applied. The intensity of the (−2,3,5) reflection was measured in 10° increments about the diffraction vector; as a result, empirical absorption correction factors ranging from 1.00 to 1.12 were applied (the linear absorption coefficient is 8.3 cm^{-1}).

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[13] The atomic scattering factors were taken from the tabulations of Cromer and Waber;[14a] anomalous dispersion corrections were by Cromer.[14b] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[15]

The structure was solved by direct methods. The positions of the hydrogen atoms were determined by Fourier difference techniques. Full-matrix least-squares refinement of all positional and thermal parameters (anisotropic for Zr, N, and C; isotropic for H) with the 2459 reflections with $I > 2\sigma(I)$ converged at

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.023$$

$$R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.025$$

The two largest peaks in the final difference Fourier had magnitudes of approximately 0.3 e $Å^{-3}$ and were located near Zr and N(1).[16]

Registry No. Ia, 70024-35-0; Ib, 69039-12-9; Ic, 69039-11-8; IIa, 70024-36-1; IIb, 70024-37-2; IIc, 70024-38-3; $Zr(NMe_2)_4$, 19756-04-8; $Hf(NMe_2)_4$, 19782-68-4.

Supplementary Material Available: Tables of final positional parameters (as fractional coordinates), thermal parameters, and structure factor amplitudes (observed and calculated) (22 pages). Ordering information is given on any current masthead page.

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Some Complexes of Cobalt(III) with 3,6-Diaza-1,9-nonanediamine, an Unsymmetrical Flexible Tetraamine Ligand

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As a part of our continuing investigation of the stereochemistry of complexes with flexible tetradentate ligands, we have synthesized and characterized some complexes with the unsymmetrical tetraamine ligand 3,6-diaza-1,9-nonanediamine, 2,2,3-tet. The ligand 2,2,3-tet is a structural isomer of 3,7-diaza-1,9-nonanediamine, 2,3,2-tet, complexes of which have been extensively studied.[2] Our interest in unsymmetrical ligands arises from our expectation that the differing terminal chain lengths will give rise to geometrical specificity in complexes with these ligands. Thus, while it is well established that the symmetrical ligand 2,3,2-tet readily forms trans and unsymmetrical-cis complexes, it is not possible to control which of the terminal donor atoms moves in the course of well-known trans–cis isomerization reactions.[3] We expect that internal strain will favor the displacement of one of the terminal donors; i.e., either the "short" or the "long" terminal ring should be preferentially displaced from the plane of the tetraamine ligand in the parent trans complex. We report herein the synthesis of several complexes, details of the electronic spectra, details of a ^1H NMR study of several examples, and the results of a strain-energy minimization calculation.

Experimental Section

Synthetic Procedures. Preparation of 3,6-Diaza-1,9-nonanediamine, 2,2,3-tet. A 1-mol sample of acrylonitrile was refluxed overnight with 1.5 mol (excess) of *N*-(2-aminoethyl)ethylenediamine in 250 mL of benzene. After evaporation of the benzene, the product was hydrogenated with Raney nickel as the catalyst in ammoniacal absolute ethanol until the precise amount of hydrogen to effect reduction had been taken up. The mixture was then filtered to remove the Raney nickel and then the product was vacuum distilled at 140–145 °C (9 mm).

Preparation of *trans*-Dichloro(3,6-diaza-1,9-nonanediamine)cobalt(III) Chloride, *trans*-[Co(2,2,3-tet)Cl_2]Cl. 3,6-Diaza-1,9-nonanediamine (1.5 g, 0.1 mol) was added to a solution of $CoCl_2{\cdot}6H_2O$ (2.4 g, 0.1 mol) in 200 mL of water. A stream of air previously passed through KOH solution to remove CO_2 was bubbled through the solution for 16 h. To the red solution was added 25 mL of concentrated HCl, and it was evaporated to near dryness on a steam bath. After the solution was cooled, the crude green product was removed by filtration, washed with ethanol, recrystallized from hot water, and dried at 110 °C for 24 h. Anal. Calcd for $CoC_7H_{20}N_4Cl_3$: C, 25.81; H, 6.20; N, 17.21. Found: C, 25.73; H, 6.48; N, 17.16.

Preparation of *uns-cis*-(Valinato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *uns-cis*-[Co(2,2,3-tet)val]$(ClO_4)_2$. The pH of a solution containing 1.17 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 0.46 g (4 mmol) of L-valine in 10 mL of water was adjusted to 5.5. The solution was heated at 60 °C with stirring for 1 h. The pH was then adjusted to 8.5 and the stirring continued for 2 h. The complex crystallized upon addition of $LiClO_4$. The solution was filtered and the crystals were washed with ether and air-dried. Anal. Calcd for $CoC_{12}H_{30}N_5Cl_2O_{10}$: C, 26.96; H, 5.66; N, 13.11. Found: C, 26.61; H, 5.74; N, 12.79.

Preparation of *trans*-Bis(acetato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,2,3-tet)$(OAc)_2$]ClO_4. A solution containing 1.3 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 5.2 g (8 mmol) of sodium acetate was warmed at 60 °C for 2 h after which excess potassium perchlorate was added and the solution cooled. The large red crystals were removed by filtration, washed with acetone, and air-dried. Anal. Calcd for $CoC_{11}H_{26}N_7ClO_8$: C, 30.23; H, 6.00; N, 12.83. Found: C, 29.98; H, 5.87; N, 12.58.

Preparation of *trans*-Bis(sarcosine)(3,6-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,2,3-tet)$(sarc)_2$]$(ClO_4)_3$. To a solution containing 1 g of *trans*-[Co(2,2,3-tet)Cl_2]Cl and 1.5 g of sarcosine in 15 mL of water was added 5 N NaOH to adjust the pH to 5.5. The solution was heated at 40 °C for 16 h. On addition of 1 g of potassium perchlorate and cooling of the solution, the red crystals formed and were removed by filtration. Anal. Calcd for $CoC_{13}H_{34}N_6Cl_3O_{16}$: C, 22.46; H, 4.93; N, 12.10. Found: C, 22.57; H, 4.93; N, 11.91.

Preparation of *uns-cis*-(Oxalato)(3,6-diaza-1,9-nonanediamine)cobalt(III) Iodide, *uns-cis*-[Co(2,2,3-tet)ox]I. To a constantly stirred solution containing 1.30 g (4 mmol) of *trans*-[Co(2,2,3-tet)Cl_2]Cl was added 0.75 g (4 mmol) of potassium oxalate hydrate in 14 mL of water. The solution was warmed at 60 °C for 3 h and filtered and the filtrate evaporated at 60 °C until crystals began to form. The solution was placed in the refrigerator for 3 h. The needlelike crystals

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Table I. Electronic Spectral Parameters for Some Trans Cobalt Tetraamine Complexes

complex	λ_{max}, nm (ϵ, M^{-1} s^{-1}) band I	band II	band III	ref
[Co(2,3,2-tet)Cl$_2$]Cl		425 (35)	625 (35)	*a*
[Co(2,3,2-tet)(sarc)$_2$](ClO$_4$)$_3$	359 (73)	439 (34)	550 (74)	*b*
[Co(2,3,2-tet)(OAc)$_2$]ClO$_4$	361 (82)	443 (29)	543 (70)	*b*
[Co(3,2,3-tet)Cl$_2$]Cl		450 (45)	640 (34)	*a*
[Co(3,2,3-tet)(sarc)$_2$](ClO$_4$)$_3$	371 (88)	463 (49)	563 (63)	*b*
[Co(3,2,3-tet)(OAc)$_2$]ClO$_4$	368 (93)	465 (46)	550 (70)	*b*
[Co(2,2,3-tet)Cl$_2$]Cl		450 (40)	655 (35)	*c*
[Co(2,2,3-tet)(sarc)$_2$](ClO$_4$)$_3$	365 (110)	445 (115)	550 (67)	*c*
[Co(2,2,3-tet)(OAc)$_2$]ClO$_4$	365 (120)	455 (95)	545 (67)	*c*
[Co(2,2,3-tet)(NO$_2$)$_2$]I		450 (37)		*c*

[a] Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* 1971, *10*, 811.
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[c] This work.

were washed with methanol and ether and air-dried. Anal. Calcd for $CoC_9H_{20}N_4IO_4$: C, 24.88; H, 4.61; N, 12.98. Found: C, 24.69; H, 4.75; N, 12.73.

Spectral Measurements. ^1H NMR. All spectra were recorded on a Varian Associates A-60D ^1H NMR spectrometer which operates at 60 MHz with a field strength of 14 092 G provided by a 6 in. electromagnet. This instrument typically operates by using the external locking method and a field sweep of 50–1000 Hz (from low to high field).

Most spectra were obtained from saturated solutions of the complexes in Me_2SO-d_6. D_2O and TFA-d_1 served as alternate solvents when Me_2SO-d_6 was unsuitable. Little or no effect on the ^1H NMR spectra was observed in different solvents with the exception of concentrated DCl which shifted the methylene resonances by 0.15 ppm downfield. Corrections were made where necessary to make comparisons. Most samples showed no signs of change or decomposition even after many months.

The reference compound employed throughout this work for the nonaqueous solvents was Me_4Si, which was either present (1%) in Me_2SO-d_6 or added to TFA-d_1. DSS was used as an internal reference in the aqueous solvents.

Electronic Spectra. The complexes were weighed and dissolved in a suitable solvent, usually Me_2SO, to concentrations that were typically 5×10^{-3} M. All measurements were carried out on a Cary Model 14 spectrophotometer using 1-cm path length quartz cells with solvent in the reference beam. Molecular sieves were used to keep the solvent free of water in order to prevent aquation of the complexes. Spectra were recorded over the range 800–330 nm.

Strain-Energy Minimization Calculations. Strain-energy minimization calculations were performed on the IIT UNIVAC 1108 with a locally modified version of Richard Boyd's program MOLBD.[4] Interaction constants given by DeHayes and Busch[5] were used; details of the method have been published elsewhere.[6] Each calculation was considered to have converged when the root-mean-square coordinate shift fell below 0.01 Å.

Results and Discussion

Electronic Spectra. The electronic spectra of some *trans*-diacido(3,6-diaza-1,9-nonanediamine)cobalt(III) complexes are summarized in Table I along with those of some previously reported *trans*-diacido(tetraamine)cobalt(III) complexes. These spectra are characterized by three bands. The Co(III) ion in both the trans and uns-cis complexes is in a pseudooctahedral environment, and, therefore, there are two spin-allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. The latter is of higher energy and is assigned to band I in both trans and uns-cis complexes. In D_{4h} complexes the $^1T_{1g}$ (O_h) excited state is split into ^1E_g and $^1A_{2g}$ components. This is reflected in the trans complexes by the appearance of band II. Thus, band III is assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition, and band II is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition.[7] Clearly, the electronic spectra support the *trans*-Co(2,2,3-tet) configuration assignments.

Table II. Electronic Spectral Parameters for Some Uns-cis Cobalt Tetraamine Complexes

complex	λ_{max}, nm (ϵ, M^{-1} s^{-1}) band I	band II	ref
[Co(2,2,2-tet)ox]$^+$	357 (179)	497 (179)	*b*
[Co(2,3,2-tet)ox]ClO$_4$	360 (175)	500 (140)	*a*
[Co(2,3,2-tet)val]I$_2$	353 (144)	495 (136)	*a*
[Co(3,2,3-tet)ox]ClO$_4$	363 (177)	512 (118)	*a*
[Co(3,2,3-tet)val]I$_2$	358 (139)	503 (106)	*a*
[Co(2,2,3-tet)ox]I	363 (190)	510 (150)	*c*
[Co(2,2,3-tet)val](ClO$_4$)$_2$	355 (160)	485 (125)	*c*

[a] Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* 1971, *10*, 968.
[b] Froebe, L. R. Ph.D. Thesis, University of Pittsburgh, 1970.
[c] This work.

The electronic spectra of *trans*-diacido(3,6-diaza-1,9-nonanediamine)cobalt(III) complexes bear a strong resemblance to that of *trans*-$[Co(2,2,2\text{-tet})Cl_2]^+$.[8] We note that the molar absorbtivity of band II, at about 450 nm, is greater than that for band III, at 550 to 650 nm for both the trans 2,2,3-tet and 2,2,2-tet complexes, but the molar absorbtivity of band III is greater than that for band II for all other *trans*-diacido(tetraamine)cobalt(III) complexes known to us. We do not know the origin of this phenomenon but suggest that it is related to distortion of the Co–N bond at the junction of two fused five-membered chelate rings.

Electronic spectra for some *uns-cis*-Co(2,2,3-tet) complexes are shown in Table II along with some examples from previous investigations. The electronic spectra confirm the cis assignments, but they do not establish whether a complex is s-cis or uns-cis.

Proton Magnetic Resonance. The ^1H NMR spectrum of *trans*-$[Co(2,2,3\text{-tet})Cl_2]Cl$ in Me_2SO-d_6 solution exhibits amine resonances at chemical shifts of 6.75, 6.00, 5.75, and 4.95 ppm with integrated area ratios of 1:1:1:3, respectively. This is similar to the amine resonances of *uns-cis*-$[Co(2,3,2\text{-tet})glyH]I_2$.[10]

Part of the methylene resonance spectrum is also characteristic of *uns-cis*-$[Co(2,2,2\text{-tet})Cl_2]Cl$. The main α-methylene resonance is found at 3.12 ppm and has an integrated area of 6. This resonance is assigned to the α_5-methylene protons of the terminal five-membered chelate ring and to those α_5-methylene protons of the intermediate five-membered chelate ring next to the terminal five-membered ring. The β-methylene resonance occurs at a chemical shift of 2.02 ppm with an integrated area of 2, and the α_6-methylene resonance is split into two signals, one with a chemical shift of 2.55 ppm and integrated area of 2 and the other at 2.75 ppm also with an area of 2. The remaining α_5-methylene resonance occurs at a chemical shift of 2.82 ppm with an area of 2.

In the ^1H NMR spectrum of *trans*-$[Co(2,2,3\text{-tet})(OAc)_2]ClO_4$ in neutral D_2O solution, the amine resonances are resolved at 6.75, 6.10, 5.68, and 5.40 ppm with integrated area ratios of 1:2:2:1, respectively. The β-methylene resonance occurs at a chemical shift of 2.00 ppm with an integrated area of 2. The α_6-methylene resonances are found at 2.50 and 2.75 ppm, both with integrated area of 2. The α_5-methylene resonances were observed at 2.83, 2.90, 3.05, and 3.16 ppm each with integrated area of 2. The last three resonances appear to result from the splitting of the 3.12-ppm resonance of *trans*-$[Co(2,2,3\text{-tet})Cl_2]Cl$, possible because of increased contact with the axial acetato ligands.

The ^1H NMR spectrum of *uns-cis*-$[Co(2,2,3\text{-tet})val](ClO_4)_2$ exhibits amine resonances at chemical shifts of 7.05, 6.25, 5.9, 5.1, 4.1, and 3.75 in the ratio of 1:1:1:2:1:2, respectively. The last resonance is due to the amine protons of the valine ligand. The α_5-methylene protons are represented by an intense, broad signal at 2.84 ppm with an integrated area of 8. The α_6-methylene resonance occurs at a chemical shift of 2.40 ppm

Table III. ^1H NMR Spectra of Some Co(2,2,3-tet) Complexes[c]

complex	methylene resonances, ppm				
	α_5		α_6		β
trans-[Co(2,2,3-tet)Cl_2]Cl	3.12 (6)	2.82 (2)	2.75 (2)	2.55 (2)	2.02 (2)
trans-[Co(2,2,3-tet)$(OAc)_2$]ClO_4	3.16 (2)	2.89 (6)	2.75 (2)	2.50 (2)	2.00 (2)
uns-cis-[Co(2,2,3-tet)val]$(ClO_4)_2$		2.84 (8)		2.35 (4)	1.74 (2)
uns-cis-[Co(2,2,3-tet)ox]I[a]		2.76 (8)		2.34 (4)	1.77 (2)
uns-cis-[Co(2,2,3-tet)ox]I[b]		2.80 (8)		2.49 (4)	2.01 (2)

[a] In Me_2SO-d_6. [b] In DCl.

Table IV. Summary of Minimized Strain Energies (kcal mol^{-1}) for Some [Co(2,2,3-tet)Cl_2]$^+$ Ions

	trans *RR,SS* (2,2,3-tet)	trans *RR* (2,2,3-tet)	cis *RS* (2,2,$\underline{3}$-tet)	cis *SS* (2,2,$\underline{3}$-tet)	cis *RS* ($\underline{2}$,2,3-tet)	cis *RR* ($\underline{2}$,2,3-tet)
ΣR_{ij}[a]	1.861	1.793_0	1.882_4	1.819_9	1.6203	1.586_0
$\Sigma\theta$[b]	4.756	4.787_0	6.205_7	7.371_0	4.2540	6.597_7
$\Sigma\phi$[c]	9.746	9.797_2	10.032_1	9.987_2	9.759_7	9.896_3
ΣNB[d]	7.285	7.024_5	7.459_1	6.253_6	6.077_8	5.814_0
Σ	23.648	23.401_7	25.579_3	25.431_6	21.711_8	23.894_0

[a] ΣR_{ij} = bond deformation strain energy. [b] $\Sigma\theta$ = angle deformation strain energy. [c] $\Sigma\phi$ = torsional strain energy. [d] ΣNB = nonbonded strain energy.

while the β-methylene resonance occurs at a chemical shift of 1.74 ppm. The chemical shifts of the valine ligand are 1.05 ppm for the methyl groups, 2.25 ppm for the methylene protons, and 3.75 for the amine protons.

The ^1H NMR spectrum of *uns-cis*-[Co(2,2,3-tet)ox]I was poorly resolved due to low solubility in Me_2SO-d_6. The β-methylene resonance had a chemical shift of 1.77 ppm. The α_6-methylene resonance occurred at a chemical shift of 2.76 ppm and is partially obscured by the Me_2SO resonance. The α_5-methylene proton resonance appears as a shoulder at 2.34 ppm.

It has been shown that *uns-cis*-(oxalato)(3,7-diaza-1,9-nonanediamine)cobalt(III) and *uns-cis*-(oxalato)(4,7-diaza-1,10-decanediamine)cobalt(III) readily isomerize to the corresponding trans dichloro complexes in aqueous or methanolic HCl.[11] Accordingly, the ^1H NMR of *uns-cis*-(oxalato)(3,6-diaza-1,9-nonanediamine)cobalt(III) was examined in D_2O–DCl after sufficient time had elapsed to result in a green solution typical of the trans dichloro species. The β-methylene resonance is at 2.16 ppm, the α_6-methylene resonance is at a chemical shift of 2.64 ppm, and the α_5-methylene resonance is at 2.95 ppm. The integrated area ratio is 2:4:8, respectively. The amine resonances are observed at about 5.0 ppm.

The contrast between the ^1H NMR of a sample derived from the acid chloride-induced isomerization of *uns-cis*-[Co(2,3,2-tet)ox]$^+$ and that of samples from the original synthesis suggests that the configurations of these complexes are not the same. The near equivalence of the α_5 and amine proton resonances observed in the former is consistent with the *R,S* (meso) configuration, with a gauche bridging ethylene linkage. This is to be expected in light of the results of the strain-energy minimization calculation (vide infra). Moreover, these different ^1H NMR spectra suggest that racemic *trans-RR,SS*-[Co(2,2,3-tet)Cl_2]$^+$ is the lowest energy trans isomer and is found in the original synthesis.

The results obtained for the ^1H NMR investigation of 2,2,3-tet complexes are summarized in Table III. As expected, the spectra of trans complexes, which contain two adjacent coplanar five-membered chelate rings as in the 2,2,3-tet complexes, exhibit resonances that are shifted toward low field or high chemical shift values. Even after application of a correction of 0.15 ppm for solvent effects in D_2O, the highest chemical shifts are still near 3.00 ppm. These indicate that the protons of adjacent five-membered rings undergo severe bond compression and angle strain. In the uns-cis complexes, the α_5-methylene resonances have values of 2.84, 2.82, and 2.76 ppm, which are higher than that obtained for various *s-cis*-Co(2,2,2-tet) complexes. This fact may indicate that bond compression and angle strain have been relieved in the uns-cis complexes indicated by the upfield shifts via the formation of one of the *uns-cis*-(3,6-diaza-1,9-nonanediamine)cobalt(III) species.

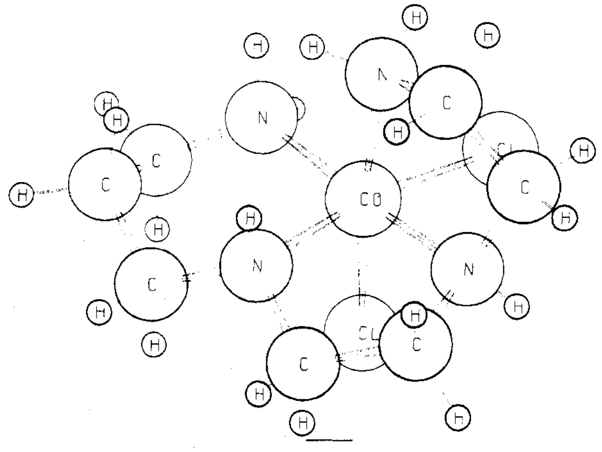

Figure 1. *uns-cis-RS*-[Co($\underline{2}$,2,3-tet)Cl_2]$^+$.

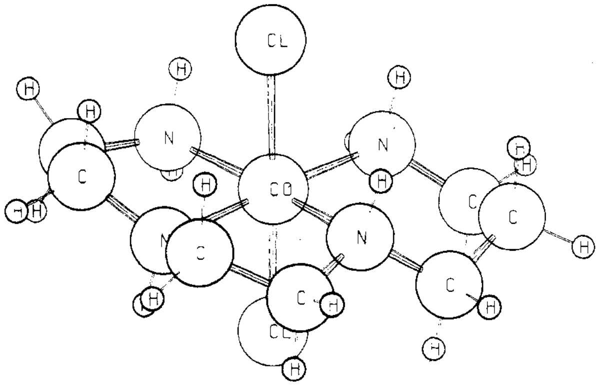

Figure 2. *trans-RS*-[Co(2,2,3-tet)Cl_2]$^+$.

Strain-Energy Minimization. The lowest lying isomer is found to be *uns-cis-R,S*-[Co($\underline{2}$,2,3-tet)Cl_2]$^+$,[9] in which the five-membered chelate ring is displaced from the plane of the cobalt ion and the secondary donors (Table IV, Figure 1); it

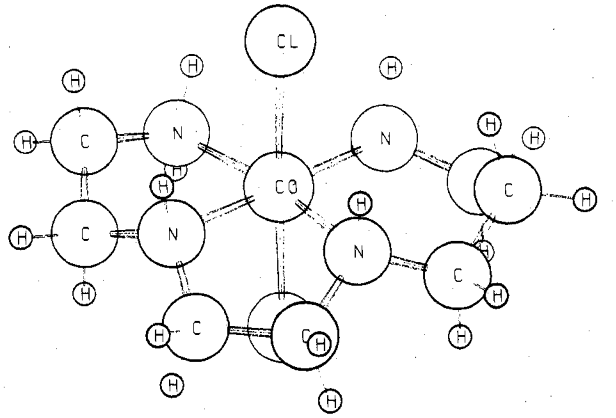

Figure 3. *trans-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$.

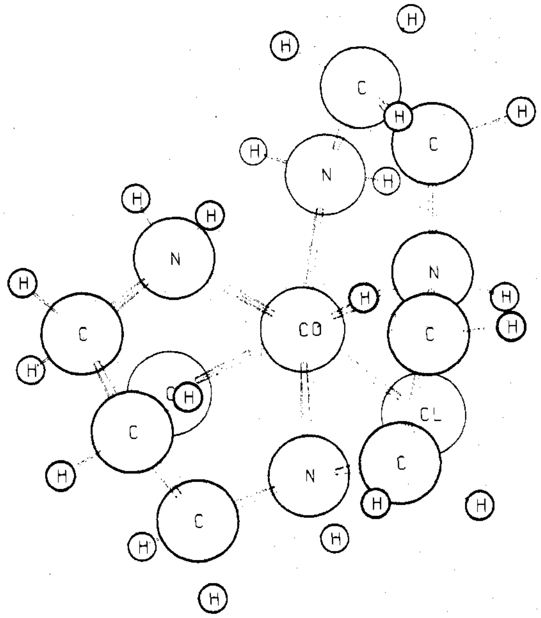

Figure 4. *uns-cis-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$.

lies almost 2 kcal/mol below the other complexes in this series. From Table IV we find that the complex *trans-RS*-[Co(2,2,3-tet)Cl$_2$]$^+$ (Figure 2) lies about 0.2 kcal/mol below *trans-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$ (Figure 3); we doubt that this difference is significant. Both of the complexes in which the six-membered chelate ring is displaced from the plane of the cobalt ion and the secondary donors (Table IV, Figures 4 and 5) are nearly 4 kcal/mol higher in energy than the least-strained isomer; the strain energy calculated for the remaining isomer, *uns-cis-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$, with the five-membered chelate ring displaced from the plane (Figure 6) is comparable with that found for the trans isomers. While we cannot unequivocally state which of the trans isomers is found in the original reaction mixture, we note that the racemic (*RR,SS*) isomer is found in the 2,2,2-tet (triethylenetetraamine, 3,6-diaza-1,8-octanediamine) and 3,2,3-tet (4,7-diaza-1,10-decanediamine) systems and that the *R,S* (meso) isomer is found in the 2,3,2-tet system.[12]

We do not find significant or systematic variations in cobalt–donor atom bond lengths, which lies within the range 2.01–2.05 Å for Co–N and 2.32–2.34 Å for Co–Cl. Similarly, all of the L–Co–L′ bond angles are within the range 90 ± 4°. While we recognize that the potential functions chosen imply very low angle-deformation energies about the central ion, we are encouraged by the observation that coordinates calculated by using this set of functions[13] lie within the error estimates of a *subsequent* structure determination of the similar *uns-cis*-(2,4-pentanedionato)(4,7-diaza-1,10-decanediamine)cobalt(III) cation.[14]

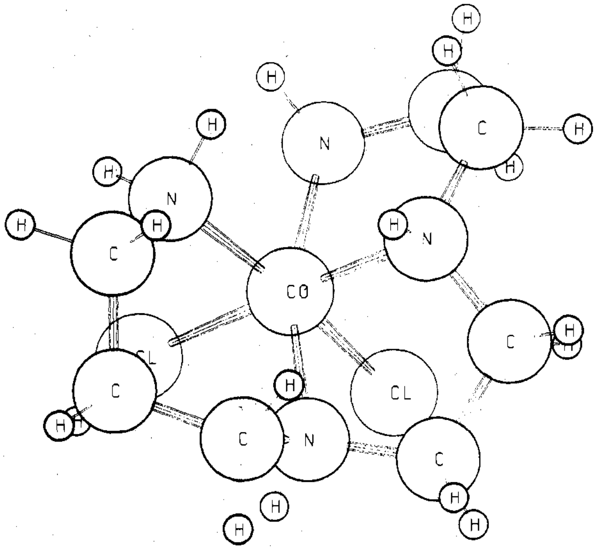

Figure 5. *uns-cis-RS*-[Co(2,2,3-tet)Cl$_2$]$^+$.

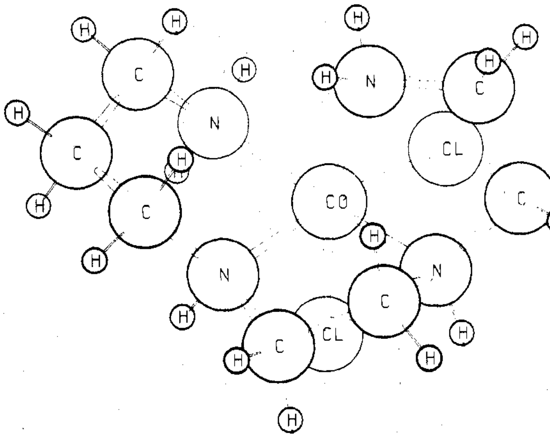

Figure 6. *uns-cis-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$.

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Registry No. *trans*-[Co(2,2,3-tet)Cl$_2$]Cl, 70235-81-3; *uns-cis*-[Co(2,2,3-tet)val](ClO$_4$)$_2$, 70235-83-5; *trans*-[Co(2,2,3-tet)-(OAc)$_2$]ClO$_4$, 70235-85-7; *trans*-[Co(2,2,3-tet)(sarc)$_2$](ClO$_4$)$_3$, 70235-87-9; *uns-cis*-[Co(2,2,3-tet)ox]I, 70235-88-0; 2,2,3-tet, 70209-08-4; acrylonitrile, 107-13-1; *N*-(2-aminoethyl)ethylenediamine, 111-40-0; *trans*-[Co(2,2,3-tet)(NO$_2$)$_2$]I, 70235-89-1; *trans-RS*-[Co(2,2,3-tet)Cl$_2$]$^+$, 70285-96-0; *uns-cis-RS*-[Co(2,2,3-tet)Cl$_3$]$^+$, 70332-14-8; *uns-cis*-[*RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$, 70285-97-1; *uns-cis-RS*-[Co(2,2,3-tet)Cl$_2$]$^+$, 70285-98-2; *uns-cis-RR,SS*-[Co(2,2,3-tet)Cl$_2$]$^+$, 70285-99-3.

References and Notes

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to the plane of the cobalt ion and the secondary donor atoms as the plane of the complex. We distinguish among the methylenic protons by means of subscripts: α_5 protons belong to a methylene group (adjacent to an amine) in the five-membered chelate rings, and α_6 protons are the corresponding protons in six-membered chelate rings. Protons labeled β are the central protons of a six-membered chelate ring. We distinguish among the various cis isomers by underscoring the chelate ring displaced from the plane of the complex, e.g., $[Co(\underline{2},2,2\text{-tet})Cl_2]^+$ is the familiar uns-cis configuration of the β isomer of $[Co(trien)Cl_2]^+$. The more familiar nomenclature is not readily applicable when there exists the possibility of more than one s-cis or uns-cis isomer which are independent of any other coordinated ligand.

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Ligating Ability of the Coordinated Thiolato Sulfur Atom.[1] Interactions between Soft Metal Centers and the Thiolatocobalt(III) Complexes $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$

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Recent interest in the efficacy of low-valent sulfur as an electron-transfer bridge[2-8] has led us to investigate the ligating ability of coordinated thiols—ligation of a coordinated thiol to a second metal center is the first step in the formation of an inner-sphere electron transfer precursor complex. Busch[9] and more recently Blinn[10] have qualitatively studied the ligating ability of *fac*-$Co(SCH_2CH_2NH_2)_3$ which functions as a tridentate ligand toward a variety of hard and soft metal centers. For a closer correspondence to the conditions and chemistry of extant redox studies[2-8] wherein only one thiolato sulfur atom bridges oxidant and reductant, we have investigated the ligating abilities of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ (hereafter referred to as Co(cys) and Co(tga), respectively). These complexes form strong adducts only with soft metal centers such as $[Ag(aq)]^+$ and $[CH_3Hg(aq)]^+$. The relevance of these specific studies has been extended by recent observations of Lane and coworkers[8,11] on reduction of Co(cys) and Co(tga) by the soft species Cu(I); while Cu(I) readily reduces Co(tga) via formation of a very stable precursor complex,[8] Co(cys) is not detectably reduced by Cu(I) but rather forms an unusual tetrameric complex (two cobalt(III) centers bridged by two Cu(I) centers) which provides a model for type 3 copper in multicopper oxidases.[11]

This study reports quantitative equilibrium constants for association of the title complexes with $[Ag(aq)]^+$ and $[CH_3Hg(aq)]^+$, as well as qualitative observations on association with other metal centers. The results of this study indicate that thiolato sulfur coordinated to cobalt(III) retains a high degree of Lewis basicity toward soft metals. Some unexpected behavior is noted in the $Co(cys)/[CH_3Hg(aq)]^+$ equilibrium which may be indicative of the formation of a three-coordinate Hg(II) species—the existence of such species has recently been reviewed.[12] Also, a convenient, accurate spectrophotometric technique for the standardization of aqueous $[CH_3Hg(aq)]^+$ solutions is presented.

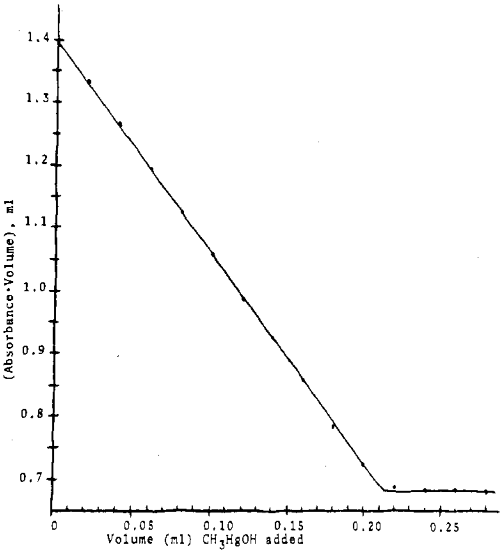

Figure 1. Spectrophotometric titration (λ 450 nm, l = 1.00 cm) of Co(tga) (initially 5.00×10^{-3} M) with CH_3HgOH in acid (pH ca. 0), a plot of absorbance × volume vs. volume (mL vs. mL).

Experimental Section

All common laboratory chemicals were of reagent grade. Water, $HClO_4$ and $LiClO_4$ were of previously specified purity.[2] Extensively recrystallized perchlorate salts of Co(cys) and Co(tga) were available from previous studies.[2,3,13,14] Silver perchlorate (G. F. Smith) solutions were standardized with sodium thiocyanate. Solutions of CH_3HgOH were prepared by the reaction of Ag_2O with CH_3HgCl in aqueous solution and then standardized by spectrophotometric titration (Figure 1) with a solution of Co(tga) (prepared from an accurately weighed sample of recrystallized $[Co(tga)]ClO_4$) at 450 nm where the molar extinction coefficients of Co(tga) and $[Co(tga)HgCH_3]^{2+}$ are 93.6 ± 0.9 and 45.5 ± 0.7 $M^{-1}\ cm^{-1}$, respectively (vide infra).

All solution studies were conducted in $HClO_4/LiClO_4$ media held at constant ionic strength at ambient temperature (22 ± 1 °C). Equilibrium constants governing association with silver(I) were determined by potentiometrically monitoring $[Ag(aq)]^+$ as aliquots of aqueous $AgClO_4$ solution were added to solutions of the cobalt complex. All potentiometric measurements were conducted in Nalgene plasticware, with continual stirring, by using a Beckman Research pH/mV instrument equipped with an Orion solid-state Ag_2S working electrode and an Orion double junction (saturated NaCl and saturated $NaClO_4$ solutions in the inner and outer chambers, respectively) reference electrode with Ag/AgCl internal couple. This system exhibited Nernstian behavior throughout the concentration range of interest: calibration curves were determined each working day. Equilibrium constants governing association with methylmercury ion were determined by titrating with base an acidic solution containing both the cobalt(III) complex and $[CH_3Hg(aq)]^+$ while simultaneously monitoring the optical density and pH of the solution. A typical titration curve is shown in Figure 2; at the beginning of the titration methylmercury is bound to the thiolatocobalt(III) complex, at the end of the titration it is bound to hydroxide, and in the intermediate region the methylmercury center is distributed according to the equilibrium

$$(CoSR)HgCH_3{}^{n+} + OH^- = CH_3HgOH + CoSR^{(n-1)+} \quad (1)$$

The steepness of the titration curve in the intermediate region permits determination of only two to four informative absorbance–pH data points per experiment. Spectrophotometric data were obtained by using a Cary 14 or Cary 118B spectrophotometer; pH data were obtained under a nitrogen atmosphere by using a Beckman pH/mV instrument equipped with a Sensorex thin probe combination electrode.

Solid samples of many adducts were prepared by mixing aqueous solutions of a thiolatocobalt(III) complex and a soft metal center in the presence of poorly coordinating anions. Table A[15] gives elemental analysis data for solid samples of the representative adducts $[(Co(cys))_2Ag](ClO_4)_5$, $[(Co(cys))_2PtCl_2]Cl_4$, $[Co(tga)AgOH_2](NO_3)_2$, and $[Co(tga)AgOH_2](NO_3)(SiF_6)_{1/2}$.

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