

Since we have tetradentate planar ligands (formula A), we can also expect the formation of the square-planar complexes. Copper(II) and palladium(II) prefer this type of coordination so that the stability of complexes CuL and PdL of VIII may be explained in that way.

The (M→L) π -bonding effect of all compounds is given by the extensive resonance within the π -electron system and by the strong electrophilic effect of the cyano group. From the viewpoint of the metal ion, the (M→L) π -bonding effect increases with the increasing number of d electrons. This may explain the stability of some d¹⁰ complexes.

The existing differences in the stability of zinc, cadmium, and mercury(II) complexes may be explained by the action of the chelate cage effect. The most stable complexes are formed by zinc (ionic radius 0.74 Å); see the complexes of VI, Table III. The appearance of the chelate cage effect is given by the rigid planar structure of all compounds (see formula A).

Cobalt(II) produces a rapid catalytic oxidation of IV at pH 8.1. This reaction is highly selective and sensitive and will be described separately.

Comparison with recently published 3-(4-antipyrinyl-azo)pentane-2,4-dione¹¹ shows that a similar compound, *i.e.*, 1,5-bis(4-antipyrinyl)-3-acetylformazan, may be formed too. However, the cleavage of pentane-2,4-dione occurs with much greater difficulty than that of cyanoacetic acid.

Conclusion

The investigated compounds form most stable complexes with zinc, copper(II), and palladium(II). Complex ZnH₂L of VI and complexes CuL and PdL of VIII show good prospects for use as a highly selective means for these metals.

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Conformational Analysis of Coordination Compounds. IV. Conformational Energies and Activation Energies for Ring Inversion of Ethylenediamine Complexes

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The free energy differences between the various configurations of M(en)₃ have been calculated for a number of M-N bond lengths. The marked preference for configurations of the types D($\delta\delta\delta$), L($\lambda\lambda\lambda$), D($\delta\delta\lambda$), and L($\lambda\lambda\delta$) which occurs for M-N = 2.0 Å was found largely to be removed for complexes with M-N = 2.3 Å. The calculations included for the first time an estimation of an entropy contribution to the conformational energies arising from differences in the vibrational freedom of the chelate rings in the various configurations. The calculations also included a study of the lowest energy transition state for ring inversion. This was found to be of the envelope type and to provide a barrier to inversion of about 5 kcal mol⁻¹ for M-N = 2.0 Å increasing to about 7 kcal mol⁻¹ for M-N = 2.3 Å. The results of the calculations were used as the basis for a rationalization of the observed nmr spectra of the tris-ethylenediamine complexes of a number of metal ions. It was concluded that the room-temperature spectra were the result of rapid ring inversion, the variation with the metal ion being due to a number of factors controlling the effective chemical shift difference between the axial and equatorial methylene protons.

The nmr spectra of diamagnetic complexes of the type M(en)₃ exhibit widely differing CH resonances depending on the central metal ion. For the N-deuterated ruthenium(II) complex, detailed fine structure has been observed and analyzed in terms of an AA'BB' system.¹ For the equivalent cobalt(III) complex a broad unresolved band has been observed,² for rhodium(III) and iridium(III) a narrow band with definite fine structure, and for platinum(IV) a very sharp peak with ¹⁹⁵Pt satellites.³ For the above complexes, even for the ruthenium(II) complex with the well-resolved fine structure, it has not been possible to determine from the published spectra

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the rate of ring inversion or whether one configuration is markedly preferred over the other possible structures.

The ethylenediamine chelate rings have puckered conformations with either δ or λ chirality. To date, no reliable estimate has been made of the activation energy for the inversion from one chirality to the other. However, experimental data are available for the relative free energies of the four configurations D($\delta\delta\delta$) { = L($\lambda\lambda\lambda$) }, D($\delta\delta\lambda$) { = L($\lambda\lambda\delta$) }, D($\delta\lambda\lambda$) { = L($\lambda\delta\delta$) }, and D($\lambda\lambda\lambda$) { = L($\delta\delta\delta$) } for cobalt complexes where the M-N bond length is 2.0 Å.⁴⁻⁷ No information is

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currently available for the systems with different M-N bond lengths. However, it was thought that the configurational energy differences and the activation energy for ring inversion and, therefore, the observed nmr spectra might be dependent upon the M-N bond length. To test this hypothesis, *a priori* calculations of these energies have been made for M-N bond lengths of 2.0, 2.1, 2.2, and 2.3 Å.

Previously, conformational energy calculations have been restricted to estimations of enthalpy differences. However, in this paper, entropy contributions have also been estimated. These arise from differences in the freedom of the chelate rings to undergo ring deformation vibrations in the various configurations.

Energy Calculations

In an earlier paper dealing with the conformational energies of the various configurations of $\text{Co}(\text{en})_3^{3+}$, a set of empirical van der Waals energy equations was derived from the available experimental energy data.⁸ However, the derivation was based on the incorrect premise that statistically there is no preference for the "mixed" configurations $\text{D}(\delta\delta\lambda)$ and $\text{D}(\delta\lambda\lambda)$. In fact, according to statistics, the configurations listed above should exist with a 1:3:3:1 ratio. The previously determined set of van der Waals energy equations has been modified to allow for an entropy contribution to the free energy differences from this statistical weighting and also to allow for an entropy contribution from the differences in vibrational freedom of the chelate rings in the four configurations.

The relative free energies have been estimated from the experimental data⁸ for the cobalt-(*R*)-propylenediamine-(*S*)-propylenediamine system studied by Dwyer, Sargeson, and James: for the 1:1 ratio of the ligands: $\text{D}(\delta\delta\delta)$, 0; $\text{D}(\delta\delta\lambda)$, 0; $\text{D}(\delta\lambda\lambda)$, 0.52; $\text{D}(\lambda\lambda\lambda)$, 1.6 kcal mol⁻¹; for the 2:1 ratio of the ligands, allowing for the statistical preference for the *R* isomer: $\text{D}(\delta\delta\delta)$, 0; $\text{D}(\delta\delta\lambda)$, -0.06, $\text{D}(\delta\lambda\lambda)$, +0.58; $\text{D}(\lambda\lambda\lambda)$, 1.6 kcal mol⁻¹. Values have also been estimated from the experimental data^{5,7} for the cobalt-ethylenediamine-(*R*)-propylenediamine systems by a similar method to that outlined in the previous paper⁸ allowing for the fact that, in $\text{Co}(\text{en})_2(\text{R}-\text{pn})^{3+}$, the $\lambda\lambda\lambda$, $\lambda\delta\lambda$, and $\delta\delta\lambda$ configurations would have a statistical weighting of 1:2:1. The energies calculated from the relative concentrations of the separated fractions were found to vary over wide limits depending on which set of experimental data was chosen. In addition, each set of free energies suggested, contrary to other substantive evidence, that the $\text{D}(\delta\delta\lambda)$ configuration was markedly preferred over the $\text{D}(\delta\delta\delta)$. These inconsistencies could be due to the difficulty experienced in correctly identifying the composition of the separated fractions.⁷ For these reasons we have chosen the free energy data from the cobalt-(*R*)-propylenediamine-(*S*)-propylenediamine system as a basis for our studies.

The empirical van der Waals curves were derived

by the method outlined previously.⁸ The following values were determined for the parameter r_{min} : H...H, 2.50 Å; C...H, 3.10 Å.

The empirical curves have been applied to the methylcyclohexane system by the method described previously⁸ to test their validity.⁹ The free energy difference which included an entropy term due to the difference in the freedom of vibration for the axial and equatorial conformations was calculated to be 1.5 kcal mol⁻¹, which is to be compared with an experimental value¹⁰ of 1.7 kcal mol⁻¹.

Calculations of the torsional and angle-bending energies have also been described previously.¹¹ The force constants for the angle-bending energies, which were listed elsewhere,¹¹ have not been varied with the M-N bond length. However the geometrical model⁸ used previously has been modified for the present investigations. Here the geometry of the ring has been specified by a constant set of bond lengths and four geometrical parameters, θ , ϕ , z_1 , and ω , where θ and ϕ are the internal ring angles $\angle\text{N}_1\text{C}_1\text{C}_2$ and $\angle\text{C}_1\text{C}_2\text{N}_2$, z_1 is the z coordinate of the carbon atom C_1 , and ω is the dihedral angle between the $\text{N}_1\text{C}_1\text{C}_2$ and $\text{C}_1\text{C}_2\text{N}_2$ planes. This particular set of parameters was chosen so that the torsional arrangement about the $\text{C}_1\text{-C}_2$ bond could be specified directly (by ω) rather than as a function of z_1 and z_2 . As before, the coordinates of each ring and its substituents have initially been calculated with the coordinate bonds lying in the xy plane, making equal angles with the x and y axes.

The distribution of ligands in the D tris complexes is approximately defined by a C_3 axis of the octahedron, $C_3(x, z, -y)$, which relates the basic (x, y) , $(z, -x)$, and $(-y, -z)$ positions of the rings. Thus, once the geometry of each ring and its substituents has been calculated in the xy position, the coordinates are simply rotated about this axis to their appropriate octahedral positions. In a number of special cases, for example, the minimum-energy structures of the $\text{D}(\delta\delta\delta)$ and $\text{D}(\lambda\lambda\lambda)$ configurations, this axis also strictly relates the individual geometries of the rings and defines their relative orientations. However, in this general investigation, the rings were permitted to vary independently to minimize their interactions and, where necessary, to distort from these strictly octahedral positions. The reorientation procedure for each ring involved successive rotations of the coordinates of the ring and its substituents about the three octahedral axes. ϕ_x , ϕ_y , and ϕ_z are used subsequently to specify these rotations (Figure 1).

In the present study, each of the seven parameters was permitted to vary concurrently in the following ranges: θ and ϕ , 104.5–114.5°; z_1 , 0–1.6 Å; ω , 0–70°; ϕ_x , ϕ_y , and ϕ_z , -10 to +10°. The wide ranges of z_1 and ω were chosen in order to include all the possible envelope-type conformations that could correspond to the lowest energy transition state in the chelate ring

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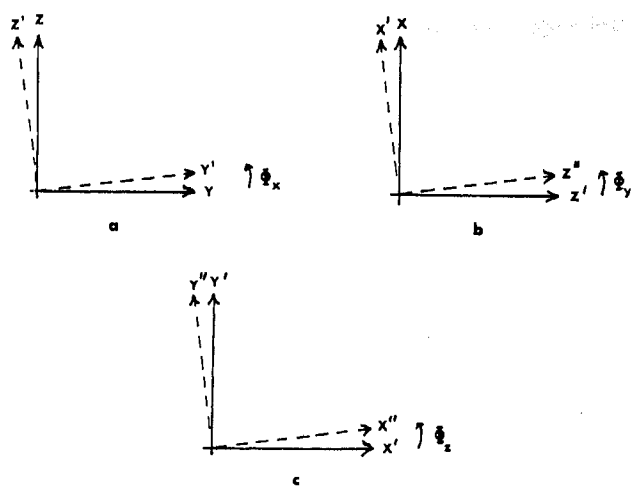


Figure 1.—The reorientation procedure used to transform the atomic coordinates by successive rotations about the octahedral axes: (a) $\Phi_x(x, y, z \rightarrow x', y', z')$, (b) $\Phi_y(x, y', z' \rightarrow x'', y'', z'')$, and (c) $\Phi_z(x'', y'', z'' \rightarrow x''', y''', z''')$.

inversion. Approximate minima and transition states were chosen on this basis and, where necessary, refined using progressively smaller increments until the parameter increments had the following values: θ and ϕ , 1° ; z_1 , 0.05 \AA ; ω , 2.5° ; ϕ_x , ϕ_y , and ϕ_z , 2.5° .

Each of the seven significant variables used to define the geometry and orientation of each ring may be associated with an independent mode of vibration of the ring. Since the scanning method of locating the energy minima determines the precise shape of the n -dimensional energy surface in the region of the minimum-energy conformations and the lowest energy transition states, this information may be used to fit an approximate Hooke's law vibration term (eq 1) to the surface for each of these variables. The entropy of this vibration may be associated with the entropy contribution to the free energy as it expresses the statistical freedom of the ring in a particular conformation. This has been calculated from eq 1-3, where k_ξ is the force constant for the deformation

$$E_\xi = \frac{1}{2}k_\xi(\Delta\xi)^2 \quad (1)$$

$$\Delta E = \frac{1}{2\pi c} \sqrt{\frac{k_\xi}{\mu}} \quad (2)$$

$$S^0_\xi = \frac{N\Delta E/T}{e^{\Delta E/kT} - 1} + R \ln \frac{1}{1 - e^{-\Delta E/kT}} \quad (3)$$

tion, ξ is the deformation parameter, ΔE is the spacing of the vibrational energy levels, c is the velocity of light, μ is the reduced mass of the vibrating atoms, S^0 is the entropy associated with the vibration, N is Avogadro's number, and k is the Boltzmann constant.

Results

The effect of the different M-N bond lengths on the conformational properties of the tris-ethylenediamine complexes depends on two factors: (i) the changes in the conformational properties of the in-

dividual chelate rings and (ii) the changes in the interactions between rings.

Initial calculations were carried out for an isolated ethylenediamine ring where the only contributors to the conformational energy are the ring strain terms. As in earlier calculations for cobalt(III), the results suggest that the ethylenediamine ring can exist in two enantiomeric skew conformations (δ and λ) separated by an energy barrier corresponding to an envelope transition state with $\omega = 0^\circ$. The chiral puckered rings were found to exist in a wide range of symmetric and unsymmetric conformations with energies lying within $0.2 \text{ kcal mol}^{-1}$ of the minimum energy. On the other hand, the achiral transition state was found to be under considerable torsional and angular strain and its flexibility is therefore severely limited. The detailed geometry of the minimum-energy and transition-state conformations of the isolated ring are shown in Table I together with the limiting values of the

TABLE I
THE CHANGE IN GEOMETRY AND ENERGY OF ISOLATED DIAMINE CHELATE RINGS AS THE FIXED M-N BOND LENGTH CHANGES FROM 2.0 TO 2.3 \AA ^a

M-N, \AA	z_1 , \AA	ω , deg	θ , ϕ , deg	ΔH	$T\Delta S$	ΔG
(a) Puckered Ring						
2.0	0.35 (0.15-0.55)	57.5 (52.5-62.5)	107.5 (105.5-108.5)	0.0	0.0	0.0
2.1	0.35 (0.15-0.55)	60.0 (55.0-65.0)	107.5 (106.5-109.5)	0.0	-0.05	0.05
2.2	0.40 (0.20-0.60)	62.5 (57.5-70.0)	108.5 (106.5-110.5)	0.15	-0.05	0.20
2.3	0.40 (0.20-0.60)	65.0 (60.0-70.0)	109.5 (107.5-111.5)	0.50	-0.10	0.60
(b) Envelope						
2.0	1.00 (0.85-1.10)	0	110.5 (109.5-111.5)	4.20	-0.05	4.20
2.1	1.00 (0.85-1.10)	0	111.5 (110.5-112.5)	4.75	-0.05	4.80
2.2	1.00 (0.85-1.10)	0	111.5 (110.5-112.5)	5.35	-0.05	5.40
2.3	1.00 (0.85-1.10)	0	112.5 (111.5-112.5)	6.05	-0.10	6.15

^a The figures in parentheses represent the ranges of values of the geometrical parameters corresponding to conformations within $0.2 \text{ kcal mol}^{-1}$ of the minimum energy. The energies are expressed in kilocalories per mole and T has been taken as 300°K .

geometrical parameters for conformations whose energies are within $0.2 \text{ kcal mol}^{-1}$ of the minimized values.

The minimum-energy structures found for the various configurations of $M(\text{en})_3$ are presented in Table II, and the enthalpy, entropy, and free energy associated with these structures are given in Table III.

The relevant features of the interaction systems in the tris complexes with $M-N = 2.0 \text{ \AA}$ and their significance to the total energy have already been described in detail.⁸ The interaction systems in the complexes with longer M-N bonds are qualitatively similar. However, the strength of the interactions is dramatically reduced for the longer M-N bond lengths, leading to smaller energy differences between the configurations. In the case with $M-N = 2.3 \text{ \AA}$, the interactions are so small that the enthalpies of

TABLE II
GEOMETRIES OF THE MINIMUM-ENERGY
CONFIGURATIONS OF $M(en)_3^a$

	ω , deg	α , Å	θ ; ϕ , deg
M-N = 2.0 Å			
$\delta\delta\delta$	δ 55	0.35 (0.20-0.50)	107.5 (105.5-109.5)
$\delta\delta\lambda$	δ 55	0.25 (0.20-0.30)	106.5 (105-107.5); 108.5 (107.5-109.5)
	λ 55	-0.35 (0.30-0.40)	107.5 (105.5-109.5)
$\delta\lambda\lambda$	δ 55	0.35 (0.30-0.40)	106.5 (105.5-109.5)
	λ 55	-0.30 (0.30-0.35)	106.5 (105.5-107.5); 108.5 (107.5-109.5)
$\lambda\lambda\lambda$	λ 55	-0.35 (0.30-0.40)	106.5 (104.5-108.5)
M-N = 2.3 Å			
$\delta\delta\delta$	δ 65	0.40 (0.25-0.55)	109.5 (107.5-111.5)
$\delta\delta\lambda$	δ 65	0.30 (0.25-0.40)	109.5 (107.5-111.5)
	λ 65	-0.40 (0.35-0.45)	109.5 (107.5-111.5)
$\delta\lambda\lambda$	δ 65	0.40 (0.35-0.45)	109.5 (107.5-110.5)
	λ 65	-0.35 (0.25-0.40)	109.5 (107.5-110.5)
$\lambda\lambda\lambda$	λ 65	-0.40 (0.30-0.50)	109.5 (107.5-110.5)

^a ϕ_x , ϕ_y , and ϕ_z deviate by less than 2.5° from 0° for all the conformations in the table. The figures in parentheses represent the ranges of values of the geometrical parameters corresponding to conformations within 0.2 kcal mol⁻¹ of the minimum energy. For ω , this range was found to be $\pm 2.5^\circ$. The results for M-N = 2.1 and 2.2 Å were found to be systematically intermediate between those for M-N = 2.0 and 2.3 Å.

TABLE III
RELATIVE CONFIGURATIONAL ENERGIES FOR $M(en)_3^a$

	ΔH	$T\Delta S$	$T\Delta S^b$	ΔG
M-N = 2.0 Å				
$\delta\delta\delta$	0.0	0.0	0.0	0.0
$\delta\delta\lambda$	0.6	-0.2	0.65	0.15
$\delta\lambda\lambda$	1.1	-0.3	0.65	0.75
$\lambda\lambda\lambda$	1.2	-0.3	0.0	1.5
M-N = 2.3 Å				
$\delta\delta\delta$	0.0	0.0	0.0	0.0
$\delta\delta\lambda$	0.0	-0.1	0.65	-0.55
$\delta\lambda\lambda$	0.0	-0.2	0.65	-0.45
$\lambda\lambda\lambda$	0.0	-0.2	0	0.2

^a In kilocalories per mole. T has been taken as 300°K. The results for M-N = 2.1 and 2.2 Å were found to be systematically intermediate between those for M-N = 2.0 and 2.3 Å. ^b Statistical entropy term.

the four conformational isomers are not significantly different.

The δ and λ conformations in these complexes are separated by an energy barrier associated with a transition-state conformation of the envelope type. The transition-state conformation is completely analogous to that already described for the isolated ring except that, in the complexes, the conformation is modified by the severe interactions of the two ring carbon atoms and their substituents with an amine group of one of the other rings. As the M-N bond length increases, these interactions become much smaller but the ring strain energy of the envelope increases dramatically. The two opposing effects cause an overall increase in the enthalpies of the transition-state structures ($t\delta\delta$), ($t\delta\lambda$), and ($t\lambda\lambda$) in the order M-N = 2.0, 2.1, 2.2, and 2.3 Å and lead to the entropy contribution becoming less negative. As a result, there is a general

increase in the free energy of the transition-state complexes as M-N increases.

The minimum-energy "ground-state" configurations ($\delta\delta\delta$), ($\delta\delta\lambda$), ($\delta\lambda\lambda$), and ($\lambda\lambda\lambda$) are affected by similar variations in the interaction and ring strain energies. However, in these complexes the reduction in interaction energy as M-N increases more than compensates for the accompanying small increases in ring strain energy and there is, as a result, a slight decrease in the free energy of each isomer in the order M-N = 2.0, 2.1, 2.2, and 2.3 Å. Because of the divergence of the ground-state and excited-state energies the average free energy of activation for ring inversion from a δ to a λ conformation in these complexes increases regularly with M-N. The activation energies for M-N = 2.0-2.3 Å lie in the approximate range 5-7 kcal mol⁻¹.

Discussion

Energy Calculations.—The amount of strain involved in forming an isolated ethylenediamine chelate ring is determined by the geometrical requirements of the NMN and NCCN fragments of the ring. If we assume that their optimum geometries are defined by the parameter values $\alpha = 90^\circ$, θ , $\phi = 109.5^\circ$, and $\omega = 60^\circ$, then the optimum NN distances for M-N = 2.0 Å are 2.83 and 2.79 Å, respectively, for the two fragments. Since the NN distances differ by only 0.04 Å, the ring can be formed without significant strain in either fragment. However, in this "unstrained" conformation $\angle MNC$ is 101.3° which is much smaller than the normal tetrahedral angle of 109.5°. In order to relieve the strain in the MNC angles, the ring tends to flatten causing a general slight decrease from the optimum values in the torsional and remaining bond angles. As the M-N bond length increases, the optimum NN distance associated with the NMN fragment increases markedly, and, before the ring can be formed at all, it is necessary either to decrease α or to increase the NN distance in the NCCN fragment by increasing ω or θ and ϕ . The last alternative is the least energetically favorable. The decrease in α , which also serves to relieve the increased strain in the MNC angles, and the increase in ω both are effective, and the minimum-energy conformations for M-N = 2.3 Å are found to have values of α and ω in the vicinity of 80 and 65°, respectively.

In the tris complexes, these tendencies are modified by the nonbonded interactions with the other chelate rings. The increased puckering of the conformation for the longer M-N bonds does not lead to more severe interactions because the increased M-N bond length has the effect of displacing the atoms in the chelate ring away from the other rings. In fact, the interactions become so slight that the geometry of the rings in $M(en)_3$ with M-N = 2.3 Å is close to that for an isolated ring.

The factors governing the energies of the isolated transition state ($\omega = 0^\circ$) are similar to those previously described for the minimum-energy skew conformations. Here the optimum NN distances for M-N = 2.0 Å

are 2.83 Å (NMN) and 2.52 Å (NCCN). Because of the large discrepancy between the optimum NN distances, large angular strain in the angles α , θ , and ϕ is necessary before the ring can be formed. Increases in the M-N bond length are accompanied by further changes in these angles, the increases in energy being magnified relative to the minimum-energy conformations because the ring in the envelope conformation is already under great angular strain. The actual conformation of the ring with $\omega = 0^\circ$ is determined by the torsional strain about the N-C bond and the angular strain in the angles MNC. In the minimum-energy geometry of a perfectly flat chelate ring all the torsional angles are zero and $\angle\text{MNC} = 121.5^\circ$. The torsional strain in the NC bonds and the angular strain in $\angle\text{MNC}$ may both be relieved, while maintaining $\omega = 0^\circ$, by forming an envelope conformation.

Interpretation of Nmr Spectra.—The above results indicate that the barriers to ring inversion between the δ and λ conformers are too small to prevent rapid ring inversion on the nmr time scale. (An increase in the activation energy for ring inversion to 12–15 kcal mol⁻¹ from the 5–7 kcal mol⁻¹ calculated would be required.) Consequently, we conclude that *all of the M(en)₃ complexes undergo rapid ring inversion at room temperature and that the observed nmr spectra are those of the equilibrium populations of conformers.* A similar conclusion has recently been obtained by Ho and Reilley¹² from a study of the temperature-dependent nmr spectrum of paramagnetic Ni(en)₃²⁺.

The nmr spectra in these complexes are determined by the *effective* chemical shift difference between nonequivalent protons together with the effective coupling constants between these protons. In a single ethylenediamine chelate ring in one conformation, say δ , there exists a chemical shift difference between each geminal pair of methylene protons, H_a and H_e, due to their axial or equatorial position with respect to the NMN plane to the ring. This *intrinsic* chemical shift difference is presumably different for each metal ion and may be expected to depend on the oxidation state of the metal as well as M-N distance in the complex. The geminal coupling between the methylene protons and the vicinal coupling between the two pairs of protons result in magnetic nonequivalence and an expected AA'BB' spectrum. The vicinal coupling constants depend on the dihedral angles between the coupled protons and, consequently, on ω , which has been shown to vary with the M-N distance and, therefore, with the metal ion.

With a low barrier to ring inversion, the consequence of equilibrium between δ and λ conformers must be considered. For a single chelate ring in a complex of the type M(en)X₄, where the δ and λ are equally stable and enantiomeric, the effective chemical shift difference disappears because each proton spends equal time in the axial and equatorial environments which are strictly equivalent for the two chiralities. Under these conditions the AA'BB' spectrum would collapse

to a single line. In an M(en)₃ complex, however, there are two ways in which an effective chemical shift difference can be maintained.

(1) If each configuration were of equal energy, an effective chemical shift difference might still exist due to the inherent magnetic nonequivalence described previously;³ *i.e.*, the environment of an axial proton in a δ conformer is not identical with that of an axial proton in a λ conformer due to the presence of the other two chelate rings. The only direct experimental evidence on this possibility indicates that the effect is very small in Pt(en)₃⁴⁺, since only a single narrow resonance line is observed, indicating a very small effective chemical shift difference.

(2) If various configurations are not of equal energy, the effective chemical shift will be a weighted average of the populations of the various conformations. For example, if the D($\delta\delta\delta$) and D($\delta\delta\lambda$) forms are of similar energy and significantly more stable than the D($\delta\lambda\lambda$) and D($\lambda\lambda\lambda$) configurations, as suggested by the calculations for M-N = 2.0 and 2.1 Å, then each proton will be in a δ conformation five-sixths of the time and in a λ conformation one-sixth of the time, with the result that the effective chemical shift difference between H_a and H_e will be only two-thirds of the intrinsic chemical shift difference. For the longer M-N bond lengths this chemical shift difference will be further reduced as the λ conformations will be more populated. Because the entropy differences between the D($\delta\delta\delta$) and the other configurations are relatively small, the AA'BB' will be only slightly dependent on temperature, except at very low temperatures where the rate of ring inversion is slow.

Ring inversion will also result in averaged effective coupling constants, but the effect of this averaging on the spectrum is small. The spectrum is determined by parameters *N*, *K*, *L*, and *M* which are sums and differences of the individual coupling constants.¹ Inversion to an enantiomeric conformer leaves these parameters unchanged except for a change in the sign of *M*. Consequently, if the two conformers δ and λ are of equal energy, *M* would be zero and the AA'BB' spectrum would consist of 20 instead of 24 lines.

With the assumption of rapid ring inversion the various spectra of the M(en)₃ complexes must be interpreted according to the following factors: (1) the intrinsic chemical shift difference in a single conformation, (2) the relative populations of the various configurations, and (3) the coupling constants determined by the dihedral angle ω and the relative populations.

The above *a priori* calculations, which are based solely on intramolecular interactions, are not expected to account for differences in configurational energies for different metal ions better than a few tenths of 1 kcal, particularly as variations in solvation energies are likely to be substantial when comparing, say, Pt(en)₃⁴⁺ and Ru(en)₃²⁺. As the effective chemical shift difference depends strongly on the relative populations of the various configurations, the reliability of the calculated relative populations is not sufficient to allow

(12) F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).

for a quantitative interpretation of the spectra. It is possible, however, to account qualitatively for some of the differences between the spectra due to expected trends in the intrinsic chemical shift difference and to differences in the ring geometry revealed by the calculations.

The largest effective chemical shift difference is observed for $\text{Ru}(\text{en})_3^{2+}$ (0.23 ppm), while the smallest (~ 0 ppm) is observed for $\text{Pt}(\text{en})_3^{4+}$. This may be due to the different oxidation states of the metal. The metal d-electron density has the largest radial extension in ruthenium(II), whereas the higher oxidation state of platinum(IV) results in substantial radial contraction of the d-electron density. The axial protons of the ligand are directed toward the t_{2g} lobes of the d electrons and the equatorial protons are directed away from the metal. Consequently the axial protons in the ruthenium(II) complex are more effectively shielded relative to the equatorial protons than are the axial protons in the platinum(IV) complex. The result is a larger intrinsic chemical shift difference in the ruthenium(II) complex. The variation in the effective chemical shift difference for the different metal ions could also be due to a variation in the long-range diamagnetic anisotropic shielding of the axial and equatorial protons by the M-N bonds. The axial protons are substantially closer to the electrical center of gravity of these bonds and are oriented at a greater angle to them. The above shielding effects would both contribute to the axial protons resonating at higher field than the equatorial and, therefore, are consistent with the assignment of the spectrum of $\text{Ru}(\text{en})_3^{2+}$, in which the axial protons were found to occur at higher field.¹

This suggested larger intrinsic chemical shift difference for ruthenium(II) is magnified by the changes in ring geometry caused by the larger M-N distance of ruthenium(II) compared with platinum(IV).¹³ As the M-N distance increases, the chelate ring becomes more puckered and the dihedral angle ω increases. This causes the axial protons to be more susceptible to the diamagnetic shielding arising from the metal ion, further increasing the intrinsic chemical shift difference. An increase in ω also causes a change in the coupling constants, particularly the axial-equatorial and equatorial-equatorial coupling. This change can be predicted using the Karplus relation.¹ Calculations using the coupling constants and chemical shift difference obtained for $\text{Ru}(\text{en})_3^{2+}$ indicate that a change in ω from 55 to 63° has only a small effect on the spectrum.

Finally, the relative populations of the various configurations may be shifted by solvation effects. There is evidence from crystal structure studies that specific strong hydrogen bonding involving the amine protons

(13) The Ru-N distance in $\text{Ru}(\text{en})_3^{2+}$ is not yet available. In $\text{Ru}(\text{NH}_3)_6^{2+}$ the Ru-N distance has been found¹⁴ to be 2.14 Å. In *trans-cis*- $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ the Pt-N distance¹⁵ is 2.06 Å.

(14) H. M. Cleary and J. A. Ibers, paper presented at the American Crystallographic Association's Winter Meeting, Tulane University, New Orleans, La., Mar 1-5, 1970.

(15) C. F. Liu and J. A. Ibers, *Inorg. Chem.*, **9**, 773 (1970).

can stabilize unfavorable conformers.¹⁶ It is possible that, in solution, solvent interactions could similarly reduce the energy differences between the configurations and, in the limit that the δ and λ conformers become energetically equivalent, could result in the disappearance of the effective chemical shift difference. It is perhaps of importance to note that the platinum(IV) complex, which exhibits a sharp methylene resonance, is a relatively strong acid ($\text{p}K_a = 5.5$) and capable of much stronger hydrogen bonding than, say, $\text{Ru}(\text{en})_3^{2+}$, which shows a relatively large effective chemical shift difference.

Each of the above factors could serve to increase the effective chemical shift difference of $\text{Ru}(\text{en})_3^{2+}$ and may account for the observation of well-resolved fine structure in its spectrum compared with $\text{Pt}(\text{en})_3^{4+}$. The trivalent metal complexes present intermediate cases as the intrinsic chemical shift differences and the strengths of hydrogen bonding with the solvent for these complexes are likely to be intermediate between those of $\text{Ru}(\text{en})_3^{2+}$ and $\text{Pt}(\text{en})_3^{4+}$. The trivalent metal ion complexes exhibit intermediate spectra in terms of both the position (Pt^{4+} , 3.26; Rh^{3+} , 2.93; Co^{3+} , 2.83; Ir^{3+} , 2.77; Ru^{2+} , 2.55 ppm downfield from DSS in D_2O) and the shape of the methylene resonance. The variation of the chemical shift is due to a number of factors, the most important being the diamagnetic shielding from the metal ion and the M-N bonds. Because the radial distribution of the t_{2g} electrons is more restricted for cobalt(III) than for rhodium(III) and iridium(III), the first of these factors would tend to make the methylene resonance for the cobalt complex appear at the lower field. The fact that it is intermediate between the resonances for the rhodium and iridium complexes could be due to the order of shielding from the M-N bonds. The values of $\Delta\chi_{\text{M-N}}$ for these complexes are presently not known. However, the variation in the shielding from the M-N bonds may also provide a satisfactory rationalization of the variation in band shapes for the cobalt, rhodium, and iridium series. Because the three complexes have identical charges and would have similar structures, it is unlikely that solvation effects would play an important part in distinguishing the three complexes. The degree of puckering of the chelate rings and the relative stabilities of the various configurations would also not differ greatly. If the shielding from the t_{2g} electrons was the most important factor in determining the variation in the effective chemical shift difference, the methylene resonance for $\text{Co}(\text{en})_3^{3+}$ would be sharper than those for rhodium and iridium. The markedly broader cobalt(III)-methylene resonance could be partly due to a larger intrinsic chemical shift difference which derives from the differences in the shielding from the M-N bonds, but it mainly results from the coupling of the protons with the cobalt nucleus.¹⁷

(16) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968).

(17) J. K. Beattie, *ibid.*, **10**, 426 (1971); J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

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A Neutron Diffraction Study of Uranyl Nitrate Dihydrate^{1a}

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The crystal structure of uranyl nitrate dihydrate, $\text{UO}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$, has been determined by neutron diffraction. The structure is monoclinic with $a = 14.124$ (13), $b = 8.432$ (8), $c = 7.028$ (7) Å, $\beta = 108.0$ (1)°, and space group $P2_1/c$ with 4 formula weights per unit cell. This is in disagreement with a previously reported X-ray study. In the present study the structure was solved with three-dimensional data by applying Patterson and Fourier techniques. The four uranium atoms per unit cell are located on special positions (a) and (b) of the space group. Each uranyl group is surrounded by a nearly perpendicular planar oxygen hexagon. This hexagon consists of two oxygen atoms from each of two equivalent bidentate nitrate groups and two oxygen atoms from equivalent water molecules. This arrangement is similar to that reported for the uranyl nitrate hexahydrate. The structural units are bound together by hydrogen bonds from the oxygen of the water molecule to the uncoordinated oxygen atom of the nitrate group and to the oxygen atom of the uranyl group.

Introduction

An X-ray diffraction study of $\text{UO}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$ has been reported by Vdovenko, *et al.*,² but the U–O bond lengths they reported are not in agreement with the lengths of similar bonds found in other compounds. Table I lists the U–O distances determined by Vdovenko, *et al.*,² in $\text{UO}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$, by Taylor and Mueller³ in a neutron investigation of $[\text{UO}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$, and by Zachariasen and Plettinger⁴ in an X-ray study

revealed in Table I are real and (2) obtain the positions of all atoms in the complex, including hydrogen atoms, and thereby ascertain the role of the hydrogen bonding in the compound.

Experimental Section

Large flat crystals of uranyl nitrate dihydrate were grown in a uranyl nitrate–nitric acid–water solution with the following composition (by weight): 28.8% uranyl nitrate, 54.5% nitric acid, and 16.7% water. This composition is dictated by the phase diagram established by Gaunt, *et al.*⁵ Two samples were analyzed by the Karl Fischer method, which established the water content in the samples to be 8.44 and 9.20%. The analysis clearly showed the material was the dihydrate because the calculated water content is 8.34% for the dihydrate and 12.05% for the trihydrate. One of the analyzed samples was stored in a desiccator, and the other was exposed to humid air prior to the titration, which may account for the difference in percentages of water content. Therefore, some protection for the crystal was considered necessary during data collection.

A crystal, $10.5 \times 5.1 \times 4.8$ mm (approximately a parallel-piped), weighing 0.740 g, was coated with a thin layer of silicone oil, encapsulated in a vanadium can, and mounted on the Argonne automated four-circle diffractometer along a nonmajor axis. A beam of neutrons with a wavelength of 1.063 Å was produced making use of the (110) plane of a beryllium single crystal to monochromate the beam. The wavelength was obtained by measuring several known reflections of a standard sodium chloride crystal and calculating the wavelength by a least-squares technique. Preliminary investigation of the reciprocal lattice revealed monoclinic symmetry with the following systematic extinctions: $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. These data uniquely determined the space group as $P2_1/c$. Lattice parameters were obtained at the room temperature, $25 \pm 3^\circ$, from neutron diffractometer measurements of 15 reflections. Results from a least-squares refinement, using a computer program written by Heaton and Gvildys,⁶ were $a = 14.124$ (13), $b = 8.432$ (8), $c =$

TABLE I
U–O BOND DISTANCES^a FOUND IN SIXFOLD-COORDINATED
URANYL ION COMPLEXES (Å)

Bond type	Vdovenko ²	Taylor and Mueller ³	Zachariasen and Plettinger ⁴
	$\text{UO}_2(\text{H}_2\text{O})_2\text{-}$ $(\text{NO}_3)_2$	$[\text{UO}_2(\text{H}_2\text{O})_2\text{-}$ $(\text{NO}_3)_2] \cdot 4\text{H}_2\text{O}$	$\text{Na}[\text{UO}_2\text{-}$ $(\text{C}_2\text{H}_3\text{O}_2)_3]$
U–O (uranyl)	1.9 (1)	1.770 (7)	1.74 (4)
		1.749 (7)	1.70 (4)
U–O (ligand)	2.0 (1)	2.504 (5)	2.47 (2)
	2.1 (1)	2.547 (6)	2.51 (2)
		2.397 (3)	

^a Values in parentheses are standard errors that occur in the last recorded decimal place. (This system will be used throughout the paper.)

of $\text{Na}[\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_3]$. Since all three compounds exhibit sixfold oxygen coordination about the linear uranyl ion, the chemically similar bonds should be about equal in length.

The present neutron study of $\text{UO}_2(\text{H}_2\text{O})_2(\text{NO}_3)_2$ was instigated in order to (1) determine if the differences

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