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*-$CH_3 \cdots NO_2$ 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 Ĉelap 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 Ĉelap 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) Ĉelap, M. B.; Radanović, D. J.; Nikolić, T. I.; Janić, T. J. *Inorg. Chim. Acta* **1968**, *2*, 52.

Contribution from The Queen's University of Belfast,
Belfast BT9 5AG, Northern Ireland

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

Kevin P. Wainwright

Received July 27, 1979

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

---

(1) The full names and structures of these compounds are given in D. H. Busch, *Acc. Chem. Res.*, **11**, 394 (1978).

(2) Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977).

(3) L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 2968 (1977).

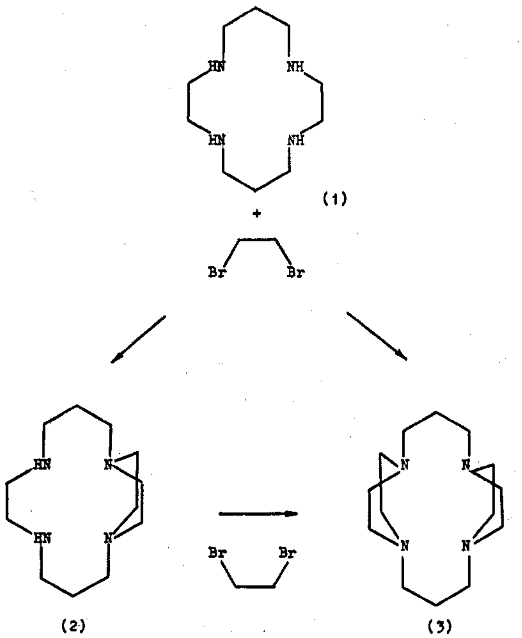
(4) L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).

(5) L. Fabbrizzi, *Inorg. Chem*, **16**, 2667 (1977).

(6) D. D. Watkins, D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **15**, 387 (1976).

0020-1669/80/1319-1396$01.00/0

Scheme I



Scheme I. The distribution is largely in favor of the monobridged species (**2**), although repeated treatment of **2** with 1,2-dibromoethane yields useful amounts of the dibridged compound **3**. The formation of these two compounds suggests that it may be possible to modify the set of ligands [12]aneN_4 to [15]aneN_4 in a way which will preserve constancy of donor type and total saturation, while allowing the effects of incremental changes in ring size on trans-bonded systems to be studied.

Experimental Section

Carbon-13 NMR spectra were recorded at ambient temperature by using a Bruker WH90 Fourier transform spectrometer operating at 22.6 MHz. All samples were run in $CDCl_3$ with Me_4Si as internal standard. Mass spectra were obtained at 70 eV by using an AEI MS 902 spectrometer.[7] Electronic spectra were recorded by using a Unicam SP-8000 spectrophotometer.

[14]aneN_4 (**1**) was prepared according to the procedure of Barefield.[8] 1,2-Dibromoethane was from Aldrich and was used without further purification.

Compound 2. [14]aneN_4 (3 g, 15 mmol) and 1,2-dibromoethane (5.92 g, 2.72 mL, 31.5 mmol) were heated at reflux in ethanol (60 mL) for 60 h. The solvent was then removed by evaporation under reduced pressure and the sticky residue dissolved in water (15 mL). The aqueous solution was basified with 10 M NaOH until precipitation of the free amines was complete and then extracted with chloroform (4 × 50 mL). The chloroform solution was dried ($MgSO_4$) and evaporated to dryness in a vessel from which the products could subsequently be sublimed directly. A sublimation probe was inserted, and sublimation for 4 h at 40 °C (0.1 torr) resulted in the separation of impure **3** (0.1 g) from the mixture as a viscous oil. This was washed from the probe with ethanol and stored for further purification. Continued sublimation at 70 °C for another 12 h resulted in the isolation of pure **2**. It can be collected directly from the probe as hygroscopic white needles (1.1 g). Anal. Calcd for $C_{12}H_{26}N_4$: C, 63.7; H, 11.6; N, 24.8. Found: C, 63.4; H, 11.6; N, 24.9. Or it can be washed from the probe with ethanol and precipitated, upon the addition of concentrated HCl, as white crystals of the nonhygroscopic tetrahydrochloride (1.8 g). Anal. Calcd for $C_{12}H_{30}Cl_4N_4$: C, 38.7; H, 8.12; N, 15.1. Found: C, 38.8; H, 8.07; N, 14.9. The residual material which does not sublime at temperatures below 70 °C is impure [14]aneN_4 (2 g) which can be recovered for further use.

Compound 3. The reaction of [14]aneN_4 (9 g, 45 mmol) with 2 equiv of 1,2-dibromoethane (17.76 g, 8.16 mL, 94.5 mmol) was carried out as described above. A single sublimation at 70 °C yielded a 9:1 mixture (3.5 g) of compounds **2** and **3**. This mixture was dissolved in ethanol (70 mL) and heated at reflux with 1,2-dibromoethane (2.92 g, 1.34 mL) for a further 60 h. The ethanol was then removed and the residue dissolved in water, basified, and extracted into chloroform as before. After the solution was dried ($MgSO_4$) and the solvent evaporated, sublimation of the residue at 70 °C (0.1 torr) for 8 h gave a 6:4 mixture (1.0 g) of compounds **2** and **3** as a viscous hygroscopic oil. This mixture was washed from the probe with ethanol, and, after the precise amounts of **2** and **3** present were determined,[9] just sufficient nickel(II) perchlorate-6-water to complex compound **2** alone[10] was added (details concerning this complexation process, which leads to the formation of Ni(**2**)$(ClO_4)_2$, are given below). The precipitated complex of **2** was removed by filtration and the filtrate evaporated to dryness, leaving impure **3**. **3** was extracted from this residue with chloroform and the resulting solution dried before evaporating it to dryness in a sublimation apparatus. Sublimation at 50 °C (0.1 torr) for 8 h gave pure **3** as a hygroscopic viscous oil. It was washed from the probe with anhydrous ethanol and precipitated as its tetrahydrochloride (also hygroscopic) by introducing dry HCl into the solution. Anal. Calcd for $C_{14}H_{32}Cl_4N_4$: C, 42.2; H, 8.09; M, 14.1. Found: C, 42.5; H, 8.46; N, 14.6.

Ni(2)$(ClO_4)_2$. Nickel(II) perchlorate-6-water (0.5 g) dissolved in ethanol (15 mL) was added dropwise to a solution of **2** (0.3 g) in refluxing ethanol (15 mL). The orange crystalline product that formed was recrystallized once from water, yielding the pure product (0.6 g, 94%). Anal. Calcd for $C_{12}H_{26}Cl_2N_4NiO_8$: C, 29.8; H, 5.42; N, 11.6; Cl, 14.6. Found: C, 29.9; H, 5.36; N, 11.6; Cl, 14.6.

Ni(3)$(ClO_4)_2$. This compound was prepared by a method analogous to that given above. The orange crystalline product was recrystallized once from ethanol, giving the pure compound in 80% yield. Anal. Calcd for $C_{14}H_{28}Cl_2N_4NiO_8$: C, 33.0; H, 5.53; N, 11.0. Found: C, 33.1; H, 5.90; N, 10.9.

Results and Discussion

The extent to which [14]aneN_4 is converted into its bridged derivatives is only on the order of 30%. This occurs because the desired substitution reaction and the competing elimination reaction are both accompanied by quarternization of the unreacted amine groups, rendering them unavailable for participation in the bridging process. Thus the reaction is self-inhibiting. The use of various acid scavengers to avoid this, as well as variations in solvent, reaction temperature, and reaction time failed to achieve higher conversion rates.

Evidence for the structure of compound **2** was obtained from its ^{13}C NMR spectrum. This shows only a single resonance (at 25.9 ppm) downfield from the carbon of Me_4Si, arising from the central carbon in the 1,3-diaminopropane residue. Bridging across one of the 1,3-diaminopropane residues would lead to the nonequivalence of these carbons and hence to two signals. Compound **3** also shows a single resonance for these carbon atoms (at 23.7 ppm). Although this is not diagnostic for the structure proposed, since the alternative compound would also give only a single resonance, the general similarity of the complete spectrum of **3** to that of **2** gives no reason to suggest that **2** has undergone structural rearrangement during the formation of the second bridge.

Only square-planar nickel(II) complexes of **2** and **3** could be prepared. Interaction of azide, thiocyanate, and cyanide ions with the orange, diamagnetic perchlorate salts of Ni(**2**)$^{2+}$ and Ni(**3**)$^{2+}$ in hot aqueous solution produced no conversion of the low-spin nickel(II) species to the high-spin form. Even the presence of equilibrium quantities of the diacido species

---

(7) Compounds **2** and **3** both showed molecular ion peaks at the expected *m/e* values.

(8) E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Synth.*, **16**, 220 (1976).

(9) This is most easily done by recording the ^{13}C NMR spectrum of the entire mixture and observing the relative intensities of the signals due to the central carbons of the 1,3-diaminopropane residues (see Results and Discussion). With a knowledge of the total weight of the mixture the amounts of each component can then be calculated.

(10) The rate of complexation of Ni^{2+} with the monobridged ligand is significantly faster than with the dibridged ligand. The Ni(**2**)$(ClO_4)_2$ precipitates as it forms leaving the free dibridged ligand in solution.

Table I. Energy of the d → d Band for Low-Spin Square-Planar Ni(tetraamine)$^{2+}$ Complexes in Aqueous Solution

ligand	no. of bridges	ν(d → d), cm^{-1}
[14]aneN$_4$[a]	0	22 470
Me$_4$-[14]aneN$_4$[b]	0	19 570
2	1	21 690
3	2	23 260

[a] Data taken from ref 5. [b] 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane. Data taken from ref 12.

seems unlikely since extraction of the aqueous solution with hot chloroform failed to transfer any of these normally chloroform soluble species[3] into the organic phase. There are at least two possible reactions for this: The effect of the bridge may simply be to impose a prohibitive steric barrier toward the addition of axial substituents; however, this is improbable since the addition of excess cyanide ion results in the liberation of the ligand and the formation of Ni(CN)$_4^{2-}$, in the usual way, after only a few minutes of heating. Alternatively, the effect of the bridge may be to reduce ligand flexibility to the point where the macrocyclic hole is incapable of expanding to accept the slightly larger high-spin nickel(II) ion. In this case one would expect the in-plane ligand field to be enhanced upon the introduction of the bridge. In fact this is observed. The frequency of the single d → d absorption band in the spectra of low-spin nickel(II) complexes is related to the in-plane ligand field strengths, with higher frequencies being indicative of higher ligand field strengths.[11] In Table I the ligand field absorptions of nonbridged, monobridged, and dibridged complexes are compared, and the correlation which exists between increased bridging and increased ligand field strength, at least in this series of compounds, can readily be seen. The low-spin nickel(II) complex of *N,N′,N″,N‴*-Me$_4$-[14]aneN$_4$ is chosen for inclusion in the table since it is the only complex involving tertiary nitrogen donors in a macrocyclic array for which data are available.[12]

Attempts to induce the Ni(**2**)(ClO$_4$)$_2$ system to fold, by refluxing it in ethanolic solution with the potentially cis-bidentate ligand 1,10-phenanthroline, were unsuccessful, which suggests that this manner of bridging provides an effective means of blocking the possibility of a macrocycle folding. Preliminary experiments on the [13]aneN$_4$ system have already shown that corresponding bridged products can be derived from this system also.

Registry No. 1, 295-37-4; **2**, 72952-82-0; **2**·4HCl, 72952-83-1; Ni(**2**)(ClO$_4$)$_2$, 72984-97-5; **3**·4HCl, 72952-84-2; Ni(**3**)(ClO$_4$)$_2$, 72967-86-3; 1,2-dibromoethane, 106-93-4.

---

(11) F. P. Bossu and D. W. Margerum, *Inorg. Chem.*, **16**, 1210 (1977).

(12) E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

A New Synthetic Method for 2-Alkylpentaboranes(9)

Donald F. Gaines* and Michael W. Jorgenson

Received February 13, 1979

Following the synthesis of μ-SiMe$_3$B$_5$H$_8$,[1] the first example of a group 4 element bridging two adjacent boron atoms in a borane by a three-center two-electron bond, a number of other bridge-substituted group 4 derivatives of pentaborane(9), including μ-SiR$_3$-, μ-GeR$_3$-, μ-SnR$_3$-, and μ-PbR$_3$B$_5$H$_8$, have been prepared.[1,2] Attempts to prepare the corresponding carbon-bridged derivatives, μ-CR$_3$B$_5$H$_8$, under conditions similar to those utilized in the preparation of the other bridged group 4 derivatives were, however, notably unsuccessful. We report here the results of Fenske–Hall molecular orbital calculations[3] on μ-CH$_3$B$_5$H$_8$ and the synthesis of 2-allylpentaborane(9), 2-[CH$_2$CHCH$_2$]B$_5$H$_8$, and 2-benzylpentaborane(9), 2-[C$_6$H$_5$CH$_2$]B$_5$H$_8$, via synthetic routes that appear to require the formation of short-lived carbon-bridged intermediates.

Table I. Energy Differences between Related Molecular Orbitals for Isomers of SiH$_3$B$_5$H$_8$, CH$_3$B$_5$H$_8$, and FB$_5$H$_8$

MO[a]	substituent	$\Delta_{1,2}$,[b] eV	$\Delta_{2,\mu}$,[c] eV
3e	CH$_3$	+0.15	−0.96
	SiH$_3$	−0.33	−0.29
	F	−2.08	
e$_x$	CH$_3$	+1.13	+1.73
	SiH$_3$	+0.66	+1.25
	F	+0.38	
a$_{1x}$	CH$_3$	+1.12	+1.05
	SiH$_3$	+1.50	−0.14
	F	−1.91	

[a] Idealized molecular orbital symmetry assignment. [b] (Energy of MO of 1-XB$_5$H$_8$) − (energy of MO of 2-XB$_5$H$_8$) = $\Delta_{1,2}$; positive values imply a net stabilization. [c] (Energy of MO of 2-XB$_5$H$_8$) − (energy of MO of μ-XB$_5$H$_8$) = $\Delta_{2\mu}$.

Results and Discussion

Recent theoretical calculations, having proven useful in rationalizing the reactivity and relative stabilities of known pentaborane(9) derivatives,[4a] were extended to include the unknown μ-CH$_3$B$_5$H$_8$ in order to reveal any anomalous changes in the energy levels of the MO's or the charge distributions. In accord with previous semiempirical calculations based on photoelectron spectral data,[4b] an examination of the shifts of three primary molecular orbitals, cage 3e, substituent e$_x$, and substituent–boron σ bond a$_{1x}$, allows a qualitative understanding of the observed trends in isomer stabilities since the other MO energy values generally remain invariant. The differences in the calculated energies of these respective MO's in 2-CH$_3$- and μ-CH$_3$B$_5$H$_8$ (unknown) as compared to the 2-SiH$_3$- and μ-SiH$_3$B$_5$H$_8$ (least stable) couple are tabulated in Table I. These results, in contrast to the striking differences between 2-FB$_5$H$_8$ and the unknown 1-FB$_5$H$_8$, suggested that the nonexistence of μ-CH$_3$B$_5$H$_8$ could not be attributed to energy differences.

Calculations also showed the individual atom charges on carbon in the known 1- and 2-CH$_3$B$_5$H$_8$'s and the unknown μ-CH$_3$B$_5$H$_8$ to be −0.152, −0.246, and −0.064 e, respectively, and on silicon in the 1-, 2-, and μ-SiH$_3$B$_5$H$_8$'s to be +0.810, +0.726, and +0.907 e, respectively. The relative trends for carbon and silicon are virtually identical except that carbon is negatively charged and the silicon is positively charged. The charges on both carbon and silicon are most positive in the bridged position. This tendency for positive charge to increase on the substituent when it is located in a bridged position suggested that further synthetic investigations were warranted.

The supposition[5] that only relatively electropositive groups can occupy bridged positions led to the examination of reactions of B$_5$H$_8^-$ with organic compounds known to produce relatively stable carbonium ions. Due to the spatial require-

---

(1) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 4249 (1967).

(2) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **90**, 6617 (1968).

(3) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972); R. F. Fenske, *Pure Appl. Chem.*, **27**, 61 (1971).

(4) (a) D. F. Gaines and M. W. Jorgenson, unpublished results. (b) J. A. Ulman and T. P. Fehlner, *J. Am. Chem. Soc.*, **98**, 1119 (1976).

(5) D. F. Gaines, *Acc. Chem. Res.*, **6**, 416 (1973).

0020-1669/80/1319-1398$01.00/0