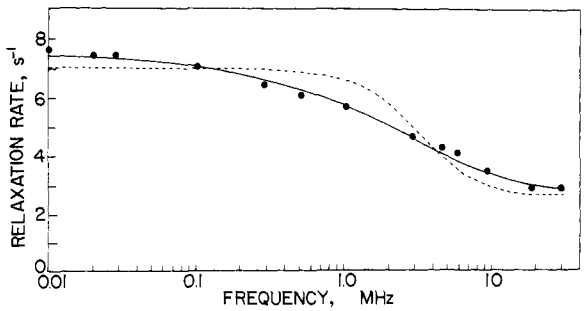


Figure 1. The water proton nuclear magnetic relaxation rate as a function of magnetic field strength plotted as proton Larmor frequency for a 0.28 mM solution of bovine serum albumin labeled with 4.6 nitroxides per protein molecule at pH 6.4 and 286 K. The solid circles are the experimental points and the solid line the calculated curve for the translational diffusion model[9] assuming the diffusion coefficient for water at the surface of $(3.0 \pm 0.6) \times 10^{-6}$ cm^2 s^{-1} and the minimum distance of approach of the spins of $(1.9 \pm 0.3) \times 10^{-8}$ cm. The dotted curve was calculated on the basis of a rotational diffusion model[2] using a rotational correlation time of $(0.6 \pm 0.2) \times 10^{-10}$ s and an average radius of the water diffusional unit of $(1.8 \pm 0.1) \times 10^{-8}$ cm. The sample contained 1 mM sodium azide.

water, the measurement provides the self-diffusion coefficient for water at the protein surface. Further, the results are not dependent upon the electron spin relaxation time of the nitroxide as long as it remains large compared with the other correlation times entering the problem such as the protein rotational correlation time or the correlation time for the relative diffusion of the nitroxide and the solvent protons. This condition will generally be satisfied for nitroxide radicals.[3] A representative dispersion plot of the data is shown in Figure 1 along with the computed fit to the data. Other models such as rotational diffusion[2,4] gave much poorer fits to the dispersion plots. The analysis, to be completely described elsewhere,[8] follows the development of Freed very closely,[9] and the solid line through the data points is based on this force-free diffusion model. The water molecule translational diffusion coefficient in the immediate vicinity of the nitroxide determined from this analysis is $(3.0 \pm 0.6) \times 10^{-6}$ cm^2 s^{-1} at 286 K. This is to be compared with a value of $(16 \pm 3) \times 10^{-6}$ cm^2 s^{-1} for pure water obtained from an aqueous solution of a spin label, which agrees with the published results of others.[10]

Though the data set is quite sufficient for this analysis, we take this result as an approximation because the theory has not specifically included the excluded volume effect required by the finite size of the surface, in this case the protein particle, and pair correlation effects between particles.[5,7] The neglect of these effects can be shown to result in a calculated diffusion constant that is somewhat smaller than the correct value and a calculated distance between the centers of the interacting particles that is larger than the correct value.[8] This result also represents an average of the diffusion coefficient over distance from the nitroxide that is initially weighted by the usual sixth power of the distance. However, the actual weighting as a function of distance from the surface is considerably weaker because the average required is over volume so that the distance dependence falls to approximately inverse third power dependence. The method, therefore, provides a characterization of water mobility at the surface defined as the first several monolayers of water. Further confirmation of our results is achieved by taking the limiting form of the equations which is independent of the model chosen[6] and obtaining the translational diffusion coefficient from the slope of a plot of relaxation rate vs. the square root of frequency. We obtain $D = (2.2 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1} for the data below 0.6 MHz in Figure 1. A similar analysis for an aqueous solution of spin label gives $D = (18 \pm 4) \times 10^{-6}$ cm^2 s^{-1}.

The method employed here is perfectly general as a means for providing local relative diffusion coefficients. The same strategy should be equally useful and valid for the characterization of nonaqueous solvent mobility on any surface that could be labeled with a radical having the appropriately long electron relaxation time.

Experimental Section. Nuclear magnetic relaxation rates were made on a field cycling instrument built in this laboratory with the collaboration of Drs. Seymour Koenig and Rodney Brown, III, and is described elsewhere.[11] The spin-label samples were prepared as described by Twining et al.[12] using 3-[[(2,5-dioxo-1-pyrrolidinyl)oxy]carbonyl]-2,5-dihydro-2,2,5,5-tetramethyl-1*H*-pyrrolyl-1-oxy (Molecular Probes) which reacts with free amino groups on proteins.[13] The spin-label concentration was measured by double integration of the ESR spectra. The protein solutions contained 1 mM sodium azide as a preservative and the albumin (Sigma, essentially fatty acid free) concentration was calculated from $\epsilon_{280} = 4.34 \times 10^{-4}$ L mol^{-1} cm^{-1}. The solutions were unbuffered, and the pH was adjusted by adding 0.01 N NaOH. The parameters were determined using a nonlinear least-squares simplex procedure.

Acknowledgment. We gratefully acknowledge the technical assistance of Scott Kennedy and useful discussions with Professor Jack Freed. Aid with the field cycling aspects of the spectrometer provided by Dr. Seymour Koenig and Dr. Rodney Brown, III, is acknowledged with pleasure. Use of ESR spectrometers in the laboratories of Dr. David Thomas and Dr. John Lipscomb is appreciated. This work was supported by the National Institutes of Health and the National Science Foundation.

Registry No. Water, 7732-18-5.

(8) Polnaszek, C. F.; Bryant, R. G. *J. Chem. Phys.*, submitted for publication.
(9) Freed, J. H. *J. Chem. Phys.* **1978**, *68*, 4034-4037.
(10) Gillen, K. T.; Douglass, D. C.; Hoch, M. J. R. *J. Chem. Phys.* **1972**, *57*, 5117-5119.
(11) Brown, R. D., III; Brewer, C. F.; Koenig, S. H. *Biochemistry* **1977**, *16*, 3883-3893.
(12) Twinning, S. S.; Sealy, R. C.; Glick, D. M. *Biochemistry* **1981**, *20*, 1267-1272 (1981).
(13) Gaffney, B. J. In "Spin Labeling Theory and Applications"; Berliner, L. J., Ed.; Academic Press: New York, 1976; Vol. 1, pp 183-238.

Atropisomerism in Metal Chelates. Preparation and Partial Resolution of (3,4-Diacetyl-2,5-hexanedionato)bis[((2,2′,2″-triaminotriethyl)amine)cobalt(III)] Ion

Yoshiharu Nakano*

Department of Chemistry, Ibaraki University
Bunkyo 2-1-1, Mito 310, Japan

Yuzo Yoshikawa

Department of Chemistry, Faculty of Science
Nagoya University
Chikusa-ku, Nagoya 464, Japan

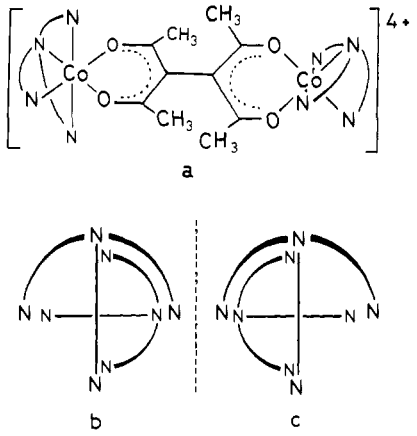
Received October 3, 1983

One of the authors (Y.N.) has reported a series of optically active complexes (atropisomers), the chirality of which arises from the restricted rotation of an aromatic ring group.[1]

In the present study, we are interested in a new type of atropisomer, containing 1,1,2,2-tetraacetylethane[2] (taeH$_2$).[3] Tetraacetylethane adopts an interesting dienolic form in which the two planer acetylacetone units are perpendicularly joined back to back in the crystal.[4] The acetylacetone moieties are able to form stable

(1) Nakano, Y.; Sato, S. *Inorg. Chem.* **1982**, *21*, 1315.
(2) Rabjohn, N. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 869.
(3) In this paper the following abreviations are used: taeH$_2$ for 1,1,2,2-tetraacetylethane or 3,4-diacetyl-2,5-hexanedione, acacH for acetylacetone or 2,4-pentanedione, tren for tris(2-aminoethyl)amine.

0002-7863/84/1506-0429$01.50/0



a

b c

Figure 1. (a) A structure of the twin complex, $[\{Co(tren)\}_2(tae)]^{4+}$. (b) The side view of tren parts from the right-hand side of (a). (c) The mirror image of (b).

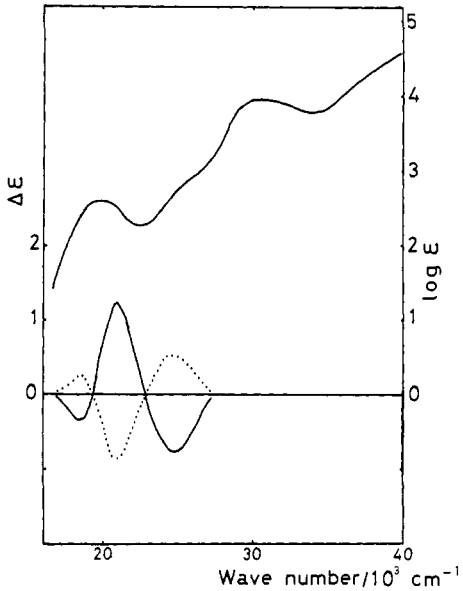


Figure 2. Absorption and circular dichroism spectra of partially resolved complexes.

coordination compounds. We have selected the Co(tren) system as the partner of 1,1,2,2-tetraacetylethane anion (tae). Molecular model of the resulting twin complex (see Figure 1) shows a novel structure in which the two units of $[Co(acac)(tren)]^{2+}$ types are bound to tae at right angles to each other. Although the unit itself has a symmetry plane neglecting the conformational structure of a chelate ring, the symmetry is invalidated in the twin complex. Therefore it is expected that the twin complex can be resolved into optically active isomers.

The complex was prepared analogously to β-diketonato complexes and gave compatible IR, ^1H NMR, ^{13}C NMR, and absorption spectra and elemental analysis data with the expected twin structure. The red complex was subjected to recycling chromatography on an SP-Sephadex (C-25, φ 4.4 × 90 cm) column using an aqueous 0.25 M sodium $(+)_{589}$-tartrate solution as eluent. The flow rate of the elution was about 80 mL per hour. After the 20th recycling the adsorbed complex could not be separated into two bands, but the circular dichroism spectrum of the initial part (solid line shown in Figure 2) of the elution curve showed the mirror image of that of the last part (dotted line). The rotatory strength of the latter fraction is significantly weaker than that of the former, indicating partial resolution. Success in resolution confirms that the complex has the expected structure as shown in Figure 1, and the two units of $[Co(acac)(tren)]^{2+}$ types cannot rotate freely around the central C–C bond of tae.

Since the two units of $[Co(acac)(tren)]^{2+}$ types are bound perpendicularly and two acetylacetonato-ring units cannot conjugate to each other, the absorptivity of the twin complex must be 2 times that of $[Co(acac)(tren)]^{2+}$. Comparing the obtained CD spectrum to that of naphthyl derivative, we can assign the two peaks, 18 500 and 20 800 cm^{-1}, to $B_1 \leftarrow A_1$ and $B_2 + A_2 \leftarrow A_1$ transitions, respectively. Complete CD spectra and the other detailed characterizations will be reported on later.

Registry No. $[\{Co(tren)\}_2(tae)]^{4+}$, 88211-16-9.

(4) Schaefer, J. P.; Wheatly, P. J. *J. Chem. Soc. A* **1966**, 528.
(5) Circular dichroism spectra of the series will be published elsewhere.

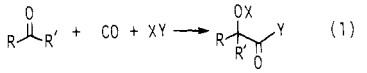
Catalytic Incorporation of Carbon Monoxide into a Ketonic Carbon. Conversion of Cyclobutanones to Disiloxycyclopentenes with Hydrosilane and Carbon Monoxide in the Presence of Cobalt Carbonyl[1]

Naoto Chatani, Hidenori Furukawa, Toshikazu Kato, Shinji Murai,* and Noboru Sonoda

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan

Received October 20, 1983

Carbonylation of carbon–carbon double bonds with the aid of transition-metal complexes is a popular catalytic reaction,[2] which finds fruitful application in industry, hydroformylation of olefins being a representative example.[2,3] In contrast, catalytic carbonylation of carbon–oxygen double bonds (i.e., carbonyl group) with carbon monoxide remains almost unexplored. Of the two available reaction sites in a carbon–oxygen double bond, C-carbonylation (eq 1) is more important than O-carbonylation,[4]



(1)

since the former could bring about carbon-chain extention.[5] Investigation devoted to finding effective catalyst systems that would enable the conversion of formaldehyde to glycolaldehyde (eq 1, R = R′ = X = Y = H), or to ethylene glycol, via C-carbonylation have been made.[6] Few examples are known of the transition-metal catalyst system that is effective for C-carbonylation of higher aldehydes[7,8] (eq 1, R = alkyl; R′ = H).

(1) For previous papers of this series: (a) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370. (b) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* **1983**, *2*, 1883.
(2) Wender, I.; Pino, P. "Organic Syntheses via Metal Carbonyls"; Wiley: New York, 1977; Vol. II. Farbe, J. "New Syntheses with Carbon Monoxide"; Springer-Verlag: New York, 1980.
(3) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1. Siegel, H.; Mimmele, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 178.
(4) Marko, L.; Szabo, P. *Chem. Tech. (Berlin)* **1961**, *13*, 482; *Chem. Abstr.* **1962**, *56*, 7102. Marko, L. *Proc. Chem. Soc.* **1962**, 67. Polievka, M.; Mistrik, E. *J. Chem. Zvesti* **1972**, *26*, 149; *Chem. Abstr.* **1972**, *77*, 113388. Weil, T. A.; Metlin, S.; Wender, I. *J. Organomet. Chem.* **1973**, *49*, 227. Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.
(5) The following *unknown* reaction may illustrate the importance of C-carbonylation:

$$CH_3COCH_3 + H_2O + CO \rightarrow (CH_3)_2C(OH)COOH \rightarrow CH_2{=}C(CH_3)COOH + H_2O$$

(6) Yukawa, T.; Wakamatsu, H. Brit. Pat. 1 408 857, 1974. Spencer, A. *J. Organomet. Chem.* **1980**, *194*, 113. Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. Parker, D. G.; Pearce, R.; Prest, D. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1193. Suzuki, T.; Kudo, K.; Sugita, N. *Nippon Kagaku Kaishi* **1982**, 1357; *Chem. Abstr.* **1982**, *97*, 144126. Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377. See also: *Chem. Eng. News* **1983**, *61*, 41.

0002-7863/84/1506-0430$01.50/0