Other derivatives of this series are under investigation to substantiate these findings.

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ethanol–water (w/w) at 20° (G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933)). The distances between the removable protons in these acids are similar: 4.6 ± 0.2 A in IV, 5.15 A in glutaric acid, and 4.66 A in succinic acid.

(11) National Science Foundation Fellow, 1964–1966.

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Kinetics of Ligand Exchange in Tetrahedral Complexes. Triphenylphosphine Exchange with Dihalobis(triphenylphosphine)cobalt(II) and -nickel(II) by Proton Magnetic Resonance[1]

Sir:

Relatively little is known of the kinetics of ligand substitution in tetrahedral coordination compounds. There have been no reports of such studies on divalent first-row transition metal complexes of this stereochemistry where the importance of ligand-field effects may be assessed. We report here a proton magnetic resonance (pmr) study of the kinetics of triphenylphosphine (TPP) exchange with the dihalobis(triphenylphosphine)cobalt(II) and -nickel(II) compounds of known pseudo-tetrahedral structure.[2-6] The pmr spectra of compounds of this type have been reported previously;[7-9] however, quantitative kinetic data were not obtained and an erroneous conclusion was reached[9] regarding the relative lability of the cobalt and nickel complexes.

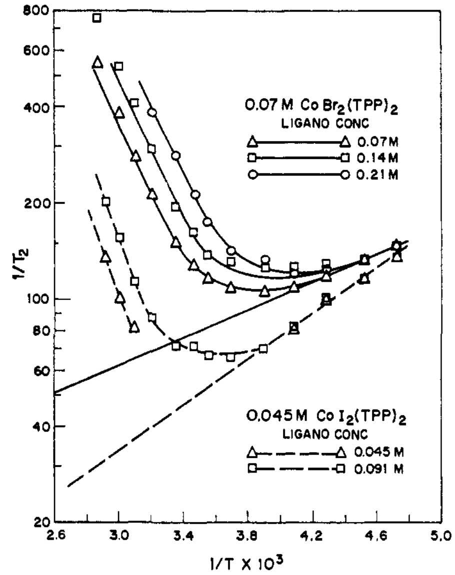

Figure 1. Plot of log ($1/T_2$) *vs.* $1/T$ for deuteriochloroform solutions of $CoBr_2(TTP)_2$ and $CoI_2(TPP)_2$ with various concentrations of excess triphenylphosphine (TPP) as indicated. The points for $CoI_2(TPP)_2$ at a TPP concentration of 0.045 *M* between $1/T$ = 3.2 and 4.0 were omitted because of precipitate formation in this range.

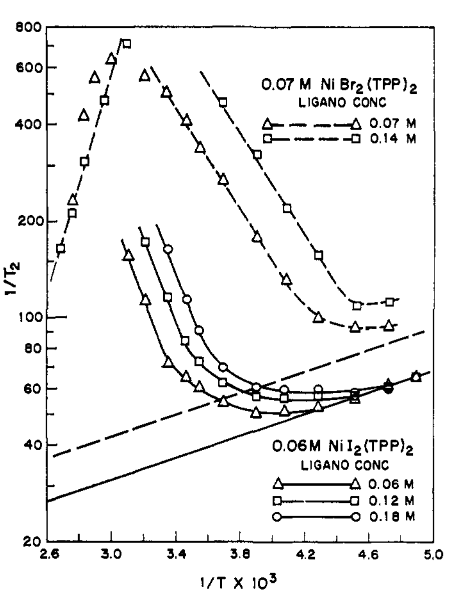

Figure 2. Plot of log ($1/T_2$) *vs.* $1/T$ for deuteriochloroform solutions of $NiBr_2(TPP)_2$ and $NiI_2(TPP)_2$ with various concentrations of excess triphenylphosphine(TPP) as indicated.

The present experiments were carried out on deuteriochloroform solutions of the complexes $MX_2(TPP)_2$, (M = Co, Ni; X = Br, I) containing known concentrations of excess TPP, using a Varian A-60A spectrometer equipped with a variable-temperature probe. In these solutions (except for $NiBr_2(TPP)_2$ above about 40°) separate resonances are observable for free TPP and for the isotropically shifted[7,8] coordinated ligand protons. Kinetic parameters were obtained from the measured line widths at half-height, $\Delta\nu_{1/2}$ (cps), of the downfield shifted phenyl *meta* proton resonance of coordinated TPP. In such a system the effective transverse relaxation time of a ligand proton, T_2, is given by $(1/T_2) = \pi\Delta\nu_{1/2}$. This is related to T_{2M}, the transverse relaxation time in the absence of exchange, and τ_M, the average residence time of a ligand in the complex, by eq 1.[10,11]

$$\frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \qquad (1)$$

Figures 1 and 2 show plots of log ($1/T_2$) *vs.* $1/T$ for the cobalt and nickel compounds, respectively, in the presence of various concentrations of excess TPP. $CoI_2(TPP)_2$ is the least labile of the complexes studied and at low temperatures shows the expected[9,10] decrease in $1/T_{2M}$ as the temperature increases. At higher temperatures $1/T_2$ increases as the exchange term, $1/\tau_M$, becomes important. Values of $1/T_{2M}$ in this region were obtained by extrapolation of the low-temperature behavior; however, for $NiBr_2(TPP)_2$ the

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[1] This research was supported by the National Science Foundation through Grant GP3397.

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

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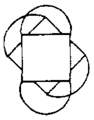
Geometry of the $[Y(CF_3COCHCOCF_3)_4]^-$ Ion. A New Eight-Coordinate Stereoisomer in the Dodecahedral Class

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 tetrakis-acetylacetonatozirconate(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.



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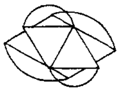

II

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

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