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Crystal Structure of Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]I$_2$ and Related Strain Energy Minimization Calculations

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The absolute configuration of Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]I$_2$ has been determined by X-ray methods ($P4_1$, $a = b = 8.878$ Å, $c = 21.398$ Å, $Z = 4$, $R_1 = 5.2\%$, $R_2 = 5.5\%$ (for 1472 unique data with $I \geq 3\sigma(I)$); the amino acid contains trans methyl groups with the *R* and *S* configurations about the N and C centers, respectively; the ethylenediamine chelates adopt δ and λ conformations. Strain energy minimization calculations predict the stability order Δ-*S*(*R*), Δ-*R*(*S*), Δ-*S*(*S*), Δ-*R*(*R*) and correctly predict the energy difference between the Δ-*S*(*R*) and Δ-*R*(*S*) isomers (observed 1.0 kcal mol^{-1}; calculated 0.8). The structure of the energy-minimized and crystal Δ-*R*(*S*) cations agree closely. Similar agreement is found between the calculated and observed structures of the Δ-*S*-[Co(en)$_2$(sar)]$^{2+}$ (sar = sarcosinato) cation. Calculations predict the stability order *S*(*R*), *S*(*S*), *R*(*S*), *R*(*R*) for the Δ-β_2-*RR*-[Co(trien)(*N*-Me-alaO)]$^{2+}$ cation and the three isolated isomers[6] are assigned. Structures and relative energies of the configurational isomers of Δ-β_2-[Co(trien)(sar)]$^{2+}$ are discussed.

Introduction

In a recent study of the Δ-[Co(en)$_2$(*N*-Me-(S)-alaO)]$^{2+}$ ion[1] (en = ethylenediamine, *N*-Me-(*S*)-alaO = *N*-methyl-(*S*)-alaninato anion) it was shown that at pH >12 mutarotation about the C center of the alaninato chelate occurred and that at equilibrium the Δ-*R*:Δ-*S* ratio was ca. 4. No mutarotation was observed for either isomer in more neutral solutions, pH <7, and it was concluded that the stereochemistry about the alaninato *N*-methyl center was controlled by the adjacent chiral metal and carbon centers in both ions. However, whereas in the Δ-*R* cation this leads to the stereospecific trans arrangement of the methyl groups, in the Δ-*S* species two alternatives are possible: the trans configuration which involves considerable strain in an adjacent ethylenediamine ring but avoids intramethyl group interactions and the cis configuration where the reverse situation obtains. Previous experience with the [Co(en)$_2$(sar)]$^{2+}$,[2] β_2-[Co(trien)(sar)]$^{2+}$,[3] β_2-[Co(trien)(pro)$^{2+}$],[4,5] and [Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$ [6] ions and an examination of molecular models suggested that chelate ring–methyl group interactions would dominate the issue and predicted that a cis arrangement would occur in the minor Δ-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$ component. However, strain energy calculations predicted that the trans structure would be stabilized in the Δ-*S* ion. It was therefore of some importance to determine the structure and this paper describes these results.

The agreement found between the X-ray and strain energy minimized structures for the Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$ ion (vide infra) prompted us to reexamine our results for the Δ-β_2-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$,[6] Δ-[Co(en)$_2$(sar)]$^{2+}$,[2] and Δ-β_2-[Co(trien)(sar)]$^{2+}$ [3] ions. These data are briefly discussed at the end of the paper.

Experimental Section

A. Crystallography and Data Collection for Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]I$_2$. The complex crystallized from water as deep red distorted octahedra.[1] Preliminary cell dimensions and the space group were determined from precession photographs and the final parameters and diffractometer orientation matrix refined by least-squares procedures[7] from the setting angles of 12 high-angle reflections measured on a Picker FACS-1 four-circle diffractometer.

Cell data:[8] $CoI_2C_8N_5O_2H_{24}$, mol wt 535.1, space group $P4_1$ ($00l$ reflections absent for $l \neq 4n$), $a = b = 8.8784$ (4) Å, $c = 21.3982$ (13) Å, $V = 1686.7$ Å^3, $Z = 4$, $d_c = 2.11$ g cm^{-3}, d_m(by flotation) $= 2.12$ g cm^{-3}, λ(Cu Kα_1) = 1.54051 Å, $\mu = 423.6$ cm^{-1}, $F(000) = 258$.

Cell parameters and all reflection data were collected from a typical crystal bounded by the eight faces of the [101] form and having dimensions $0.023 \times 0.016 \times 0.016$ cm^3, parallel to *a*, *b*, and *c* respectively. It was mounted with the *a* axis parallel to the ϕ axis of the diffractometer system. Diffraction data for $3° \leq 2\theta \leq 126°$ were collected at room temperature (20 ± 1°) using graphite-monochromated Cu Kα radiation ($\bar{\lambda} = 1.5418$ Å) with a tube takeoff angle of 3°. Intensity measurements were made using the θ–2θ scan technique, scanning at a rate of 2°/min from 1° below the calculated position of the Cu Kα_1 maximum to 1° above that for Cu Kα_2. Backgrounds were counted for 10 sec at both ends of the scan range. Three moderately high-angle reflections, monitored after every 40 reflections, each showed a time-dependent decrease of about 13% in intensity over the period of data collection. The time dependence of the intensity decrease was corrected during data reduction by applying scale factors calculated from the three standards to each block of 40 reflections. This procedure assumes the intensity decrease to be independent of the scattering angle. Absorption corrections using a numerical integration method[9] over a grid of $10 \times 10 \times 12$ points set parallel to *a*, *b*, and *c*, respectively, were applied. Transmission coefficients varied from 0.3 to 0.12.

A total of 2234 reflections were measured and corrected for Lorentz and polarization effects in the usual manner.[10] After sorting and merging equivalent reflections, 1472 unique data remained with $I \geq 3\sigma(I)$[11] and these were used for the structure refinement.

B. Structure Solution. The heavy-atom positions were determined from an unsharpened Patterson synthesis and the initial positions of all the nonhydrogen atoms were obtained from the first heavy-atom Fourier map. Refinement by full-matrix methods, with the *z* coordinate of I(1) fixed and by using anisotropic thermal parameters

Table I. Fractional Atomic Positional and Thermal Parameters for Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]I$_2$

(i) Refined Positional and Anisotropic Thermal Parameters[a]

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	0.2826 (2)	0.3948 (1)	0.0	0.0125 (2)	0.0071 (2)	0.0020 (1)	0.0008 (2)	−0.0003 (1)	0.0002 (1)
I(2)	0.0788 (2)	0.0807 (1)	0.3466 (1)	0.0091 (2)	0.0086 (2)	0.0016 (1)	−0.0008 (2)	−0.0002 (1)	0.0002 (1)
Co(1)	0.5661 (3)	0.8980 (3)	−0.0041 (1)	0.0064 (4)	0.0052 (3)	0.0010 (1)	0.0007 (3)	0.0000 (1)	0.0002 (1)
C(1)	0.724 (3)	1.169 (2)	0.022 (1)	0.015 (4)	0.006 (3)	0.003 (1)	−0.001 (3)	−0.003 (1)	−0.001 (1)
C(2)	0.607 (3)	1.150 (3)	0.074 (1)	0.014 (4)	0.008 (3)	0.002 (1)	0.005 (3)	−0.001 (1)	−0.002 (1)
C(3)	0.289 (2)	0.818 (3)	−0.064 (1)	0.007 (3)	0.015 (4)	0.001 (1)	−0.005 (3)	0.001 (1)	0.001 (1)
C(4)	0.334 (2)	0.972 (2)	−0.089 (1)	0.010 (3)	0.005 (2)	0.002 (1)	0.000 (2)	−0.001 (1)	0.001 (1)
C(5)	0.719 (2)	0.618 (2)	0.011 (1)	0.010 (3)	0.004 (2)	0.002 (1)	0.001 (2)	0.000 (1)	0.000 (1)
C(6)	0.695 (2)	0.691 (3)	0.075 (1)	0.002 (2)	0.013 (3)	0.002 (1)	0.000 (2)	0.000 (1)	0.001 (1)
C(7)	0.613 (2)	0.641 (3)	−0.095 (1)	0.006 (3)	0.014 (3)	0.002 (1)	0.001 (3)	0.000 (1)	−0.002 (1)
C(8)	0.876 (3)	0.558 (3)	0.002 (1)	0.014 (4)	0.014 (4)	0.002 (1)	0.008 (3)	0.001 (1)	0.000 (2)
N(1)	0.752 (2)	1.019 (2)	−0.005 (1)	0.009 (2)	0.009 (2)	0.001 (1)	−0.002 (2)	−0.001 (1)	0.000 (1)
N(2)	0.483 (2)	1.064 (2)	0.044 (1)	0.009 (2)	0.004 (2)	0.002 (1)	0.002 (2)	0.000 (1)	0.000 (1)
N(3)	0.375 (2)	0.789 (2)	−0.005 (1)	0.005 (2)	0.006 (2)	0.002 (1)	0.002 (2)	0.000 (1)	0.000 (1)
N(4)	0.497 (2)	0.982 (2)	−0.084 (1)	0.006 (2)	0.005 (2)	0.002 (1)	0.000 (2)	0.000 (1)	0.000 (1)
N(5)	0.675 (2)	0.722 (2)	−0.040 (1)	0.009 (2)	0.008 (2)	0.001 (1)	−0.002 (2)	0.000 (1)	0.002 (1)
O(1)	0.744 (2)	0.631 (2)	0.121 (1)	0.008 (2)	0.015 (3)	0.002 (1)	0.003 (2)	0.000 (1)	0.002 (1)
O(2)	0.618 (1)	0.816 (1)	0.073 (1)	0.008 (2)	0.006 (2)	0.001 (1)	0.006 (2)	0.001 (1)	0.001 (1)

(ii) Calculated Hydrogen Atom Coordinates and Isotropic Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2	Atom	*x*	*y*	*z*	*B*, Å^2
H(1)	0.820	0.973	0.018	2.9	H(13)	0.303	0.982	−0.131	2.8
H(2)	0.784	1.027	−0.043	2.9	H(14)	0.288	1.048	−0.064	2.8
H(3)	0.816	1.211	0.038	4.1	H(15)	0.538	0.929	−0.115	2.4
H(4)	0.686	1.235	−0.010	4.1	H(16)	0.526	1.074	−0.087	2.4
H(5)	0.650	1.095	0.108	3.9	H(17)	0.759	0.755	−0.058	2.8
H(6)	0.574	1.245	0.089	3.9	H(18)	0.520	0.598	−0.083	3.4
H(7)	0.431	1.123	0.020	2.7	H(19)	0.593	0.709	−0.135	3.5
H(8)	0.422	1.028	0.073	2.7	H(20)	0.681	0.564	−0.107	3.4
H(9)	0.320	0.818	0.027	2.3	H(21)	0.657	0.531	0.008	2.8
H(10)	0.393	0.692	−0.001	2.3	H(22)	0.903	0.491	0.035	5.0
H(11)	0.312	0.741	−0.094	3.4	H(23)	0.884	0.505	−0.037	5.0
H(12)	0.183	0.814	−0.056	3.4	H(24)	0.948	0.639	0.001	5.0

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

for all atoms, converged with $R_1 = [\sum\|F_o| - |F_c\|/\sum|F_o|] = 0.058$. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement where F_o and F_c were the observed and calculated structure factor amplitudes and *w* the weights taken as $[\sigma(F)]^{-2}$.[12] The nonhydrogen scattering factors used were those compiled by Cromer and Waber[13] while corrections for anomalous dispersion of the cobalt and iodine atoms were taken from Cromer.[14]

A difference Fourier synthesis calculated at this stage of the refinement exhibited significant electron density maxima (>0.5 e Å^{-3}) at ca. 50% of the expected hydrogen atom locations. It was decided, therefore, that hydrogen atom contributions should be included in the scattering model. Accordingly, coordinates for all 24 hydrogen atoms were determined by calculation (tetrahedral disposition, C–H = 0.95 Å, N–H = 0.87 Å).[15] For methyl group C(8), no clear maxima attributable to hydrogens were observed in the difference map, and the hydrogens were located so as to define a staggered configuration with respect to the C(5)–N(5) bond. Methyl group C(7) was generated from the positions of N(5), C(7), and the most clearly defined (H(19)) of the three associated methyl hydrogens in the map. Each hydrogen atom was assigned an isotropic Debye factor 1.1 times that of its parent "heavy atom", with scattering factors taken from the compilation of Stewart, Davidson, and Simpson.[16] In subsequent refinement the hydrogen atom parameters were not permitted to vary but were recalculated from time to time according to the procedure outlined above. To establish the absolute configuration of the cation, the signs of the anomalous part of the cobalt and iodine scattering factors were reversed and the structure again refined to convergence. The Δ configuration model resulted in $R_1 = 0.052$, $R_2 = 0.055$ compared with 0.059, 0.059, respectively, for the Λ configuration ($R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$). The choice of the Δ cobalt configuration is justified to greater than the 95% significance level according to Hamilton's *R* factor test.[17]

A weighting scheme analysis showed that the minimized function was independent of $|F_o|$ and $(\sin\theta)\lambda^{-1}$. The final estimated standard error in an observation of unit weight [defined as $\sum w|F_o - F_c|^2/(n - s)$] was 1.24. The final difference synthesis showed eight peaks of height greater than 1 e Å^{-3} in size [maximum 1.25 e Å^{-3}] and all were associated with iodide ions. The final atom parameters, together with their estimated standard deviations, are given in Table I. A table of the final observed and calculated structure factors is available as supplementary material.

C. Strain Energy Minimization Calculations. Both the method and parameters were identical with those used in the study of the Δ-β_1-[Co(trien)(glyO)]$^{2+}$ (glyO = glycinato) isomers.[18] The starting models were generated from the Δ-β_2-[Co(trien)(*N*-Me-alaO)]$^{2+}$ cations,[6] with other combinations of the two en ring conformations generated by a modification of the method of Wiberg and Boyd.[19] Tables of final minimized cartesian coordinates are available from the authors.

Results and Discussion

The Crystal Structure of Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]I$_2$. The crystal structure consists of discrete Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]$^{2+}$ cations and iodide anions, Figures 1 and 2.[20] Relevant bond lengths and angles are given in Table II. The minor component of the mutarotation experiment at pH ~12[1] therefore contains trans methyl groups with *R* and *S* configurations about adjacent N and C centers, respectively. Furthermore, the two ethylenediamine chelate rings have mirror image conformations.

Most bond lengths and angles, Table II, agree with those found in similar structures[18,21–25] although some significant distortions occur. The Co–N(5)–C(7) angle (120.2°) differs markedly from the regular tetrahedral value due to the proximity of the N(3)–C(3)–C(4)–N(4) ethylenediamine ligand to C(7). A similar, although smaller, distortion was found in Λ-β_2-*SS*(*S*)-[Co(trien)((*S*)-pro)]ZnCl$_4$ resulting from a similar cause.[22] The *N*-methyl carbon atom (C(7)) is almost equidistant from N(3) and N(4) (3.15 and 3.20 Å, respectively) and is 3.35 Å from C(3). The distances of the two carbon atoms C(2) and C(1) from the N(1)–Co–N(2) plane of the second ring (Co–N(1)–C(1)–C(2)–N(2)) are −0.53 and 0.18

Table II. Crystal and Energy-Minimized Structural Parameters for the Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$ Ion

	Crystal	Minimized
	Distances, Å	
Co–N(1)	1.969 (16)[a]	1.975
Co–N(2)	1.940 (16)	1.976
Co–N(3)	1.954 (15)	1.968
Co–N(4)	1.955 (15)	1.966
Co–N(5)	1.990 (16)	2.008[b]
Co–O(2)	1.869 (12)	1.888
N(1)–C(1)	1.46 (3)	1.49
C(1)–C(2)	1.53 (3)	1.50
C(2)–N(2)	1.49 (3)	1.49
N(3)–C(3)	1.50 (2)	1.50
C(3)–C(4)	1.53 (3)	1.50
C(4)–N(4)	1.46 (3)	1.50
N(5)–C(5)	1.48 (2)	1.51
N(5)–C(7)	1.49 (3)	1.50
C(5)–C(6)	1.54 (3)	1.50
C(5)–C(8)	1.50 (3)	1.51
C(6)–O(1)	1.20 (2)	1.22
C(6)–O(2)	1.30 (3)	1.29
	Bond Angles, Deg	
N(1)–Co–N(2)	84.6 (7)	86.7[b]
N(1)–Co–N(3)	176.6 (6)	177.0
N(1)–Co–N(4)	92.9 (6)	91.1
N(1)–Co–N(5)	91.1 (7)	91.1
N(1)–Co–O(2)	90.7 (6)	90.5
N(2)–Co–N(3)	92.9 (7)	90.6
N(2)–Co–N(4)	93.1 (6)	91.6
N(2)–Co–N(5)	169.5 (7)	172.0
N(2)–Co–O(2)	85.5 (6)	87.0
N(3)–Co–N(4)	85.0 (6)	87.8
N(3)–Co–N(5)	91.8 (7)	93.9[b]
N(3)–Co–O(2)	91.3 (6)	90.6
N(4)–Co–N(5)	96.6 (6)	95.2[b]
N(4)–Co–O(2)	176.0 (6)	177.9
N(5)–Co–O(2)	85.1 (6)	86.3[b]
Co–N(1)–C(1)	110.5 (13)	108.6
N(1)–C(1)–C(2)	107.4 (17)	107.9
C(1)–C(2)–N(2)	104.0 (16)	107.7
C(2)–N(2)–Co	109.9 (13)	106.6
Co–N(3)–C(3)	111.4 (12)	108.9
N(3)–C(3)–C(4)	108.3 (16)	109.3
C(3)–C(4)–N(4)	106.9 (15)	109.4
C(4)–N(4)–Co	110.6 (11)	107.3
Co–N(5)–C(5)	109.6 (11)	108.4
Co–N(5)–C(7)	120.2 (13)	119.6[b]
C(5)–N(5)–C(7)	112.2 (15)	109.3
N(5)–C(5)–C(6)	111.0 (15)	109.8
N(5)–C(5)–C(8)	111.4 (17)	110.8
C(6)–C(5)–C(8)	113.3 (17)	109.9
C(5)–C(6)–O(1)	119.9 (19)	120.9
C(5)–C(6)–O(2)	113.6 (15)	119.2
O(1)–C(6)–O(2)	126.5 (18)	120.0
C(6)–O(2)–Co	119.5 (11)	115.5[b]

[a] The figures in parentheses are the esd's in the least significant figures shown. [b] Minimized strain energies are ⩾0.2 kcal mol^{-1}.

Å, respectively, while the corresponding values for C(4) and C(3) are −0.52 and 0.08 Å. Repulsion between C(3) and C(7) is suggested with a consequent depression of C(3) toward the N(2)–Co–N(4) plane of about 0.10 Å. The effect of the close approach of C(7) to the en ring is further shown by differences in the torsion angles for the two rings; Table III (ϕ(N(3)–C(3)–C(4)–N(4)) = 44.0°; ϕ(N(1)–C(1)–C(2)–N(2)) = 51.1°). The carboxyl moiety of the alaninato ring is planar in agreement with that found for a number of other cobalt–amino acid structures.[17,21–25] The C(1)–C(6)–O(2) angle is expanded by 6.5° (compared with 4° in L-glutamatobis(ethylenediamine)cobalt(III) perchlorate[25]) at the expense of the internal angle C(5)–C(6)–O(2) while the remaining angle at C(6) remains close to 120°.

One intermolecular hydrogen bond binds the carbonyl oxygen O(1) of one cation to N(4) of another (2.87 (2) Å), Table IV. Via this bond, each molecule becomes part of an infinite helix twisted about the 4$_1$ axis at (00*l*), Figure 1. The helices pack together as parallel rods and are held together in the crystal by van der Waals forces with the iodide ions fitting into the interstices. The closest contacts for the iodide anions are listed in Table IV.

Energy Minimization Calculations. (i) Comparison of Crystal and Minimized Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]$^{2+}$ Cations. Comparisons of bond lengths and bond angles (Table II) for the crystal and energy-minimized N-(*R*)C(*S*) cations (Figure 2) show excellent agreement except about the carboxylate part of the alaninato chelate; this latter section is involved in intermolecular hydrogen bonding, Figure 1, and therefore some disagreement is not unexpected. Good agreement is also found for the intraatomic nonbonded contacts and torsion angles (Table III) especially considering that the H atoms in the crystal structure were placed in calculated positions and were not refined. Two features deserve particular comment. The distortion resulting from the proximity of the *N*-methyl group and the N(3)–C(3)–C(4)–N(4) ligand is reproduced in the minimized structure (angle Co–N(5)–C(7) = 120.2 (13)° (crystal), 119.6° (0.9 kcal mol^{-1}, minimized); ϕ(N(3)–C(3)–C(4)–N(4)) = 44.0° (crystal), 45.9° (0.3 kcal mol^{-1}, minimized)), and although the extension of the Co–N(5) bond, 1.990 (16) Å, is crystallographically barely significant (2σ), it is reproduced in the minimized cation (2.01 Å, 0.4 kcal mol^{-1}). The resulting flattening of the N(3)–C(3)–C(4)–N(4) ethylenediamine ring compared to its N(1)–C(1)–C(2)–N(2) counterpart is partially reproduced in the minimized structure (distances from N–Co–N plane: C(4), 0.52 Å (crystal), 0.43 Å (minimized); C(3), 0.08 Å (crystal), 0.18 Å (minimized); C(2), 0.53 Å (crystal), 0.47 Å (minimized); C(1), 0.18 Å (crystal), 0.21 Å (minimized).

(ii) Analysis of Minimized Strain Energy Components for the Four Δ-[Co(en)$_2$(*N*-Me-alaO)]$^{2+}$ Cations. Contributions to the total strain energy for the four isomers with λ and δ ethylenediamine ring conformations are given in Table V. Figure 3 shows the minimized structures with dotted lines representing nonbonded repulsive contacts of >0.3 kcal mol^{-1}. As anticipated in the Introduction, the Δ-*S*(*R*) ion with staggered methyl groups and minimal interatomic nonbonded contacts, Figure 3a, is favored. It is highly likely that this corresponds to the isomer present to 80% under equilibrium conditions at pH >12.[1] By contrast the cis methyl groups of the least stable *R*(*R*) isomer (Figure 3d), interact strongly with each other and with the adjacent N(3)–C(3)–C(4)–N(4) ethylenediamine ligand and this isomer is not observed at equilibrium. Surprisingly to us, and in agreement with the structural study, the second most stable isomer is the *R*(*S*) ion, Figure 3b. Apparently the stabilization resulting from the trans configuration of the methyl groups is more than sufficient to offset the increased strain resulting from nonbonded repulsions with the ethylenediamine moiety. Also the calculated energy difference between the two trans ions, 1.0 kcal mol^{-1}, compares very favorably with that observed, 0.8 kcal mol^{-1}.[1] The difference in strain energy between the trans *R*(*S*) and cis *S*(*S*) ions is not large (0.3 kcal mol^{-1}), but none of the latter ion was observed in the mixture.[1]

The calculated stability relationships, Table V, result in large part from the proximity of the *N*-methyl group to the ethylenediamine ring and/or to the methyl group on C(5). The number and severity of the nonbonded H···H, C···H, and C···C contacts increase in the order *S*(*R*) < *R*(*S*) ~ *S*(*S*) < *R*(*R*) for the Δ configuration, as shown by the dotted lines in Figure 3 and by Table III. Both effects also appear as distortions of the Co–N(5)–C(7) angle, *S*(*S*) 115.6° (0.3 kcal mol^{-1}), *S*(*R*) 117.6° (0.6), *R*(*S*) 119.6° (0.9), *R*(*R*) 119.7° (0.9), and

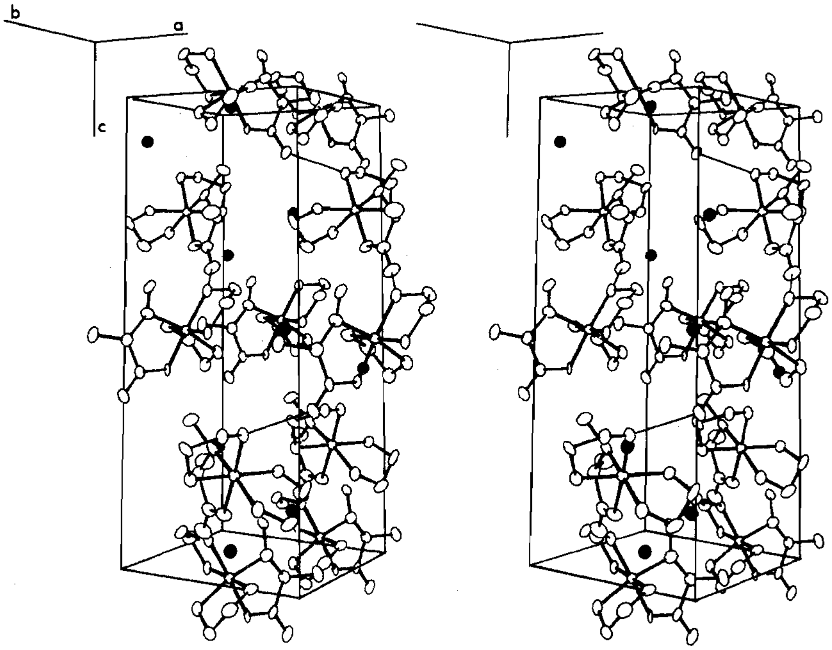

Figure 1. Stereoscopic packing diagram of Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]I_2. The iodide ions are shaded and I(1) has almost the same *z* coordinate as the cobalt.

Table III. Nonbonded and Torsional Interactions for the Crystal and Energy-Minimized Structures of the Δ-$[Co(en)_2(N\text{-}Me\text{-}alaO)]^{2+}$ Cations

(i) Nonbonded Interactions,[a] Å

Atoms	(*RS*) crystal[b]	(*RS*) minimized	(*SR*) minimized	(*SS*) minimized	(*RR*) minimized
C(7)· · ·C(8)	3.22	3.32	3.71	2.80 (0.7)	2.79 (0.7)
C(7)· · ·H(21)	2.49	2.46 (0.5)	2.43 (0.6)	3.36	3.07
C(8)· · ·H(17)	2.45	2.45 (0.5)	2.44 (0.5)	3.02	3.29
H(1)· · ·H(20)	4.79	4.83	2.40 (0.1)	2.27 (0.3)	4.62
H(2)· · ·H(17)	2.42	2.25 (0.3)	3.74	3.67	2.25 (0.3)
H(2)· · ·H(19)	3.68	3.90	2.43 (0.1)	2.17 (0.5)	4.79
H(2)· · ·H(20)	4.54	4.51	2.25 (0.3)	2.42 (0.1)	3.85
H(7)· · ·H(14)	2.15	2.20 (0.4)	2.24 (0.3)	2.27 (0.3)	2.20 (0.4)
H(8)· · ·H(9)	2.20	2.22 (0.4)	2.20 (0.4)	2.18 (0.5)	2.22 (0.4)
H(9)· · ·H(12)	2.26	2.26 (0.3)	2.29 (0.2)	2.29 (0.2)	2.26 (0.3)
H(10)· · ·H(18)	2.12	2.21 (0.4)	4.68	4.81	3.82
H(10)· · ·H(21)	2.67	2.85	4.10	2.16 (0.5)	4.22
H(11)· · ·H(17)	4.13	4.07	2.46 (0.3)	2.21 (0.4)	4.07
H(11)· · ·H(18)	2.07	2.21 (0.4)	4.36	4.49	3.61
H(11)· · ·H(19)	2.68	2.32 (0.2)	3.85	4.15	2.18 (0.4)
H(15)· · ·H(19)	1.88	2.10 (0.7)	2.08 (0.8)	2.28 (0.3)	3.41
H(15)· · ·H(20)	3.54	3.63	3.48	3.69	2.07 (0.8)
H(17)· · ·H(19)	2.17	2.40 (0.1)	2.43	2.42 (0.1)	2.95
H(17)· · ·H(21)	2.84	2.90	2.87	2.22 (0.4)	2.18 (0.5)
H(18)· · ·H(23)	3.61	3.72	3.92	2.26 (0.3)	3.18
H(18)· · ·H(24)	4.46	4.52	2.76	2.50	2.25 (0.3)

(ii) Torsion Angles (φ), Deg

Atoms	(*RS*) crystal[c]	(*RS*) minimized (trans)	(*SR*) minimized (trans)	(*SS*) minimized (cis)	(*RR*) minimized (cis)
Co-N(1)-C(1)-C(2)	34.7	34.8 (0.6)	34.1 (0.6)	35.1 (0.6)	34.6 (0.6)
Co-N(2)-C(2)-C(1)	45.2	43.5 (0.3)	44.1 (0.3)	43.6 (0.3)	43.5 (0.3)
Co-N(3)-C(3)-C(4)	−26.9	−30.5 (0.8)	−37.2 (0.5)	−37.8 (0.5)	−30.9 (0.7)
Co-N(4)-C(4)-C(3)	−41.9	−38.6 (0.4)	−40.1 (0.4)	−38.6 (0.4)	−38.5 (0.4)
Co-N(5)-C(5)-C(6)	−11.2	−7.9 (1.5)	0.8 (1.5)	−27.0 (0.9)	−7.9 (1.5)
Co-N(5)-C(7)-H(18)	−63.2	−66.1 (0.0)	−173.4 (0.1)	−172.7 (0.1)	173.1 (0.1)
Co-O(2)-C(6)-O(1)	174.9	173.2 (0.1)	−174.9 (0.1)	172.1 (0.1)	166.4 (0.3)
N(1)-O(1)-C(2)-N(2)	−51.1	−51.9 (0.1)	−52.0 (0.1)	−52.1 (0.1)	−51.8 (0.1)
N(3)-C(3)-C(4)-N(4)	44.0	45.9 (0.3)	51.4 (0.1)	50.9 (0.1)	46.1 (0.3)
N(5)-C(5)-C(6)-O(1)	169.6	−170.2 (0.4)	176.4 (0.5)	−155.8 (0.0)	−165.9 (0.3)
N(5)-C(5)-C(8)-H(22)	179.9	−177.1 (0.0)	177.4 (0.0)	−175.4 (0.0)	−178.1 (0.0)

[a] Figures in parentheses are strain energies ⩾0.1 kcal mol^{-1}. [b] Proton positions for the crystal structure were calculated using C-H and N-H bond lengths of 0.95 and 0.87 Å, respectively. [c] Esd's in crystal angles are ~1.7°.

of the N(5)-C(5)-C(8) angle, *R*(*S*) 110.8° (0.04), *S*(*R*) 111.2° (0.07), *S*(*S*) 114.7° (0.6), *R*(*R*) 115.1° (0.7). Significant torsional contributions about C(3)-C(4) and N(3)-C(3) are also present, but again less for the isomers with the *S* nitrogen configuration, Table III(ii). Thus all dihedral angles in the Co-N(3)-C(3)-C(4)-N(4) chelate ring are consistently less than the corresponding angles in the Co-N(1)-C(1)-C(2)-N(2) chelate for the *R*(*S*) and *R*(*R*) isomers

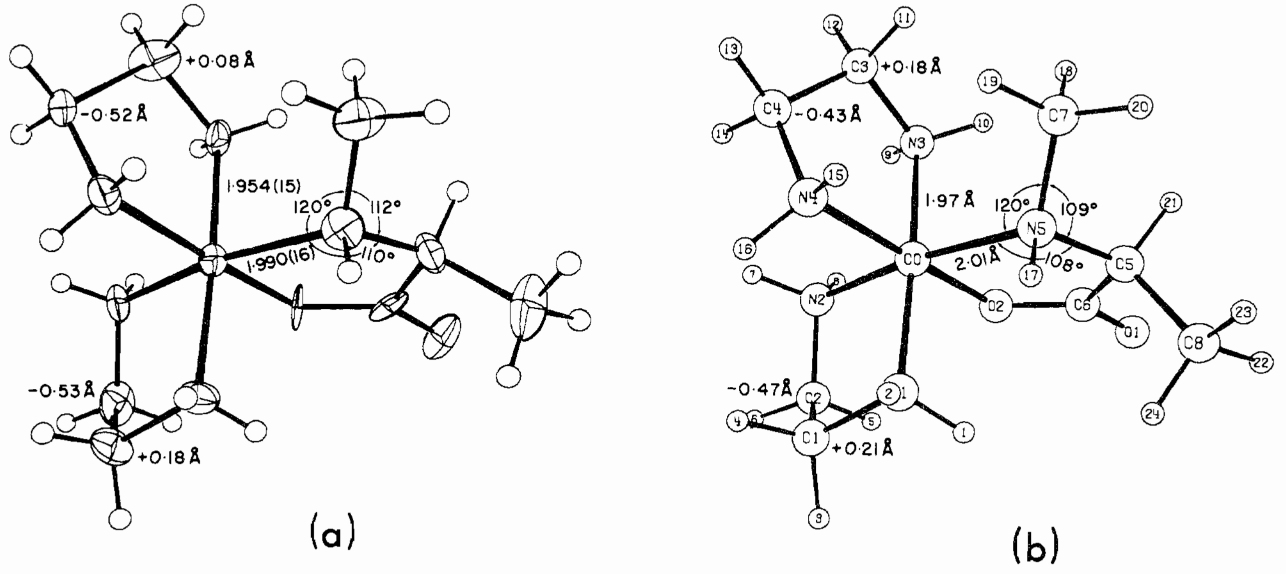

Figure 2. (a) Crystal structure and (b) energy-minimized structure for the Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]$^{2+}$ cation showing atom-numbering scheme, thermal ellipsoids, and distances of the ethylenediamine C atoms from the mean planes of their respective chelate rings.

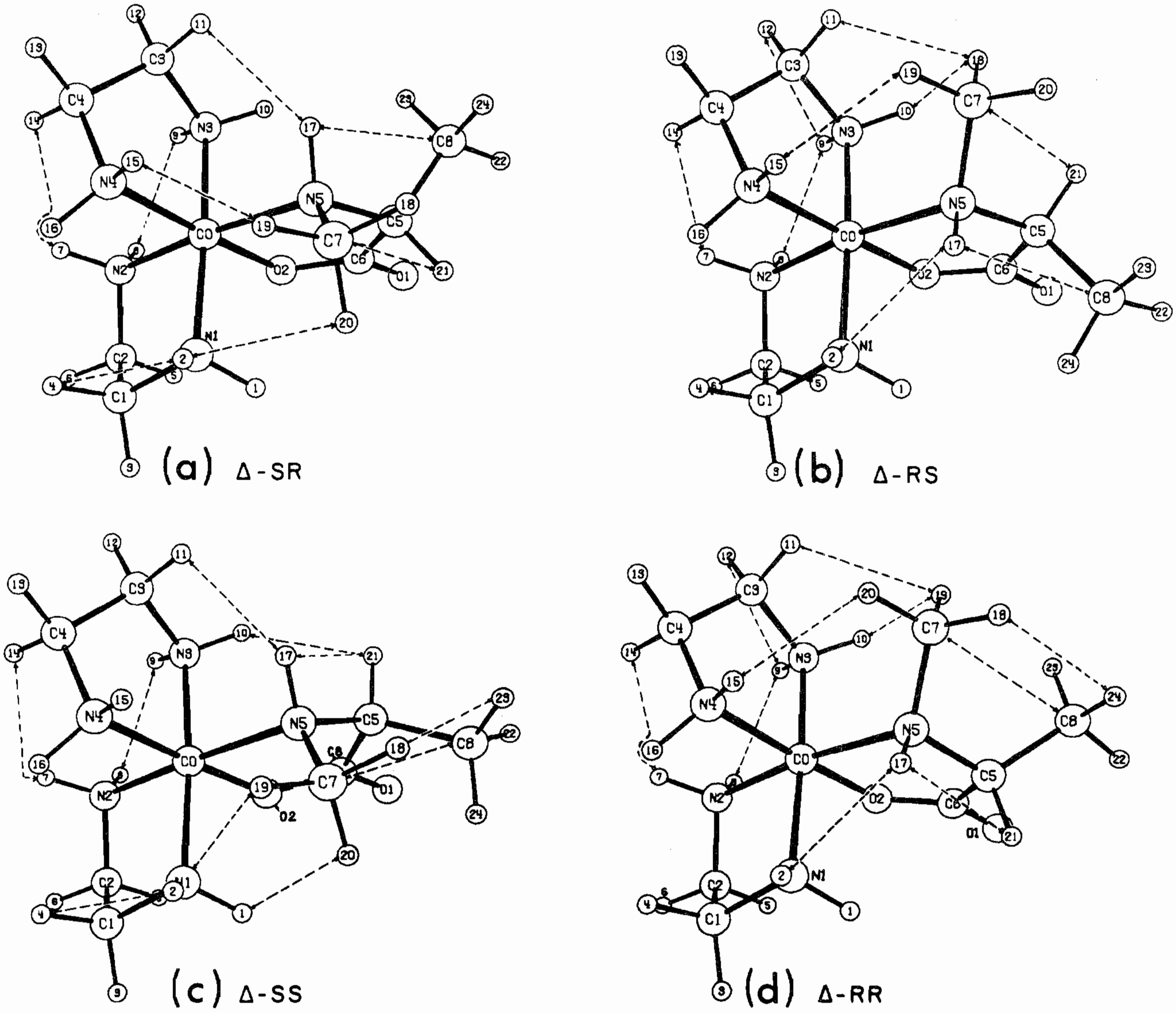

Figure 3. Minimized structures for the four Δ-[Co(en-λ)(en-δ)(*N*-Me-alaO)]$^{2+}$ cations. Dotted lines show interatomic repulsions >0.3 kcal mol^{-1}.

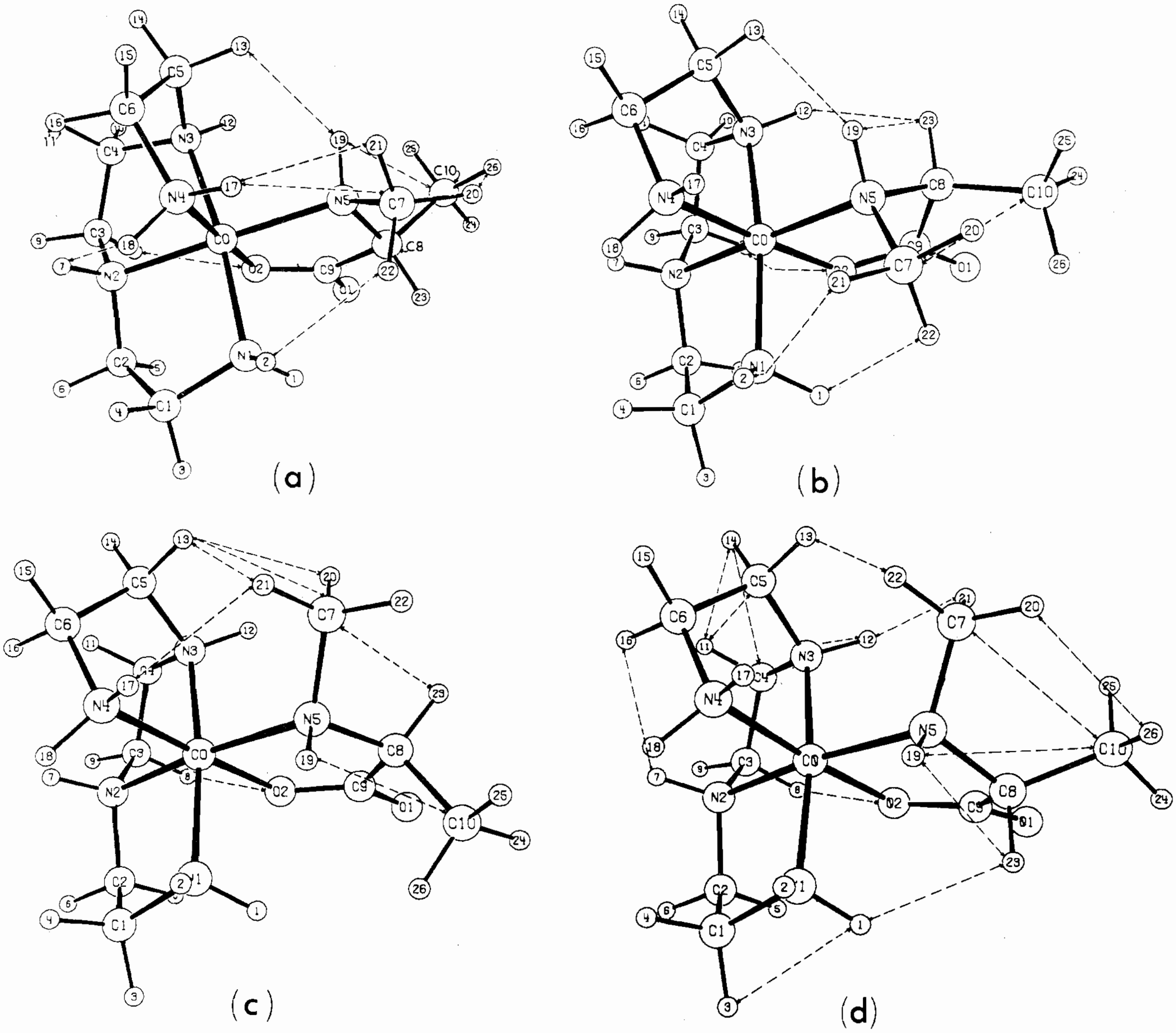

Figure 4. Minimized structures for the four Δ-β_2-RR-[Co(trien)(N-Me-alaO)]$^{2+}$ cations. Configurations about the N and C centers of the N-Me-alaO chelate are (a) N(S)C(R), (b) N(S)C(S), (c) N(R)C(S), and (d) N(R)C(R). Dotted lines show interatomic repulsions >0.3 kcal mol^{-1}.

Table IV. Intermolecular Contacts (<3.8 Å) in Δ-R-[Co(en-λ)(en-δ)(N-Me-(S)-alaO)]I$_2$

Atoms A···B	d(A···B), Å	Symmetry operation[a]
O(1)···N(4)	2.87 (2)	$z-y, x, {}^1/_4+z$
I(1)···N(2)	3.56	$x, y-1, z$
I(1)···N(3)	3.59	x, y, z
I(2)···N(3)	3.59	$1-y, x, {}^1/_4+z$
I(2)···N(1)	3.63	$1-x, 1-y, {}^1/_2+z$
I(2)···N(5)	3.70	$1-x, 1-y, {}^1/_2+z$
I(2)···N(1)	3.74	$1-y, x-1, {}^1/_4+z$

[a] To move atom B into contact with atom A.

indicating a flattening of this ring system. A comparison for the $R(S)$, $R(R)$ and $S(R)$, $S(S)$ pairs shows that a change in configuration about the C-methyl center does not seriously affect the puckering of the ethylenediamine ring.

The N-methylalaninato ring was refined starting from both planar and puckered conformations.[26] Except for the $S(R)$ cation the planar situation was unstable, refining to a puckered ring, Table III(ii), ϕ(Co–N(5)–C(5)–C(6)). Even the $S(R)$ species gave an alternative structure containing the puckered alaninato ring (ϕ(Co–N(5)–C(5)–C(6)) = −28°) of identical overall strain energy (5.3 kcal mol^{-1}). Twisting about N(5)–C(5) reduces the torsional strain (by 0.4 kcal mol^{-1}) but shortens the H(2)···H(20) distance and distorts the N(4)–Co–N(5) (96.4°, 0.6 kcal mol^{-1}) and N(5)–Co–O(2) (85°, 0.4 kcal mol^{-1}) angles about Co. Such a result illustrates the cooperative nature of the minimization method. An estimate of the barrier for the planar to puckered ring conversion using the Boyd–Wiberg approach[19] (1.5 kcal mol^{-1}) indicates that the two conformations would rapidly interconvert at room temperature.

Table V. Energy Terms for the Δ-[Co(en-λ)(en-δ)(N-Me-alaO)]$^{2+}$ Cations (kcal mol^{-1})

	Trans N(S)-C(R)	Trans N(R)-C(S)	Cis N(S)-C(S)	Cis N(R)-C(R)
Bond deformations	0.93	0.94	1.11	1.15
Angle deformations	3.13	3.63	4.17	5.15
Nonbonded interactions	−2.86	−2.71	−1.78	−1.81
Torsional strain	4.09	4.47	3.12	4.60
Out-of-plane deformation	0.0	0.0	0.0	0.0
Total strain energy	5.3	6.3	6.6	9.1
Energy differences	0.0	1.0	1.3	3.8

Table VI. Strain Energy Minima for Δ-β_2-[Co(trien)(*N*-Me-alaO)]$^{2+}$ Cations (kcal mol^{-1})

RR (trien)				*RS* (trien)			
N center	C center	SE[a]	SED[b]	N center	C center	SE[a]	SED[b]
S	*R* (trans)	8.7	0	*S*	*R* (trans)	11.7	3.0
S	*S* (cis)	9.3	0.6	*S*	*S* (cis)	12.6	3.9
R	*S* (trans)	10.6	1.9	*R*	*S* (trans)	14.5	5.8
R	*R* (cis)	12.7	4.0	*R*	*R* (cis)	16.3	7.6

[a] Calculated strain energy. [b] Strain energy differences.

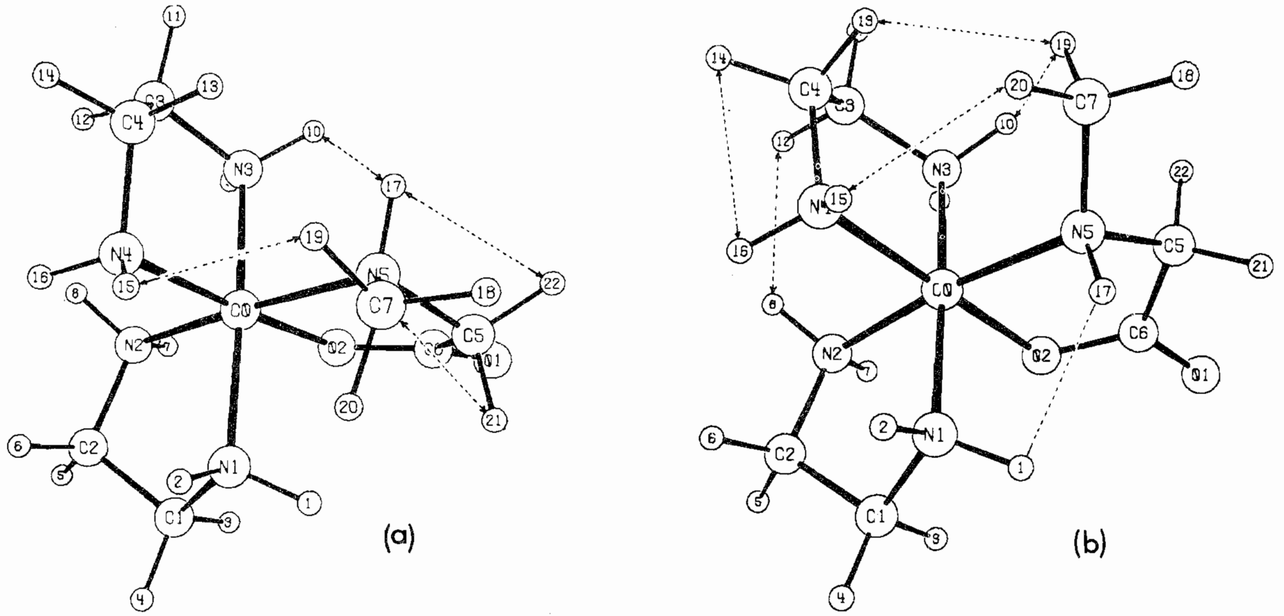

Figure 5. Minimized structures for the (a) Δ-*S*- and (b) Δ-*R*-[Co(en-δ)(en-λ)(sar)]$^{2+}$ cations. Dotted lines show interatomic repulsions >0.3 kcal mol^{-1}.

Energy calculations were also carried out on isomers containing the $\delta\delta$, $\lambda\lambda$, and $\delta\lambda$ conformations of the ethylenediamine rings. The $\delta\delta$ and $\delta\lambda$ structures optimized to within 0.1 kcal mol^{-1} of that found for the $\lambda\delta$ species, but the four $\lambda\lambda$ structures converged to strain energies of ca. 1 kcal mol^{-1} lower than the others, due largely to a release of torsional strain. For example, in the Δ-*R*(*S*)-$\lambda\delta$ isomer, Figure 3b, twisting about N(5)–C(5) of the near-planar alaninato ring (ϕ(Co–N(5)–C(5)–C(6)) = 7.9°, 1.5 kcal mol^{-1}) is prevented by the close H(2)···H(17), H(8)···H(9), and H(9)···H(12) contacts; in the corresponding $\lambda\lambda$ conformer the relief of both inter- and intraethylenediamine contacts allows the alaninato ring to take up the more preferred staggered conformation (ϕ(Co–N(5)–C(5)–C(6)) = 25°, 1.0 kcal mol^{-1}). Torsional strain energies within the two ethylenediamine rings are the same for both structures. The absence of the Δ-$\lambda\lambda$ conformation in the crystal, and perhaps in solution, may be due to the stabilization of Δ-δ ethylenediamine rings by hydrogen bonds between amine protons and anions or water molecules in the lattice.[27] Indeed hydrogen-bond packing forces in the crystal of Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]I_2 involve both N(4) and N(3) of the δ ring (Figure 1 and Table IV).

Structures and Relative Energies of the Δ-β_2-[Co(trien)-(*N*-Me-alaO)]$^{2+}$ Ions. The existence of both *R* and *S* configurations about the *N*-methyl center in the analogous Δ-β_2-[Co(trien)(*N*-Me-alaO)]$^{2+}$ system warranted reexamination. The three isomers found for this ion were previously assigned the *RR*-*S*(*R*), *RR*-*S*(*S*), and *RS*-*S*(*S*) configurations with mutarotation at pH 6.5–7.0 being assigned to inversion at the secondary N center which fuses the chelates in the same coordination plane of β-trien rather than at the *N*-methyl center.

The minimized strain energies of all eight isomeric ions are given in Table VI. Two general conclusions can be made: the *RS* trien isomers are ca. 3–4 kcal mol^{-1} less stable than the corresponding *RR* trien isomers, and isomers containing the *R* *N*-methyl configuration are less stable than those with the preferred *S* *N*-methyl center. Furthermore, compared to the [Co(en)$_2$(*N*-Me-alaO)]$^{2+}$ ions, the relative stabilities of the trans methyl *R*(*S*) and cis methyl *S*(*S*) isomers are reversed. This last result arises from the increased rigidity of the apical trien ring to conformational inversion compared to the corresponding ethylenediamine ring. Detailed comparisons of the strain energy contribution for the Δ-β_2-*RR*-[Co(trien)(*N*-Me-alaO)]$^{2+}$ ions, Table VII, with those for the corresponding ethylenediamine ions, Table V, shows that the difference resides largely in the nonbonded, bond angle, and torsional contributions. Relative to the cis-*S*(*S*) methyl structures where methyl–apical chelate ring interactions are at a minimum, the trans-*R*(*S*) ethylenediamine structure, Figure 3b, is stabilized more than is the corresponding trien ion, Figure 4c. The H(13)···H(21) (2.17 Å, 0.5 kcal mol^{-1}), H(17)···H(21) (2.18 Å, 0.5 kcal mol^{-1}), and O(2)···H(8) (2.35

Table VII. Energy Terms for the Four Δ-β_2-*RR*-[Co(trien)(*N*-Me-alaO)]$^{2+}$ Cations (kcal mol^{-1})

	Methyl configurations[a]			
	S(*R*) (trans)	*S*(*S*) (cis)	*R*(*S*) (trans)	*R*(*R*) (cis)
Bond deformations	1.00	1.10	1.07	1.15
Angle deformations	5.05	5.58	5.34	6.75
Nonbonded interactions	−2.61	−2.28	−2.46	−2.10
Torsional strain	5.31	4.94	6.66	5.92
Out-of-plane deformation	0.00	0.00	0.00	0.00
Total strain energy	8.7	9.3	10.6	12.7
Energy differences	0.0	0.6	1.9	4.0

[a] The first designation refers to the N center and the second (in parentheses) to the C center.

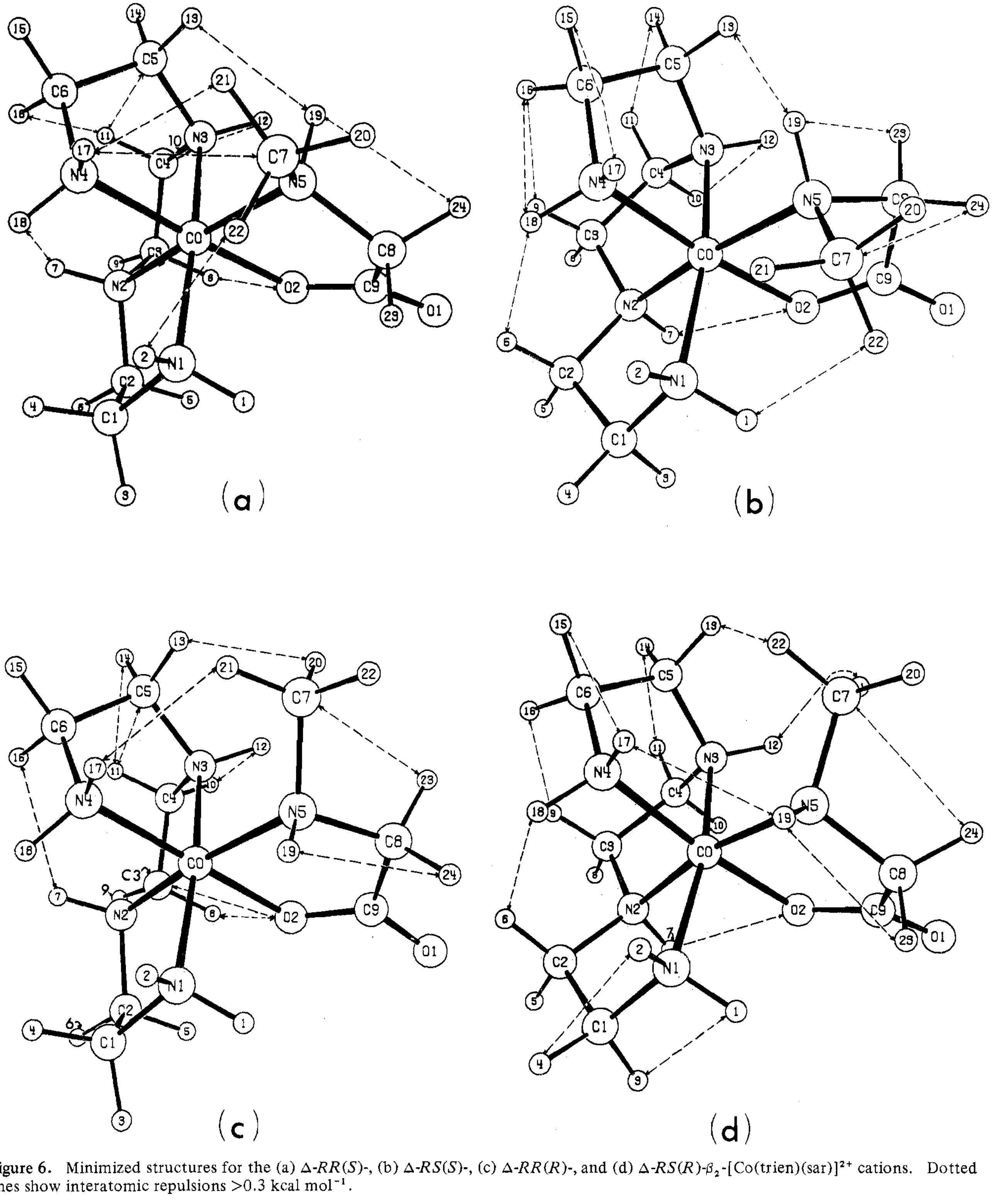

Figure 6. Minimized structures for the (a) Δ-*RR*(*S*)-, (b) Δ-*RS*(*S*)-, (c) Δ-*RR*(*R*)-, and (d) Δ-*RS*(*R*)-β_2-$[Co(trien)(sar)]^{2+}$ cations. Dotted lines show interatomic repulsions >0.3 kcal mol^{-1}.

Å, 0.5 kcal mol^{-1}) interactions are larger in the trans-*R*(*S*) trien structure and torsional strain about N(5)–C(8) and C(8)–C(9) of the alaninato ring cannot be compensated for elsewhere and results in a strained, near-planar, ring system (ϕ(Co–N(5)–C(8)–C(9)) = 3.9°, 1.5 kcal mol^{-1}).

The experimental results[6] can be reinterpreted as follows. Isolated Δ-β_2-$[Co(trien)(N\text{-Me-}(S)\text{-alaO})]I_2 \cdot 2H_2O$ ($[\alpha]_{546}$ −462°) may be assigned the Δ-*RR*-*S*(*S*) configuration with cis methyl groups (PMR (*N*-methyl) 2.8 ppm). Mutarotation at pH 6.5–7.0 results in an equilibrium mixture of the Δ-*RR*-*S*(*S*) and Δ-*RR*-*R*(*S*) (PMR (*N*-methyl) 3.0 ppm) ions, and further mutarotation at carbon at pH ~12 forms the most stable Δ-*RR*-*S*(*R*) ion (PMR (*N*-methyl) 3.0 ppm). The coincidence of the *N*-methyl PMR absorptions for the latter two ions with trans methyl groups agrees with that found for *R*(*S*)- and *S*(*R*)-$[Co(en)_2(N\text{-Me-alaO})]^{2+}$ of known structure and lends strong support to the assignments. Saburi and Yoshikawa have come to the same conclusion as a result of comparing the PMR spectra[6] with those of the related 5-(*S*)-methyl-[28] and 5(*R*),6(*R*)-diaminocyclohexane-substituted[29] triethylenetetramine complexes where stereospecificity about the secondary N centers is ensured.

Table VIII. Energy Terms for the Δ-[Co(en-δ)(en-λ)(sar)]$^{2+}$ Isomers (kcal mol^{-1})

	N(*S*)	N(*R*)
Bond deformations	0.71	0.78
Angle deformations	3.09	3.67
Nonbonded interactions	−3.20	−2.64
Torsional strain	3.16	3.67
Out-of-plane deformation	0.00	0.00
Total strain energy	3.8	5.5
Energy differences	0.0	1.7

Table IX. Energy Terms for Δ-β_2-[Co(trien)(sar)]$^{2+}$ Isomers (kcal mol^{-1})

	trien, sar configurations			
	RR, S	*RS, S*	*RR, R*	*RS, R*
Bond deformations	0.83	0.97	1.04	1.01
Angle deformations	5.28	6.12	8.12	5.24
Nonbonded interactions	−2.78	−2.13	−1.71	−1.98
Torsional strain	5.02	5.67	6.33	6.61
Out-of-plane deformation	0.00	0.00	0.00	0.00
Total strain energy	8.3	10.6	10.9	13.8
Energy differences	0.0	2.3	2.6	5.5

Relative Energies and Structures of the Δ-[Co(en)$_2$(sar)]$^{2+}$ and Δ-β_2-[Co(trien)(sar)]$^{2+}$ Ions. Previously it was shown that the configuration about the asymmetric N center of the chelated sarcosinato (*N*-methylglycinato) moiety in Δ-[Co(en)$_2$(sar)]$^{2+}$ [2] and in Δ-β_2-*RR*-[Co(trien)(sar)]$^{2+}$ [3] was controlled by the metal ion configuration. Only the Δ-*S* ions were observed[2,3] and for Δ-*S*-[Co(en)$_2$(sar)]I$_2$·2H$_2$O the structure was confirmed by an absolute X-ray study.[21] Crude strain energy calculations based on rigid Dreiding stereomodels and considering only nonbonded interactions indicated that the Δ-*R* species was less stable by 8–10 kcal mol^{-1}.[2,3]

Use of the present force field[18] and method[30] gives the minimized strain energies listed in Tables VIII and IX. The Δ-*S* ions are clearly more stable than the Δ-*R* species, in agreement with experiment, but the calculated energy differences are now not large suggesting that the Δ-*R* ions could be present in concentrations (~5% Δ-*R*-[Co(en)$_2$(sar)]$^{2+}$, ~1% Δ-β_2-*RR*(*R*)-[Co(trien)(sar)]$^{2+}$) detectable by PMR, ion-exchange, or polarimetric methods. However, careful ion exchange of equilibrated solutions of the two complexes using Dowex 50W-X2 and Sephadex SP-25 cation-exchange resins and NaClO$_4$–HCl (pH 4) or Na$_2$HPO$_4$–NaH$_2$PO$_4$ (pH 6.2) eluents failed to show any isomer separation. The actual ΔG differences therefore probably exceed ~2 kcal mol^{-1}.

For the Δ-[Co(en)$_2$(sar)]$^{2+}$ ions strain energy calculations were carried out on all combinations of ethylenediamine ring conformations with the following results (minimized energies in kcal mol^{-1}): $\delta\lambda$-*S*, 3.8; $\delta\lambda$-*R*, 5.5; $\lambda\delta$-*S*, 4.15; $\lambda\delta$-*R*, 6.0; $\lambda\lambda$-*S*, 3.8; $\lambda\lambda$-*R*, 4.7; $\delta\delta$-*S*, 4.25; $\delta\delta$-*R*, 6.4. Thus the *S* configuration about the N center of chelated sarcosine is stabilized compared to *R* irrespective of the ethylenediamine ring conformation, and the $\delta\lambda$-*S* ion found in the crystal[21] is also of minimum energy. The $\lambda\lambda$-*S* ion minimizes to the same energy and the preference for the δ ring may well result from H bonding as discussed above for the Δ-*R*-[Co(en-λ)(en-δ)(*N*-Me-(*S*)-alaO)]$^{2+}$ structure.

Minimized structures for the Δ-*R*- and Δ-*S*-[Co(en-δ)(en-λ)(sar)]$^{2+}$ cations and for the *RR*(*S*), *RS*(*S*), *RR*(*R*), and *RS*(*R*) Δ-β_2-[Co(trien)(sar)]$^{2+}$ cations are given in Figures 5 and 6, respectively. For Δ-*S*-[Co(en)$_2$(sar)]$^{2+}$ the minimized and X-ray structures agree closely; all angular distortions are reproduced to within 2 esd's. The only significant differences are a slight flattening of the Co–N(3)–C(3)–C(4)–N(4) ethylenediamine ring (ϕ(Co–N(3)–C(3)–C(4)) = 37.2° (crystal), 33.9° (minimized)) and a more pronounced twisting of the sarcosinato ring (ϕ(Co–N(5)–C(5)–C(6)) = 11.4° (crystal), 24.0° (minimized)). For each ion the *R* configuration of the amino acid results in increased nonbonded repulsions between the CH$_3$ group and the apical chelate ring which appear as angular and torsional distortions. Thus the angles about the Co atom, N(3)–Co–N(5) and N(4)–Co–N(5), are further distorted in the N(*R*) structures: Figure 5b, 93.4° (0.2 kcal mol^{-1}), 95.2° (0.4); Figure 5a, N(*S*), 91.7° (0.0); 93.9° (0.2); crystal structure, N(*S*), 91.6° (0.0), 93.7° (0.2), respectively. The same angles in the Δ-β_2-*RR*-[Co(trien)(sar)]$^{2+}$ ions are as follows: Figure 6c, N(*R*), 97.1° (0.7), 94.3° (0.3); Figure 6a, N(*S*), 92.8° (0.1), 95.0° (0.4). The *N*-methyl group also bends away from the apical chelate ring: Co–N(5)–C(7) angle, Figure 5b, N(*R*), 120.0° (1.0); Figure 5a, N(*S*), 117.5° (0.6); Figure 6c, N(*R*), 120.3° (1.0); Figure 6a, N(*S*), 119.0° (0.8). The apical ethylenediamine chelate ring also flattens in the N(*R*) configuration: ϕ(N(3)–C(3)–C(4)–N(4)), Figure 5b, N(*R*), −44.7°; Figure 5a, N(*S*), −51.5°; crystal, N(*S*), −50.7°; ϕ(N(3)–C(5)–C(6)–N(4)), Figure 6c, N(*R*), 47.4°; Figure 6a, N(*S*), 50.3°. These effects correspond closely with those examined above for the Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$ ion.

Summary

In those cases where experimental information is available the strain energy minimization results presented above correctly predict the stability order and relative energy differences for configurational isomers of [Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$, β_2-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$, [Co(en)$_2$(sar)]$^{2+}$, and β_2-[Co(trien)(sar)]$^{2+}$. In some instances it also correctly predicts the conformations of the chelate rings found in the crystalline state. The calculated structures closely correspond with those found in the crystal except in the vicinity of the amino acid carboxyl residue where H bonding could well play an important role.

Registry No. Δ-*R*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]I$_2$, 54932-93-3; Δ-*S*-[Co(en)$_2$(*N*-Me-(*R*)-alaO)]$^{2+}$, 54932-94-4; Δ-*S*-[Co(en)$_2$(*N*-Me-(*S*)-alaO)]$^{2+}$, 54932-95-5; Δ-*R*-[Co(en)$_2$(*N*-Me-(*R*)-alaO)]$^{2+}$, 54932-96-6; Δ-β_2-*RR*(*S*)-[Co(trien)(*N*-Me-(*R*)-alaO)]$^{2+}$, 23391-67-5; Δ-β_2-*RR*(*S*)-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$, 23443-87-0; Δ-β_2-*RR*(*R*)-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$, 54932-97-7; Δ-β_2-*RR*(*R*)-[Co(trien)(*N*-Me-(*R*)-alaO)]$^{2+}$, 54932-98-8; Δ-β_2-*RS*(*S*)-[Co(trien)(*N*-Me-(*R*)-alaO)]$^{2+}$, 23293-44-9; Δ-β_2-*RS*(*S*)-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$, 30856-72-5; Δ-β_2-*RS*(*R*)-[Co(trien)(*N*-Me-(*S*)-alaO)]$^{2+}$, 54932-99-9; Δ-β_2-*RS*(*R*)-[Co(trien)(*N*-Me-(*R*)-alaO)]$^{2+}$, 54933-00-5; Δ-(*S*)-[Co(en)$_2$(sar)]$^{2+}$, 46359-48-2; Δ-(*R*)-[Co(en)$_2$(sar)]$^{2+}$, 54910-23-5; Δ-*RR*(*S*)-β_2-[Co(trien)(sar)]$^{2+}$, 46750-37-2; Δ-*RS*(*S*)-β_2-[Co(trien)(sar)]$^{2+}$, 54933-01-6; Δ-*RR*(*R*)-β_2-[Co(trien)(sar)]$^{2+}$, 54933-02-7; Δ-*RS*(*R*)-β_2-[Co(trien)(sar)]$^{2+}$, 54933-03-8.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC40803+.

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(11) $\sigma(I) = [\mathrm{CT} + (T_\mathrm{p}/T_\mathrm{b})^2(B_1 + B_2)]^{1/2}$, where CT is the integrated peak intensity counted for T_p seconds and B_1 and B_2 are the background intensities each measured for $T_\mathrm{b}/2$ seconds.

(12) Standard deviations for each structure amplitude were calculated as $\sigma(F_\mathrm{o}) = \{[\sigma(I)/Lp]^2 + (\rho|F_\mathrm{o}|^2)^2\}^{1/2}/2|F_\mathrm{o}|$, where Lp is the appropriate Lorentz and polarization correction and ρ (0.001) is an instrumental "uncertainty" factor.

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Synthesis and Characterization of Some Halocopper(I)–Alkyl Sulfide Complexes Including the Crystal Structure of μ-(Diethyl sulfide)-bis(diethyl sulfide)tetra-μ-iodo-tetracopper(I), $[(C_2H_5)_2S]_3[CuI]_4$[1]

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Dimethyl sulfide reacts with copper(I) iodide, bromide, and chloride to yield a series of 1:1 complexes. Similar reaction with diethyl sulfide produces a homologous series of complexes with a ligand to copper ratio of 3:4. Treatment of copper(I) iodide and bromide with *n*-butyl sulfide results in a complex which is operationally characterized as halo[bis(di-*n*-butyl sulfide)]copper(I). The unusual stoichiometry of the diethyl sulfide complexes was definitively established by a X-ray diffraction determination of the crystal and molecular structure of $[(CH_3CH_2)_2S]_3[CuI]_4$. Refinement using full-matrix least-squares techniques revealed a structure consisting of infinite chains of sulfide-bridged Cu_4I_4 cores, each of which resembles a distorted cube with alternating vertices of copper and iodine. Individual copper–sulfur distances clearly reflect the presence of both bridging (Cu–S distances 2.331 (8) and 2.337 (6) Å) and terminal (Cu–S distances 2.297 (10) and 2.298 (9) Å) ligands. Each copper atom exists in a distorted tetrahedral environment provided by three bridging iodine atoms and a diethyl sulfide ligand. The intramolecular copper···copper distances range from 2.741 (6) to 2.901 (5) Å. The average copper–iodine distance is 2.692 Å. Crystallographic data are as follows: space group $P2_1/a$; unit cell $a = 13.201$ (4) Å, $b = 11.573$ (3) Å, $c = 18.466$ (5) Å, $\beta = 104.21$ (2)°; $V = 2735$ Å^3; d_calcd for $Z = 4$ is 2.508 g/cm^3. A total of 2018 independent reflections with $F^2 \geq 3\sigma$ were used to refine the structure to final values of $R_F = 0.058$ and $R_{wF} = 0.075$.

The coordination chemistry of copper(I) has been studied extensively in recent years and a multiplicity of stoichiometries has been observed. Complexes with ligand to copper ratios of 1:1, 2:1, 3:1, 4:1, and 3:2 are known for a variety of monodentate ligands.[2] Much of this work and particularly the structural studies have focused on complexes of the copper(I) halides with tertiary phosphine and arsine ligands.[2b,3-5] A number of sulfur-coordinated copper(I) complexes are known and several have been structurally characterized.[6,7] The ligands in these instances, however, have involved either bidentate disulfides or ligand systems such as thioureas, phosphine sulfides, or related compounds, in which the sulfur center participates in extensive π bonding. Complexes of copper(I) halides with simple alkyl sulfides are not well-known.[8] Here we report the preparation and characterization of several halocopper(I)–alkyl sulfide complexes including the single-crystal X-ray structure determination of one such complex, μ-(diethyl sulfide)-bis(diethyl sulfide)tetra-μ-iodo-tetracopper(I)], $[(C_2H_5)_2S]_3[CuI]_4$.

Experimental Section

General Data. Copper(I) halides were purchased from Alfa Inorganics, Inc., and used as received. Alkyl sulfides were obtained from either Aldrich Chemical Co. or Fairfield Chemical Co. and were employed without additional purification. Elemental analyses and molecular weights were determined at Galbraith Laboratories, Knoxville, Tenn.

Spectra. Raman spectra were obtained on a Cary Model 82 laser Raman spectrometer equipped with rotating sample cells. Unless otherwise noted, a slit width of 3 cm^{-1} and a scanning rate equal to the ratio of the slit width to time constant were employed. Red (6471 Å) or green (5145 Å) excitation was provided by Coherent Radiation Laboratory Model 52 krypton and argon ion lasers, respectively. Reported frequencies are precise to ±1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer employing Nujol mulls supported on polyethylene plates or as potassium bromide disks. Frequencies are precise to ±1 cm^{-1}.

$[(C_2H_5)_3PCuI]_4$ was prepared as described by Wells.[3]

Preparation of $(CH_3)_2SCuI$. Copper(I) iodide (47.5 g, 0.250 mol) was placed in a 250-ml flask equipped with a Teflon-coated stirrer bar and a condenser. In a well-ventilated hood, dimethyl sulfide (100 ml) was added gradually over a 5-min period through the top of the condenser. A mildly exothermic reaction occurred upon mixing. The resulting mixture was stirred for 2 hr at room temperature, refluxed for 1 additional hr, and then gravity filtered. The filtrate was treated with 250 ml of petroleum ether (bp 30°–60°) and chilled to −20° for 3 hr. The crystalline precipitate that formed was collected by suction filtration, washed with 100 ml of petroleum ether, and air-dried.