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The Infrared Spectra and Conformational Analysis of Geometric Isomers of Diethylenetriamine Complexes

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Geometric isomers of diethylenetriamine (dien) complexes of the type $[M^{III}dien\ X_3]$ with $M^{III}=Cr$, Co, Rh, and X=halogen have been prepared. The infrared spectra of these and other compounds, e.g. *[Pd dien Cl]Cl, [Pd et₄dien Br]Br (et₄dien: $[(C_2H_5)_2NCH_2CH_2]_2NH$), and $[Mo\ dien\ O_3]$ are recorded. An empirical assignment of infrared bands to the normal modes of vibration is made using N-deuterated compounds. The regions* 1450, 1250, *and* 850-700 cm^{-1} *provide a means for differentiation of geometric isomers. A comparison with the spectrum of square complexes allows the assignment of the facial and meridional structure to the complex salts. The most probable ring conformation has been determined as k'k for the meridional and kk (or its enantiomer k'k') for the facial isomeric structure.*

Introduction

Hexacoordinated diethylenetriamine complexes of transition group elements have been known for a long time.[1] However, geometric isomers of this type of compounds have been prepared only recently.[2,3] For complexes with one diethylenetriamine molecule attached to the central metal, two geometric isomers are possible. The tridentate ligand either occupies a face of the coordinate octahedron in such a way that the molecule is bent into a triangular form (facial or 1,2,3 isomer), or it is arranged around the central atom like a circumference of a sphere (meridional or 1,2,6 isomer). In either case the ligand forms fused five-membered rings together with the central metal with conformations which are expected to be different for both isomers. The infrared spectra of these compounds are reported only fragmentarily; therefore also the problem of band assignments to fundamental modes of vibration is not solved. However, all these questions have been thoroughly investigated for the corresponding ethylenediamine complexes. Their geometric isomers have been known since the early days of coordination chemistry. The infrared spectra and ring conformations have also been very well studied.[4-7]

In this paper a thorough study of diethylenetriamine complexes is presented, comparable to earlier studies on ethylenediamine compounds. An empirical assignment of infrared bands is made, using also N-deuterated materials. The results are compared with the tentative assignment for square diethylenetriamine complexes of Pd^{II}.[8] Some spectral regions are identified as useful for determining facial and meridional isomers. Infrared spectra also distinguish different ring conformations which are conceivable for the different isomers. Relevant results obtained from the corresponding ethylenediamine complexes are used in the discussion of pertinent problems which is felt to be justified in view of the similar atomic groupings in the ethylenediamine and diethylenetriamine molecule.

Experimental Section

Materials. The synthesis of the complex compounds followed the course described in literature.[2,3,9,10] In some cases the preparations were modified in order to simpify the method or to obtain higher yields of products. For example, the chloride, [Pd dien Cl]Cl, was obtained in higher (*ca.* 45%) yield, by direct reaction of stoichiometric amounts of $K_2[PdCl_4]$ and diethylenetriamine in aqueous solution. The molybdenum compound $[Mo\ dien\ O_3]$, was supplied by Dr. Marzluff.[11]

The only compound for which no detailed synthesis is available, is the facial isomer of $[Cr\ dien\ Cl_3]$. We therefore describe one which is based on the preliminary method given by House.[3]

(1,2,3)[Cr dien Cl_3]. A suspension of finely powdered $[Cr\ urea_6]Cl_3 \cdot 3H_2O$ (2 g) in absolute ethanol (50 ml) together with a diethylenetriamine solution (0.38 ml in 10 ml ethanol) is heated on a steam bath. The solvent should evaporate very slowly.

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Table I. Infrared Absorption Bands (cm^{-1}) of monodiethylenetriamine Complexes [a]

Assignment	(1,2,6)-RhdienCl$_3$	(1,2,6)-RhdienCl$_3$ N-deut.	(1,2,3)-RhdienCl$_3$	(1,2,6)-RhdienBr$_3$	(1,2,3)-RhdienBr$_3$	(1,2,6)-RhdienI$_3$	(1,2,6)-CrdienCl$_3$	(1,2,3)-CrdienCl$_3$	(1,2,6)-CodienCl$_3$	(1,2,3)-ModienO$_3$	(1,2,3)-ModienO$_3$ N-deut.	[PddienCl]Cl	[PddienCl]Cl N-deut.
ν_{NH_2}, ν_{NH}	3283 s 3220 s 3160 sh 3143 s	2455 s 2405 sh 2380 s 2320 s	3250 s 3225 s 3205 s 3180 sh 3137 s	3280 s 3225 s 3183 s 3123 m	3275 m 3235 sh 3222 s 3190 s 3125 s	3270 s 3215 s 3168 s 3120 m	3290 s 3228 s 3130 s	3300 ms 3275 s 3254 s 3225 s 3134 ms	3287 s 3233 s 3185 mw 3150 m, br	3247 s 3210 m 3112 s	2422 s 2390 m 2335 sh 2305 s	3210 s 3127 s 3060 s	2408 s 2360 s, br 2307 s 2238 s
ν_{CH_2}	2970 mw 2955 m 2940 m 2910 m 2880 w	2972 w 2945 mw 2875 w	2988 w 2955 mw 2910 vw 2878 w	2990 w 2968 vw 2943 m 2880 sh	2935 w	2977 w 2955 vw 2924 m	3000 mw 2951 m 2887 mw	2996 w 2980 w 2945 mw 2900 sh	2950 w 2915 ms 2850 m	2986 w 2957 vw 2937 mw 2925 m	3002 w 2985 w 2958 w 2935 sh 2924 m	2955 vw 2935 vw 2885 mw	2982 mw 2955 mw 2873 mw
δ_{NH_2}	1580 s 1563 sh	1180 s 1163 m	1578 s, br 1555 sh	1575 sh 1567 s	1575 s, br	1568 s	1570 s	1580 s, br	1572 s, br	1620 w 1595 s	1197 s, sh 1187 s	1597 s	1190 s 1177 s
δ_{CH_2}	1480 w [c] 1448 s	1448 s	1487 ms 1449 s 1421 m	1443 s	1485 ms 1446 s 1422 m	1441 s	1448 s 1441 s	1490 s 1460 s 1428 ms	1480 vw [c] 1448 s	1485 m, sp 1460 s, sp 1440 m, sp	1490 ms 1461 s 1442 m	1483 w [c] 1468 ms 1450 s	1470 w 1450 s, br
ω_{CH_2}	1386 w 1371 w 1336 m	1380 w 1361 mw 1352 m	1396 m 1368 mw 1355 m	1382 mw 1365 vw 1351 m	1394 m 1366 mw 1356 m	1381 w 1369 vw 1352 m	1391 mw 1362 mw	1398 m 1373 mw 1360 mw	1382 vw 1368 w 1348 m	1391 w 1370 mw 1340 m, sp 1334 m, sp	1379 w 1361 w 1349 w	1387 m, br 1353 m, sp	1380 mw 1369 mw 1349 m
ω_{NH_2}	1308 m	1015 m	1308 ms	1300 m	1304 ms	1300 m	1312 ms	1330 m 1305 ms	1302 s	1317 s	1014 w, sh	1310 ms	1020 s
γ_{CH_2}	1287 m	1270 w 1259 vw	1299 m 1290 mw 1250 w	1283 mw 1255 sh	1295 m 1288 w 1253 w	1283 mw 1273 sh	1291 m 1285 sh	1312 w 1292 m 1252 w	1284 w	1293 ms 1256 mw 1247 mw	1302 ms 1280 m 1256 ms	1322 mw [c] 1298 mw 1285 mw	1280 mw [c] 1269 vw 1260 mw
ω_{NH}	1250 ms	990 m		1243 ms		1243 m	1251 ms		1244 s			1250 m	998 mw
ω_{NH_2}	1142 s	922 ms [b]	1182 ms 1160 w	1135 sh 1120 s	1174 ms 1159 m	1130 m	1140 s 1130 m	1170 w 1148 s	1130 s	1187 s 1148 ms	913 s	1168 mw 1152 s	929 s, br [b]
γ_{NH_2}	1120 s	870 ms [b]	1145 s	1110 s	1141 s	1120 s	1110 s	1126 s	1112 s	1128 s	885 m, sh [b]	1147 s, sh	875 ms [b]
C—C C—N C_r—N	1088 s 1079 s 1049 ms 1033 ms	1093 s 1080 sh 1030 s	1085 sh 1071 s 1045 w 1030 s	1080 s, br 1043 m 1028 s	1070 s, sp 1035 m, sh 1029 s	1080 s 1066 ms 1040 sh 1030 s	1087 s 1060 vw 1035 s	1071 s 1022 s 1010 w	1090 s 1060 ms 1040 sh 1030 s	1075 s 1043 s 1032 s	1078 s 1068 s 1037 s	1103 s, sp 1087 s 1056 s 1030 vw	1095 s 1073 m 1043 mw 1030 sh
γ_{NH_2}	1002 s	795 s	1002 m	990 ms	1009 mw 982 w	990 ms 984 ms	972 s	490 m	990 s	999 s, sp	798 m	1000 mw 994 ms	825 s, br
ρ_{CH_2} ρ_{NH_2} ρ_{NH} and C—N	918 m 889 mw 858 mw 847 m 680 vw	905 w, sh	919 mw 906 w 868 mw 787 m 758 m 669 m	912 m 880 mw 848 w 835 m 685 vw	899 m 863 m 782 m 750 m 690 w 657 m	912 m 878 mw 848 w 831 m	916 mw, sp 892 m, sp 852 mw, sp 830 m, sp 675 m 655 mw, br	902 mw 870 mw 861 m 785 m 703 s 635 mw 610 m	928 ms, sp 900 mw 870 m, sp 844 ms 720 w, br	896 mw, sp 883 w 875 mw, sp 785 mw 630 sh	893 m, sp [b] ? [d] 585 mw 548 m	930 m, sp 891 mw, sp 865 mw 838 m, sp 735 m 691 mw	? [b] 657 vw 610 w 588 mw
ν(M—N)	573 mw 540 w	530 mw 510 w	572 mw 541 mw	570 w 512 mw	566 mw 534 mw	570 w 499 mw	539 ms 478 ms 457 ms	541 ms 498 mw 457 m	570 ms 518 w 498 m	525 w 476 mw, br 453 mw, br	440 m, br	558 m 516 m 483 m	492 m 455 mw
δ_{ring}	470 mw	440 mw	480 w	468 mw	476 mw 457 w	468 w 448 vw	420 mw	431 m	452 w	380 ms 367 m	377 ms 363 m	451 mw	440 w
δ(N—M—N)	412 mw	410 mw	413 mw	410 vw	410 mw	399 vw	340 m	350 ms	418 m	348 ms	345 ms	389 m	380 m
M—hal.	320 s	315 s	320 s 296 s				300 s	310 s 298 s	330 s 320 s	837 s, br ν(Mo—O)	840 s, br ν(Mo—O)	331 s	331 s
unassign.		1222 vw 1208 vw	1226 w		1224 w			1232 w		638 m, br δ(O—Mo—O)?	633 m δ(O—Mo—O)? 1224 vw		1228 m 1210 w

[a] Intensities: s, strong; m, medium; w, weak; vw, very weak; sp, sharp; br, broad; sh, shoulder. [b] Covers also ρ-CH$_2$. [c] Combination (?). [d] Covered by δ(O–Mo–O).

Optimal conditions are obtained if the solution reaches dryness only after some 45 min. Accelerated evaporation cuts down the conversion of the starting materials. The resulting sticky fluid material is heated at 100° for another three hours. During this time the gum changes into a violet oil which at room temperature is dissolved in 12 *M* HCl solution (10ml). After filtration from some greenish residue (perhaps starting material) ethanol (10 ml) is added to the filtrate so that no precipitate is formed. The mixture is allowed to stand for 2-3 days at room temperature. Dark green, shiny crystals are formed which are collected on a fritted glass filter, washed with alcohol and dried over silica. The compound is insoluble in water or alcohol.

Anal. Calcd. for $C_4H_{13}N_3Cl_3Cr$: C, 18.37; H, 5.01; N, 16.07; Cl, 40.65; Cr, 19.90. Found: C, 18.21; H, 5.17; N, 16.19; Cl, 40.50; Cr, 19.87.

Deutero derivatives were prepared in the usual way[6] by recrystallization from heavy water. This process was repeated until practically no NH_2 groups were detected in the infrared spectrum. This procedure can be applied only if the complexes are sufficiently soluble in water. It was made certain that no hydrolysis occurred during recrystallization. This was checked by recording the ultraviolet spectrum in which loss of coordinated halogen should be detected immediately.

Infrared Spectra. The infrared spectra of crystals in KBr pellets or in nujol suspensions were recorded on a Perkin-Elmer grating infrared spectrophotometer, Model 521.

Infrared Spectra and Band Assignments. In Table I the maxima and relative intensities of infrared absorption bands for a series of mono-diethylenetriamine complexes are listed which are selected as representatives for an infrared investigation of geometric isomers. The assignments of the bands to the fundamental modes of vibrations is discussed in detail in this section. Use is made of relevant results obtained for the free ethylenediamine molecule and its coördinated forms. An tentative band assignment for the free diethylenetriamine molecule in carbon tetrachloride solution was made by Segal and Eggerton,[12] planar complexes with this amine as a ligand have been investigated by Watt and Klett.[8] According to preceding investigations the fundamental vibrations of such molecules are considered in five categories with

(12) L. Segal and F. V. Eggerton, *Appl. Spectr.*, *15*, 148 (1961).

bands occurring in the following spectral regions:[6]

(1) $NH_2(NH)$ and CH_2 stretching vibrations (ν)	3500-2800 cm^{-1}
(2) $NH_2(NH)$ deformations (bending δ, twisting γ, wagging ω, rocking ρ)	1650- 600 cm^{-1}
(3) CH_2 deformations	1500- 800 cm^{-1}
(4) skeletal stretching vibrations, involving C–C, C–N, and (for secondary amines) C_2N stretches	1100- 800 cm^{-1}
(5) skeletal stretching vibrations (metal-nitrogen and metal-halogen stretches) and ring deformations (bending N–C–C–N and N–M–N)	<600 cm^{-1}

(1) *$NH_2(NH)$ and CH_2 Stretching Vibrations.* A maximum of five NH stretching vibrations per diethylenetriamine are expected. In general the facial (1,2,3) isomers display a larger splitting than their meridional (1,2,6) analogues. Indeed for halogen (1,2,3) complexes five bands are found in the NH stretching region (3300-3050 cm^{-1}) while (1,2,6) isomers show only three strong bands which may be accompanied by a shoulder or another weak absorption. A more detailed assignment is proposed by Gentile *et al.*[13] for nine-coordinated complexes who locate the NH stretching mode of the secondary amine group in the interval between the asymmetric and the symmetric NH_2 stretching mode of the primary amine group. However, this seems not to be true for square complexes which have their ν–(NH) at the low frequency end of this region.[8] A decision on octahedral complexes could be made if corresponding et_4dien complexes were investigated. Nitrogen deuteration shifts these bands by a factor of $\nu_{NH_2}/\nu_{ND_2} = 1.34\text{-}1.36$ which is in close agreement with the value 1.37 obtained from the harmonic oscillator approximation. In Figure 1 the infrared spectrum of a typical complex is presented together with that of its N-deuterated compound. The CH_2 stretching vibrations have lower intensities compared to the NH_2 stretching modes and are hardly recognizable for some (1,2,3) isomers.

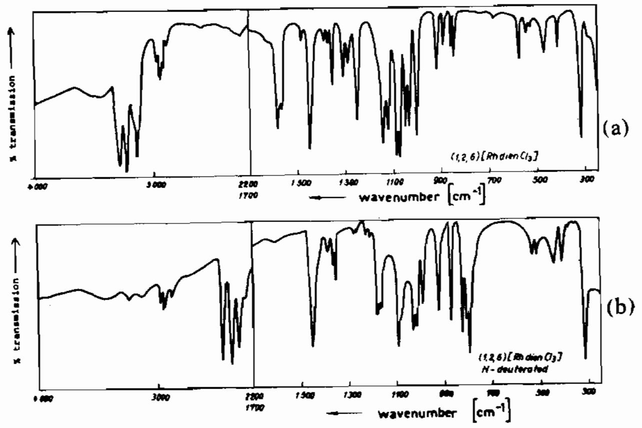

Figure 1. Infrared spectra of (a) (1,2,6)[RhdienCl$_3$] and (b) its N-deuterated complex in KBr medium.

(2) *$NH_2(NH)$ Deformations.* The assignment of NH_2 and CH_2 deformations follows the frequency sequence proposed for ethylene-diamine complexes,[6,8,14] according to which these vibrational modes have the energetic order

$$\text{bending} > \text{wagging} > \text{twisting} > \text{rocking}$$

The spectrum of the deutero complexes also helps to establish the assignment to different NH_2 deformation modes. For bending frequencies a larger isotope effect is expected than for other vibrational mechanisms, since the latter modes are strongly coupled with corresponding CH_2 deformations.

Each NH_2 group gives rise to one of the deformation modes mentioned above. For the NH group only a wagging and a rocking mode can occur. In few cases more bands than theoretically possible are observed in particular regions. The origin of these weak bands may be explained by interacting molecules in the crystal or by combinations of bands with lower frequency. A decision is difficult to make since solution spectra, even if they were obtainable from compounds of such limited solubility, would probably not provide useful information because of the existence of a number of rotational isomers.

(2a) *NH_2 Bending (δ–NH_2).* This vibrational mode is found in the region 1550-1600 cm^{-1}. It was proposed[4,5] to use this region as a means for differentiation of *cis-* and *trans-*isomers of bis-ethylenediamine complexes. Also diethylenetriamine complexes exhibit a larger splitting of δ–NH_2 for (1,2,3) than for (1,2,6) isomers. However, this effect is too weak to be used for an assignment of the geometric isomers. The isotope shift of these bands are also close to the theoretical factor $\nu_{NH_2}/\nu_{ND_2} = 1.37$.

(2b) *NH_2 Wagging and Twisting (ω–NH_2, γ–NH_2).* Since the spectrum of ethylenediamine and diethylenetriamine complexes are almost identical for wave numbers higher than about 1400 cm^{-1}, the assignment of the bands in this region is made on the basis of earlier work.[4-6,8] In the region of lower energy the spectrum differs more distinctly for the two molecules.[12] For an assignment of these bands the spectrum is compared with that of the corresponding deutero compounds. In the region 1350-950 cm^{-1} five bands can be shown to be shifted by deuteration. One at 1300 cm^{-1} is observed in all compounds, it is assigned to the first ω–NH_2, the second one is found between 1170-1120 cm^{-1} in close neighborhood to another strong absorption at 1150-1100 cm^{-1} which is due to γ–NH_2. The ω and γ region also has been proposed as characteristic for recognizing *cis-trans* bisethylenediamine isomers.[15,16] We notice that facial diethylenetriamine complexes have three well-resolved, approximately equally spaced bands between 1200-1100 cm^{-1}, while their meridional components show only two absorptions.

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(13) P. S. Gentile, J. Carlotto, and T. Shankoff, *J. Inorg. Nucl. Chem.*, *29*, 1427 (1967).

(14) G. W. Watt and D. S. Klett, *Inorg. Chem.*, *5*, 1278 (1966).

(15) M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.*, *81*, 6412 (1959).

(16) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.* (A), 546 (1967).

All meridional complexes display a medium strong absorption band at 1250 cm^{-1} which is absent (or has only very weak intensity, possibly due to a γ–CH_2 component which is to be expected in this region) in the spectra of their facial counterparts. Such an absorption is not present in corresponding ethylenediamine complexes. On deuteration this band shifts by a factor of 1.26, losing in intensity. It is assigned to the NH wagging mode which should appear at higher wave numbers than the corresponding rocking vibration. This assignment is confirmed by the spectrum of $[\mathrm{Pd\,et_4dien\,Br}]^+$, a compound in which all primary amine groups are ethyl-substituted. Among all NH_2 and NH vibrations only this ω–NH mode maintains its position while the others assigned to NH_2 vibrations disappear. Watt and Klett[8] assign this band to γ–CH_2; their ω–NH mode occurs at about 1450 cm^{-1}. This does not agree with our findings of isotope shifts for deuterated compounds.

(2c) *NH_2 Rocking (ρ–NH_2).* Two NH_2 rocking bands at frequencies around 850 cm^{-1} are observed in the spectrum of (1,2,6) isomers. These are shifted to lower wave numbers and have higher intensities for the corresponding (1,2,3) isomers (see Figure 2a). In this region two additional bands are found which are more pronounced in the spectra of Pd^{II} and Cr^{III} compounds. The latter are shifted on deuteration by a factor of ~ 1.2. Since all other NH_2 and NH vibrational modes have been detected this absorption can be only due to a NH rocking frequency or a C–N ring skeletal vibration in which the nitrogen atom is predominantly involved. In (1,2,3) complexes this absorption is always more intense and shifted to lower wave numbers.

We prefer this assignment to that given for Pd^{II} complexes[8] since these bands can be considered as doublets which occur in the spectra of both isomers but at different wave lengths.

(3) *CH_2 Deformations.* (3a) *CH_2 Bending (δ–CH_2).* The δ–CH_2 is expected[17] for all 1,2-disubstituted ethanes in the region 1500-1400 cm^{-1}. For (1,2,6) diethylenetriamines this absorption is found at 1450 cm^{-1} generally accompanied by another weak absorption which possibly is a combination band. The spectrum of (1,2,3) isomers, however, exhibits a band triplet in this region which is rather specific for the facial isomeric structure (see Figure 2b).

(3b) *Other CH_2 Deformation Modes (ω–, γ–, ρ–CH_2).* Other low energy bands which are hardly affected by N-deuteration are assigned to wagging, twisting and rocking CH_2 modes, respectively. All these band intensities are relatively small. Their positions do not vary for the two steric isomers. Only the ρ–CH_2 mode shows a more pronounced splitting and a shift to smaller wave numbers for the (1,2,3) component. For these bands the same is true as for the ρ–NH_2: they hardly can be distinguished by the present method from low energy C–N stretches.

(4) *C–C and C–N Skeletal Vibrations.* The high intensity bands at 1100-1000 cm^{-1} are assigned to C–C and C–N ring vibrations.[4,6,18] Meridional complexes show in general three to four bands, while facial isomers have only two strong bands in this region. A more detailed analysis of these absorptions is not possible on the basis of the present experimental results.

(5) *M–N and NCCN Skeletal Vibrations.* Metal-nitrogen stretches occur in the region 600-450 cm^{-1}.[6,19] The isotope shift of these absorption bands is usually larger[6] than the theoretical value $\nu_{M-NH_2}/\nu_{M-ND_2} =$ 1.05-1.06. Two other absorptions weakly influenced by a deuteration are assigned to N–M–N bending and N–C–C–N ring deformations.[6,16,19] Although some δ–(N–M–N) frequencies are very high this assignment is preferred to a δ–(NCC) deformation[8] because of the large dependence of the band positions on the central metal. On the other hand, these bands do not vary much with the geometry of the compounds. Since different ring conformations are expected for the two isomers, the skeletal deformations δ–(NCC) should also be different. Also metal-halogen stretching modes are detected in this region which display a higher splitting for *cis*- than for *trans*-complexes.[16]

This completes the band assignment which can be made on the basis of the present results. At this stage of investigation, more detailed assignments would be for the most part fortuitous. The bulk of infrared bands, however, has been interpreted with some certainty.

Detection of Geometric Isomers. The infrared spectrum can be used as a straightforward means for detecting and assigning facial and meridional geometric isomers of monodiethylenetriamine complexes. As indicated in the preceding section, several spectral regions may be used for such an assignment. According to our experience three regions are most appropriate for this purpose. In Table II band characteristics are presented which differ essentially in these regions. Figure 2 illustrates parts of the spectrum for a typical pair of isomers.

Table II. Spectral Regions for Detecting Diethylenetriamine Geometric Isomers

	CH_2 bending 1500-1400 cm^{-1}	NH wagging *ca.* 1250 cm^{-1}	NH_2 rocking 850-700 cm^{-1}
(1,2,3)	3 bands	—	1-2 bands 700-800 cm^{-1}
(1,2,6)	1 band	1 band	2 bands at 850 cm^{-1}

Notice that the spectrum of the square Pd^{II} compound in which the ligand assumes the shape of a chain agrees well in all regions with the spectrum of the meridional isomers. Those compounds characterized by this group of infrared spectra are then assign-

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[17] S. Mizushima, I. Ichishima, I. Nakagawa, and J. V. Quagliano, *J. Phys. Chem.*, *59*, 293 (1955).

[18] A. D. Allen and C. V. Senoff, *Canad. J. Chem.*, *43*, 888 (1965).

[19] M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc.* (A), 592 (1967).

ed with certainty to the meridional structure while the others represent their geometric counterparts. This assignment agrees in all cases with that made earlier using the visible and ultraviolet spectrum.[2,3] It seems comprehensible that the vibrational modes of the secondary amine group are particularly dependent on whether the chelating ligand has a linear or a triangular form. This explains the noticeable difference of the spectrum in the 1250 cm^{-1} region. It is also worth emphasizing that facial isomers always show more numerous bands and a larger band splitting in their spectra. From this a lower point symmetry can be concluded for this steric isomer.

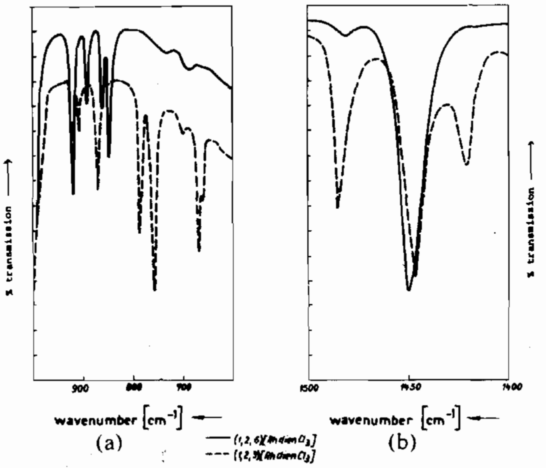

Figure 2. Different spectral regions used for differentiation of the facial and meridional [RhdienCl$_3$] isomer.

The Conformation of the Chelating Ring Systems. The infrared spectrum represents a powerful tool for a conformational analysis of ring systems,[20] and was applied to ethylenediamine complexes to determine conformations of five membered chelating rings,[5,21] although decisions in ambiguous cases can be made only by X-ray analysis.[22] Thorough infrared investigations have shown that 1,2-disubstituted ethanes coordinated to metal ions are present in their gauche forms.[17,21] This has been confirmed by X-ray data.[23]

Corey and Bailar[7] investigated the stereochemistry of individual rings in bis- and tris-ethylenediamine complexes. Their notation is used in the following (another more reasonable but less common notation was introduced by Douglas[24]). Possible gauche forms of the ethylenediamine molecule are either k or its mirror image k′. They can be converted into each other by an internal rotation about the C–C axis. An equivalent notation may be used for the diethylenetriamine molecule. If diethylenetriamine is considered to consist of two ethylenediamine moieties, the ethylenediamine moiety being that portion of the molecule having the structure $H_2N{-}CH_2{-}CH_2{-}NH{-}$, the notation of Corey and Bailar can be used as applied to bisethylenediamine complexes. For the tridentate ligand two coupled rings are formed by coordination, each assuming either the k or k′ form. As can be illustrated by an atomic model, four possible forms can be constructed which are suitable for coordination preserving the two ethylenediamine parts in their gauche forms. There are two symmetric forms kk′ and k′k, which are not identical but have a mirror plane going through the secondary amine group. The other two forms kk and k′k′ are asymmetric; they are enantiomeric and energetically equivalent to each other. It is therefore not possible to distinguish between these latter forms by the infrared spectrum or on the basis of energy arguments by constructing ring models. It can be shown that under the conditions mentioned only one ring system is possible which is suitable for (1,2,6) meridional coordination, that is the k′k form with a reflection plain as symmetry element. All other ring systems have to abandon the molecular gauche form or deviate essentially from the tetrahedral valence angle for carbon atoms. The most likely ring conformation for (1,2,3) facial isomers is obtained by the asymmetric kk or k′k′ form. The kk′ conformation which may also be thought of as possible for facial isomers is ruled out because of the steric hindrance due to hydrogen atoms which approach each other appreciably in this ring structure. The kk′ conformation also would belong to a symmetric situation which would be as high as proposed for (1,2,6) complexes. However, the infrared spectrum of facial isomers exhibits in all regions a higher band splitting which points to a larger number of unequivalent atomic groups in the molecule. From this it is concluded that the atomic groups are arranged in different point symmetries in the two isomers, the facial complex belonging to a lower symmetry. Such an arrangement is achieved if for the (1,2,6) complex k′k and for the

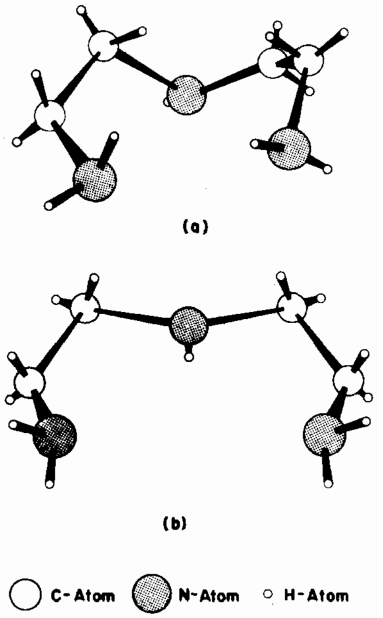

Figure 3. Ring conformations determined for (a) the facial (asymmetric k′k′) and (b) the meridional (symmetric k′k) diethylenetriamine geometric isomers.

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(1,2,3) complex kk or its enantiomeric form k'k' ring conformation is assumed. The molecular structure of (1,2,3)[Mo dien O_3] has been determined with high accuracy by X-ray analysis.[25] According to this work the diethylenetriamine ring in our notation has the kk conformation.

In Figure 3 the preferred conformation of the chelating rings are illustrated for both geometric isomers. Notice that for the asymmetric form both enantiomers are equally possible for energetic reasons. In the symmetric structure two NH_2 and CH_2 groups, respectively, are equivalent. Therefore NH_2 and CH_2 stretching or bending vibrations are always found less numerous in the spectrum of (1,2,6) structures than for (1,2,3) structures. The disappearance of the ω–NH mode in the spectrum of the facial isomer is not easy to explain. This band is either shifted to other wave numbers where it cannot be discovered below other more intense absorptions or the transition loses its infrared activity.

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