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Variable-Temperature Studies of Order/Disorder Transitions in the Thiourea Pyridinium Halide Crystals by XRD and Solid-State ^{2}H NMR

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Variable-temperature single-crystal X-ray experiments have been performed on the thiourea pyridinium chloride, bromide, and iodide inclusion compounds. Two phases were found for the chloride, three for the bromide, and two for the iodide. As previously reported for the bromide, at room-temperature all three halides were found to form orthorhombic crystals in space group *Cmcm*. For each compound, the pyridinium cation is disordered in the square cross section thiourea channels. On cooling, the chloride undergoes a phase change between 200 and 230 K to give an orthorhombic form in *Pbca* with the *a* axis doubled and the pyridinium ions partially ordered. The bromide undergoes a phase change between 170 and 165 K to a partially ordered form in space group $Cmc2_1$ with the *a* axis tripled. A second phase change occurs between 140 and 150 K to a fully ordered phase in space group $P2_1cn$ with cell dimensions approximately the same as the room-temperature form. The iodide undergoes a single-phase transition at 120−130 K to a fully ordered form isomorphous with the low-temperature form of the bromide. The phase transitions have also been studied by VT ^{2}H NMR of the perdeuteriopyridinium salts. These data have been correlated with the XRD data and with models for the motion of the pyridinium cation.

Introduction

Thiourea has been known from 1947 to form inclusion compounds with a variety of organic guest molecules.[1,2] Usually, the structures have hexagonal channels, the walls of which are a double helix of H-bonded thiourea molecules.[3] These channels fit together in a honeycomb-like system with hexagonal or rhombohedral symmetry. The guest molecules are located in the channels in an array that may be either commensurate or incommensurate with the thiourea array.[4,5] Even when host and guest are commensurate, the guest molecule is frequently disordered.[6] Recently, using variable-temperature (VT) single-crystal X-ray diffraction and ^{13}C solid-state NMR spectroscopy, we have studied the stepwise ordering on cooling of cycloheptane and cyclooctane guests in these channels.[7]

Thiourea pyridinium halides were first prepared by Phillips[8] and the room-temperature structure of the bromide was determined by Truter and Vickery.[9] In this complex, the thiourea molecules form H-bonded ribbons, with four ribbons forming the four sides of a square cross-sectional channel in which the pyridinium ions are located. There is no H-bonding between the ribbons. Where four channels meet, a second type of smaller channel is created in which the bromide anions are located. The pyridinium cation is at a site of crystallographic symmetry 2/*m*, and therefore must have rotational disorder, but the very large anisotropic displacement parameters suggest that the disorder is more complex than this structure requires. We therefore instigated a study of these complexes with VT single-crystal X-ray diffraction and VT ^{2}H solid-state NMR.

Experimental Section

Preparation. d_5-Pyridinium halide (chloride, bromide, and iodide) bis(thiourea) clathrates were prepared by initially adding 99% d_5-pyridine dropwise with stirring to a stoichiometric amount of concentrated hydrohalo-acid. The reaction mixture was left to cool, and lyophilized overnight. The crude

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Table 1. d_5-Pyridinium Iodide Bis(thiourea) Clathrate: Crystal Data and Experimental Details

temperature (K)	110	295
formula	$(S{=}C(NH_2)_2)_2{\cdot}C_5H_6NI$	
M_r	359.25	
crystal size (mm)	0.2 × 0.2 × 0.15	0.6 × 0.3 × 0.2
crystal habit	needle	
crystal system	orthorhombic	
space group	$P2_1cn$	$Cmcm$
a (Å)	14.869(4)	15.119(6)
b (Å)	11.312(5)	11.230(6)
c (Å)	8.305(4)	8.327(6)
volume (Å$^{3)}$	1396.89	1413.73
Z	4	4
radiation wavelength (Å)	0.7107	0.7107
ρ_{calc} (g cm^{-3})	1.708	1.688
μ (mm^{-1})	25.35	25.05
$\theta_{min}, \theta_{max}$ (°)	$2.26 \rightarrow 26.52$	
h_{min}, h_{max}	$-18 \rightarrow 0$	$-18 \rightarrow 18$
k_{min}, k_{max}	$0 \rightarrow 14$	$0 \rightarrow 13$
l_{min}, l_{max}	$0 \rightarrow 14$	$-9 \rightarrow 9$
measured data	1445	2163
unique data	1445	717
observed data ($I > 3\sigma(I)$)	1274	695
R_{merge}		0.0202
no. parameters refined	151	52
resid. electron density (eÅ^{-3})	−1.02, 0.86	−1.34, 0.70
R, R_W	0.0350, 0.0379	0.0436, 0.0661

pyridinium halide was purified by recrystallization from ethanol. Stoichiometric quantities of thiourea and the deuterated pyridinium salt were dissolved in the minimum quantity of boiling ethanol, and on cooling, yellow-white needlelike crystals of the clathrate separated. The crystals were filtered, washed with ethanol, and dried under vacuum. For the XRD measurements, the clathrates were recrystallized from ethanol. Elemental analysis was performed by the Analytical Service of the Inorganic Chemistry Laboratory. C,H,N were determined by combustion and halogens by ICP-AES. Results are consistent with a thiourea−pyridinium ratio of 2:1. (exp/calcd d_5-pyridinium iodide bis(thiourea) clathrate ($C_7H_9D_5N_5S_2I$): H+D, 3.60−3.65/4.09%; C, 23.02/23.08%; N, 18.17−18.96/19.22%; I, 33.69−33.87/ 33.84%. d_5-Pyridinium bromide bis(thiourea) clathrate ($C_7H_9D_5N_5S_2Br$): H+D, 4.32−4.39/4.69%; C, 26.41−26.45/26.50%; N, 21.50−21.54/22.07%; Br, 24.48−24.55/25.18%. d_5-Pyridinium chloride bis(thiourea) clathrate ($C_7H_9D_5N_5S_2Cl$): H+D, 4.70−4.91/5.46%; C, 26.67−30.98/30.82%; N, 23.32−24.54/25.67%; Cl, 10.77−10.84/12.99%).

Single-Crystal X-ray Diffraction. For measurements at room temperature, suitable crystals were mounted on a glass fiber with Superglue. For measurements at 265 K and below, the crystals were placed in a drop of perfluoropolyether oil in a fiber loop. The crystals were then placed in the cold gas stream of an Oxford Cryosystems Cryostream cooler on a MAR or an Enraf-Nonius DIP2020 image plate diffractometer or a MACH3 serial diffractometer and cooled to the required temperature. The low-temperature limit of the Cryostream coolers in our laboratory varied from time-to-time within the region 80−90 K. The variable-temperature measurements that led to the identification of the different phases of these compounds are described in detail in the Supporting Information.

Single-crystal X-ray diffraction intensity data sets were obtained for all different phases. Relevant details of the crystallography for the different systems are given in Tables 1−3 and more extensively in the Supporting Information Tables S1−7. Data reduction included Lorentz and polarization corrections. The frames from the image plate (MAR or DIP2020) diffractometers were processed with the HKL (Denzo)[10] software. A semiempirical (ψ-scan)[11] absorption correction was applied to the MACH3 data, but no correction was used with the image plate data where the interframe scaling takes some account of absorption effects. All structures were solved by direct methods (SIR92[12]) which yielded all non-hydrogen atom positions for each of the three salts (except the atoms of the pyridinium cation in the ambient temperature structures). Positional and first isotropic, and then atomic displacement, parameters for the non-hydrogen atoms were refined to convergence by the least-squares method, minimizing $\sum w(F_{obs} - F_{calc})^2$ for all observed reflections. The full normal matrix was used together with a Chebychev polynomial weighting scheme.[13] Restraints were applied to the anisotropic displacement parameters and to the geometry of the pyridinium ions to stabilize the refinement. Hydrogen atoms were included in the models at geometrically idealized positions when there was reasonable indication of H-atom positions in the difference electron density. Final residuals are given in Tables 1−3. At ambient temperature, the pyridinium cations are necessarily disordered from the space group symmetry, and the chosen atomic positions are barely resolved maxima in an annulus of diffuse difference electron density.

Except where indicated to the contrary, the Oxford CRYSTALS[14] system was used for all crystallographic calculations and CAMERON[15] was used for crystallographic drawings. Scattering factors were taken from International Tables for Crystallography.[16] The atomic coordinates, atomic displacement parameters, bond distances and angles, and interionic contact and H-bond distances, Tables S1 − S7, are available as Supporting Information.

Solid-State ^{2}H NMR. All ^{2}H NMR spectra were recorded at 61.42 MHz with a Bruker MSL400 spectrometer employing a wideline probe with a 7 mm horizontal solenoid coil. The temperature control unit was a Bruker B−VT1000 equipped with a copper−constantan thermocouple and a digital reference. The temperatures were accurate to within ±1 K and were stable to ±0.1 K. The sample was thermally equilibrated for at least 30 min at each temperature before spectral accumulation was commenced. About 1 g of sample was packed into a 7 mm diameter glass tube, topped with a wad of glass wool, and sealed with epoxy resin. The quadrupolar spin−echo technique with standard precautions and phase recycling was used for acquiring all spectra. All spectra were recorded with quadrature detection. Typically, 3.0 μs 90° pulses and spin−echo delay times of $\tau = 25$ μs were employed.

The spectra of the iodide clathrate were recorded at 5 K intervals from 110 to 180 K, and then 10 K intervals to 200 K and 20 K intervals to 400 K. The spectra of the bromide were recorded at 10 K intervals from 120 to 330 K, and the spectra of the d_5-pyridinium chloride bis(thiourea) clathrate were recorded at 20 K intervals from 140 to 400 K. Powder pattern simulations were performed using local software, calculating the line-shapes arising from motions in the fast limit (rate > 10^7 Hz) using order parameter theory.[17,18] Calculated patterns were corrected for power roll-off due to finite radio frequency pulses by applying a Bloom-type correction[19] in the frequency domain. Further details on the ^{2}H NMR spectroscopy and simulations can be found elsewhere.[20]

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Table 2. d_5-Pyridinium Bromide Bis(thiourea) Clathrate: Crystal Data and Experimental Details

temperature (K)	100	150	295
formula	$(S{=}C(NH_2)_2)_2{\cdot}C_5H_6NBr$		
M_r	312.25		
crystal size (mm)	0.45 × 0.45 × 0.8	0.22 × 0.25 × 0.95	0.15 × 0.15 × 0.35
crystal habit	needle		
crystal system	orthorhombic		
space group	$P2_1cn$	$Cmc2_1$	$Cmcm$
a (Å)	14.431(2)	44.128(6)	14.771(7)
b (Å)	10.984(2)	10.7890(6)	10.897(4)
c (Å)	8.291(5)	8.351(1)	8.368(2)
volume (Å^3)	1314.21	3975.99	1346.95
Z	4	12	4
radiation wavelength (Å)	1.5418	0.7107	0.7107
ρ_{calc} (g cm^{-3})	1.58	1.57	1.53
μ (mm^{-1})	7.08	3.35	3.29
$\theta_{min}, \theta_{max}$ (°)	5.06 → 75	0 → 75	0 → 25
h_{min}, h_{max}	−18 → 0	−54 → 54	−1 → 19
k_{min}, k_{max}	0 → 13	0 → 13	−1 → 14
l_{min}, l_{max}	−18 → 0	0 → 10	−2 → 10
measured data	1579	6034	1140
unique data	1400	2176	853
observed data ($I > 3\sigma(I)$)	1366	1912	580
R_{merge}	0.03	0.04	0.025
no. parameters refined	137	209	41
resid. electron density (eÅ^{-3})	−0.51, 0.78	−2.11, 0.92	−0.304, 0.594
R, R_W	0.035, 0.050	0.059 0.057	0.041, 0.047

Table 3. d_5-Pyridinium Chloride Bis(thiourea) Clathrate: Crystal Data and Experimental Details

temperature (K)	110	265
formula	$(S{=}C(NH_2)_2)_2{\cdot}C_5H_6NCl$	
M_r	267.80	
crystal size (mm)	0.1 × 0.22 × 0.65	0.1 × 0.22 × 0.65
crystal habit	needle	
crystal system	orthorhombic	
space group	P*bca*	$Cmcm$
a (Å)	29.021(1)	14.563(8)
b (Å)	10.418(1)	10.561(4)
c (Å)	8.374(5)	8.398(2)
volume (Å$^{3)}$	2531.67	1291.65
Z	8	4
radiation wavelength (Å)	1.5418	1.5418
ρ_{calc} (g cm^{-3})	1.405	1.377
μ (mm$^{-1)}$	5.60	5.485
$\theta_{min}, \theta_{max}$ (°)	3.05 → 73.92	5.17 → 74.43
h_{min}, h_{max}	−28 → 0	−18 → 18
k_{min}, k_{max}	0 → 10	0 → 13
l_{min}, l_{max}	0 → 8	0 → 10
measured data	2026	1478
unique data	2026	733
observed data ($I > 3\sigma(I)$)	1861	672
R_{merge}		0.046
no. parameters refined	137	42
resid. electron density (eÅ^{-3})	−0.47, 0.82	−0.81, 0.87
R, R_W	0.073, 0.0980	0.0817, 0.0558

Results

Single-Crystal X-ray Diffraction. Examination of the unit cell dimension of the three clathrates at ambient temperature confirms the work of Truter and Vickery.[9] The compounds are isomorphous and in space group $Cmcm$. On cooling, each behaves somewhat differently.

At 120 K, the iodide transforms to a phase with a primitive lattice, space group $P2_1cn$, which persists to 85 K, our lower temperature limit. The nonstandard space group setting was chosen for the low-temperature form so that the crystal directions were self-consistent at all temperatures. The bromide transforms at 165 K to a new phase with the a axis tripled. The lattice remains C-centered, but (from the subsequent structure analysis) the space group is changed to $Cmc2_1$. Below 150 K, a third phase is formed in space group $P2_1cn$ that is the same as that found for the iodide. For the chloride complex below 200 K, a new phase is formed with space group $Pbca$ and a doubled a axis. On further cooling to the low-temperature limit of the Cryostream (90 K), no other changes are observed. A full data set was collected at 110 K. On returning to 265 K, the crystal returns to the room-temperature form. For each compound, the variations of unit cell dimension with temperature are detailed in the Supporting Information.

Thus each of the three clathrate compounds shows one (or two) reversible thermal events on cooling. For the chloride, the event occurs over a quite broad temperature range in the region 200−230 K. For the bromide, there are two events, one at 165−170 K and the other at 140−150 K, both of which occur in a much smaller temperature range than for the chloride. For the iodide, the change occurs in the region 120−130 K and is quite sharp, but argueably not as sharp as that for the bromide. Since all of the crystals undergo these phase changes with the retention of crystallinity to a very high degree, it has been possible to determine the structures of the phases above and below the transition temperatures.

The low-temperature forms of the bromide and iodide are assumed to represent the fully ordered form of the structure. At 100 K, the crystals are orthorhombic, with space group $P2_1cn$ (a nonstandard setting of space group No. 33, $Pna2_1$) and one pyridinium cation, one bromide anion, and two thiourea molecules in the asymmetric unit (Figure 1). The principal structural motif is a bowed hydrogen-bonded thiourea ribbon. Each ribbon contains two crystallographically distinct thiourea molecules. Four ribbons, each with its long axis parallel to the c axis and mean plane parallel to (110), $(\bar{1}10)$, $(1\bar{1}0)$, and $(\bar{1}\bar{1}0)$, form a channel parallel to the c axis with an approximately square cross section. For a given channel, two adjacent ribbons have their convex surfaces facing into the channel and the remaining two have their concave surfaces facing into the channel. In each channel, there is a stack of pyridinium cations. The nitrogen atoms of the pyridinium cations are unambiguously located and are H-bonded to the sulfur atoms S(2) (for

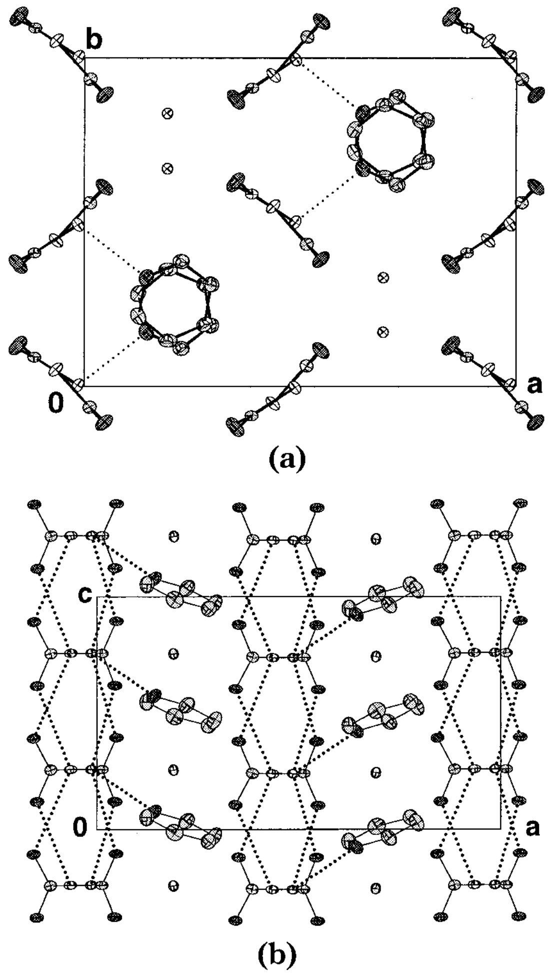


Figure 1. Structure at 110 K of the bis(thiourea) pyridinium bromide: views along the (a) *c* and (b) *b* axes. Similar diagrams of the iodide are given in the Supporting Information.

Table 4. Orientation of the Plane of the Pyridinium Cations

	ab	*ac*	*bc*
Cl 110 K	157.1	71.5	103.1
Br 110 K	156.8	78.7	109.9
I 110 K	157.0	81.4	111.2
Br 150 K (ring 1)	158.3	73.7	103.9
Br 150 K (ring 2)	163.7	73.7	90.0
Cl RT	161.9	71.9	90.0
Br RT	165.5	76.1	90.0
I RT	173.2	83.3	90.0
Br RT simulated	167.4	77.1	90.0
I RT simulated	170.6	80.6	90.0

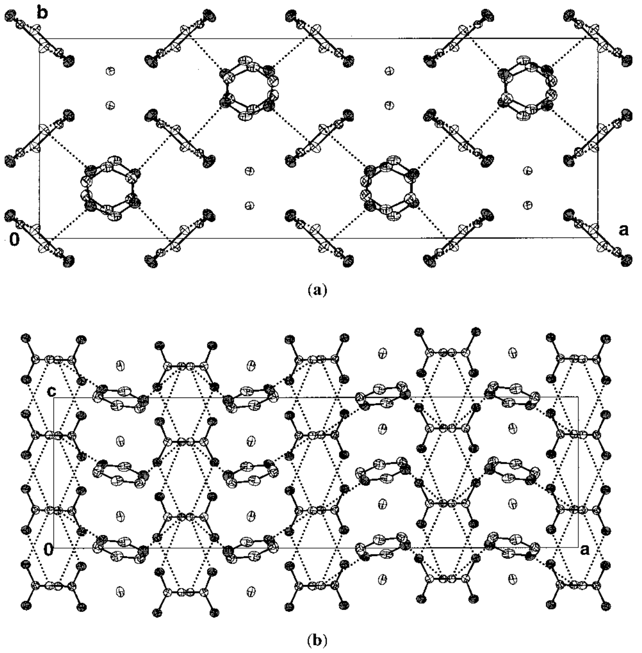


Figure 2. Bis(thiourea) pyridinium chloride at 110 K: views along the (a) *c* and (b) *b* axes.

the bromide N−H···S, 3.260(5) Å, cf. N−H···S within the thiourea ribbons, 3.331(5)−3.383(5) Å, Table S2i; for the iodide N−H···S, 3.285(6) Å, cf. N−H···S within the thiourea ribbons, 3.337(6)−3.394(6) Å, Table S5i) on the convex surface of the ribbon. This hydrogen bonding results in a displacement of the pyridinium ions from the center of the channels (to the left in Figure 1). These displacements are along the *a* axis, the polar direction of the crystal. The orientations of the pyridinium cations in the channels are conveniently described by the angles that the normals to the pyridinium plane make with the *bc*, *ac*, and *ab* crystal planes. These angles are given in Table 4. Viewed along the *b* axis, (Figure 1), the pyridinium cations form a herringbone pattern. The anisotropic displacement parameters of the thiourea molecules are of a magnitude consistent with the temperature of the analysis, those of the pyridinium group are a little larger than those of the thiourea molecule, and those of the pyridinium group in the iodide a little larger than those in the bromide.

Where four channels come together, a second type of channel, parallel to the *a* axis, is created and is filled with bromide anions (Figure 1). The six shortest contacts to the anions are two cis contacts to two thiourea sulfur atoms and four contacts (possibly N−H···X H-bonds) to the nitrogen atoms of two other thiourea molecules, to give a pseudo-square-planar arrangement. These short contacts suggest sheets parallel to the *ab* plane. The halide ions do not form short contacts to neighboring sheets. The halide ion environments are not significantly different in the higher temperature forms of the clathrates.

These ordered low-temperature structures contrast with the structure of the chloride salt found between 200 and 85 K. The latter appears to have some residual disorder. The structure is basically similar to that of the bromide and iodide but (1) the crystals are centrosymmetric, *Pbca*, (2) the thiourea ribbons are flat rather than bowed, (3) the pyridinium nitrogen atoms are not unambiguously identifiable, and (4) the pyridinium cations appear to be central in the channels (Figure 2). None of the atoms of the pyridinium cation makes sufficiently close approaches to the sulfur atoms for S···H−N H-bonds to be identified. The shortest contacts from the ribbon sulfur atoms to the pyridinium atoms are S(10) to two symmetry related atoms N(35), (3.654 and 3.730 Å), S(20) to N(31) (3.614 Å); cf. S(10) to N(10) and N(11), S(20) to N(20) and N(21) within the thiourea ribbons at distances of about 3.3−3.4 Å (Table S7 g). The pyridinium cations in the channels have their planes inclined at an angle of 157.1° to the *ab* plane and 71.5° to the *ac* plane, Table 4. These angles of inclination of the pyridinium cation are remarkably similar to those found in the ordered low-temperature

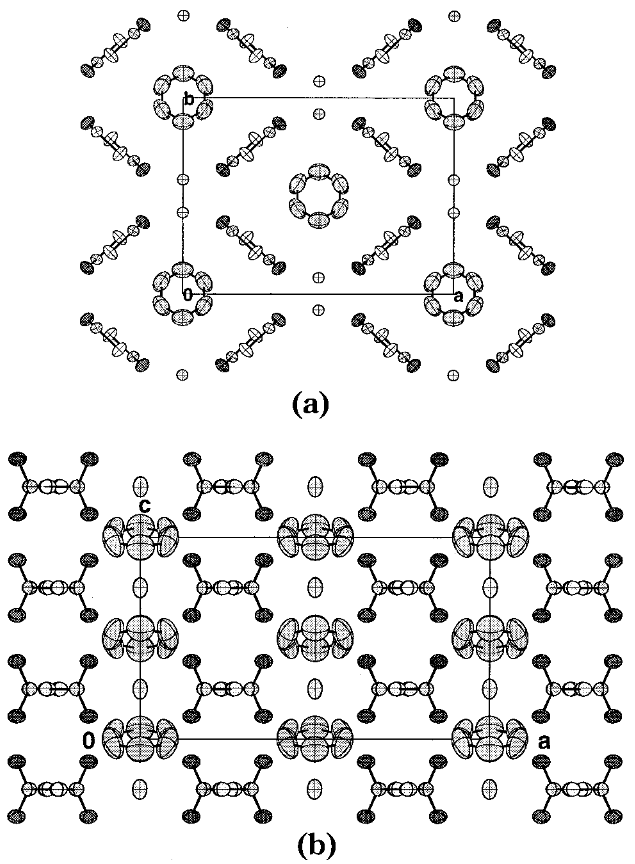


Figure 3. Room-temperature structure of the bis(thiourea) pyridinium chloride: views along the (a) *c* and (b) *a* axes. Similar diagrams of the bromide and iodide are given in the Supporting Information.

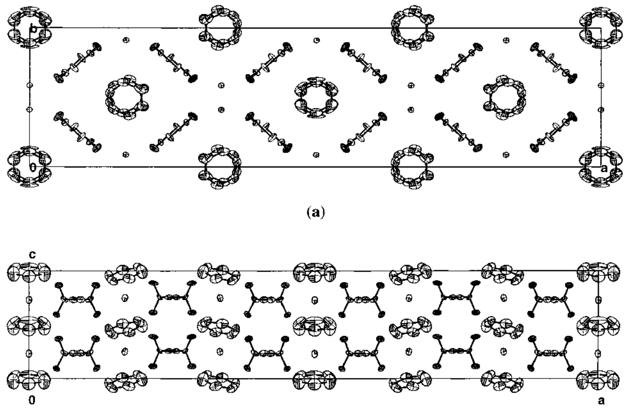
forms of the bromide and iodide. The behavior of the pyridinium cation is best described as a 2-fold rotational disorder of the ring that allows the cation to be H-bonded to the thiourea sulfur atoms in either the $+a$ or the $-a$ directions, thus making the *a* axis nonpolar (in contrast with the situation in the low-temperature structures of the bromide and iodide). If the disorder is dynamic, the nitrogen atom position interchange can be achieved by either a 120° in-plane reorientation or a 180° out-of-plane flip.

The structure of the ambient temperature form of each of the halide salts is that previously described by Truter and Vickery.[9] The structure of the chloride is shown in Figure 3. (Analogous drawings of the bromide and iodide are included in the Supplementary Material.) The structures reveal the same general structural features (the thiourea ribbons, the pyridinium channels, and the halide channels) as the low-temperature forms. However the symmetry is much higher. The pyridinium cations are at sites of symmetry $2/m$, and the hexagonal ring is described by only two independent atoms. One is in the mirror plane, and the other one lies in a general position. Thus, the hexagonal ring has the same relationship to each of the four surrounding thiourea ribbons. The isotropic displacement parameters for these atoms are very large and do not represent the TLS motion of a planar hexagonal entity, The ribbons are flat, and the anisotropic displacement ellipsoids, most noticeably of the sulfur atoms, are elongated perpendicular to the ribbon plane. The whole picture is strongly symptomatic of a disordered structure in which the various displacements in the disorder are quite small. Very comparable anisotropic displacement parameters amongst the structures suggest that the dynamic behavior of the three halides at ambient temperature is very similar.

A model that reproduces the essential features of the ambient temperature halide structures may be obtained from the low-temperature structures in the following manner. First, the origin of the asymmetric unit was shifted so that the coordinates of the halide ion were the same as those in the high-temperature structure; then the symmetry operators of space group *Cmcm* were applied. For the iodide, the resulting crystal structure was then refined against the room-temperature structure amplitudes with the following simplifications. The hydrogen atoms were ignored. The pyridinium ion was refined as a group defined by the coordinates of the center of the group, the direction cosines of the least-squares best plane of the group, and a single isotropic temperature factor. The thiourea groups were defined by one carbon atom, one nitrogen atom, and two-half-occupancy sulfur atoms, all with isotropic temperature factors. Only the iodide ion was refined anisotropically. The refined structure has well-behaved temperature factors and an *R* value of 0.052. This model has 4-fold disorder of the pyridinium ions with each pyridinium cation hydrogen bonded to any one of the four surrounding thiourea chains. Dynamically, the pyridinium group might be presumed to execute a series of in-plane reorientations and/or out-of-plane flips from one H-bonding position to another while simultaneously the thiourea ribbon flexes as pyridinium cations H-bond to one side or another.

Examination of the difference electron density map obtained using F_{calc} and phases based only on the halide and thiourea suggests that the pyridinium cation might be represented equally well by a torus of diffuse electron density rather than individual atoms. The pyridinium cation in the bromide was modeled in this way and the structure refined. The difference electron density calculated at the convergence of the refinement shows some vestiges of individual atomic peaks. Therefore, the model was refined to include partially occupied atomic sites embedded in the torus of diffuse density. The structure was further refined, and the difference electron density was calculated.

The bromide has an intermediate phase in the temperature range 150−165 K. The crystals, the structure of which was determined at 150 K, are orthorhombic with space group $Cmc2_1$, and one and a half pyridinium cations, one and a half bromide anions, and three thiourea molecules in the asymmetric unit (Figure 4). The *b* and *c* axes are approximately the same as those at 90 K, but the *a* axis is trebled. The overall structure is very similar to that at 90 K; the thiourea molecules form H-bonded ribbons, the ribbons form channels filled with pyridinium cations, and when these channels pack together, a second type of channel is formed and filled with the bromide ions. There are, however, subtle differences. The ribbons come together to form two types of square channel; one bounded only by S(4), S(5) type ribbons (**A** channels) and the second bounded by two adjacent S(3) ribbons and two S(4), S(5) ribbons (**B** channel). There are twice as many **B** as **A** channels.



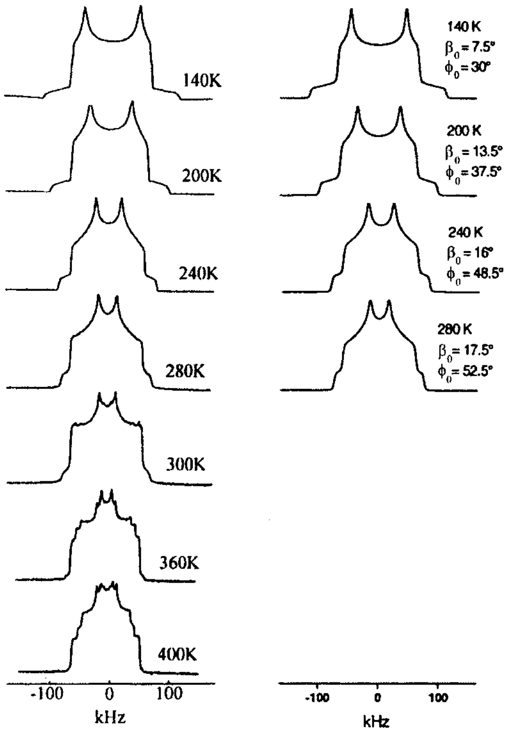
(a)

(b)

Figure 4. Structure of the bis(thiourea) pyridinium bromide at 150 K: views along the (a) *c* and (b) *b* axes

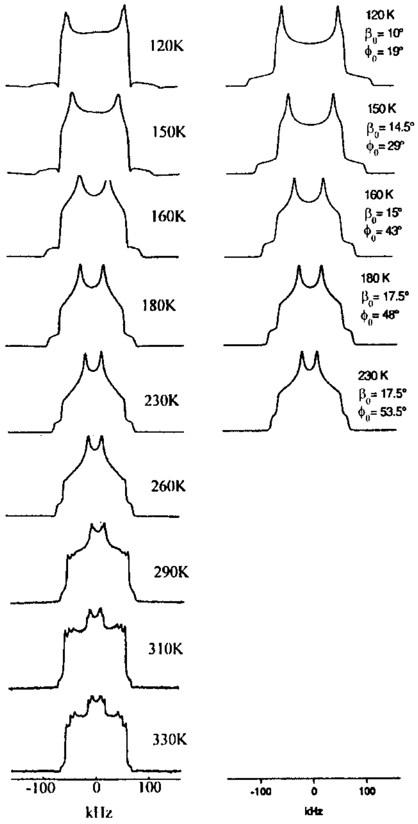
The pyridinium cations containing C(21−26) stack in the **B** channels and those containing C(30−33) (that is the pyridinium cation lying about the crystallographic mirror plane) stack in the **A** channels. Both pyridinium cations have atomic displacement ellipsoids that are noticeably larger than those found in the thiourea molecules. The ellipsoids of the cation containing C(30−33) are larger than those of the other cation. It is impossible to distinguish the nitrogen atom in either type of cation. The C(21−26) pyridinium cations appear to be behaving in a manner similar to the cations in the low-temperature form of the chloride, whereas the C(30−33) cations seem to be behaving in a manner similar to the cations in the ambient temperature structures.

Solid-State ^{2}H NMR. Many of the structures described above display a significant disorder of the pyridinium molecules, and in order to obtain some information about the dynamics involved we have performed variable temperature ^{2}H NMR experiments. In ^{2}H NMR spectroscopy, the spectrum is dominated by the interaction between the ^{2}H quadrupole moment eQ and the electric field gradient (EFG) described by a tensor with principal component eq_{zz}. The strength of the quadrupolar interaction can be measured by the nuclear quadrupolar coupling constant χ $(=e^2q_{zz}Q/h)$. Molecular motions may reduce the values of the principal components of the EFG tensor (V_{xx}, V_{yy}, and V_{zz}) and hence the width and shape of the spectral lines. EFG tensor values can be extracted from the characteristic splitting of the spectra and compared to the values for a static pyridine molecule[21] to give insight into the nature of the motion involved. Line-shape simulations can be performed to test specific motional models. This is particularly valuable if the molecular motions are in the range 10^4−10^7 s^{-1} where the line-shapes are highly sensitive to both the rate and the geometry of the motion.[17,18]



(a) (b)

Figure 5. Experimental (a) and simulated (b) deuterium NMR line-shapes between 140 and 400 K for the bis(thiourea) pyridinium chloride clathrate.



(a) (b)

Figure 6. Experimental (a) and simulated (b) deuterium NMR spectra for the bis(thiourea) pyridinium bromide clathrate.

Samples of the ^{2}H NMR spectra of d_5-pyridinium chloride, bromide, and iodide bis(thiourea) clathrates at different temperatures are shown in Figures 5−7 respectively; more complete information is included in the Supporting Information, Figures S8 − S10. At low temperature, the spectra for all of the clathrates have a similar appearance, and are narrowed compared to that characteristic of a static pyridinium ion. This

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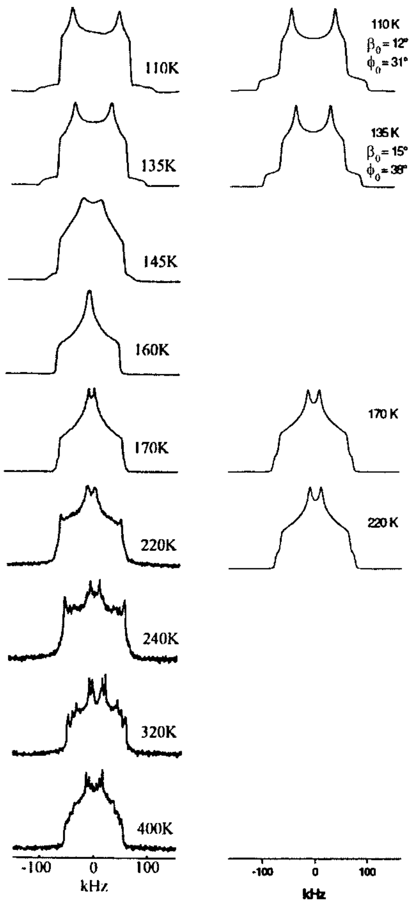
[21] Barnes, R. G.; Bloom, J. W. *J. Chem. Phys.* **1972**, *57*, 3082.



(a) (b)

Figure 7. Experimental (a) and simulated (b) deuterium NMR line-shapes between 140 and 400 K for the bis(thiourea) pyridinium iodide clathrate.

provides direct evidence that motional averaging is taking place at these temperatures. The line-shapes are compatible with a motion that is mainly confined in the plane of the pyridinium ring and taking place in the fast limit relative to the ^{2}H NMR time scale (>10^7 Hz). The amplitude of the motion can be seen to increase with temperature, resulting in a reduction in the nuclear quadrupolar coupling constant χ and in an increase in the asymmetry parameter η of the spectrum. The in-plane motion does not affect the value of the component of the EFG tensor lying perpendicularly to the ring plane (V_{yy}), and the observed values are, at least at the very low temperatures, close to that characteristic of the static tensor (~66 kHz). As the temperature increases, there is an increasing low-amplitude, out-of-plane motion resulting in smaller values for this component, and reducing the breadth of the spectra. One of the simplest ways to include in the simulation such a contribution is to assume a wobbling motion resulting in the reduction of the nuclear quadrupole coupling constant.[22,23] The amplitude of the wobbling component is expected to increase with the temperature. For the simulation presented here, the wobbling motion was modeled by the reorientation of the normal of the pyridinium ring over the surface of a cone of half-angle β_0. The simulations displayed in Figures 5−7 have been obtained from the continuous libration motion including the out-of-plane contribution as a wobbling type motion. If the same model of motion is assumed in the three clathrates, it is possible to compare the extent of this motion directly from the reduction of the principal values of the EFG tensor, or from the estimation of the angular range.

However, as the motions are in the fast limit, several models of motion are in general compatible with the observed line-shapes.[24] The first and simplest in-plane motion to be considered involves a continuous libration of the pyridinium ring over a restricted angular range between two azimuthal angles, $\pm\phi_0$, assuming a square potential well. Alternatively, the line-shapes can be simulated using a model involving a large number of discrete sites to mimic the continuous character of the motion.[20,25] The low-temperature motions can be also simulated using a model with discrete jump processes between distinct sites equally spaced and populated in the plane of the pyridinium ring. With a model involving only two positions, the observed line-shapes for pyridinium chloride match the simulated pattern with the two sites separated by an angular range of ±20° at 140 K and ±35° at 240 K. Other discrete models can be used and lead to similar results. Increasing the number of sites and the angular range gives results similar to those obtained using the continuous restricted libration motion considered before.

The temperature dependence of the deuterium line-shape is simplest for the pyridinium chloride with a continuous variation of line-shape from 140 to 260 K. Between 200 and 230 K, in the temperature range where the phase transition is observed by XRD, the changes in the spectra seem to offer no evidence of any phase change or other significant event. However, simulation indicates a larger temperature coefficient of the increase in the extent of both the in-plane and wobbling motions between 140 −200 K than between 240−280 K. Above 300 K the onset of a new motion is detected, superposed on the in-plane libration. Between 300 and 340 K, the "shoulder" of the spectrum tends to increase, providing evidence for out-of-plane motion with intermediate rate relative to the NMR time scale. At higher temperatures the shoulders decrease reflecting a further averaging of the EFG tensor, and the powder pattern appears to be the superposition of at least three different spectra giving a complex line-shape. This does not match the simulation model with simple motions and it does not prove possible to provide a detailed description of the motion in this temperature regime.

The temperature dependence of the deuterium pattern for the bis(thiourea) bromide clathrate is very similar to that of the chloride (Figure 6). Spectra corresponding to the fast limit of the in-plane motion are found in the temperature range 120−260 K. These can be simulated using the same combination of in- and out-of-plane motion, as used for the other clathrates, with an increasing extent as the temperature is raised. Between 150 and 160 K, the line-shapes in the spectrum

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(22) Aliev, A. E.; Harris, K. D. M.; Mahdyarfar, A. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2017.

(23) Facey, G. A.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem.* **1995**, *99*, 12249.

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(25) Armstrong, P. A.; Bell, A. T.; Reimer, J. A. *Solid State NMR* **1993**, *2*, 1.

are significantly narrowed, notably ν_{xx} and ν_{zz}, indicating that the angular range of the in-plane motion has increased more in this 10 K temperature region than between 120 and 150 K or between 160 and 230 K. This behavior, found near the transition temperature resulting in the formation of the intermediate phase, can be seen clearly in the simulations. The angle of in-plane libration ϕ_0 shows a large increase (from 29° at 150 K to 43° at 160 K). There is also a discontinuous jump in the value of β_0 at the transition. Spectra between 180 K and 260 K are still modelled in the fast limit; the onset of further intermediate time scale motion occurring only above 260 K. Line-shapes above 270 K show a close resemblance to those in the high-temperature spectra found for the bis(thiourea) pyridinium chloride clathrate. Between 280 and 330 K, the spectra are virtually identical to the spectra of the chloride in the same temperature range, indicating that the motions involved are likely to be closely similar.

For the bis(thiourea) pyridinium iodide, a regime of fast in-plane motion is evident between 110 and 140 K. The line-shapes can be simulated in a manner similar to those for the pyridinium chloride and bromide and show significantly larger amplitudes of in-plane libration (ϕ_0), though not wobbling of (β_0), compared to the chloride and bromide clathrates at the same temperatures. In the temperature range 145–155 K, the line-shapes are perturbed with the onset of some additional motion. The spectra are suggestive of motions at intermediate rates, but no significant diminution of the signal intensity and no extra line broadening are observed compared to those of the previous spectra. Moreover the spectrum at 160 K appears to be a completely nonaxial powder pattern with an effective asymmetry parameter η close to 1, yet spectra above 170 K are in the fast limit and display a different powder pattern. These unusual line-shapes could be attributed to the phase change detected between 120 and 130 K in the X-ray investigation though it is unclear why X-ray and NMR techniques detect it at such different temperatures. The line-shapes recorded between 170 and 200 K are characteristic of fast-limit spectra, and can be simulated as resulting from a 180° ring flip around the C_2 axis of the pyridinium ring, (see 170 K simulation in Figure 7). Above 200 K the spectra show the onset of further motions at an intermediate rate. This is indicated by the general reduction in signal strength, the distortion of the line-shapes, and the sensitivity to the length of the echo delay time. The high-temperature spectra are the result of the superposition of several averaged EFG tensors with different principal values and large apparent asymmetry parameters, giving rise to extremely complex line-shapes. This additional motion does not reach the fast limit regime at 400 K; there is still evidence of intermediate rate character in the spectra.

These spectra most closely resemble a combination of typical solid and liquid crystalline lineshapes.

Conclusions

Crystallographic data at low temperatures (110–120 K) show the existence of a fully ordered phase for the bis(thiourea) pyridinium iodide and bromide complexes. In the same temperature range, the solid-state NMR line-shapes are consistent with in-plane librations of the pyridinium ions coupled with a small out-of-plane wobble motion. The amplitudes of these motions are consistent with the amplitudes of the atomic displacement parameters found in the crystallographic structure determination. The extent of these motions increases as the temperature is raised. For the bis(thiourea) pyridinium chloride clathrate, residual disorder has been found in the structure determined at 110 K. Notably, the position of the nitrogen cannot be defined unambiguously. The ordered low-temperature form has not been observed for the chloride salt, but this may be because the ordering takes place below 90 K, i.e., below the temperature range studied here. At 140 K, the lowest temperature at which solid-state NMR spectra were recorded, the line-shapes for the chloride salt indicate an extent of motion similar to that found for the bromide at the same temperature. Above 140 K, the narrowing of the line-shape is more marked for the iodide compound, followed by the bromide, and then the chloride. These differences in the extent of the motion are consistent with the relative amplitudes of the atomic displacement parameters, and reflect the different degree of disorder affecting the three compounds.

For the bis(pyridinium) iodide, the phase change detected between 120 and 130 K from the variation in the X-ray diffraction pattern is apparently observed in the solid-state ^{2}H NMR experiments at higher temperature (140–150 K). This difference in the transition temperatures detected by the two techniques can be rationalized if a gradual phase change is assumed. NMR is sensitive to a much shorter range order than X-ray diffraction patterns, and only the onset of a fully ordered new phase will give rise to new sharp diffraction peaks in the X-ray diffraction pattern. By contrast, the phase changes observed for the bis(thiourea) pyridinium chloride and bromide are only observable by more subtle variations in the degree of the temperature dependence of the line-shapes, corresponding to discontinuities in the temperature dependence of the motional amplitudes of simple simulation models. From the ^{2}H NMR VT experiments, the bis(thiourea) pyridinium iodide has been found to have an additional motion, a 180° ring flip in the fast limit, detected in the temperature range 170–190 K but not clearly observed in the two other clathrates (though it may be present at higher temperatures in the superposition of spectra which we are unable to deconvolute).

The atomic displacement parameters for the phases present at room temperature have similar shape for the three halides, suggesting that the dynamic behavior is similar in all compounds. This observation is also consistent with the similarity found for the deuterium line-shapes for the three clathrates above 300 K. These line-shapes suggest a complex motion involving the fast libration found at low temperature with an additional out-of-plane contribution at the higher temperature. It is pertinent to note that the onset of such intermediate regime motion does not correspond to any detected phase change for any of the clathrates. It occurs at approximately the same temperature for the chloride and bromide (~280 K) and at lower temperature for the iodide (~200 K). This provides further evidence as already observed,[26] that substantial molecular motion may take place without any major change in crystal lattice or symmetry.

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Supporting Information Available: Tables of X-ray data collection and refinement parameters, atomic position parameters, and anisotropic displacement parameters, as well as bond lengths and angles, torsional angles and hydrogen bonds for the bis(thiourea) pyridinium iodide at 295 K (table S1) and 110 K (S2), bis(thiourea) pyridinium bromide at 295 K (S3), 150 K (S4), and 100 K (S5), bis(thiourea) pyridinium chloride at 295 K (S6) and 110 K (S7); full details of variable-temperature XRD and a complete set of VT d_5-pyridinium solid-state NMR spectra and simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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