Inorg. Chem. **1991**, *30*, 1720–1722

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Nature of the Phase Change in Solid $Ce_2(O^iPr)_8(^iPrOH)_2$, As Determined by Variable-Temperature X-ray Diffraction and ^2H NMR Spectroscopy

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Received October 4, 1990

The temperature dependence of the unit cell edge lengths of $Ce_2(O^iPr)_8(^iPrOH)_2$ shows a reversible phase change at about −90 °C. The availability of single-crystal structure determinations at −155 and +25 °C reveals a planar centrosymmetric $Ce_2(O^iPr)_2(^iPrOH)_2$ substructure with hydrogen bonds from alcohol to alkoxide bonded to different metals. While these hydrogens are localized at −155 °C, they are disordered at 20 °C. Solid-state variable-temperature ^2H NMR studies reveal that this disorder is dynamic, not static. Line shape analysis permits a determination of the hydrogen position (5.5° off of the O–O line) as well as the frequency of interconversion ($>10^6$ s^{-1}) between the two degenerate hydrogen-bonded structures.

Introduction

A variety of benefits follow from using low temperatures for collection of single-crystal X-ray data for structure determination. Generally, these are incremental improvements rather than detection of wholly new phenomena unobserved at 25 °C. We report here a case where the availability of fully refined X-ray structures on the same composition of matter at both room temperature and low temperature clearly expands our understanding of a solid-state phase transition. Moreover, solid-state ^2H NMR spectroscopy reveals mechanistic details associated with this phase transition.

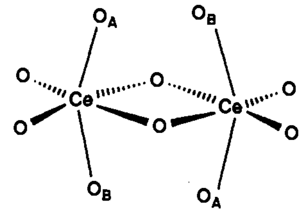
Results

Variable-Temperature X-ray Diffraction Study. The recent report[1] of the structure of $Ce_2(O^iPr)_8(^iPrOH)_2$ at 20 °C revealed an edge-shared octahedral structure. We have independently carried out a structure determination of this same material, but at −155 °C, and were surprised to find (in comparison to the +20 °C data) a 10% difference in the *c*-axis unit cell length, compared to the more typical 0.5% difference in the *b* axis.[2] The space group is the same at both temperatures. Along with this change, the crystals are thermochromic, being yellow at room temperature and colorless at −155 °C. We investigated the temperature dependence of the cell constants in more detail and found (Figure 1) evidence for a well-defined reversible phase change at approximately −90 °C. Particularly noteworthy is the *shrinkage* of the *a*- and *b*-axis lengths as a consequence of warming through the phase change.

While we have encountered such phase changes with considerable frequency over some 15 years of low-temperature crystallography, we have seldom investigated the phenomenon on a molecular level. The availability of a full structure determination both above[1] and below[2] the transition temperature offers the potential for understanding the molecular origin of the phase change in the present case. A number of points warrant consideration:

(1) The 20 °C structure determination exhibits a number of isopropyl groups with planar geometry at the central carbon. This implausible result is often observed when either static disorder or large amplitude librational motion is present in the solid. This problem is encountered with some frequency in structural studies of metal alkoxides. These effects alone are not expected to account for behavior of the magnitude of that shown in Figure 1.

(2) A major difference between the centrosymmetric molecular structures determined at 20 °C and at −155 °C is the equivalence[1] of the Ce–O_A and Ce–O_B distances (1.6σ) at 20 °C and their inequivalence[2] (40σ) at −155 °C. Moreover, at −155 °C, the hydroxyl hydrogens were located on the oxygens involved in the longer Ce–O distances.[2] The distinction between the alkoxides and the two alcohol groups is well-defined and thus exhibits long-range order. We suggest that the equality of Ce–O_A and Ce–O_B distances observed at 20 °C originates from thermally induced static disorder *or* from dynamic intramolecular proton transfer occurring in the solid state at 20 °C.



In order to better understand the molecular origin of this phase change, we sought direct evidence that could discriminate between the static and dynamic scenarios. For this, one needs a spectroscopic technique with a threshold time scale that would be crossed in the event of proton transfer.

Solid-State NMR Studies. Solid-state deuterium NMR spectroscopy is such a technique because of the sensitivity of the solid-state ^2H line shape to dynamics.[3] The ^2H NMR spectra were recorded at 293 and 104 K (Figure 2). The narrow resonance in the center of each spectrum is apparently due to a photoreduction of the sample and/or to free deuterated 2-propanol,[4] despite attempts to protect the sample from light. The ^2H spectrum of O-deuterated 2-propanol at 104 K has a quadrupole coupling constant of approximately 178 kHz, which is larger than that obtained from the spectrum of the cerium sample. Therefore, the resonance in the middle of Figure 2a,c, especially at the lower temperature, is not due to the free alcohol.

There are two parameters diagnostic of deuteron motion. These are the relative relaxation rates of the sample and relative widths of the spectrum at low and high temperatures. It is known that dynamics play an important role in facilitating deuteron relaxation.[6] Therefore, if the T_1 at the lower temperature is longer, it may be concluded that the dynamics which helped in the relaxation mechanism at room temperature have been substantially slowed at the lower temperature. The second indicator is observed through direct measurement of the inner "horn" (i.e., two tallest peaks) separation of the spectra at the two temperatures. As is true for any inhomogeneous line broadened by dynamics, lowering

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(1) Toledano, P.; Ribot, F.; Sanchez, C. *Acta Crystallogr.* **1990**, *C46*, 1419.

(2) Vaartstra, B. A.; Huffman, J. C.; Gradeff, P. S.; Hubert-Pfalzgraf, L. G.; Daran, J. C.; Parraud, S.; Yunlu, K.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3126.

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(4) We have commented earlier that alcohol loss from $Ce_2(O^iPr)_8(^iPrOH)_2$ occurs readily and complicates recording the infrared spectra of solid samples.[2] The compound is also quite photosensitive.[5]

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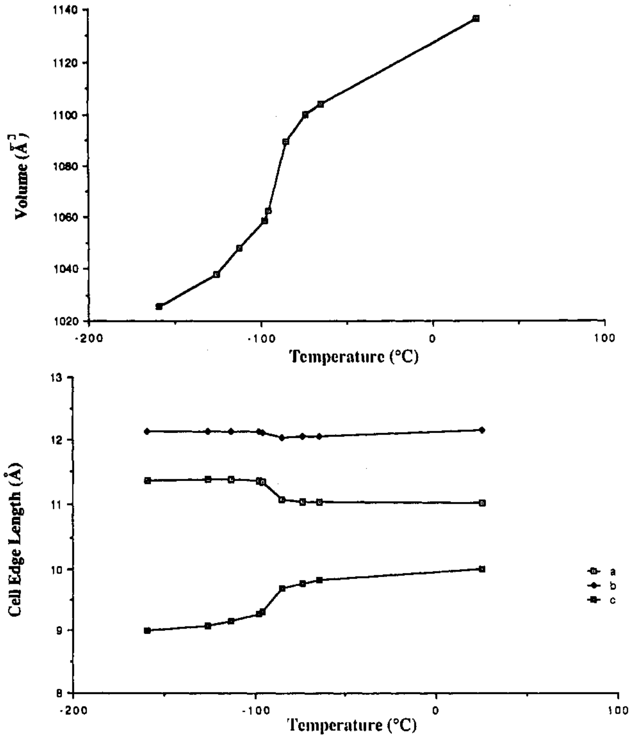

Figure 1. Temperature dependence of the unit cell dimensions and cell volume of $Ce_2(O^iPr)_8(^iPrOH)_2$.

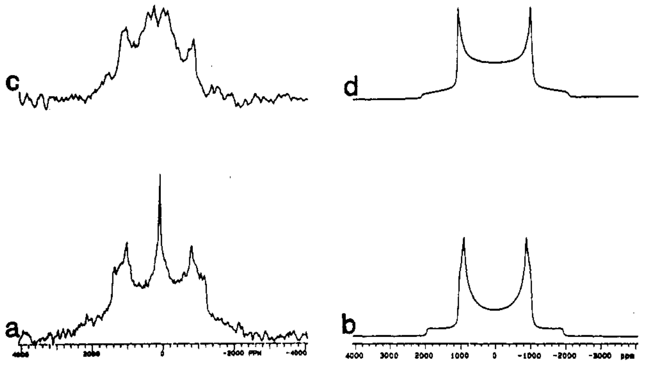

Figure 2. Solid-state ^2H NMR spectra of $Ce_2(O^iPr)_8(^iPrOD)_2$ at (a) 296 K and (c) 104 K. Both spectra are an accumulation of 1024 transients. The simulated spectra for rate constants of 10^6 (b) and 10^1 (d) correspond to the room-temperature and low-temperature experimental spectra, respectively.

the temperature serves to increase the line width.[7] This is due to a slowing of the motion responsible for the narrowing or averaging of the spectrum at room temperature. This phenomenon is also evident in solid-state deuterium NMR experiments as an increase in the inner horn separation with a decrease in temperature. Therefore, motion can also be established if the inner horn separation at room temperature is smaller than at lower temperatures. Both of these factors are evident in the solid-state variable-temperature ^2H NMR spectra of $Ce_2(O^iPr)_8(^iPrOD)_2$. While the T_1's were not directly measured at the two temperatures, arrayed pulse delay experiments clearly showed that the recycle delay for the sample at room temperature, 293 K, was on the order of 10^5 times faster than that at 104 K. In addition, the observed inner horn separation (Figure 2) is 20 kHz narrower at 293 K than at 104 K.

Given that the presence of motion has been established, one can now consider the geometry and rate of that motion. We have modeled this as proton jumping between sites a and b as shown in Figure 3. This model assumes that the O–Ce–Ce–O atoms

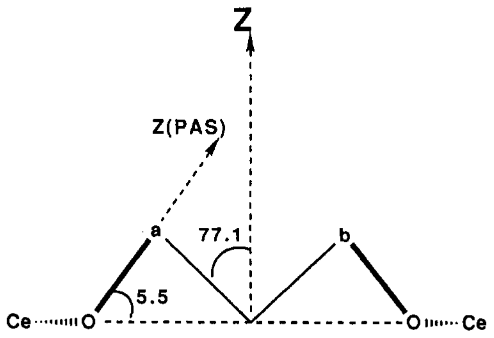

Figure 3. Structural model for the jump of a deuteron between sites a and b. The view is into the edge of the Ce–O–O–Ce plane and shows the z axis of the deuteron principal-axis system (z(PAS)) and the Z axis of the jump from site a to site b.

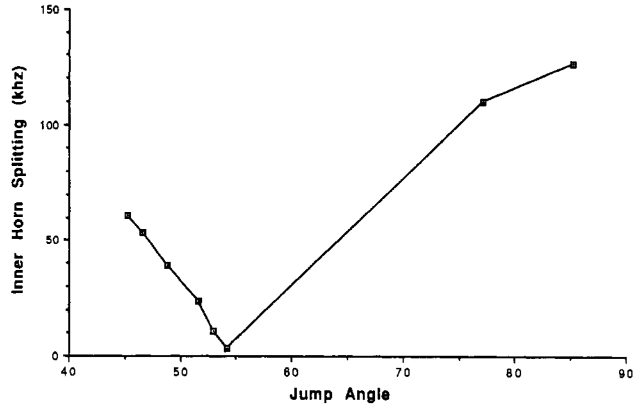

Figure 4. Plot of the calculated inner horn splitting obtained with varying jump angle, θ_j. The rate used was 10^7, thus simulating the fast-limit motion.

are planar (known from the X-ray structure determination) and that the jump axis for the proton is perpendicular to this plane and bisects the O–O direction (Z in Figure 3). A two-site model such as this can be simulated. The basis for the dynamics simulation program used is summarized in a paper by Greenfield et al.[8] and incorporates the rate, the geometry of the motion, and the relative populations of the two sites involved. The type of motion is described by means of the Euler angles needed to go from the principal-axis system (PAS) of the quadrupolar coupling tensor (here, assumed to be along the O–H bond) to the Z axis of the jump frame (Figure 3). For this model, these angles are $(0,\theta,0)$, where θ is $(90 - \angle O\text{–}O\text{–}H) \pm \theta_j$, the jump angle. Because the splitting of the inner horns at 293 K is not much smaller than at 104 K, one can immediately conclude that the proton does not lie far out of the Ce–O–O–Ce plane. This follows because proton hopping wholly in the Ce–O–O–Ce plane (which has inversion symmetry along the O···O line) can be shown rigorously to have no influence on line shape. For this two-site problem, the kinetic matrix is a 2 × 2, with site a able to go to site b, and vice versa, and both sites being equally weighted. Varying the rate of jumping, k, duplicates the static deuterium spectrum (104 K) for $k = 10$, given an experimentally determined (104 K) quadrupolar coupling constant of 171.9 kHz and an asymmetry parameter, η, of 0.0. The motionally averaged spectrum (293 K) is satisfactorily simulated when $k = 10^6$. There is no further narrowing of the simulated spectrum with $k > 10^6$. The dependence of the splitting of the horns on jump angle θ_j in this fast-exchange limit is shown in Figure 4. The line shape of the simulated spectra also changes as the jump angle changes, giving an independent criterion for choosing the optimized calculated jump angle of 77.1°. The O–O distance from the X-ray structure (2.748 Å) and a typical O–H distance (0.97 Å)[9] were then used to calculate an O···O–H

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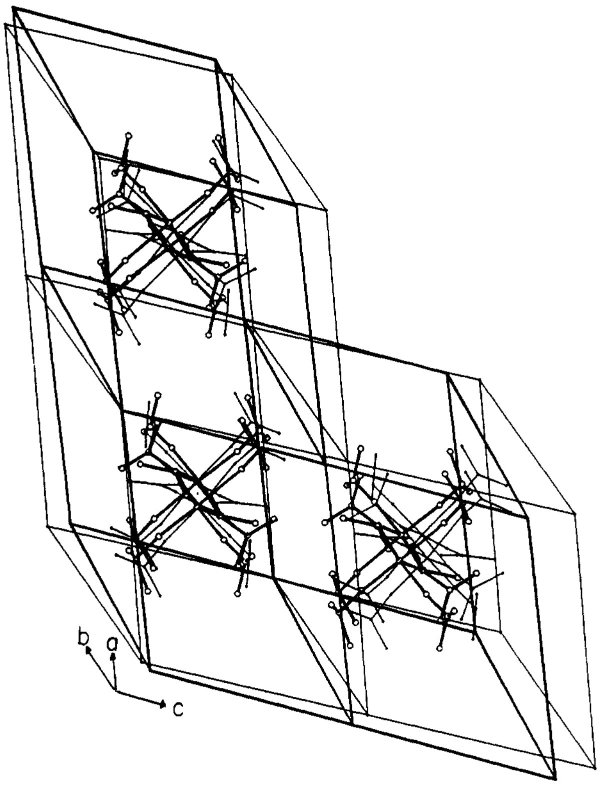

Figure 5. Superposition of three unit cells of $Ce_2(O^iPr)_8(^iPrOH)_2$ at 25 °C (light lines) and −155 °C (heavy lines). See text for criteria used in the superposition.

angle of 5.5° (Figure 3). It is well established from neutron crystallography that hydrogen bonds tend to be nearly linear at hydrogen.[9] Thus, the experimentally determined O···O–H angle of 5.5° is in accord with this trend and lends support to the model chosen for simulating the dynamic ^2H NMR spectra.

As mentioned, the complex undergoes a phase change at −90 °C. This phase change could manifest itself as an intermediate exchange line shape in the ^2H NMR spectrum. Thus, spectra were recorded at −85, −92, and −112 °C. Comparison of these spectra does not reveal any differences other than that expected by lowering the temperature (i.e., slowing the rate of deuteron hopping). Thus, the phase change causes no discontinuity in the solid-state ^2H NMR spectra and therefore must not significantly disturb the deuteron motion or the O–O–H bond angle.

Discussion

In the frequent occurrence that a proton of a coordinated alcohol is not detected in an X-ray structure determination,[10] one can hope that the alcohol will be recognized by its long (compared to alkoxide) M–O distance and its significantly bent M–O–R angle. However, when proton transfer is rapid in the solid state, as we report here, dynamic disorder blurs both of these criteria.

The problem we address here in the room-temperature structure determination of alkoxo/alcohol complexes is less likely to cause problems when the metal is in its highest oxidation state; there is no chance that the room-temperature structure of the cerium compound would lead to the conclusion that the compound is $[Ce^V(O^iPr)_5]_2$. However, when the metal is in less than its highest oxidation state, identical M–O bond lengths could lead to misidentification of $M^{n+}(OR)_n(ROH)$ as $M^{n+1}(OR)_{n+1}$. A closely related example is present in the recent literature.[11] For the case of cerium, disorder would also obscure the truth if the compound were a reduced $[Ce(OR)_3(ROH)_2]_n$ species. The value of low-temperature data collection is thus enhanced for alkoxo/alcohol compounds.

Conclusions which can be drawn from the solid-state deuterium spectra of this complex are that (1) there is motion of the deuteron at room temperature and thus the disorder is dynamic and (2) the angle the O–D bond makes with the Ce–O–O–Ce plane is approximately 5.5°. The jumping motion at room temperature is very fast, being at least 10^6 s^{-1}, and is practically stopped at 104 K.

We have analyzed the orientation of intermolecular contacts in solid $Ce_2(O^iPr)_8(^iPrOH)_2$ in an effort to establish the origin of the highly anisotropic cell edge length changes. Figure 5 shows the best least-squares fit of the structures as determined at 20 and at −155 °C. In this comparison, the centroids of the Ce_2 units in the cells nearest the origin are constrained to be identical. The angular orientations of the cells at the two temperatures have been chosen so as to minimize the square of the distance between the centers of the molecules translated along *a* and along *c*; these are also shown in Figure 5. This drawing reveals that the Ce···Ce direction lies roughly along the *b*-axis direction. The alkoxides in the $(^iPrO)_2Ce(\mu\text{-}O^iPr)_2Ce(O^iPr)_2$ plane determine the size of the molecule along the *b* direction. Since they are in a plane perpendicular to the plane of the hydrogen-bonded $Ce_2(O^iPr)_2(^iPrOH)_2$ unit, they are least influenced by changes in hydrogen-bond dynamics. The relatively normal temperature dependence of the *b*-axis length is thus explained. The plane of the hydrogen bonding bisects the *a*/*c* angle of the unit cell. The onset of hydrogen-bond dynamics would therefore have maximum influence in the *a* and *c* directions. It is in these directions that movement of the hydrogen bonds in two adjacent molecules will interact.

Finally, Steiner, Mason, and Saenger have stated "...it is unlikely that static disorder transforms to order on cooling..." and concluded that, when cooling does create order, the disorder must be of the dynamic type.[12] The present work supports this conjecture.

Experimental Section

Synthesis of $Ce_2[OCH(CH_3)_2]_8[DOCH(CH_3)_2]_2$. Oxygen-deuterated $Ce_2(O^iPr)_8(^iPrOD)_2$ was prepared from $Ce_2(O^iPr)_8(^iPrOH)_2$ (0.60 g) in $(CH_3)_2CHOD$ (2 mL) together with enough pentane to totally dissolve the compound. The solution was stirred in the dark for 30 min at 25 °C. After vacuum removal of the volatiles, this procedure was repeated two times, to give material that showed negligible OH intensity by ^1H NMR spectroscopy.

Solid-State NMR Spectroscopy. The complex was packed into a 5-mm air/tight rotor in a nitrogen atmosphere drybox, protected from light. The spectra were recorded at 61.42 MHz on a previously described[13] home-built 400-MHz spectrometer modified with a TecMag pulse generator and ADC, using MacNMR software. The pulse sequence used was a quadrupole echo, $90°-\tau-90°$, with a τ delay of 50 μs.

Acknowledgment. This work was supported in part by the Department of Energy and by NSF Grant CHE 89 21632.

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