

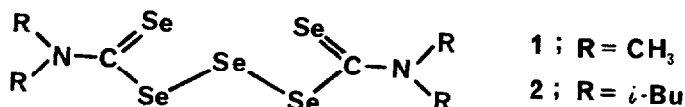
STRUCTURE AND INTRAMOLECULAR DYNAMICS OF
BIS(DIISOBUTYLSELENOCARBAMOYL) TRISELENIDE
AS IDENTIFIED IN SOLUTION BY THE ^{77}Se -NMR SPECTROSCOPY

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Summary: A novel intramolecular four co-ordinated structure of the title compound was identified in the solution at low temperature, which was found to undergo the rapid interconversion to the chain structure on raising the temperature.

The N-methyl protons in bis(dimethylselenocarbamoyl) triselenide (1) show the magnetic equivalence in the ^1H - and ^{13}C -NMR spectra at room temperature.¹ This is in sharp contrast to other dimethyldiselenocarbamate derivatives, exhibiting non-equivalent N-methyl signals due to the restricted rotation about the N-CSe bond.^{1,2} We have now revealed the exact nature of such an unusual behaviour of bis(selenocarbamoyl) triselenides, based on the ^{77}Se -NMR spectrum and its temperature variation, by using N-isobutyl derivative (2)³ to overcome the solubility problem encountered in (1).



A typical ^{77}Se -NMR spectrum of (2) at room temperature is given in Fig. 1b. Only two broad resonances at $\delta = 655.1$ and 251.2 ppm (referenced to the signal position of MeSeMe in CDCl_3) are observed for (2).⁴

On lowering the temperature the peaks due to (2) sharpen and down at -50°C change to two sharp signals with the relative integrated area of 4:1 and each with clearly resolved satellite signals about the central peaks (Fig. 1c). The intensity of the outer satellite peaks surrounding the mother signal of the higher-field (Fig. 1d) is 22.1% relative to the central peak, which corresponds

up to four times of the relative intensity observed in the satellite peaks of lower-field signal (5.4%).⁵ Such an AB satellite pattern and the intensity ratio, especially the satellite intensities, indicate that one ⁷⁷Se nucleus is coupled with four equivalent selenium nuclei. Thus the structure of (2) at low temperature is uniquely defined as the intramolecular four co-ordinated structure (3).

The X-ray structure of a compound of the selenocarbamoyl triselenide family has been reported to be a trapezoid planar four co-ordinated complex, in which two of the center atoms to the ligand bonds are intramolecular and the other two are weak intramolecular bonds.⁶ However, the present results show that four ligands bonds are all equivalent in the solution at low temperature. One might suspect a possibility of the rapid interconversion between two trapezoid structures, which could also give rise to the four equivalent selenium atoms on the NMR time scale. However, in such a case, the intensity of the satellite

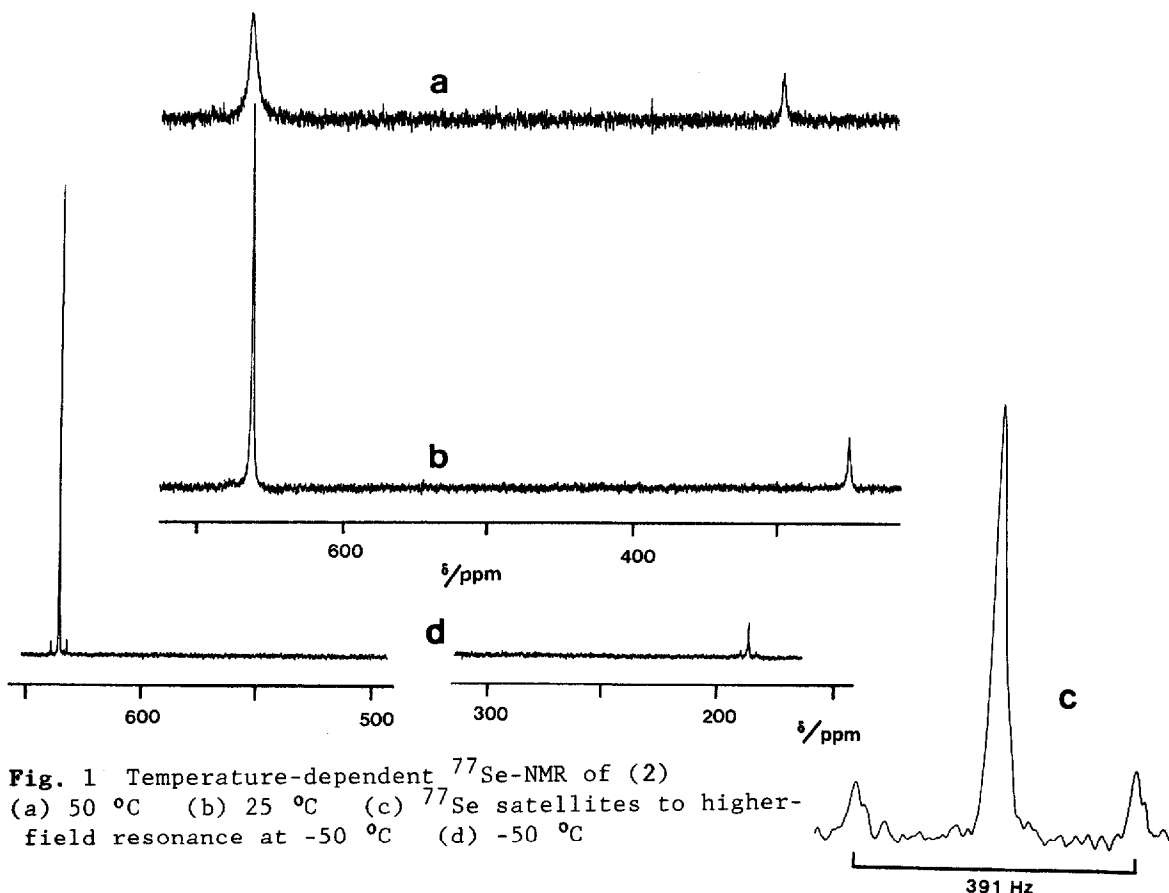


Fig. 1 Temperature-dependent ⁷⁷Se-NMR of (2)
 (a) 50 °C (b) 25 °C (c) ⁷⁷Se satellites to higher-field resonance at -50 °C (d) -50 °C

peak should be 14 % at most (twice of the natural abundance), because at any instant the central selenium atom bounds two other selenium atoms and if the interconversion is rapid, the satellite signals should disappear.

The central selenium atom resonates remarkably high field, indicating this selenium atom is involved as negatively charged valency. It is reasonable to assume that the contribution of the resonance form (3A) is important, in which the lone pair electrons in the two selenocarbonyl groups are donated to the central selenium atom in the triselenide moiety to develop the negative charge in the central selenium.⁷ The magnitude of the Se-Se coupling constant (391 Hz) is the largest one-bond Se-Se coupling so far observed,⁸ indicating the considerable contribution of another resonance form (3B) with formal Se=Se double bonds.

The temperature dependent ⁷⁷Se NMR spectra of (2) clearly indicate a dynamic process involved in the selenium atoms, as the signals show line broadening as the temperature is increased from -50 °C to 50 °C. On these temperature change the chemical shifts of the central selenium atom dramatically shifts to lower field as shown in Fig. 2. These observation is most reasonably explained in terms of a rapid interconversion between the co-ordinated structure (3) and the triselenide chain structure (2) with increasing temperature. Since

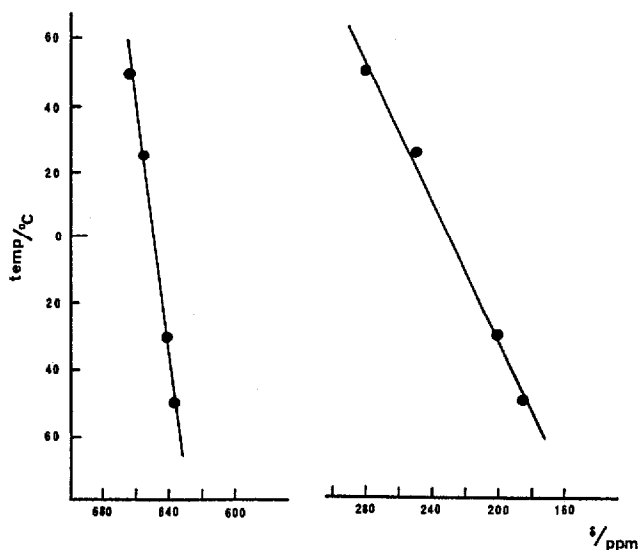
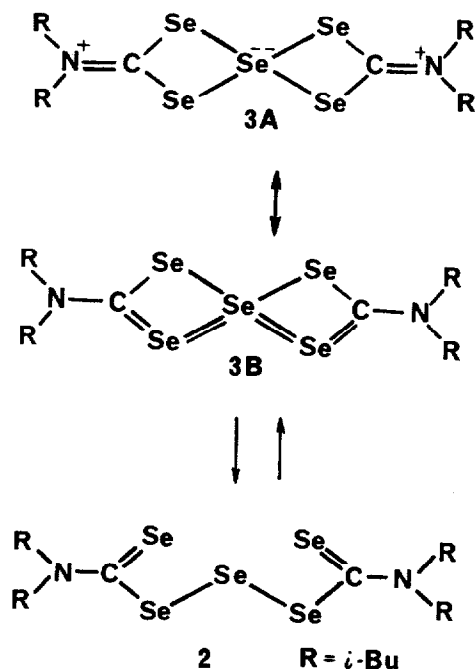


Fig. 2 Temperature dependence of ⁷⁷Se chemical shifts of (2)



the chemical shifts of the central selenium atom in (2) should be much more lower field than that of the central selenium atom in (3), the increased population of the chain structure at high temperature would bring about the down field shift of the resonance of the central selenium atom.

The ^{13}C -NMR spectra have also supported the four co-ordinated structure of (2) at low temperature. At $-50\text{ }^\circ\text{C}$ the Se-C=Se carbon exhibited only one set of satellite signal ($J=185\text{ Hz}$). When the ^{13}C -NMR spectra of methyl dimethyldiselenocarbamate have been measured for comparison, the Se-C=Se carbon showed two sets of satellite signals, one due to the C=Se coupling ($J=232\text{ Hz}$) and another to the C-Se coupling ($J=147\text{ Hz}$). These observations are in consistent with the results obtained from the ^{77}Se -NMR spectra.

References and Notes

1. K. Kobayashi, H. Tukada, K. Kikuchi, and I. Ikemoto, *Bull. Chem. Soc. Jpn.*, **59**, 1741 (1986).
2. K. A. Jensen and J. Sandstrom, *Acta Chem. Scand.*, **23**, 1911 (1969); G. Schwenker and H. Rosswag, *Tetrahedron Lett.*, **1967**, 4237.
3. L. Henriksen, *Synthesis*, **1982**, 771.
4. There appear two other sharp resonances at $\delta=852.3$ and 719.8 ppm . These are assigned to bis(diisobutylselenocarbamoyl) diselenide, which might be formed by decomposition of (2).
5. The selenium nuclei in (2) are still under a dynamic process which is not frozen at this temperature. Therefore, 5.4% could be reasonably regarded as the natural abundance of ^{77}Se nuclei (7.6%).
6. S. Esperas, S. Husebye, and A. Rolandsen, *Acta Chem. Scand., Ser. A*, **29**, 608 (1975); R. O. Gould, C. L. Jones, W. J. Savage, and T. A. Stephenson, *J. Chem. Soc., Dalton*, **1976**, 908.
7. The central selenium atom of (3A) is in the oxidation state +2. A similar situation of the selenium valency is seen in halogenoselenates (II). The X-ray structure of the halogenoselenate (II) salt has been reported to involve a square planar anion SeCl_4^{2-} : B. Krebs, E. Luhrs, L. Stork, and R. Willmer, *Acta. Cryst.*, **A43**, C145 (1987).
8. I. Johansen and H. Eggert, *J. Am. Chem. Soc.*, **106**, 1240 (1984); I. Johansen, L. Henriksen, and H. Eggert, *J. Org. Chem.*, **51**, 1657 (1986); H. Eggert, O. Nielsen, and L. Henriksen, *J. Am. Chem. Soc.*, **108**, 1725 (1986); M. N. Carnell, F. Grein, M. Murchie, J. Passmore, and C-M. Wong, *J. Chem. Soc., Chem. Commun.*, **1986**, 225; I. Johansen, H. Eggert, S. Gronowitz, and A.-B. Hornfeldt, *Chem. Scripta*, **27**, 359 (1987).

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