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 22. On 4 June 1984, temperatures in Atlanta during the daylight hours averaged 28°C and peaked at 32°C. The winds were out of the northwest, and by the end of the day O₃ at a DNR monitoring station in Conyers had peaked at 0.147 ppmv.
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 24. To simulate present-day AHC and NO_x levels, the initial AHC and NO_x concentrations were set at 0.68 and 0.096 ppmv, respectively, in accordance with early morning observations from downtown Atlanta, and the total AHC and NO_x surface emissions from 0800 to 1900 LST were set at 34 and 28 kg km⁻², respectively. The emissions and their distribution as a function of time were chosen to correspond to the emissions an air column would encounter if it followed a trajectory from downtown Atlanta to Conyers. The chemical speciation of the initial mix of AHCs and NO_x and of the emissions was based on the apportioning factors or "reactivities" recommended by EPA (19).
 25. Because all NHCs may not be as reactive and may not produce as much O₃ as isoprene, our treatment of all NHCs as isoprene may have caused us to overestimate the effect of NHCs on O₃ for a given NHC emission rate. However, even if isoprene were the only NHC species to produce O₃ [a very unlikely eventuality (11)], our conclusion regarding the importance of NHCs would still be valid; our calculations indicate that the daytime emission rate for isoprene alone [30 kg km⁻² (13)] is sufficient to significantly affect urban O₃ levels.
 26. F. W. Lurman, B. Nitta, K. Ganesan, A. C. Lloyd, *Atmos. Environ.* **18**, 1133 (1984).
 27. Lurman *et al.* (26) claimed to have shown that NHCs are unimportant through model simulations of the Tampa Bay-St. Petersburg area. Model simulations were reported with only AHC sources and with both AHC and NHC sources. Because the maximum O₃ level calculated with both sources was only about 10% larger than that calculated with only the AHC source, the authors concluded that NHCs were not important. However, as Trainer *et al.* (12) have shown, these results can be misleading; if the system is not limited by hydrocarbons, then the O₃ production rate will respond nonlinearly to the addition of AHCs as well as NHCs.
 28. We thank N. Faust for the LANDSAT data. Supported in part under NSF grant ATM-8600888.

14 June 1988; accepted 9 August 1988

The Structure and Symmetry of Crystalline Solid Solutions: A General Revision

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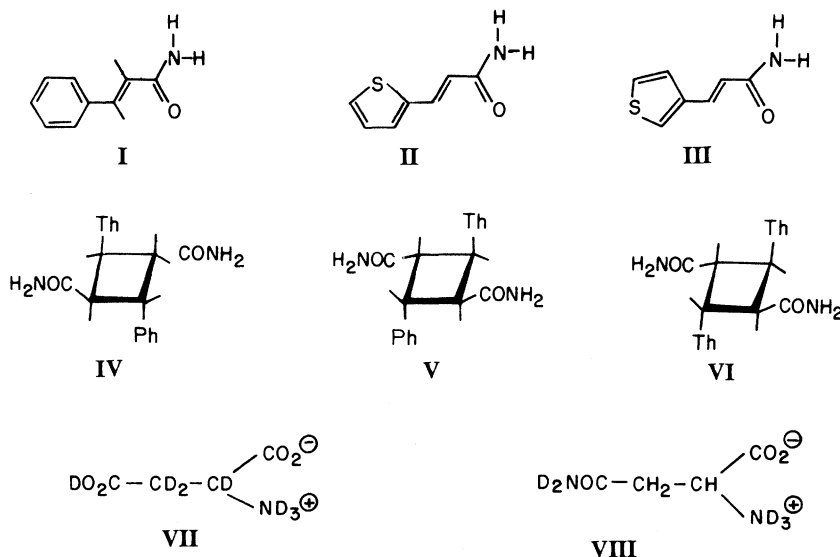
Mixed single crystals composed of host and guest organic molecules of similar structures and shapes are shown to comprise sectors with different host-guest distributions and to have symmetries lower than that of the host crystal. These properties are determined by the structure of the guest and the surface structures of the crystal faces through which the guest molecules are occluded. This general concept is illustrated by studies of three mixed crystal systems, (*E*)-cinnamamide-(*E*)-2-thienylacrylamide, (*E*)-cinnamamide-(*E*)-3-thienylacrylamide, and (*S*)-asparagine-(*S*)-aspartic acid, with x-ray and neutron diffraction and solid-state photochemistry.

MIXED CRYSTALS COMPOSED OF host and guest molecules of similar molecular structures and shapes have been generally observed to exhibit the same symmetries as those of the host crystals. Moreover, Kitaigorodsky proposed that guest molecules will occupy all symmetry-related sites with equal probability (1). These assumptions are the outcome of considerations of bulk thermodynamic properties, and, to our knowledge, no diffraction studies to the contrary have been reported.

We have shown that the adsorption and occlusion of minor amounts of additive during crystal growth are dictated by interactions between the additive and substrate molecules at the crystal surface (2). In cases where the additive is a substrate molecule with an altered moiety or functional group and these interactions are unfavorable, addi-

tive occlusion will be limited (0.01 to 1.0%). We show that for solid solutions, produced by the occlusion of large amounts of guest, the nature of the occlusion is also

dictated by a mechanism dependent on surface symmetry and structural considerations. Thus the guest may be adsorbed and preferentially occluded at different subsets of surface sites on the various faces, leading to a mixed crystal composed of distinct sectors coherently compounded together. Each sector exposes to solution its bounding crystal face. By our proposed mechanism, we anticipate that the symmetry of each sector will, in general, be lower than that of the host crystal, as illustrated here by low-temperature diffraction studies of three mixed-crystal systems (see scheme 1), (*E*)-cinnamamide (I)-(*E*)-2-thienylacrylamide (II), (*E*)-cinnamamide-(*E*)-3-thienylacrylamide (III), and the amide-acid system (*S*)-asparagine (VII)-(*S*)-aspartic acid (VIII), and by studies of the photochemical behavior of the first system. With these examples we show that



Scheme 1

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a reduction in crystal symmetry occurs that is at variance with the rule proposed by Kitaigorodsky.

The (*E*)-cinnamamide-(*E*)-2-thienylacrylamide system was chosen for the following reasons. The phenyl ring can be easily replaced by a thienyl ring (3), which contains sulfur as a heavy x-ray scatterer and whose carbon atom positions do not directly coin-

cide with the atoms of the phenyl ring. The packing arrangement of cinnamamide (4), space group $P2_1/c$, $Z = 4$ (where Z is the number of molecules per unit cell) (Fig. 1a) and the crystal habit, delineated by {011}, {100}, and {001} faces, is such that different guest distributions and space group symmetries were expected for the various crystal sectors. Let us consider the herringbone

arrangement between cinnamamide molecules, as represented by contacts between molecules 1 and 4 and molecules 2 and 3. These contacts involve aromatic C-H groups and π electrons of the neighboring phenyl ring. Replacement of such a C-H group by a sulfur atom could cause repulsion between the sulfur lone-pair electrons and the π electrons.

The {011} faces of cinnamamide crystals comprise four different types of surface sites (Fig. 1b). In accordance with the principles of additive adsorption, thienylacrylamide can easily be adsorbed at site 1, as the sulfur atom emerges from the crystal bulk. The molecular conformation used is II (scheme 1) taken from the native crystal structure (5), which shows no disorder. In contrast, the guest may less easily occupy site 3, at which the sulfur atom would have to point into the bulk. The two remaining sites, 2 and 4, would have their thienyl rings lying almost parallel to the {011} face, and their ease of adsorption should be determined by the tilt of the rings with respect to that face. Any inequality in the guest occupancies of the four sites would result in a reduction of crystal symmetry; preferential occlusion at site 1 would yield space group $P1$. Alternatively, selective adsorption and occlusion through the {001} faces would lead to symmetry Pc , as these faces expose only two different types of surface sites, 1, 2 and 3, 4, where the two molecules of each type are related by glide symmetry (see Fig. 1, a and b). For the (001) face, stereochemical arguments suggest that 2-thienylacrylamide is more easily adsorbed at sites 1, 2 than at 3, 4. However, all four sites at the {100} faces will be equally favorable for adsorption. Thus we argue that the mixed crystal will be divided into six sectors of reduced symmetries (Fig. 1c), with the structures of the sectors related to one another by the original point symmetry ($2/m$) of the host crystal. Thus the two sectors of type A, with faces (011) and (01 $\bar{1}$), will be congruent, of symmetry $P1$, and enantiomorphic to the two sectors of type $\bar{A}$, with faces (0 $\bar{1}1$) and (0 $\bar{1}\bar{1}$). The two sectors of type B, with faces (001) and (00 $\bar{1}$), should assume symmetry Pc and be of opposite polarity in the ac plane.

To test these expectations, we grew mixed crystals from a solution containing cinnamamide and 2-thienylacrylamide (7:3 ratio by weight). Approximately 7.5 to 8.0% of the additive was occluded in the host crystal, as shown by high-performance liquid chromatography (HPLC) (6). A crystal specimen 5 by 3 by 2 mm was chosen for the x-ray diffraction study. The sectors had to be separated from each other to prevent superposition of the diffraction patterns, because

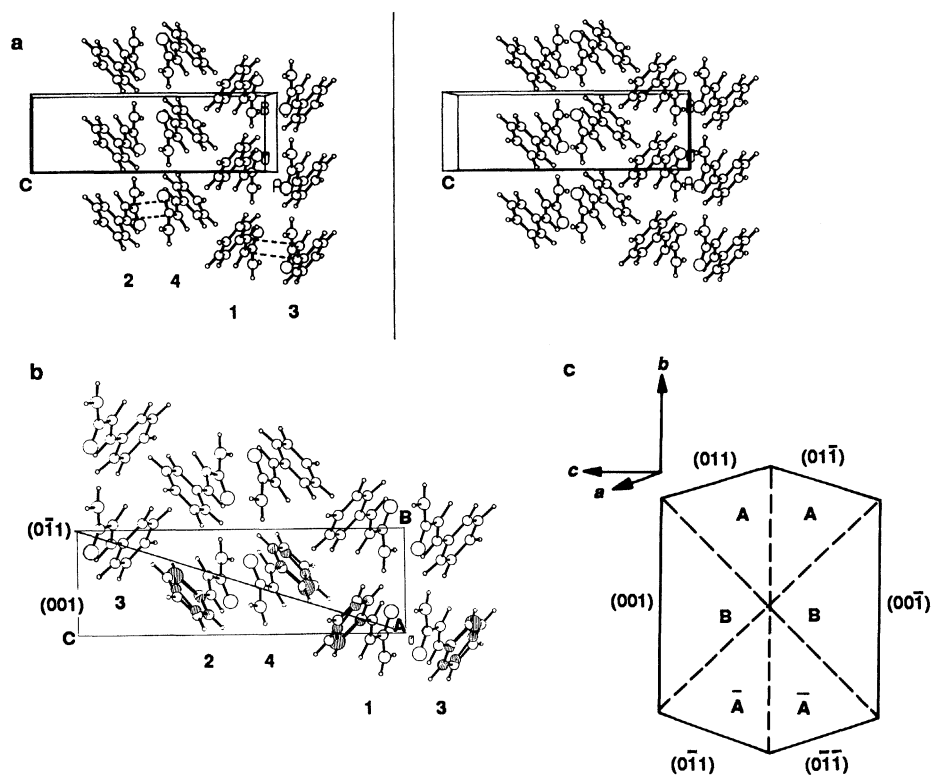


Fig. 1. (a) Stereoscopic view of the packing arrangement of cinnamamide viewed along a . The four symmetry-related molecules are labeled. (b) Packing arrangement of cinnamamide showing the four different types of surface sites at the (011) face. Shown in shaded molecules are the 2-thienyl rings in the positions they would assume were they to replace a cinnamamide molecule. (c) Morphological representation of a cinnamamide-thienylacrylamide crystal with segments of reduced symmetry.

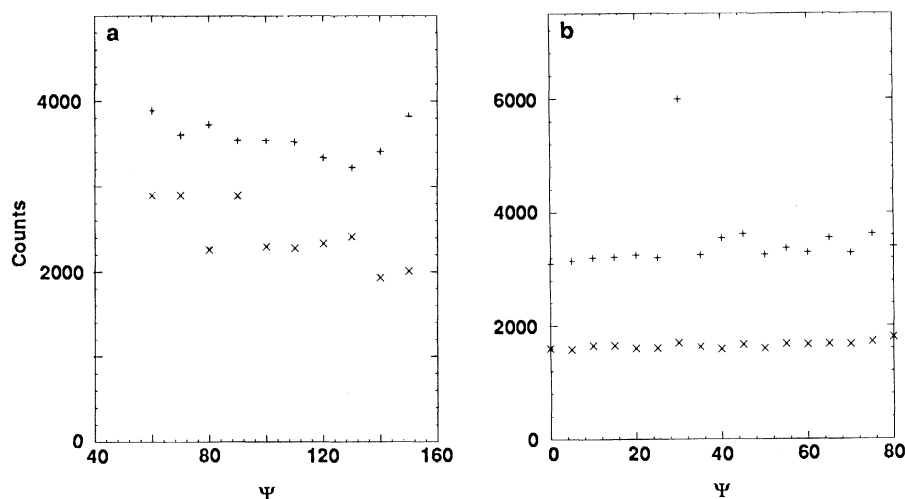


Fig. 2. Record of Ψ scans of symmetry "forbidden" reflections (intensity, +; background, $\times$): (a) Ψ scan of reflection (605) from segment $\bar{A}$ of cinnamamide-2-thienylacrylamide; (b) Ψ scan of reflection (030) from a crystal of cinnamamide-3-thienylacrylamide. Note the effect of multiple diffraction at $\Psi = 30^\circ$.

Table 1. Crystallographic data for the cinnamamide–2-thienylacrylamide system. Numbers in parentheses are standard errors.

Crystal segment	Unit cell angles (°)			Internal agreement $R_m(F^2)^*$ for two point groups		Agreement factors $R(F)^\dagger$ for two space groups	
	α	β	γ	1	2/m	P1	P2 ₁ /c
A	90.018(6)	92.749(30)	89.871(4)	0.041	0.043	0.040	0.042
$\bar{A}$	89.969(20)	92.697(5)	90.113(4)	0.039	0.044	0.039	0.045
B	89.998(2)	92.703(2)	90.005(2)				
Pure cinnamamide‡	89.999(2)	92.721(2)	90.008(2)				

* $R_m(F^2) = \Sigma |F^2 - F_c^2| / \Sigma F_c^2$, where F^2 is the average of the set of observed symmetry-related structure factors and F_c^2 is the i th individual observed structure factor of that set. $^\dagger R(F) = \Sigma |F_{\text{obs}} - F_{\text{calc}}| / \Sigma F_{\text{obs}}$. ‡ Cell dimensions of pure cinnamamide at 100 K are $a = 9.476$ Å, $b = 5.071$ Å, $c = 15.652$ Å, $\beta = 92.721^\circ$.

Table 2. Asparagine/aspartic acid. Indices of internal agreement $R_m(F^2)$ between F_{obs}^2 values for different point groups; agreement indices $R(F)$ and $R_G(F)$ of refined structures for a total of 4837 reflections assuming different space groups and the ratio $R_G/R_G(P12_11)$ for the Hamilton test (11).

Space and point groups	$R_m(F^2)^*$	$R(F)$	$R_G(F)^\dagger$	$R_G/R_G(P12_11)$
P2 ₁ 2 ₁ 2 ₁ (222)	0.0282	0.0349	0.0234	1.068
P12 ₁ 1(121)	0.0185	0.0330	0.0219	1.000
P112 ₁ (112)	0.0249	0.0352	0.0237	1.082
P2 ₁ 11(211)	0.0267	0.0353	0.0239	1.091

*See Table 1. $^\dagger R_G(F) = [\Sigma w(F_{\text{obs}} - F_{\text{calc}})^2 / \Sigma w F_{\text{obs}}^2]$, where $w = 1/\sigma^2(F)$.

an uncut crystal would mask the reduction in crystal class (that is, the 2/m symmetry of the crystal sectors) (7). The deviation of unit cell angles γ and α from 90° (Table 1), in particular $\gamma(\bar{A}) = 90.113(4)^\circ$ and $\gamma(A) = 89.871(4)^\circ$, is evidence in favor of symmetry P1 for crystals A and $\bar{A}$ (the parenthetical numbers are the standard error as the variation in the last digit). These two angles are nearly complementary to each other [$\gamma(\bar{A}) = 180^\circ - \gamma(A)$], because the x-ray data of the two sectors were measured with respect to a fixed axial system of the original crystal. This complementary relation is true also of the α angle (Table 1). These angles are indicative of the enantiomorphic relation of crystal sectors A and $\bar{A}$ and are striking in comparison to the α and γ angles of pure cinnamamide, which are closer to 90° , and of sector B with anticipated Pc symmetry (Table 1).

Additional evidence for space group P1 as opposed to P2₁/c is provided by the internal agreement between the structure factors $F_0^2(hkl)$ of the measured reflections; if we assume Laue symmetry $\bar{1}$ rather than 2/m (corresponding to P1 and P2₁/c, respectively), there is better agreement for both A and $\bar{A}$ sectors (Table 1). The loss of the glide plane and the twofold screw axis is also manifested by the presence of the “forbidden” reflections ($h0l$), $l = 2n + 1$, and ($0k0$), $k = 2n + 1$. Diffractometer ψ scans (8) for these symmetry “forbidden” reflections (Fig. 2a) confirmed the presence of residual, if weak, intensities (9). Taken to-

gether, these observations indicate that the F_{obs}^2 data obey the symmetry constraints of space group P1 rather than those of P2₁/c.

To further establish the symmetries of sectors A, $\bar{A}$, and B, we refined their crystal structures by least-squares adjustment of the occupancy factors of the two species at each site, with geometric constraints applied to the molecules (10). For both A and $\bar{A}$ the space group P1 gave the lower $R(F)$ factor (Table 1) [significant by the Hamilton test (11) with $P < 0.005$]. If we assume P1 symmetry, the refined occupancies of the thienylacrylamide molecules for sector $\bar{A}$ at the four independent sites 1, 2, 3, and 4 (see Fig. 1b) were 0.155(2), 0.055(2), 0.025(2), and 0.074(3), respectively, with an average of 0.077(1). The thienylacrylamide occupancies (12) at the corresponding sites 2, 1, 4, and 3 of sector A were 0.139(2), 0.046(2), 0.022(2), and 0.106(2), respectively, with an average occupancy of 0.078(1). The occupancies of the corresponding sites of A and $\bar{A}$ agree well with the relative ease of thienylacrylamide adsorption described earlier and with the total guest concentration as determined by HPLC. Analysis of the diffraction data measured from sector B by assuming space groups P2₁/c or Pc yielded similar agreement factors, with $R(F)$ values for the two space groups of 0.045 and 0.044, respectively (13).

The reduction in symmetry for cinnamamide on occlusion of 2-thienylacrylamide was independently demonstrated by topochemical (2π - 2π) photocyclodimerization (14).

Irradiation with monochromatic light of mixed crystals of these components grown from the melt led to the formation of racemic mixtures of dimers (IV and V) together with some homodimer (VI) (3). (In IV, V, and VI, Ph is phenyl and Th is thienyl.) There is no energy transfer between guest and host in this system, so that the product distribution reflects the molecular occupancies in the crystal (14). The present structural analysis indicated that irradiation of sectors A and $\bar{A}$ should yield optically active dimers of opposite chirality. Thienylacrylamide molecules at sites 1 and 4, which are related to each other by twofold screw symmetry, will photoreact with cinnamamide molecules at sites 3 and 2, respectively, to yield the chiral mixed dimer (IV). On interchange of the cinnamamide and thienylacrylamide molecules at the four sites, the reaction will yield the enantiomorphic product (V). The molar ratio of the two enantiomorphic dimerization products expected from the refined molecular occupancies at sites 1, 2, 3, and 4 are $(0.155 + 0.074)/(0.055 + 0.025) = 2.86:1$ or 48% enantiomeric excess (ee) for sector $\bar{A}$ and $(0.139 + 0.106)/(0.046 + 0.022) = 3.60:1$ or 56% ee for sector A. The circular dichroism spectrum of photodimers obtained from A and $\bar{A}$ type sectors (Fig. 3a) shows that the respective photoproducts are indeed optically active and enantiomeric. Furthermore, the ee, as determined by gas chromatography, is in the range of 40 to 60% (Fig. 3b), as expected from the molecular occupancies. According to the crystal structures of sectors A and $\bar{A}$, the absolute configuration of the major photodimer from a crystal piece taken from the $+b$ end of the crystal should be (V), and, by symmetry, that from the $-b$ end should be (IV) (15). As expected, dimers from the B sectors yield the racemic mixture, in agreement with the retention of the glide plane for these pieces.

We were unable to establish unambiguously by x-ray diffraction analysis that the symmetry of the B sector was reduced to Pc . On the other hand, x-ray diffraction measurements of an analogous system, the solid solution (*E*)-cinnamamide–(*E*)-3-thienylacrylamide with expected symmetry Pc , indicated that crystallization of host (*E*)-cinnamamide from a solution containing this amide and (*E*)-3-thienylacrylamide (III) yielded thin {001} plates of the host containing as much as 15% of the guest. We interpreted this change in morphology in terms of a preferred occlusion of the guest through the {001} faces. In accordance with the stereochemical arguments for ease of additive adsorption presented earlier, we expect preferential occlusion through only one-half of the sites on that face and thus a

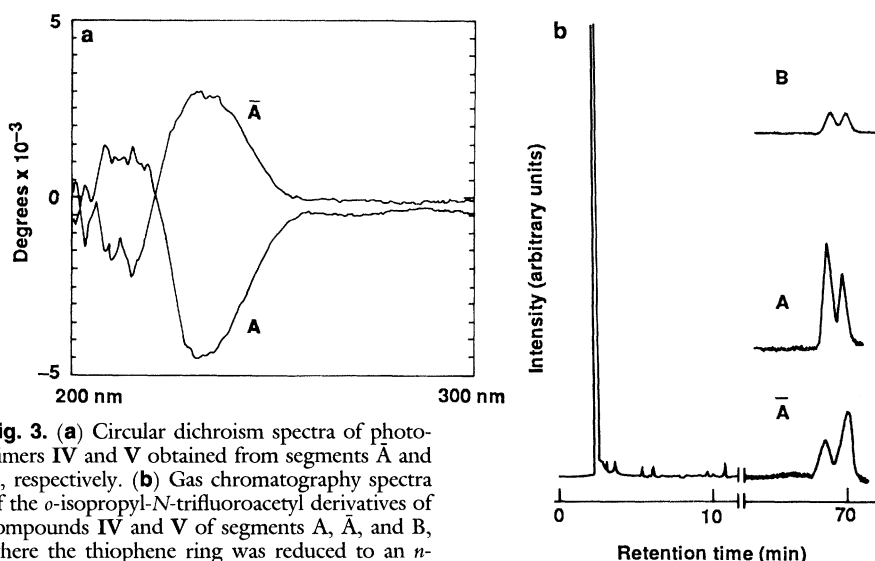


Fig. 3. (a) Circular dichroism spectra of photodimers IV and V obtained from segments $\bar{A}$ and A, respectively. (b) Gas chromatography spectra of the *o*-isopropyl-*N*-trifluoroacetyl derivatives of compounds IV and V of segments A, $\bar{A}$, and B, where the thiophene ring was reduced to an *n*-butyl group (Chirasil-L-valine capillary column).

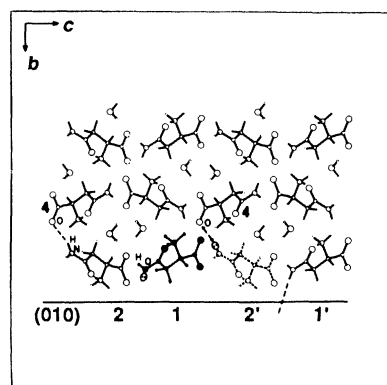


Fig. 4. Packing arrangement of (*S*)-asparagine- H_2O viewed down the *a*-axis. The crystal is delineated by the (010) face. The four symmetry-related molecules are shown. The surface sites 1' and 2' designate asparagine (asn) replaced by guest aspartic acid (asp). The N-H $\cdots$ O (carboxylate) bond between asn at surface site 2 and asn at site 4 is replaced by O(hydroxyl) $\cdots$ O(carboxylate) repulsion between asp at site 2' and asn at site 4.

reduction in symmetry to Pc for the solid solution. The Ψ scans demonstrated the loss of the 2_1 axis for the (010) and (030) reflections, which definitely show residual intensities (Fig. 2b). Preliminary refinements indicate the occupancies of the two independent guest molecules to be 0.109(3) and 0.143(2).

Another solid solution that lent itself to a diffraction analysis is the (*S*)-asparagine- H_2O -(*S*)-aspartic acid system, in which as much as 16% of the aspartic acid guest may be occluded in the amide (16). Adsorption of aspartic acid at translationally related sites 2 and 2' on the (010) face of the host (Fig. 4) is unfavorable, as the normal N-H $\cdots$ O hydrogen bonds between host molecules would be replaced by O(guest) $\cdots$ O(host) lone-pair repulsions (17). This poor contact is shown at site 2'. Sites 1 and 2 are related

by a twofold screw axis along *c*. Aspartic acid may be adsorbed at sites 1 and 1' (related to each other by translation) on this face, because only at these sites do the lone-pair lobes of the hydroxyl oxygen atom emerge from the crystal face. This allowed adsorption is shown at site 1'. Thus aspartic acid should preferentially occupy sites of type 1 rather than of type 2, and the space group of the mixed crystal grown through the (010) face would be the monoclinic $P12_11$ instead of the orthorhombic $P2_12_12_1$ of the host crystal.

We performed a neutron diffraction study of asparagine C-H (protonated) (VIII) containing aspartic acid C-D (deuterated) (VII). If the guest was occluded from both sides of the crystal, the two opposite halves of the plate would be related by the original point symmetry (222) of the host crystal, and the reduction in symmetry would be masked in a manner analogous to that of a twinned crystal. We obtained a homogeneous sector without cutting the crystal by blocking the (0 $\bar{1}$ 0) face from additive occlusion and growing the crystal unidirectionally along +*b*. The neutron intensities on single crystals of pure asparagine and mixed crystals cooled to 16 K were measured for a hemisphere of reflections to $\sin \theta/\lambda = 0.75 \text{ \AA}^{-1}$ (where θ is the diffraction angle and λ is wavelength) at the Brookhaven High-Flux Beam Reactor. Initial evidence for space group $P12_11$ can be seen from agreement between symmetry-related reflections by assuming point groups 222, 121, 112, and 211 (Table 2). The crystal structure was refined by least squares analysis (18) in a manner analogous to that adopted for cinnamamide-thienylacrylamide, by assuming space groups $P2_12_12_1$, $P12_11$, $P112_1$, and $P2_111$. The lowest $R(F)$ index was found for $P12_11$ which, according to the Hamilton

test (11), describes the symmetry with $P < 0.005$ (Table 2). The occupancies of the aspartic acid at the two independent sites, 1 and 2 (Fig. 4), in this space group were 0.173(2) and 0.132(2), respectively, in accordance with the stereochemical arguments given above.

The above results indicate that a general revision in the approach to the structural, spectroscopic, and physical properties of mixed crystals is called for, in particular to include the effects of the growth history and morphology of the crystal and the structure of the guest. The reduction of symmetry may allow centrosymmetric or nonpolar crystals to be transformed into polar ones for technical applications such as pyroelectricity and nonlinear optics (19).

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6. The analyses were done on a Waters HPLC equipped with a Nucleosil 10- μ m Rp. 18 column, with 30% acetonitrile in 0.05M buffer acetate, pH 4.0, as eluent, at a flow rate of 1 ml/min, with an ultraviolet detector (254 nm).
7. The intensities of the x-ray reflections of crystal pieces cut from sectors A(011) and $\bar{A}(0\bar{1}1)$ were measured over a full sphere of reciprocal space out to $\sin \theta/\lambda = 0.56 \text{ \AA}^{-1}$ at 100 K on a Rigaku automatic diffractometer with a rotating copper anode source. To reduce systematic errors, in particular the effect of multiple diffraction, we measured each sector in three different orientations.
8. In a Ψ scan about a reciprocal vector $d^*(hkl)$, the crystal is rotated about d^* in diffracting position. The diffracted intensity $I(hkl)$ is measured as a function of rotation.
9. The intensities of the symmetry-“forbidden” reflections have an average $\langle I/\sigma(I) \rangle$ value of 5.3, where I is the net intensity of each reflection. That these residual intensities were not solely due to multiple diffraction was shown by diffractometer Ψ scans.
10. The crystal structures were refined as follows. The molecular geometries of cinnamamide and thienylacrylamide were determined from x-ray structure refinements of low-temperature (100 K) data sets from pure crystals. We refined the mixed-crystal structures by structure-factor least-squares analysis (18) by assuming $P2_1/c$ symmetry and by treating cinnamamide and thienylacrylamide molecules as rigid bodies with geometries transferred from the pure crystal structures and with partial occupancies summing to unity. An $R(F)$ value of 0.045 for sector $\bar{A}$ was obtained with all 2231 reflections and 91 refined variables. Occupancies of 0.922(1) and 0.078(1) were obtained for the cinnamamide and thienylacrylamide molecules, respectively, in agreement with the HPLC analysis (see text). (To the accuracy of our measurement, no disorder in the sulfur position was observed.) The geometry of the $P2_1/c$ structure was retained but the four sites were assigned individual occupancy factors, in order to generate the initial model for the $P1$ crystal structure. Only the four occupancies of the cinnamamide and thienylacrylamide molecules were refined (the total occupancy at each molecular site constrained to a value of one), resulting in $R(F) = 0.038$, which is

- significantly lower than $R(F) = 0.045$ for the $P2_1/c$ symmetry. The $R(F)$ values for the 152 symmetry-“forbidden” reflections $[(h0l), l = 2n + 1, \text{ and } (0k0), k = 2n + 1]$ refined to 0.20; for a true $P2_1/c$ structure this value would be equal to 1. An analogous refinement was performed for sector A. Refinement led to $R(F) = 0.042$ for space group $P2_1/c$ and to $R(F) = 0.040$ for space group $P1$. $R(F)$ for the 151 “forbidden” reflections was 0.35.
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 13. The refined occupancies of the sites 1, 2 and 3, 4 for space group Pc were 0.100(1) and 0.039(1), respectively.
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14 April 1988; accepted 13 July 1988

[Cr₄S(O₂CCH₃)₈(H₂O)₄](BF₄)₂·H₂O: Ferromagnetically Coupled Cr₄S Cluster with Spin 6 Ground State

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Data on the preparation, structure, and magnetism of the new complex [Cr₄S(O₂CCH₃)₈(H₂O)₄](BF₄)₂·H₂O are presented. The metal-sulfur M₄S core structure is similar to that found in M₄S[S₂As(CH₃)₂]₆ (where M is cobalt or zinc) compounds and in beryllium basic acetate. However, the six-coordinate metal ions in the new Cr₄S system distinguish it from these structures. The tetranuclear chromium complex is the first example of a new structural type. Its magnetic spin $S = 6$ ground state, a striking example of intramolecular ferromagnetic coupling, was determined by variable-temperature magnetic susceptibility measurements. Long-range antiferromagnetic intercluster ordering was found below 170 millikelvin.

INTRAMOLECULAR MAGNETIC COUPLING is a phenomenon that has ramifications in physics (1), chemistry (2, 3), materials science (4), biology (5), and geology (6). Transition-metal cluster compounds containing two or more metal centers provide fertile ground for detailed investigation of such magnetic coupling. Early work on molecular systems recognized only antiferromagnetic coupling (spin pairing), where the magnetic moment of the ensemble of (atomic) paramagnets in the molecule is lowered from the maximally attainable value. In 1968 it was realized (7) that ferromagnetic intramolecular coupling is also possible (8). The magnetic properties of bi- and trinuclear Cr(III) complexes have been intensely studied (9). In trinuclear systems, the basic chromium acetate cation [Cr₃O(O₂CCH₃)₆(H₂O)₃]⁺ is the prototypical complex for study of antiferromagnetic

interactions between the spin $s = 3/2$ Cr(III) ions (10). In fact, in di-, tri-, and tetranuclear complexes containing Cr(III), antiferromagnetic coupling is almost invariably found.

We report here a new and unusual tetranuclear sulfur-centered [Cr(III)]₄ complex that exhibits intramolecular ferromagnetic coupling with a ground state that has the maximal spin $S = 6$. The compound also exhibits weak intercluster antiferromagnetic interactions, leading to long-range antiferromagnetic ordering of the $S = 6$ clusters in the solid state below 170 mK. Data on the preparation, structure, and magnetism of the new complex, [Cr₄S(O₂CCH₃)₈(H₂O)₄](BF₄)₂·H₂O (I) are presented.

The reaction of chromium metal powder [or Cr(CO)₆] with sulfur in refluxing acetic acid: acetic anhydride (1:1) yields a mixture of soluble cationic species composed primarily of the well-known green basic chromium acetate cation and a new blue cation (11). The basic chromium acetate can be separated from the blue species by ion-exchange chromatography on Dowex 50W-X2. Elution with 0.1M HBF₄ yields the green basic chromium acetate cation. Subsequent elu-

tion with 0.5M HBF₄ yields the blue cation, which can be crystallized as the BF₄[−] salt by evaporation and then recrystallized from methanol (11). The visible spectrum is consistent with a Cr(III) complex. Elemental analysis indicates the composition [Cr₄S(O₂CCH₃)₈(H₂O)₄](BF₄)₂·H₂O.

The structure of I was solved by single-crystal x-ray diffraction techniques (12) (Tables 1 and 2). The structure (Fig. 1) consists of a central four-coordinate sulfur (S) atom bound to four Cr atoms that are in an approximate tetrahedral array. This core is, in a sense, an inverse cluster with the S ligand in the center and the four metal ions on the outside. The Cr-Cr distances average 3.83 Å (range, 3.72 to 3.91 Å). Each Cr atom is six-coordinate with a nearly octahedral arrangement of five oxygen (O) donors and the central S atom. The one water ligand on each Cr lies *trans* to the central S atom. The bridging acetate ligands provide the remaining O atoms bonded to each Cr atom. The overall symmetry of the cation is nearly D_{2d} , whereas that of the inner Cr₄S core is nearly T_d . The structure is related to that of beryllium basic acetate (13), Be₄O(O₂CCH₃)₆, although in the latter structure the Be atoms are tetrahedrally four-coordinated rather than octahedrally six-coordinated as in the Cr₄S complex. The tetrahedral central S atom is found in Zn₄S[S₂P(OCH₃)₂]₆ (14) and in the compounds M₄S[S₂As(CH₃)₂]₆ (M = Co, Zn) (15), which also have the basic beryllium acetate structure. In contrast, the basic chromium acetate cation, [Cr₃O(O₂CCH₃)₆(H₂O)₃]⁺, has an O atom in the center of an

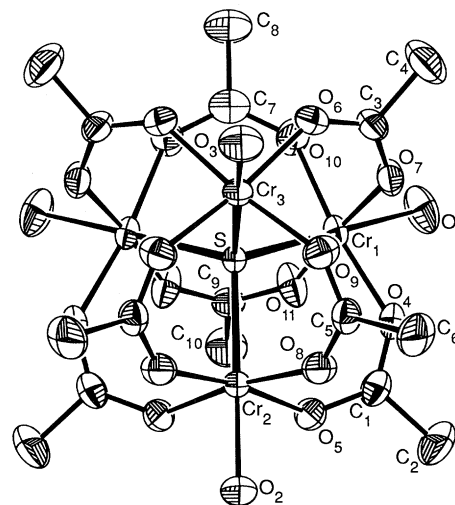


Fig. 1. Perspective drawing of the [Cr₄S(O₂CCH₃)₈(H₂O)₄]²⁺ cation in [Cr₄S(O₂CCH₃)₈(H₂O)₄](BF₄)₂·H₂O with nonhydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are omitted. Unlabeled atoms are related to labeled atoms by the crystallographic mirror plane which contains Cr₂, Cr₃, O₂, O₃, C₇, C₈, C₉, and C₁₀.

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