3.0 (aromatic protons). The dibromide **10** was contaminated with **7** and was easily converted to this substance by dehydrobromination with boiling ethanolic potassium hydroxide.

The properties and reactions of **3** provide clear evidence for the assigned structure. At least one of the double bonds must have the *trans* configuration, in view of the presence of a strong band at 958 cm^{-1} in the infrared spectrum and the observed J value of 17 cps in the nmr spectrum. The di-*trans* stereochemistry is excluded by the complexity of the olefinic pattern of the nmr spectrum. The mono-*trans* configuration **3** is confirmed by the fact that H^5 and H^6 (see **8**) in the adducts are *trans*-oriented (J = 14–19 cps). The corresponding protons in the precursor **5** are therefore also *trans*, the stereochemistry expected to be formed from the mono-*trans* compound **3** by a thermal disrotatory cyclization process.[4,11,15] On the other hand, all-*cis*-1,2:3,4:7,8-tribenz[10]annulene or the corresponding di-*trans* compound should have given *cis*-fused adducts.[3,11,16]

It appears that the ten-membered ring in **3** is nonplanar and does not represent a delocalized ten-π-electron system. A reason for the greatly increased stability of **3**, as compared with [10]annulene itself,[3,4] is presumably that the isomerization to the 9,10-dihydronaphthalene derivative in this case involves disruption of the cyclic delocalization of a benzene ring.

Acknowledgment. We are indebted to the Royal Society (London) for generous financial support and to Drs. P. J. Garratt and D. H. Williams for valuable discussions.

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Nuclear Magnetic Resonance and Superconductivity in the Clathrate Salt $[Ag_7O_8]^+HF_2^-$

Sir:

The electrical conductivity, superconductivity, and crystal structure of a number of silver oxide clathrate salts having the formula $[Ag_7O_8]^+X^-$ have been reported recently.[1] Among them was the material Ag_7O_8F, a black metallic substance having a cubic crystal structure as shown in Figure 1.[2,3] As can be seen from this figure, the structure consists of face-sharing Ag_6O_8 polyhedra enclosing alternately Ag^+ and F^- ions, with interatomic distances as given in the figure caption. By virtue of its structure, the lack of any abundant silver or oxygen nuclear species of sizable nuclear magnetic moment, and the large F^-–F^- separation, the nuclear dipole magnetic fields acting on an F^- ion in Ag_7O_8F will be quite small, the expected root-mean-square second-moment broadening being approximately 0.2 G. It was then with some surprise that the 22-G-wide ^{19}F nmr spectrum shown in Figure 2 was observed at 4.2°K in material of nominal composition Ag_7O_8F. In addition, a proton nuclear resonance with two satellites was also seen. Our work suggests that these spectra are characteristic of the HF_2^- ion, and that preparation of the compound Ag_7O_8F is accompanied by the formation of more or less $Ag_7O_8HF_2$. This explains in part the variability of composition of "Ag_7O_8F" reported by Náray-Szabó and Popp.[4]

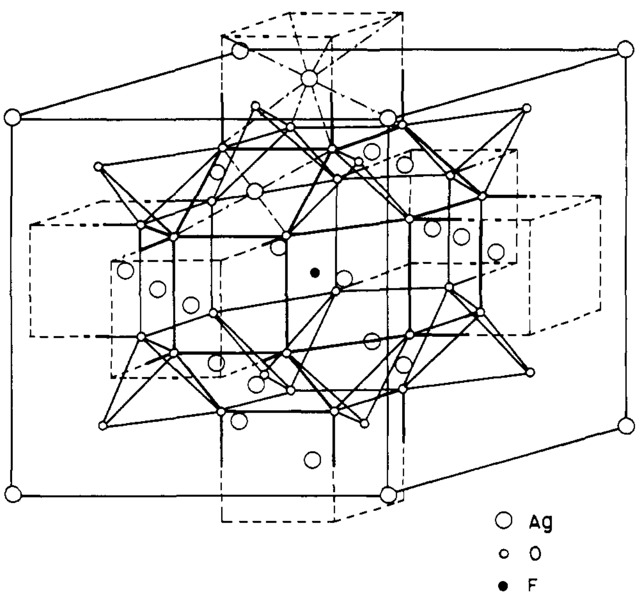

Figure 1. The crystal structure of Ag_7O_8F. In this structure, the distance from one fluoride ion to the next in an adjacent cage is 6.97 Å and to the twelve nearest neighbor silver ions is 3.49 Å; the distance to the nearest neighbor oxide ions is 4.09 Å.

The unusually good resolution of the four ^{19}F lines in $Ag_7O_8HF_2$ is attributed to the low extraionic dipolar magnetic fields mentioned above. By contrast, in measurements made on $NaHF_2$ and KHF_2, the four components of the ^{19}F resonance could not be individually resolved.[5] The four-line pattern centered near the unperturbed fluorine resonance and three transitions near the unperturbed proton resonance are those expected for a system of randomly oriented, linear symmetric HF_2^- ions.[5] The peaks in the spectrum arise from absorption by nuclei in those ions lying in a plane perpendicular to the applied magnetic field. The assumption of an end-to-end distance of 2.26 Å[6] in a linear, symmetric HF_2^- ion leads to predicted resonances[5] at the positions shown in Table I. The agreement between the calculated and experimentally observed splittings confirms that the resonances are those of the HF_2^- ion, the small differences between calculated and observed values being attributed to the combined effects of vibrational or torsional zero-point motions of the ion, indirect nuclear exchange or nuclear pseudo-dipolar coupling, and the possibilities that the over-all length of the ion is greater than 2.26 Å or that the ion is

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[1] M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, and D. B. McWhan, *Phys. Rev. Letters*, **17**, 917 (1966).

[2] C. Kung-Du, *Sci. Sinica* (Peking), **12**, 139 (1963).

[3] I. Náray-Szabó, G. Argay, and P. Szabó, *Acta Cryst.*, **19**, 180 (1965).

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[6] L. Helmholz and M. T. Rodgers, *J. Am. Chem. Soc.*, **61**, 2590 (1939).

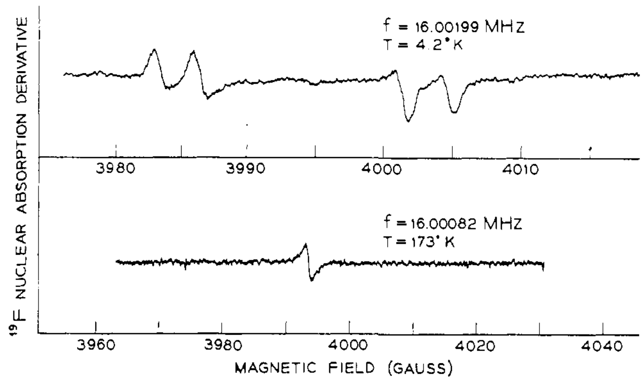

Figure 2. The ^{19}F nmr spectrum of $Ag_7O_8HF_2$ at 4.2°K (upper), and at 173°K (lower).

asymmetric.[5] A ^{19}F nmr signal with splittings characteristic of the spin 1 deuteron also was seen in $Ag_7O_8DF_2$.

Table I. Predicted and Observed Positions of ^{19}F and ^{1}H Resonances in $Ag_7O_8HF_2$

	Calcd, G	Obsd, G
Fluorine peaks		
1	$(H_0)_F + 10.88$	$(H_0)_F + 11.0$
2	$(H_0)_F + 8.60$	$(H_0)_F + 7.85$
3	$(H_0)_F - 8.60$	$(H_0)_F - 7.85$
4	$(H_0)_F - 10.88$	$(H_0)_F - 11.0$
Proton peaks		
1	$(H_0)_H + 18.45$	$(H_0)_H + 17.64$
2	$(H_0)_H$	$(H_0)_H$
3	$(H_0)_H - 18.45$	$(H_0)_H - 17.64$

Spectral changes were noted as the sample temperature was raised above 4.2°K, so that above 100°K only a single line of width 2 G was observed. This apparent narrowing is evidently caused by a thermally excited rotation of the HF_2^- ion. The minimum frequency of reorientation which would be needed to produce the observed narrowing[7] is approximately $[\Delta\omega(1.6°)]^2/\Delta\omega(100°) \sim 6 \times 10^6$ sec^{-1}, where $\Delta\omega(1.6°)$ is the overall splitting of the resonance at 1.6°K, and $\Delta\omega(100°)$ is the line width above the narrowing temperature, *e.g.*, the line width at 100°K. Preliminary results of free induction decay studies from 100 to 300°K indicate that the activation energy is approximately 150°K. However, it is possible that the height of the rotational barrier depends upon the crystal structure and takes a different value on crossing the phase transformation found at 80°K in $Ag_7O_8HF_2$.[8] A study of the nuclear relaxation in $Ag_7O_8HF_2$ which should provide a more detailed picture of the rotation process is now underway.

Dc measurements of the resistivity of multiply twinned "single" crystals of $Ag_7O_8HF_2$ demonstrated a small resistivity anomaly at about 220°K and a large discontinuity at 80–100°K, which is most likely associated with the phase change at 80°K. The resistivity of the single-crystal samples at 300°K is 2.3×10^{-2} ohm cm and drops by a factor of about 30 on cooling to 4.2°K; the crystals become superconducting at 1.0–1.5°K.

$Ag_7O_8HF_2$ is a member of the mixed valence class of compounds,[9] having an average silver oxidation of $+2^3/_7$. Inasmuch as Ag^{2+} has the $4d^9$ configuration, its presence in any coordination will make $Ag_7O_8HF_2$ paramagnetic. However, our measurement of the magnetic susceptibility of $Ag_7O_8HF_2$ in the range 1.4–296°K shows only the temperature-independent Pauli paramagnetism ($\chi_g = 0.38 \times 10^{-6}$ cgs) characteristic of a metal lacking local moments. The explanation lies in the fact that the cubically coordinated silver is Ag^+, and, of the six silvers in the neutral Ag_6O_8 unit, five are diamagnetic ($4d^8$ in square-planar coordination), and the sixth is $4d^{10}$. Since, however, all six silvers are structurally equivalent, the two electrons distinguishing the sixth silver must resonate among all six silvers equally, thus forming a conduction band involving the $4d_{x^2-y^2}$ orbitals of silver and the 2p orbitals of oxygen. From this, the Pauli paramagnetism and the high electrical conductivity of $Ag_7O_8HF_2$ follow. The positions of the ^{19}F resonances observed here are within the normal range of chemical shifts, suggesting that there is very little conduction electron density at the bifluoride ion. Measurement of the Hall effect in $Ag_7O_8NO_3$ gives the number of charge carriers per six Ag as between 2 and 3, in accord with the above explanation.

It is also interesting to speculate on the connection between superconductivity and the dynamics of the ion motion. Earlier samples, which were thought to be solely the fluoride and which we now know to have contained a paramagnetic impurity, showed superconducting transitions at about 0.3°K.[1] However, samples in which the ^{19}F nmr spectrum contains only lines characteristic of the HF_2^- ion show superconductivity transition temperatures of 1.0–1.5°K. Since the superconducting transition temperatures in the nitrate and fluoroborate salts are 1.04 and 0.15°K, respectively, low-lying modes of vibration or libration of the anions within the Ag_6O_8 cages may be important in determining the electron–electron attraction leading to superconductivity in these compounds.

The HF_2^- salt was prepared by first neutralizing a quantity of hydrofluoric acid with Ag_2CO_3, filtering, and then adding an equal volume of 48% hydrofluoric acid. Electrolysis of this solution in a platinum dish using a 1-cm^2 platinum foil anode at 45 V led to the rapid growth of large shiny black needles. *Anal.* Calcd for $Ag_7O_8HF_2$: Ag, 81.89; F, 4.12. Found: Ag, 81.83; F, 4.28. The unit cell of this material at room temperature is cubic, with $a = 9.824$ Å. Superconducting transition temperatures were measured with a mutual inductance technique at ^{3}He temperatures. The nmr samples were prepared by sieving the coarse polycrystalline powder and using that fraction which passed through a 100-mesh screen. The nmr measurements were made at frequencies of 16 and 56 MHz with crossed-coil nuclear induction spectrometers.

Acknowledgments. We wish to thank D. B. McWhan and H. J. Levinstein for helpful discussions and suggestions, and G. W. Hull, C. Nanney, Mrs. Ann Cooper,

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(7) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961, p 424.

(8) H. J. Levinstein has investigated microscopically the diffuse reflectance of white light from crystals of $Ag_7O_8HF_2$ from room temperature to 4.2°K and finds an obvious and reversible change in surface texture at 80°K.

9. M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, in press.

and R. C. Sherwood for making measurements on our samples.

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Crystal Structure of Bullvalene at 25°[1]

Sir:

The self-interconversion of bullvalene has been studied by nmr in solution,[2] where it was found that at 120° all protons are magnetically indistinguishable, while at −85° the spectrum corresponds to that for a single valence tautomer. A solid-state nmr investigation of bullvalene indicated that the line width decreases with increase of temperature above 0°.[3] This effect was interpreted[3] either as indicating reorientation about a molecular axis or as valence tautomerism occurring in the crystal. Crystal structure analyses on two bullvalene–$AgBF_4$ complexes[4,5] have provided evidence for only a small amount of valence tautomerism occurring in these solid complexes. The Ag^+ ions complex to several double bonds and the resulting "freezing" of these bonds in definite positions reduces the number of self-rearrangement pathways. We have investigated the crystal structure of bullvalene itself at 25 ± 3° to determine whether there are unique positions for the bullvalene molecules in the crystal at this temperature and to investigate the extent of valence tautomerism in the solid.

Bullvalene ($C_{10}H_{10}$) crystallizes as transparent plates belonging to the monoclinic system. The most obvious choice of unit cell is virtually orthogonal ($\beta' = 90°\ 20'$), but this cell does not correspond to a conventional description for any space group. A simple transformation of reciprocal and real lattice axes leads to the following cell dimensions (Mo Kα, λ 0.7107 Å) at 25°: $a = 6.21 \pm 0.03$, $b = 20.73 \pm 0.05$, and $c = 10.52 \pm 0.04$ Å; and $\beta = 148°\ 18' \pm 30'$. The transformed cell belongs to the space group $P2_1/c$, with four molecules of $C_{10}H_{10}$ in the unit cell. Intensity data were obtained by equiinclination Weissenberg photographs and visual estimates. A total of 988 independent structure amplitudes was obtained. The crystal structure was solved by the symbolic addition technique,[6,7] and at the present stage of refinement, the crystallographic R factor is 0.14 on 988 reflections.

A view of the crystal structure looking down the b axis is shown in Figure 1. The packing is highly efficient and the definition of individual atoms indicates that motion of an entire bullvalene molecule about a molecular axis is not an important facet of the structure at this temperature. The agreement among the dimensions of chemically equivalent features within the bullvalene molecule is in accord with the estimated standard deviations (C–C distance ±0.02 Å, C–C–C angles ±1°). The mean C═C, C(sp^2)—C(apex), C(sp^2)—C(three-membered ring), and C—C (within the three-membered ring) distances are 1.33, 1.51, 1.45, and 1.54 Å, respectively. The angles at the apical carbon atom are close to tetrahedral, and those at the carbon atoms participating in the double bonds are all significantly greater than 120° (mean 126°); the average internal angle in the three-membered ring is 60° and the average external angle at the three-membered ring is 122°. There are no anomalous features in a three-dimensional difference map to indicate unusual atom vibrations, and indeed, well-defined positions can be found for most hydrogen atoms.

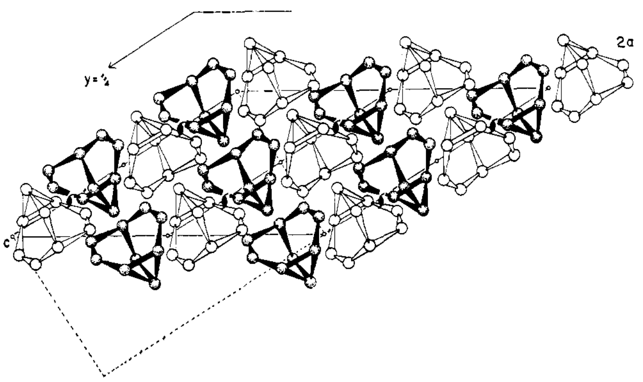

Figure 1. A view of the contents of two unit cells looking down the b axis. The bonds in the bullvalene molecules above $y = 1/2$ are shaded in black. In this projection, one of the atoms in the three-membered ring completely obscures another atom in one-half of the molecules and is completely obscured by that atom in the other half. The a' and c' axes of the pseudo-orthogonal cell are marked by discontinuous lines at the lower portion of the drawing.

We conclude that the packing forces prevent substantial valence tautomerism from occurring in the bullvalene crystal at 25°. The rearrangement observed in the 3:1 bullvalene–$AgBF_4$ complex[4] must be due to less restrictive packing forces in that crystal.[7a]

Acknowledgment. The bullvalene used in this study was obtained through the courtesy of Union Carbide Research Institute.

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[1] Work supported by U. S. Public Health Service Grant GM 12470-03.

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[8] Author to whom inquiry should be addressed.

Topography of Nucleic Acid Helices in Solutions. V. The Interactions of L-, D-, and DL-Amino Acid Derivatives with Nucleic Acid Helices. Demonstration of an Asymmetric Surface[1]

Sir:

We wish to report the synthesis and the interactions of several amino acid amides of the general structure I,

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[1] For part IV in this series see E. J. Gabbay and R. R. Shimshak, *Biopolymers*, in press.