amine, on absorbing light, is converted to I·⁻ and the radical cation of the amine.

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Nathan Kornblum, Francis W. Stuchal
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907
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Detection of Rapid Optical Inversion in "Labile" Cobalt(II) Chelates Using Proton Magnetic Resonance

Sir:

Detailed kinetic and mechanistic studies[1] of optical inversion in tris metal chelates with bidentate ligands generally require the capability of physically separating the isomers. Thus past investigations have been restricted to the "nonlabile" transition metal ions (optical lifetimes $\gtrsim 10^2$ sec). To date virtually nothing is known about the optical lifetimes of chelates of the "labile" metal ions, such as cobalt(II). In particular, it is not even known whether the optical lability is determined by bulk ligand exchange or by some intramolecular process.

Recently[2] it has been shown that for complexes of mixed, symmetric bidentate ligands, $M(CC)_2(DD)$ (CC, DD = dissimilar, symmetric diketonates), the magnetically inequivalent terminal CC methyl groups display slightly different chemical shifts. Optical inversion, which is accompanied by exchange of these methyl groups,[3] was then monitored by observing the collapse of the two methyl signals as the temperature was raised. These observations for mixed β-diketonates of Al(III)[2] and Ga(III)[4] have demonstrated that optical inversion can be studied in complexes with lifetimes as short as $\sim 10^{-2}$ sec. Since only kinetic processes with lifetimes comparable to the chemical shift difference can be obtained from nmr line-width analysis,[5] the limitations to detecting much shorter lifetimes is due to the very small methyl chemical shift differences ($\sim$10 Hz) usually observed in diamagnetic compounds.[4]

We have been able to obtain the lower limit of the rate of optical inversion[3] of (4,7-dimethyl-1,10-phenanthroline)bis(acetylacetonate)cobalt(II),[6] $Co(AA)_2$-(4,7-phen), using proton nmr.[7] Examination of the physical principles which allow the detection of such short lifetimes ($<10^{-6}$ sec) indicates that this method will have some general applicability for cobalt(II) complexes.

The nmr spectrum of a paramagnetic complex differs from that of an analogous diamagnetic compound in that the combination of the contact interaction (arising from delocalized unpaired electrons) and the dipolar interaction (resulting from an anisotropic g-tensor) leads to a sizable, nonlinear expansion of the chemical shift scale.[8] Thus at 300°K, the proton spectrum of this paramagnetic ($S = {}^3/_2$) chelate[6] exhibits six peaks spread over $\sim$80 ppm, where all peaks can be unambiguously identified by relative areas and by phenanthroline methyl substitution. The two AA methyl peaks are equivalent on the nmr time scale at this temperature. As the temperature is lowered, all peaks shift (see Table I), and the AA methyl peak broadens and splits into two equal peaks, each of which progressively decreases in width. The rate of signal collapse is concentration independent and thus first order. Standard analysis[5,9] of the line widths yields $k^{298} \sim 5 \times 10^6$ sec^{-1}, $E_a \sim 13$ kcal/mol, and log $A \sim 16$. The addition of a slight excess of either 4,7-phen, or $(AA)^-$ in the form tetra-n-butylammonium acetylacetonate does not alter either the paramagnetic peak positions or line widths, suggesting that the kinetic process does not directly involve bulk ligand exchange.

Two aspects of our present observations are noteworthy. Firstly, the chemical shift difference between the two AA methyl groups is $\sim$40 ppm at 240°K ($\sim 10^3$ greater than for diamagnetic complexes), and it is this large shift difference which allows us to monitor such a rapid kinetic process. The origin of this magnified magnetic inequivalence of the AA methyl groups can be traced to the expected g-tensor anisotropy[10,11] which characterizes Co(II). Since the symmetry of the complex is only C_2, both axial and rhombic contributions[12] to the dipolar shifts must be considered. Calculations of the axial, $(3\cos^2\chi - 1)r^{-3}$, and the rhombic geometric factors, $(\sin^2\chi \cos 2\Omega)r^{-3}$, for the necessarily *cis* configuration for the complex, which determine the *relative* dipolar shifts,[12] reveal that a basic characteristic of such mixed complexes is that the AA ligands are so disposed relative to the C_2 symmetry axis that, while the geometric factors for the inequivalent AA methyl groups are quite large, they *always* have *opposite signs.* This is true for both the axial and rhombic geometric factors. Thus the dipolar interaction guarantees a large chemical shift difference between the terminal methyl groups. This observation is valid not only for AA^- but can be shown to be a feature of the XX ligand of any $Co(XX)_2(YY)$ complex. We therefore propose that this nmr method will have general applicability in elucidating the kinetics of rapid intramolecular rearrangements, of which optical inversion in $Co(XX)_2(YY)$ type complexes is only one example.

A second point of interest is that, as the data in Table I illustrate, the Curie law[8] is not obeyed, with the 2,9-H shift in fact *decreasing* with decreasing tempera-

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, pp 646–651.

[2] J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

[3] The analysis in ref 2 has shown that the rate of optical inversion, k_0, and the rate of nmr signal averaging, k_{nmr}, are not necessarily identical but related by the nature of the transition state. Since $k_{nmr} \leq k_0$,[2] the observed k_{nmr} is a lower limit to k_0.

[4] T. J. Pinnavaia, J. M. Sebeson, II, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969).

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," The McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

[6] J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

[7] The complex was prepared in a conventional manner[6] and dissolved in $CDCl_3$. The proton nmr spectra were run on a Varian HR-100 spectrometer.

[8] D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

[9] Only data in the region of slow exchange were employed in the analysis.

[10] J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

[11] Thus the analogous magnetically isotropic Ni(II) complex, which is expected to be less labile, exhibits only a single peak for both AA methyl groups between −70 and 55°.

[12] G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

Table I. Isotropic Shifts for Co(AA)$_2$(4,7-phen) in CDCl$_3$[a]

Position	303°K	263°K	223°K	203°K
2,9-H	−56.10	−51.35	−38.00	−27.70
3,8-H	−19.67	−23.80	−30.05	−33.80
4,7-CH$_3$	+10.23	+12.06	+14.62	+16.33
5,6-H	−23.66	−25.50	−27.00	−27.40
AA-CH	+23.25	+26.26	+28.02	+30.10
CH$_3$			+2.54	+2.36
AA	−11.47[b]	−13.65[b]		
CH$_3$			−40.72	−45.92

[a] Shifts in ppm at 100 MHz, referenced against diamagnetic ligand. [b] Averaged proton nmr signal.

ture. Whether this anomaly is related to the nature of the transition state in the form of a temperature-dependent equilibrium between octahedral and five-coordinated species is not known at this time. The two species would be expected to exhibit very different isotropic shift patterns. Alternatively, the thermally accessible Kramers doublets for the octahedral complex[13] may possess widely differing magnetic anisotropies, so that varying the temperature alters the population of the accessible states. This latter mechanism has been predicted[10,13] and observed[14] for some six-coordinated Co(II) chelates.

A more extensive investigation into solvent and substituent effects in progress should shed further light on the mechanism of this rearrangement and on the origin of the non-Curie behavior of the shifts.

(13) J. P. Jesson, *J. Chem. Phys.*, 47, 582 (1967).

(14) G. N. La Mar and J. P. Jesson, unpublished data.

Gerd N. La Mar
Shell Development Company
Emeryville, California 94608

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Chemistry of Bicyclo[5.1.0]oct-2-yl Cations

Sir:

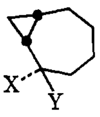
Much research has been done to determine the structure(s) of the minimum energy conformation(s) of various substituted cyclopropylcarbinyl cations. Product studies in the bicyclo[*n*.1.0]alk-2-yl systems (n = 3–4)[1b–c] indicate that there is only one conformationally stable interaction of the electron-deficient p orbital with the cyclopropane ring. We wish to report the solvolytic chemistry of *endo*- and *exo*-bicyclo-[5.1.0]oct-2-yl 3,5-dinitrobenzoates (**1a,b**) in which, by contrast, a minimum of two structurally distinct cations are formed as intermediates.

The results of our product studies are given in Table I. The slightly differing product distribution from the two solvolyses is similar to that observed by Cope[1d] in acetic acid solution and provides evidence for at least two intermediate cations. We do not wish to stress any importance to these results, however, because kinetic and scrambling studies appear to provide in this system an even more sensitive probe for differing cationic intermediates.

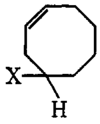
Table I. Products from Solvolysis[a] of *endo*- and *exo*-Bicyclo[5.1.0]oct-2-yl 3,5-Dinitrobenzoates (**1a,b**)

Products	% yield from *endo*-DNB **1a**	% yield from *exo*-DNB **1b**
endo-DNB **1a**	4 (unreacted)	0
exo-DNB **1b**	6	13 (unreacted)
Δ^3-DNB **2a**[c]	6	2
endo-OH **1c**[c]	47 (56)[b]	44 (52)[b]
exo-OH **1d**[c]	16 (19)[b]	30 (35)[b]
Δ^3-OH **2b**[c]	21 (25)[b]	11 (13)[b]

[a] 80% aqueous acetone buffered with 1.1 equiv of lutidine at 100°. [b] Normalized to 100%, standard deviation ±3%. [c] These products were stable to the reaction conditions.



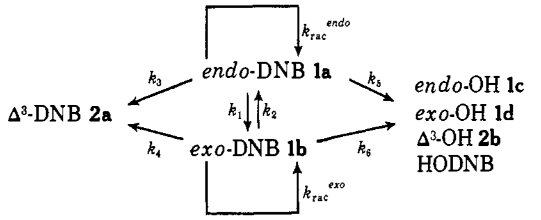
1a, *endo*-DNB; X = DNB; Y = H
b, *exo*-DNB; X = H; Y = DNB
c, *endo*-OH; X = OH; Y = H
d. *exo*-OH; X = H; Y = OH
e, *endo* D-DNB; X = DNB; Y = D
f, *exo*-D-DNB; X = D; Y = DNB



2a, Δ^3-DNB; X = DNB
b, Δ^3-OH; X = OH

Both titrimetric and polarimetric kinetic studies were conducted. The data were analyzed according to Scheme I. The titrimetric study of *endo*-DNB **1a** showed slightly curved first-order plots after approximately three half-lives due to slight instability of the small amount of returned *exo*-DNB **1b**. This curvature was resolved into observed rate constants with a nonlinear iterative regression analysis. Solvolysis of *exo*-DNB **1b** gave good first-order plots.

Scheme I. Kinetic Scheme for Solvolysis of *endo*- and *exo*-3,5-Dinitrobenzoates **1a,b**



In the racemization rate studies, the total optical rotation of the solution *vs.* time was measured and observed to follow good first-order kinetics over two half-lives. The quantity, k_{rac}, reported in Table II, was calculated as the difference between k_α^{obsd} and either k_7 or k_8. The values for k_6 were calculated by assuming $k_2 \approx 0$. Even though we believe that k_2 may be as high as 25% of k_8, our data do not distinguish whether products from *exo*-DNB **1b** arise solely from k_6 or partly from k_6 and k_2; under the reaction conditions for the solvolysis of **1b**, **1a** is so reactive that, at best, it can only achieve a steady-state concentration.

We also studied the products from the solvolyses of *endo*-D- and *exo*-D-DNB **1e,f**. After 81% reaction, the alcoholic products and unreacted starting material from *endo*-D-DNB **1e** retained unscrambled deuterium atoms. The results for *exo*-D-DNB **1f** are given in Table III. The per cent racemization of unreacted *exo*-D-

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(1) (a) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *J. Amer. Chem. Soc.*, 90, 5338 (1968); (b) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (c) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, Abstracts of Paper, p K011; (d) A. C. Cope, S. Moon, and C. J. Park, *J. Amer. Chem. Soc.*, 84, 4850 (1962); (e) unpublished results of C. D. Poulter, E. C. Friedrich, and S. Winstein, University of California, Los Angeles, Calif.; (f) unpublished results of C. D. Poulter and S. Winstein, University of California, Los Angeles, Calif.