slope of the curve for the corresponding iodide complex was assumed and the line was located with the aid of the apparent second-order kinetic behavior (*vide infra*) in the low-temperature region. The qualitative conclusions of LaLancette and Eaton[8] regarding the nickel systems, namely that the lability of the coordinated phosphine increases in the order I < Br < Cl, are corroborated by our data for both cobalt and nickel. As seen from the figures, exchange invariably sets in at lower temperatures for the bromides than for the iodides. Contrary to an earlier report[9] dealing with the diiodobis(tri-*p*-tolylphosphine) compounds, $MI_2(TTP)_2$, a comparison of the corresponding cobalt and nickel complexes shows the latter to be considerably more labile, with exchange becoming apparent at lower temperatures. Preliminary results of ours with TTP complexes indicate a behavior entirely analogous to that found for the TPP compounds. The earlier line-width study[9] was made on solutions of the $MI_2(TTP)_2$ compounds, however, without added excess TTP no doubt causing the results to be highly sensitive to any solvolysis or decompostion in solution.

For an exchange process first order in complex concentration, we have $1/\tau_M = k_1$, where k_1 is the pseudo-first-order rate constant; however, for second-order kinetics, $1/\tau_M = k_2[\text{ligand}]$. The data presented in the figures indicate that the exchange reactions are second order within experimental error. Experiments at different complex concentrations gave results identical with those reported. Table I gives values of the second-order rate constants, k_2, extrapoloated to 25°, and values of ΔH^* and ΔS^* obtained from linear plots of log (k_2/T) *vs.* $1/T$. The fairly sizable negative values of ΔS^* are to be expected for a bimolecular process with a pentacoordinate transition state. For the most labile of the complexes studied, $NiBr_2(TPP)_2$, the line widths decrease as expected with increasing temperature above 40°, the temperature at which the resonances of the free and coordinated TPP merge (Figure 2).

Table I. Kinetic Parameters for Triphenylphosphine Exchange with the Complexes $MX_2(TPP)_2$

MX_2	k_2 (25°)	ΔH^*, kcal/mole	ΔS^*, eu
$CoBr_2$	8.7×10^2	7.7	−19.3
CoI_2	2.6×10^2	9.1	−17.0
$NiBr_2$	6.9×10^3	4.7	−25.1
NiI_2	6.4×10^2	6.9	−22.5

While ligand-field stabilization (LFS) is by no means the only factor affecting the rates of ligand exchange in transition metal complexes, it does serve to explain certain observations: for instance, why octahedral d^8 nickel(II) with a fairly large ground-state LFS energy forms complexes more robust than those of octahedral d^7 cobalt(II). Our results for the same two metals in roughly tetrahedral environments show the opposite behavior consistent with the greater LFS of tetrahedral cobalt(II) compared with nickel(II) (the LFS energies of either a square-pyramidal or trigonal-bipyramidal transition state are roughly the same for these cases[12]). The present tetrahedral complexes

(12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

also contrast with their octahedral counterparts which generally show first-order kinetics in their substitution reactions.

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Geometry of the $[Y(CF_3COCHCOCF_3)_4]^-$ Ion. A New Eight-Coordinate Stereoisomer in the Dodecahedral Class

Sir:

Recently, we have undertaken an investigation of the solid state and solution properties of several anionic eight-coordinate β-diketonate complexes of yttrium(III) and the lanthanides.[1-3] In the course of preparing crystalline samples for various studies, it was discovered that certain relatively large but flexible organic cations, such as $(C_6H_5)_4As^+$ or $C_5H_{10}NH_2^+$, give rise to a polymorphism not observed when simple inorganic cations (Na^+, K^+, Cs^+) are employed.[1,4] It is possible that this polymorphism might be due to a form of geometric isomerism for the eight-coordinate anions never before observed in tetrachelate metal atom complexes. In connection with this possibility, we note that, previously, there has been evidence for only two of the various possible arrangements of four bidentate ligands around a central metal atom. These are I, the D_2 square antiprismatic configuration which occurs, for example, in the crystal structure of the tetrakisacetylacetonatozirconate(IV) molecule and, II, the D_{2d} dodecahedral configuration which occurs, for example, in the crystal structure of the tetraoxalatozirconate(IV) anion.[5,6] In no case, however, have both of these configurations been found for a given metal–ligand system, nor has any other of the possible configurations been known to exist.
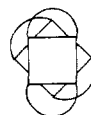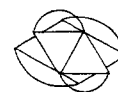
I   II

Here we report the crystal and molecular structure of $Cs[Y(HFA)_4]$.[7] This remarkable compound, which has been shown before[3] to sublime without decomposition at temperatures ranging from 180 to 230°, is now found to possess a unique dodecahedral arrangement of ligand molecules about the central yttrium atom.

Crystals of $Cs[Y(HFA)_4]$ were obtained as described previously.[3] On the basis of Weissenberg and precession photographs, taken with Cu $K\alpha$ radiation, the compound was found to have Laue symmetry mmm with lattice constants $a = 8.683 \pm 0.007$, $b = 21.52 \pm 0.02$, $c = 17.58 \pm 0.01$ A. From the measured density, $\rho = 2.1$ g/cc, and observed systematic absences, $hk0$, $h + k \neq 2n$, $h0l$, $l \neq 2n$, and $0kl$, $k \neq 2n$, the space

(1) S. J. Lippard, *Proc. Intern. Congr. Coord. Chem.*, *9th*, 476 (1966).
(2) F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, in press.
(3) S. J. Lippard, *J. Am. Chem. Soc.*, **88**, 4300 (1966).
(4) H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, **86**, 5125 (1964).
(5) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1965).
(6) G. L. Glen, J. V. Silverton, and J. L. Hoard, *ibid.*, **2**, 250 (1963).
(7) HFA = hexafluoroacetylacetonate, $CF_3COCHCOCF_3^-$.

group was ascertained to be Pbcn with four molecules per unit cell.

Using the equiinclination Weissenberg technique, intensity data were collected for successive layers $0kl$ through $6kl$ using Cu Kα radiation. The intensities were estimated visually against a calibrated strip prepared from the same crystal. Absorption and anomalous dispersion corrections were applied along with the usual Lorentz-polarization corrections and, after placing the data on an absolute scale by Wilson's method, a three-dimensional Patterson function was computed. From the Patterson map, both the cesium and yttrium atoms were located on twofold axes in the crystal. The rest of the structure was solved by successive least-squares and Fourier calculations.[8] At the present stage of refinement, the conventional R factor[9] is 0.14 for 750 observed reflections. The individual isotropic temperature factors for the fluorine atoms range from 12 to 20 A^2, and, in addition, there is evidence for rotational disorder of the trifluoromethyl groups on the difference Fourier maps.

The basic structure of the [Y(HFA)$_4$]$^-$ anion is shown in Figure 1. Eight oxygen atoms surround the central yttrium atom at an average distance of 2.33 $\pm$ 0.04 A in a dodecahedral configuration. The angular dodecahedral parameters,[10] θ_A and θ_B, are 40 $\pm$ 2 and 67.5 $\pm$ 2°, respectively. Unlike all other dodecahedral complexes known to contain four bidentate chelating ligand molecules, however, the β-diketonate groups span the g edges of the dodecahedron rather than the m edges,[10] resulting in over-all idealized D$_2$ symmetry for the anion.[11] Although it is at present not possible to provide a detailed explanation for this behavior, it is interesting to note that the D$_2$ dodecahedral structure found for the [Y(HFA)$_4$]$^-$ ion may be derived from the D$_2$ antiprismatic structure, I, via a slight distortion of the latter structure in the manner shown below. One possible cause of this distortion

I, D$_2$ antiprismatic   III, D$_2$ dodecahedral
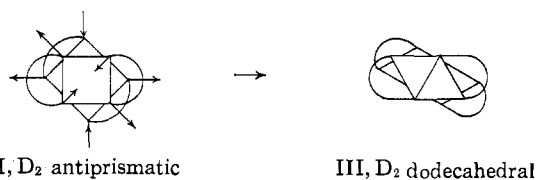
might be the close association of the Cs$^+$ ions with the [Y(HFA)$_4$]$^-$ anions found to occur in the crystal structure, for each cation is surrounded by eight fluorine atoms from two neighboring anions (Cs–F, 3.3 A). Taken collectively, these cations serve to link together infinite columns of discrete dodecahedral [Y(HFA)$_4$]$^-$ ions in the lattice. This packing interaction may also be related to the unusual volatility[3] of the compound.

Other X-ray crystallographic studies are currently in

(8) Programs for the IBM 7094 used in this work, in addition to various local programs written at the Brookhaven National Laboratory and kindly made available to us, were Burnham's GNABS absortion program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program and ORFFE error function program.

(9) Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(10) Cf. J. L. Hoard and J. V. Silverton, Inorg. Chem., 2, 235 (1963), for a definition of the nomenclature used here.

(11) Recently, M. Cefola, W. Hamilton, R. Lalancette, and S. LaPlaca (to be published) have determined the crystal structure of NH$_4$[Pr(TTA)$_4$]·H$_2$O (TTA = thenoyltrifluoroacetonate) and also find the ligand molecules to span the same four dodecahedral g edges. The over-all symmetry in their anion is less than D$_2$, however, since the attachment of one of the four asymmetric TTA ligand molecules is reversed from that of the other three.
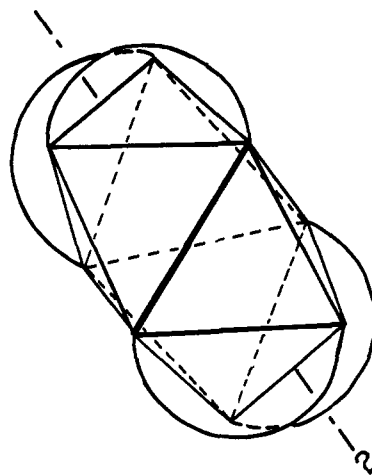
Figure 1. Schematic representation of the structure of the [Y(HFA)$_4$]$^-$ ion, assuming idealized D$_2$ symmetry. Half-circles indicate the pattern of ring attachment. The crystallographically required twofold axis is also shown.

progress to explore further the possibility that geometric isomerism might occur in certain eight-coordinate β-diketonate Y(III) complexes.

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Photochromism of Synthetic and Naturally Occurring 2H-Chromenes and 2H-Pyrans

Sir:

In the course of investigation of spectroscopic and photochromic properties of 1,3,3-trimethylindolinobenzospiropyran and its derivatives,[1] 2H-chromene (I) and a number of its simple derivatives were synthesized or obtained from other sources.

I   II   III
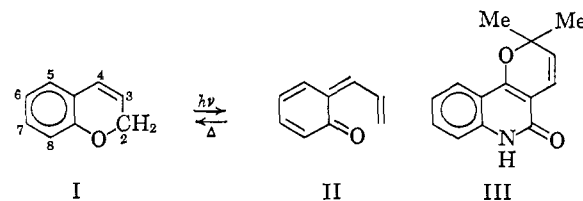
We wish to report that the latter compounds are photochromic and propose structure II for the colored form. This seems to be the only logical possibility and is in agreement with the following observations. Photochromism was observed in over 25 molecules, irrespective of the presence, location, and nature of

(1) R. S. Becker and J. K. Roy, J. Phys. Chem., 69, 1435 (1965).