

Communications to the Editor

Chiral Discrimination and Solid-State ^{13}C NMR. Application to Tri-*o*-thymotide Clathrates[†]

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In recent years there has been great interest in the study of chiral recognition in host-guest systems.^{1,2} One such host, tri-*o*-thymotide (TOT) (Figure 1, inset), when recrystallized from a suitable racemic solvent, spontaneously resolves into *P*-(+) and *M*-(-) TOT crystals, each preferentially including *d* or *l* guest molecules. Whether chiral discrimination occurs or not, determination of the enantiomeric excess is often a lengthy and destructive procedure, as it involves recovery of guest material from a single crystal, or a portion thereof. We show that for one family of host-guest systems, the TOT clathrates of secondary butyl compounds, solid-state ^{13}C NMR gives a very direct indication of chiral discrimination, including the possibility of quantitative analysis. Also, some important differences between the dynamic states of the major and minor enantiomers are revealed by the NMR measurements.

TOT was prepared and recrystallized as reported previously,³ and TOT clathrates of 2-chloro-, 2-bromo-, and 2-iodobutane and 2-butanol were prepared by slow evaporation from the racemic guest materials.

Solid-state ^{13}C NMR spectra⁴ for these solid clathrates are shown in Figure 1a-e. Although the solution spectrum of the symmetric trimer is straightforward, in the solid the host molecule loses its threefold symmetry and all lines become triplets, many of which are completely resolved. Many of the observable guest resonances are distinct doublets, e.g., C₂ for all of the guests, C₄ for the chloride, bromide and iodide; C₁ is obscured by the host lattice spectrum. Significant enantiomeric excesses have been reported for the chloride and bromide,^{2b,c} and it is known that the *S*-(+) guest prefers the *P*-(+) configuration of the host molecules.^{2c} Our powdered samples contain equal numbers of *P*-(+) and *M*-(-) TOT crystallites, so that the major lines of the C₂ and C₄ guest

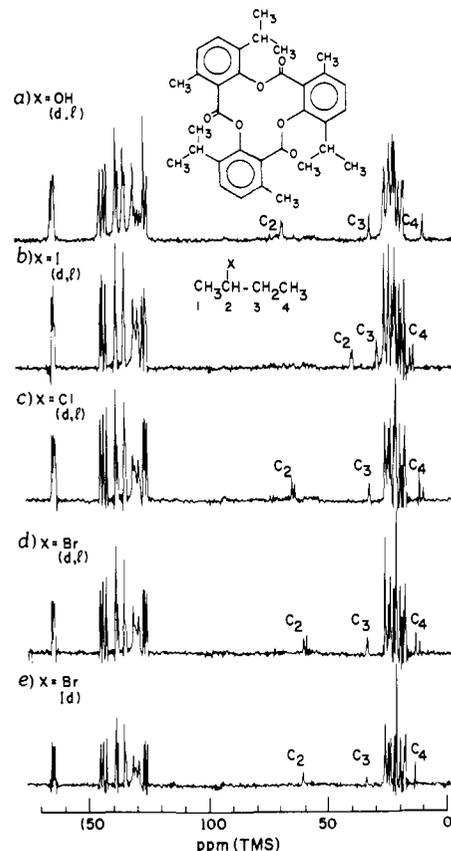


Figure 1. Solid-state ^{13}C NMR spectra obtained for TOT clathrates. Number of scans = 400; cross-polarization time = 5 ms; 2K data points were collected at 20 kHz sweep rate and fid's were zero filled to 8K before Fourier transformation.

doublets should be assigned to *P*-(+)-*S*-(+) and *M*-(-)-*R*-(-) host-guest combinations. The minor doublet component should therefore correspond to *P*-(+)-*R*-(-) and *M*-(-)-*S*-(+) host-guest combinations. This assignment was confirmed by preparing TOT clathrates from optically pure 2-bromobutanes.⁵ Figure 1e shows the spectrum obtained for TOT-*d*-2-bromobutane, which was identical with that obtained for TOT-*l*-2-bromobutane. For both these systems the minor enantiomer is essentially absent. Therefore, in optically mixed systems, solid-state NMR offers a very direct way of establishing enantiomeric excess, providing account is taken of the cross-polarization time-dependent line intensities. From the relative peak sizes of the methyl resonances, enantiomeric excesses of 47% and 35% were found for 2-chloro- and 2-bromobutane, respectively, in good agreement with values reported in ref 2e. For 2-iodobutane and 2-butanol, the NMR results indicate essentially equal populations, again in agreement with previous measurements.^{2e,h}

It should be noted that for guest molecules for which little or no enantiomeric excess was found,^{2b} i.e., the 2-butanol and 2-iodobutane, some of the ^{13}C lines are still doublets. The observation of the line splittings, therefore, has no direct bearing on the presence of interaction energy differences for the various host cavity-guest enantiomer combinations.

Some further insight into the chiral discrimination of TOT-sec-butyl compounds can be obtained from the application of the

[†]NRCC No. 24184.

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(4) Spectra were obtained at 45.3 MHz on a Bruker CXP-180 NMR spectrometer, cross-polarization times of 5 ms were used, rf field amplitudes being 50 kHz. Magic angle spinning rates of ~3 kHz were achieved by using Kel-F spinners of the Andrew-Beams type. First-order spinning sidebands were suppressed with the technique of Hemminga and de Jager (Hemminga; Jager *J. Magn. Reson.* **1983**, *51*, 339).

(5) Helmkamp, G. K.; Joel, C. D.; Sharman, H. *J. Org. Chem.* **1956**, *21*, 844. Optical purities were measured on a JASCO Model ORD/UV-5 instrument.

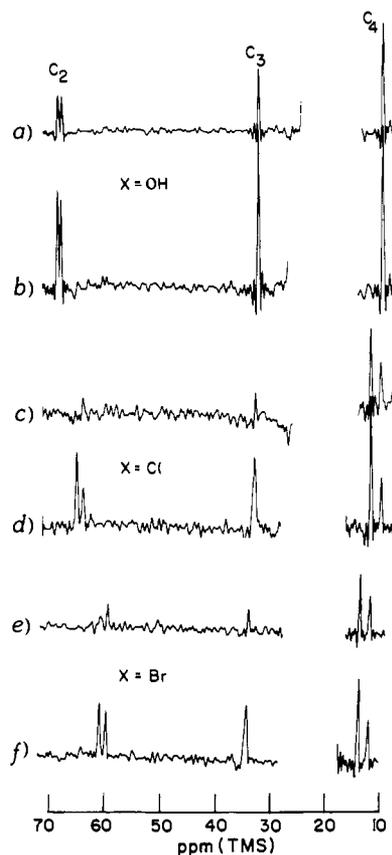


Figure 2. Solid-state ^{13}C NMR spectra obtained for TOT clathrates. Only the guest lines are shown, under normal (b, d, f) and dipolar dephasing (a, c, e) conditions.

dipolar dephasing technique.⁶ The ratio I_{DD}/I of ^{13}C line intensities obtained under dipolar dephasing and normal CP/MAS conditions is a semiquantitative measure of the dynamic state of the molecule or molecular group. For example, for rigidly held methylene or methine carbons $I_{\text{DD}}/I = 0$, whereas for a methyl group rotating about its threefold axis $I_{\text{DD}}/I \approx 0.6$ when a dipolar dephasing time of $40 \mu\text{s}$ is used. More extensive molecular motion further increases I_{DD}/I up to a maximum value of 1.

In Figure 2 the guest lines are shown under normal and dipolar dephasing conditions. For the chloride and bromide the C_2 methylene carbons have $I_{\text{DD}}/I \sim 0$ for the major enantiomer and a value of ~ 0.4 for the minor enantiomer. The I_{DD}/I ratios for the methyl carbons show a similar trend. The major enantiomer value is ~ 0.6 , that for the minor enantiomer ~ 0.9 . The observations suggest that the major enantiomer is held essentially rigidly in the TOT cage (except for small angle librations), whereas the minor enantiomer is more mobile, the I_{DD}/I values suggesting some sort of single-axis rotation for the encaged molecules. In case of the alcohol, the C_2 methylene carbons for the two enantiomers dephase to the same extent ($I_{\text{DD}}/I \sim 0.4$) so that both enantiomers have the same degree of rotational freedom in the cage. Chiral discrimination, therefore, is related to the tightness of fit of a guest molecule in the cage, which ultimately must relate back to nonspecific guest-host van der Waals interactions and which seems to be reflected more by the dynamic guest properties than the static equilibrium guest positions determined by diffraction techniques. Of course, although diffraction techniques can detect positional disorder as for the major 2-bromobutane enantiomer guest in the TOT cages, no information can be obtained about the motion taking place between disorder sites. The minor 2-bromobutane enantiomer could not be located at all, presumably because of excessive disorder.

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In the case of the *sec*-butyl compounds studied here, the differences in guest dynamics between major and minor enantiomers is especially pronounced, the major enantiomer being static in the cage, whereas the minor enantiomer is mobile. For many other guest-host systems the differences may be rather less pronounced, and perhaps more detailed information will be required, i.e., the degree of motional anisotropy and motional rates, in accordance with the concept of a guest-host dynamic coupling coefficient proposed by Lehn⁷ in the case of solution complexes.

Registry No. TOT, 4399-52-4; (\pm)-2-chlorobutane, 53178-20-4; (\pm)-2-bromobutane, 5787-31-5; (\pm)-2-iodobutane, 52152-71-3; (\pm)-2-butanol, 15892-23-6.

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Ruthenium(IV) and Osmium(IV) Chalcogen Complexes of Carbon Monoxide

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The ability of ruthenium and osmium complexes in the +2 and to a lesser extent in the +3 oxidation states to coordinate π -acid ligands such as carbon monoxide is well documented.²⁻⁴ We wish to report that a series of Ru(IV) and Os(IV) complexes of sterically hindered thiolate and selenolate ligands^{5,6} bind CO to provide rare examples of $\text{M}^{\text{IV}}(\text{CO})$ compounds. These compounds, $\text{M}(\text{SR})_4(\text{CO})$,^{7,8} are readily prepared at room temperature and atmospheric pressure by flushing CO over methylene chloride solutions of $\text{M}(\text{SR})_4(\text{CH}_3\text{CN})$.⁶

$\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (**1**) has been structurally characterized by X-ray diffraction.⁹ The overall structure (Figure 1) is similar to that of the parent complex,⁶ $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CH}_3\text{CN})$ (**2**), with the CO occupying the axial position of the trigonal-bipyramidal coordination sphere.¹⁰ The Ru-S

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(5) 2,3,5,6-Tetramethylbenzenethiolate = $[\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}]^-$; 2,4,6-triisopropylbenzenethiolate = $[\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2]^-$.

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(7) Typical synthesis: A methylene chloride solution of $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CH}_3\text{CN})$ (1.0 g, 0.92 mM) was stirred in an atmosphere of CO for 10 min. EtOH was then added slowly to crystallize the product which was filtered in air. Black crystals of $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CO})$ were acquired in 75% yield.

(8) $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$: IR (CHCl_3) 2040 cm^{-1} , UV/vis (CHCl_3) 408 (63700), 320 (sh) (14700), 270 nm (sh) (16700). IR $\text{Ru}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_4(\text{CO})$ (CHCl_3) 2032 cm^{-1} ; Os($\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (CHCl_3) 2020 cm^{-1} .

(9) $\text{Ru}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_4(\text{CO})$ (CHCl_3) crystallizes from $\text{CHCl}_3/\text{EtOH}$ in the triclinic space group $P1$ with $a = 12.507$ (1) Å, $b = 17.297$ (4) Å, $c = 11.200$ (6) Å, $\alpha = 98.01$ (4)°, $\beta = 97.76$ (4)°, $\gamma = 110.56$ (1)°, $V = 2202$ (3) Å³, $Z = 2$. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by using normal Patterson and difference Fourier methods. Final least-squares refinement gave $R = 0.064$ and $R_w = 0.082$ for 2592 reflections with $|F_o| > 3\sigma(|F_o|)$.