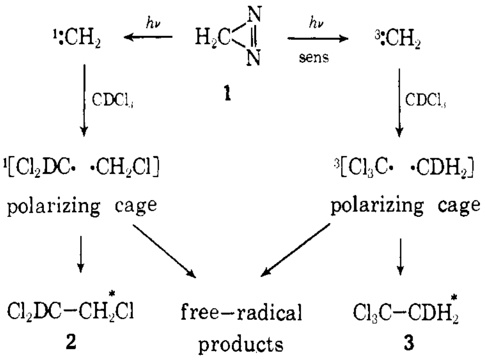
tential insertion products are simple. When diazirine is photolyzed in $CDCl_3$ solution a CIDNP spectrum is observed (Figure 1b). The dominating emission signal is attributed to spin-polarized 1-deuterio-1,1,2-trichloroethane (**2**), formed by chlorine abstraction and in-cage coupling of the resulting radical pair, [$Cl_2DC\cdot \cdot CH_2Cl$]. The observed signal direction is the same as in the case of the chloromethyl–trichloromethyl radical pair.[1] The factors determining the signal direction (in-cage coupling, negative *a* value, negative Δg) are the same for both radical pairs. Consequently, the emission signal observed for **2** establishes the singlet as the initial spin multiplicity of the parent radical pair and thus of the methylene involved in its formation.

When the decomposition of **1** in $CDCl_3$ is photosensitized, a new signal is observed, a 1:1:1 triplet in strongly enhanced absorption (Figure 1a). This signal has the chemical shift of 1,1,1-trichloroethane; its splitting pattern indicates the presence of a nucleus of spin 1 in the molecule; the magnitude of the observed coupling ($J \sim 1.9$ Hz) identifies this interaction as a geminal proton–deuteron coupling. The observed product, 2-deuterio-1,1,1-trichloroethane (**3**), is obviously formed by abstraction of the deuterium atom from deuteriotrichloromethane and recombination of the resulting radical pair (Scheme I). Since the polarized protons originate in the radical with negative Δg[11] and a negative *a* value, an absorption signal is compatible with a radical pair initially of triplet spin multiplicity and consequently with $^3CH_2$ as intermediate.

Scheme I[a]



[a] An asterisk denotes polarization.

It is noteworthy that the spectrum obtained during the photosensitized decomposition of **1** (Figure 1a) does not exhibit a signal of **2**. Earlier, we had observed that $^3CH_2$ (as well as $^1CH_2$) abstracts chlorine atoms from CCl_4.[1] Now we find that in $CDCl_3$, where hydrogen abstraction competes with halogen abstraction, $^3CH_2$ rather selectively abstracts hydrogen. We view the halogen abstraction by $^3CH_2$, a relatively stable ground-state[14] species, as kinetically unfavorable but certainly thermodynamically feasible.

Of equal significance is the complete absence (within the limit of detectability) of spin-polarized **3** in the singlet spectrum (Figure 1b). Barring the fortuitous cancellation of an enhanced absorption signal by a signal in enhanced emission of equal intensity, this observation means that $^1CH_2$ selectively abstracts chlorine atoms, that no triplet methylene is formed in the direct irradiation, and that the reactions of $^1CH_2$ with $CDCl_3$ are faster than the intersystem crossing to the triplet ground state.[15] The absence of an enhanced signal, of course, does not mean that the corresponding product is not formed; it only means that this product is not formed *via* a reaction sequence which allows the generation and observation of polarized nuclear spins. Consequently, our CIDNP evidence should not be interpreted as an argument against the well-established (one step) insertion reaction of methylene into carbon–hydrogen bonds.[16]

Concluding, we recall the results of Setser and coworkers, who inferred a similar specificity of singlet and triplet methylene for gas-phase reactions.[7] Their conclusion was based on kinetic studies of the photodecomposition of ketene and diazomethane in the presence of simple chloro-substituted alkanes and inert gases. It is gratifying and encouraging that an entirely different technique leads to essentially identical conclusions for the corresponding liquid-phase reactions.

Acknowledgment. The author is deeply indebted to Dr. Saul Meiboom and Mr. Richard Hewitt for their patient guidance during the use of a modified pmr spectrometer.

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[11] $g_{CH_3} = 2.0026$,[12] $g_{CCl_3} = 2.0091$.[13]

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Received June 7, 1971

X-Ray Determination of the Absolute Configuration of Metal Complexes in Quasiracemic Crystals. Λ-(−)$_{546}$-Cobalt(III) Acetylacetonate

Sir:

The number of dissymmetric metal complexes whose absolute configurations have been unambiguously established by X-ray methods is still quite small, and nearly all of the compounds studied to date are diamine complexes.[1] X-Ray studies of a wider variety of metal chelates are needed in order to test empirical spectroscopic criteria[2,3] for relating optical rotatory power and absolute configuration. We report here a simple X-ray method for determination of the absolute configuration of metal complexes in quasiracemic crystals and its application to Λ-(−)$_{546}$-cobalt(III) acetylacetonate.[4] The only other tris-β-diketonate complex

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(4) The designation of absolute configuration is in accord with the IUPAC recommendations, *Inorg. Chem.*, **9**, 1 (1970).

whose absolute configuration has been established by single-crystal X-ray methods is Λ-$(+)_{589}$-*trans*-tris-[(+)-3-acetylcamphorato]chromium(III).[5]

Crystallization of a mixture of partially resolved $\mathrm{Co(acac)_3}$[6] ($[M]_{546} = -20{,}200$) and racemic $\mathrm{Al(acac)_3}$ from benzene–hexane (~1:10 v/v) gives quasiracemic monoclinic crystals which contain an excess of $(-)_{546}$-$\mathrm{Co(acac)_3}$ and which display lattice parameters ($a = 13.96 \pm 0.02$, $b = 7.53 \pm 0.01$, $c = 16.32 \pm 0.02$ Å, $\beta = 98.66 \pm 0.05°$) nearly identical with those for the isomorphous crystals of racemic $\mathrm{Co(acac)_3}$ and racemic $\mathrm{Al(acac)_3}$.[7] However, the quasiracemic crystals show only the space group symmetry $P2_1$ instead of $P2_1/c$, that observed for the racemic acetylacetonates. In the quasiracemic $\mathrm{Co(acac)_3}$–$\mathrm{Al(acac)_3}$ mixed crystals, unequal substitution of cobalt in the two enantiomeric sites suffices to reduce the space group symmetry from the centrosymmetric $P2_1/c$ to the noncentrosymmetric $P2_1$ without requiring any change in atomic coordinates. For the crystal used in this determination, the reflections $l = 2n + 1$ on $h0l$, normally extinct for $P2_1/c$, appeared weakly but were quite sharp.

Intensity data on 268 reflections from the four layers $h0l$, $h\bar{1}l$, $0kl$, and $\bar{1}kl$ were estimated visually from multiple-exposure precession photographs taken with Ni-filtered Cu Kα radiation. Intralayer scaling of the intensities was performed with corrections for Lorentz-polarization and spot extension being applied.

Since the quasiracemic crystal is isomorphous with the racemic trisacetylacetonates of Co(III),[7] Al(III),[7] and Mn(III),[8] refinements of the site occupancies and interlayer scale factors (six parameters) were carried out using the previously published structural parameters for these three complexes. The results of these refinements, which employed only the real part of the scattering factors for $\mathrm{Co^0}$, $\mathrm{Al^0}$, $\mathrm{C^0}$, and $\mathrm{O^0}$,[9,10] are summarized in Table I. It is quite clear that there is no significance in the apparent differences in the results for the three models; the small size of the data set does not support any distinction between them. However, as can be seen in Table II, all three models display the same relationship between the residuals for the two enantiomeric possibilities; the model with excess Λ-$\mathrm{Co(acac)_3}$ in the crystal gives the lowest residuals. The imaginary part of the scattering factor[10] for Co and Al was included in these calculations.

Table I. Results of Refinements

Model	[Co]/[Al]	% resolution of $\mathrm{Co(acac)_3}^a$	Residuals R^b	Residuals $R_w{}^c$
$\mathrm{Co(acac)_3}$	0.969	60.4	0.127	0.135
$\mathrm{Al(acac)_3}$	0.886	51.6	0.124	0.128
$\mathrm{Mn(acac)_3}$	0.496	83.6	0.134	0.136

[a] % resolution = $\{[(-)_{546}\text{-Co(acac)}_3] - [(+)_{546}\text{-Co(acac)}_3]\}/\{[(-)_{546}\text{-Co(acac)}_3] + [(+)_{546}\text{-Co(acac)}_3]\}$. [b] $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = (1/\sigma_F)^2$.

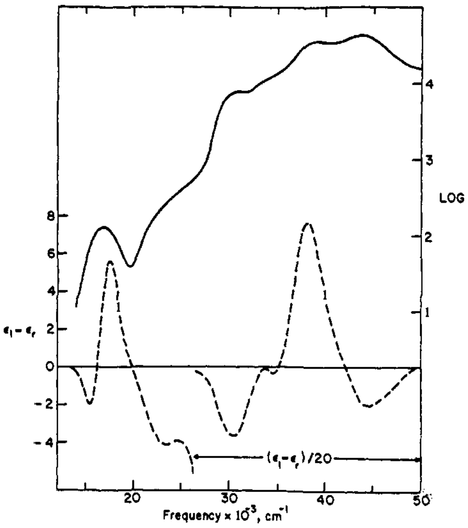

Figure 1. The absorption spectrum (—) and circular dichroism (---) of partially resolved Λ-$(-)_{546}$-$\mathrm{Co(acac)_3}$ ($[M]_{546} = -15{,}500$) in ethanol solution.

The Λ configuration for $(-)_{546}$-$\mathrm{Co(acac)_3}$ is further supported by Bijvoet analysis of 19 Friedel pairs of reflections. In every case the sign of the observed difference in intensity for a Friedel pair matches that calculated for the model having an excess of Λ-$\mathrm{Co(acac)_3}$.

Table II. Comparison of Enantiomeric Models

Model	Λ-$\mathrm{Co(acac)_3}$ in excess R	Λ-$\mathrm{Co(acac)_3}$ in excess R_w	Δ-$\mathrm{Co(acac)_3}$ in excess R	Δ-$\mathrm{Co(acac)_3}$ in excess R_w
$\mathrm{Co(acac)_3}$	0.124	0.130	0.135	0.136
$\mathrm{Al(acac)_3}$	0.118	0.124	0.134	0.134
$\mathrm{Mn(acac)_3}$	0.130	0.131	0.142	0.140

The circular dichroism (CD) spectrum[11] of Λ-$(-)_{546}$-$\mathrm{Co(acac)_3}$ (Figure 1) exhibits a negative band at 15,500 cm^{-1} and a more intense, positive band at 17,500 cm^{-1}; these may be assigned, respectively, on the basis of the polarized crystal spectrum of $\mathrm{Co(acac)_3}$,[12] to the $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{A}_2$ and $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}$ components of the lowest energy, spin-allowed d–d transition ($^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{T}_{1g}$ in O_h). Thus, the empirical spectroscopic rules based on the sign of the CD of the E component[2] and the sign of the dominant Cotton effect[3] both predict that $(-)_{546}$-$\mathrm{Co(acac)_3}$ has the Λ configuration, in accord with the X-ray results. Also in agreement with the spectroscopic rules is the absolute configuration of Λ-$(-)_{546}$-*trans*-tris-[(+)-3-acetylcamphorato]cobalt(III), Λ-$(-)_{546}$-*trans*-Co((+)atc)$_3$, which has been established on the basis of the X-ray crystal structure of Λ-$(+)_{589}$-*trans*-Cr((+)-atc)$_3$[5] and isomorphism between the other three Cr((+)atc)$_3$ diastereomers (Δ-trans, Λ-cis, and Δ-cis) and the corresponding Co((+)atc)$_3$ diastereomers.[13] It is interesting that the spectroscopic rules apply to $\mathrm{Co(acac)_3}$ and Co((+)atc)$_3$ despite the presence of relatively low-energy charge-transfer and π–π^* transitions. Recent spectroscopic assignments of the ab-

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solute configuration of cobalt(III) β-diketonates[14] are therefore now on a firm basis. The validity of the spectroscopic criteria for chromium tris-β-diketonates has been confirmed by the X-ray analysis of Λ-$(+)_{589}$-*trans*-Cr((+)atc)$_3$[5] and also by our preliminary studies of Δ-$(-)_{589}$-Cr(acac)$_3$ in quasiracemic crystals.

Further, it is noted that the CD bands of $(-)_{546}$-Co(acac)$_3$ at 44,400 and 38,200 cm^{-1} (Figure 1) may be assigned,[11] respectively, to the A_2 and E components of the exciton-split π–π^* transition, and that the sign of the rotatory power of these bands also predicts[20] the Λ configuration.

Finally, we emphasize several advantages of the method of determining absolute configurations in quasiracemic crystals. This method avoids a full X-ray analysis on a compound whose molecular structure is already known,[21] and it avoids the necessity of completely resolving the compound, a task of considerable difficulty in the case of nonpolar, electrically neutral complexes. Relatively little effort is required in cases where the crystal structure of a suitable racemic crystal has already been determined and, once such a structure is available, the method can be applied to an entire series of isostructural complexes. Our work in this area is continuing.

Acknowledgment. The support of this research by National Science Foundation Grant No. GP-16280 is gratefully acknowledged.

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[14] The Λ configuration has been (or may be) assigned to the $(-)_{546}$-cis and $(-)_{546}$-trans cobalt(III) complexes with the anions of (+)-hydroxymethylenecamphor,[15,16] (+)-3-acetylcamphor,[13,16,17] (+)- and (−)-hydroxymethylenecarvone,[18] 5-methylhexane-2,4-dione,[19] and 1-phenylbutane-2,4-dione.[11]

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Received June 1, 1971

Catalysis in Dipolar Aprotic Solvents. A Proton-Relay Mechanism Resembling the Mechanism of Action of Serine Enzymes[1]

Sir:

We are investigating the catalyzed hydrolysis of *p*-nitrophenol acetate (PNA) in dipolar aprotic solvents, and have found that in acetonitrile containing imidazole and benzoate ion, the dominant rate term is first order in substrate, imidazole, and benzoate ion. Crystallographic studies of a number of hydrolytic enzymes indicate that chymotrypsin, trypsin, elastase, subtilisin, and papain have a common mechanism of action involving a proton-relay mechanism.[2] An aspartate carboxyl is hydrogen bonded to an imidazole ring which is in the active site and hydrogen bonded to a serine (cysteine in papain) which functions as the nucleophile in the first step of hydrolysis. It therefore appears that proton transfer accompanies nucleophilic attack by the serine hydroxyl which is therefore expected to be much more nucleophilic than a normal serine hydroxyl. Since the active sites of enzymes would be expected to have solvent properties considerably different from aqueous solutions and may resemble dipolar aprotic solvents containing small amounts of water, our results appear to be of considerable interest.

Our early studies[3] were concerned with catalysis by imidazole. We have demonstrated in a range of dipolar aprotic solvents that hydrolysis of PNA is both first and second order in imidazole.[3,4] Recently, we have investigated the mechanisms of catalysis by mixtures of imidazole (IM) and carboxylate ions in acetonitrile and the results appear to be important in understanding enzyme action and biochemical evolution.

All the studies reported here were carried out by following the appearance of *p*-nitrophenol in acetonitrile at constant salt concentration, $[(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-] + [(\text{CH}_3)_4\text{N}^+\text{C}_6\text{H}_5\text{CO}_2^-] = 0.01\ M$, [PNA] is approximately $10^{-4} M$, $[\text{H}_2\text{O}] = 1.0\ M$, and $T = 30.1°$. When imidazole alone is added, the hydrolysis of PNA follows the rate laws in eq 1 and 2.[4] Analysis of k_{obsd} at [IM]

$$v = k_{\text{obsd}}[\text{PNA}] \qquad (1)$$

$$k_{\text{obsd}} = k_1[\text{IM}] + k_2[\text{IM}]^2 \qquad (2)$$

$= 0.015\text{–}0.20\ M$ yields $k_1 = 3.1 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ and $k_2 = 1.3 \times 10^{-2}\ M^{-2}\ \text{sec}^{-1}$.

When benzoate ion is added, there is marked catalysis,[4] and the infinity point corresponds to complete reaction. With $[\text{C}_6\text{H}_5\text{CO}_2^-] = [\text{C}_6\text{H}_5\text{CO}_2\text{H}]$ we find the dependence of k_{obsd} in eq 3 in studies both (1) at

$$k_{\text{obsd}} = k_1[\text{IM}] + k_2[\text{IM}]^2 + k_2[\text{IM}][\text{RCO}_2^-] \qquad (3)$$

constant concentration of imidazole and varied concentrations of benzoate ion ($k_2' = 1.0\ M^{-2}\ \text{sec}^{-1}$), and (2) at constant concentration of benzoate ion and varied concentrations of imidazole ($k_2' = 1.0\ M^{-2}\ \text{sec}^{-1}$). Although there may be a term in benzoate ion alone, $k_1'[\text{RCO}_2^-]$, it is experimentally indistinguishable from zero in these experiments. Change of $[\text{C}_6\text{H}_5\text{CO}_2^-]/[\text{C}_6\text{H}_5\text{CO}_2\text{H}]$ from 10:1 to 1:1 keeping $[\text{C}_6\text{H}_5\text{CO}_2^-]$ constant has a small effect on the rate of hydrolysis of PNA. Preliminary experiments with acetate ion indicate behavior qualitatively similar to benzoate ion.

In the presence of initially added *p*-nitrophenol, there is no significant change in the rate of hydrolysis. Since we are measuring the rate of appearance of *p*-nitrophenol, this result, our other results with imidazole and *N*-methylimidazole, and basicity relations in acetonitrile[5] all indicate that the mode of catalysis represented by k_2' involves the carboxylate ion acting as a general base to abstract a proton from imidazole which func-

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