An alternative to the McConnell approximation[7] would involve a knowledge of the tensor elements of the ^{183}W spectra, obtained in a solid-state NMR experiment. This approach has been used to evaluate local anisotropic contributions from carbon atoms in organometallic π systems.[17] In this model, one could regard the situation as being equivalent to having three mutually perpendicular current loops around the tungsten atoms; the local anisotropic contributions to the chemical shifts of nearby protons would therefore be calculable. Such an approach has been successfully tested on alkynes[6] and, in principle, is more reliable for proximate protons when the dipole approximation often breaks down.

Registry No. $W_2(NMe_2)_6$, 54935-70-5; $Mo_2(NMe_2)_6$, 51956-20-8; $W_2(O_2CNMe_2)_6$, 61091-29-0; $[(n\text{-}C_4H_9)_3P]_2(C_6H_5CO_2)_2Mo_2Br_2$, 59493-09-3.

(17) Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902.

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Structural Assignments and Stereospecificity of the *cis*-Dinitrobis(sarcosinato(1−)-*O*,*N*)cobaltate(III) Ion

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The stereospecific coordination of chiral ligands manifests itself in the preferred formation of one of the possible diastereoisomers. Frequently the configurations of the ligands produce steric interactions which cause either the Λ or Δ isomer to be preferentially formed. Ligands with donor atoms which become chiral on coordination behave in a similar way. In such cases the configuration of the donor atom for a given isomer is enforced by the remaining part of the chelate ring and vice versa. If the absolute configuration of the donor atom is fixed, the absolute configuration of the complex will be stereoselectively controlled by the donor atom chirality.

We are interested in metal complexes with forced configurations of donor atoms. Recently we[2a] have found that nonbonding interactions between N-CH_3 groups of sarcosine exclude the existence of tris(sarcosinato)cobalt(III) *fac* isomers and *mer* isomers with *SSS* and *RRR* configurations at the secondary nitrogen atoms and several other combinations with similar interactions, while very small stereoselectivity is exhibited by the analogous asparaginato chelate. In a cobalt(III) complex with nonequivalent chiral centers, i.e., (sarcosinato)bis((*S*)-(+)-valinato)cobalt(III),[2b] the stereochemical selection of geometric isomers is determined primarily by the steric requirements of the N-CH_3 group of sarcosine, while the degree of stereoselectivity corresponds to the small structural differences arising from the axial or equatorial disposition of the two isopropyl groups of valine. These results prompted us to study the forced configuration of the donor atoms in relation to the internal stereoisomerism in bis(chelate) octahedral complexes.

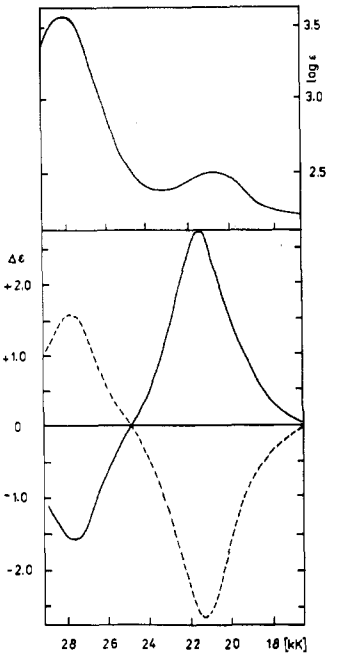

Figure 1. Electronic absorption spectrum of the cis(NO_2),trans(N),cis(O) isomer (—) and circular dichroism spectrum of the Λ (—) and Δ (-----) isomers.

Results and Discussion

Complexes of the type $Co(\overset{\frown}{N\,O})_2(NO_2)_2^-$, where $\overset{\frown}{N\,O}$ is an unsymmetrical bidentate ligand, can exist in five geometrical isomers: trans(NO_2),trans(N),trans(O); trans(NO_2),cis(N),cis(O); cis(NO_2),cis(N),cis(O); cis(NO_2),trans(N),cis(O); cis(NO_2),cis(N),trans(O). Among these isomers the three cis(NO_2) isomers can exhibit enantiomeric (or Δ,Λ) relationships. Accordingly, the number of isomers is up to 8. On the assumption that the secondary nitrogen atom of sarcosine becomes chiral by coordination, the total number of isomers will be 26, excluding conformational isomers. That is, coordination of inert secondary nitrogen atoms can give rise to an *RR* isomer, to an *SS* isomer, and normally to one *RS* isomer—except for the Δ and Λ "all-cis" isomers of C_1 symmetry for which the two chelate rings are not equivalent and give two *RS* isomers each.

Čelap et al.[3] studied a series of the above-mentioned type of complexes and found that the topology of the complexes obtained depended on the temperature, which seems to play an important role in the isomerization. A mixture of isomers has been obtained by a substitution reaction at 60 °C. At higher temperatures only the cis(NO_2),trans(N),cis(O) isomers could be obtained.[3] It is evident from a study of models that these isomers exhibit a minimum of nonbonding interactions between the nonpolar amino acid side chains and that the steric volume of the α-amino acid substituents does not influence the geometry of the complexes obtained.

The sarcosine complex was prepared under conditions which lead to several geometrical isomers, but only two isomers were obtained. Their electronic absorption spectra (Figure 1) do not show splitting of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, which suggests that the carboxylate groups are in cis positions. The low-energy band located at about 20 800 cm^{-1} is shifted by 600 cm^{-1} in comparison with other amino acid complexes (see ref 3). This shift may be due to the lower ligand field of the secondary

(1) (a) Prague Institute of Chemical Technology. (b) Ain Shams University. (c) University of Massachusetts.
(2) (a) Jursík, F.; Sýkorová, D.; Hájek, B. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2333. Jursík, F.; Archer, R. D.; Hájek, B. *Ibid.* **1978**, *43*, 819. (b) Jursík, F.; Sýkorová, D.; Hájek, B. *Ibid.* **1976**, *41*, 3363.
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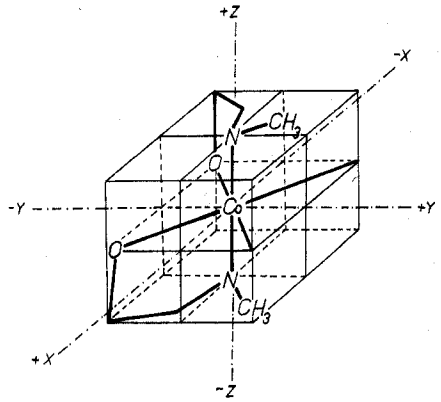

Figure 2. Schematic structure which shows the contributions of the CH_2 and NH–CH_3 groups to the optical activity of Λ isomer.

nitrogen atom. Therefore, it follows that the $[Co(Sar)_2(NO_2)_2]^-$ ions (where Sar = sarcosinate anion) could exist as pairs of enantiomers and one was resolved into Λ and Δ isomers.

The first complex obtained by the anion-exchange procedure was resolved into optical isomers, whose absolute configurations were deduced from their CD (circular dichroism) spectra (Figure 1) by using McCaffery and Mason's proposition[4] that complexes with C_2 symmetry can be related to the absolute configuration of $Co(en)_3^{3+}$, where en = ethylenediamine, by CD spectral similarity. This proposal has been verified for $(+)_{589}$-*cis*-$Co(l\text{-pn})_2(NO_2)_2^+$, where pn = 1,2-propylenediamine, by X-ray crystallography[5] and used for amino acid complexes,[6] which is appropriate because amino acid and diamine complexes of cobalt(III) exhibit similar circular dichroism characteristics.[7] The Sar chelate in question appears to have C_2 symmetry, too, as noted from the NMR results below; thus a comparison of the dominant circular dichroism peak of E_a parentage allows the determination of the relative absolute configuration. The dominant positive circular dichroism band from the first ligand field band for $(+)_{589}$-$Co(Sar)_2(NO_2)_2^-$ with $\Delta\epsilon = +2.71$ is analogous to Λ-$Co(en)_3^{3+}$, and the $(+)_{589}$ isomer has been assigned as Λ. Similarly, the negative band with $\Delta\epsilon = -2.71$ for the $(-)_{589}$ isomer indicates a Δ absolute configuration. Both circular dichroism spectra bear a mirror-image relationship reflecting the enantiomeric character of the two isomers obtained from the first fraction. The circular dichroism spectra of both isomers were interpreted in more detail by utilizing the octant rule of Hawkins and Larsen.[8] From the regional signs (Figure 2) it follows that the N_R-CH_3 groups (vide infra) of the two sarcosinato ligands are in (−) octants while the CH_2 groups are in (+) octants. The CD intensities then arise from two negative and two positive contributions on the assumption that these are additive to the d-d circular dichroism. For a determination of the magnitude of the CH_2 and N_R-CH_3 contributions, the CD intensities of both $[Co(Gly)_2(NO_2)_2]^-$ (where Gly = glycinate anion) and the complex currently under investigation were compared. As follows from the octant rule, any contribution to optical activity of the former comes from the two CH_2 groups ($\Delta\epsilon = +4.25$).[9] On the other hand, the CD intensity

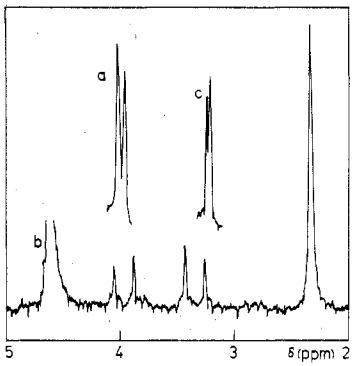

Figure 3. ^1H NMR spectrum of the Λ-cis(NO_2),trans(N),cis(O) isomer: (a) NH–CH_3 group signal (Me_2SO-d_6) and (b) spectrum in D_2O. The NH–CH_3 group signal (D_2O) of the isomer obtained from the second band is inset as c.

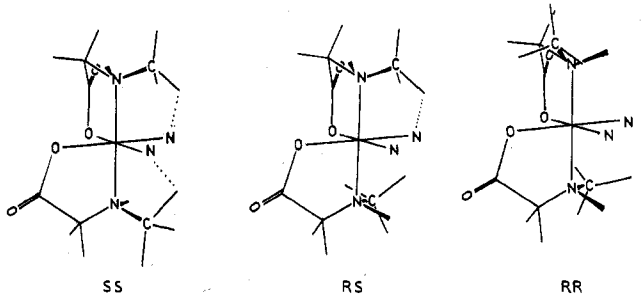

Figure 4. Steric situations arising from different nitrogen atom configurations in the Λ-cis(NO_2),trans(N),cis(O) isomer.

of $[Co(Sar)_2(NO_2)_2]^-$ results from both the CH_2 group and N_R-CH_3 group contributions. Subtracting the CH_2 group contributions (+4.25) from the CD band intensity of $[Co(Sar)_2(NO_2)_2]^-$ (+2.71), we obtain a −1.54 contribution for an N_R-CH_3 group. Also comparing these two contributions, i.e., +4.25 and −1.54, it follows that the CD band intensity of $[Co(Sar)_2(NO_2)_2]^-$ results primarily from the CH_2 groups. Furthermore, the vicinal effect from this *R*-chiral nitrogen atom is greater than that of the *R*-chiral carbon atom of (*R*)-α-alanine (−0.79).[9]

The geometrical arrangement and configuration of the nitrogen atoms were determined from the ^1H NMR spectra. The Me_2SO-d_6 spectrum of the complex obtained from the first fraction shows a doublet at 2.2 ppm, while in D_2O it shows a sharp singlet at 2.4 ppm (Figure 3). This signal belongs to the *N*-CH_3 group because the NH proton does not undergo D-H exchange in Me_2SO-d_6, where the NH is observed as a broad peak between 5.5 and 5.7 ppm. This latter signal disappears in D_2O. Therefore, the doublet is the result of coupling between the *N*-CH_3 and NH protons. Hence, it follows that both secondary nitrogen atoms of sarcosine have the same configuration, either *RR* or *SS* (which excludes the *RS* isomer), although accidental degeneracies could alter this conclusion were it not for the other facts detailed below. Furthermore, because the $-CH_2$ group protons of both sarcosine molecules exhibit the same geometric and magnetic conditions, the complex apparently has a C_2 axis. From this fact and the electronic spectral observations it can be concluded that the configuration of the complex is cis(NO_2),trans(N),cis(O). This conclusion is also confirmed by the change of the 3.60-ppm ABX multiplet, which originates from the coupling of the AB (CH_2) protons with the X (NH) ones, in Me_2SO into a symmetrical AB quartet for the CH_2 protons when measured in D_2O.

The symmetrical AB quartet observed for the CH_2 group in the Λ-*RR*-cis(NO_2),trans(N),cis(O) isomer in D_2O is logical for CH_2 groups attached to dissymmetric nitrogen atoms in

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a complex where both Sar ligands are equivalent.

From the ^{1}H NMR spectra, it follows that both sarcosine nitrogen atoms are coordinated stereospecifically as Λ-*RR* or Λ-*SS* and Δ-*RR* or Δ-*SS*. To distinguish between the *RR* and *SS* configurations, we utilized the different stereochemical situations arising from nonbonding interactions between *N*-CH_3 and freely rotating NO_2 groups (Figure 4). From this point of view it is necessary to take into account all factors influencing the thermodynamic stability of the isomers, i.e., the axial or equatorial arrangements of the *N*-CH_3 groups, the conformations of the chelate rings, the conformations of the N(H)–C(H_3) bond, and finally the mutual positions of the *N*-CH_3 group with its neighboring atoms. If the Λ-cis-(NO_2),trans(N),cis(O) isomer obtained from the first fraction has both nitrogen atoms in an *S* configuration, it can be seen from Dreiding models (Figure 4) that interactions arise between the *N*-CH_3 and NO_2 groups. On the other hand, the interactions between the above-mentioned groups are minimal when the nitrogen atom configuration is *RR* and the NH–CH_3 bond is in a gauche or staggered conformation. From the ^{1}H NMR spectrum and molecular model studies it follows that the racemic complex obtained from the first fraction is composed of the Λ-*RR* and Δ-*SS* isomers. Accordingly, the *RS* isomer, in which the N_s-CH_3 group is always in interaction with the NO_2 group (Figure 4), can be excluded.

The second complex (fraction 2 from the anion-exchange column) exhibits an analogous electronic absorption spectrum, which is characteristic for a cis(NO_2) and a cis(O) configuration. Therefore, this complex must have a cis(NO_2),cis(N),cis(O) configuration. Its cis(N),cis(O) topology was confirmed from the ^{1}H NMR spectrum; i.e., the CH_2 groups are not equivalent. As above, the nitrogen atoms in this complex can have one of three configurations, i.e., *RR*, *SS*, or *RS*. A nonbonding interaction study with models excludes the *SS* configuration due to the *N*-CH_3···NO_2 interactions and the *RR* arrangements which leads to interaction between two *N*-CH_3 groups. The tentatively lowest degree of repulsive interactions corresponds to the *RS* isomer. The doublet nature of the CH_3 signal in the ^{1}H NMR spectrum of this isomer supports this fact (Figure 3c). Only a small quantity of this isomer was obtained. Thus, more detailed characterization was excluded.

Conclusion

The geometry of the primary dinitrobis(sarcosinato(1−)-*O*,*N*)cobaltate(III) isomer has been determined from electronic absorption and ^{1}H NMR spectroscopies as cis(NO_2),trans(N),cis(O). The absolute configurations of the resolved isomers have been determined from circular dichroism spectra. The *N*-CH_3 groups of sarcosine in the Λ isomer preferentially adopt *R* configurations (and *S* in the Δ isomer). Only very small amounts of other isomers are formed.

Experimental Section

Sarcosine was purchased from Fluka. The electronic absorption spectra were measured on a Specord UV VIS (Zeiss, Jena, GDR) apparatus. The ^{1}H NMR spectra were obtained from a Varian XL-100 spectrometer. The circular dichroism spectra were measured by using a Cary 60 spectropolarimeter fitted with a CD accessory. A Perkin-Elmer 241 spectropolarimeter was employed for measurement of optical activity.

Preparation of Complexes. Na[Co(Sar)$_2$(NO_2)$_2$] was prepared according to a procedure described by Čelap et al.[10] The reaction mixture obtained at 60 °C was cooled to 20 °C, diluted to 200 mL, and poured on an anion-exchange column (Dowex 50W-X1, 2 × 30 cm, in Cl^- form). The column was washed with water and was then eluted with a 0.01 M solution of NaCl. The reaction mixture separated into two bands of different intensity. These were eluted separately, and the eluates were concentrated in vacuo. First, NaCl was separated by the addition of a small amount of ethanol. Further concentration allowed the complex from the first fraction to crystallize and be separated by filtration. It was washed with a small amount of cold water, then with ethanol, and finally with ether and dried in air. Anal. Calcd for $C_6H_{12}N_4O_8CoNa$: C, 20.58; H, 3.46; N, 16.00. Found: C, 20.60; H, 3.45; N, 15.97.

An insufficient amount of solid complex was obtained from the second fraction; accordingly this complex was not analyzed.

The complex obtained from the first fraction was resolved into diastereoisomers by using the method of Čelap et al.[10]

Registry No. $(-)_{589}$-Δ-*SS*-Co(Sar)$_2$(NO_2)$_2^-$, 73002-70-7; $(+)_{589}$-Λ-*RR*-Co(Sar)$_2$(NO_2)$_2^-$, 73017-44-4; *RS*-CO(Sar)$_2$(NO_2)$_2^-$, 73068-32-3; Na[Co(Sar)$_2$(NO_2)$_2$], 72843-86-8.

(10) Čelap, M. B.; Radanović, D. J.; Nikolić, T. I.; Janić, T. J. *Inorg. Chim. Acta* **1968**, *2*, 52.

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Bridging Alkylation of Saturated Polyaza Macrocycles: A Means for Imparting Structural Rigidity

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Considerable attention has been afforded to the ligand field parameters exhibited by the saturated tetraaza macrocycles forming the series [12]aneN$_4$ to [16]aneN$_4$[1] when bound in a square-planar manner to a metal ion.[2,3] In the cases of [14]aneN$_4$ to [16]aneN$_4$ it has been possible to determine these parameters accurately, and the results obtained have been of use in establishing the optimum ring size for a particular metal ion.[4] However, owing to the propensity that the smaller of these ligands have for folding and thus for adopting a cis rather than a trans configuration about the metal, particularly where the mismatch between metal ion size and macrocyclic hole size becomes large, it has not been possible to complete this data set down to the potentially most interesting case of [12]aneN$_4$ where, if deviations from planarity can be prevented, very high ligand field strengths may be expected. No complex in which [12]aneN$_4$ is bound in a planar manner has yet been isolated, although there are data to suggest[5] that *trans*-Ni([12]aneN$_4$)$^{2+}$ is present to a small extent in equilibrium, under certain conditions, with the more abundant *cis*-Ni([12]aneN$_4$)$^{2+}$. [13]aneN$_4$ binds trans in association with cobalt(III)[2] and iron(II)[6] and with low-spin nickel(II)[3] but folds whenever attempts are made to convert from low-spin nickel(II) to the larger high-spin nickel(II) by introducing axial ligands.

During the course of work in this laboratory it was observed that the interaction of 1,2-dibromoethane with [14]aneN$_4$ results in the bridging of adjacent secondary amine donors by way of ethano bridges, thus providing a means for structurally reinforcing the backbone of saturated ligands without introducing unsaturation. The introduction of such a bridge, or bridges, effectively creates a steric barrier, which molecular models strongly suggest as being sufficient to prohibit the possibility of the ligand binding in anything other than the trans fashion. The products of this reaction are indicated in

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