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(14) We note this proposal is also supported by aluminum halide catalysis of the isomerization of *trans*-$Mo(CO)_2(diphos)_2$.[11a]
(15) Under the conditions employed in this work, k_{obsd} for *trans*-$Mo(CO)_2(diphos)_2$ is 10^3 times slower than that observed in ref 13 (compare $k_{obsd} = 1.88 \times 10^{-3}$ min^{-1} at 25.7 °C in THF containing 1% *tert*-butyl alcohol with 3.0×10^{-2} s^{-1} at 20 °C in THF–MeOH–LiCl[13]). This is, presumably, a reflection of the less polar media.
(16) The small temperature dependence of k_{obsd} for *trans*-$Mo(CO)_2(diphos)_2$ is a result of the negative $\Delta S^{\ddagger}$ for the isomerization.[13]

Contribution from the Department of Chemistry,
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Tris(3-nitroso-2,4-pentanedionato)cobalt(III): Strong Evidence for a Facial Geometry Analogous to Ferroverdin

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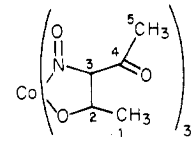
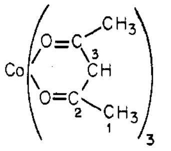
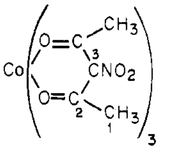
During investigations of the selective interactions of Na[$Co^{III}(acac)_2(NO_2)_2$][1] (acac = acetylacetonato) with biomolecules,[2] we neutralized an acid solution of the complex (0.04 mol of complex in 200 mL of 0.8 M HNO_3, 15 min) and obtained an orange product, I. This product is soluble in common organic solvents, including CCl_4, but insoluble in water or in acid solutions. The material, obtained in 34% yield, was formulated as $C_{15}CoH_{18}N_3O_9$, mol wt 443. Anal. Calcd: C, 40.7; H, 4.1; N, 9.5. Found: C, 40.5; H, 3.9; N, 9.3 [mol wt (cryoscopically, benzene) 407].



I



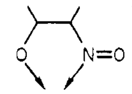
II



III

The IR spectrum of I contains a pronounced carbonyl stretching band at 1715 cm^{-1} (KBr pellet, Perkin-Elmer 621 instrument). The ^{1}H NMR spectrum of I ($DCCl_3$; all ^{1}H and ^{13}C NMR signals in ppm referenced downfield from TMS and obtained using Varian A-60 or CFT-20 instruments) contains only two equal-intensity signals at 2.78 and 2.38 ppm assignable to methyl groups. No signals are present at 5.3 ppm, consistent with the absence of the methine proton at C(3). The addition of strong ligands such as pyridine and tri-*n*-butylphosphine in large excess did not change the ^{1}H NMR spectrum of I.

On the basis of this data, we formulated I as the facial N-bonded isomer of tris(3-nitroso-2,4-pentanedionato)cobalt(III). The properties of this complex correspond exactly with those of that prepared from an authentic sample of 2,3,4-pentanetrione 3-monoxime.[3,4] Furthermore, we were able to recover 2,3,4-pentanedionetrione 3-monoxime[5] from I (in 40% yield) by treatment with sodium sulfide, acidification, extraction into methylene chloride, and addition of ligroin to induce crystallization. Recent studies[4,6] of I and related Co(III) compounds which contain the chelating function



agree that coordination to Co(III) involves ligating oxygen and nitrogen atoms.

It is of some interest that studies of Fe(II) and Ni(II) octahedral complexes of chelates which can be expected to coordinate via the N of a nitroso group and by an O forming a five-membered ring also show the formation of the facial isomer.[7-9] One of these compounds,[7] ferroverdin, is a naturally occurring green low-spin iron(II) pigment. The causes for the predominance of the *facial* geometry are not known. However, there have been no previous assignments of the overall geometry of the tris cobalt(III) complexes. On the basis of the ^{1}H NMR data for I, the facial geometry is strongly suggested. In view of the isoelectronic nature of the d^6 Co(III) and Fe(II) centers, we felt it would be worthwhile to further explore the geometry of I and also to investigate one example of the tris(*O*-nitrosophenolate)cobalt(III) complexes which have been so widely studied.[6] The narrow range of chemical shifts and/or ^{1}H,^{1}H couplings of ^{1}H NMR spectra of diamagnetic Co(III) complexes could obscure the presence of a meridional isomer.

The proton-decoupled natural-abundance ^{13}C NMR spectrum of I ($DCCl_3$) contains five distinct signals. The upfield signals at 28.44 and 30.76 ppm are of equal intensity and are readily identified as the C(1) and C(5) methyl carbons of I. For spectral comparison, tris(acetylacetonato)cobalt(III), II, and tris(3-nitroacetylacetonato)cobalt(III),[10] III, were prepared and characterized by elemental analysis. The ^{13}C peak positions are as follows: In II: C(1), 26.06 ppm; C(2), 189.44 ppm; C(3), 97.13 ppm. In III: C(1), 26.42 ppm; C(2), 190.06 ppm; C(3), not observed down to 250 ppm. Both C(1) and C(5) in I are shifted downfield, but an exact assignment of the two upfield signals is not possible. The C(3) signal of II is comparable in intensity to that for C(1), consistent with the presence of a C–H bond at C(3). However, the C(3) signal of I is shifted downfield by almost 60 ppm on nitrosation to 155.58 ppm and is appreciably diminished in intensity as expected from the absence of any C–H bonds. The C(2) resonances in II and III are both at ~189 ppm and the signal of one of the carbonyl carbons of I is also found in this region at 189.01 ppm. We tentatively assign this signal to C(2). The resonance of the other carbonyl carbon, C(4), is found well downfield at 211.34 ppm in a shielding range characteristic of some aliphatic ketones.

The information we have obtained could also be accommodated by a rapidly isomerizing mixture of facial and meridional isomers. However, addition of tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)[11] (0.03 M) to a solution of I (0.19 M in $DCCl_3$) caused downfield shifts of both methyl ^{1}H NMR resonances (2.38 to 2.96 and 2.78 to 3.28 ppm). The resonance at 3.28 ppm was clearly resolved (~1 Hz) into two signals of equal intensity. Such a finding would require a facile isomerization but a slow racemization—a highly unlikely set of circumstances particularly in view of the known chemistry of cobalt(III) complexes. Similarly, we find that the ^{13}C NMR spectrum of tris(2-nitroso-1-naphtholato)cobalt(III)[6] contains six strong equiintensity signals (corresponding to the six carbons which have a directly bound hydrogen) and two weaker signals (two resonances were not observed). On the basis of the results obtained with I, it is most reasonable to conclude that the complex has the facial geometry.

It thus appears that some intrinsic stability is associated with the *facial* geometry in all octahedral systems thus far investigated. One might speculate that the NO group might have a large trans effect and the mutually trans NO groups in the meridional isomer would be unstable. However, a trans arrangement is found in a square-pyramidal Cu(II) complex.[12] Clearly, an understanding of the preference for the facial isomer in octahedral systems must await further investigations.

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Registry No. I, 63864-72-2; II, 13681-88-4; III, 15169-25-2; $Na[Co^{III}(acac)_2(NO_2)_2]$, 14024-47-6; ^{13}C, 14762-74-4.

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B-Dimethylaminomethyl-Substituted 1,2,5,6-Bis(boratazonia)cyclohexane

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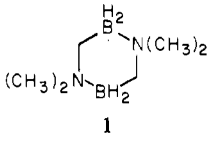
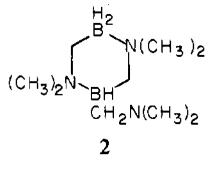
Modification of synthesis conditions[1,2] of the valence saturated, BCN sequenced heterocycle **1** by addition of 1,2-dimethoxyethane (glyme) results in the isolation of a new *B*-dimethylaminomethyl derivative, **2**, a low melting solid, stable in air, and readily water soluble to give a strongly basic solution. The synthesis and characterization are described.

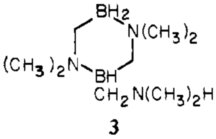


1



2

Formally named as a cyclohexane anologue, 1-dimethylaminomethyl-1,2,5,6-bis(boratazonia)cyclohexane, **2**, reacts as a typical tertiary amine to form proton salts, **3**, and a simple borane adduct, **4**. It reacts with methylene chloride nominally to exchange trimethylamine for methylene dichloride to give a new *B*-dichloromethyl derivative



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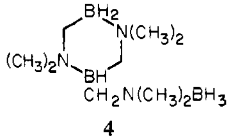

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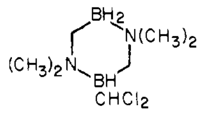

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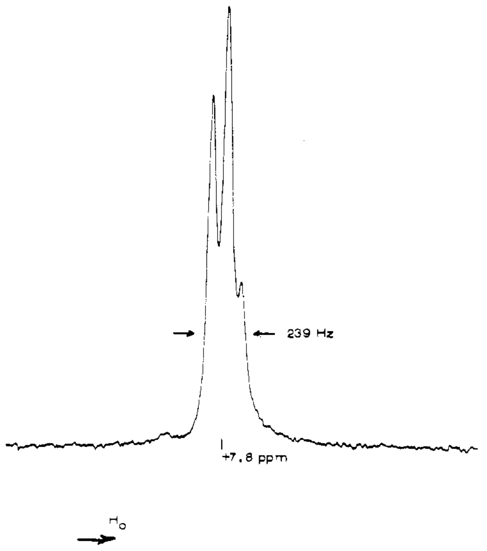

Figure 1. A 28.874-MHz ^{11}B NMR of $H(CH_3)_2NCH_2\overline{BHCH_2N(CH_3)_2BH_2CH_2N}(CH_3)_2{}^+PF_6{}^-$ in acetonitrile.

Results

Characterization of Structures. Elemental analyses and infrared spectral data support structures **2** through **5**, but key structural data are the mass spectra of **2** and **5** and the ^{11}B NMR spectrum of **3**. Structural representations show only ring sequences; a rapidly converting chair form structure for **1** in solution is likely since the chair form obtains for the solid state.[3]

Mass spectral data, Table I, for the dimethylamino derivative, **2**, shows a significant parent ion at *m/e* 199. Because boron hydrides often have mass patterns with the P − 1 as the highest significant peak,[4] it is reasonable, in view of the structure proposed, to assume that the 199 peak arises by proton abstraction from the plasma to give the P − 1 peak of the ammonium salt **3**. Lower mass fragments correspond very closely to the splitting pattern observed for the parent heterocycle, **1**. The highest mass peak at 141 for this residue pattern arises from loss of the very stable methylenedimethylammonium ion, $(CH_3)_2N{=}CH_2{}^+$, from the parent. Relative ratio of the 141 to 140 peaks is close to the 2:1 statistical distribution expected ratio for B_2 species. The similar ratio of the 139 to 138 peaks is difficult to explain short of facile loss of H_2 from the P − 1 or highest fragment of **1**. Indeed, Hseu and Larsen[3] report that $B_2C_6H_{17}N_2$ fits well the high-resolution mass numbers for the 138, 139 peaks. The fragmentation pattern observed at lower excitation voltage by these workers compares generally with that reported here at a higher ionization voltage; the greater abundancies of the higher mass species are reasonably expected for an acid–base