reagents with **3** are shown to provide further evidence in support of this comparison.[31]

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Registry No. **1a**, 82112-95-6; **1b**, 82112-98-9; **1c**, 67507-30-6; **1d**, 83311-96-0; **2a**, 82112-93-4; **2b**, 82112-96-7; **2c**, 67507-09-9; **2d**, 82112-97-8; **2e**, 67507-15-7; **2f**, 67507-13-5; **3**, 83311-98-2; Li(C_6H_3-($CH_2NMe_2)_2$-*o,o'*), 66479-07-0; *o,o'*-($Me_2NCH_2)_2C_6H_3Br$, 66479-06-9; $PdBr_2$(c-1,5-C_8H_{12}), 12145-47-0; *cis*-[$PtCl_2(SEt_2)_2$], 15442-57-6.

Supplementary Material Available: Listings of observed and calculated structure factors for $C_{13}H_{22}IN_2PtBF_4$ (**3**) and positional and thermal parameters, bond distances, and bond angles for **3** (Table II) and an ORTEP drawing giving a stereoview of **3** (Figure 3) (29 pages). Ordering information is given on any current masthead page.

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NMR Spectroscopic Studies on Chalcogen Compounds. 4.[1] Carbon-13 Isotope Effect on Selenium-77 and Tellurium-125 Nuclear Shielding and Its Correlation with C–Se Bond Distances. Tellurium-123 Isotope Effect on Tellurium-125 Nuclear Shielding

Willy Gombler

Contribution from the Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, D-4630 Bochum, Germany. *Received February 10, 1982*

Abstract: A one-bond isotope effect of ^{13}C on the nuclear shielding of ^{77}Se and ^{125}Te was observed for the first time. Thirty values for Se(II) and Se(IV) compounds containing sp^3-, sp^2-, and sp-hybridized carbon were measured, and a wide range of low frequency shifts was found between −0.012 and −1.099 ppm. A correlation was established between the isotope shift and the C–Se bond distance for CF_3- and CH_3-substituted selenium compounds. The isotope shift of the linear molecules SeCO, SeCS, and SeCSe is inversely dependent on the force constant of the C=Se bond. This is attributed to different vibrational amplitudes. The CSe bond order plays an important role for the isotope shift and appreciable substituent effects were observed. Five Te(II) and Te(IV) compounds were studied. The isotope shifts are larger than for the corresponding Se compounds, and the results can be qualitatively interpreted in analogy to those found for the selenium compounds. The isotope shift can be temperature dependent; this was shown, for example, on liquid samples of CF_3SeCN and SeCO. This behavior is explained by a substantial contribution of vibrationally excited states. Furthermore, an isotope effect of ^{123}Te on the screening of ^{125}Te (and vice versa) in $CF_3TeTeCF_3$ was detected, and the coupling constant $^1J(^{125}\mathrm{Te}-^{123}\mathrm{Te})$ was determined.

Introduction

Numerous isotope shift effects in nuclear magnetic resonance spectroscopy have been observed,[2-5] and theoretical aspects of this effect have been considered.[6,7] Recently, several interesting papers on ^{18}O-induced isotope shifts in ^{13}C[3,8-10] and ^{31}P[11,12] NMR spectra have been published (see also review article ref 4). The data provide evidence for the dependence of the isotope shift on substituents and bond order. However, the effect of ^{13}C on the chemical shift of an adjacent nucleus has been found only in ^{19}F, ^{59}Co, ^{13}C,[13,14] and ^{111}Cd[15] NMR spectroscopy. This paper reports for the first time the observation of ^{13}C isotope effects on the nuclear screening of ^{77}Se and ^{125}Te and the correlation of one-bond isotope shifts with bond distances. Furthermore, the isotope effect of ^{123}Te on ^{125}Te (and vice versa) nuclear screening in $CF_3TeTeCF_3$ was detected.

In a current investigation of CF_3-substituted selenium and tellurium compounds[16] and compounds containing a C=Se double

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Table I. ^{13}C Isotope Effects on ^{77}Se and ^{125}Te Chemical Shifts

compound	$^1\Delta^{77}Se(^{13/12}C)$/ppm	r(C-Se)/pm
1, CF_3SeCl_3	−0.012	203[17]
2, $(CF_3)_2SeO$	−0.121	
3, CF_3SeCN	−0.170 (CF_3Se)	198.4[18]
4, $CF_3SeSO_2CF_3$	−0.172	
5, $CF_3SeSeCF_3$	−0.175	201.8[19]
6, CF_3SeBr	−0.178	
7, $CF_3SeSCCl_3$	−0.180	
8, $CF_3SeSCFCl_2$	−0.180	
9, CF_3SeSCF_2Cl	−0.180	
10, CF_3SeSCF_3	−0.180	
11, CF_3SeCH_3	−0.181 (CH_3Se)	
12, CF_3SeCF_3	−0.191	197.8[20]
13, CF_3SeH	−0.193	
14, $CF_3SeCFCl_2$	−0.204 (CF_3Se)	
15, $(CF_3Se)_3N$	−0.215	197.3[21]
16, $CH_3SeSeCH_3$	−0.220	195.4[22]
17, CF_3SeCl	−0.227	
18, CH_3SeCH_3	−0.228	194.3[23]
19, CF_3SeCH_3	−0.230 (CF_3Se)	
20, $(CF_3Se)_2NH$	−0.254	
21, $CF_2ClSeCl$	−0.270	
22, $CF_2ClSeCF_2Cl$	−0.271	
23, $CF_3SeCFCl_2$	−0.341 ($CFCl_2Se$)	
24, CF_3SeCN	−0.438 (SeCN)	185.4[18]
25, Se=C=Se	−0.633	169.2[24]
26, $Se{=}C(NH_2)_2$	−0.649	186[25]
27, Se=C=S	−0.650	169.5[26]
28, Se=C=O	−0.887	171.1[27]
29, $Se{=}CF_2$	−0.988	174.3[28]
30, $Se{=}C(t\text{-}Bu)_2$	−1.099	

compound	$^1\Delta^{125}Te(^{13/12}C)$/ppm
31, $(CF_3)_2TeO$	−0.057
32, $(CF_3)_2TeBr_2$	−0.092
33, $CF_3TeTeCF_3$	−0.320
34, CF_3TeCF_3	−0.330
35, CH_3TeCH_3	−0.341

bond,[1] interest arose in the isotope effect, since relatively large values could be expected due to the large chemical shift ranges of both nuclei. A large number of compounds has been studied to gain more information about the influence of hybridization, bond order, structure, and substituents on the isotope effect.

Experimental Section

The NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 47.71, 65.51, and 78.92 MHz for ^{77}Se, ^{123}Te, and ^{125}Te, respectively. A broadband (26–105 MHz) 10-mm probe was used, and the samples were measured at 296 K (except $SeCF_2$, 243 K). The fluorine nuclei of the CF_3 groups and the protons of the CH_3 groups attached to the resonant nucleus ^{77}Se, ^{123}Te, or ^{125}Te were decoupled. For most compounds several measurements were carried out. A digital resolution of 0.1 Hz per data point was chosen. The accuracy of the values is ±0.002 ppm.

The preparation or origin of the compounds has been reported in ref 1 and 16. The liquid substances were condensed in 10-mm NMR sample tubes, about 10% C_6D_6 was added as an internal lock substance, and the tubes were sealed under vacuum. $(CF_3)_2SeO$ was dissolved in dimethylformamide, $SeC(NH_2)_2$ was dissolved in a 1:1 mixture of DMF and CH_3OH, and $(CF_3)_2TeBr_2$ and $(CF_3)_2TeO$ were dissolved in CD_3CN, which served also for locking. CF_3SeCl_3 was prepared from CF_3SeCl and Cl_2 (molar ratio 1:2); the excess of chlorine served as a solvent and ensured the presence of CF_3SeCl_3 in equilibrium with CF_3SeCl and Cl_2.

A typical fluorine-decoupled ^{77}Se NMR spectrum of a compound CF_3SeX consists, for example, of a large singlet of the $^{12}CF_3{}^{77}SeX$ isotopomer and a weak doublet of total relative intensity of 1.1%, which is attributed to the isotopomer $^{13}CF_3{}^{77}SeX$ in its natural abundance. The frequency difference between the doublet signals is the coupling constant $^1J(^{77}Se–^{13}C)$. The center of the doublet is at lower frequency than the singlet, the difference being the isotope shift as defined in eq 1.

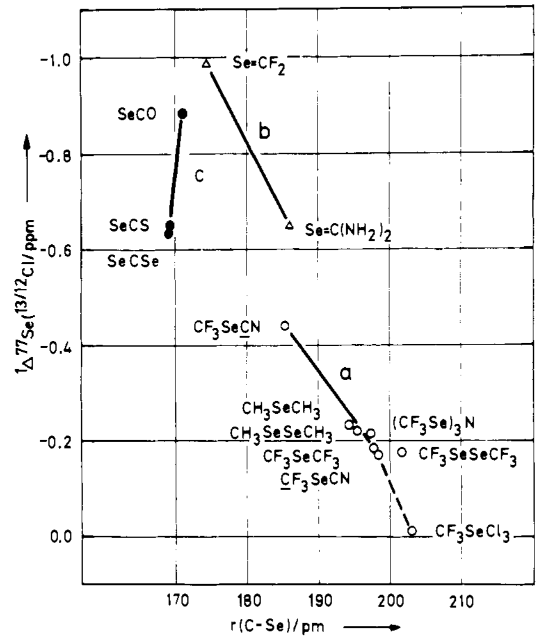

Figure 1. Correlation of ^{13}C-induced isotope shifts on ^{77}Se shielding with C–Se bond distances of compounds containing selenium bonded to (a) sp^3-, (b) sp^2-, and (c) sp-hybridized carbon. For curve b, the values of only two compounds were available until now.

Results and Discussion

All observed one-bond ^{13}C-induced isotope effects $^1\Delta$ listed in Table I exert a low-frequency (high-field) shift on the nucleus N in question. This can be rationalized by the shorter bond length for the heavier isotope-bearing species and is due to anharmonic vibrational potential.[7] Low-frequency isotope shifts are in general quoted as positive values in the literature. This is, however, in contradiction to the definition of chemical shift scales.[29] Therefore, the isotope shifts reported here are defined by eq 1 so

$$^1\Delta N(^{k/1}N')/\text{ppm} = \delta_N(^kN') - \delta_N(^1N') \qquad (1)$$

that low-frequency isotope shifts bear a negative sign like chemical shifts. Isotope shifts may be defined in general by this equation in which the following abbreviations are used: $^n\Delta$, isotope shift via n bonds; N, resonant nucleus; $(^{k/1}N')$, pair of isotopes for which the effect is observed (k and 1 are given in the order of decreasing masses. If a signal is due to several isotopomers, which contain isotopes without a magnetic moment, the weighted average mass for these isotopes should be given, e.g., $^1\Delta^{125}Te(^{127.7/123}Te)$).

The $^1\Delta^{77}Se(^{13/12}C)$ values (Table I) are spread over an unusually wide range and therefore could be used for analytical purposes. At first glance the results for the selenium compounds can be characterized as follows: (a) A drastic difference was found between the values for a C=Se double and C–Se single bond. Thus the bond order plays an important role. (b) Within groups of related compounds appreciable substituent effects are observed, e.g., isotope shifts between −0.170 and −0.254 ppm are found for the compounds CF_3SeX, whereas for the series Se=C=E (E = Se, S, O) the values range from −0.633 to −0.887 ppm, and compounds of the type $Se{=}CR_2$ exhibit values between −0.649 and −1.099 ppm. (c) There is no simple general correlation between the isotope effect and the electronegativity of substituents.

To advance the application of the isotope shift effect, it is useful to correlate the shifts with molecular physical properties, e.g., bond distances and bond energies. However, only a few molecular structures of the compounds under consideration have been de-

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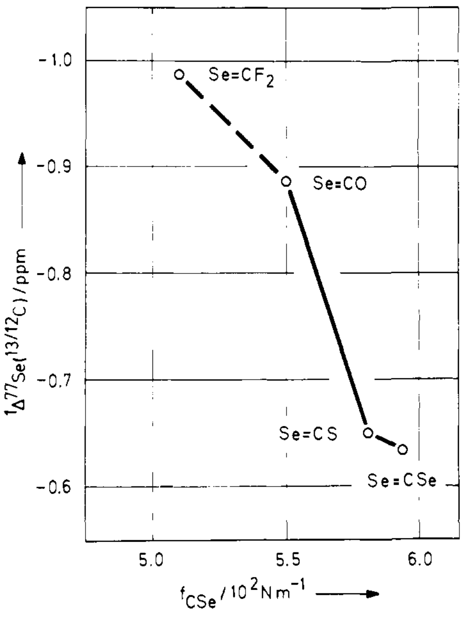


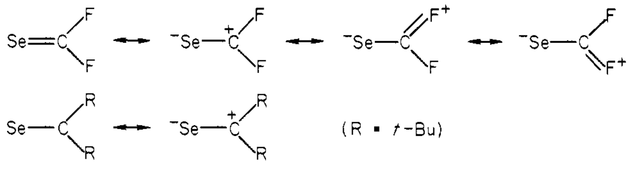
Figure 2. Correlation of ${}^{13}C$-induced isotope shifts on ${}^{77}Se$ shielding with force constants of C=Se double bonds in $SeCF_2$, SeCO, SeCS, and SeCSe.

termined, and bond energies are not known. The most important result of this work is that the ${}^1\Delta^{77}Se({}^{13/12}C)$ values of a series of closely related compounds RSeX, including the structurally different compound CF_3SeCl_3, are inversely dependent on the C–Se bond distance (Figure 1). This is the first example in which a one-bond isotope effect correlates with the internuclear distance. An analogous inverse dependence of geminal ${}^2H$ isotope effect on the internuclear distance r(H–E–H) via two bonds (${}^2\Delta^1H({}^{2/1}H)$) has been found in the ${}^1H$ NMR spectra of some molecules containing first-row elements E.[2] In contrast to these findings, Aydin and Günther recently observed that isotope effects ${}^1\Delta^{13}C({}^{2/1}H)$ of cycloalkanes (C_3–C_7 rings) are proportional to the p character of the C–D bond and suggested that the ${}^1\Delta$ values increase with the C–D bond length.[30] These authors also report upfield and downfield isotope shifts via three bonds. This shows that the isotope shift in polyatomic molecules is not yet completely understood.

In the series of compounds Se=C=E (E = O, S, Se) with almost constant C=Se bond distances, different isotope shifts are found (Figure 1, curve c). This reveals that besides the C=Se bond length further molecular properties associated with the C=Se bond determine the isotope effect in these compounds. Since the isotope effect is due to different vibrational behavior of different isotopomers,[7] we can assume two possible reasons: (1) The anharmonicity of the vibration should be much larger in SeCO than in SeCS and SeCSe. (2) The vibrational amplitudes of the C=Se bond may be important for the isotope shift. (Average bond extensions and angle deformations are also discussed in ref 4 to affect the isotope shift.)

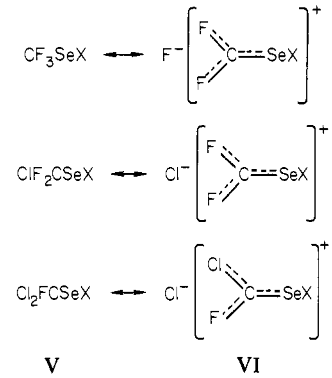
Considering qualitatively the different masses in Se=C=E, the vibrational amplitudes of the C=Se entity should decrease in the order SeCO > SeCS > SeCSe. As the vibrational amplitude is inversely dependent on the force constant, the isotope shift should decrease in the same order, if it depends on the vibrational amplitude. The plot of ${}^1\Delta^{77}Se({}^{13/12}C)$ vs. C=Se force constants (**28**, 5.50; **27**, 5.82; **25**, 5.94 × 10^2 N m^{-1} [27]) shows in fact an inverse dependence (Figure 2). These first experimental results support the hypothesis that vibrational amplitudes are of importance in determining isotope shifts. Although Se=CF_2 differs in symmetry from the SeCE compounds and therefore is not strictly comparable with those molecules, nevertheless its ${}^1\Delta^{77}Se({}^{13/12}C)$ value and the force constant ($f_{CSe} = 5.10 \times 10^2$ N m^{-1} [28]) fit the curve in Figure 2.

The dependence of the isotope effect on the electronegativity of substituents is not clear. Although in the linear molecules Se=C=E the more electronegative substituent causes the larger isotope shift, no simple correlation is found for the series CF_3SeX and the compounds Se=CR_2 (R = F, NH_2, *t*-Bu). At first glance inverse dependences seem to exist for the series SeCE on the one hand and $SeCF_2$ and $SeC(t\text{-}Bu)_2$ on the other (Table I), but mesomeric effects in $SeCF_2$ can explain the contrary dependences as follows. The larger isotope shift for $SeC(t\text{-}Bu)_2$ suggests that its C=Se bond distance is shorter than in $SeCF_2$. The extrapolation of curve b in Figure 1 (which can show only a first trend since no more than two points are available) leads to an estimated C=Se bond length of 170 pm in $SeC(t\text{-}Bu)_2$. In fact, the longer C=Se bond in $SeCF_2$ (and analogously in $SeC(NH_2)_2$) can be explained by the possibility of mesomeric structures of type III and IV in which the CSe bond length should be larger, although these structures are not conceivable in $SeC(t\text{-}Bu)_2$. Obviously mesomeric effects overwhelm inductive effects in $SeCF_2$ and $SeC(NH_2)_2$.



I II III IV

The only available ${}^{13}C$ isotope shifts of the Se(IV) and Te(IV) compounds CF_3SeCl_3, $(CF_3)_2TeBr_2$, and $(CF_3)_2TeO$ are smaller than the values of the comparable two-coordinated compounds $(CF_3)_2Se$, CF_3SeCl, and $(CF_3)_2Te$, the three-coordinated compound $(CF_3)_2SeO$ giving an intermediate value between CF_3SeCl_3 and CF_3SeCl (or CF_3SeCF_3). The C–Se bond distance in solid CF_3SeCl_3[17] is considerably larger than that in CF_3SeCF_3 (gas),[20] and thus the correlation between ${}^1\Delta$ and r(C–Se) gains considerable support. A value for r(C–Se) in $(CF_3)_2SeO$ intermediate between CF_3SeCF_3 and CF_3SeCl_3 can be predicted. Furthermore, the isotope shifts of **14**, **22**, and **23** reveal that the ${}^{13}C$ isotope effect is different in CF_3Se, CF_2ClSe, and $CFCl_2Se$ groups. The values are increasing in this order. This can be understood if the possible mesomeric structures V and VI are considered. The ${}^{19}F$ shielding in these groups decreases in the order CF_3Se > CF_2ClSe > $CFCl_2Se$, and this has been explained by the participation of structures VI.[16] In these structures the C–Se bond should be shorter than in structures V and therefore the isotope shift should be larger the more structures VI are involved.



V VI

The ${}^1\Delta^{125}Te({}^{13/12}C)$ values of **33**, **34**, and **35** are larger than the corresponding ${}^1\Delta^{77}Se({}^{13/12}C)$ values of **5**, **12**, and **18** by a factor of 1.8, 1.7, and 1.5, respectively. The larger sensitivity of the ${}^{125}Te$ nucleus toward isotopic substitution is expected because of the larger chemical shift range. A good linear correlation between $\delta({}^{125}Te)$ and $\delta({}^{77}Se)$ for analogous species is known, the slope of the plot being ca. 1.8.[31] Molecular structures of the investigated

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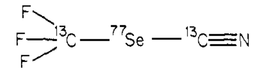
Table II. Temperature Dependence of ^{13}C Isotope Effects on ^{77}Se Chemical Shifts in CF_3SeCN and SeCO

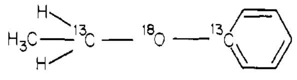
	$^{1}\Delta^{77}Se(^{13/12}C)$/ppm		
temp/K	CF_3SeCN	CF_3SeCN	Se=C=O
233			−0.970
263	−0.171	−0.464	−0.928
283	−0.169	−0.444	−0.888
296	−0.171	−0.438	−0.887
310	−0.171	−0.437	

tellurium compounds are not yet known, and therefore a correlation between the isotope shifts and the C–Te bond distance cannot be established. However, since both Se(IV) and Te(IV) compounds exhibit smaller isotope shifts than the Se(II) and Te(II) compounds, one is bound to conclude that an analogous dependence probably does exist.

In the present work the effect of $^{13}C/^{12}C$ substitution on the resonant chalcogen nucleus ^{77}Se is investigated in compounds containing >C—Se— and >C=Se entities. Risely and Van Etten[3] studied the inverse effect of the chalcogen $^{18}O/^{16}O$ substitution on the resonant nucleus ^{13}C in bond types >C—O—R and >C=O. The results of both studies show that the isotope shift is larger for double bonds than for single ones. An analogous effect $^{1}\Delta^{31}P(^{18/16}O)$ has also been observed by Cohn and Hu[12] for P=O double and P–O single bonds. However, a notable difference is found if one tries to relate the isotope shifts to the carbon–atom hybridization. It has been argued that for phenetole the ^{18}O isotope effect on ^{13}C is smaller when the s character in the carbon orbital is larger.[3] By contrast, in CF_3SeCN the resonant nucleus ^{77}Se experiences a larger ^{13}C isotope effect with larger s character in the carbon orbital (Δ values in ppm):



$^{1}\Delta^{77}Se(^{13/12}C) =$ −0.170 −0.438



$^{1}\Delta^{13}C(^{18/16}O) =$ −0.025 −0.016

These rather contradictory results show that one should be careful in explaining isotope shifts merely on the basis of hybridization. The larger isotope shift for the sp-hybridized C atom in CF_3SeCN can also be caused simply by the shorter C–Se bond distance (cf. Table I). Moreover, the CN group is lighter than the CF_3 group. Hence the vibrational amplitudes of the Se–CN entity should be larger than those of the CF_3Se entity and should therefore cause a larger isotopic shift (vide supra). An analogous explanation can be given for the above $^{1}\Delta^{13}C(^{18/16}O)$ values of phenetole. More work is needed to explore the role of the hybridization in the bond for which the isotope shift is observed. Since the isotope shift depends in a complex manner on many variables, its correlation with a single parameter may be successful only for a series of closely related compounds.

It is worthwhile to comment on the isotope shifts of CF_3SeCH_3. From other isotope shifts in Table I a larger value for the CH_3Se than for the CF_3Se entity would be expected, but the C–Se coupling constants allow an unequivocal assignment. The larger isotope shift for the F_3C–Se group can possibly be explained by the participation of mesomeric structures of type VI, which lead to a shorter F_3C–Se bond distance. It should also be mentioned that the here reported isotope shifts do not correlate with the coupling constants $^{1}J(^{125}Te-^{13}C)$ and $^{1}J(^{77}Se-^{13}C)$. The coupling constants of compounds containing a C=Se entity are reported in ref 1; those of CF_3SeX compounds will be reported and discussed together with other coupling constants of these compounds in a further publication.

CF_3SeCN and SeCO have been investigated in the liquid state at different temperatures to obtain information about the temperature dependence of the isotope shift in polyatomic molecules. The results are summarized in Table II. The isotope shifts $^{1}\Delta^{77}Se(^{13/12}C)$ in the three different types of C–Se bonds show different temperature dependences. Whereas the CF_3Se entity gives a constant value, the isotope shifts of the SeCN and SeC groups decrease with increasing temperature. This is in agreement with theory and implies that higher vibrational energy levels contribute to the isotope shift because of anharmonic vibration. The population of the vibrational energy level N_1 for the Se–C bond within the quoted temperature range is about 5–8% and 6–10% for the SeCN and Se=C entities, respectively. This was estimated from the equation $\ln(N_1/N_0) = -\Delta E/(kT)$ by using the vibrational frequencies ν(Se–CN) = 533 cm^{-1} [32] and ν(Se=C) = 463.7 cm^{-1}.[33] Should the vibrational excited states only cause the temperature dependence of the isotope shift, then the plot $^{1}\Delta^{77}Se(^{13/12}C)$ vs $\ln(N_1/N^0)$ should result in a linear correlation. For SeCO this is approximately borne out by experiment, but for CF_3SeCN a bent curve results. This nonlinearity suggests that a further effect determines the temperature dependence of the isotope shift. This effect may be the intermolecular interaction of the molecules. The found temperature dependence of the ^{77}Se chemical shifts (CF_3SeCN, +0.026 ppm/K; SeCO, −0.123 ppm/K; both are average values for the investigated temperature range) support this suggestion. The different signs of the values indicate that different interaction mechanisms may be involved. In conclusion, these qualitative considerations show that vibrational excitation can substantially contribute to the isotope shift $^{1}\Delta^{77}Se(^{13/12}C)$ in liquid polyatomic compounds and that association of the molecules complicates the quantitative description of the temperature dependence of the isotope shift.

$CF_3TeTeCF_3$ contains two equivalent Te atoms so that the spin–spin coupling constant $^{1}J(^{125}Te-^{125}Te)$ cannot be obtained from the satellite spectrum of the most abundant magnetically active isotopomer $^{12}CF_3{}^{125}Te^{125}Te^{12}CF_3$. Theoretically this coupling might be measured in the isotopomer $^{13}CF_3{}^{125}Te^{125}Te^{12}CF_3$, but the concentration of these species was too low to be observed. Tellurium-123, however, is a second isotope of Te with a magnetic moment ($I = {}^{1}/_{2}$, natural abundance 0.89%) and the isotopomer $^{12}CF_3{}^{125}Te^{123}Te^{12}CF_3$ gives the coupling constant $^{1}J(^{125}Te-^{123}Te)$. These satellites have about the same intensity as the ^{13}C satellites. The coupling was observed in the ^{125}Te and ^{123}Te NMR spectrum, and values of 206.5 and 207.0 Hz, respectively, were measured. From this coupling constant a value for $^{1}J(^{125}Te-^{125}Te)$ of 249.3 Hz can be calculated by using the magnetogyric ratios of ^{125}Te ($\gamma = -8.453 \times 10^7$ rad T^{-1} s^{-1}) and ^{123}Te ($\gamma = -7.011$ rad T^{-1} s^{-1}). The ^{19}F-decoupled ^{125}Te NMR spectrum consists of a strong singlet and two weak doublets. The singlet arises from isotopomers that contain besides one ^{125}Te isotope any of the nonmagnetic isotopes of tellurium with masses 120, 122, 124, 126, 128, 130 or a second magnetic ^{125}Te (weighted average mass 127.7). The doublet with the small coupling constant is assigned to the isotopomer $^{12}CF_3{}^{125}Te^{123}Te^{12}CF_3$, the other to the isotopomer $^{13}CF_3{}^{125}Te^{128.0}Te^{12}CF_3$ (the weighted average mass of 128.0 is obtained when ^{123}Te and ^{125}Te are excluded). The center of the inner, tellurium-123-induced doublet, is shifted to high frequency with respect to the strong singlet, whereas the carbon-13-induced doublet is shifted to low frequency. This observation is in agreement with theory since the shift inducing isotopes ^{123}Te and ^{13}C are lighter and heavier in comparison to $^{127.7}Te$ and ^{12}C, respectively. The notation, according to eq 1, for this isotope shift is $^{1}\Delta^{125}Te(^{127.7/123}Te)$. The ^{123}Te NMR spectrum exhibits a similar pattern, and analogously an isotope shift $^{1}\Delta^{123}Te(^{127.9/125}Te)$ is derived. This shift is smaller than the above one because the fractional change in mass is smaller: $CF_3TeTeCF_3$, $^{1}\Delta^{125}Te(^{127.7/123}Te) = -0.042$ ppm; $^{1}\Delta^{123}Te(^{127.9/125}Te) = -0.018$ ppm.

Conclusion

Although the isotope shift in NMR spectroscopy is a complex function of many variables, in a series of closely related compounds only one parameter like the bond distance or the force constant can dominate the isotope effect. Thus the isotope shift can serve

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for the estimation of these molecular physical properties. Furthermore, it has been shown that even the effect of isotopes of such a heavy element as tellurium can be studied with high-field (5.8 T) NMR spectrometers.

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Metallopolymer Photochemistry. Photophysical, Photochemical, and Photoelectrochemical Properties of $(bpy)_2Ru^{II}<$ Sites Bound to Poly(4-vinylpyridine)

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Abstract: The photochemical and photophysical properties of the polymer-bound chromophore $Ru(bpy)_2(PVP)_2^{2+}$ (PVP is poly(4-vinylpyridine)) have been investigated in homogeneous solution. Results have been obtained with polymers both dilute and concentrated in chromophore. Lifetime and quantum yield data are interpreted in terms of models of excited-state behavior previously proposed for analogous monomeric poly(pyridyl) complexes of Ru(II). Excited-state sites within the metallopolymers undergo oxidative and reductive electron-transfer quenching. The quenching reactions were investigated by Stern–Volmer quenching and conventional microsecond flash photolysis. Sensitization of n-TiO_2 to visible light has been observed on a semiconductor coated with a film of the metallopolymer.

Introduction

We have described the synthesis and characterization of a variety of poly(pyridyl) complexes of ruthenium(II) bound to poly(4-vinylpyridine) (PVP), including the title compound $Ru(bpy)_2(PVP)_2^{2+}$ (bpy is 2,2′-bipyridine).[1,2] Synthetic procedures were developed that allowed for variation in the extent of the loading of the metal complex onto the PVP backbone. The earlier work also showed that systematic modifications could be made in the coordination environment of the polymer-bound metal complex site. Our investigations of these materials led to the conclusion that, for the most part, the inherent chemical and physical properties of the monomers were maintained in the polymeric materials either in solution or as films on electrodes. Some notable exceptions did appear. One example relevant to the present work was the observation of an apparent onset of electronic communication between sites based on measurements involving both ground and excited states of $Ru(trpy)(bpy)(PVP)^{2+}$ (trpy is 2,2′-2″-terpyridine) as the loading of the metal complex in the polymer exceeded a critical value.[1] In terms of chemical properties, when differences occurred between monomeric and polymeric sites, they were attributed to two major factors: (1) the ability to control the spatial separation of the sites in the polymers by diluting them along the polymer backbone and (2) the effect of the local polymeric environment on the reactivity properties of the sites.

One of our principal interests in metallopolymers containing poly(pyridyl)ruthenium(II) groups is in their photochemical properties. The metal to ligand charge-transfer (MLCT) excited states of $Ru(bpy)_3^{2+}$ have an extensive redox photochemistry. The photoredox properties have provided a basis for energy conversion processes based on molecular excited states.[3] The basic photochemical and photophysical properties of the MLCT excited states of Ru(II) poly(pyridyl) complexes[4-6] have been shown to exist for Os(II) as well.[7]

Compared to monomers, metallopolymeric analogues appear to offer at least three advantages: (1) the presence of multiple chromophoric sites in a fixed chemical matrix, (2) the ability to prepare materials containing both catalytic and chromophoric sites, and (3) the ability to create an interface by physical adsorption on electrodes or on particles in solution. A preliminary report has appeared that describes the preparation of polymer-bound $Ru(bpy)_3^{2+}$ units by means of a polystyrene backbone to which 2,2′-bipyridine had been attached.[8] The Ru sites in the polymer

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