensors for SeCN\(^-\) are much smaller than those for CSe\(_2\), a consequence of the smaller paramagnetic term in the shielding perpendicular to the \(C_{\infty}\) axis of SeCN\(^-\) compared to that of CSe\(_2\). High-level ab initio calculations show that the smaller paramagnetic term results from the lower symmetry of the MOs of SeCN\(^-\) and from the fact that there are fewer low-lying unoccupied MOs for SeCN\(^-\) compared to CSe\(_2\). The shielding parallel to the \(C_{\infty}\) axis of SeCN\(^-\) is less than expected for linear molecules, suggesting that this component is sensitive to intermolecular effects. This work has shown that multinuclear magnetic resonance studies of solids can offer much information about solid selenocyanate salts; it is hoped that this study will encourage further studies of these and related ligands.

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References


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