

Tellurium-125 NMR of Te(II) and Te(IV) Dithiocarbamates

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Abstract

^{125}Te chemical shifts for $\text{Te}(\text{R}_2\text{NCS}_2)_2$ and $\text{Te}(\text{R}_2\text{NCS}_2)_4$ compounds were found to be separated by ca. 1400 ppm. When R is an alkyl group, the electronic contributions to the chemical shifts appear to be very small for both oxidation states of tellurium. The chemical shifts of these compounds display a positive temperature dependence consistent with the major contributions arising from paramagnetic shielding.

Introduction

The ^{125}Te NMR studies of a large number of tellurium compounds have been particularly useful in gauging the sensitivity of the chemical shifts to the chemical environment and the oxidation state of the tellurium nucleus [1–21]. Indeed the compounds with tellurium in the –2, +2 and +4 oxidation states cover a chemical shift range of approximately 4700 ppm [6].

The limited value of IR and UV–Vis spectroscopy in the characterization of tellurium dithiocarbamates [19, 22, 23] has directed our attention to the application of ^{125}Te NMR. Although these compounds are well known and $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ has been used as a ^{125}Te chemical shift reference [7, 11, 21], the ^{125}Te NMR spectroscopy of tellurium(II) and tellurium(IV) dithiocarbamates hitherto has not been subject to close examination.

As part of our continuing studies into the oxidation of thiols by metal ions which is applicable to the curing of polysulfide sealants used in advanced aircraft, we have undertaken the ^{125}Te NMR characterization of a number of tellurium dithiocarbamates.

Experimental

Preparation of Compounds

Bis(dithiocarbamato)tellurium(II), $\text{Te}(\text{R}_2\text{NCS}_2)_2$ [24, 25] compounds, tetrakis(dithiocarbamato)tellurium(IV), $\text{Te}(\text{R}_2\text{NCS}_2)_4$ [26] compounds,

chlorotris(diethyldithiocarbamato)tellurium(IV), $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Cl}$ [27] and thiocyanatotris(diethyldithiocarbamato)tellurium(IV), $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{NCS}$ [22] were prepared by standard literature methods with the elemental (C, H, N, S) analyses being consistent with the given formulae. Sodium pyrrole-*N*-carbodi-thioate was prepared in accordance with the method of El A'mma and Drago [28].

Iodotris(diethyldithiocarbamato)tellurium(IV), *Te(Et₂NCS₂)₃I*

Potassium iodide (1.4 g, 8.4 mmol) dissolved in methanol (50 ml) was added with stirring to $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Cl}$ (1.0 g, 1.6 mmol) in methanol (80 ml). A fine crystalline precipitate formed immediately and the reaction mixture was filtered after 0.25 h, the residue was washed with methanol and dried first with suction and then *in vacuo*. Yield 0.82 g (73%), melting point ca. 147 °C (decomp.). *Anal.* Calc. for $\text{C}_{15}\text{H}_{30}\text{N}_3\text{I}_2\text{S}_6\text{Te}$: C, 25.76; H, 4.32; N, 6.01; S, 27.51. Found: C, 25.69; H, 4.22; N, 5.97; S, 27.35%.

Reaction of Te⁰ with (Et₂NCS₂)₂

An equimolar mixture of tellurium powder (0.63 g) and tetraethylthiuram disulfide (1.5 g) was stirred for 1 week at 20 °C in dichloromethane (500 ml). The resultant mixture was filtered and reduced in volume to ca. 20 ml to which 20 ml of petroleum ether (60–80) and 30 ml of acetone were added. The mixture was then allowed to evaporate, at room temperature, to ca. 20 ml, then filtered and the residue washed with acetone. The red crystalline solid was dried under suction. Yield 1.3 g (61%), melting point 164.5–165 °C (lit. [25] 164 °C).

Elemental analyses were performed by Analytische Laboratorien, Elbach, F.R.G.

NMR Measurements

NMR spectra were measured on a Bruker AM 300 spectrometer. Resonance frequencies were derived directly from the synthesizer output required to centre the observed signals from ^{125}Te and ^1H (TMS) using existing software. Frequencies are given relative to ^1H (TMS, 100 MHz exactly). This method is more accurate and versatile than conventional double

resonance experiments and is only limited, in the present case, by the line widths and the temperature sensitivity of the ^{125}Te chemical shifts. The chemical shifts were calculated relative to TeMe_2 assuming a resonance frequency equal to 31.549802 MHz as determined from double resonance experiments [2]. Variable temperature measurements were made relative to the chemical shifts of methanol and ethylene glycol. Delays of approximately 0.5 h were required for each change in temperature. Line widths were measured without proton decoupling after temperature equilibration and represent upper limits, particularly for values < 100 Hz.

MAS measurements were made using the standard solid accessory retuned for ^{125}Te . Operating conditions were optimized for telluric acid.

Results and Discussion

Because of the different solubilities of the compounds in deuterated solvents, signals were obtained for a variety of concentrations. However the dependence of ^{125}Te chemical shifts on the concentration of the tellurium dithiocarbamates was found to be relatively low as indicated by $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ which showed a variation of 2.4 ppm over a concentration range of 0.0025–0.25 M in CDCl_3 . This compares with a slightly higher value of 10 ppm reported for Te_2Me_2 in benzene, over the range of 0.02–2 M [29].

The ^{125}Te line widths were found to vary from 10–1390 Hz (Table I). Similar line widths have been reported for organotellurium trihalides and the reduction of line widths at low temperatures was attributed to a spin-rotation relaxation mechanism [8, 14]. At relatively narrow line widths a significant contribution can be expected from temperature variations (*vide infra*). The considerably large line widths for the $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{X}$ series also suggests the possibility of a contribution from fast exchange reactions with a closely related species.

The reason for the unusually large line width of $\text{Te}(\text{i-Pr}_2\text{NCS}_2)_4$ is not known but the possibility of an anomalous paramagnetic contribution was ruled out after comparisons were made of the bulk magnetic susceptibility of this compound with that of $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ using the method of Evans [30].

The ^{125}Te chemical shifts of $\text{Te}(\text{R}_2\text{NCS}_2)_2$ compounds (where R = Et, i-Pr, n-Pr and i-Bu) resonate over a narrow range (< 11 ppm) indicating similar electronic effects from the substituent alkyl groups (Table I). In fact, the solvent effects observed for $\text{Te}(\text{n-Pr}_2\text{NCS}_2)_2$ in CDCl_3 and CD_3COCD_3 have a more substantial effect on the ^{125}Te chemical shifts. A slightly larger chemical shift is observed for $\text{Te}(\text{Bz}_2\text{NCS}_2)_2$ but this does not represent a significant departure from other tellurium(II) compounds. By contrast, $\text{Te}(\text{pyrrCS}_2)_2$ appears at considerably larger chemical shifts which may be attributed to the presence of the pyrrole ring. Unlike most alkyl

TABLE I. ^{125}Te NMR Data for Tellurium Dithiocarbamates

Compound	Resonance frequency (MHz) ^{a, b}	Chemical shift (ppm) ^{a, c}	Temperature (K)	Concentration (M)	Solvent	Line width (Hz)
$\text{Te}(\text{Bz}_2\text{NCS}_2)_4$	31.531849	-569.05	305	0.02	CDCl_3	30
$\text{Te}(\text{Et}_2\text{NCS}_2)_4$	31.532098	-561.14	305	0.01	CD_3COCD_3	94
$\text{Te}(\text{n-Pr}_2\text{NCS}_2)_4$	31.532100	-561.09	300	0.015	CD_3COCD_3	140
$\text{Te}(\text{i-Bu}_2\text{NCS}_2)_4$	31.532650	-543.65	305	0.06	CD_3COCD_3	10
$\text{Te}(\text{i-Pr}_2\text{NCS}_2)_4$	31.537089	-402.96	300	0.07	CDCl_3	1100
	31.536961	-407.00	280			380
	31.536835	-411.00	260			245
	31.536658	-416.63	296	0.01	CD_3COCD_3	430
$\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{I}$	31.542911	-218.41	300	0.07	CDCl_3	1390
$\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{Cl}$	31.544910	-155.05	300	0.08	CDCl_3	1000
$\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{NCS}$	31.545745	-128.59	300	0.07	CDCl_3	710
$\text{Te}(\text{Et}_2\text{NCS}_2)_2$	31.576228	837.60	300	0.25	CDCl_3	18
	31.575928	827.39	300	0.006	CD_3COCD_3	69
$\text{Te}(\text{i-Pr}_2\text{NCS}_2)_2$	31.576083	833.00	300	0.04	CDCl_3	700
$\text{Te}(\text{n-Pr}_2\text{NCS}_2)_2$	31.576189	836.36	300	0.035	CDCl_3	35
	31.575955	828.94	300	0.004	CD_3COCD_3	40
$\text{Te}(\text{i-Bu}_2\text{NCS}_2)_2$	31.576448	844.57	305	0.03	CD_3COCD_3	39
$\text{Te}(\text{Bz}_2\text{NCS}_2)_2$	31.577092	864.98	305	0.1	CDCl_3	105
$\text{Te}(\text{pyrrCS}_2)_2$	31.585054	1117.33	300	0.01	CDCl_3	17

^aResonance frequencies and chemical shifts are estimated to be accurate to 5 percent of the line widths.

^bCorrected to

$^1\text{H}(\text{TMS}) = 100$ MHz.

^cReferenced to $\text{TeMe}_2 = 31.549802$ MHz [2].

dithiocarbamates, pyrCS₂⁻ coordinates as a mono-anion with little evidence for the delocalization of electrons from the nitrogen atom to the sulfur atoms [31]. The low chemical shift dependency on the substituent alkyl group is not a reflection on the insensitivity of the ¹²⁵Te chemical shifts but is attributable to the attenuation caused by the remoteness of the groups from the metal ion. This is supported by the large chemical shift range (ca. 690 ppm) established for Te(RS)₂ compounds [21].

Chemical shifts of other nuclei coordinated to dithiocarbamates have also been reported. They include ¹⁹⁹Hg [32, 33], ¹¹³Cd [33] and ⁵⁹Co [34]. By comparison with ¹²⁵Te, their chemical shifts show greater fluctuations for the alkyl substituted dithiocarbamates as well as a poor correlation with the inductive effects of the substituent groups (Table II). These observations are consistent with an unsuccessful attempt to correlate Taft parameters of substituted groups with the oxidation potentials of transition metal dithiocarbamates which led to the conclusion that the electronic contributions were perturbed by steric effects [35].

TABLE II. Comparisons with the Chemical Shifts of Other Metal Nuclei

M(R ₂ NCS ₂) _{2/3} R =	δ(¹²⁵ Te) (ppm) ^a	δ(¹⁹⁹ Hg) (ppm) ^b	δ(¹¹³ Cd) (ppm) ^b	δ(⁵⁹ Co) (ppm) ^c
Me		180		6830
				6840
Et	837.60	177	383	6790
i-Pr	833.00	224	419	
n-Pr	836.36			
i-Bu	844.57	143	389	
n-Bu		173	386	6750
pyrr	1117.33			7200

^aThis work.

^bRef. 33.

^cRef. 34.

The tellurium(IV) dithiocarbamates occur at negative ¹²⁵Te chemical shifts relative to TeMe₂ and the corresponding tellurium(II) analogs (Table I). Like the tellurium(II) analogs, their chemical shifts are not strongly influenced by the nature of the alkyl substituent group. The exception is Te(i-Pr₂NCS₂)₄ which occurs at a significantly less negative chemical shift compared to the rest of the series.

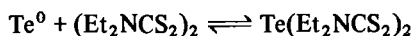
The ¹²⁵Te chemical shift of Te(Et₂NCS₂)₄ in CDCl₃ has been previously reported at 841.2 ppm (versus TeMe₂, Table I) [19] as opposed to -561.14 ppm (versus TeMe₂). We have found that Te(R₂NCS₂)₄ compounds readily decompose in CDCl₃ to form Te(R₂NCS₂)₂ and (R₂NCS₂)₂ probably aided by the presence of adventitious HCl in the solvent. This has required some of the ¹²⁵Te chemical shifts to be reported for CD₃COCD₃ solutions.

The decomposition of Te(Et₂NCS₂)₄ was shown to be reversible by the addition of excess (Et₂NCS₂)₂ to a CDCl₃ solution of Te(Et₂NCS₂)₂ which resulted in the detection of Te(Et₂NCS₂)₄ in addition to Te(Et₂NCS₂)₂.



Furthermore, the addition of a tenfold molar excess of both (i-Pr₂NCS₂)₂ and (Et₂NCS₂)₂ to Te(Et₂NCS₂)₂ in CDCl₃ solution generated five well separated resonance lines assignable to Te(Et₂NCS₂)₄, Te(Et₂NCS₂)₃(i-Pr₂NCS₂), Te(Et₂NCS₂)₂(i-Pr₂NCS₂)₂, Te(Et₂NCS₂)(i-Pr₂NCS₂)₃ and Te(i-Pr₂NCS₂)₄ (Fig. 1). The experiment does not indicate whether the ligand exchange occurs in the Te(II) or the Te(IV) state.

The mixture may also be generated from the addition of tellurium metal to a solution of (R₂NCS₂)₂ since Te(Et₂NCS₂)₂ can be prepared in good yield utilizing the following reaction



The lines in Fig. 1 show progressive broadening as the ratio of i-Pr₂NCS₂⁻/Et₂NCS₂⁻ increases. This is also accompanied by a significant and almost regular

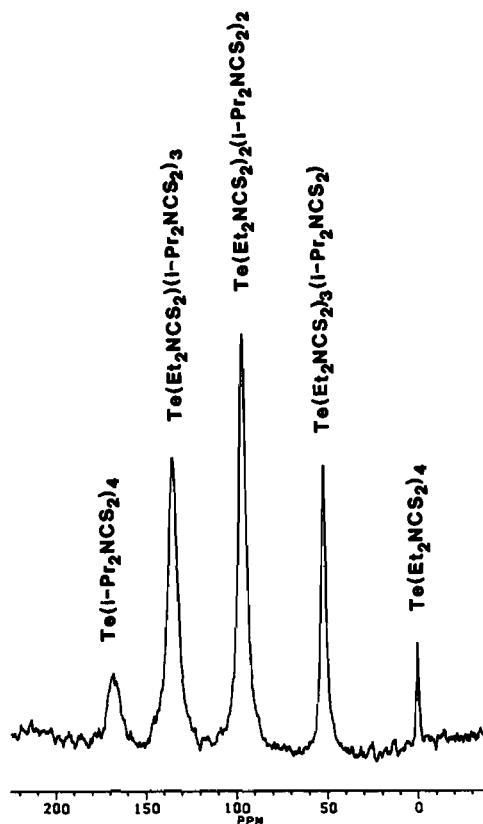


Fig. 1. ¹²⁵Te NMR of an equilibrium mixture of Te(Et₂NCS₂)₂ (0.08 M), (Et₂NCS₂)₂ (0.8 M) and (i-Pr₂NCS₂)₂ (0.8 M) in CDCl₃.

increase in the ^{125}Te chemical shift indicating that the comparatively large difference in chemical shifts between $\text{Te}(\text{i-Pr}_2\text{NCS}_2)_4$ and other $\text{Te}(\text{R}_2\text{NCS}_2)_4$ compounds listed in Table I is due to the individual contributions of the $\text{i-Pr}_2\text{NCS}_2^-$ ligands (probably through steric effects) rather than an anomalous structure of $\text{Te}(\text{i-Pr}_2\text{NCS}_2)_4$. A similar dependence in line widths is also observed.

The inclusion of a more electronegative substituent than the dithiocarbamate ligand, as in the $\text{Te}(\text{Et}_2\text{NCS}_2)_3\text{X}$ series, has the effect of resulting in a more positive chemical shift. This is consistent with a more negative paramagnetic shielding term (σ_p) as the unbalance in the valence p orbital population term (Pu) is increased (assuming the d orbital populations (Du) are unimportant) [29, 36–38]

$$\sigma_p = \frac{-2e^2h^2}{3m^2c^2\Delta E} (\text{Pu}\langle r^{-3} \rangle_p + \text{Du}\langle r^{-3} \rangle_d)$$

where the constants have their usual meaning, ΔE is the mean electronic excitation energy and the $\langle r^{-3} \rangle$ terms refer to the valence p and d electron radii.

The temperature dependence of the ^{125}Te chemical shifts of both tellurium(II) and tellurium(IV) dithiocarbamates are shown in Figs. 2–4 and they vary between 0.40 ppm/K and 0.85 ppm/K over the temperature range 275–325 K. This temperature dependence is considerably larger than that previously reported for tellurium compounds namely, TeMe_2 (–0.128 ppm/K) and TeCl_4 (–0.167 ppm/K) [8] which is in contrast to the tellurium dithio-

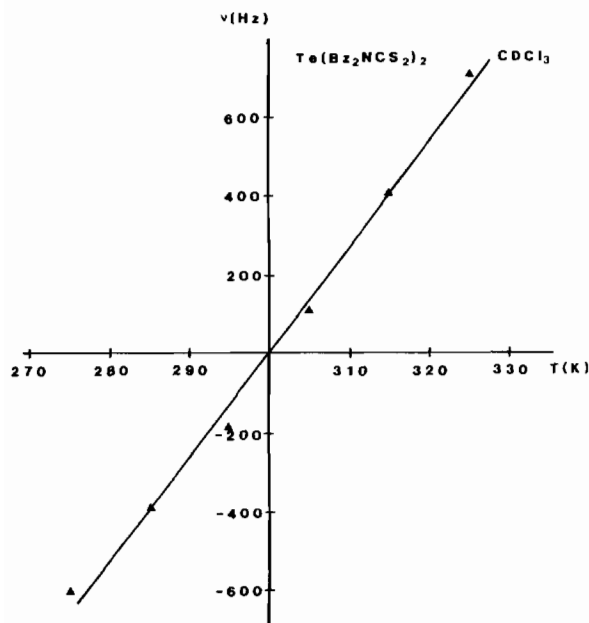


Fig. 2. Temperature dependence of ^{125}Te chemical shift for $\text{Te}(\text{Bz}_2\text{NCS}_2)_2$ in CDCl_3 calculated at 0.85 ppm/K. Resonance frequencies corrected to $^1\text{H}(\text{TMS}) = 100$ MHz.

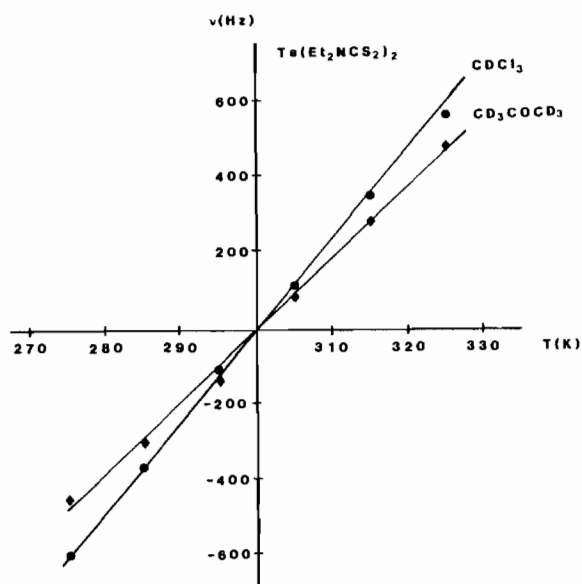


Fig. 3. Temperature dependence of ^{125}Te chemical shifts for $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ in CDCl_3 and CD_3COCD_3 calculated at 0.76 ppm/K and 0.60 ppm/K respectively. Resonance frequencies corrected to $^1\text{H}(\text{TMS}) = 100$ MHz.

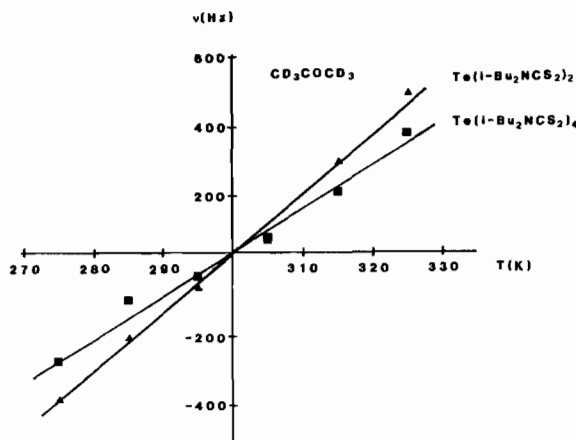


Fig. 4. Temperature dependence of ^{125}Te chemical shifts for $\text{Te}(\text{i-Bu}_2\text{NCS}_2)_2$ and $\text{Te}(\text{i-Bu}_2\text{NCS}_2)_4$ in CD_3COCD_3 calculated at 0.54 ppm/K and 0.40 ppm/K respectively. Resonance frequencies corrected to $^1\text{H}(\text{TMS}) = 100$ MHz.

carbamates, show anomalous negative dependency if the paramagnetic shielding contribution were the dominating factor [18].

The origin of temperature dependence lies in the sensitivity of the paramagnetic shielding term. As the temperature increases, the statistical occupancy of the higher energy ground vibrational levels increases and the separation between the ground state and the excited state (ΔE) decreases and this leads to an increase in the chemical shift [39, 40] as indicated by the above equation. The positive temperature coefficients of the tellurium dithiocarbamates is

consistent with this treatment and the magnitudes are of the same order as those obtained for cobalt(III) [40] and platinum [39] compounds.

It has been suggested that variations in ΔE between tellurium compounds may be the dominant factor affecting ^{125}Te chemical shifts, rather than p orbital imbalance which, at times, appears to be inconsistent with the observed trends in the chemical shifts when the electronic effects of the substituent groups are considered [17]. However, in the case of the tellurium dithiocarbamates, the relative variations in the temperature dependence of the ^{125}Te chemical shift from compound to compound are much greater than the chemical shift variation at any one temperature within a series (Figs. 2–4). Thus the chemical shifts are not reflected in the ΔE variations as shown by the temperature dependence.

The results also indicate that the temperature dependence of ^{125}Te chemical shifts is influenced by solvent (Fig. 3). Solvent interactions with tellurium dithiocarbamates may occur particularly when a ketone is involved as carbonyl groups are known to coordinate to tellurium [41]. A similar effect of CD_3COCD_3 on ^{125}Te chemical shifts has been previously observed [12].

An attempt was made to measure the solid state ^{125}Te NMR spectra of these compounds. ^{13}C magic angle spinning measurements of $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ were indistinguishable from that previously reported [42]. We have, as yet, been unsuccessful in detecting a ^{125}Te signal for this compound as well as $\text{Te}(\text{Et}_2\text{NCS}_2)_4$ despite a number of attempts, namely (i) multiple 30° pulse accumulations extending over 8 h with 5, 20 and 300 s delays between pulses; (ii) single 90° pulse experiments following a relaxation delay of 12 or 60 h using either cross-polarization or simple high power decoupling conditions [43]. Similar single pulse experiments on telluric acid gave a signal to noise ratio of ca. 30:1.

Conclusions

The electronic effects of substituent groups (R) in $\text{Te}(\text{R}_2\text{NCS}_2)_2$ and $\text{Te}(\text{R}_2\text{NCS}_2)_4$ compounds appear to be considerably weakened by their distance from the tellurium ion and consequently there is little difference in the ^{125}Te chemical shifts when R = Et, i-Pr, n-Pr, i-Bu and Bz compared with $\text{Te}(\text{pyrrCS}_2)_2$. This generalization may also be valid for the transition metal dithiocarbamates.

Temperature dependence measurements of ^{125}Te chemical shifts are consistent with the effect of temperature on the energy separation between the ground and excited states of tellurium. However, these energy differences do not correlate well with the differences in the chemical shifts. The magnitude of this dependence is not significantly different from

that of other nuclei with large chemical shift ranges (such as ^{59}Co [40] and ^{195}Pt [39, 44]) but it is much larger than the ^{13}C and ^1H temperature dependent chemical shifts [45, 46].

Although $\text{Te}(\text{Et}_2\text{NCS}_2)_2$ has previously been used as a reference for ^{125}Te chemical shifts the temperature and solvent dependence of tellurium dithiocarbamates shown in this study indicate that these compounds are unsuitable for this purpose.

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