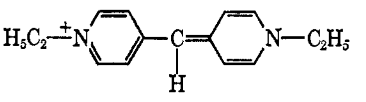
Pyridocyanine XI. 4-Benzylpyridine methiodide was prepared by the method of Koenigs, *et al.*[36] This methiodide (3 g) was treated with 25 ml of concentrated aqueous NaOH in the presence of ether. On shaking, the ether layer became orange-red. A portion of the ether extract was examined for visible absorption. The identity of pyridocyanines XI and XIX was established by Sprague and Brooker,[37] and their properties are included in Table I.


XIX

Acknowledgment. This work was supported by the Optical Systems Branch of the National Aeronautics and Space Administration in part on Grant No. NGR 09-010-008. Thanks are given to the National Science Foundation for partial contribution toward the purchase of the nmr spectrometer and mass spectrograph. In addition, appreciation is expressed to Drs. Felix Geiger and A. D. Britt for their assistance with the esr determinations.

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[36] E. Koenigs, K. Köhler, and K. Blindow, *Chem. Ber.*, **58**, 933 (1925).

[37] R. H. Sprague and L. G. S. Brooker, *J. Amer. Chem. Soc.*, **59**, 2697 (1937).

Structure and Conformational Analysis of Coordination Complexes. The αα Isomer of Chlorotetraethylenepentaminecobalt(III)

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Abstract: A procedure for the quantitative conformational analysis of metal complexes is elaborated and applied to the αα isomer of the chlorotetraencobalt(III) ion (tetraen = 1,4,7,10,13-pentaazatridecane). The crystal structure of this ion as the chloride perchlorate salt was determined. The unit cell is monoclinic, space group $P2_1/c$, with $a = 9.85$ (1), $b = 13.80$ (1), $c = 13.91$ (1) Å, and $\beta = 119.3$ (1)°. The central secondary nitrogen of the ligand is coordinated *trans* to the chloro group. The remaining nitrogen atoms coordinate so that the ligand is attached to three octahedral faces which share a common vertex at the central secondary nitrogen. The complex ion has an approximate mirror symmetry which is destroyed in detail by an unexpected envelope conformation of a chelate ring having a primary nitrogen atom. Energy minimization calculations have shown that this is not the lowest energy conformation to be expected in the gas phase, and close contacts in the crystal confirm that it is due to crystal packing. Where these particular contacts are absent, the computed geometry agrees with that observed to within several standard deviations. The lattice chloride ion forms three hydrogen bonds to hydrogen atoms of both primary amino groups and the central secondary amino group of the same cation. This trigonal interaction has been postulated for anion to complex ion pairs in solution, but has not been previously detected in the solid state.

By consideration of a few nonbonded interactions, Corey and Bailar[1] were able to predict that metal complexes with flexible rings were able to adopt preferred conformations. These studies yielded an energy difference between conformations, but since they assumed a rigid structure they are unable to predict detailed molecular geometry. Considerable success has recently been obtained with more complete force fields in organic[2-4] and polymer[5] molecules using efficient energy search and minimization techniques. These studies have demonstrated the value of the quantitative approach for hydrocarbon, heterocyclic, and biopolymer molecules in the reliable prediction of their molecular geometry, thermodynamic properties, and vibrational spectra.

One of these procedures[3] has been applied to the molecular structures of three isomeric cobalt complexes of 1,4,7,10,13-pentaazatridecane (tetraethylenepentamine ≡ tetraen) of the type $[Co(tetraen)Cl]^{2+}$. It was hoped that the very unusual conformational features of these complexes could be traced to an intra- or intermolecular source and that accurate "gas state" geometries and energy differences could be calculated for these kinds of compounds. The results of a less general quantitative procedure for carbon- and nitrogen-substituted ethylenediamine complexes of the type $Co(NH_3)_4en$ have recently appeared.[6] In this procedure the strain energy of the complex is explored as a function of selected and independent geometric variables one at a time. A partial energy surface of the molecule is found from which the minima are deduced. The results described below were obtained by minimization of the strain energy allowing the atomic Cartesian coordinates to vary simultaneously. This method

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[1] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[2] J. E. Williams, P. J. Strang, and P. von R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

[3] R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

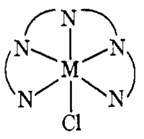
[4] S. Lifson and A. Warshel, *ibid.*, **49**, 5116 (1968).

[5] H. A. Scheraga, *Advan. Phys. Org. Chem.*, **6**, 103 (1968).

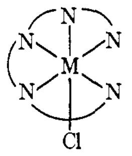
[6] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969).

yields the equilibrium energy and geometry very efficiently, but does not map the energy surface. It is general, however, in the sense that the algorithm is not particular to each molecule, but that it only requires trial coordinates and a force field for the minimization.

The general coordination modes of the isomers established by structure analysis are shown below.[7]



αα



αβ

The αα isomer as drawn has a plane of symmetry and it was of interest to see if this was true in the crystal and whether or not it persisted in the "gas phase" calculations. The structure and calculations both show that it is destroyed by intermeshing of the hydrogen atoms on the adjacent middle rings. The proton nmr spectrum is consistent with a symmetrical complex and interconversion between the unsymmetrical forms must be rapid on this time scale.[8] The αβ isomer is asymmetric, and in addition to the stereochemistry generated by the topology of the coordinated ligand, there is the possibility of the existence of diastereoisomers arising from alternative configurations about the *sec*-N atom which joins chelate rings in the same plane. The two possible diastereoisomers have been isolated and the chemistry, structure analysis, and conformational analysis of these[9,10] and the structure and conformational analysis of the αα isomer have been reported briefly.[10] The details of the latter work are given below.

Experimental Section

Crystals of [Co(tetraethylenepentamine)Cl]ClClO$_4$ were kindly supplied by Dr. A. M. Sargeson and Dr. P. Marzilli. Preliminary precession photographs showed the crystals to be monoclinic, space group P2$_1$/c. The unit cell constants obtained from calibrated precession photographs are a = 9.85 (1), b = 13.80 (1), c = 13.91 (1) Å, and β = 119.3 (1)° (Mo Kα, λ 0.7107 Å). Estimated standard deviations are given in parentheses. The calculated and measured densities are 1.79 and 1.78 g/ml (U = 1637.8, Z = 4).

Two crystals were used for collection of the Mo Kβ, three-axis, integrated film data. A crystal with dimensions 0.16 × 0.2 × 0.2 mm was used to collect the levels $0kl$–$5kl$ by rotation about a using the equiinclinational, multiple film, Weissenberg technique. A crystal of dimensions 0.15 × 0.3 mm × 0.3 mm was used to collect the levels $h0l$–$h4l$ and $hk0$–$hk3$ using an integrating precession camera. The integrated reflections were measured with a Nonius II microdensitometer. Interfilm and interlayer scale factors were determined by a least-squares procedure described by Rae,[11] developed by Paul,[12] and extended locally.[13] The data were corrected for Lorentz and polarization effects, but not for absorption (μ for Mo Kα = 14.3 cm^{-1}). A total of 1922 unique intensities were obtained from the 2787 intensities measured. The unique reflections constitute 50% of those accessible to Cu Kα radiation and they include 377 reflections whose intensities were too weak to measure.

Determination and Refinement of the Structure.[14] The cobalt site was found from the three-dimensional Patterson function and used to compute a first approximation electron density synthesis. The three chlorine sites were readily obtained from this synthesis. The next synthesis phased on the four heavy atoms revealed all the remaining nonhydrogen atoms. Three cycles of full-matrix least-squares refinement varying scale, positional, and isotropic thermal parameters yielded a discrepancy index of the observed reflections, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of 0.144. A number of data errors were corrected at this stage and refinement was resumed using anisotropic temperature factors for the four heavy atoms. A weighting scheme with the weights, $w(F_o) = \sigma^{-2}(|F_o|)$, obtained during data reduction was used. Three cycles of refinement converged with R_1 = 0.098. A difference map was calculated whose highest peak was 0.8 electron/Å^3. The hydrogen atoms were not revealed, but on including them at their calculated positions[15] in the next structure factor calculation, R_1 dropped to 0.094. A refinement cycle with the hydrogen parameters fixed yielded R_1 = 0.091. The corresponding values of $R_2 = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$ for these three R_1 values were 0.101, 0.097, and 0.092. Application of Hamilton's R-factor significance test[16] shows that the inclusion of the hydrogen atoms is significant at the 0.005 level ($\mathcal{R}_{92,1400,0.005}$ = 1.043). The inclusion of the hydrogens had the effect of contracting the carbon–carbon and carbon–nitrogen bond lengths by 0.02–0.06 Å in the two subsequent least-squares cycles. The shifts were less than one-third of the standard deviations in the final cycle. The final structure factor calculation[17] after this cycle was made with recalculated hydrogen positions and gave R_1 = 0.089 and R_2 = 0.086. The error in an observation of unit weight, $\sqrt{\Sigma w(|F_o| - |F_c|)^2/(n - m)}$, was 1.24, where $n - m$ is the excess of reflections over refined parameters. For correctly assigned weights on an absolute scale this quantity is ideally unity. The slightly higher observed value is due to an overweighting of the low angle and high intensity data in the data reduction procedure. The quantity $(\Sigma w(|F_o| - |F_c|)^2)/k$, computed in ranges of k reflections as a function of sin θ/λ and of F_o, is constant at 1 ± 0.3 for both plots except in the low angle (2.0) and high intensity (3.1) ranges. In these ranges F_o tends to be less than F_c, the result most probably of an uncorrected extinc-

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[7] The trivial αβ nomenclature is extended from that used for trien complexes: A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 4, 45 (1965). The tetraen ligand viewed from the two ends has either α,β or *trans* characteristics considering the first four donor atom arrangements. The remaining coordination possibilities β,β and β, *trans* are not reproduced here.

[8] A. M. Sargeson and P. A. Marzilli, private communication.

[9] M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 891 (1969).

[10] M. R. Snow, Proceedings of the XIIth International Conference on Coordination Chemistry, Sydney, 1969, Communication W4.

[11] A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

[12] G. L. Paul, SUFFAC, a FORTRAN IV program for the least-squares determination of film factors, School of Chemistry, University of Sydney, 1966.

[13] SUFFAC was modified to allow for the estimation of standard deviations from the agreement between multiple observations during interfilm scaling. The expression $\sigma^2(I_{hi}) = \Sigma^n(\bar{I}_h/k_i - I_{hi})^2/(n - 1)$ was formed in ranges of log $\bar{I}_h$ where $\sigma(I_{hi})$ is the standard deviation of the raw density of the h reflection on the ith film, k_i is the scale factor to place this density on the scale of the first film, n is the number of intensities in each log $\bar{I}_h$ range, and $\bar{I}_h$ is the mean of the scaled intensities. It was found that these plots could be well fitted by a weighting scheme $w(I_{hi}) = 1/\sigma^2(I_{hi})$, with a four-parameter scheme of the form $\sigma(I_{hi}) = aI_{hi} + b$ (when $I_{hi} \geq c$), and $\sigma(I_{hi}) = d$ (when $I_{hi} < c$). All subsequent corrections to I_{hi} were also applied to $\sigma(I_{hi})$; $w(\bar{I}_h) = \Sigma w(I_{hi})$ and the weighted mean intensity were output.

[14] (a) Computer programs used in solving and refining the structure were as follows: PREPFLS and FOURIER, local modifications of the data packing and Fourier programs of F. R. Ahmed, Division of Pure Physics, NRC, Ottawa; FUORFLS modification of ORFLS (least-squares) by M. R. Taylor, Flinders University of South Australia; BLANDA and PLANET geometry routines by J. F. Blount, University of Sydney; ORTEP plot routine by C. K. Johnson, and ORNL. (b) Source of atomic scattering factors: Co^{2+} and Cl$^-$, P. A. Doyle and P. S. Turner, *Acta Crystallogr.*, **A24**, 390 (1968), $\Delta f'$(Co) and $\Delta f'$(Cl) for Mo Kα radiation were +0.3 and +0.1 electron; O, N, and C, J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202, and H. R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[15] Positions calculated by a modification of PLANET. The hydrogen atoms were placed at the expected electron density maxima appropriate to the scattering curve of Stewart, *et al.*: C–H = 1.02, N–H = 0.95, H–C–H and N–N–H = 109° 28′; for secondary N–H the X–N–H angles were made equal and obtuse.

[16] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[17] Calculated and observed structure factors will be deposited with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022.

Table I. Final Least-Squares Parameters[a]

Atom	x	y	z	B, Å^2
Co	−0.01673 (16)	0.16183 (10)	0.19979 (11)	
Cl_1	−0.05011 (35)	0.30210 (22)	0.10645 (23)	
Cl_2	−0.46152 (36)	0.41213 (25)	0.24635 (25)	
Cl_3	0.01129 (36)	0.39314 (22)	0.39834 (23)	
O_1	−0.4021 (11)	0.3222 (8)	0.3064 (8)	5.06 (23)
O_2	−0.4260 (11)	0.4890 (9)	0.3249 (8)	6.37 (25)
O_3	−0.6230 (13)	0.4046 (9)	0.1800 (9)	6.65 (27)
O_4	−0.3921 (12)	0.4304 (9)	0.1795 (9)	6.25 (26)
N_1	0.1462 (10)	0.1209 (7)	0.1651 (7)	2.58 (18)
N_2	0.1545 (10)	0.2195 (8)	0.3334 (7)	2.38 (20)
N_3	0.0136 (11)	0.0478 (8)	0.2920 (7)	2.55 (20)
N_1'	−0.1800 (10)	0.1019 (7)	0.0649 (7)	2.11 (19)
N_2'	−0.1876 (10)	0.2005 (7)	0.2290 (7)	2.25 (18)
C_1	0.2956 (16)	0.1723 (13)	0.2355 (12)	5.26 (36)
C_2	0.2861 (16)	0.2408 (12)	0.3137 (11)	4.71 (32)
C_3	0.1973 (13)	0.1552 (10)	0.4319 (9)	2.78 (24)
C_4	0.1669 (13)	0.0522 (9)	0.3957 (9)	2.76 (24)
C_1'	−0.3382 (15)	0.1070 (11)	0.0584 (10)	3.54 (29)
C_2'	−0.3347 (12)	0.1971 (9)	0.1247 (9)	2.87 (23)
C_2'	−0.1843 (12)	0.1360 (9)	0.3161 (9)	2.30 (22)
C_4'	−0.1198 (15)	0.0372 (11)	0.3135 (10)	3.11 (28)
N_1'–H_1[b]	−0.1857	0.1346	0.0029	4.0
N_1'–H_2	−0.1540	0.0359	0.0634	4.0
N_1–H_1	0.1124	0.1348	0.0898	4.0
N_1–H_2	0.1626	0.0532	0.1773	4.0
N_2'–H	−0.1698	0.2652	0.2556	4.0
N_3–H	0.0145	−0.0075	0.2518	4.0
N_2–H	0.1185	0.2794	0.3462	4.0
C_1'–H_1	−0.4244	0.1136	−0.0218	5.0
C_1'–H_2	−0.3569	0.0463	0.0919	5.0
C_2'–H_1	−0.3450	0.2578	0.0799	5.0
C_2'–H_2	−0.4252	0.1940	0.1406	5.0
C_3'–H_1	−0.2950	0.1282	0.3033	5.0
C_3'–H_2	−0.1158	0.1667	0.3916	5.0
C_4'–H_1	−0.2051	−0.0034	0.2523	5.0
C_4'–H_2	−0.0824	0.0036	0.3876	5.0
C_4–H_1	0.2528	0.0272	0.3815	5.0
C_4–H_2	0.1634	0.0109	0.4553	5.0
C_3–H_1	0.1318	0.1737	0.4675	5.0
C_3–H_2	0.3126	0.1638	0.4879	5.0
C_2–H_1	0.2726	0.3091	0.2824	6.5
C_2–H_2	0.3876	0.2370	0.3872	6.5
C_1–H_1	0.3255	0.2099	0.1856	6.5
C_1–H_2	0.3796	0.1222	0.2795	6.5

Anisotropic Thermal Parameters[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.00876 (26)	0.00087 (9)	0.00252 (10)	0.00004 (12)	0.00307 (12)	−0.00025 (8)
Cl_1	0.01659 (58)	0.00143 (17)	0.00482 (23)	0.00038 (25)	0.00553 (29)	0.00076 (16)
Cl_2	0.01158 (57)	0.00377 (22)	0.00524 (23)	−0.00123 (27)	0.00494 (30)	−0.00058 (20)
Cl_3	0.01692 (59)	0.00201 (19)	0.00440 (22)	0.00045 (25)	0.00573 (29)	0.00007 (17)

[a] The estimated standard deviations are given in parentheses in this and succeeding tables. [b] The hydrogen atomic positions were recalculated after the last least-squares cycle. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Bond Lengths in the Crystal

Co–N_1	1.972 (10)	N_1–C_1	1.486 (22)	C_1–C_2	1.478 (24)
Co–N_2	1.961 (10)	N_2–C_2	1.480 (19)	C_3–C_4	1.488 (19)
Co–N_3	1.958 (10)	N_2–C_3	1.509 (16)	C_1'–C_2'	1.538 (20)
Co–N_1'	1.955 (10)	N_3–C_4	1.490 (16)	C_3'–C_4'	1.513 (19)
Co–N_2'	1.988 (10)	N_3–C_4'	1.491 (18)	Av[a]	1.504 (14)
Av[a]	1.967 (6)	N_1'–C_1'	1.518 (18)	Cl_2–O_1	1.449 (12)
Co–Cl_1	2.263 (3)	N_2'–C_2'	1.461 (16)	Cl_2–O_2	1.438 (12)
		N_2'–C_3'	1.491 (16)	Cl_2–O_3	1.395 (12)
		Av[a]	1.491 (6)	Cl_2–O_4	1.422 (12)
				Av[a]	1.426 (10)

[a] Average for each bond type with standard deviation calculated from internal agreement.

tion effect. This is not expected to significantly affect the positional coordinates. The final fractional atomic coordinates and thermal parameters are listed in Table I. Tables II–IV contain the important bond length, bond angle, and intermolecular contact data.

Description of the Structure

In the crystal the complex cations are arranged so that their Co–Cl bonds are perpendicular to the *a* axis. The cations are held together by electrostatic interactions and hydrogen bonds to the chloride and perchlorate anions. The crystal is anhydrous. There are no vectors shorter than 3.5 Å between nonhydrogen atoms of different cations, but there are a number of such anion to cation vectors. The first three of these (Table IV) are chloride (Cl_3)–nitrogen hydrogen bonds bonding the chloride ion to an octahedral face of the complex. The three N–H groups are those of the uppermost octahedral face in Figure 2, Cl_3 lies directly above Co and was omitted for clarity. The Cl_3 to N and Cl_3 to H distances of Table IV lie well within the

Table III. Comparison of Bond Angles in the Crystal with Those Calculated by Energy Minimization

Atoms	Crystal angle, deg	Calculated set 1 parameters[a]	Calculated set 2 parameters[a]
Cl$_1$–Co–N$_1$	90.6 (3)	88.8	90.0
Cl$_1$–Co–N$_2$	90.6 (3)	90.4	89.9
Cl$_1$–Co–N$_3$	174.61 (3)		
Cl$_1$–Co–N$_1$′	89.6 (3)	90.0	90.1
Cl$_1$–Co–N$_2$′	89.4 (3)	88.3	90.1
N$_1$–Co–N$_2$	85.7 (4)	87.4	88.0
N$_2$–Co–N$_3$	85.6 (4)	88.4	88.3
N$_3$–Co–N$_2$′	87.3 (4)	88.6	88.3
N$_1$′–Co–N$_2$′	86.0 (4)	87.4	87.9
N$_3$–Co–N$_1$	94.4 (4)	92.1	91.7
N$_3$–Co–N$_1$	92.9 (4)	94.4	91.6
N$_2$–Co–N$_2$′	96.7 (4)	95.6	93.9
N$_1$–Co–N$_1$	91.6 (4)	89.5	90.2
Co–N$_1$–C$_1$	111.3 (9)	110.5	109.8
N$_1$–C$_1$–C$_2$	112.9 (13)	109.3	109.7
C$_1$–C$_2$–N$_2$	112.8 (13)	110.4	110.6
C$_2$–N$_2$–C$_3$	114.0 (10)	113.5	112.7
N$_2$–C$_3$–C$_4$	109.6 (10)	110.3	110.8
C$_3$–C$_4$–N$_3$	107.8 (10)	110.3	110.7
C$_4$–N$_3$–C$_4$	112.5 (9)	113.4	112.3
N$_3$–C$_4$′–C$_3$′	109.8 (10)	111.1	110.7
C$_4$′–C$_3$′–N$_2$′	111.0 (10)	111.1	110.7
C$_3$′–N$_2$′–C$_2$′	113.7 (9)	113.9	112.6
N$_2$′–C$_2$′–C$_1$′	109.9 (10)	110.0	110.5
C$_2$′–C$_1$′–N$_1$′	106.4 (10)	108.7	109.8
C$_1$′–N$_1$′–Co	111.9 (8)	110.1	109.9
Co–N$_2$–C$_2$	109.2 (8)	106.4	106.0
Co–N$_2$–C$_3$	110.3 (7)	108.9	109.1
Co–N$_3$–C$_4$	110.9 (7)	107.4	108.3
Co–N$_3$–C$_4$′	110.2 (7)	108.6	108.0
Co–N$_2$′–C$_2$′	108.3 (7)	106.2	105.9
Co–N$_2$′–C$_3$′	108.9 (7)	108.9	109.2
	Angles within the Perchlorate Ion		
O$_1$–Cl$_1$–O$_2$	108.4 (4)	O$_2$–Cl$_1$–O$_3$	109.3 (4)
O$_1$–Cl$_1$–O$_3$	108.9 (4)	O$_2$–Cl$_1$–O$_4$	110.5 (4)
O$_1$–Cl$_1$–O$_4$	110.0 (4)	O$_3$–Cl$_1$–O$_4$	109.8 (4)

[a] See Table V.

Table IV. Important Intermolecular Contacts (to 3.5 Å) in the Crystal[a]

Atoms X···H–Y		Atoms Y–H···X		X–Y distance, Å	X···H distance, Å[b]
Cl$_3$	N$_1$ (1)	N$_1$	Cl$_3$ (IV)	3.42	2.6
Cl$_3$	N$_3$ (I)	N$_3$	Cl$_3$ (IV)	3.32	2.4
Cl$_3$	N$_1$′ (I)	N$_1$′	Cl$_3$ (IV)	3.24	2.3
O$_1$	C$_1$ (II)	C$_1$	O$_1$ (V)	3.35	2.8
O$_1$	C$_2$ (II)	C$_2$	O$_1$ (V)	3.32	3.0
O$_2$	N$_1$ (I)	N$_1$	O$_2$ (IV)	3.25	2.8
O$_2$	C$_1$ (I)	C$_1$	O$_2$ (IV)	3.13	2.5
O$_3$	C$_1$ (II)	C$_1$	O$_3$ (V)	3.48	2.7
O$_3$	C$_2$ (II)	C$_2$	O$_3$ (V)	3.32	2.4
O$_3$	C$_4$′ (III)	C$_4$′	O$_3$ (VI)	3.16	2.6
O$_4$	C$_4$ (I)	C$_4$	O$_4$ (IV)	3.34	2.3

[a] Transformations are (I) $-x, \frac{1}{2} + y, \frac{1}{2} - z$, (II) $-1 + x, y, z$; (III) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (IV) $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; (V) $1 + x, y, z$; (VI) $-1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$. [b] Only the shortest of the possible X···H distances are given.

ranges (3.15 to 3.51 Å and 2.17 to 2.82 Å) established by neutron diffraction[18] for hydrogen bonds with these atoms. This trigonal hydrogen bonded system is the first solid state example of a model proposed to account for the circular dichroism spectra of (+)tris(ethylenediamine)cobalt(III) gegenion solutions[19] as well as ion-pair association constants with optically active anions.[20] The most stable ion pairs are formed with (+)Co(en)$_3$$^{3+}$ (lel conformation[1]), in which the N–H bonds parallel the C$_3$ axis in a manner resembling that here, rather than with the (−)Co(en)$_3$$^{3+}$ ion, where the N–H bonds are oblique to the C$_3$ axis.

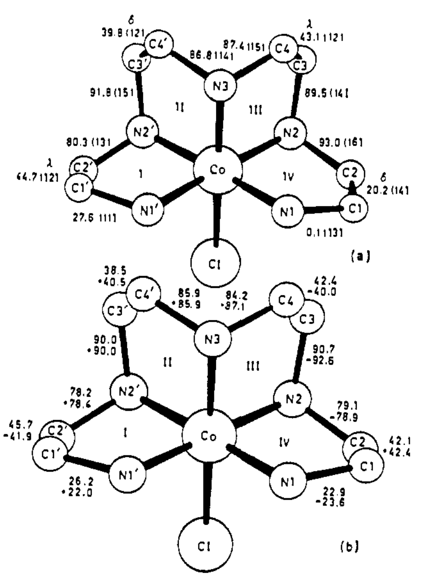

Figure 1. Comparison of the $\alpha\alpha$-chlorotetraethylenepentaminecobalt(III) ion as found in the crystal (a) and calculated for the gas phase (b). The torsion (dihedral) angle about the C–C and C–N bonds are given[21] with the proposed IUPAC symbol for the configuration of each chelate ring.[22] In (b) the angles calculated with set 1 parameters appear above those with set 2 parameters (Table V) and share the same signs.

The remaining close contacts in Table IV all involve perchlorate oxygens. These interactions are all repulsive as judged by the nonbonded potential functions given in Table VI. (For this comparison nitrogen functions can safely be used for oxygen.) Except for the O$_3$–C$_4$′ contact the remainder are all centered on chelate rings III and IV of the complex (Figures 1a and 2; see ref 21, 22). The effect of these repulsive contacts is to distort these chelate rings, particularly ring IV as compared with ring I. That these distortions are due to packing is shown by comparison with Figure 1b, the energy minimized conformation calculated for the gas state (see below).

Conformational Analysis

The conformational energy of the isomer was computed by the strain energy formalism.[2,3] The strain energy, U, was taken as a summation over the relevant internal coordinates with four energy types

$$U = \Sigma(E_r + E_\theta + E_\phi + E_{\mathrm{nbd}}) \qquad (1)$$

These represent bond length distortion strain, bond angle distortion strain, torsional energy of rotation

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(18) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin Inc., New York, N. Y., 1968, p 263.

(19) S. F. Mason and B. J. Norman, *J. Chem. Soc., A*, 307 (1966).

(20) K. Ogino, *Bull. Chem. Soc. Jap.*, **42**, 447 (1969).

(21) The torsion angles are defined as follows. Traveling around the ligand chain from N$_1$′ to N, the torsion angle formed by the atoms A, B, C, and D is the angle which the ABC plane is rotated from the BCD plane. The angle is positive when the AB bond must be rotated clockwise to lie on the BCD plane: W. Klyne and V. Prelog, *Experientia*, **16** 521 (1960); F. H. Allen and D. Rogers, *Acta Crystallogr.*, **B25**, 1326 (1969).

(22) IUPAC Information Bulletin Number 33, 1968, p 68. The chelate ring conformations are assigned for an arbitrary absolute configuration since the crystal has a center of symmetry.

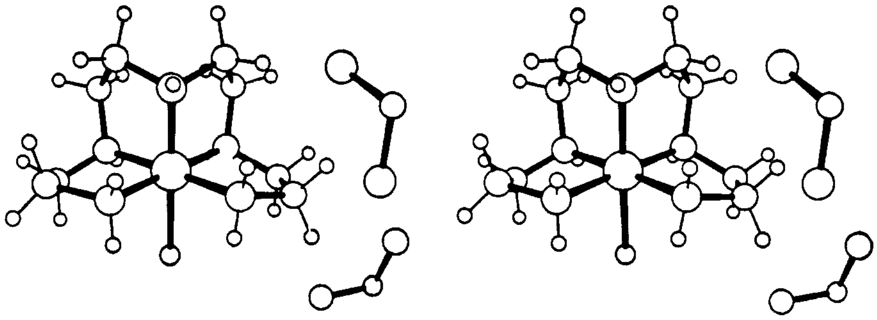

Figure 2. Stereo pair of $\alpha\alpha$-chlorotetraethylenepentaminecobalt(III) ions showing interactions of (partial) perchlorate ions with rings I and II of the complex ions. The oxygens shown are O_4, O_2, O_1, and O_3, from top to bottom.

about bonds, and nonbonded interactions, respectively.

Since the number of terms contributing to the strain energy is potentially large,[23] efficient practical application of the method depends on choosing a partial, but adequate force field. The majority of the possible interactions are of the E_{nb} type,[23] and these were reduced in three ways.

(i) The geminal 1,3 nonbonded interactions of the polyamine ligand were omitted. These interactions between atoms bonded to the same atom are strongly repulsive,[24] though they tend to balance each other about the tetrahedral centers. If the molecule is not highly strained neglect of these terms should not be serious. The use of harmonic bond angle bending functions (see below) should result in an underestimation of the strain energy on closure of the angle and an overestimation on bond angle opening from the strain-free position. The results of this and other studies on metal complexes have not so far shown any marked trends of this type.[9,25,26] The N···N and N···Cl interactions about the cobalt ion were included in the force field.

(ii) The longer range nonbonded interactions were omitted when the criterion $[d_{ij} - p(w_i + w_j)] > 0$ was met. Here d_{ij} is the distance apart of the ith and jth atoms, w_i is the van der Waals radius,[27] and p is a factor taken equal to 1.16. This value of p serves to omit through-bond and through-atom interactions in polyamine complexes as well as reduce the large number of very weakly attractive terms.

(iii) No nonbonded interactions involving the cobalt ion were included.

All possible bond angle terms were included with the exception of those for linear X–Co–X situations. A program was written in FORTRAN IV to find and code the potential functions for these E_{nb} and E_θ terms as well as all possible E_r terms for the energy minimization procedure. Input consisted of a bonding connection matrix, atomic coordinates (either fractional crystal coordinates and cell data or orthogonal coordinates), and the unique potential function parameters. Some 268 interactions were found in this way and the possibility of overlooking important interactions by manual searching was eliminated. The torsional energy terms, E_ϕ, were included only for rotations about the ligand skeleton bonds. The 12 terms of this type were manually added to the previous list bringing the total number of interactions to 280.

Minimization Procedure. In Boyd's procedure[3] the strain energy, $U(r, \theta, \phi, d)$, is expanded about the equilibrium strain energy, $U'(r', \theta', \phi', d')$, in a Taylor series. Representing the t internal coordinates by the general symbol c_i

$$U_c = U'_{c'} + \sum_{i=1}^{t} \frac{\partial U}{\partial c_i}\delta c_i + \frac{1}{2} \sum_{i=1}^{t} \frac{\partial^2 U}{\partial c_i^2}\delta c_i^2 \qquad (2)$$

where cross terms have been neglected and $c_i' = c_i + \delta c_i$. Transformation to Cartesian coordinates, $g_i(1 \leq i \leq 3q)$, and application of the necessary condition for a minimum (or maximum) in U', $\partial U'/\partial g_i = 0$, to eq 2 gives $3q$ equations of the type

$$\left.\frac{\partial U'}{\partial g_i}\right|_{g_{i'}} = \left.\frac{\partial U}{\partial g_i}\right|_{g_{i'}} + \left.\sum_{j=1}^{3q} \frac{\partial^2 U}{\partial g_i \partial g_j}\delta g_i\right|_{g_{i'}} = 0 \qquad (3)$$

These equations ($A = C\delta_g = 0$ in matrix notation) are linear in the shifts, $\delta g = g_i' - g_i$, and may be solved after removing six equations to prevent rotation and translation of the molecule. From three to ten iterations of eq 3 were found necessary to reach the equilibrium conformation since eq 2 is only approximate. Convergence to the equilibrium conformation was judged by the root mean square of the shifts of the coordinates, $\sqrt{\Sigma_i \delta g_i / 3q}$. A value less than 0.005 Å was taken to indicate convergence. The rms shifts were rather high in the early cycles and tended to oscillate (*e.g.*, 0.43, 0.1, 0.45, 0.16, 0.29, 0.04, 0.02, 0.0003). In the calculation with the $\alpha\alpha$ isomer of tetraethylenepentaminecobalt(III) chloride the crystal coordinates were used as the trial starting coordinates and the possibility of obtaining a conformation away from the true minimum was real. The calculations were repeated using partial shifts, δg(applied) = 0.25 δg(calculated), and the identical conformation resulted. For a cycle of minimization, calculation of the derivatives and shifts (eq 3) required 14 sec of CDC 6400 time to which 11 sec must be added if the strain energies of the interactions are also computed.

Energy Functions

Bond Stretch and Bend. The bond angle and bond length distortions were represented by harmonic ap-

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(23) For complexes with q total atoms and central coordination number r formed from noncyclic ligands with s four-covalent skeleton atoms the number of interactions of each type will be $E_r + E_{\text{nba}} = q(q - 1)/2$, $E_\theta = [6s + r(r - 1)/2]$, $E_\phi = (s - 1 + r)$. For chlorotetraethylenepentamine isomers of cobalt(III) where $q = 38$, $r = 6$, and $s = 13$, 814 interactions are possible.

(24) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(25) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

(26) K. R. Butler, P. F. Crossing, and M. R. Snow, unpublished calculations on tris-substituted (ethylenediamine)cobalt(III) complexes.

(27) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

proximations of the form $E(c) = {}^1/_2A(c - B)^2$; $c = r$ or θ, where A is a Urey–Bradley force constant, and B is the value of c in the absence of the force field, *i.e.*, a strain-free value. For the ligand bonds B was set equal to the average bond length for each bond type in the crystal (C–C, C–N, Table III) or the internuclear separation (C–H, N–H).[28] The absences of geminal nonbonded interactions in the ligand force field results in only a very slight strain in these bonds. This was confirmed for the C–N and C–C bonds where equilibrium values on minimization were only from 0.005 to 0.01 Å greater than the strain-free parameters. For the cobalt–nitrogen bond, however, considerable strain developed whether or not the geminal N···N or N···C nonbonded interactions were included. For these bonds B was set 0.05 Å less than the calculated equilibrium Co–N bond length, using the force constant derived for hexaminocobalt(III) salts[29] to reproduce the average observed bond length of the $\alpha\alpha$ isomer (1.97 Å). The unstrained bond angles were assigned standard tetrahedral or octahedral values as appropriate. Two sets of bond angle force constants were used (Table V); for both sets the N–C–X (X = C or H) bonding constants were set equal to those for C–C–X.

Table V. Force Constants[a]

Interaction	Parameters *A*	*B*	Ref
	Bond Length[b]		
Co–N	2.0, 1.7	1.925	29
Co–Cl	1.41	2.20	29
C–N	6.0	1.49	*c*
C–C	5.0	1.50	*d*
C–H	5.0	1.09	*d*
N–H	5.64	1.03	29
	Bond Angle[b]		
Co–N–H	0.2	1.911	*c*
Co–N–C	0.2, 0.4	1.911	*c*
N–Co–N	0.05, 0.68	1.571	*c*, 29
N–Co–Cl	0.05, 1.00	1.571	*c*, 29
H–C–H	0.32, 0.52	1.911	*d, e*
H–N–H	0.53	1.911	29
H–C–C	0.55, 0.65	1.911	*d, e*
N–C–C	0.80, 1.00	1.911	*d, e*
N–C–H	0.55, 0.65	1.911	*d, e*
C–N–H	0.55, 0.65	1.911	*d, e*
	Torsional		
C–C	2.48		30
C–N	1.58		30

[a] Functions used are given in the text. The energy units are all appropriate to erg/molecule. Thus the A parameters are in mdyn/Å and the B parameters are in Å and radians for bond length and angle terms, respectively. [b] Two sets of calculations were carried out: the left-hand A column is force field 1; the right hand is force field 2, which differs from force field 1 only where a second number is given. [c] Estimate. [d] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, New York, N. Y., 1956, Chapter 12. [e] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

Torsion. The energy terms involved in twisting about bonds in the ligand skeleton were deduced from the experimental barriers to rotation[30] in ethane, 2.88, and methylamine, 1.98 kcal/mol^{-1}. Following Scheraga[31] the barrier was considered to be of two parts, nonbonded and quantum mechanical components of the form

$$E_\phi = E_{\text{nb}} + {}^1/_2A(1 + \cos 3\phi)$$

where A is that part of the experimental barrier not accounted for in E_{nb} and ϕ is the torsion angle measured from the eclipsed configuration as zero. Calculations for ethane using the parameters of Tables V and VI (set 1 of bending parameters) showed the E_{nb} term to be 0.4 kcal/mol^{-1}. For the coordinate bonds the situation is very complex and experimental barriers are not available. For a Co–N bond a threefold set of atoms on N rotates over a fourfold set on Co. If the atoms within the fourfold set can be regarded as equivalent the total torsional energy can be written[32] as

$$E_\phi = E_{\text{nb}} + \sum_{i=1}^{3} \frac{1}{2}A_i[1 + a_i \cos 4(\phi + k) + b_i \cos 8(\phi + k) + c_i \cos 12(\phi + k)]$$

where $k = (i - 1)120°$ and A_i is the barrier to rotation of the ith bond of the threefold set over the fourfold set. For hexaminocobalt(III), where the atoms within both sets are equivalent, this expression reduces to

$$E_\phi = E_{\text{nb}} + \frac{3}{2}A[1 + 3c(\cos 12\phi)]$$

This 12-fold barrier must be small in hexaminocobalt(III) since Kim[33] has presented solid state nmr evidence that the ammonia ligands are freely rotating at temperatures below 20°K. In other situations these barriers may be significant. In this study only E_{nb} has been included and the results suggest that the excluded terms are not important in determining isomer geometry.

Table VI. Nonbonded Interaction Parameters[a]

Atoms	$A \times 10^{-3}$	B	C	d_{min}, Å	d_{contact}, Å	Ref
H–H	6.6	4.08	49.2	2.97	2.40	*b*
H–C	31.4	4.20	121.1	3.15	2.90	*b*
H–N	28.1	4.32	99.2	3.03	2.75	*b*
H–Cl	33.8	3.85	265.0	3.33	2.95	*c*
C–C	237.0	4.32	297.8	3.50	3.40	*b*
C–N	212.1	4.44	244.0	3.37	3.25	*b*
C–Cl	230.0	3.96	652.0	3.68	3.45	*c*
N–N	186.4	4.55	200.0	3.27	3.10	*b*
N–Cl	213.0	4.06	534.0	3.57	3.30	*b–d*

[a] Buckingham function, $E_{\text{nb}} = A\exp(-Bd) - C/d^6$. d_{min} is the minimum of this funtion and d_{contact} is the mean of contact distances observed in crystals.[27] [b] A. M. Liquori, A. Damiani, and G. Elefante, *J. Mol. Biol.*, **33**, 439 (1968). [c] J. L. De Coen, A. M. Liquori, A. Damiani, and G. Elefante, *Nature*, **216**, 910 (1967). [d] From the geometric means of the parameters of the Cl–Cl (see footnote *c*) and N–N functions.

Nonbonded Energies. A great many functional forms and associated parameters have been used in conformational analysis to represent these energies.[2,5,6] The majority of authors agree that these functions should contain repulsive and attractive terms and

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(28) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 270 and 276.

(29) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 1707 (1966).

(30) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

(31) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

(32) The procedure for the Fourier expansion is due to E. Tannerbaum, R. J. Myers, and N. D. Gwinn, *ibid.*, **25**, 42 (1956).

(33) P. H. Kim, *J. Phys. Soc. Jap.*, **15**, 445 (1960).

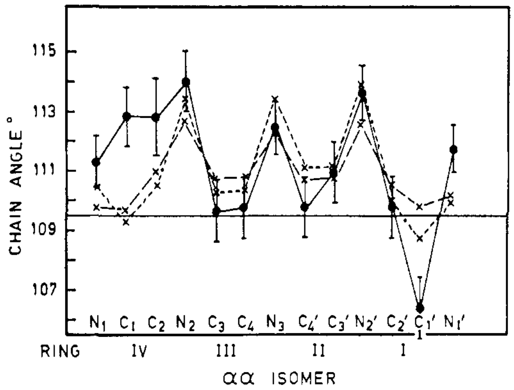

Figure 3. Plot of the bond angles in the ligand skeleton of the αα-chlorotetraethylenepentaminecobalt(III) ion at the indicated atoms: (a) in the crystal (—), (b) calculated for the gas phase with force set 1 (----), and (c) force set 2 (- -) of Table V.

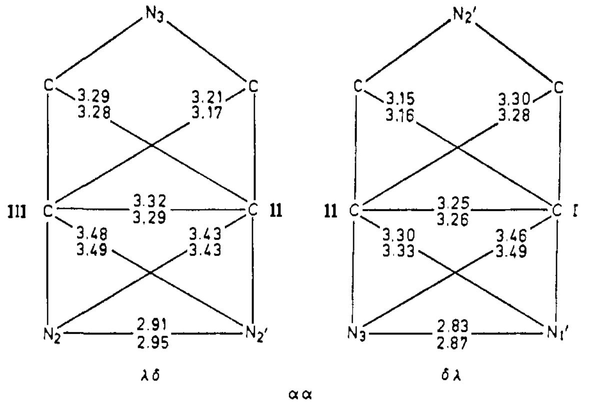

Figure 4. Comparison of the intraligand nonbonded distances (Å) between chelate rings III and II and between II and I. The crystal distances appear above those calculated using force set 1 of Table V.

therefore an overall minimum. The division of the available curves into hard and soft types has recently been criticized[2] on the grounds that this division will not necessarily be so for the complete range of the functions. Many of these competing functions have very similar and relatively flat shapes near their minima. The position of these minima would appear therefore to be the most important factor in choosing a function, especially since only the first and second derivatives of the functions are used in determining the equilibrium geometry. The problem of locating this minimum has been discussed by Brant[34] who concludes that the sum of the van der Waals contact radii in crystals sets a lower limit in d and that it should lie 0.2 Å above this value. Comparison of the $d_{\min}$ and van der Waals constant distances in Table VI shows that the former exceed the latter by from 0.1 (C–C) to 0.57 Å (H–H). These differences generally decrease with the repulsive exponent B of the potential function, consistent with the expectation that the least compressible atoms will have their minima closest to their crystal contact distances. Very few of the nonbonded interactions included in minimization lie away from the flat region of the minimum. The geometry of the complex will therefore not be greatly affected by the detailed parameters since the first and second derivatives will be very slowly changing in this region. This conclusion would not hold so well for the relative strain energy of a series of isomers unless considerable cancellation of like terms occurred.

Results and Discussion

The distortion of ring IV of the complex (Figure 1) caused by the lattice makes a strict comparison of the crystal and energy minimized geometry difficult. The packing distortion is manifest not only in the geometry of the immediately affected area, but also in a perturbation of the remainder of the molecule *via* coupled interactions. Use of the smaller force constants of set 1 (Table V) yields a better correlation of crystal and energy minimized geometry (Figures 1, 3, and 4 and Table III). These comparisons all indicate the absence of a mirror plane in the complex, and also that deviations from mirror symmetry are greater with force constant set 1. These force constants give excellent agreement for the intraligand nonbonded distances in the undistorted region (Figure 4). A similar comparison using set 2 force constants shows almost mirror symmetry for rings II and III and larger deviations from crystal values, while the II–I distances are very similar to those given in Figure 4. The largest nonbonded interactions are between hydrogen atoms and are shown in Table VII.

Table VII. Hydrogen Nonbonded Interactions Greater than 0.35 kcal/mol

Rings	Atoms	Distance, Å, and energy, kcal/mol Set 1 parameters	Set 2 parameters
I–II	$C_1'H_2$ $C_4'H_1$	2.10 (0.67)	2.08 (0.76)
III–IV	C_1H_2 C_4H_1	2.11 (0.66)	2.07 (0.77)
II–III	$C_4'H_2$ C_4H_2	2.22 (0.36)	2.18 (0.44)
II–III	$C_3'H_2$ C_3H_1	2.17 (0.47)	2.11 (0.64)

The range of the Co–N bond lengths was 1.965 to 1.971 Å for calculations with both sets of force constants. This range, 0.006 Å, is less than a typical standard deviation and no correlation with observed distances was found. The mean bond lengths in Table II are closely comparable with those of recently determined polyamine cobalt(III) complexes.[35,36] The angles at the cobalt ion are not well reproduced by calculations with either force field set (Table III). There is a distinct tendency for the N–Co–N angles within a chelate ring to be overcalculated and for the N–Co–N angles outside chelate rings to be undercalculated. Such a result would appear to indicate that the effective N–Co–N force constant was too high. The correlation was not improved by removing the N···N and N···Cl nonbonded interactions from calculations with force constant set 2. These interactions are repulsive (0.04–0.4 kcal), and although they serve to effectively increase the N–Co–N force constant, the complete set of bond angles calculated did not differ by more than 0.4° from the previous calculation with them included in the force field. In complexes where there is little lattice distortion, these angles are well represented by calculations with set 2 parameters whether or not the N···N nonbonded

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[34] D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.*, 23, 47 (1967).

[35] H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, 8, 1293 (1969), and references therein.

[36] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, 7, 1362 (1968).

interactions are included.[25,37] It would appear therefore that the N···N-type interactions are not essential to the force field and that in this case the poorer agreement is connected with the effects of lattice distortion. The angles in the ligand skeleton (Figure 3, Table III), apart from the distorted ring IV, are reproduced to within 0–2 standard deviations of the crystal values by both force fields. The calculation with set 1 force constants again has a better correlation, though for less crystal distorted complexes[37] better correlation is obtained using set 2. Both calculated and observed angles show that most angular strain occurs at the secondary nitrogen atoms where the ligand is turning from one chelate ring to the next. Bond angles of the types X–Y–H and H–X–H have a range 106.5–110.5°, with the vast majority very close to 109.5°. The lowest values are associated with the H–C–H angles of C_3, C_4, C_3', C_4'; not surprisingly these are the hydrogen atoms with the strong repulsive contacts in Table VII. This result justifies the procedure for adding the hydrogen atoms to the X-ray structure factor calculation.

The total strain energy of the complex ion at equilibrium was 20.21 (set 1), 20.93 (set 2), and 18.05 (set 2 omitting N···N and N···Cl nonbonded interactions) kcal/mol. This last strain energy is made up of E_r (1.08), E_θ (2.24), E_ϕ (7.7), and E_{nb} (7.02 kcal/mol) terms, of which the last two are most important. The distorted complex in the crystal has an energy of approximately 2.5 kcal/mol above the minimized strain energy calculated above. The major term is the unfavorable bond torsion energy (1.8 kcal/mol) of the envelope ring conformation. The usefulness of the strain energies in determining equilibria between isomers of metal complexes will be discussed elsewhere.[25,37]

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[37] The $\alpha\beta S$ and $\alpha\beta R$ isomers of chlorotetraethylenepentaminecobalt(III): M. R. Snow, manuscript in preparation.

Prediction of Molecular Geometries and Relative Stabilities in Chelate Complexes. Application to Cobalt(III) Triethylenetetramine-(*S*)-prolinato Complexes

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Adelaide, South Australia 5000. *Received November 7, 1969*

Abstract: The technique of conformational potential energy minimization has been successfully applied to a series of β-[Co(trien)(*S*-Pro)]$^{2+}$ complexes (trien = triethylenetetramine, *S*-Pro = L-proline). A general force field has been used including contributions from nonbonded interactions, bond angle bending, torsional potentials, and bond stretching. A modified Newton–Raphson method of minimization, due to Boyd, has been used to vary all the independent coordinates simultaneously. This method is superior to steepest descents techniques in that the parameter shifts are calculated directly. The calculated geometries of these strained molecules agree very well with the geometries obtained from crystal structure analysis studies. The method has been particularly successful in reproducing major angular distortions and the detailed conformations of the puckered chelate rings. Predicted energy differences between the isomers have been found to be in good agreement with experiment. The geometries and relative stabilities of other related isomers are predicted.

Although the techniques of minimization of conformational potential energy have been used for some time in organic chemistry it is only recently with the availability of high speed digital computers that the minimization techniques have greatly improved.[2–5] A parallel improvement has occurred in our knowledge of potential functions particularly for bond length and angular deformation force constants. However, throughout this development at no stage have cooperative minimization techniques been applied to inorganic structures, although some studies have been made on the conformational analysis of chelate systems.

The pioneering work of Mathieu[6] and Corey and Bailar[7] on chelate ring conformations indicated the importance of nonbonded interactions as a factor in determining isomer stabilities, and this was later supported by similar simple calculations and equilibrium measurements.[8] One of the problems in these studies

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[2] (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

[3] M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

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[5] R. H. Boyd, *ibid.*, **49**, 2574 (1968).

[6] J. P. Mathieu, *Ann. Phys.* (Paris), **19**, 335 (1944).

[7] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[8] A. M. Sargeson, "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1966, p 303.