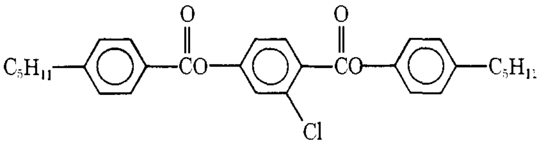
lesteric characteristics, in contrast to the majority of cholesteryl-based materials, which are left-handed. Furthermore, they are very tightly "wound"; that is, they have a small optical pitch which affects ultraviolet radiation. In order to measure the optical pitch of these compounds and avoid the ultraviolet molecular absorption, it is necessary to measure the optical pitch of binary mixtures of a chiral nematic compound with a similar-type optically inactive nematic compound. Ideally, the mixtures should consist of the chiral nematic and its racemate.[15] From a practical point of view, we chose the dipentyl phenylene diester **18**



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because of its structural similarity to the chiral nematic esters, especially with respect to the phenylene diesters, as well as its low, broad nematic range (39–122°). Thus, monotropic chiral nematics are rendered "enantiotropic" and high-melting materials are rendered "lower melting." Furthermore, the melting-point-depression effect of mixtures enables many measurements to be made at or near room temperature.

All the optical-pitch values,[16] except for one example, are smaller than any previously reported (0.357 μm);[3] indeed, the symmetrical phenylene diesters display values (0.15–0.18 μm) approximately half that magnitude and which are the smallest known to date. Compound **3** is similar in size to its Schiff-base counterpart[3] but has an optical-pitch value 50% smaller (0.24 vs. 0.357 μm).

Note also that the "tighter" the helix, that is, the lower the optical pitch, the more optically active group(s) as a percent of the molecular size. Thus, the symmetrical phenylene diesters **9–11** with two chiral centers have the smallest optical pitch values and the highest percentage of optical activity, and the simple esters have intermediate values. In addition, the importance of having the chiral alkyl group attached directly to the aromatic system without an intervening oxygen atom or other functionality has been demonstrated and supports our premise that, in general, chiral alkyl (as opposed to alkoxy) groups, and specifically the chiral 2-methylbutyl group, favor chiral nematics with small optical-pitch values. Furthermore, the distance of the chiral center from an aromatic ring, the number of chiral centers, and the size of the molecule are critical factors affecting the magnitude of the optical-pitch value. Since these new chiral nematic esters are right-handed cholesterics, encompass a broad spectrum of temperature ranges, are based on the relatively stable ester linkage, and have very small optical-pitch characteristics such that they can be "diluted" to become color active, these materials offer more stable useful alternatives to and complement the well-known cholesteric liquid crystals based on the cholesteryl moiety.

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(15) Separate measurements employing chiral nematic unsymmetrical phenylene diesters **13** and **14** and their respective racemates led to the same optical-pitch values as obtained using **18** instead of the racemates. Similarly, the use of a nematic simple ester, 4′-hexyloxyphenyl 4-pentylbenzoate, with chiral nematic simple ester **4**, having the same molecular weight, gave values identical with those obtained with **18**, a somewhat longer molecule.

(16) The optical-pitch measurements were made at 28° using a Cary Model 14 spectrometer to scan transmitted light of Grandjean films of mixtures of chiral nematics and **18** absorbing between 350 and 1600 nm. The inverse optical pitch, 1/λ, is plotted against the weight percent chiral nematic in the mixture. Extrapolation to 100% chiral nematic gives the inverse optical pitch for the pure chiral nematic compound. The optical-pitch values (λ or $\bar{n}p$) are given in Table I.

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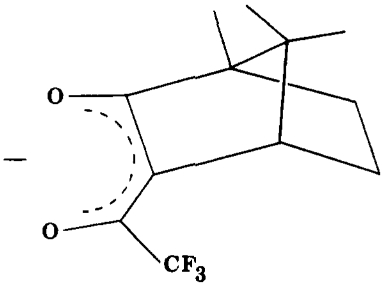
The Structure of an Adduct of a Chiral Lanthanide Nuclear Magnetic Resonance Shift Reagent

Sir:

Complexes between trivalent lanthanide ions and optically active β-diketones have been used to facilitate the determination of enantiomeric purity by NMR methods.[1] Chiral lanthanide complexes were first reported to be useful probes by Whitesides and Lewis.[2] In addition to the well-known lanthanide induced isotropic shifts, the presence of asymmetric centers in the β-diketonato ligands produces a differential shift between the resonances of equivalent nuclei in an enantiomeric pair. Although other optically active β-diketones have been investigated as potential ligands,[3] the most widely used chiral shift reagents are based on 3-trifluoroacetyl-*d*-camphor[4,5] (I).

Despite the wide interest in and use of these reagents, no determination of the structure of a chiral lanthanide shift reagent has previously been reported and little is known about the detailed bonding and steric requirements of these complexes. Without such information chiral shift reagent



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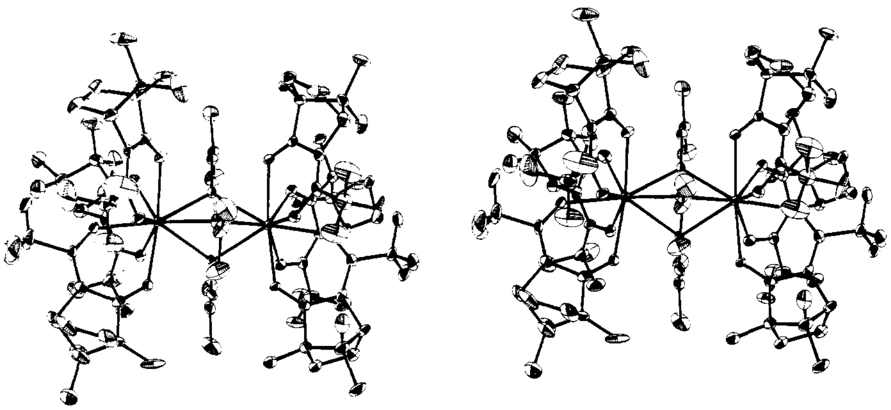

Figure 1. A stereoscopic drawing of the (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$ dimer. Average bond lengths and angles of interest are: Pr-O(facam), 2.46 (3) Å; Pr-O(DMF), 2.60 (2) Å; Pr-Pr, 4.078 (9) Å; Pr-O(DMF)-Pr, 103.6 (1.8)°.

chemistry will remain a poorly understood art, and little progress can be made toward such important goals as the determination of absolute configurations by NMR. We have synthesized and have obtained in crystalline form an adduct between DMF and Pr(facam)$_3$. The successful determination of the crystal structure, reported herein, reveals the asymmetric unit to be the dimer (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$, with the DMF oxygen atoms forming bridges between the two Pr(facam)$_3$ moieties, indicating that steric bulk of the ligands probably is not as important as once thought.[6]

Both the ligand, Hfacam, and the complex, Pr(facam)$_3$, were synthesized following the methods of Feibush et al.[7] The adduct was prepared by saturating hot, reagent grade, DMF with the unsolvated complex and allowing the solution to slowly cool to room temperature. Excellent, air-stable, light-green crystals were then obtained from the slow isothermal evaporation of a hexane solution of the adduct of composition $Pr_2C_{81}H_{105}O_{15}N_3F_{18}$.

Preliminary photographic studies of a crystal with dimensions 0.24 × 0.26 × 0.35 mm mounted on the end of a glass fiber and unprotected from the ambient atmosphere revealed the Laué symmetry $2/m$ and a systematic extinction consistent with the monoclinic space groups $P2_1$ ($C^2{}_2$, No. 4) or $P2_1/m$ ($C^2{}_{2h}$, No. 11).[8] The presence of only one enantiomer of the chiral ligand in the complex eliminated from consideration the centrosymmetric space group, and the asymmetric space group $P2_1$ was assumed throughout the structure determination and refinement procedure. Precision lattice constants[9] of a = 17.930 (6) Å, b = 19.403 (6) Å, c = 13.049 (4) Å, and cos β = −0.0189 (6) giving β = 91°5′ together with a measured density of 1.44 (2) g cm^{-3} indicated the unit cell contained two of the dimeric units (ρ_c = 1.45 g cm^{-3}). Ambient laboratory temperature was 20 ± 1°.

The intensities of all independent reflections in the range $0.03 \leq (\sin\theta)/\lambda \leq 0.649$ were measured by the θ-2θ scan technique using a fully automated Picker four-circle diffractometer equipped with a molybdenum target X-ray tube and a Zr-foil filter ($\lambda K\alpha_1$ 0.70926 Å). After correction for background, the intensities of the 10,491 independent reflections were directly reduced to a set of relative scattering amplitudes, $|F_o|$. The 8779 reflections satisfying the criterion $|F_o| \geq 3.0\sigma(|F_o|)$ were used to develop and refine the structure by the heavy-atom method. The standard deviation of each structure amplitude, $\sigma(|F_o|)$, was obtained from a consideration of only counting statistics.

The parameters of the 119 independent carbon and heavier atoms in the asymmetric unit were refined utilizing a block diagonal, least-squares minimization of the function $\Sigma w(|F_o| - k|F_c|)^2$, with empirical weights ($w = \sigma^{-2}$) calculated in a manner previously described.[10] Refinement of the fully anisotropic model converged to a conventional R of 0.0709 and a weighted R of 0.0908.

A stereoscopic computer drawn model of the (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$ molecule as it exists in the crystal is displayed in Figure 1. The oxygen atoms of the DMF ligands are equally shared by the two Pr atoms and act as bridges between the two Pr(facam)$_3$ moieties. In contrast to the pattern displayed in $[Pr_2(fod)_6(H_2O)]\cdot H_2O$,[11] the facam ligands have been blocked by the larger DMF molecules from participating in the bridging and are further restricted to positions that are almost entirely on the hemisphere of each Pr atom that is opposite to the bridging network. No short interligand approach distances are observed in the structure, indicating steric crowding is not a serious problem and may not be as dominant a factor in determining the stereochemistry of lanthanide shift reagents as was once believed. Further evidence that this arrangement does not produce undue strain or instability within the dimer may be inferred from the lack of any observable decomposition of the unprotected sample crystal during the several months required to study it.

Each Pr atom is nine-coordinate with the oxygen atoms occupying the vertices of a distorted monocapped square-antiprism. This structure determination represents the first documented case in which a lanthanide NMR shift reagent has a coordination number (CN) greater than eight. Horrocks has concluded, based solely on intramolecular steric considerations, that expansion beyond CN = 8 is unlikely in lanthanide shift reagent complexes because of demanding steric requirements of the bulky β-diketonato ligands.[12] Based on the structural results reported herein and the observed stability of the dimer, it can be seen that even in this molecule, which contains large facam ligands, there is still sufficient space in the coordination sphere of Pr(III) to adequately accommodate three DMF ligands without resulting in serious steric interactions. While intramolecular steric factors are doubtlessly of prime importance, the influence of other factors such as the nucleophilic strength of the substrate ligand, intermolecular packing considerations, and hydrogen bonding may ultimately decide the CN exhibited by a higher coordinate complex in a crystalline arrangement.[13]

It is also clear from the study of this structure that there is sufficient room for nine donors to be accommodated in the coordination sphere of Pr(III), even when three facam ligands are present. This suggests that considerably bulkier ligands than facam can be utilized and still leave ample room for a single additional nucleophile, so long as the monodentate nucleophile is not unusually large. On the other hand, the "pocket" in the coordination sphere of Pr(facam)$_3$ appears to be sufficient in size to accommodate quite large nucleophiles.

Acknowledgment. We wish to thank Ms. P. R. Blum for synthesizing the ligand, Hfacam, and the complex (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$ used in this work.

Supplementary Material Available. Table I, atomic coordinates in (facam)$_3$Pr(DMF)$_3$Pr(facam)$_3$, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-1586.

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Excitons in One-Dimensional Tetracyanoplatinite Salts

Sir:

Although the recent flurry of activity[1] on the electronic properties of metal chain compounds has been mainly concerned with the so-called "partly oxidized" (i.e., mixed valence[2]) platinum salts, in the solid state quite a lot of ordinary divalent square planar platinum salts form stacks in which the metal atoms are also brought into reasonably close proximity. These compounds are of course insulators, not metals, but they do have extremely unusual optical properties which are clearly the result of the one-dimensional character of their crystal lattices. The purpose of this note is to draw attention to a strikingly simple correlation between the structural and optical parameters in one set of Pt(II) salts, the tetracyanoplatinites, which strongly suggests that the lowest excited states of one-dimensional single valence platinum compounds can be described as neutral Frenkel excitons, propagating along the stacks.

Briefly stated, the unusual optical properties of the tetracyanoplatinites are the following: in dilute aqueous solution the isolated $Pt(CN)_4{}^{2-}$ ion has major absorption bands at 35,800 (ϵ = 1480), 39,200 (ϵ = 10700), and 46,100 cm^{-1} (ϵ = 22100).[3] It does not appear to have any further absorption bands, even weak ones, at lower energies. Nevertheless, many tetracyanoplatinite salts, particularly those of group 1A and 2A cations are intensely colored and, moreover, exhibit strong visible luminescence. Polarized single-crystal reflection spectra[4] of Mg, Ca, Sr, and Ba tetracyanoplatinites demonstrate that at room temperature the visible absorption consists of a single broad band, polarized almost entirely parallel to the metal atom chains, whose oscillator strength in that direction has the order of magnitude of unity. The frequency of the band varies very markedly from one salt to another; it lies lowest in $MgPt(CN)_4 \cdot 7H_2O$, which also has the shortest Pt–Pt spacing (3.13 Å[5]). That the frequency in fact varies monotonically with Pt–Pt spacing is demonstrated by the extensive set of structural and optical data collected by Moreau-Colin.[6]

Since the tetracyanoplatinites are insulating crystals in which the molecular units remain clearly distinguishable, it seems a priori probable that the lowest crystal excited states should be neutral Frenkel excitons formed from simple molecular transitions, coupled by the intermolecular interaction potential. The simplest approximation to the latter is the point multipole expansion. Because the intense low energy crystal absorption band is polarized parallel to the Pt chains, its origin must lie in an allowed transition polarized perpendicular to the planes of the units, i.e., A_{2u} in the double group D^*_{4h}, which could arise either from a metal-to-ligand charge transfer ($d_{z^2} \rightarrow a_{2u}\pi^*$) or a $d_{z^2} \rightarrow p_z$ transition of the metal or, perhaps more likely, some admixture of the two. The molecular transition dipole vectors within each stack then being parallel to one another, the resulting crystal transition should suffer a Davydov shift to lower energy which in the point dipole approximation,[7] and assuming only interactions between nearest neighbors in the stack, would be $2e^2|M|^2/R^3$, where M is the transition dipole moment in the free ion and R is the Pt–Pt spacing within the stack. This possibility was mooted some years ago[8] but without definitive evidence.

An obvious means of testing whether the observed bands are indeed still Davydov components would thus be to plot their energies against R^{-3}. This we have done in Figure 1, for both tetracyanoplatinites and tetracyanopalladites, using the data of Moreau-Colin.[6] The result is such an excellent linear correlation that there can be no doubt of the essential correctness of the original hypothesis. Furthermore the extrapolated frequencies of the transitions at $R = \infty$ (i.e., for the free ions) are 44,800 and 52,900 cm^{-1} for $Pt(CN)_4{}^{2-}$ and $Pd(CN)_4{}^{2-}$, respectively, well within the range of energy of the intense transitions of both ions in solution.

Yet more confirmation comes from the assignments of the relevant states in the free ions. A spin-orbit calculation[3]