Vibrational Spectra of the Tris(1,2-ethanediamine)rhodium(III) Cation. I. Normal Coordinate Analysis of the Parent Compound, Three Deuterated, and Four ^{15}N Substituted Species *

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A normal coordinate analysis of the tris(1,2-ethanediamine)-rhodium(III) cation, the $N\text{-}d_{12}$, $C\text{-}d_{12}$ and $N,C\text{-}d_{24}$ deuterated, and the four corresponding ^{15}N substituted species has been accomplished as a 37 body problem (including all atoms). The complex with the three chiral five-membered rings in the more stable δ conformation and the same absolute configuration Λ as in $(+)_{589}\text{-}[Co(en)_3]^{3+}$ was selected for the analysis among the four possible combinations of Λ,Λ absolute configuration with δ,Λ ring conformation; resulting in D_3 symmetry of the complex ion. By fitting 38 force constants in the GVFF (General Valence Force Field) approximation to reproduce more than 500 observed frequencies, the normal modes of vibration for the observed bands can be described in terms of the potential energy distribution (PED) between the symmetry coordinates. The force field and vibrational modes related to the Rh$-$N bonds and N$-$Rh$-$N angles are discussed in some detail.

A large amount of data has been collected on the vibrational spectra of metal chelates of 1,2-ethanediamine (en). However, the interpretation of these results is still very unsatisfactory and band assignments and interpretations are usually made without any assistance from normal coordinate calculations. A partial calculation considering only the nine skeletal atoms was performed by Ashley and Torrible [1] for Ti(en) tetrahalide complexes and used as a basis for assigning the IR spectrum in the region above 300 cm^{-1}. A more detailed cal-

culation has been reported by Omura, Nakagawa and Shimanouchi [2] for the IR active species of several bis(en) metal chelates, but in this case the force constants were refined to fit the frequencies especially in the region below 600 cm^{-1}. Attempts to give detailed assignments of IR and Raman spectra based upon complete normal coordinate calculations have, to our knowledge, not been published.

In the present paper the results of a complete normal coordinate treatment of this ion and seven isotopically labelled species are discussed with special emphasis on the force constants and the vibrational modes involving the central part of the complex compounds. The IR and Raman spectra in the solid state and in solution including polarization measurements of the Raman bands of the parent molecule [Rh(en)$_3$]$^{3+}$ and the three deuterated species will be dealt with in separate papers.[3] The shifts observed by ^{15}N isotopic substitution are also included here. Hence, this is the first of several papers concerning the vibrational characteristics of the [Rh(en)$_3$]$^{3+}$ cation.

STRUCTURE

By investigation of X-ray powder photographs of active racemates it was shown by Andersen *et al.*[4] that $(+)_{589}\text{-}[Co(en)_3]^{3+}$ and $(-)_{589}\text{-}[Rh(en)_3]^{3+}$ have the same absolute configuration Λ. Since a three-dimensional analysis of $(+)_{589}\text{-}[Co(en)_3]Cl_3.H_2O$ [5] revealed the ligand conformation to be δ, i.e. that the

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C−C direction within each chelate ring is approximately parallel to the threefold axis of the complex ion (*lel* arrangement), the same must necessarily be true for the rhodium complex in the solid state. The complex has accordingly the symmetry D_3 with the six nitrogen atoms of the three ligands bonded nearly octahedrally to the central rhodium atom. The present calculations have therefore been based upon a Λ-$(\delta\delta\delta)$, or Λ-*lel*$_3$, model for the [Rh(en)$_3$]$^{3+}$ ion.

The Cartesian coordinates were constructed in the following way. The [Rh(en)$_3$]$^{3+}$ ion was located in a three-dimensional coordinate system with the rhodium atom *in origo* and with the six nitrogen atoms placed upon the X, Y, and Z axes assuming N−Rh−N angles of 90°. The unknown coordinates were then calculated by a vector analytical method [6] applied to one of the ligands only. Transcription of (x,y,z) coordinates to the trigonal coordinate system [6] (x′,y′,z′) proceeded *via* the orthonormal transformations

$$x' = (2/3)^{\frac{1}{2}}z - 6^{-\frac{1}{2}}y - 6^{-\frac{1}{2}}x$$
$$y' = -2^{-\frac{1}{2}}y + 2^{-\frac{1}{2}}x$$
$$z' = 3^{-\frac{1}{2}}z + 3^{-\frac{1}{2}}y + 3^{-\frac{1}{2}}x$$

and finally the coordinates obtained (x′y′,z′) were rotated ±120° around the Z′ axis to give the coordinates of the two other ligands.

The average Rh−N distance in (+)$_{589}$-tris-[(−)-*trans*-1,2-cyclohexanediamine]rhodium (III) nitrate trihydrate was found [7] to be 2.08 Å. Since the Rh−N bond length was very close to 1.99 Å in both dimethylglyoxime [8,9] and ethylenimine [10] complexes, the rounded value of 2.00 Å was adopted in the present calculation. The values used for the ligand distances and bond angles are mostly standard values: r(N−H) = 1.01 Å, r(C−H) = 1.09 Å, r (C−C) = 1.53 Å, r(C−N) = 1.47 Å, $\angle$H−N−H = $\angle$H−C−H = 111°, $\angle$Rh−N−C = 105°, $\angle$N−C−C = 111°, $\angle$Rh−N−H = 115°, $\angle$N−C−H = 107°, $\angle$Rh−N−C−C = 33°.

NORMAL COORDINATE ANALYSIS

The normal coordinate analysis was performed as a 37-body problem using Wilson's GF matrix method as treated in the program of Schachtschneider and Snyder.[11] The potential
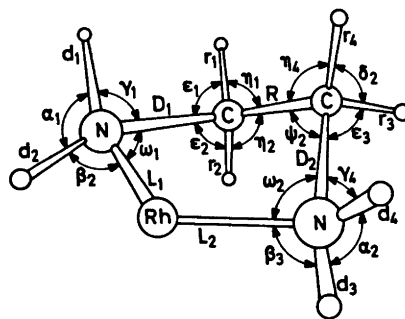

Fig. 1. Internal coordinates of the chelate ring I. Additional coordinates are: Torsion around the Rh−N bonds τ_1 and τ_2, the N−C bonds π_1 and π_2, and around the C−C bond Δ. Torsion aound the Rh−N bonds (τ_1 and τ_2) have been defined as C−N−Rh−N torsion within a chelate ring. Torsion around the N−C bonds (π_1 and π_2) have been defined as Rh−N−C−C torsion, and around the C−C bond (Δ) as N−C−C−N torsion.

function employed was of the GVFF type originally developed for hydrocarbons,[12] extended to molecules containing the X−CH$_2$−CH$_2$−X moiety [13–16] also present in [Rh(en)$_3$]$^{3+}$. The internal coordinates of the chelate ring are shown in Fig. 1, while the internal NRhN deformation coordinates are separately given in Fig. 2. The symmetry coordinates listed in Table 1 were derived making use of the D_3 symmetry of the complex. The redundancies
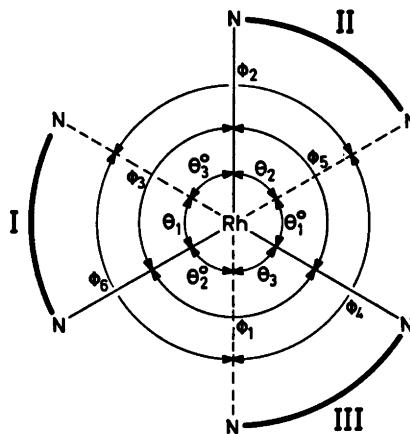

Fig. 2. The internal NRhN deformation coordinates. The numbers I, II, and III refer to the three chelate rings.

Table 1. Symmetry coordinates for the tris(1,2-ethanediamine)Rh(III) cation. The numbers I, II, and III refer to the chelate rings. The symbols used are defined in section (c) of this Table for the chelate ring I and similar expressions are used for the other chelate rings.

(a) Chelate rings

Species A_1

$S_1 - S_{22} = [Sx(I) + Sx(II) + Sx(III)]/\sqrt{3}$ (x = a, b, c, d, ..., v)

Species A_2

$S_1 - S_{20} = [Sx'(I) + Sx'(II) + Sx'(III)]/\sqrt{3}$ (x = a, b, d, e, ..., u)

Species E

$S_1 = [2Sa(I)\text{-}Sa(II)\text{-}Sa(III)]/\sqrt{6}$ $S_2 = [Sa'(II)\text{-}Sa'(III)]/\sqrt{2}$

$S_3 = [2Sb(I)\text{-}Sb(II)\text{-}Sb(III)]/\sqrt{6}$ $S_4 = [Sb'(II)\text{-}Sb'(III)]/\sqrt{2}$

$S_5 = [2Sc(I)\text{-}Sc(II)\text{-}Sc(III)]/\sqrt{6}$

$S_6 = [2Sd(I)\text{-}Sd(II)\text{-}Sd(III)]/\sqrt{6}$ $S_7 = [Sd'(II)\text{-}Sd'(III)]/\sqrt{2}$

$S_8 = [2Se(I)\text{-}Se(II)\text{-}Se(III)]/\sqrt{6}$ $S_9 = [Se'(II)\text{-}Se'(III)]/\sqrt{2}$

$S_{10} = [2Sf(I)\text{-}Sf(II)\text{-}Sf(III)]/\sqrt{6}$ $S_{11} = [Sf'(II)\text{-}Sf'(III)]/\sqrt{2}$

$S_{12} = [2Sg(I)\text{-}Sg(II)\text{-}Sg(III)]/\sqrt{6}$ $S_{13} = [Sg'(II)\text{-}Sg'(III)]/\sqrt{2}$

$S_{14} = [2Sh(I)\text{-}Sh(II)\text{-}Sh(III)]/\sqrt{6}$ $S_{15} = [Sh'(II)\text{-}Sh'(III)]/\sqrt{2}$

$S_{16} = [2Si(I)\text{-}Si(II)\text{-}Si(III)]/\sqrt{6}$ $S_{17} = [Si'(II)\text{-}Si'(III)]/\sqrt{2}$

$S_{18} = [2Sj(I)\text{-}Sj(II)\text{-}Sj(III)]/\sqrt{6}$ $S_{19} = [Sj'(II)\text{-}Sj'(III)]/\sqrt{2}$

$S_{20} = [2Sk(I)\text{-}Sk(II)\text{-}Sk(III)]/\sqrt{6}$ $S_{21} = [Sk'(II)\text{-}Sk'(III)]/\sqrt{2}$

$S_{22} = [2Sl(I)\text{-}Sl(II)\text{-}Sl(III)]/\sqrt{6}$ $S_{23} = [Sl'(II)\text{-}Sl'(III)]/\sqrt{2}$

$S_{24} = [Sm(II)\text{-}Sm(III)]/\sqrt{2}$ $S_{25} = [2Sm'(I)\text{-}Sm'(II)\text{-}Sm'(III)]/\sqrt{6}$

$S_{26} = [2Sn(I)\text{-}Sn(II)\text{-}Sn(III)]/\sqrt{6}$ $S_{27} = [Sn'(II)\text{-}Sn'(III)]/\sqrt{2}$

$S_{28} = [So(II)\text{-}So(III)]/\sqrt{2}$ $S_{29} = [2So'(I)\text{-}So'(II)\text{-}So'(III)]/\sqrt{6}$

$S_{30} = [2Sp(I)\text{-}Sp(II)\text{-}Sp(III)]/\sqrt{6}$ $S_{31} = [Sp'(II)\text{-}Sp'(III)]/\sqrt{2}$

$S_{32} = (Sq(II)\text{-}Sq(III))/\sqrt{2}$ $S_{33} = [2Sq'(I)\text{-}Sq'(II)\text{-}Sq'(III)]/\sqrt{6}$

$S_{34} = [2Sr(I)\text{-}Sr(II)\text{-}Sr(III)]/\sqrt{6}$ $S_{35} = [Sr'(II)\text{-}Sr'(III)]/\sqrt{2}$

$S_{36} = [Ss(II)\text{-}Ss(III)]/\sqrt{2}$ $S_{37} = [2Ss'(I)\text{-}Ss'(II)\text{-}Ss'(III)]/\sqrt{6}$

$S_{38} = [2St(I)\text{-}St(II)\text{-}St(III)]/\sqrt{6}$ $S_{39} = [St'(II)\text{-}St'(III)]/\sqrt{2}$

$S_{40} = [2Su(I)\text{-}Su(II)\text{-}Su(III)]/\sqrt{6}$ $S_{41} = [Su'(II)\text{-}Su'(III)]/\sqrt{2}$

$S_{42} = [2Sv(I)\text{-}Sv(II)\text{-}Sv(III)]/\sqrt{6}$

(b) Symmetry coordinates involving NRhN deformation (δNRhN)

Species A_1

$S_{23} = [\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6]/\sqrt{6}$

$S_{24} = [\theta_1 + \theta_2 + \theta_3 + \theta_1° + \theta_2° + \theta_3°]/\sqrt{6}$

$S_{25} = [\theta_1 + \theta_2 + \theta_3 - \theta_1° - \theta_2° - \theta_3°]/\sqrt{6}$

Species A_2

$S_{21} = [\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6]/\sqrt{6}$

Species E

$S_{43} = [2\phi_1 + 2\phi_2 - \phi_3 - \phi_4 - \phi_5 - \phi_6]/\sqrt{12}$

$S_{44} = [\phi_3 - \phi_4 + \phi_5 - \phi_6]/2$

$S_{45} = [2\theta_1 - \theta_2 - \theta_3 + 2\theta_1° - \theta_2° - \theta_3°]/\sqrt{12}$

$S_{46} = [\theta_2 - \theta_3 + \theta_2° - \theta_3°]/2$

Table 1. Continued.

(c) Local symmetry coordinates of the chelate ring I

Symmetry coordinate	Symbol	Description
$Sa(I) = (L_1 + L_2)/\sqrt{2}$	$\nu_s RhN$	Symm. RhN stretch
$Sa'(I) = (L_1 - L_2)/\sqrt{2}$	$\nu_{as} RhN$	Asym. RhN stretch
$Sb(I) = (D_1 + D_2)/\sqrt{2}$	$\nu_s CN$	Symm. CN stretch
$Sb'(I) = (D_1 - D_2)/\sqrt{2}$	$\nu_{as} CN$	Asymm. CN stretch
$Sc(I) = R$	νCC	CC stretch
$Sd(I) = (d_1 + d_2 + d_3 + d_4)/2$	$\nu_s NH$	Symm. NH stretch
$Sd'(I) = (d_1 + d_2 - d_3 - d_4)/2$	$\nu_s NH$	Symm. NH stretch
$Se(I) = (d_1 - d_2 + d_3 - d_4)/2$	$\nu_{as} NH$	Asym. NH stretch
$Se'(I) = (d_1 - d_2 - d_3 + d_4)/2$	$\nu_{as} NH$	Asym. NH stretch
$Sf(I) = (r_1 + r_2 + r_3 + r_4)/2$	$\nu_s CH$	Symm. CH stretch
$Sf'(I) = (r_1 + r_2 - r_3 - r_4)/2$	$\nu_s CH$	Symm. CH stretch
$Sg(I) = (r_1 - r_2 + r_3 - r_4)/2$	$\nu_{as} CH$	Asym. CH stretch
$Sg'(I) = (r_1 - r_2 - r_3 + r_4)/2$	$\nu_{as} CH$	Asym. CH stretch
$Sh(I) = (\omega_1 + \omega_2)/\sqrt{2}$	$\delta_s RhNC$	Symm. RhNC deformation
$Sh'(I) = (\omega_1 - \omega_2)/\sqrt{2}$	$\delta_{as} RhNC$	Asym. RhNC deformation
$Si(I) = (\psi_1 + \psi_2)/\sqrt{2}$	$\delta_s NCC$	Symm. NCC deformation
$Si'(I) = (\psi_1 - \psi_2)/\sqrt{2}$	$\delta_{as} NCC$	Asym. NCC deformation
$Sj(I) = (\alpha_1 + \alpha_2)/\sqrt{2}$	δNH_2	NH_2 deformation
$Sj'(I) = (\alpha_1 - \alpha_2)/\sqrt{2}$	δNH_2	NH_2 deformation
$Sk(I) = (\delta_1 + \delta_2)/\sqrt{2}$	δCH_2	CH_2 deformation
$Sk'(I) = (\delta_1 - \delta_2)/\sqrt{2}$	δCH_2	CH_2 deformation
$Sl(I) = (\beta_1 + \beta_2 + \beta_3 + \beta_4)/2$	$[Sl(I) + Sn(I)]/\sqrt{2} = \delta NH_2$	NH_2 deformation
$Sl'(I) = (\beta_1 + \beta_2 - \beta_3 - \beta_4)/2$	$[Sl'(I) + Sn'(I)]/\sqrt{2} = \delta NH_2$	NH_2 deformation
$Sm(I) = (\beta_1 - \beta_2 + \beta_3 - \beta_4)/2$	$[Sm(I) + So(I)]/\sqrt{2} = \varrho NH_2$	NH_2 rock
$Sm'(I) = (\beta_1 - \beta_2 - \beta_3 + \beta_4)/2$	$[Sm'(I) + So'(I)]/\sqrt{2} = \varrho NH_2$	NH_2 rock
$Sn(I) = (\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)/2$	$[Sl(I) - Sn(I)]/\sqrt{2} = \omega NH_2$	NH_2 wag
$Sn'(I) = (\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4)/2$	$[Sl'(I) - Sn'(I)]/\sqrt{2} = \omega NH_2$	NH_2 wag
$So(I) = (\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)/2$	$[Sm(I) - So(I)]/\sqrt{2} = t NH_2$	NH_2 twist
$So'(I) = (\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)/2$	$[Sm'(I) - So'(I)]/\sqrt{2} = t NH_2$	NH_2 twist
$Sp(I) = (\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4)/2$	$[Sp(I) + Sr(I)]/\sqrt{2} = \delta CH_2$	CH_2 deformation
$Sp'(I) = (\varepsilon_1 + \varepsilon_2 - \varepsilon_3 - \varepsilon_4)/2$	$[Sp'(I) + Sr'(I)]/\sqrt{2} = \delta CH_2$	CH_2 deformation
$Sq(I) = (\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4)/2$	$(Sq(I) + Ss(I)]/\sqrt{2} = \varrho CH_2$	CH_2 rock
$Sq'(I) = (\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4)/2$	$[Sq'(I) + Ss'(I)]/\sqrt{2} = \varrho CH_2$	CH_2 rock
$Sr(I) = (\eta_1 + \eta_2 + \eta_3 + \eta_4)/2$	$[Sp(I) - Sr(I)]/\sqrt{2} = \omega CH_2$	CH_2 wag
$Sr'(I) = (\eta_1 + \eta_2 - \eta_3 - \eta_4)/2$	$[Sp'(I) - Sr'(I)]/\sqrt{2} = \omega CH_2$	CH_2 wag
$Ss(I) = (\eta_1 - \eta_2 + \eta_3 - \eta_4)/2$	$[Sq(I) - Ss(I)]/\sqrt{2} = t CH_2$	CH_2 twist
$Ss'(I) = (\eta_1 - \eta_2 - \eta_3 + \eta_4)/2$	$[Sq'(I) - Ss'(I)]/\sqrt{2} = t CH_2$	CH_2 twist
$St(I) = (\tau_1 + \tau_2)/\sqrt{2}$	$\tau_s RhN$	Symm. RhH torsion
$St'(I) = (\tau_1 - \tau_2)/\sqrt{2}$	$\tau_{as} RhN$	Asym. RhN torsion
$Su(I) = (\pi_1 + \pi_2)/\sqrt{2}$	$\tau_s NC$	Symm. NC torsion
$Su'(I) = (\pi_1 - \pi_2)/\sqrt{2}$	$\tau_{as} NC$	Asym. NC torsion
$Sv(I) = \varDelta$	τ_{cc}	CC torsion

Table 2. Valence force constants for the [Rh(en)$_3$]$^{3+}$ cation.

Force type	Constants symbol	Group	Coordinate(s) involved	Atoms common to interacting coordinates	Value[a] Initial	Final
Stretch	K_r	CH$_2$	C—H	—	4.55[b]	4.706
	K_d	NH$_2$	N—H	—	6.42[c]	5.669
	K_R	CH$_2$—CH$_2$	C—C	—	4.39[b]	3.581
	K_D	CH$_2$—NH$_2$	C—N	—	4.97[c]	4.692
	K_L	RhN$_6$	Rh—N	—	2.31[d]	1.607
Stretch-stretch	F_r	CH$_2$	C—H, C—H	C	0.01[b]	0.0398
	F_d	NH$_2$	N—H, N—H	N	0[c]	0.0307
	F_{RD}	CH$_2$—CH$_2$—NH$_2$	C—C, C—N	C	0.10[b]	0.391
	F_{LL}	RhN$_6$	Rh—N, Rh—N, *cis*	Rh	0.05[d]	0.250
	F'_{LL}	RhN$_6$	Rh—N, Rh—N, *trans*	Rh		−0.0868
Bend	H_δ	CH$_2$	<HCH	—	0.55[b]	0.554
	H_α	NH$_2$	<HNH	—	0.64[c]	0.547
	H_η	CH$_2$—CH$_2$	<HCC	—	0.656[b]	0.651
	H_ε	CH$_2$—NH$_2$	<HCN	—	0.656[b]	0.732
	H_γ	CH$_2$—NH$_2$	<CNH	—	0.578[c]	0.692
	H_ψ	CH$_2$—CH$_2$—NH$_2$	<CCN	—	1.13[b]	1.087
	H_β	Rh—NH$_2$	<HNRh	—	0.19[e]	0.458
	H_ω	Rh—NH$_2$—CH$_2$	<RhNC	—	0.77[f]	0.755
	$H_\phi=H_\theta$	RhN$_6$	<NRhN	—	0.20[f]	1.100
Stretch bend	$F_{R\eta}$	CH$_2$—CH$_2$	C—C, <HCC	C—C	0.328[b]	0.301
	$F_{R\varepsilon}$	CH$_2$—CH$_2$—NH$_2$	C—C, <HCN	C	0.079[b]	0.101
	$F_{R\psi}$	CH$_2$—CH$_2$—NH$_2$	C—C, <CCN	C—C	0.42[b]	0.250
	$F_{D\varepsilon}$	CH$_2$—NH$_2$	C—N, <HCN	C—N	0.36[c]	0.473
	$F_{D\gamma}$	CH$_2$—NH$_2$	C—N, <HNC	C—N	0.16[c]	0.385
	$F_{D\eta}$	CH$_2$—CH$_2$—NH$_2$	C—N, <HCC	C		0.141
	$F_{D\psi}$	CH$_2$—CH$_2$—NH$_2$	C—N, <CCN	C—N	0.42[b]	0.466
	$F_{L\omega}$	Rh—NH$_2$—CH$_2$	Rh—N, <RhNC	Rh—N		0.216
	$F_{D\omega}$	Rh—NH$_2$—CH$_2$	C—N, <RhNC	C—N		0.0984
Bend-bend	F_η	CH$_2$—C	<HCC, <HCC	C—C	−0.021[b]	−0.0324
	F_ε	CH$_2$—N	<HCN, <HCN	C—N	−0.031[c]	−0.0218
	F_γ	NH$_2$—C	<HNC, <HNC	C—N	−0.05[c]	−0.128
	F_β	NH$_2$—Rh	<HNRh, <HNRh	N—Rh		0.0856
	$F_\phi=F_\theta$	RhN$_6$	<NRhN, <NRhN at right angles	Rh—N		−0.200
	$F'_\phi=F'_\theta$	RhN$_6$	<NRhN, <NRhN coplanar	Rh—N		0.200
	f_η^t	CH$_2$—CH$_2$	<HCC, <CCH	C—C	0.127[b]	0.0996
Torsion	H_τ	RhN$_6$	Rh—N	—		0.205
	H_π	CH$_2$—NH$_2$	C—N	—	0.058[c]	0.060
	H_Δ	CH$_2$—CH$_2$	C—C	—	0.058[c]	0.127

[a] In units of mdyn/Å (stretch constants) mdyn/rad (stretch-bend interaction constants) and mdyn Å/(rad)^2 (bending and torsion constants). [b] Refs. 12 and 17. [c] Ref. 18. [d] Ref. 19. [e] Ref. 2. [f] Ref. 20.

$7A_1+4A_2+11E$ included here were in the calculations eliminated directly by the program. The initial force constants, based on values for similar molecules [12,17–20] are listed in Table 2 for comparison with the final GVF constants. The calculated frequencies are given in Table 3, which also includes an approximate description of the vibrational modes based upon the PED (potential energy distribution) of each vibration among the symmetry coordinates. The PED

among the force constants, $K_h J_{\lambda h}/\lambda$ [11] was also calculated to estimate the significant force constants for each vibration, but are not listed in order to save space.

Treatment of [Rh(en)$_3$]$^{3+}$ under the point group D_3 reduces the 105 normal modes of vibration to the irreducible representation $\Gamma = 18A_1(R) + 17A_2(IR) + 35E(R,IR)$, where (R) and (IR) indicate the Raman and infrared active modes, respectively. The eight isotopic

species considered here accordingly give us potentially 144 A_1, 136 A_2, and 280 E frequencies, or a total of 560 frequencies which we have tried to fit to the minimum number of force constants in an internally consistent approximation.

Method of calculation. Since the experimental Raman data included semiquantitative depolarization ratios for many bands, it was decided to perform exploratory calculations of the A_1 block separately and obtain a fit of the calculated frequencies to those of the polarized Raman bands. The force field obtained was then transferred to species A_2 and E after having properly utilized the molecular symmetry, and a provisional assignment of approximately one half of the 560 fundamentals made. Least squares refinements of each species separately disclosed the presence of inconsistencies which led to the introduction of new interaction force constants and revision of the assigned fundamentals. An examination of the Jacobian elements indicated that several of these were very poorly determined while others were essential to insure satisfactory convergence. The following constraints were now made to the calculations. (i) The force constants were not allowed to deviate beyond some fixed limits found valid for similar molecules (*vide infra*). (ii) The final force field should as far as possible be truly convergent, *i.e.* obtained by allowing all force constants to vary simultaneously. (iii) The standard error (excluding NH/ND and CH/CD stretching) for each species (A_1, A_2, E) in any of the four isotopic molecules should not exceed a fixed limit (1 % intended). (iv) The number of force constants should be held as low as possible. With these constraints it was possible to assign almost all fundamentals and explain the significant bands in the observed spectra, by using a 38-parameter GVFF.

Force field related to RhN$_6$. The approach developed here is based mainly upon the general considerations by Claassen [21] to molecules of formula XY$_6$ and the results for hexamine complexes derived from Ru, Rh, Ir, and Os [19] and Ni.[22] The vibrations involving Rh−N stretching could only be fitted satisfactorily by including the three force constants K_L (Rh−N stretching), F_{LL} (bond with a bond at right angles to it), and F'_{LL} (bond with opposite

bond). No improvement was obtained by introducing different interaction force constants F_{LL} for interactions within a chelate ring and interaction between Rh−N bonds of two different chelate rings. The interaction force constants $F_{L\phi}$ and $F_{L\theta}$ were found to be small and omitted in the final calculations.

The force constants for N − Rh − N deformation were initially introduced with different values for deformation within a chelate ring and deformation between two rings. This was considered important since all equilibrium values for N−Rh−N angles were put equal to 90° which is a reasonable but nevertheless conjectural value, being at variance with an Λ-$(\lambda,\lambda,\lambda)$ (ob_3) isomer [7] of the |Rh(-chxn)$_3$|$^{3+}$ cation. However, as the calculations proceeded it became clear that this distinction was not warranted and accordingly the constraint that all $H\theta = H\phi$ was introduced. To be consistent the interaction constants were constrained in the same way, *i.e.* all interactions involving deformation of the RhN$_6$ part of the chelate were considered equal whether the deformation occurs within a chelate ring or between two chelate rings. The force constants $H\theta$, $F\theta$, and $F'\theta$ were now determined by trial and error. These constraints ensured convergence of the remaining force field (*vide supra*). The standard error of the final set did not exceed 1.1 % for each species (A_1, A_2, E) in any of the eight compounds.

The description of the low frequency modes in terms of *PED* on symmetry coordinates were not sufficient for an understanding of the vibrational spectrum of [Rh(en)$_3$]$^{3+}$ in this region. Accordingly, we finally calculated the elements of the transformation matrix L_x between the Cartesian displacement vector X and the normal coordinate vector Q.

RESULTS AND DISCUSSION

Some features considered to be of general interest will be pointed out from the results of the normal coordinate analysis. Nevertheless, in the following discussion it should be kept in mind that (i) the experimental frequencies used are not unambiguously classified to their species from the Raman polarization ratios and (ii) certain constraints have been imposed on the force field. Undoubtedly, these sources

of error are only partly counterbalanced by attempting alternative assignments of fundamentals in all cases of reasonable doubt and systematic attempts to evaluate the significance of the force field during the calculations as discussed above.

Potential constants. Let us compare the values of the initial and the final valence force constants listed in the last two columns of Table 2. The agreement is very satisfactory for force constants related to the ethylenediamine ligand provided allowance is made for the somewhat larger variation observed for interaction force constants than for pure stretch and bending constants. Appreciable changes are noted for some of the force constants involving the amino groups (*e.g.* K_d, H_α and F_γ), but this is easily understandable as a result of the coordination to Rh. The changes in K_R and K_D are mainly the result of the increase in K_{RD} following complex formation. From the overall pattern we may conclude this part of the force field to be essentially comparable to that of similar molecules.

Very similar changes have been observed for the Urey-Bradley force constants of bis(en) metal chelates [3] compared with those found for unchelated aliphatic amines.[10] Thus, for example, the value of the N−H stretching force constant was found to decrease from 6.3 mdyn/Å in amines to *ca.* 5.7 mdyn/Å in chelated 1,2-ethanediamine. In the GVFF developed here, K_D decreased from 6.42 mdyn/Å in aliphatic amines to 5.669 mdyn/Å in [Rh(en)$_3$]$^{3+}$ in complete harmony. This behaviour is hardly coincidental but rather reflects a mutual consistence between the present and previous calculations.

An evaluation of the force field related to the central part of the [Rh(en)$_3$]$^{3+}$ ion is much more difficult, since data suitable for comparison have not been reported. The differences between initial and final GVF constants (Table 2) for the RhN$_6$ group are therefore largely due to an unprecedented choice of the initial value rather than real discrepancies. From an assignment of five fundamentals for [Rh(NH$_3$)$_6$]-Cl$_3$ in the low frequency region, assuming O_h symmetry and treating the NH$_3$ molecules as single masses, Griffith [19] calculated the force constant for Rh−N stretching, K_L, to be 2.3−2.5 mdyn/Å and the interaction force

constant for two Rh−N *cis* bonds, F_{LL}, to be 0.05 mdyn/Å. We have attempted to evaluate the force field in more detail using the GVF expressions given by Claassen [21] with suitable approximations, but the derived force constants have in many cases complex solutions and are very dependent on the details of the sophistication. Such calculations have been successfully carried out by Müller *et al.*[22] for the [Ni(NH$_3$)$_6$]$^{2+}$ ion indicating values of 0.87, 0.12, and 0.00−0.01 mdyn/Å for Ni−N stretch, *cis* Ni−N and *trans* Ni−N stretch-stretch interactions, respectively. The values obtained here for K_L, K_{LL}, and F'_{LL} of 1.607, 0.250, and −0.0868 mdyn/Å are considered quite reliable since they depend heavily upon the assignment of the fundamentals involving Rh−N stretching which in fact are some of those most reliable in the experimental material (*cf.* Schmidt and Müller [23]).

From these results we conclude that K_L decreases somewhat from [Rh(NH$_3$)$_6$]$^{3+}$ to [Rh(en)$_3$]$^{3+}$ but this trend does not necessarily reflect a weaker bond in the latter compound but may be due to an erroneous choice of the Rh−N bond length in our calculations. The value of F_{LL} appears to increase to the fivefold value on changing the ligand from NH$_3$ to 1,2-ethanediamine, but if we consider instead the ratio K_L/F_{LL} it compares favourably with [Ni(NH$_3$)$_6$]$^{2+}$. In short, the values are not unreasonable, but unsatisfactory for deductions regarding the detailed nature of the bonds in the complex.

The GVF constant for N−Rh−N deformation was found to be 1.10 mdyn Å/(rad)^2, considerably higher than the corresponding values for [Ni(NH$_3$)$_6$]$^{2+}$ [22] and for dimethylglyoxime chelates [19] which are in the range 0.10−0.30 mdyn Å/(rad)^2. However, in the UBFF approximation the appropriate range for 1,2-ethanediamine chelates is 0.16−0.40 mdyn/Å (in-plane bending) and 0.53−0.90 mdyn Å (out-of-plane bending) [3] suggesting the value obtained here to be significant. The numerical values of the interaction force constants F_ϕ and F'_ϕ and of the force constant for Rh−N torsion are also considerably higher than expected from other complex compounds [22] and suggest a considerable stiffening of [Rh(en)$_3$]$^{3+}$. The high values of the bending force constants H_β and H_ω and of the interaction

Table 3. Calculated (ν_{calc}, cm⁻¹) and observed (ν_{obs}, cm⁻¹) fundamentals and main potential energy distribution (PED, %) for [Rh(en)₃]³⁺ from a 38-parameter GVFF based upon the spectra of [Rh(en)₃]Cl₃ and 7 isotopic species.[a]

[Rh(en)₃]³⁺ Species and No.	ν_{calc}[b]	ν_{obs}[c]	¹⁵N shift[d] calc	¹⁵N shift[d] obs	PED[e]	N-d₁₂[Rh(en)₃]³⁺ No.	ν_{calc}[b]	ν_{obs}[c]	¹⁵N shift[d] calc	¹⁵N shift[d] obs	C-d₁₂[Rh(en)₃]³⁺ No.	ν_{calc}[b]	ν_{obs}[c]	¹⁵N shift[d] calc	¹⁵N shift[d] obs	N,C-d₂₄[Rh(en)₃]³⁺ No.	ν_{calc}[b]	ν_{obs}[c]	¹⁵N shift[d] calc	¹⁵N shift[d] obs
A_1 ν_1	3235	3245	10	10	ν_{as}NH(100)	ν_3	2398	2397	14	10	ν_1	3235	3245	10	0	ν_1	2399	2391	15	8
ν_2	3175	3150	6		ν_sNH(100)	ν_4	2306	2339	9	10	ν_2	3175	3192	6	8	ν_2	2306	2330	9	5
ν_3	2973	2968	0	6	ν_{as}CH(99)	ν_1	2973	2972	0	10	ν_3	2234	2238	0	4	ν_3	2233	2233	0	2
ν_4	2911	2906	0	5	ν_sCH(99)	ν_2	2911	2907	0	10	ν_4	2128	2155	0	3	ν_4	2128	2137	0	1
ν_5	1609	1607	5	3	δNH₂(97)	ν_8	1189	1187	6	10	ν_5	1609	1605	5	3	ν_5	1208	1202	8	10
ν_6	1473	1469	0	2	δCH₂(100)	ν_5	1472	1469	0	3	ν_9	1089	1069	3	3	ν_7	1085	1090	1	0
ν_7	1373	1375	1	0	ωCH₂(73)	ν_6	1352	1353	1	3	ν_{10}	967	950	3	3	ν_{11}	846	838	4	1
ν_8	1327	1332	3	3	tCH₂(62),tNH₂(32)	ν_7	1318	1307	2	0	ν_{11}	927	925	8	15	ν_{10}	925	929	11	4
ν_9	1297	1292	2	3	tNH₂(46), tCH₂(37)	ν_9	845	844	0	2	ν_6	1309	1315	3	0	ν_9	1000	1002	10	12
ν_{10}	1183	1182	2	3	ωNH₂(72)	ν_{10}	976	970	11	10	ν_7	1258	1258	3	6	ν_8	1039	1048	2	8
ν_{11}	1059	1061	14	10	νCN(80), νCC(13)	ν_{11}	1055	1057	10	10	ν_8	1110	1103	8	2	ν_6	1168	1169	0	9
ν_{12}	996	1007	3	6	ϱCH₂(53), νCC(16)	ν_{12}	1106	1106	3	6	ν_{12}	882	892	5	5	ν_{12}	783	780	1	0
ν_{13}	871	883	4	6	νCC(49), νCN(20)	ν_{13}	790	808	0	3	ν_{13}	773	771	2	4	ν_{13}	741	751	6	1
ν_{14}	749	750	4		ϱNH₂(87)	ν_{14}	592	587	6	5	ν_{14}	716	719	2	0	ν_{14}	578	570	6	7
ν_{15}	547	545	14	12	γ_sRhN(68)	ν_{15}	504	512	12	14	ν_{15}	543	536	14	14	ν_{15}	499	502	10	8
ν_{16}	308	315	5	7	δNRhN(31), δ_sNCC(19) τCC(15)	ν_{16}	278	273	2		ν_{16}	287	285	5	8	ν_{16}	266	260	3	2
ν_{17}	272	272	3	0	δNRhN(36), δ_sRhNC(27), ν_sRhN(12)	ν_{17}	259	268	2	3	ν_{17}	256	260	3	5	ν_{17}	237	244	3	3
ν_{18}	200	195	2		δNRhN(62), τCC(13)	ν_{18}	191	183	2	3	ν_{18}	173	170	1	3	ν_{18}	170	170	1	1
A_2 ν_{19}	3235	3230	10	30	ν_{as}NH(100)	ν_{31}	2397	2397	14	10	ν_{19}	3234	3210	10	10	ν_{19}	2397	2390	14	15
ν_{20}	3174	3145	5		ν_sNH(100)	ν_{33}	2303	2279	7	8	ν_{20}	3174	3170	6	8	ν_{20}	2303	2290	7	4
ν_{21}	2966	2964	0		ν_{as}CH(99)	ν_{19}	2966	2966	0	0	ν_{21}	2214	2225	0	0	ν_{21}	2213	2196	0	0
ν_{22}	2909	2890	0		ν_sCH(99)	ν_{20}	2909	2905	0	0	ν_{23}	2124	2135	0	0	ν_{23}	2124	2132	0	0
ν_{23}	1607	1607	5	3	δNH₂(97)	ν_{26}	1184	1187	6	10	ν_{23}	1606	1605	5	4	ν_{23}	1192	1190	8	10
ν_{24}	1460	1459	0		δCH₂(98)	ν_{23}	1459	1466	1	0	ν_{27}	1065	1066	1	0	ν_{25}	1075	1080	1	1
ν_{25}	1334	1330	1	3	ωCH₂(65), tNH₂(21)	ν_{24}	1305	1307	1	0	ν_{29}	889	890	5	5	ν_{24}	1115	1113	4	3
ν_{26}	1300	1305	3	5	tNH₂(45), tCH₂(37)	ν_{25}	945	956	2	10	ν_{24}	1287	1290	2	2	ν_{27}	968	971	8	8
ν_{27}	1217	1217	0		tCH₂(59), tNH₂(32)	ν_{28}	1254	1270	2	4	ν_{28}	922	922	4	6	ν_{28}	863	824	0	7
ν_{28}	1170	1163	4	1	ωNH₂(84)	ν_{29}	879	888	2	0	ν_{25}	1230	1229	3	4	ν_{29}	808	1004	0	12
ν_{29}	1031	1028	11	8	νCN(81)	ν_{27}	1039	1038	15	18	ν_{26}	1093	1088	6	4	ν_{26}	993	1004	10	10
ν_{30}	816	812	4	6	ϱCH₂(59), ϱNH₂(26)	ν_{30}	791	795	4	5	ν_{31}	693	694	6	5	ν_{30}	682	673	6	4
ν_{31}	779	785	7	6	ϱNH₂(58), ϱCH₂(11)	ν_{31}	655	650	7	7	ν_{30}	769	785	5	3	ν_{31}	627	628	5	10
ν_{32}	592	580	5	6	δ_{as}NCC(35), δ_{as}RhNC(15), ϱCH₂(22)	ν_{32}	532	539	3	4	ν_{32}	510	511	3	3	ν_{32}	468	480	3	3
ν_{33}	441	445	6	4	ν_{as}RhN(84)	ν_{33}	423	431	4	4	ν_{33}	426	417	4	4	ν_{33}	413	413	4	4
ν_{34}	253	240	4		τRhN(41), δNRhN(39)	ν_{34}	222	226	2	0	ν_{34}	242	242	3	0	ν_{34}	216	220	3	0
ν_{35}	111	110	1		δNRhN(55), τRhN(34)	ν_{35}	107	113	0		ν_{35}	102	106	0		ν_{35}	99	94	0	

Table 3. Continued.

In the table below the modes of the E species are listed by diminishing frequency for the d₀ cation (columns I, II); for the deuterated/isotopic species the modes are re‑ordered by their own frequencies, the correspondence to the d₀ mode being given by the accompanying ν‑label (ν′, ν″). Small integer columns (PED contributions z_{ik} and ^{15}N shifts) are omitted.

ν	PED	I	II	ν′	III	IV	ν″	V	VI
ν₃₆	ν_as NH(100)	3245	3232	ν₄₀	2972	2971	ν₃₆	2390	2391
ν₃₇	ν_as NH(100)	3230	3230	ν₄₁	2966	2966	ν₃₇	2387	2390
ν₃₈	ν_s NH(100)	3150	3174	ν₄₂	2907	2907	ν₃₈	2304	2330
ν₃₉	ν_s NH(100)	3145	3173	ν₄₃	2905	2905	ν₃₉	2302	2290
ν₄₀	ν_as CH(99)	2968	2971	ν₃₆	2390	2390	ν₄₀	2225	2255
ν₄₁	ν_as CH(99)	2964	2966	ν₃₇	2387	2387	ν₄₁	2211	2196
ν₄₂	ν_s CH(99)	2906	2911	ν₃₈	2304	2305	ν₄₂	2127	2132
ν₄₃	ν_s CH(99)	2890	2909	ν₃₉	2302	2302	ν₄₃	2123	2132
ν₄₄	δNH₂(99)	1607	1606	ν₅₀	1187	1185	ν₄₄	1196	1190
ν₄₅	δNH₂(99)	1607	1604	ν₅₁	1187	1181	ν₄₅	1183	1190
ν₄₆	δCH₂(94)	1469	1478	ν₄₄	1474	1464	ν₄₈	1074	1077
ν₄₇	δCH₂(96)	1459	1464	ν₄₅	1467	1464	ν₄₉	1066	1069
ν₄₈	tCH₂(56), ωCH₂(31)	1374	1380	ν₄₆	1385	1375	ν₅₁	1004	1003
ν₄₉	ωCH₂(69), tCH₂(13)	1357	1355	ν₄₇	1352	1338	ν₅₆	843	838
ν₅₀	ωCH₂(47), tCH₂(38)	1310	1318	ν₄₈	1307	1305	ν₄₆	1155	1150
ν₅₁	tCH₂(65), tCH₂(22)	1305	1303	ν₅₂	1058	1058	ν₅₂	993	1003
ν₅₂	tNH₂(88)	1293	1296	ν₅₆	962	959	ν₅₅	894	893
ν₅₃	tCH₂(54), tNH₂(33)	1227	1242	ν₄₉	1270	1256	ν₅₄	959	929
ν₅₄	ωNH₂(77), ωCH₂(14)	1173	1181	ν₅₅	980	979	ν₅₃	978	980
ν₅₅	ωNH₂(80), ωCH₂(14)	1163	1167	ν₅₇	888	882	ν₅₇	818	828
ν₅₆	νCN(92)	1059	1065	ν₅₃	1051	1062	ν₄₇	1106	1103
ν₅₇	νCN(92)	1028	1028	ν₅₄	1038	1034	ν₅₀	1027	1027
ν₅₈	ϱCH₂(86), ϱNH₂(12)	980	980	ν₅₈	864	867	ν₅₉	768	765
ν₅₉	νCC(61), νCN(15)	880	901	ν₅₉	830	823	ν₅₈	788	790
ν₆₀	ϱCH₂(59), ϱNH₂(37)	812	820	ν₆₀	777	775	ν₆₀	639	645
ν₆₁	ϱNH₂(93)	750	751	ν₆₂	587	585	ν₆₂	573	570
ν₆₂	ϱNH₂(64), ϱCH₂(35)	728	731	ν₆₃	587	580	ν₆₃	551	544
ν₆₃	δNCC(59), δRhNC(22)	664	663	ν₆₁	650	648	ν₆₁	622	628
ν₆₄	νRhN(64), δRhNC(14), δNCC(13)	506	507	ν₆₄	475	475	ν₆₅	475	468
ν₆₅	δNRhN(36), δRhNC(18), τRhN(11), τCC(10)	445	435	ν₆₅	424	422	ν₆₄	420	413
ν₆₆	δNCC(26), τCC(25)	397	402	ν₆₆	390	397	ν₆₇	395	398
ν₆₇	δNRhN(41), νRhN(20)	357	359	ν₆₇	333	343	ν₆₈	337	328
ν₆₈	νRhN(86)	296	291	ν₆₈	273	274	ν₆₉	270	270
ν₆₉	δNRhN(87)	184	173	ν₆₉	176	168	ν₆₉	165	170
ν₇₀	δNRhN(48), τRhN(40)	120	120	ν₇₀	113	119	ν₇₀	118	120

(Species: E)

[a] The fundamentals of the tris(1,2-ethanediamine)rhodium(III) cation have been arranged according to their species with diminishing frequencies, those of the deuterated compounds to give, as fas as possible, matching PED's. The stated PED's are only approximative and small contributions have been neglected. [b] Iteration based upon all eight isotopic species. [c] Solvent data used wherever available. [d] Shift following ^{15}N substitution of all six nitrogen atoms. [e] The PED is defined as $z_{ik} = 100 F_{ii} L_{ik}^{2}/\lambda_{k}$.

force constant $F_{\mathrm{L}} = 0.209$ mdyn/rad (cf.[22] [Ni(NH$_3$)$_6$]$^{2+}$: 0.09 mdyn/rad) suggest a strong chelation of the ligand.

Normal modes mainly confined to the ligand. From the results given in Table 3 the following values seem to be typical for 1,2-ethanediamine bonded to Rh^{3+}: δCH$_2$ 1470 cm^{-1}, ωCH$_2$ 1370 cm^{-1} and 1330 cm^{-1}, tCH$_2$ 1230 and 1330 cm^{-1}, and ϱCH$_2$ 820 and 980 cm^{-1}. The results of free 1,2-ethanediamine based upon *cis* C_{2v} symmetry,[24,25] later proved incorrect, [26,27] correspond to the following ranges: δCH$_2$ 1445 $-$ 1469, ωCH$_2$ 1298 $-$ 1318, tCH$_2$ 880 $-$ 1360, and ϱCH$_2$ 761 $-$ 815 cm^{-1}. The only major discrepancy concerns the assignment of a tCH$_2$ mode to 880 cm^{-1} in free 1,2-ethanediamine [25] which appears to be too low. Previous assignments of the modes in [Rh(en)$_3$]$^{3+}$ complexes have been based upon the results of N-deuteration [28,29] using polarized radiation.[30]

Our calculations confirm the coupling between the two amine groups of 1,2-ethanediamine to be much smaller, and the separation between the in-phase and the out-of-phase combination usually does not exceed 50 cm^{-1}. The following regions are typical for 1,2-ethanediamine chelated to Rh^{3+}: δNH$_2$ 1600 $-$ 1610 cm^{-1}, tNH$_2$ 1290 $-$ 1310 cm^{-1}, ωNH$_2$ 1165 $-$ 1185 cm^{-1}, and ϱNH$_2$ 730 $-$ 780 cm^{-1}. As before, these regions apply only to modes which are reasonably localized; they may easily be displaced by 100 cm^{-1} upon coupling with neighbouring modes. The δNH$_2$ mode in [Rh(en)$_3$]$^{3+}$ chelates has been attributed by other authors to bands in the 1500 $-$ 1600 cm^{-1} region.[28,29] This can hardly be correct since [3] (i) the bands in this region (in contrast to the results described recently by Gouteron [30]) disappear by removal of the coordinated water, (ii) the bands are not observed in solution (*cf.* Krishnan and Plane [31]) and (iii) these assignments disagree with the results of the normal coordinate analysis, which consistently place them above 1600 cm^{-1}.

The C$-$C and C$-$N stretching vibrations in [Rh(en)$_3$]$^{3+}$ are coupled to other vibrations, but the C$-$N stretching modes are usually found in the region 1020 $-$ 1070 cm^{-1}. Previous assignments have been based upon comparison with free 1,2-ethanediamine, and locate the modes in question within the region 1000 $-$ 1100 cm^{-1}.[28,29]

Normal modes mainly confined to the central RhN$_6$ region. The six rhodium-nitrogen stretching coordinates form a basis with the reduced representation: $A_1 + A_2 + 2E$ of the point group D_3. Previous investigations [29,30] have identified the symmetrical Rh$-$N stretching vibration of species A_1 as the very strong Raman band at ca. 545 cm^{-1}. Our calculations confirm this band to consist mainly of ν_sRhN (68 %), but weakly coupled to the δNCC (11 %) and δRhNC (14 %) deformational modes. Inspection of the L matrix shows that stretching of the RhN bonds is followed by a closing of the RhNC angles and opening of the NCC angles in such a way that the distance between the rhodium atom and the midpoint of the C$-$C bond is almost unaltered. It should be noted that this band is unambiguously identified by the major shift on ^{15}N substitution (Table 3). It has recently been proposed [32] that the other strong fundamental of species A_1 in the 280 $-$ 320 cm^{-1} region of the Raman spectra of tris(ethylenediamine) complexes (*i.e.* ν_{17} at 272 cm^{-1}) should have substantial RhN stretching character. This is not confirmed by our calculations, which indicate the contribution of ν_sRhN to this band to be only 12 %.

Our calculations show that two bands near 450 cm^{-1} in [Rh(en)$_3$]$^{3+}$ attributed [30] to species A_2 and E can be assigned as the fundamentals ν_{33} and ν_{65}. The former of these arises from ν_{as}RhN (84 %) coupled to δNCC (14 %), *i.e.* corresponds to an almost pure Rh$-$N stretching vibration of species A_2. This was previously assigned [28-30] to bands at *ca.* 100 cm^{-1} higher frequencies.

One of the Rh$-$N stretching vibrations of species E was attributed [29] to a band near 500 cm^{-1}, but this band was assigned by Gouteron [30] to a a ligand deformation. The major shifts observed on ^{15}N substitution (Table 3) leave no doubt that this band must arise mainly from Rh$-$N stretching. However, the calculations indicate that in addition to νRhN (64 %) the PED contains δNCC (13 %) and δRhNC (14 %), and accordingly the fundamental comprises both proposals mentioned above. The other Rh$-$N stretching vibration of species E is calculated to lie around 290 cm^{-1}, which complies with a weak band in the spectrum of [Rh(en)$_3$]$^{3+}$ but may very well need future revision since the ^{15}N shifts are not decisive.

The remaining fundamentals of this region show no features of special interest. However, it should be mentioned that the fundamental ν_{32} of species A_2 was previously attributed to Rh−N stretching [28-30] while our calculations indicate mainly ring deformation coupled to CH_2 rocking. On successive removal of 1, 2, and 3 hydrogen atoms with KNH_2 this band is displaced towards higher frequencies.[23] Since coordination of ethylenediamine anions is undoubtedly much stronger than coordination of neutral ethylenediamine, this shift merely reflects the increase in force constants for δRhNC and δNCC following deprotonation.

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