demonstrated by the data in Table I. The pK values for *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ are about 6.4 and 9.8.[8] One would expect that the pK for *cis*-$[Cr(C_2O_4)_2(DMSO)H_2O]^-$ would be not less than 6.4 and, therefore, the species studied in the pH range 1–4 would not change.

The activation parameters for the first step of the aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$ imply a mechanism with more bond making than bond breaking in the transition state. This is consistent with the idea that the activation enthalpy should be lower if the entering group is forming a bond with the metal during the transition state. If the entering group is forming a bond in the transition state, stringent steric requirements have to be met and the entropy of activation should be relatively negative. The second step in the aquation reaction has activation parameters which imply more of a concerted reaction.

Solvolysis of *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ in DMSO.—The possible reaction scheme for the solvolysis of *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ in DMSO would be a set of reactions similar to those presented for the aquation of *cis*-$[Cr(C_2O_4)_2(DMSO)_2]^-$. The arguments with respect to the *cis* isomers being the more stable thermodynamically have been presented. There can be no argument that the spectrum of the intermediate supports this because of the inaccuracy of the calculated intermediate spectrum.

The activation parameters for this solvolysis reaction in DMSO, shown in Table II, have small standard deviations in general and probably indicate a dissociation mechanism. The data taken with small amounts of water added to DMSO indicate no importance due to presence of water in DMSO. If the observed rate constants are composites of several different rate constants, the several different rate constants must have activation parameters that are within experimental error of the observed activation parameters, because the standard deviation of the observed parameters is quite small.

Acknowledgment.—The authors wish to express their thanks to the University Research Committee of Washington State University for funds to support this research.

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[8] R. E. Hamm and D. M. Grant, *J. Am. Chem. Soc.*, **78**, 3006 (1956).

CONTRIBUTION FROM THE SCHOOL OF CHEMICAL SCIENCES, UNIVERSITY OF EAST ANGLIA,
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The Stereospecific Coordination of Sarcosine

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The classical resolution[1] of the (±)sarcosinatobis(ethylenediamine)cobalt(III) ion has been repeated, and the mutarotation of the optically active coordinated sarcosine was not observed. Circular dichroism, rotatory dispersion, and pmr evidence has been collected to show that sarcosine is coordinated stereospecifically, and this result is supported by a conformational analysis of the possible isomers.

Introduction

The possibility of resolving a quaternary ammonium salt where one of the substituents is a metal ion probably was entertained first by Meisenheimer and co-workers.[1] These authors claimed to have resolved the $(Co(en)_2sar)^{2+}$ ion (en = ethylenediamine, sar = sarcosine) where both the configuration about the cobalt and that about the N atom are asymmetric (Figure 1). This work is quoted widely as an outstanding example of asymmetry engendered in the ligand by coordination, and some discussion of its experimental validity is relevant here since at least two attempts to reproduce some of Meisenheimer's most significant results have been unsuccessful.[2]

Disregarding the conformations of the ligands there are four possible isomeric forms of the ion, $(+)(Co(en)_2(+)sar)^{2+}$, $(+)(Co(en)_2(-)sar)^{2+}$, $(-)(Co(en)_2(+)sar)^{2+}$, and $(-)(Co(en)_2(-)sar)^{2+}$, denoted by Meisenheimer as (Co+N+) (Co+N−), (Co−N+), and (Co−N−). This nomenclature will be retained to avoid confusion with the original literature. Meisenheimer, *et al.*, resolved the complex with the π-bromocamphorsulfonate ion ((+)BCS) and obtained two BCS diastereoisomers designated as (Co−N±), $[M]_D$ −923°, and (Co+N±), $[M]_D$ +2020°, respectively, containing variable amounts of water and alcohol. They maintained that although the cobalt configurations were separated the internal diastereoisomers arising from the coordinated sarcosine were not. However, in one instance recrystallization of a diastereoisomer fraction, $[M]_D$ +2020°, from water gave a fraction, $[M]_D$ +2290°, whose rotation in aqueous solution decreased to +2130° after 2 hr and then to +2020° on standing overnight. The authors considered that this fraction contained the (Co+N+)

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[1] J. Meisenheimer, L. Angermann, and H. Holsten, *Ann.*, **438**, 261 (1924).

[2] (a) F. Basolo, Ph.D. Thesis, University of Illinois; (b) this work.

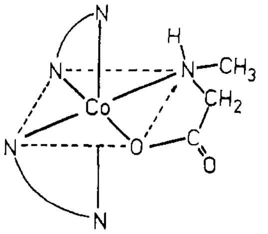

Figure 1.—Sarcosinatobis(ethylenediamine)cobalt(III) ion.

isomer and that the activity due to the asymmetric configuration about the N atom was lost on standing in aqueous solution. Another fraction of recrystallized diastereoisomer claimed to be (Co+N−), $[\mathrm{M}]_{\mathrm{D}}$ +1775°, increased its rotation in aqueous solution to +1825° after 2 hr but did not increase further. In another instance recrystallization of the (Co−N±) diastereoisomer, $[\mathrm{M}]_{\mathrm{D}}$ −923°, gave a fraction $[\mathrm{M}]_{\mathrm{D}}$ −860° whose rotation reverted to −930° after 2 hr in aqueous solution. This fraction was considered to be the (Co−N+) isomer, but the (Co−N−) diastereoisomer was not detected. However, all the diastereoisomer fractions gave complex iodides or dithionates with essentially the same magnitude of rotation, (−)-$(\mathrm{Co(en)_2sar})\mathrm{I_2}\cdot 1.5\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ −1505°, (−)$(\mathrm{Co(en)_2sar})\mathrm{S_2O_6}\cdot\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ −1555°, (+)$(\mathrm{Co(en)_2sar})\mathrm{I_2}\cdot 1.5\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ +1485°, (+)$(\mathrm{Co(en)_2sar})\mathrm{S_2O_6}\cdot\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ +1530°. No mutarotation of the resulting salts was observed except in one instance where the (−) dithionate isomer decreased in rotation $[\mathrm{M}]_{\mathrm{D}}$ from −1565 to −1100° and in 24 hr rose again to −1300°.

These results obtained by Meisenheimer do not appear to be internally consistent, and this fact coupled with the failure of other attempts to repeat this work and the more recently realized possibility of stabilizing the proton on the sarcosine N–H prompted the present study.

The possibility of stabilizing the proton on the N atom arises from a consideration of the kinetics of interchange of hydrogen isotopes with similar cobalt(III) complex ions.[3–6] In all instances the rate law is of the form

$$R = k(\text{complex})(\mathrm{OH^-})$$

and for an ion such as $(\mathrm{Co(ND_3)_6})^{3+}$ the half-life for exchange of deuterium with the solvent water at pH 4.7 and 20° is 57 min.[3] The exchange rates for ions of lower over-all charge are even lower. Therefore if Meisenheimer's recrystallizations are carried out in solutions at pH 2–3, the proton should be kinetically inert and little or no mutarotation should occur by this process. The possibility of Co–N and C–N bond rupture leading to mutarotation is excluded on the grounds that these processes would be even slower than the N–H bond rupture.

Experimental Section

All rotations were measured in a 1-dm tube with a Bellingham & Stanley visual polarimeter and/or a Perkin-Elmer 141 photoelectric polarimeter. The circular dichroism curves were measured with the Dichrographe.

***dl*-Sarcosinatobis(ethylenediamine)cobalt(III) Iodide.**—$(\mathrm{Co(en)_2CO_3})\mathrm{I}$ (11.0 g) neutralized with HCl (16 ml, 5.0 *N*) was then treated with sarcosine (3.6 g) and NaOH (42.0 ml, 1.0 *N*). The mixture was heated at 75° for 5 hr and the solution (30 ml) cooled and filtered to remove $(\mathrm{Co(en)_3})\mathrm{Cl_3}$ (2.7 g). The filtrate, treated with NaI (14 g), gave pink crystals on standing overnight which were collected and washed with 80% aqueous alcohol, then with acetone, and recrystallized from hot water. *Anal.* Calcd for $(\mathrm{Co(C_2H_8N_4)_2CH_3NHCH_2COO})\mathrm{I_2}$: C, 16.14; H, 4.26; N, 13.44. Found: C, 15.95; H, 4.54; N, 13.30.

Resolution of *dl*-(Co(en)$_2$sar)I$_2$.—The complex (13.03 g) in water (30 ml at 40°) was treated with a suspension of silver (+)-bromocamphorsulfonate monohydrate (21.7 g) in water (30 ml). After shaking the mixture for 15 min the AgI was filtered off and washed with cold water. The filtrate and washings were combined and evaporated to 30 ml when methanol (90 ml) was added. After 2 hr a fine flocculent precipitate was collected which was washed with ethanol and acetone and dried under vacuum (14.5 g, $[\alpha]^{20}_{\mathrm{D}}$ +31°. Four recrystallizations of this diastereoisomer from aqueous ethanol finally gave a fraction with $[\alpha]^{20}_{\mathrm{D}}$ −107° which was twice recrystallized from 10^{-3} *M* $\mathrm{HClO_4}$–ethanol to give (−)$(\mathrm{Co(en)_2sar})(+)(\mathrm{BCS})_2\cdot\mathrm{H_2O}$ (0.36 g), $[\alpha]^{20}_{\mathrm{D}}$ −107° (from a 1.0% solution in water or 10^{-3} *M* $\mathrm{HClO_4}$), $[\mathrm{M}]^{20}_{\mathrm{D}}$ −970°. *Anal.* Calcd for $(\mathrm{Co(C_2H_8N_2)_2CH_3NHCH_2COO})$-$(\mathrm{C_{10}H_{14}O_4BrS})_2\cdot\mathrm{H_2O}$: C, 35.80; H, 5.79; N, 7.73. Found: C, 35.85; H, 5.66; N, 7.65.

The filtrate was evaporated to dryness, $[\alpha]^{20}_{\mathrm{D}}$ +116°, and recrystallized from aqueous ethanol twice and from 10^{-3} *M* $\mathrm{HClO_4}$–ethanol to give (+)$(\mathrm{Co(en)_2sar})(+)(\mathrm{BCS})_2\cdot\mathrm{H_2O}$ (0.44 g), $[\alpha]^{20}_{\mathrm{D}}$ +227° (from a 1.0% solution in water or 10^{-3} *M* $\mathrm{HClO_4}$), $[\mathrm{M}]^{20}_{\mathrm{D}}$ +2050°. *Anal.* Found: C, 35.56; H, 5.89; N, 7.91. Both the (−)(+) and (+)(+) diastereoisomers were recrystallized from 10^{-3} *M* $\mathrm{HClO_4}$–ethanol and from water without change in rotation; solutions of the diastereoisomers in water showed no change in rotation over 12 hr at 20° and the rotations were identical with those in 10^{-3} *M* $\mathrm{HClO_4}$.

(−)Sarcosinatobis(ethylenediamine)cobalt(III) Iodide–1.5 Water.—The combined diastereoisomer fractions with $[\alpha]^{20}_{\mathrm{D}}$ −107° (1.4 g), dissolved in 10^{-3} *M* $\mathrm{HClO_4}$ (15 ml), were treated with NaI (2.5 g) and allowed to cool at 5° for 12 hr. The iodide salt which crystallized out was collected and washed with ethanol and acetone. The iodide was fractionally crystallized from 10^{-3} *M* $\mathrm{HClO_4}$ and dried under vacuum to give (−)$(\mathrm{Co(en)_2sar})\mathrm{I_2}\cdot 1.5\mathrm{H_2O}$. All fractions gave $[\alpha]^{25}_{\mathrm{D}}$ −281° (from a 0.1% solution in 10^{-3} *M* $\mathrm{HClO_4}$, $\mathrm{H_2O}$, or 0.1 *M* $\mathrm{NaHCO_3}$), $[\mathrm{M}]^{25}_{\mathrm{D}}$ −1540°. *Anal.* Calcd for $(\mathrm{Co(C_2H_8N_2)_2CH_3NHCH_2COO})\mathrm{I_2}\cdot 1.5\mathrm{H_2O}$: C, 15.34; H, 4.60; N, 12.78. Found: C, 15.23; H, 4.59; N, 12.66.

(+)Sarcosinatobis(ethylenediamine)cobalt(III) Iodide–1.5 Water.—The combined diastereoisomer fractions with $[\alpha]^{20}_{\mathrm{D}}$ +227° were treated as for the *levo* isomer to give (+)$(\mathrm{Co(en)_2sar})\mathrm{I_2}\cdot 1.5\mathrm{H_2O}$ (0.3 g), $[\alpha]^{25}_{\mathrm{D}}$ +275° (0.1% solution in 0.001 *M* $\mathrm{HClO_4}$, $\mathrm{H_2O}$, or 0.1 *M* $\mathrm{NaHCO_3}$), $[\mathrm{M}]^{25}_{\mathrm{D}}$ +1510°. *Anal.* Found: C, 15.24; H, 4.74; N, 12.66.

Fractional recrystallization of this isomer from dilute acid solutions did not alter the specific rotation.

Results and Discussion

Meisenheimer's experimental procedure was repeated and two diastereoisomers, (+)$(\mathrm{Co(en)_2sar})$-$((+)\mathrm{BCS})_2\cdot\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ +2050°, and (−)$(\mathrm{Co(en)_2}$-$\mathrm{sar})((+)\mathrm{BCS})_2\cdot\mathrm{H_2O}$, $[\mathrm{M}]_{\mathrm{D}}$ − 970°, were obtained. The rotations of solutions of these salts in water did not alter over 12 hr nor did several recrystallizations of the salts from 10^{-3} *M* $\mathrm{HClO_4}$–alcohol change their

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(3) J. S. Anderson, H. V. A. Briscoe, and N. L. Spoor, *J. Chem. Soc.*, 361 (1943).

(4) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).

(5) H. Block and V. Gold, *J. Chem. Soc.*, 966 (1959).

(6) J. W. Palmer, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

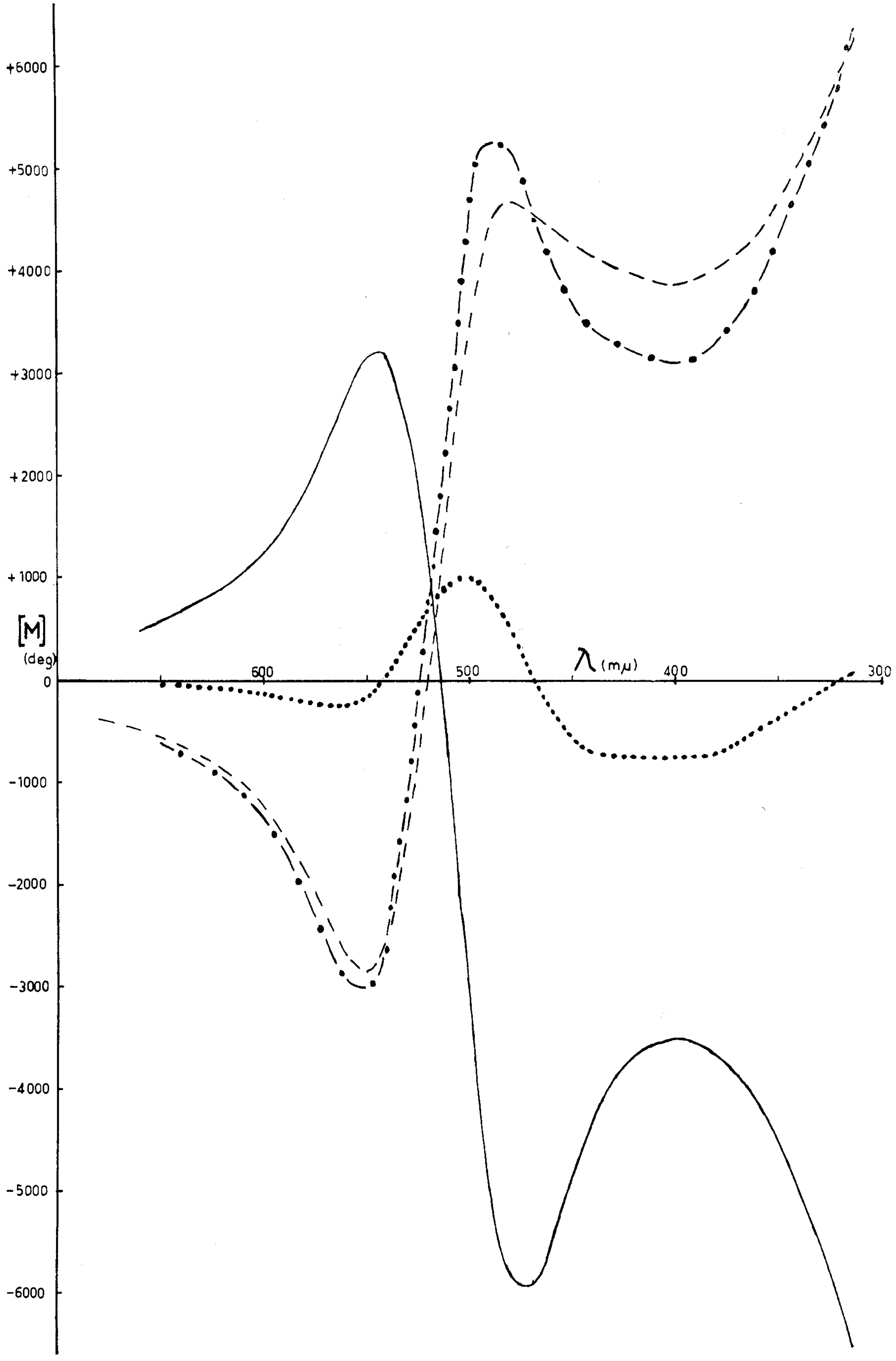

Figure 2.—The rotatory dispersion (RD) curves for the ions $(+)(\mathrm{Co(en)_2gly})^{2+}$ ———, $(-)(\mathrm{Co(en)_2sar})^{2+}$ ---------, $(-)_{436}(\mathrm{Co(NH_3)_4sar})^{2+}$ . . . . . . and the composite curve for $(-)(\mathrm{Co(en)_2sar})^{2+} + (-)(\mathrm{Co(NH_3)_4sar})^{2+}$ ·—·—·—.

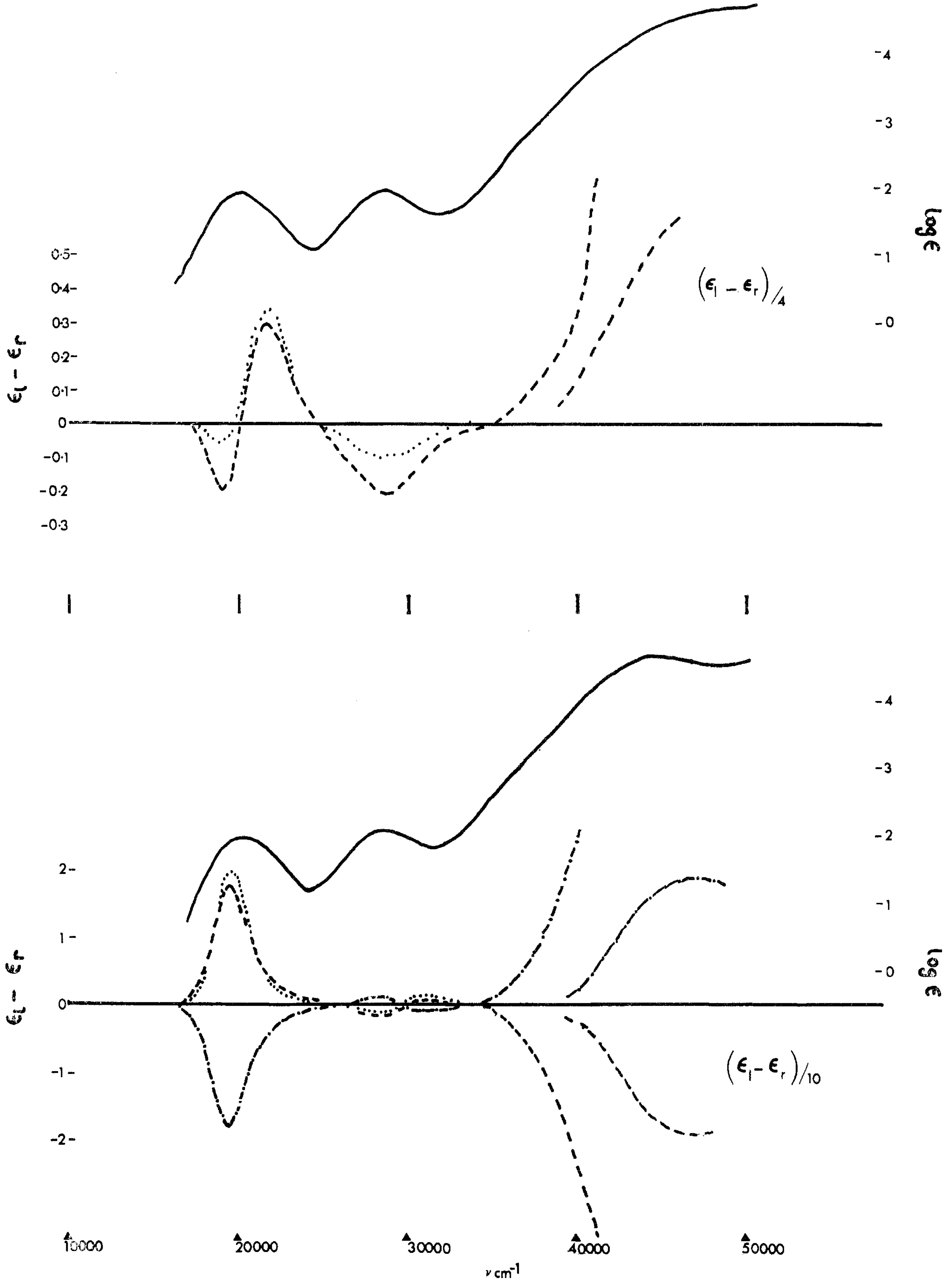

Figure 3.—The circular dichroism ($\epsilon_l - \epsilon_r$) and visible and ultraviolet absorption (log ϵ) curves for $(-)_{436}$(Co(NH$_3$)$_4$sar)(NO$_3$)$_2$ (upper) in HClO$_4$ (0.1 M) -------- in the presence of SeO$_3^{2-}$ (0.1 M, pH 6) and (lower) (+)(Co(en)$_2$sar)I$_2$ in H$_2$O --------- and in SeO$_3^{2-}$ (0.1 M, pH 6)...... and (−)(Co(en)$_2$sar)I$_2$ in H$_2$O ·—·—·—.

molecular rotations. Despite repeated recrystallization of the pure diastereoisomers from water alone no change in rotation was observed for the solutions of the salts even after several days. Thus while the diastereoisomer rotations given above agree with Meisenheimer's initial products, Meisenheimer's subsequent products with both higher and lower optical rotations and the mutarotations of these products were not observed.

The diastereoisomers were converted to the iodides in 10^{-3} M $HClO_4$ solution to give $(Co(en)_2sar)I_2\cdot 1.5H_2O$, $[M]_D$ $-1540°$, and $(Co(en)_2sar)I_2\cdot 1.5H_2O$, $[M]_D$ $+1510°$. The same rotations were observed for solutions of these salts in 10^{-3} M $HClO_4$, H_2O, and 0.1 M $NaHCO_3$, and the rotations remained unchanged after fractionation of the salts from 10^{-3} M $HClO_4$. Also, the values agree with those recorded by Meisenheimer. The failure to observe any change in rotation in the most alkaline solution (pH 8.8) indicates that either the optical isomer contains an equilibrium concentration of the (+) and (−) Co–sarcosine configurations or that the ligand is coordinated stereospecifically in one configuration. The $(Co(NH_3)_4sar)^{2+}$ ion racemizes rapidly at pH 7 ($t_{1/2}$ $\sim$ 5 min),[7] and it would be expected that the sarcosine moiety in $(Co(en)_2sar)^{2+}$ would mutarotate under the same conditions.

The rotatory dispersion (RD) curves and the circular dichroism (CD) curves of $(+)(Co(en)_2sar)I_2\cdot 1.5H_2O$ and $(-)(Co(en)_2sar)I_2\cdot 1.5H_2O$ are given in Figures 2 and 3 and show clearly the mirror image relationship of the two ions. In Figure 2 the RD curves of $(-)$-$(Co(NH_3)_4sar)^{2+}$, $(+)(Co(en)_2gly)^{2+}$ (gly = glycine), and $(-)(Co(en)_2sar)^{2+}$ are also compared. The composite curve arising from the superposition of those for $(-)(Co(en)_2sar)^{2+}$ and $(-)(Co(NH_3)_4sar)^{2+}$ is almost the mirror image of that of $(+)(Co(en)_2gly)^{2+}$, and this implies that the configuration about the N atom in the first ion is optically active and that sarcosine coordinates stereospecifically in the D and L configurations of the Co(III) ion. A similar trend was observed in the CD curves and the approximately additive nature of these optical effects has previously been observed by Liu and Douglas.[8]

Some justification for this view also arises from a consideration of the detailed stereochemistry in the Dreiding models of these ions depicted in Figure 4. Sarcosine with the configuration shown in Figure 4b, where the methyl group interacts strongly with the adjacent en ring, should be configurationally less stable than the arrangement in Figure 4a, where the methyl group is staggered between the two en rings and the nonbonded atomic interactions are thereby reduced. These considerations hold regardless of the conformation of the Co–sarcosine ring and imply that only one configuration of sarcosine (a) is stable in the D configuration about the Co atom. Similarly, the L configuration leads to the enantiomorphic form for the coordinated sarcosine, and no mutarotation should be observed if the interaction between the CH_3 group and the Co–en ring leads to D(a) being more stable than D(b) by 3 kcal/mole.

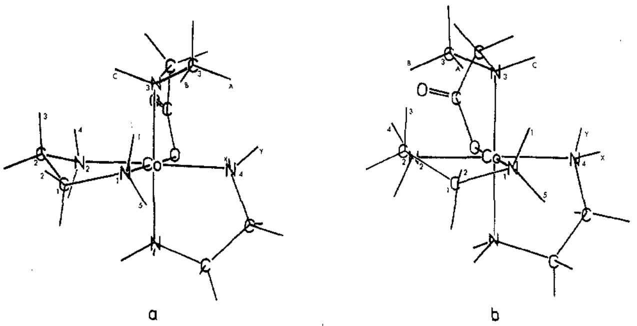
a b

Figure 4.—The configurations of coordinated sarcosine in the L-$(Co(en)_2sar)^{2+}$ ion.

To check these proposals a conformational analysis for the structures depicted in Figure 4 was carried out.[9] The structures were selected to contain those atomic arrangements in which the nonbonded interactions are minimized and the ring conformations are strain free. For instance, the methyl group is "staggered" in relation to the bonds about the sarcosine N and H_A and H_B straddle H_3 in Figure 4b. The mirror-image conformation (k^1) of the ethylenediamine leads to a greater interaction, and this arrangement was not considered. The structure in Figure 4a where the methyl group lies between the two ethylenediamine rings probably has a more stable arrangement for H_A and H_B if the methyl group partially eclipses the configuration about the sarcosine N_3. However, the calculation was carried out on the structure in Figure 4a where the methyl is completely staggered, partly to keep this factor constant for both structures and partly because it probably is a less favored configuration of the most stable diastereoisomer and the energy difference between the two structures is thereby reduced. The conformation of the sarcosine–Co ring has little effect on the position of H_A, H_B, and H_C in relation to their nonbonded interactions, and this conformation was also left constant. The following interactions were established as the most significant: structure 4b H_A–H_3, H_B–H_3, H_B–H_4, H_A–C_2, H_B–C_2, H_B–N_2, H_3–C_3; structure 4a H_A–H_1, H_B–H_X, H_X–C_3, H_B–N_4. The remaining interactions contributed little to the stability of either form.[9] The energy difference between structures 4a and 4b was assessed at 10.5 kcal/mole in favor of 4a, and although this value seems rather large it is in the same direction as the similar interaction between an axial t-butyl group and the

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[7] B. Halpern, A. M. Sargeson, and K. R. Turnbull, to be published.

[8] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[9] The total interactions considered were as follows (A). Structure 4a H_CH_1 2.72, H_CH_2 3.88, H_CH_3 2.28, H_CH_4 2.48, H_AH_1 1.80, H_AH_5 3.20, H_AH_X 2.20, H_AH_Y 3.56, H_BH_1 3.20, H_BH_5 4.08, H_BH_X 1.72, H_BH_Y 2.28, H_CH_1 3.08, H_CC_1 3.48, H_CC_2 2.80, H_CN_2 2.68, C_3H_1 2.60, C_3H_X 2.32, C_3H_Y 3.08, H_aN_1 2.68, H_aN_4 2.88, H_bN_1 3.76, H_bN_4 2.32. Structure 4b H_ZH_1 2.12, H_AH_2 2.80, H_AH_3 1.56, H_AH_4 3.00, H_BH_1 3.52, H_BH_2 3.92, H_BH_3 1.68, H_BH_4 1.64, H_CH_1 2.52, H_CH_X 2.40, H_CH_Y 3.00, H_CH_5 3.80, H_AN_1 2.64, H_AC_1 2.22, H_AC_2 2.24, H_AN_2 2.88, H_BN_1 3.60, H_BC_1 3.48, H_BC_2 2.28, H_BN_2 2.16, H_CN_1 3.12, H_CN_4 2.92, C_3H_1 2.80, C_3H_2 3.68, C_3H_3 2.00, C_3H_4 2.48. The remaining interactions were either negligible or were duplicated in both structures. The energies of the interactions were evaluated from the expression of T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

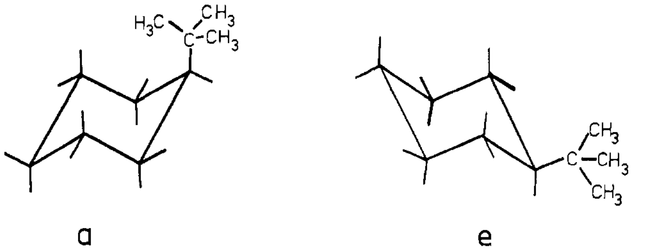

Figure 5.—The axial (a) and equatorial (e) forms of *t*-butylcyclohexane.

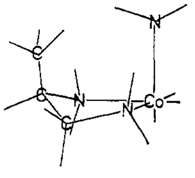

Figure 6.—Axial–axial interaction in the cobalt–(+)propylenediamine ring system.

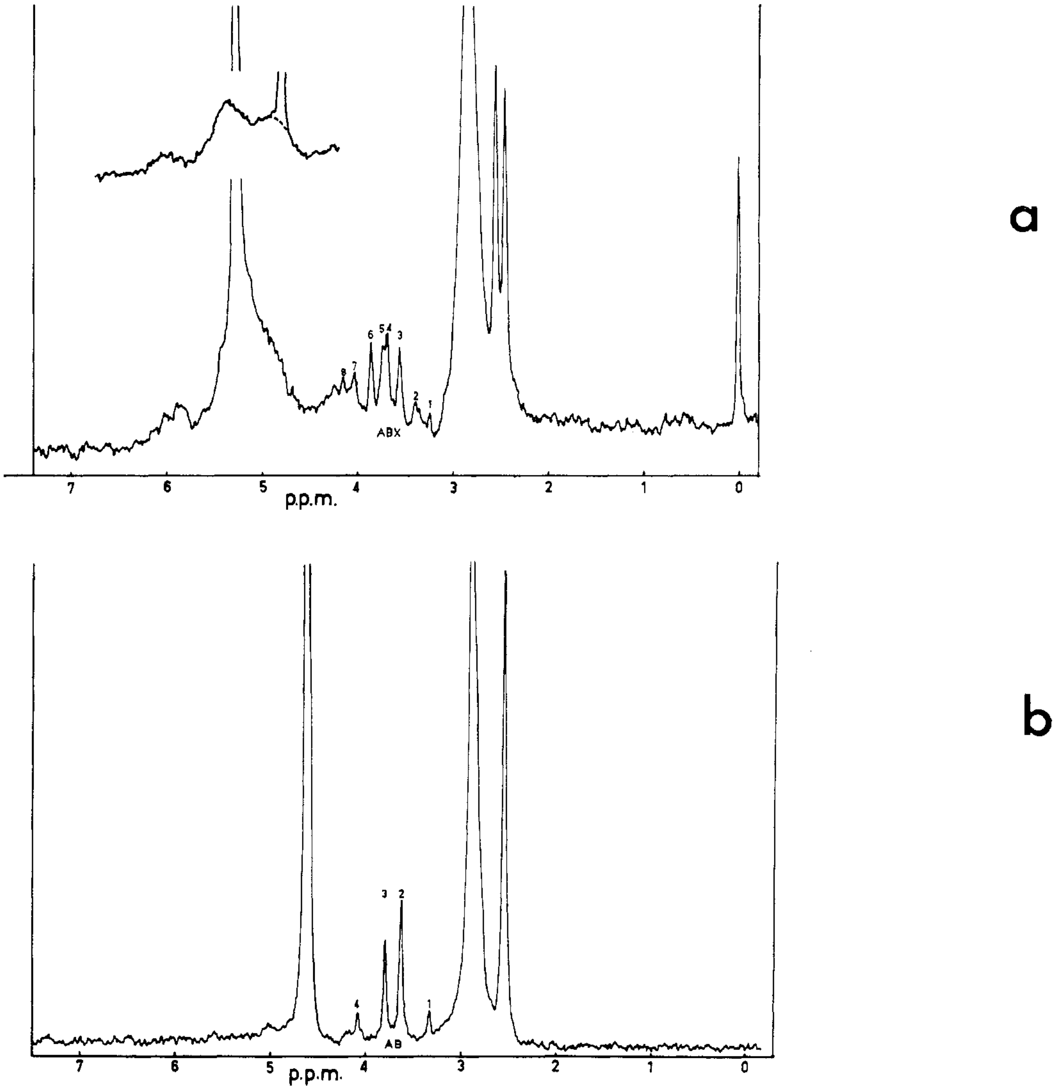

Figure 7.—Pmr spectra of D-(+)(Co(en)$_2$sar)I$_2$ in (a) 0.1 *M* D$_2$SO$_4$ and (b) D$_2$O (obtained using an R10 nmr spectrometer and sodium trimethylsilylpropanesulfonate (TPSNa) as a standard).

cyclohexane ring (Figure 5a) which has been evaluated as 4 kcal/mole less stable than that for the equatorial form (Figure 5e). The interaction between N–CH$_3$ and the ethylenediamine ring is such that the methyl group and the nearest axial proton in Figure 4b are approximately the same distance apart as the 1,3 axial *t*-butyl–proton interaction above. It is reasonable to suppose then that 4a is more stable than 4b by at least 3 kcal/mole and that the system is substantially stereospecific. It has been argued that the inverse interaction of 4b found in the Co(III)–propylenediamine complexes (Figure 6) is unfavorable to the extent of >2 kcal/mole,[10] and some evidence suggests that this conformation does not occur to any marked extent[11] if at all and that the equatorial methyl group is preferred.

Further evidence for the stereospecific attachment of sarcosine can be adduced from the pmr spectrum of the D-(Co(en)$_2$sar)$^{2+}$ ion. The environment of the N-methyl group in 4a is not equivalent to that in 4b, and two doublets should be observed if both configurations are present. It is clear from Figure 7 that only one species is present and the same spectrum was obtained

[10] E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[11] S. F. Mason and B. J. Norman, *Chem. Commun.*, 339 (1964); A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 49 (1965).

for the racemic complex. The ABX pattern at 3.7 ppm, arising from the coupling of the AB (CH_2) protons with the proton on the N atom, reduced to a simple AB system when the NH was deuterated (Figure 7b). Similarly the methyl doublet also reduced to a singlet. It is apparent from the deuterated spectra that stereospecificity is again indicated since if the other configuration of sarcosine were present two singlets should be observed for the nonequivalent methyl groups and two sets of doublet pairs for the nonequivalent $-CH_2-$ systems. This argument is supported by the pmr spectra of the D-$(Co(en)_2(+)ala)^{2+}$ (ala = alanine) and L-$(Co(en)_2(+)ala)^{2+}$ ions given in Figure 8, where the two configurations about the Co(III) ions are different for the same coordinated optically active amino acid and two doublets are observed (1.5 ppm) with different chemical shifts for the nonequivalent methyl groups. Similarly, the AB_3 quartets, attributed to the C–H proton split by the methyl group, are at different chemical shifts and the difference between the doublets and the quartets is more clearly observed in the spectrum for the "racemic" complex D,L-$(Co(en)_2(+)ala)Cl_2$ (Figure 8a), where the two quartets (1,3,3,1) are partly superimposed to give a quintet (1,4,6,4,1) and the doublet peaks are split. This situation is analogous to that for the sarcosine complex since L-$(Co(en)_2(+)ala)^{2+}$ will have a pmr spectrum identical with that of D-$(Co(en)_2(-)ala)^{2+}$. This stereospecific effect leads us to the assignment of the absolute configuration of the coordinated sarcosine in the D-$(Co(en)_2sar)^{2+}$ ion.

The circular dichroism spectra of (+)- and (−)-$(Co(en)_2sar)^{2+}$ bear a mirror-image relationship one to the other (Figure 3), indicating that these complex ions are enantiomers, with the same conformations in corresponding chelate rings. Isomeric complex ions with different chelate ring conformations, as in the case of (+)- and (−)$(Co(+pn)_3)^{3+}$, which have the lel and the ob conformation,[10] respectively, give very different circular dichroism spectra in the visible and, more particularly, in the ultraviolet region.[11]

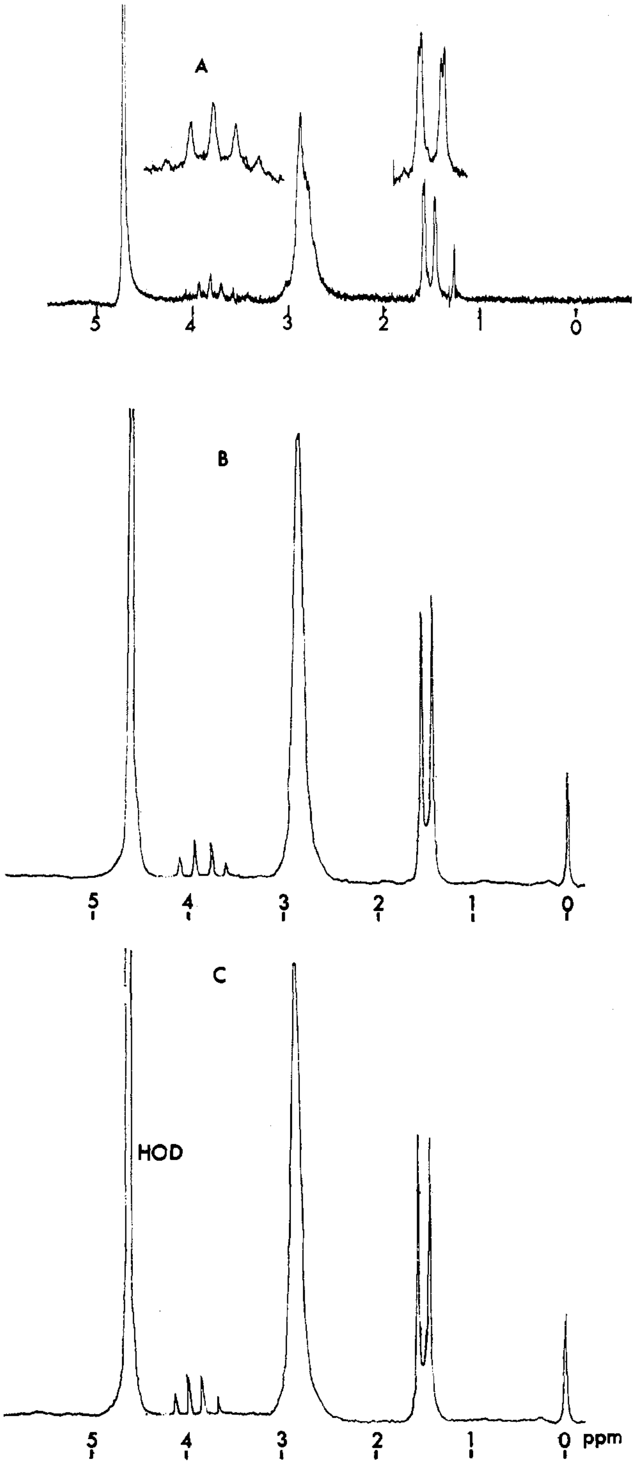

Figure 8.—Pmr spectra of $(Co(en)_2(+)ala)^{2+}$ complexes in D_2O: a, D,L-$(Co(en)_2(+)ala)Cl_2$; b, D-$(+)_{546}(Co(en)_2(+)ala)Cl_2$; c, L-$(-)_{546}(Co(en)_2(+)ala)Cl_2$ (a, A60 spectrometer; signal at 1.25 ppm is due to t-butyl alcohol; b and c obtained as in Figure 7, using sodium trimethylsilylpropanesulfonate as a standard).

The oxygen and the five nitrogen atoms bonded to cobalt(III) in (+)- and (−)$(Co(en)_2sar)^{2+}$ give these complex ions the effective chromophoric symmetry of C_{4v}, a group in which the triply-degenerate octahedral T_{1g} transition breaks down into components with A_2 and E symmetry. The A_2 component lies at the same frequency as the T_{1g} transition of $(Co(NH_3)_6)^{3+}$ and the E component is displaced to lower frequencies, as oxygen lies below nitrogen in the spectrochemical series. The net rotational strength of the components of the octahedral T_{1g} transition in the related trigonal complex ion, $(Co(en)_3)^{3+}$, is shared[12] between the A_2 and E components of $(Co(en)_2sar)^{2+}$ in the ratio of 1:2. Thus the circular dichroism spectrum in the visible wavelength region of the $(Co(en)_2sar)^{2+}$ isomer with the same absolute configuration of the chelate rings about the metal ion as $(+)(Co(en)_3)^{3+}$ should consist of two positive circular dichroism bands, the minor one lying at the same frequency as the absorption maximum of $(Co(NH_3)_6)^{3+}$ (21,200 cm^{-1}) and the major one at a lower frequency. The two circular dichroism bands are not resolved in the spectra of (+)- and (−)$(Co(en)_2sar)^{2+}$, but the circular dichroism band observed in the visible wavelength

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[12] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 132 (1965).

region tails to higher frequencies (Figure 3), suggesting the presence of two component bands with the same sign. The maximum of the observed circular dichroism band, which reflects the position of the major component, lies at a lower frequency (19,400 cm^{-1}) than that of the visible absorption band of $(Co(NH_3)_6)^{3+}$. Accordingly it is concluded that $(+)(Co(en)_2sar)^{2+}$, which gives a positive dichroism band in the visible region, has the same absolute configuration of the chelate rings around the metal ion as $(+)(Co(en)_3)^{3+}$; that is, the mirror-image of the configuration shown in Figure 4a. It follows from the RD curve analysis that the $(-)(Co(NH_3)_4sar)^{2+}$ ion has the configuration for coordinated sarcosine given in Figure 1.

The absolute configurations of both these ions are at present being determined also by an X-ray crystallographic analysis.

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Magnetic Exchange in Transition Metal Complexes. III. Vanadyl Complexes with Tridentate Schiff Bases[1]

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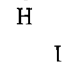
The magnetic susceptibility of a series of 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of VO^{2+} (I) has been measured between 1.4 and 300°K. For R = H, R′ = H, CH_3, Cl, Br, NO_2 and R = Cl, R′ = H, Cl, the temperature dependence of the susceptibility is characteristic of magnetically isolated exchange coupled (antiferromagnetic) pairs. The complex is presumably dimeric, with a structure like that of the corresponding copper compounds. Infrared spectra were determined in the 800–1100-cm^{-1} region, and the VO stretching frequencies are assigned. In the R = H, R′ = NO_2 complex, there is evidence for a weak intermolecular interaction between vanadyl oxygen atoms and vanadium atoms. Exchange integrals are derived by fitting the susceptibilities to the theoretical equation for coupled pairs. The results are interpreted in terms of a direct σ metal–metal interaction between unpaired spins in the $3d_{xy}$ orbitals of the vanadium atoms. This is in contrast to the analogous copper complexes, where spin coupling takes place by superexchange through the bridging oxygen atoms.

Introduction

Several 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of copper(II) have been shown to be magnetic dimers;[1] that is, the copper atoms are arranged in the crystal lattice as magnetically isolated exchange coupled pairs. The corresponding vanadyl complexes



I

with R = H, R′ = H, Cl, Br and R = NO_2, R′ = Br were reported[2,3] to have abnormally low magnetic moments (0.77–1.55 BM) at room temperature. It seems likely that these low moments result from antiferromagnetic exchange coupling between pairs of vanadyl ions, as suggested by Zelentsov.[3] In order to establish whether or not this is correct, we have determined the temperature dependence of the magnetic susceptibility of complex I with R = H, R′ = H, CH_3, Br, NO_2; R = Cl, R′ = H, Cl; and R = NO_2, R′ = H, NO_2,[4] between 1.4 and 300°K. With the exception of the R = NO_2, R′ = NO_2, H compounds, the results are in good agreement with the theoretical equation for exchange-coupled pairs. Presumably, the vanadyl complexes which show coupled-pair susceptibility have the same dimeric, oxygen-bridged structure as the copper complexes.[1,5]

Although pairwise magnetic exchange is well known in d^9 copper complexes[6] (unpaired spin in an orbital derived from the e_g set), our results represent the first demonstration of this phenomenon in a vanadyl complex (unpaired spin in an orbital derived from the t_{2g} set). The exchange integrals calculated from the susceptibility data show a quite different dependence on the substituents R and R′ than do the exchange integrals for the analogous copper complexes. The results are interpreted in terms of direct metal–metal interaction between pairs of vanadium atoms. This is in contrast to the copper complexes, where spin coupling takes place by superexchange *via* the bridging oxygen atoms.

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[1] Part II of this series: A. P. Ginsberg, R. C. Sherwood, and E. Koubek, *J. Inorg. Nucl. Chem*, in press.

[2] V. V. Zelentsov, *Dokl. Akad. Nauk SSSR*, **139**, 1110 (1961).

[3] V. V. Zelentsov, *Russ J. Inorg. Chem.*, **7**, 670 (1962).

[4] The compounds with R = H, R′ = CH_3, NO_2; R = Cl, R′ = H, Cl; and R = NO_2, R′ = H, NO_2 do not appear to have been prepared previously.

[5] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[6] See the references cited in ref 1.