

Figure 8. Halogen levels plotted as a function of EESOP calculated charge on the halogen.

that increasing the degree of sophistication of calculations is meaningless if the original charges are being calculated incorrectly by the CNDO/2 method.

Thus we returned to our EESOP calculations^{5,6} based on electronegativity-equalization methods.¹⁸ This method shows reasonable agreement in the trends on plotting BE vs. charge (Figures 7 and 8). It should be noted that the methyl analogues fit the same correlation. The limitation in this case is the requirement of treating the CF₃ moiety as a group so that correlations can only be made for BE (Ge 3d) vs. q_{EESOP} (Figure 7) and BE (halogens) vs. q_{EESOP} (Figure 8). For the germanium 3d levels, the smooth changes in the charge distribution within a series of compounds suggests that the

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changes are basically controlled by inductive effects. The absolute value of the charge depends on the relative participation of the s and p orbitals of the halogens which have been assumed to remain constant throughout both the methyl and perfluoromethyl series. The "best fit" value for the electronegativity of the CF₃ group, $\chi_{\text{CF}_3} = 9.6 + 5.32\delta_{\text{CF}_3}$, implies an overall electronegativity very similar to that of bromine which in EESOP calculation was assumed to have 15% s orbital participation in the bond to germanium. Any attempt to involve the potential term gave poorer fits with the experimental data, though the changes caused by the V term are much less pronounced than in the CNDO calculations because of the smaller calculated charges.

The halogen correlations show a reasonable fit, given our gross assumptions, except for the chlorides and, to some extent, the bromides in the CF₃ series. This is, no doubt, indicative that the oversimplified concept works least well when there are only slight changes in inductive effects and parameters that have been ignored are coming into play.

Nevertheless, our results, in general, show, as they did for the methyl series, that changes in the binding energies of the various atoms in a molecule parallel each other. Thus if all binding energies are increasing along the series (CF₃)₄Ge > (CF₃)GeF > (CF₃)₂GeF₂ > (CF₃)GeF₃, GeF₄, it seems reasonable to assume that the atoms as a whole are more tightly bound together. It is interesting that the force constants of *all* bonds also increase along this particular series, and indeed the plots of force constant (C-Ge) vs. increasing substitution of halide⁴ bear a remarkable similarity to Figures 3 and 4.

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Registry No. (CF₃)₄Ge, 55642-43-8; (CF₃)₃GeF, 66348-16-1; (CF₃)₃GeCl, 66348-17-2; (CF₃)₃GeBr, 65094-18-0; (CF₃)₃GeI, 66348-18-3; (CF₃)₂GeF₂, 56592-86-0; (CF₃)₂GeCl₂, 56593-14-7; (CF₃)₂GeBr₂, 56593-16-9; (CF₃)₂GeI₂, 754-36-9; (CF₃)GeF₃, 1512-15-8; (CF₃)GeCl₃, 1495-36-9; (CF₃)GeBr₃, 56593-15-8; (CF₃)GeI₃, 1512-08-9; GeF₄, 7783-58-6; GeCl₄, 10038-98-9; GeBr₄, 13450-92-5; (CH₃)₃GeF, 661-37-0; (CH₃)₂GeF₂, 811-70-1; (CH₃)GeF₃, 753-69-5; (CH₃)₃GeCl, 1529-47-1; (CH₃)₂GeCl₂, 1529-48-2; (CH₃)GeCl₃, 993-10-2; (CH₃)₃GeBr, 1066-37-1; (CH₃)₂GeBr₂, 1730-66-1; (CH₃)GeBr₃, 6558-57-2; (CH₃)GeI₃, 1111-91-7; (CH₃)₂GeI₂, 1184-77-6; (CH₃)₃GeI, 1066-38-2; (CH₃)₄Ge, 865-52-1.

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Solid-State High-Resolution Carbon-13 Spectra of Some Tellurium Coordination Complexes. Correlations with X-ray Crystallography

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High-resolution solid-state ¹³C NMR spectra were obtained for several tellurium coordination complexes [Te(S₂CNEt₂)_n, n = 2, 4, Te(S₂COEt)₂, and AsPh₄[Te(S₂COEt)₃]] by using cross polarization, dipolar decoupling, and magic-angle spinning. The spectra display solid-state effects that are intermolecular in origin. Methyl group chemical shifts are particularly sensitive probes of crystal symmetry, which is often reduced compared to molecular symmetry.

The combination of cross polarization,¹ dipolar decoupling, and magic-angle spinning² has allowed the observation of solid-state ¹³C NMR spectra with resolution approaching that

obtained from liquid samples. The solid-state spectra often differ from the corresponding solution spectra both in the number of individual carbon resonances and in their chemical shifts. Two main factors determine such differences: (a) the freezing of the molecules into a particular conformation generally reduces the effective molecular symmetry and (b)

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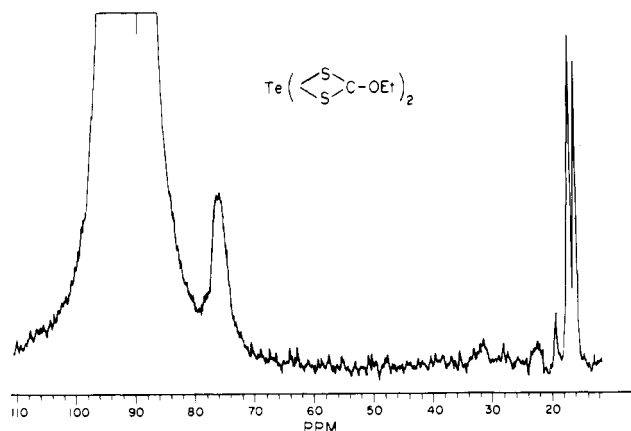


Figure 1. Solid-state high-resolution ¹³C NMR spectrum of bis(*O*-ethyl xanthato)tellurium(II).

chemically equivalent nuclei may be crystallographically inequivalent, in which case they have separate chemical shifts.

The effects of frozen conformations on solid-state ¹³C NMR spectra have been observed for a number of polymers³ as well as small molecules,⁴⁻⁶ usually polysubstituted benzenes. Frey and Opella⁷ report large differences between solution and solid-state chemical shifts of aliphatic carbons that could possibly be a consequence of crystal packing. The effects of crystallographic inequivalence have been observed by Ripmeester⁸ for polymorphic forms of the same material. In this paper we report the solid-state, magic-angle-spinning spectra of four tellurium complexes, three of which have been previously examined by X-ray crystallography. The compounds of known structure are bis(*O*-ethyl xanthato)tellurium(II),⁹ bis(*N,N*-diethyldithiocarbamato)tellurium(II)¹⁰ and tetrakis(*N,N*-diethyldithiocarbamato)tellurium(IV).¹¹

The fourth compound tetraphenylarsonium tris(*O*-ethyl xanthato)tellurate(II) has not yet been studied by X-ray crystallography, though the structure of the corresponding tetraethylammonium salt has been published.¹² Our results indicate that the number of distinct chemical shifts observed for the aliphatic carbons in these molecules reflects the (generally lower) crystal symmetry as opposed to the higher molecular symmetry which determines solution spectra.

Experimental Section

The solid-state, magic-angle-spinning spectra were obtained on an NMR spectrometer, built in our laboratories, operating at 200 MHz for protons. The probe, supplied by Chemagnetics Inc., has bullet-shaped Delrin rotors that routinely achieve spinning speeds of >4.3 kHz. Typically ~1000 transients were accumulated per spectrum; 4K data points were used, followed by 4K of zero filling. A 5-Hz line broadening was applied to the data prior to zero filling to enhance the signal-to-noise ratio.

TeO₂, K₂TeO₃, and AsPh₄Cl were obtained from Alfa Products/Ventron; KS₂COEt, NaS₂CNEt₂, and all organic solvents were from Kodak Laboratory Chemicals. Te(S₂CNEt₂)₄ was prepared by the reaction of NaS₂CNEt₂ and K₂TeO₃ in aqueous solution followed by acidification; the product was recrystallized from toluene.¹³ The

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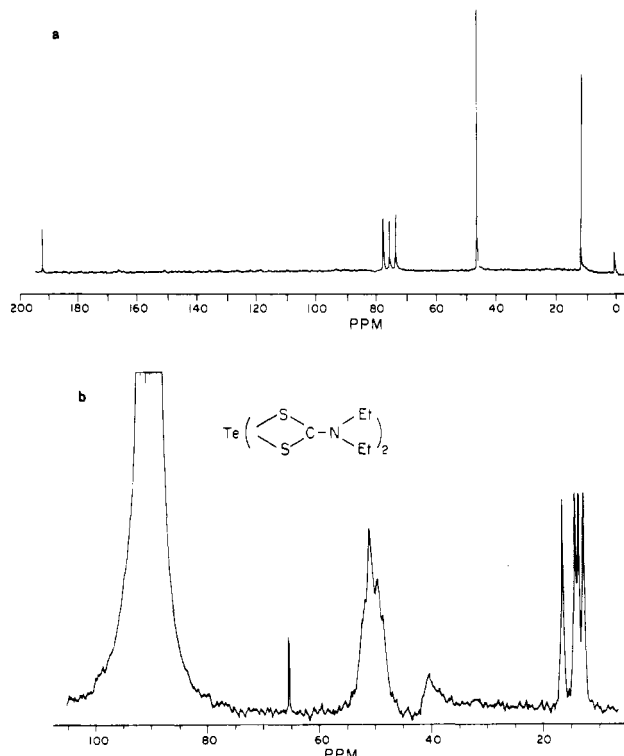


Figure 2. (a) High-resolution ¹³C NMR spectrum of bis(*N,N*-diethyldithiocarbamato)tellurium(II) in CDCl₃ solution at 15 MHz. (b) ¹³C NMR spectrum of the same material in the solid state.

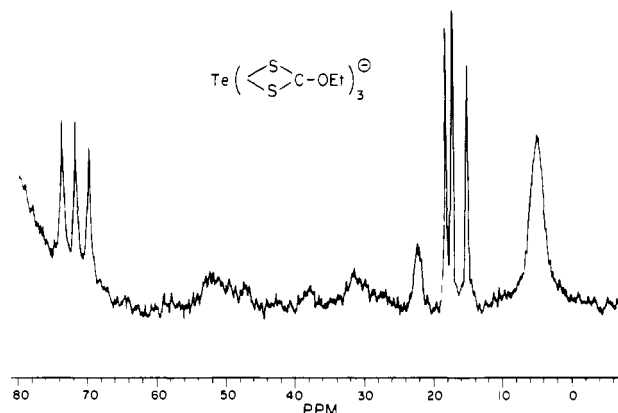


Figure 3. Solid-state high-resolution ¹³C NMR spectrum of tetraphenylarsonium tris(*O*-ethyl xanthato)tellurate(II). The peak at 5 ppm is a Delrin side band.

Table I. Methyl Group Chemical Shifts

	solid-state chem shifts ^a	soln chem shifts
bis(<i>O</i> -ethyl xanthato)tellurium(II) [Te(S ₂ COEt) ₂]	17.2, 16.1	14.09
bis(<i>N,N</i> -diethyldithiocarbamato)tellurium(II) [Te(S ₂ CNEt ₂) ₂]	16.5, 14.3, 13.6, 12.8	12.2
tetrakis(<i>N,N</i> -diethyldithiocarbamato)tellurium(IV) [Te(S ₂ CNEt ₂) ₄]	15.6	12.2
tetraphenylarsonium tris(<i>O</i> -ethyl xanthato)tellurate(II) [[AsPh ₄] ⁺ [Te(S ₂ COEt) ₃] ⁻]	18.3, 17.3, 15.1	

^a In ppm downfield from Me₄Si, with Delrin at 89.8 ppm as reference.

complexes Te(S₂COEt)₂ and Te(S₂CNEt₂)₂ were prepared from Na₂Te(S₂O₃)₂·3H₂O and the appropriate alkali-metal salt of the

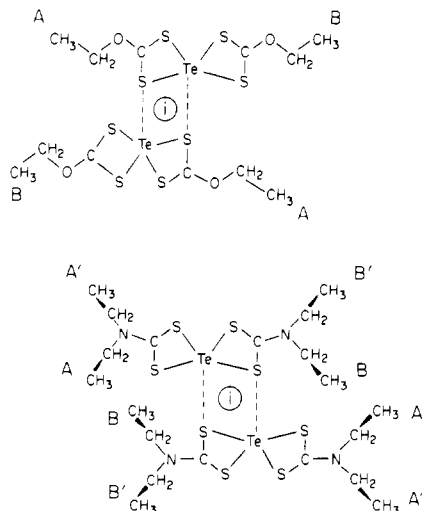


Figure 4. Dimer structure formed by the xanthate and dithiocarbamate in the solid state.

1,1-dithio ligand in aqueous solution as previously described.¹⁴

The complex $\text{AsPh}_4[\text{Te}(\text{S}_2\text{COEt})_3]$ was prepared by a modification of the method described for the tetraethylammonium salt.¹⁵ To a solution of KS_2COEt (0.64 g, 4.0 mmol) and AsPh_4Cl (1.68 g, 4.0 mmol) in 140 mL of warm methanol was added solid $\text{Te}(\text{S}_2\text{COEt})_2$ (1.48 g, 4.0 mmol). After a brief stirring, the warm solution was filtered through a fine-porosity glass frit into a flask cooled to -10°C . After the solution was further cooled overnight in a freezer, the yellow product was filtered and recrystallized from 45°C methanol to give 0.25 g of yellow microcrystals. Anal. Calcd for $\text{C}_{33}\text{H}_{35}\text{AsO}_3\text{S}_6\text{Te}$: C, 45.32; H, 4.03; S, 22.0; Te, 14.59. Found: C, 45.1; H, 3.9; S, 22.2; Te, 14.5.

Results and Discussion

The aliphatic regions of the solid-state spectra for three of the compounds are shown in Figures 1–3. The methyl regions are especially rich in fine structure. Table I summarizes the chemical shifts of the methyl groups for all of the compounds. The four compounds studied in this paper display a single methyl peak in their solution ^{13}C NMR spectra. We shall show that the multiple resonances observed in the solid-state spectra are a direct consequence of the crystal structures of these compounds.

Crystal structure determinations of bis(*O*-ethyl xanthato)tellurium(II) by Husebye⁹ and bis(*N,N*-diethyldithiocarbamato)tellurium(II) by Fabiani et al.¹⁰ show that these molecules form loose dimers in the solid state with the structures given in Figure 4.

The dimers have a center of symmetry, indicated by *i*. The ethylxanthate derivative in this configuration has two sets of centrosymmetrically related methyl groups (A and B) with different chemical environments. This difference leads to the observation of two methyl peaks separated by 1.1 ppm. The spectrum of the dithiocarbamate derivative shows four different methyl groups. We believe this to be due to a hindered rotation around the $>\text{N}-\text{CS}_2$ bond. In the absence of rapid motion around this bond, four different methyl groups (A, A', B, B') would be expected, in agreement with the observed results.

The two compounds described above are pseudopentacoordinate. True 5-coordination around tellurium is found in the salts of the complex anion tris(*O*-ethyl xanthato)tellurate(II) with bulky cations such as tetraethylammonium¹² and tetraphenylarsonium. The spectrum of the latter salt is shown in Figure 3. The three methyl groups clearly have different chemical environments, as evidenced by their separate chemical shifts. The known planar pentagonal structure of the tetraethylammonium salt¹² supports this conclusion. Furthermore, it is striking that, unlike the previous results, the methylene groups are equally sensitive to the crystalline environment, giving rise to three resolved lines.

The 8-coordinate dodecahedral tetrakis(*N,N*-diethyldithiocarbamato)tellurium(IV) gave, in contrast to the previous findings, aliphatic resonances which were rather broad and lacked fine structure. This is rather surprising since, according to the crystal structure, the methyl groups in one of the ligands are in a distinctly different environment compared to the other three.

With bis(*N,N*-diethyldithiocarbamato)tellurium(II), our conclusions are further supported by the observation of two thiocarbonyl peaks at 193 and 195 ppm. The geometry of the dimer indeed predicts the existence of two distinguishable thiocarbonyl carbons in the solid. The same compound in solution gives one thiocarbonyl peak at 194 ppm.

We have thus demonstrated that intermolecular effects such as crystal packing and aggregation in the solid state have a measurable influence on the high-resolution solid-state ^{13}C NMR spectra. These effects can be utilized for characterizing solid organometallic compounds.

Registry No. $\text{AsPh}_4[\text{Te}(\text{S}_2\text{COEt})_3]$, 79953-52-9; $\text{Te}(\text{S}_2\text{COEt})_2$, 15730-39-9; $\text{Te}(\text{S}_2\text{CNEt}_2)_2$, 15080-52-1; $\text{Te}(\text{S}_2\text{CNEt}_2)_4$, 12367-49-6.

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