Table I. Data for Compounds Characterized Solely by Crystallography

Compound	Unit cell; space group[f] (no. of nonzero reflections used)	Discrepancy indices[a,b] R_1, R_2	Working time, man hr	Elapsed time,[c] hr	Computing cost,[e] dollars
5[d]	$a = 9.252, b = 9.146, c = 12.153$ Å, $\beta = 106.25°$; $P2_1/n$ (790)	0.083 0.094	9	60	157
6[g]	$a = 7.476, b = 11.912, c = 6.606$ Å, $\alpha = 94.55$, $\beta = 110.17, \gamma = 92.38°$; $P\bar{1}$ (1283)	0.072 0.101	9	96	138
7	$a = 8.178, b = 6.800, c = 9.729$ Å, $\alpha = 101.98$, $\beta = 106.99, \gamma = 95.83°$; $P\bar{1}$ (1433)	0.082 0.102	6	60	134
8	$a = 10.401, b = 9.779, c = 6.554$ Å, $\alpha = 98.69$, $\beta = 111.76, \gamma = 82.65°$; $P\bar{1}$ (1091)	0.076 0.105	6	120	127
Mean			7.5	84	139

[a] After convergence of isotropic refinement, omitting hydrogen atoms. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. [c] From first observation that crystals had formed to termination of crystallographic study. [d] Collaboration of Dr. B. A. Frenz is acknowledged. [e] Computing was done on an IBM 360-65 machine at a cost of $325 per hr. [f] Delauney reduction indicates that there is no higher space group symmetry for the triclinic compounds. [g] This compound also crystallizes in space group $Pna2_1$ and the structure in this form has been independently determined (A. H.-J. Wang, I. C. Paul, and R. Aumann, private communication).

other products could be isolated, some in very small quantities, but all in crystalline form. In view of our previous experience, especially with compounds **4** and **5**, we decided to adopt the following strategy. No attempt whatever would be made to identify or characterize products by classical (*i.e.*, analysis or ir, nmr, or mass spectra) methods; instead, the structure would immediately be determined and refined isotropically to convergence. In this way compounds **6**, **7**, and **8** were quickly, cheaply and completely identified and characterized. The working time, total elapsed time, and direct cost are all as good as or better[7] than they would be in a classical approach. Moreover, the structures, especially of **6** and **8**, would probably have been indeterminate from spectroscopic data, anyhow.

We note also that two other products were quickly, conclusively, and without direct cost shown to be known compounds, namely *trans*-$C_8H_8[Fe(CO)_3]_2$ and $C_8H_8Fe_2(CO)_5$,[8] which presumably arise from traces of cyclooctatetraene present (*vide infra*) as an impurity in the $C_{10}H_{12}$.

Compound **6** can be considered as a derivative of barbaralone[10] derived from it by opening of the three-membered ring and insertion of $Fe(CO)_3$. We do not mean to suggest that the compound necessarily arises in that way, although it might, in view of the known reaction of semibullvalene with iron carbonyl.[11] The question of how the barbaralone itself might form would then have to be answered. The origin of compound **7** is also quite mystifying. Perhaps a part of the answer is that the bicyclodecatriene used was slightly contaminated with some 1,3,5-cyclooctatriene as well as with C_8H_8, although vpc of the ligand showed approximately 95% $C_{10}H_{12}$ and 5% C_8H_8, and no other significant component.

Compounds **4**, **5**, and **8** can be reasonably assigned parentage in the bicyclodecatriene, but it is certainly not obvious how and why they are formed.

Even today one frequently sees or reads the assertion that spectroscopic structure methods must be accorded great reverence because of the relatively immense difficulty, time requirement, and expense of crystallography. As a *generalization*, this notion is a kind of *recherche du temps perdu*, and we offer the foregoing report in evidence of this judgment.

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[7] Clearly, the working times to record and interpret various spectra would be comparable to those listed in the Table I. Elapsed times for obtaining elemental analyses commercially normally exceed those in the table by a factor of 2 or 3. Aggregate costs of instrument use for ir, nmr, and mass spectra, plus the cost of microanalyses for three elements, and the cost of duplicate molecular weight determinations usually exceed $100 at a typical American university.

[8] In the case of $C_8H_8Fe_2(CO)_5$ we were slightly delayed because our crystallographic parameters, *viz.*, *Pnma*, $a = 7.304$ Å, $b = 15.451$ Å, $c = 11.065$ Å, disagreed with those in the literature[9] with respect to a, which was reported as 7.71 Å. Professor E. B. Fleischer has informed us that the published value is a misprint.

[9] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 3158 (1966).

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An Experimental Method for the Determination of the Structure of Complex Negative Ions in Solution

Sir:

A nematic ternary middle soap phase[1] of decanol, sodium decyl sulfate, and water has been used as an orienting environment for certain small polar solute molecules.[2–6] The nuclear magnetic resonance (nmr) spectra of these solutes can be used for structural studies by determining the partially averaged dipole–dipole

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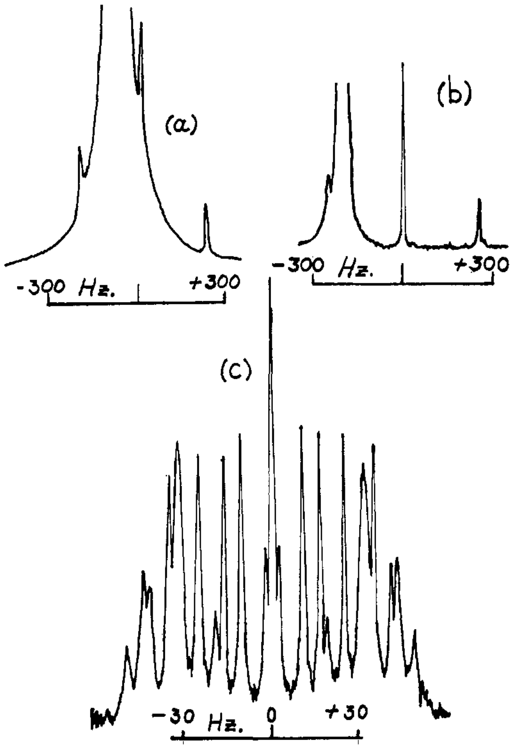

Figure 1. Proton magnetic resonance spectra from the quaternary cationic detergent phase at 33.3° and 60 MHz: (a) methanol; (b) acetate ion; (c) cacodylate ion.

coupling constants.[7] Unfortunately, this nematic phase, which is sometimes used in conjunction with sodium sulfate, is unstable in the presence of all but a few rather specific solutes. A much more general and useful property of the phase is its ability to sustain partial or complete exchange of the sodium ion for positive complex ions without loss of the nematic behavior. The phases prepared from general complex ion decyl sulfates provide an orienting medium for such positively charged ions, and since the ions are present in high concentrations, provide nmr spectra which can be used for structural studies.[8] This method is the first available for the determination of the structure of positive complex ions in aqueous solution.

The method is only applicable to positive ions since the detergent counterion (decyl sulfate) is negative. In order to make this new technique applicable to all complex ions (negative as well as positive) it has been necessary to investigate a new type of nematic phase. In this report the use of a quaternary mixture with a cationic detergent gives the necessary middle soap properties and extends the experimental method to complex negative ions.

The phase is prepared from decylammonium salts, ammonium chloride, decanol, and water. The concentrations (slightly dependent on the anion) are similar to those employed with the anionic detergent. The nematic phase may be made by neutralizing decylamine with the appropriate acid in water and then adding decanol and ammonium chloride to the required proportions. Purity of all components of the mixture is critical and consequently this simple method often fails. Preparation and recrystallization of the decylammonium salts are preferable and when possible with the compounds we have investigated the nematic phase always forms. The decanol also must be carefully purified either by distillation or fractional crystallization. In cases where the acid of the complex ion is unstable, ion exchange methods are appropriate as discussed previously for the anionic detergent[8] and differ in no essential regard from this inverse case. Complete exchange of the complex ion for the simple ion such as chloride is not necessary and, in fact, the nmr spectra may be more highly resolved with incomplete replacement.

The almost complete lack of ternary or quaternary phase diagrams for mixtures containing anionic and cationic detergents[1] requires some trial and error in finding the exact composition in the limited region of the nematic middle soap phase.

No lyotropic nematic phase has been reported as an orienting medium for nmr studies other than that in the original communication of Flautt and Lawson.[2] The phases prepared here with decylammonium chloride do orient small polar molecules as well as ions but suffer similar severe limitations in the choice of solute material. An example is given in Figure 1a for methanol oriented in a mixture having the following weight composition: *n*-decylammonium chloride, 34.2%; decanol, 3.2%; water, 55.0%; methanol, 3.7%; ammonium chloride, 3.9%. The proton magnetic resonance spectrum, recorded on a Perkin-Elmer R-10 at 60 MHz, shows clearly the triplet (D = 106.8 Hz) expected for the intramethyl dipolar coupling. This demonstration of a small oriented molecule should not be interpreted as a general and useful property of the medium.

The two negative ions chosen for demonstration of the general technique are the acetate and the cacodylate $((CH_3)_2AsO_2)^-$ ions. *N*-Decylammonium acetate was prepared as the pure salt while decylamine was combined with cacodylic acid directly when preparing the other phase. The mixtures were prepared with the following compositions: for the acetate ion, decylammonium acetate, 30.1%; *n*-decylammonium chloride, 16.1%; decanol, 2.9%; water, 46.2%; ammonium chloride, 4.7%; for the cacodylate ion, cacodylic acid, 7.1%; *n*-decylamine, 8.5%; *n*-decylammonium chloride, 16.2%; decanol, 4.0%; water, 60.9%; ammonium chloride, 3.3%.

The samples can be rotated in the probe of a conventional spectrometer as with the anionic detergent. Such rotation is possible because the cylindrical superlattice of the middle soap phase orients perpendicular to the magnetic field and thus parallel to the axis of rotation of the nmr sample tube.[1]

In Figure 1b, apart from the water peak, the triplet for the acetate ion is well resolved with a D of 153.2 Hz. The proton nuclei of the cacodylate ion have C_{2v} symmetry, assuming rapid rotation of the two methyl groups. The spectrum in Figure 1c gives D = +20.08 Hz for the intramethyl and D' = −4.83 Hz for the intermethyl dipolar couplings. The long-range J_{HCAsCH} scalar coupling has a value of J = −0.29 Hz. Since two motional constants are required for C_{2v}

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symmetry[7] and only two dipolar couplings are available, no structural information is possible for this ion.

The mechanism which allows ordering in this phase and that described by Flautt and Lawson[2] is quite different from that in thermotropic nematic phases. The small ions or molecules are located in the interstitial aqueous region of the middle soap phase and have available a very large surface area of the relatively static component of an electrical double layer. The small ions form a mobile component of the double layer and are free to exchange between the highly ordered surface of the cylindrical superstructure and the interstitial water. On the average over these motions the ions are ordered by the surface forces. For the case of sodium ion 2–5% of the ions are at the interface of the double layer region at any one time.[9]

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Implications of the Low-Temperature Nuclear Magnetic Resonance Spectrum of the 3-Picoline Diadduct of Tris[2,2,6,6-tetramethylheptane-3,5-dionato]europium

Sir:

Numerous authors[1–14] have suggested that lanthanide-induced shifts (LIS) can be rationalized on the basis of an equation of the type

$$\frac{\Delta\nu_i}{\nu_0} = K\left\langle\frac{3\cos^2\theta_i - 1}{r_i^3}\right\rangle \qquad (1)$$

where $\Delta\nu_i$ is the induced shift, ν_0 is the probe frequency, r_i is the length of a vector joining the metal with the ith proton, and θ_i is the angle that this vector makes with the unique magnetic axis, when axial symmetry of the complex is assumed. Furthermore it is commonly assumed[1–14] that this magnetic axis passes through the lanthanide ion and the donor atom of the substrate. Were this true, then the low-temperature spectrum in the slow or nonexchange region for the system Eu(dpm)$_3$(3-pic)$_2$ would exhibit a single peak for the ortho protons since both θ_i and r_i would be identical for all ortho protons. For the same reason a single meta, a single methyl, and a single para peak would be observed.

Some authors, while assuming axial symmetry for the complex, have carried out a systematic search for the location of the magnetic axis which yields the best fit of the observed data, and have found that the axis does not pass through the donor atom.[15,16] If such a model were true, and if the 3-picoline ring were not free to rotate, then two ortho, two meta, two methyl, and a single para peak would be observed in the nonexchange region.

The recently reported crystal structures of Ho(dpm)$_3$(4-pic)$_2$[17] and Eu(dpm)$_3$(py)$_2$[18,19] show that these complexes, far from having axial symmetry, possess only a C$_2$ axis passing through the lanthanide ion and the methine carbon of a chelating dpm$^-$ [20] moiety. Furthermore, each pyridine ring in Eu(dpm)$_3$(py)$_2$ experiences 11 close intramolecular contacts[18,19] so that free rotation about the Eu–N bond cannot occur. The principal axis of symmetry of such a complex does not lie along the lanthanide–substrate line but is near the C$_2$ axis. The structural results thus suggest that two ortho, two meta, and two methyl peaks, and a single para peak should be observed.

Evans[21] has recently reported that exchange between free and complexed Me$_2$SO can be stopped at −80° for the system Eu(fod)$_3$(Me$_2$SO)$_2$. In an attempt to obtain experimental evidence which could indicate which of the above models is correct, we have carried out low-temperature studies of the Eu(dpm)$_3$-(3-pic)$_2$ system in CS$_2$. Upon lowering the temperature of a sample which is 0.0240 M in Eu(dpm)$_3$ and 0.1120 M in 3-picoline in CS$_2$, the signals begin broadening and resolve into peaks due to free and complexed substrate at approximately −110°. This lower coalescence temperature confirms Evan's hypothesis[21] that the chemical exchange within the Eu(dpm)$_3$(substrate)$_n$ (n = 1, 2) system would be faster due to the weaker acceptor properties of the Eu(dpm)$_3$ shift reagent. The low-temperature spectrum reveals *two* ortho, *two* meta, and *two* methyl resonances. The chemical shifts of the resulting complexed peaks are given in Table I. We have also carried out similar

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