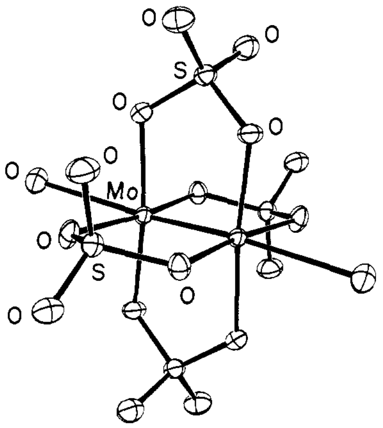


Figure 1. The structure of the $Mo_2(SO_4)_4^{3-}$ ion. Atoms are represented by their vibrational ellipsoids, contoured to enclose 50% of the electron density.

ponent of a quadruple bond in contributing to the extraordinary shortness of such bonds can be assessed by observing how the Mo–Mo bond distance changes when the bond order changes from 4.0 to 3.5 provided other factors remain essentially the same. We report here a compound in which there is an Mo–Mo bond of order 3.5 in an environment which is as nearly as possible identical with that for an Mo–Mo bond of order 4.0 in another compound.

In the course of our study of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$, which forms pink rhomboidal crystals, we observed that pale red-blue crystals are also formed. The conditions under which both types of crystals can be obtained together are as follows. Bowen and Taube's compound, $K_4Mo_2(SO_4)_4$, is dissolved in 0.1 *M* H_2SO_4. This solution is allowed to mix by diffusion through a glass frit with a saturated solution of K_2SO_4 in 0.1 *M* H_2SO_4 at 25°. The system is purged of oxygen, although it cannot be said with certainty that dissolved oxygen does not play some role in the reaction. From the X-ray structure analysis the red-blue crystals were shown to have the composition $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$.

The crystals belong to the monoclinic system, space group $C2/c$, with unit cell dimensions $a = 30.654$ (4) Å, $b = 9.528$ (2) Å, $c = 12.727$ (1) Å, $\beta = 97.43$ (1)° and $Z = 8$. Using Mo Kα radiation, 2341 reflections with $I > 3\sigma(I)$ and in the range $0 < 2\theta \leq 48°$ were collected on an automated difractometer. The structure has been refined anisotropically to $R_1 = 0.026$ and $R_2 = 0.033$. All hydrogen atoms have been located.

There are two crystallographically independent $Mo_2(SO_4)_4^{3-}$ groups lying on crystallographic centers of symmetry. The internal dimensions of the two independent units are essentially identical. Some of the water molecules are coordinated to potassium ions, as are some of the sulfate oxygen atoms, and all hydrogen atoms form hydrogen bonds. The structure of the $Mo_2(SO_4)_4^{3-}$ unit is shown in Figure 1. Each $\overline{\text{MoOSOMo}}$ ring is folded along the O···O line, with a dihedral angle of 20 ± 3°. The disposition of these folds is such as to make the idealized symmetry C_{4h}. Each molybdenum atom is approached by the oxygen atom of a water molecule approximately along the extended Mo–Mo axis, but only at a considerable distance (2.55 Å).

Important structure parameters, averaged according to C_{4h} symmetry, are: Mo–Mo, 2.164 (3) Å; Mo–O(sulfate), 2.064 (5) Å; MoO–S, 1.521 (1) Å; S–O, 1.442 (2) Å; Mo–Mo–O, 93.6 (3)°; Mo–O–S, 121.2 (3)°; MoO–S–OMo, 105.6 (3)°; MoO–S–O, 109.0 (2)°; O–S–O, 114.7 (4)°. Tables of atomic coordinates, anisotropic thermal parameters, and complete lists of bond distances and angles are available in the microfilm edition.[19]

The $Mo_2(SO_4)_4^{3-}$ structure is qualitatively very similar to that of $Mo_2(SO_4)_4^{4-}$. All distances and angles are essentially the same except for the Mo–Mo distance, which is 0.054 (6) Å longer for the bond of lower order, and the mean Mo–OS distance, which is *ca.* 0.07 Å shorter in the present structure, as would be expected for the higher mean oxidation state of the metal atoms.

$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ is paramagnetic and has epr absorption with intensity corresponding to 1 ± 0.3 electron per $Mo_2(SO_4)_4^{3-}$ unit according to preliminary data. It is intended to study the spectroscopic and magnetic properties in more detail.[20]

---

(19) Tables of atomic positional and anisotropic thermal parameters and a complete list of bond distances and angles will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring code number JACS-73-4431. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

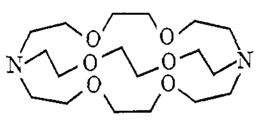
(20) We are grateful to the National Science Foundation for support of this research under Grant No. 33142X.

F. A. Cotton,* B. A. Frenz, T. R. Webb
Department of Chemistry, Texas A&M University
College Station, Texas 77843
Received March 27, 1973

^{23}Na Nuclear Magnetic Resonance Study of Exchange Rates. Sodium Cryptate in Ethylenediamine

Sir:

We wish to report the study by ^{23}Na nmr of the exchange rate of the sodium cation between two environments in solution. In ethylenediamine (EDA) as solvent, two well-defined resonance absorptions are observed below the coalescence temperature of 50° for a sample which contains dissolved sodium bromide and half the stoichiometric amount of the hexaoxadiamine macrobicyclic complexing agent, **1**. The equilibrium constant for complex ("cryptate") formation between Na^+ and **1** in several solvents[1] is large enough that we expect little free **1** in solution. The rate of exchange in water for the case of excess **1** has been studied by proton magnetic resonance by Lehn, Sauvage, and Dietrich.[2] These authors conclude that the relatively slow rate ($k = 27$ sec^{-1} at 3°) is a measure of the rate of dissociation of the cryptate complex.



1

Although chemical shifts and line widths of ^{23}Na

---

(1) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 15 (1973).

(2) J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Amer. Chem. Soc.*, **92**, 2916 (1970).

nmr lines have been related to cation exchange rates,[3,4] to our knowledge the present study is the first example in which clearly defined separate signals are obtained simultaneously for two environments of the sodium ion. In the work of Shchori, *et al.*,[4] in which complexation of Na^+ by dibenzo-18-crown-6 (DBC) in dimethylformamide (DMF) was studied, the extreme broadness of the signal of the complex prevented its observation at low temperatures even though the line width studies clearly showed that the exchange rate was slow enough.

The complexing agent, **1**, used in this work was synthesized by a modification of the method of Dietrich, Lehn, and Sauvage.[5] All measurements were made with a Varian Model DA-60 nmr spectrometer at 15.88 MHz by using the side band technique. Temperatures were measured with a calibrated thermocouple. EDA was purified by fractional freezing followed by distillation from Na-K alloy.[6] Reagent grade NaBr was used without purification.

The chemical shift at room temperature for 0.20 *M* NaBr in EDA was -13.8 ppm while that of 0.20 *M* NaBr with the stoichiometric amount of **1** was $+10.5$ ppm relative to 3 *M* NaCl in water. Line widths of these solutions were measured as a function of temperature. Addition of a potassium salt shifted the band back to its position in the absence of the complexing agent. This was expected since K^+ is more strongly complexed by **1** than is Na^+.[1] The temperature dependence of the ^{23}Na nmr spectrum is shown in Figure 1. The characteristic line broadening, coalescence, and line narrowing with increasing temperature can be used to measure the exchange rate. It was necessary to modify the usual[7] line shape expression because the transverse relaxation times in the two sites, T_{2A} and T_{2B}, are unequal. The line shape function is given by

$$v = -\gamma H_1 M_0 \left[\frac{SU + TV}{S^2 + T^2}\right]$$

with

$$S = \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}} + \frac{\tau}{T_{2A}T_{2B}} - \tau(\omega_A - \omega)(\omega_B - \omega)$$

$$U = 1 + \tau\left[\frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}}\right]$$

$$T = [p_A\omega_A + p_B\omega_B - \omega] + \tau\left[\frac{\omega_A - \omega}{T_{2B}} + \frac{\omega_B - \omega}{T_{2A}}\right]$$

$$V = \tau[p_A\omega_A + p_B\omega_B - \omega]$$

The symbols have their usual meanings.[7]

In the absence of exchange, the line shapes were Lorentzian within experimental error. Therefore, the required assumption of exponential relaxation in the absence of exchange seems justified.

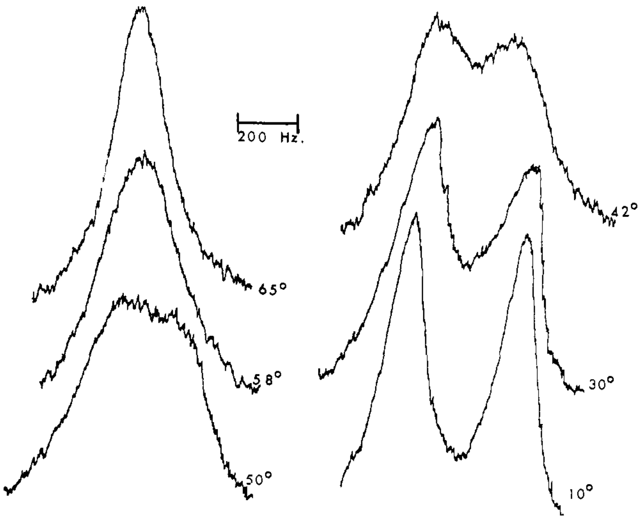


Figure 1. Temperature dependence of ^{23}Na nmr spectrum (absorption mode) for a solution of 0.4 *M* NaBr and 0.2 *M* **1** in EDA.

For the equimolar case, $p_A = p_B = 0.5$. The quantities ω_A, ω_B, T_{2A}, and T_{2B} were directly measured in separate experiments so that only τ and the amplitude of the shape function remained as adjustable parameters. However, in order to enhance the signal-to-noise ratio, it was necessary to work at partial saturation so that the true values of T_{2A} and T_{2B} are smaller than those used. The above equations were fitted to the data over the temperature range from 34 to 75° by using a generalized weighted nonlinear least-squares program.[8] Values of τ and the smoothed values of "T_2" used in the calculations are given in Table I.[9]

Table I. Temperature Dependence of Exchange Time and Line Widths

Temp, °C[a]	τ, msec[b]	σ_τ, msec[c]	$(\Delta\nu_{1/2})_A$[d]	$(\Delta\nu_{1/2})_B$[d]
75	0.20	0.04	17	33
65	0.20	0.03	22	39
56	0.39	0.05	25	43
51	0.59	0.06	29	45
44	0.99	0.08	33	48
34	1.67	0.11	38	53

[a] ±3°. [b] Solution 0.6 *M* in NaBr and 0.3 *M* in **1**. [c] Linear estimate of standard deviation of τ. [d] Half-width at half-height in hertz for: (A) 0.23 *M* NaBr, (B) 0.25 *M* NaBr + 0.25 *M* **1**.

Preliminary measurements in aqueous solutions show that the exchange rate in H_2O is similar to that in EDA. The close correspondence with the exchange rates in water[2] when **1** is in excess supports the conclusion of Lehn, Sauvage, and Dietrich[2] that the rate-limiting step is the dissociation of the complex with $k = 1/2\tau$. A similar conclusion was reached[4] for complexes of Na^+ with DBC in DMF.

From the linear variation of ln k with $1/T$, an activation energy of 12.2 ± 1.1 kcal mol^{-1} is obtained. The value 14.8 kcal mol^{-1} for $\Delta G^{\ddagger}$ at 50° is very close to the value found for aqueous solutions.[2]

Acknowledgments. This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-958. We are grateful to M. T. Lok, F. J.

---

(3) D. H. Haynes, B. C. Pressman, and A. Kowalsky, *Biochemistry*, **10**, 852 (1971).

(4) E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Amer. Chem. Soc.*, **93**, 7133 (1971).

(5) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885, 2889 (1969).

(6) M. G. DeBacker and J. L. Dye, *J. Phys. Chem.*, **75**, 3092 (1971).

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(8) V. A. Nicely and J. L. Dye, *J. Chem. Educ.*, **48**, 443 (1971).

(9) All uncertainties reported in this paper are estimates of the standard deviation.

Tehan, and K. Voorhees for their assistance in the synthesis of the complexing agent.

Joseph M. Ceraso, James L. Dye*
Department of Chemistry, Michigan State University
East Lansing, Michigan 48823

Received March 30, 1973

Cobalt-59 Nuclear Magnetic Resonance Study of Optical and Geometrical Isomerism in Tris((±)propylenediamine)cobalt(III) Complexes

Sir:

A large number of optical and geometrical isomers may be formed in tris-chelate metal complexes of chiral, bidentate ligands containing nonequivalent donor atoms. Tris((±)propylenediamine)cobalt(III) chloride, for example, forms eight optical isomers[1] each of which may form both cis and trans geometrical isomers[2] resulting in a total of 24 distinguishable structures. Conformational isomerism may also occur in a five-membered chelate ring in which the carbon–carbon bond is aligned either parallel or perpendicular to the threefold axis of the complex. The methyl groups preferentially adopt an equatorial configuration in propylenediamine complexes[3] so that the conformation of the chelate ring is determined by the optical configuration of the ligand. This preferential orientation in turn determines the distribution of optical isomers formed in a tris(pn) complex, since the λ conformation of the chelate is preferred in the Δ complex and the δ conformation preferred in the Λ complex.

The optical isomers of $Co((\pm)pn)_3^{3+}$ are easily separated chromatographically;[1] however, this technique leaves the geometrical isomers unresolved. The existence of the cis isomer has been demonstrated by an X-ray analysis of Δ-$[Co((-)pn)_3]Br_3$.[4] Attempts to prove the existence of *trans*-Δ-$Co((-)pn)_3^{3+}$ by X-ray analysis of nine different salts were unsuccessful because of the formation of insufficiently ordered crystals.[5]

Proton nuclear magnetic resonance has been a useful technique for the investigation of diastereomers of tris-chelate metal complexes.[6] Cobalt-59 decoupling is necessary in order to obtain high-resolution proton spectra of cobalt complexes;[7] however, even under these conditions no splitting due to the cis and trans isomers is observed in the pmr spectrum of Δ-$[Co((-)pn)_3]Cl_3$ at 100 MHz. On the other hand, at 251 MHz additional fine structure is observed[8] that can be attributed to the presence of the geometrical isomers; however, the presence of many nonequivalent pn ligands prevents a simple interpretation of this spectrum or an estimation of relative abundances.

Cobalt-59 nmr signals of cobalt(III) complexes occur over an extremely large frequency range;[9] therefore the ^{59}Co resonance is very sensitive to subtle details of the cobalt environment. For example, separate cobalt-59 nmr signals are observed for the geometrical isomers of complexes such as $Co(en)(NH_3)_2(OH)_2^+$ [10] and for $Co(en)_3^{3+}$ complexes with different degrees of N deuteration.[8] This sensitivity is utilized in the present work, in which separate cobalt-59 resonances are resolved for the optical and geometrical isomers of a tris-chelate complex, $Co((\pm)pn)_3^{3+}$. The existence of *trans*-$Co(pn)_3^{3+}$ is proved and relative intensities of the nmr signals are used to determine equilibrium ratios of the various isomers.

$[Co((\pm)pn)_3]Cl_3$ was prepared as described by Jenkins and Monk.[11] *Anal.* Calcd for $CoC_9H_{30}N_6Cl_3$: C, 27.88; H, 7.80; N, 21.68. Found: C, 28.03; H, 7.73; N, 21.29.[12] This complex was chromatographically separated into three fractions as described by Dwyer, Sargeson, and James.[1] (−)pn was resolved from (±)pn by the method of Dwyer, Garvan, and Shulman[13] and chromatographically pure Δ-$[Co((-)pn)_3]Cl_3$ was obtained as described by Dwyer, MacDermott, and Sargeson.[14] *cis*-Δ-$[Co((-)pn)_3]Br_3$ was crystallized according to the procedure described by MacDermott.[2]

The cobalt-59 nmr spectra were obtained on a Varian DP-60 nmr spectrometer equipped with a Varian V-4210A variable frequency rf unit which operated at 14.2 MHz. The spectrometer system included a Princeton Applied Research Model 121 lock-in amplifier which was operated at a frequency of 1500 Hz with the phases adjusted to display the first audio side band as an absorption mode signal. The field was swept with a Varian Fieldial Mark II using a 5 G sweep width and calibrated from the side band separation. The samples were contained in 15-mm o.d. test tubes and measured at the temperature of the magnet gap of 27 ± 2°. Relative integrated intensities of the peaks were measured with a planimeter, and errors are given as the mean deviation from the mean of four separate measurements.

The cobalt-59 nmr spectrum of aqueous $[Co((\pm)pn)_3]Cl_3$ is shown in Figure 1A. Figures 1B, C, and D show the cobalt-59 spectra of the three fractions of diastereomers obtained by chromatographic fractionation of $[Co((\pm)pn)_3]Cl_3$. Fraction 1 (Figure 1B) contains Δ-$Co((-)pn)_3^{3+}$ and Λ-$Co((+)pn)_3^{3+}$ and fraction 2 (Figure 1C) contains Δ-$Co((-)pn)_2((+)pn)^{3+}$ and Λ-$Co((+)pn)_2((-)pn)^{3+}$. The Δ and Λ configurations in these cases correspond to mirror image species and will exhibit identical nmr spectra. Fraction 3 (Figure 1D) consists of the remaining four racemic pairs. By inspection of Figure 1, peaks d and e are readily assigned to fraction 1, peaks b and c to fraction 2, and peak a to fraction 3. From relative integrated intensities of these lines, the ratios a:(b + c):(d + e) are

---

(1) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Amer. Chem. Soc.*, **86**, 590 (1964).

(2) T. E. MacDermott, *Inorg. Chim. Acta*, **2**, 81 (1968).

(3) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(4) H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Jap.*, **39**, 92 (1966).

(5) P. F. Crossing and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 295 (1972).

(6) G. W. Everett, Jr., and R. M. King, *Inorg. Chem.*, **11**, 2041 (1972).

(7) J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

(8) J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. L. Anet, *J. Amer. Chem. Soc.*, **94**, 757 (1972).

(9) A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, **2**, 39 (1968).

(10) F. Yajima, Y. Koike, T. Sakai, and S. Fujiwara, *Inorg. Chem.*, **11**, 2054 (1972).

(11) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951).

(12) Clark Microanalytical Laboratory, Urbana, Illinois.

(13) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

(14) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **85**, 2913 (1963).