The chemical shifts of the resonances are quite sensitive to solvent properties.[14] Hence one notes that the positions of the resonances at high temperatures are not exactly those of the weighted averages of the low-temperature resonances. This limits the accuracy with which one can calculate exchange rates from the line shapes; however, the changes are not so severe that one cannot obtain approximate activation energies using the Kubo–Sack matrix method for line-shape analysis.[15] For complex I the activation parameters for the rate of conversion of one conformation to the other were determined by matching the experimental and computed line shapes of the cyclopentadienyl resonances over a temperature range of -5.5 to $+9.5°$ for seven points and gave a value of $E_a = 12.3 \pm 1.2$ kcal/mole and $\log A = 10.6 \pm 1.0$. The methyl resonance line shape for the methallyl complex (II) was used to determine both the relative populations and the rates. A least-squares fit of five points[16–19] between 13.5 and 54.5° gave $E_a = 16.8 \pm 0.4$ kcal/mole and $\log A = 14.5 \pm 0.3$. These activation parameters for configurational interchange without *syn–anti* exchange may be compared with activation energies of 9 to approximately 20 kcal/mole for *syn–anti* exchange through a σ-bonded intermediate[20] for compounds of the form $L_2Cl_2Rh(\pi\text{-}C_4H_7)$.[21,22] We therefore conclude that opposing steric factors require that A predominate in the π-allyl complex and conformer B predominate in the π-methallyl complex. The apparently greater activation energy for the π-methallyl complex indicates further steric interactions in the transition state during interconversion of conformers.[23–25]

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[14] The chemical shift of the *anti*-proton resonance for II is highly solvent dependent: in CS_2 the major *anti* resonance is 0.10 ppm downfield from the major methyl resonance, and in C_2Cl_4 it is 0.03 ppm downfield at low temperature and merges into the methyl resonance as the temperature is raised.

[15] R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958). We are indebted to Professor Martin Saunders for supplying a computer program which carried out the matrix manipulations.

[16] Use of the *anti*-proton resonances was less reliable owing to impurity interference,[17] but it gave $E_a = 14.5 \pm 1.8$ kcal/mole and $\log A = 12.5 \pm 1.3$ and a population ratio of 14.5:1 (compared to 16:1 from the methyl resonance). The solvent dependence of the chemical shifts in these compounds makes all of the activation energy calculations somewhat less reliable than normal; nevertheless, it is felt that the difference between the π-allyl and the π-methallyl compounds is significant. We have assumed that the equilibrium constant for the interconversion of conformers is independent of temperature. This should be valid on the basis of the low-temperature behavior of both the palladium and molybdenum complexes and has also been noted in nickel–allyl complexes.[18] Considering the uncertainties and magnitudes which one expects in these E_a calculations, the values of ΔH (assuming $\Delta S \sim 0$) of 0.6 and 1.6–1.8 kcal/mole, respectively, for the allyl- and methallyl-molybdenum complexes suggest that the energy profile is effectively symmetric, such that E_a was obtained from the observed rates.

[17] Difficulty in obtaining π-allylic complexes free from impurities has been noted elsewhere.[19]

[18] H. Boennemann, B. Bogdanovic, and G. Wilke, *Angew. Chem.*, **79**, 817 (1967).

[19] C. A. Reilly and H. Thyret, *J. Amer. Chem. Soc.*, **89**, 5144 (1967).

[20] K. Vrieze and H. C. Volger, *J. Organometal. Chem.* (Amsterdam), **9**, 537 (1967).

[21] We have noted in experiments similar to those of Becconsall and O'Brien[22] that in bis(π-methallyl)palladium the temperature dependence is due to both *syn–anti* and conformational interchanges and that the line shapes could not be matched by considering the effect of a σ-bonded intermediate mechanism alone. The decomposition occurring in the palladium system makes any definitive conclusions difficult.

[22] J. K. Becconsall and S. O'Brien, *J. Organometal. Chem.* (Amsterdam), **9**, 27 (1967).

[23] The methallyl–molybdenum complex was a yellow solid which melted to an oil above room temperature and was prepared by a method similar to that for the allyl complex.[24]

[24] M. Green and M. Cousins, *J. Chem. Soc., Sect. A*, 889 (1963).

[25] We are indebted to the Climax Molybdenum Corp. for a gift of molybdenum carbonyl, the Petroleum Research Fund for financial support, and the National Science Foundation for the departmental grant which supplied the HA-100.

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New Conformers of Tris(ethylenediamine)chromium(III)

Sir:

In the conformational analysis of metal chelates, the relatively simple tris(ethylenediamine) complexes have received considerable attention.[1] In these complexes there are two ways the carbon–carbon bond of the ethylenediamine (en) ring can bend to achieve the unstrained *gauche* conformation. In the first of these the carbon–carbon bond is nearly parallel to the threefold axis of the metal complex, and in the second it forms an obtuse angle with this axis. For a Λ configuration[2] about the metal, these ring conformers are designated ∂ and λ, respectively. The Λ absolute configuration is defined by assigning it to that isomer of the complex which, when viewed down the *threefold axis*, forms a left-handed propeller. The mirror-image isomer is designated Δ. This allows the eight possible isomers: $\Lambda\partial\partial\partial$, $\Lambda\partial\partial\lambda$, $\Lambda\partial\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\lambda\lambda\lambda$, $\Delta\lambda\lambda\partial$, $\Delta\lambda\partial\partial$, $\Delta\partial\partial\partial$. The last four are mirror images of the first four, in sequence, and the members of each stereoisomeric pair, of course, have identical conformational stabilities. For this reason only the first set of four conformers will be discussed in the following comparison of stabilities.

Corey and Bailar[3] calculated the relative energies of the $\Lambda\partial\partial\partial$ and $\Lambda\lambda\lambda\lambda$ conformations of $[Co(en)_3]^{3+}$ (designated by them as kkk and k′k′k′, respectively). These calculations were based on a comparison of the nonbonded interactions in the ring systems and predicted the $\partial\partial\partial$ form to be 1.8 kcal/mole lower in energy than the $\lambda\lambda\lambda$ form. X-Ray diffraction studies of several compounds (Table I) have supported this assignment since only the $\partial\partial\partial$ conformation was found. The compounds studied included only Co(III) and Ni(II) salts. However, ter Berg[4] has shown that the salts $[M(en)_3]Cl_3 \cdot 3H_2O$ (M =

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[1] See, for example, R. D. Gillard and H. M. Irving, *Chem. Rev.*, **65**, 603 (1965); J. H. Dunlop and R. D. Gillard, *Advan. Inorg. Chem. Radiochem.*, **9**, 185 (1966); A. M. Sargeson, "Transition Metal Chemistry," Vol. 3, Marcel Dekker, Inc., New York, N. Y., 1966, p 303.

[2] The recent IUPAC proposal for nomenclature is used here.

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

[4] J. ter Berg, *Strukturbericht*, **7**, 235 (1939).

TABLE I
CONFORMATIONS OF $M(en)_3$ COMPLEXES

Compound	Ring conformation[a]	α	β
$[Ni(en)_3][NO_3]_2$	3 ∂	23.2	46.2[b,c]
$[Co(en)_3]Cl_3 \cdot 3H_2O$	3 ∂	19.7	41.2[d]
Λ-$[Co(en)_3]Cl_3 \cdot 0.5NaCl \cdot 3H_2O$	3 ∂	18.9	38.1[e]
Λ-$[Co(en)_3]Br_3 \cdot 0.5H_2O$	1 ∂	20.7	42.6[f]
	2 ∂	26.3	50.8
$[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$	1 λ	28.9	55.0[g]
Cation 1	1 λ	25.3	49.2
	1 ∂	26.4	50.8
	1 ∂	28.6	54.5
Cation 2	1 ∂	28.0	53.9
	1 λ	24.8	48.4
$[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$	2 λ	25.1	49.1[h]
	1 λ	27.0	51.8

[a] For the racemic salts this corresponds to Λ configuration around the metal. The number refers to the number of symmetry related rings with identical geometry. [b] Error assignments are described in the text. [c] References 12 and 13. [d] Reference 5. [e] References 9 and 10. [f] Reference 11. [g] Reference 7. [h] Reference 8.

Co, Cr, or Rh) and $[M(en)_3]Br_3 \cdot 3H_2O$ (M = Co or Cr) are all isomorphous. A change from the ∂∂∂ to the λλλ conformation involves a general broadening of the metal complex and would be expected to affect markedly the lattice parameters. In addition, the orientations of the amine hydrogens are strongly affected by a change in conformation. For these reasons the isomorphism of $[Co(en)_3]Cl_3 \cdot 3H_2O$ (space group P$\bar{3}$c1, $a = 11.50$ and $c = 15.52$ Å conformation ∂∂∂[5]) with the Cr(III) salt ($a = 11.49$ and $c = 15.52$ Å)[4] implies that the ∂∂∂ conformation is also present in the Cr(III) complex. In fact, it has been widely accepted that this conformation is the only one to be expected since in the several compounds previously studied all ethylenediamine rings have had this conformation.

We have completed an X-ray study of the structure of $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$.[6] This unusual salt contains two different five-coordinated $[Ni(CN)_5]^{3-}$ ions. One is a perfect square pyramid and the other is a distorted trigonal bipyramid.[7] We have also recently completed an X-ray study of $[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$.[8] Of the two crystallographically independent $[Cr(en)_3]^{3+}$ ions in $[Cr(en)_3][Ni(CN)_5] \cdot 1.5H_2O$ and a third $[Cr(en)_3]^{3+}$ ion in $[Cr(en)_3][Co(CN)_6] \cdot 6H_2O$, *none of the three has the expected ∂∂∂ conformation; instead each ion is a new, different conformer so that all three of the previously unobserved conformers (∂λλ, ∂∂λ, and λλλ) are represented.* The first $[Cr(en)_3]^{3+}$ cation in the $[Ni(CN)_5]^{3-}$ salt is shown as a projection down the usual molecular threefold axis in Figure 1(a). The conformation is Λ∂λλ (that is, only one of the carbon–carbon bonds is nearly parallel to the threefold axis). The second cation in the $[Ni(CN)_5]^{3-}$ salt is shown as the same projection in Figure 1(b). Here the conformation is Λ∂∂λ. The most unusual conformer occurs in the $[Co(CN)_6]^{3-}$ salt (Figure 1(c)), where the $[Cr(en)_3]^{3+}$ cation has the supposedly highest energy Λλλλ form (that is, none of the carbon–carbon bonds is parallel to the threefold axis).

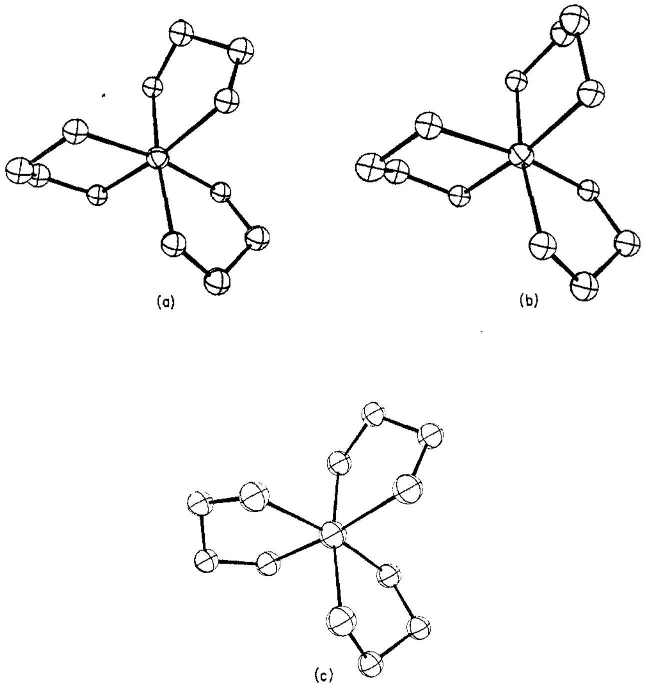

Figure 1.—Perspective drawings of the ∂λλ (a), ∂∂λ (b), and λλλ (c) conformers of $[Cr(en)_3]^{3+}$ as viewed down the usual molecular threefold axis.

Two questions must now be answered. First, why have not these conformations been observed in the previous structures, and, second, what systematic differences, if any, in the crystal environment can be invoked to explain the stabilization of a particular conformer? We believe the answers to both questions lie in the potentially large number of hydrogen bonds in which the amine hydrogens can participate.

In ethylenediamine rings with both ∂ and λ conformations there are two different kinds of amine hydrogens. One type points more or less in the axial direction and the other points out in an equatorial direction. In both the ∂ and the λ conformations, the equatorial hydrogens are free to form hydrogen bonds since they point out like the spokes of a pinwheel. The change from ∂ to λ conformation, however, makes a large difference between the respective axial hydrogens. As may be seen from molecular models, in the ∂∂∂ conformation all of the axial hydrogens are directed toward a point on the threefold axis above the molecule. Since the N–H--B hydrogen bond angles usually are between 120 and 180° (where B is the base

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[5] K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **29**, 428 (1956). These authors report the Co(III) complex is of continuously variable composition with a maximum of 3.5 waters of hydration. The Cr(III) salt is normally written with the latter hydration number.

[6] K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 949 (1966).

[7] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, submitted for publication.

[8] K. N. Raymond and J. A. Ibers, submitted for publication.

[9] K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957).

[10] K. Nakatsu, Y. Saito, and H. Kuroya, *ibid.*, **30**, 795 (1957).

[11] K. Nakatsu, *ibid.*, **35**, 832 (1962).

[12] L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 639 (1960).

[13] T. Watanabe and M. Atoji, *Kagaku* (Tokyo), **21**, 301 (1951).

of the hydrogen bond), all three axial hydrogens of the $\delta\delta\delta$ conformation cannot simultaneously form a hydrogen bond. When a basic atom is in position to bond with one hydrogen, it effectively blocks the other two. In contrast, in the $\lambda\lambda\lambda$ conformation the axial hydrogen atoms point away from the threefold axis in an outward spiral and so all three amine hydrogens are free to form hydrogen bonds. Therefore, *hydrogen bonding specifically favors the λ conformation relative to the normally more stable δ form.* In a particular tris(ethylenediamine) complex salt the $\delta\delta\delta$ conformer is then expected to be found when there are few if any basic sites in the salt to bind with the amine hydrogens. However, if there is an abundance of such sites, the energy released by the formation of a few extra hydrogen bonds (a few kilocalories per mole per bond) can make the $\lambda\lambda\lambda$ conformer the most stable. Intermediate situations might be expected to give intermediate conformers when the opposing effects (interatomic hydrogen–hydrogen repulsion and hydrogen bonding) cancel.

In $[Co(en)_3]Cl_3 \cdot 3H_2O$[5] there are N–H–Cl hydrogen bonds but more amine hydrogens than Cl^- ions, and the shortest N–Cl distances are in equatorial directions. This is true again in the salts Λ-$[Co(en)_3Cl_3 \cdot 0.5NaCl \cdot 3H_2O$[9,10] and Λ-$[Co(en)_3]Br_3 \cdot 0.5H_2O$.[11] In the latter case there are both short N–Br and N–O distances and these are all equatorial. On the basis of the hydrogen-bond model proposed earlier, the $\delta\delta\delta$ conformation would be expected to be most stable for these salts, as is observed. In $[Ni(en)_3][NO_3]_2$,[12,13] the situation is complicated by the formation of bifurcated hydrogen bonds so that each amine hydrogen is associated with a short H–O distance. However, this kind of interaction normally is weaker than the usual hydrogen bond, as Swink and Atoji pointed out in the interpretation of their infrared data.[12] The extra hydrogen bonds may then be too weak to affect the conformation, or the specific geometric requirements imposed by the planar NO_3^- anion may be important.

The hydrogen-bonding model appears to work well in explaining the stabilization of the higher energy conformers of $[Cr(en)_3]^{3+}$ in the $[Ni(CN)_5]^{3-}$ and $[Co(CN)_6]^{3-}$ salts. The complex cyanide anions and the waters of crystallization provide many possible sites for hydrogen bonding with the amine hydrogens, so the possibility of stabilizing higher energy conformers certainly exists. Of the three conformers observed, the order of increasing energy is expected to be $\delta\delta\lambda < \delta\lambda\lambda < \lambda\lambda\lambda$. The $\delta\delta\lambda$ conformer (Figure 1(b)) has only three strong hydrogen bonds (N–N or N–O less than 3.10 Å). The $\delta\lambda\lambda$ conformer (Figure 1(a)) has seven, and the highest energy $\lambda\lambda\lambda$ conformer (Figure 1(c)) has ten bonds in this range, consistent with the expected relative stabilities.

Let us define the dihedral angle α between the plane which contains the ring carbon atoms and the metal atom and the plane which contains the ring nitrogen atoms and the metal atom. This angle would be zero if the ethylenediamine ring had the eclipsed configuration. As we pointed out earlier, the coordinated ethylenediamine ring is expected to have a *gauche* configuration and α should differ from zero. In Table I we tabulate the values of α for those ethylenediamine complexes studied to date. In all cases the rings have the *gauche* configuration. We also tabulate in Table I the angle β between the two nitrogen atoms as one looks down the carbon–carbon bond. Values of β have generally been given by previous authors. Our tabulation of β is based a recalculation from the atomic parameters given in the various papers. In some cases differences as great as 10° occur between the value we calculate and the value given previously. The assigned standard deviations are, in the Cr(III) case, around 1.1°, as estimated from the variance–covariance matrix. The errors for the other complex cations are estimated to be 3–5 times greater on the assumption that the ratio of bond length errors to angle errors is constant for these very similar molecular geometries.

In conclusion, the λ conformation (for a Λ configuration of the $[M(en)_3]^{n+}$ complex) is favored in those cases where strong hydrogen bonds can be formed. The compounds studied to date indicate this is true in the solid state and it is presumably also true in solution. For this reason it is probably impossible to predict what conformers will be found in strongly hydrogen-bonding solvents, such as water. The addition of strongly hydrogen-bonding anions to solutions may also stabilize specific conformers. This could provide an alternative explanation for the changes observed in circular dichroism spectra upon the addition of such anions.[14]

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(14) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).
(15) National Institutes of Health Predoctoral Fellow 1965–1967.

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On the Applicability of the Van Vleck Formula for Polynuclear Complexes

Sir:

A recent communication by Wentworth and Saillant[1] presented magnetic suceptibility measurements on the tetrameric complex $[Cr_4(en)_6(OH)_6]I_6 \cdot 4H_2O$. The interpretation of these results was said to favor a trigonal structure with a central Cr(III) atom interacting magnetically with three Cr(III) atoms at the corners of a triangle. The basis of the interpretation

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[1] R. A. D. Wentworth and R. Saillant, *Inorg. Chem.*, **6**, 1436 (1967).