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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(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).

$$\chi_{\mathrm{m}} = \frac{N\beta^2g^2}{3kT}\left\{\begin{array}{l} \dfrac{546\exp(-27x) + 330\exp(-3x) + 180\exp(17x) + 84\exp(33x)}{13\exp(-27x) + 11\exp(-3x) + 9\exp(17x) + 7\exp(33x)} \\ \dfrac{+\ 660\exp(-21x) + 360\exp(-x) + 168\exp(15x) + 60\exp(27x)}{+\ 22\exp(-21x) + 18\exp(-x) + 14\exp(15x) + 10\exp(27x)} \\ \dfrac{+\ 540\exp(-15x) + 252\exp(x) + 90\exp(13x) + 18\exp(21x)}{+\ 27\exp(-15x) + 21\exp(x) + 15\exp(13x) + 9\exp(21x)} \\ \dfrac{+\ 336\exp(-9x) + 60\exp(3x) + 24\exp(11x)}{+\ 28\exp(-9x) + 20\exp(3x) + 12\exp(11x) + 4\exp(15x)} \\ \dfrac{+\ 60\exp(-3x) + 12\exp(5x)}{+\ 10\exp(-3x) + 6\exp(5x)} \end{array}\right\} \quad (1)$$

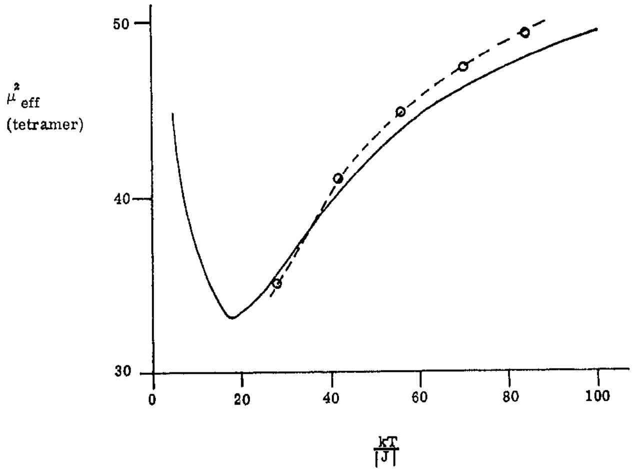

Figure 1.—A comparison of experiment with theory for the trigonal and tetrahedral models: ————, theoretical curve for trigonal model; – – – – –, theoretical curve for tetrahedral model; O, experimental results from ref 1, assuming $J = -3.57k$.

was numerical agreement with a formula due to Van Vleck[2] where the energy levels of the spin system are given by

$$E(S') = \frac{-zJ}{n-1}[S'(S+1) - nS(S+1)]$$

where n is the number of (*equivalent*) atoms in the cluster and z is the number of nearest neighbors for each *equivalent* atom.

Wentworth and Saillant used a number $Z_{\mathrm{av}} = {}^3/_2$, averaging the number of nearest neighbors for the one central Cr(III) atom ($z = 3$) and the three triangular Cr(III) atoms ($z = 1$). It must be emphasized, however, that the Van Vleck derivation depends on all the atoms in the cluster being exactly equivalent; thus using Z_{av} over nonequivalent atoms is not correct. This point has also been emphasized by Smart,[3] who shows that the Van Vleck equation is only applicable to three types of clusters: two equivalent atoms (a dimer), three equivalent atoms in an equilateral triangle, or four equivalent atoms arranged in a regular tetrahedron. Although incorrect for the trigonal case, the form of the equation used by Wentworth and Saillant ($Z_{\mathrm{av}} = {}^3/_2$, $J = -16k$) is in fact the correct expression for the energy levels in a *tetrahedral* [Cr_4] cluster, because (in that case) the product $-zJ$ is $24k$ ($z = 3$, $J = -8k$).

The method of Kambe[4] can be extended to derive the correct expression for the structure proposed by Wentworth and Saillant (eq 1, where $x = -2J/kT$). The agreement between theory and experiment in the trigonal case is much poorer than in the tetrahedral model, as shown in Figure 1. This means that, of the two structures under consideration, the regular tetrahedral arrangement of the four Cr(III) atoms is *more consistent with the magnetic data down to 77°K;* obviously, studies at lower temperatures are needed.

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[2] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter XII.

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[5] Contribution No. 3601.

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Relations between Lattice Parameter and x Value for Some Cubic Tungsten Bronzes[1]

Sir:

Several of the tungsten bronzes (M_xWO_3, where $0 < x < 1$) crystallize in cubic symmetry over part of their composition range. The cubic region is rather extensive ($0.4 < x < 1$) for the sodium tungsten bronzes,[2,3] less extensive for most of the others, and has not been observed for some of them.

A linear relation

$$a_0\ (\text{Å}) = 0.0819x + 3.7846 \qquad (1)$$

between the x value and the lattice parameter, a_0, of the sodium bronzes in the cubic region was first observed by Brown and Banks.[4]

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2228.

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[3] W. F. deJong, *Z. Krist.*, **81**, 314 (1932).

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