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Molecular structures and infrared spectra of five-coordinate copper(II) complexes including one tridentate diethylenetriamine ligand

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Abstract

The molecular structures of five-coordinate Cu(dien)L_2 (dien = diethylenetriamine; L = NO_3^-, Br^-, Cl^-, ClO_4^-) have been examined by molecular mechanics (MM2). All compounds have dien in the meridional (*mer*) position and *k,k'* (symmetric) conformation. The dien position, however, differs from the rigorous *mer* form as to the NCuN (N-terminal) being less than the expected 180°. The IR bands of these compounds in the 50–4000 cm^{-1} range have been recorded in the solid state and assigned on the basis of normal coordinate analysis (potential energy distribution) of the dien molecule. The experimental IR spectra of the studied compounds were compared with frequencies calculated by the MOPAC 6.0 package assuming dien to be coordinated in *fac* and *mer* positions. The comparison shows that in fact the dien ligand in the studied compounds should be midway between the *fac* and *mer* positions.

1. Introduction

The diethylenetriamine ligand (dien) acts as a tridentate ligand and forms a series of transition metal complexes of different types: $[M^{II}(dien)L]L$ or $[M^{III}(dien)L]L_2$, $[M^{II}(dien)L_2]$ or $[M^{III}(dien)L_2]L$ and $[M^{II}(dien)_2]L_2$ or $[M^{III}(dien)_2]L_3$, with M = Cu(II), Co(III), Cr(III), Rh(III), Mo(III), Pd(II) and L = NO_3^-, Cl^-, Br^-, I^-, ClO_4^- [1–13]. These complexes are four-, five- or six-coordinate. According to the notation of Corey and Ballar [1], two different positional isomers are known for the dien molecule in this class of compounds: facial (*fac*) and meridional (*mer*). Further the dien ligand may be in asymmetric (*kk*) or symmetric (*kk'*) conformation. A number of geometric isomers of six-coordinate diethylenetriamine complexes M(dien)L_3 has been so far prepared and the ligand conformation has been studied by their IR spectra [2–4]. It has been concluded that the *fac* and *mer* isomers for the mono-dien complexes may be distinguished by their IR spectra [4]. A recent IR study of Cr(glygly)(dien)ClO_4 has confirmed the *mer* coordination of dien to Cr(III) [5]. X-ray crystal diffraction data have shown that M(II) ions may also form complexes [6–11] in which both *fac* or *mer* conformations were detected. $[Cu(dien)_2](NO_3)_2$ for example has a crystal structure in which the Cu(II) environment is a tetragonally compressed octahedron (CuN_6). Each dien ligand is tridentate and coordinates in *fac* conformation of the terminal nitrogen atoms [8, 9].

In this work we report the IR spectra of four mono-dien Cu(II) complexes with different anions: $[Cu(dien)(NO_3)](NO_3)$ (**1**), $[Cu(dien)Br_2]$ (**2**), $[Cu(dien)Cl_2]$ (**3**) and $[Cu(dien)(ClO_4)](ClO_4)$ (**4**). Recently X-ray crystallographic data have shown that in **1** dien is in the meridional position with *kk'* conformation [12]. No structural data have been found for the other three complexes, so far. X-ray crystallographic data on Cu(II) iodo complexes of diethylenetriamine are also available [13]. We have also prepared a Cu(dien)I_2 compound. Since we were not certain whether it is the monomeric or polymeric species reported in the literature [13] we did not include it in the series of mono-dien compounds under consideration in this work.

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The study has been undertaken with the purpose of detecting the dien coordination type and of detecting which part of the coordinated dien IR spectrum is sensitive to the dien coordination type.

2. Experimental

The compounds were prepared and characterized as described elsewhere [14]. The IR spectra were recorded with an FT spectrometer Bruker IFS 113 V in PE disks in the 30–700 cm^{-1} region and in KBr pellets in the 4000–700 cm^{-1} region. The resolution in all IR measurements was better than 3 cm^{-1}.

2.1. Computational procedure

The vibrational secular determinant was set up and solved by computer programs [15–17] starting with guessed force constants. The force constants were refined via a non-linear least-square analysis between calculated and observed frequencies. A generalized valence force field (GVFF) was used. The initial set of force constants was taken from normal coordinate treatments of primary and secondary aliphatic amines. Molecular mechanics calculations were performed with the MM2 method [18]. No parameters for the diperchlorate complex were found, however, and attempts to find its molecular structure have been abandoned. The ligand geometric isomers were studied also by the MOPAC 6.0 method [19] which also gave their force fields and vibrational spectra. The input structure in the MOPAC calculations were those produced by the MM2 method with fixed NN distances as prescribed by the *mer* and *fac* positions.

3. Results and discussion

3.1. Molecular mechanics calculations

3.1.1. Geometries of the dien ligand

Figure 1 shows several structural isomers of the dien ligand: it should be noted that each isomer produces a number of conformers differing with respect to the locations of the two lone pairs of the terminal NH_2 groups and the lone pair at the imine nitrogen atom. In each case we examined the variation of the MM energy as a function of the rotation around the H_2N–C bonds. The results reported in this paper for the free dien ligand refer to the lowest energy conformer with the lone pairs located as far away as possible. The orientation of the lone pairs in a–d is unfavorable to achieve coordination to the metal ion with the exception of the omega conformer.

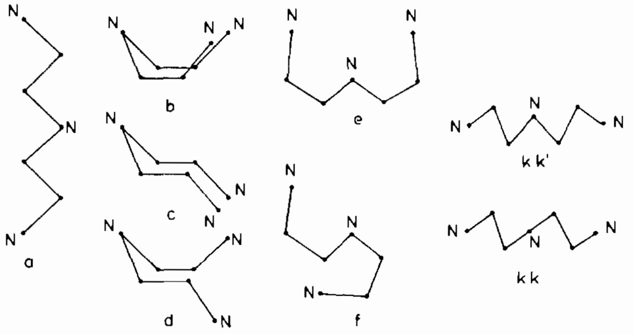

Fig. 1. Dien conformers: (a) linear; (b) boat; (c) chair; (d) intermediate; (e) omega; (f) S-like.

The results from the MM calculations for the free ligand are summarized in Table 1. It should be noted that the linear and omega conformers denoted by I and II differ as to the location of the lone pairs at the nitrogen atoms. Listed in Table 1 are only two (the lowest energy) conformers. The unlisted conformers with gauche location of the terminal lone paris offer quite unfavorable orientation of the lone pairs for their attachment to the central atom.

It is readily seen that the lowest energy conformer is the *k,k'* omega II with MM energy much lower from that of the linear conformers. In fact this conformer offers the best chances to coordinate to a central ion in a tridentate mode.

Figure 2 depicts the *mer* and *fac* coordination mode of the dien ligand. Assuming bond lengths Cu–N ≈ 2.00 Å [12] the geometric relations given in the Figure caption result. By comparing these bond lengths and valence angles with those listed in Table 1 one can readily see that the conformer best suited to bond in a *mer* mode is omega II. In fact a little shortening of the N_1N_2 length and closing of the $N_1N_2N_3$ angle is needed. The conformer best suited to coordinate in a *fac* mode is the boat form.

Table 2 lists the MM results for dien in *mer* and *fac* coordination, obtained by fixing the lengths and angles as given in the caption of Fig. 2. It is readily seen that the *mer* form is more favorable than the *fac* form and the energy gain when going from *fac* to *mer* comes from torsion (~3 kcal mol^{-1}), van der Waals (1.5 kcal mol^{-1}) and bending (0.6 kcal mol^{-1}). In fact the *fac* form is highly strained (SE = 6.5 kcal mol^{-1}), while the strain of the *mer* isomer is much lower (~1.0 kcal mol^{-1}).

3.1.2. Geometries of the Cu(dien)L_2 complexes

By positioning the two L groups (L = Cl^-, Br^-, NO_3^-, ClO_4^-) randomly in space and performing MM minimization the resulting geometry was already the *mer* coordinated *k,k'* dien conformer with five-coordinate Cu giving a distorted trigonal bipyramid (TBP) structure.

Table 3 lists the molecular structures produced by MM minimization. It is readily seen that the distortions from a regular TBP are mainly:

TABLE 1. Results from MM2 calculations for different dien conformers (see Fig. 1)

	Linear I[b]	Linear II[c]	k,k'				
			Boat	Chair	Omega I	Omega II	S-like[d]
MMX[a]	2.72	3.65	4.68	8.01	1.76	0.74	4.25
STR[a]	0.13	0.15	0.26	0.25	0.25	0.23	0.29
BND[a]	0.69	0.86	2.44	2.77	1.96	0.85	1.88
TOR[a]	−0.50	−0.42	0.52	2.38	−2.33	−2.08	−0.64
VDW[a]	2.67	2.64	1.90	2.03	2.15	2.27	2.19
ΔH_f[a]	−4.46	−3.54	−2.51	0.92	−5.43	−6.45	−2.94
SE[a]	1.08	2.01	3.04	6.37	0.12	−0.90	2.61
$R(N_1N_2)$	3.70	3.70	2.93	3.25	2.96	2.85	3.02
(Å)	3.70	3.70	2.93	3.25	2.96	2.85	3.02
	7.26	7.25	3.70	4.03	5.18	4.82	5.60
$\angle N_1N_2N_3$ (°)	158.3	157.3	78.0	70.0	123.1	113.7	135.8
$\angle$CCNC (°)	175.3	175.5	95.5	104.3	179.3	177.0	174.7

[a] In kcal mol^{-1}. [b] Linear I: with the lone pairs of the two terminal Ns above (eclipsed) and that of the NH below the plane defined by the 3N. [c] Linear II: with the 3 lone pairs of the 3N on one side (eclipsed) of the plane defined by the 3N atoms. [d] S-like and intermediate conformers gave equal MM results.

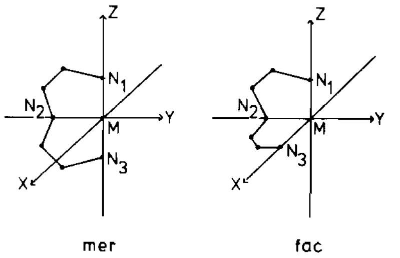

Fig. 2. The meridional (*mer*) and facial (*fac*) dien coordination to a metal ion located at the origin of a Cartesian coordinate system. For M–N = 2.0 Å the following relations result:

	mer	*fac*
N_1N_2 (Å)	2.8284	2.8284
N_2N_3 (Å)	2.8284	2.8284
N_1N_3 (Å)	4.0	2.8284
$\angle N_1N_2N_3$ (°)	90	60
$\angle N_1MN_2N_3$ (°)	180	90

(i) the $N_{ax}CuN_{ax}$ angle is always lower than 180°;

(ii) the equatorial LCuN angles are quite different.

The lower than 180° $N_{ax}CuN_{ax}$ angle can be explained by the presence of two equatorial L groups in the TBP arrangements and the possibility to reduce non-bonded repulsion if the terminal N recede away from the bulky Ls.

The inequality of the equatorial LCuN angles is due to the specific arrangement of the CH_2 groups linked to the central NH group in *k,k'* conformation. Being both on one side they increase the non-bonded repulsion on this side with the equatorial L ligand, and reduce the repulsion on the opposite side, with respect to the expected 120°.

It should be noted that the geometric structures of the studied compounds are quite similar and as to the dien conformation they are equal to that determined for the dien ligand in $[Cu(dien)(NO_3)](NO_3)$ [12]. Compared with the rigorous *mer* form where the two distortion factors discussed above are absent (see Fig. 2) it is seen that the geometries predicted by the MM method display shorter and unequal N_{ax}–N_{eq} lengths (2.5, 2.75 Å, compared with predicted 2.8284 Å in rigorous *mer*) and slightly longer N_1N_3 distances (4.03 Å, compared with 4.0 Å in rigorous *mer*).

TABLE 2. MM results (in kcal mol^{-1}) for dien ligand in *k,k'* conformation, fixed in two positions

	mer (*k,k'*)	*fac* (*k,k'*)
MME	2.65	8.19
STR	0.20	0.31
BND	1.26	1.94
S-B	0.08	0.12
TOR	−1.00	2.14
VDW	2.89	4.39
DD	−0.78	−0.72
μ	2.15	3.25
ΔH_f	4.45	1.00
SE	1.01	6.55
E_{fix}	0.06	0.12

With $CuN_1 = CuN_2 = CuN_3 = 1.00$ Å fixed:

mer		*fac*	
	$N_1N_2 = 2.8284$ Å		$N_1N_2 = 2.8284$ Å
	$N_2N_3 = 2.8284$ Å		$N_2N_3 = 2.8284$ Å
	$N_1N_3 = 4.00$ Å		$N_1N_3 = 2.8284$ Å
	$\angle N_1N_2N_3 = 90°$		$\angle N_1N_2N_3 = 60°$

3.2. Normal coordinate analysis calculations

3.2.1. IR spectrum and band assignment of dien ligand

The IR band assignment of the studied complexes was made on the basis of a normal coordinate analysis

TABLE 3. Geometric parameters for the Cu(dien)L_2 complexes, obtained from MM calculations

	Cu(dien)$^{2+}$ **(1)**	Cu(dien)Cl_2 **(2)**	Cu(dien)Br_2 **(3)**	Cu(dien)$(NO_3)_2$ **(4)**
MMX (kcal mol^{-1})	190.73	182.66	181.40	179.03
Cu–N_{ax} (Å)	2.03; 2.00	2.02; 2.04	2.04; 2.04	2.05; 2.05(2.13)
Cu–N_{eq} (Å)	2.01	1.99	2.02	2.02(1.99)
Cu–L (Å)		2.11	2.36	1.81(2.13)
∠LCuL (°)		114.3	113.4	84.0(86)
∠LCuN_{ax} (°)		97.7	97.4	96.9(93)
∠LCuN_{eq} (°)		117.0; 129.0	116.0; 130.0	111.0; 129(124; 150)
∠N_{ax}CuN_{eq} (°)	73.0; 74.0	75.0; 79.9	75.0; 79.0	75.0; 79.0(85.0)
∠N_{ax}CuN_{ax} (°)	130.0	153.0	153.0	154.0(169.0)
∠N_{ax}Cu$N_{eq}$$N_{ax}$ (°)	173.7	176.1	176.2	175.0
R(N–N) (Å)	2.41; 2.47; 3.70	2.46; 2.75; 4.03	2.46; 2.75; 4.03	2.34; 2.25; 3.60 (2.70) (3.97)
∠$N_{ax}$$N_{eq}$$N_{ax}$ (°)	98.6	101.2	101.2	94.8

Values in parentheses are taken from ref. 12.
BND(bending) = 166.6 kcal mol^{-1} for **1** and 163.5 kcal mol^{-1} for **2–4**.
STR(stretch) = 1.01 kcal mol^{-1} for **1** and 2.3–2.7 kcal mol^{-1} for **2–4**.
TOR(torsion) = 10.3 kcal mol^{-1} for **1** and 9.2–9.4 kcal mol^{-1} for **2–4**.
VDW(van der Waals) = 8.5 kcal mol^{-1} for **1** and 10.0; 8.9 and 7.1 kcal mol^{-1} for **2**, **3** and **4**, respectively.

of the free ligand and on the basis of comparison with IR spectra of these and related complexes [4, 5, 20–27]. The free dien is expected to exist in its most stable conformation (omega II). This is quite near the form present in [Cu(dien)(NO_3)](NO_3) [12]. For this reason in the normal coordinate analysis we used the structural parameters taken from the X-ray crystallographic study of [Cu(dien)(NO_3)](NO_3) [12]. Since the molecular symmetry is very low no attempt was made to classify the vibrations in symmetry blocks. 58 internal coordinates were introduced as a basis set: 19 stretchings, 33 deformations and 6 torsions. According to the theory 54 vibrational modes have to be obtained: 4 NH_2-stretchings, 1 NH-stretching, 8 CH_2-stretchings, 2 NH_2-deformations, 4 CH_2-deformations, 4 CH_2-waggings, 4 CH_2-twistings, 4 CH_2-rockings, 4 CN-stretchings, 2 CC-stretchings, 1 NH-rocking (symmetric CNH deformation), 1 NH-wagging (asymmetric CNH deformation), 2 NH_2-waggings, 2 NH_2-twistings, 2 NH_2-rockings (equivalent to H_2C-NH_2 torsions), 5 skeletal deformations (1 CNC and 4 CCN), 2 H_2C-NH_2 torsions and 2 CC torsions. The 54 calculated frequencies were assigned according to the PED on the basis of already published assignments of the vibrational modes of primary and secondary amines [28–31]. The IR spectral data of dien were taken from ref. 23. Since the dien far-IR spectrum in liquid phase (700–400 cm^{-1}) shows very broad and diffuse absorptions, some values in this region and below 400 cm^{-1} (marked by 'a' in Table 4), used during the calculations, have been taken from another study of the vibrational spectra of primary and secondary aliphatic amines [29].

In general our assignment on the basis of the normal coordinate analysis (given in Table 4) is in agreement with the results reported previously for the dien normal modes [28, 29]. The force constants are given in Table 5. A detailed analysis of the separate spectral regions is given below.

(i) NH_2 and NH stretching and deformation vibrations

According to previous investigations, primary amines can be identified by two characteristic absorption bands in the symmetric and asymmetric ν(NH) region [30]. In the IR spectrum of dien these two bands were found at 3360 and 3280 cm^{-1}, respectively (Table 4) (see also ref. 29).

The (secondary) ν(NH) vibration gives rise to a very weak absorption band located between the asym and sym $\nu(NH_2)$s, usually undetectable (the calculated value is 3324 cm^{-1}). The strong band at 1599 cm^{-1} was assigned to $\delta(NH_2)$ [28–31]. The NH_2-wagging modes in twenty primary amines were at 840–760 cm^{-1}, depending on the degree of substitution of the α-carbon atom [29]. This band can be identified by its considerable width. The NH_2-wagging mode appears in our spectra at 770 cm^{-1}, which is in agreement with ref. 29 but not with ref. 31.

The two NH_2-twisting modes were found at lower frequencies (650 cm^{-1}).

The last two NH_2 motions (NH_2-rockings) identical with torsions involving the NH_2 groups with respect to the C–N bond, were calculated at 546 cm^{-1}. It should be mentioned that the assignment of the NH_2-twisting and rocking modes is uncertain because of the very broad absorption in this region.

TABLE 4. Observed and calculated frequencies of diethylenetriamine (dien), (ν, cm^{-1})

Obs. [29, 32]	Calc.	Assignment (% PED)	
3360s	3360×2	NH$_2$-stretching	100 νNH$_2$
	3324	NH-stretching	100 νNH
3280s	3288×2	NH$_2$-stretching	100 νNH$_2$
2929vs	2932×2	CH$_2$-stretching	99 νCH$_2$
	2929×2		99 νCH$_2$
2860vs	2860×4		100 νCH$_2$
1599s	1600×2	NH$_2$-deformation	74δHNH + 8δCNH$_2$ + 4δNCH
1458s	1484×2	CH$_2$-deformation	38δNCH + 28δHCH + 12νCN
	1467×2		39δNCH + 24δHCH + 12δHNH
1360m	1370×2	CH$_2$-wagging	52δHCH + 28δCCH + 16νCC
1300m	1304		48δHCH + 30δCCH + 8δCNH + 9νCN
	1286		43δHCH + 43δCCH + 4δNCH + 4νCN
1250w	1244	CH$_2$-twisting	71δNCH + 18δCCH + 12νCN
1210w	1213		40δNCH + 20δCCH + 20δNCH
	1200×2		71δNCH$_2$ + 22δCCH + 6δCNH
1127s	1128	NH-wagging + CN-str.	60δNCH + 20δCCH + 4νCN
1060m	1060	CN-stretching	56νCN + 24δNCH$_2$
	1057		58νCN + 22δNCH$_2$
1030m	1000		48νCN + 6δNCH$_2$ + 6δCCH + 2δNCC
	980		56νCN + 14δNCH$_2$ + 10δCCH
920m	946	CH$_2$-rocking	42δCCH + 24t-CN + 33t-CC + 2νCC
	937		54δCCH + 16t-CN + 8δNCH + 8δCNH
874m	864		33δCCH + 31t-CN + 8νCN + 8δNCH
848m	849	CC-stretching	56νCC + 22δCCH + 6δNCH
	826		44νCC + 20δCCH + 6δNCH
798m	798	CH$_2$-rocking	33δCNH$_2$ + 24δCCH + 12δNCH
770m	777	NH$_2$-wagging	80δCNH$_2$ + 4δCCH + 6t-CN
	769		52δCNH$_2$ + 18δCCH + 8δNCH
735w	739	NH-rocking	52δCNH + 24δCCH + 16t-CN
650m	668	NH$_2$-twisting	80δCNH$_2$
	663		80δCNH$_2$
546w	555	NH$_2$-rocking	62t-CN + 24δCCH
	542		64t-CN + 27δCCH
460w[a]	418	skeletal	72δNCC + 8δCCH + 6t-CN
360w[a]	378		52δNCC + 18δCNC + 10δCCH
300w[a]	296		36δCNC + 30δNCC + 8t-CC
290vw[a]	280	t-CC	30t-CC + 28t-CN + 10δNCC
225vw[a]	224	t-CC	32t-CC + 20t-CN + 18δNCC
	161	skeletal	38δNCC + 25δCNC + 14t-CN
	144		44δNCC + 24t-CC + 10t-CN
	77	t-CN	54t-CN + 34t-CC
	67		30t-CN + 30δNCC + 20δCNH

s = strong, m = medium, w = weak, vw = very weak, ν = stretching, δ = deformation, t = torsion. [a]These values have been taken from ref. 29.

The asym δ(CNH) (NH-wagging) was found to have the highest contribution to the band at 1127 cm^{-1}. The position of the NH-wagging mode was not discussed previously and thus no comparison was possible.

(ii) CH$_2$ stretching and deformation vibrations

CH$_2$ group vibrations give rise to two characteristic bands at about 2929 and 2860 cm^{-1}, corresponding to asym and sym vibrations of the H atoms [30].

The strong 1458 cm^{-1} band in the dien spectrum was assigned to δ(CH$_2$). The potential energy of these motions consists predominantly of NCH and HCH displacement energy (*c.* 40 and 20%, respectively).

The bands at 1360 and 1300 cm^{-1} were assigned according PED values to CH$_2$-waggings in agreement with ref. 31.

The CH$_2$-twisting modes were calculated at 1250 and 1210 cm^{-1}. The bands at 798, 874 and 920 cm^{-1} were interpreted as CH$_2$-rocking vibrations.

(iii) Skeletal vibrations

Two bands with medium intensity were observed in the 1000–1060 cm^{-1} frequency region. According to our PED values and the usual position of the CN-stretching mode in amines, these two bands were assigned to CN-stretchings. Five skeletal deformations were determined: 4 NCC (418, 378, 161 and 144 cm^{-1})

TABLE 5. Force constants of dien (in mdyn Å^{-1}, mdyn Å rad^{-2})

Type	Value (NCA)	Value (MOPAC)	Ratio
F(CH)	4.579	2.45	1.87
F(NH)	6.123	3.31	1.85
F(CN) (NH_2 group)	5.341	2.90	1.84
F(CN) (NH group)	4.415	2.78	1.59
F(CC)	3.338	1.98	1.69
F(HNH)	0.342		
F(CNC)	0.833		
F(NCC)	0.587		
F(HCH)	0.352		
F(CCH)	0.381		
F(HNC) (NH group)	0.250		
F(HNC) (NH_2 group)	0.190		
F(NCH) (NH_2 group)	0.569		
F(NCH) (NH group)	0.558		
F(t-CC)	0.191		
F(t-CN)	0.201		
F(CNH/CNH) (NH group)	0.098		
F(CNH/CNH) (NH_2 group)	0.024		
F(CN/CN)	−0.025		

and 1 CNC (296 cm^{-1}). The CC-torsions are at 280 and 224 cm^{-1}.

The IR spectrum of dien below 400 cm^{-1} is very complicated and difficult to assign. The observed absorptions are very weak and diffuse [29]. A tentative assignment according to the PED values has been given in our study. This range will be discussed later in detail.

3.2.2. Dien vibrational spectrum from MOPAC calculations

Table 6 lists the band frequencies from the experimental spectrum and those calculated with the MOPAC 6.0 package with geometries fixed as k,k' linear I and k,k' omega II and as taken from the MM minimization procedures. The MOPAC 6.0 program performed additional minimization since the gradient norm of the geometry coming from the MM calculations was too high to obtain reliable force fields. The resulting MOPAC produced new geometry, however, was essentially not very different from the MM geometry thus giving evidence that the studied geometric isomers refer to real energy minima on the hyperspace defined by the internal coordinates.

It is readily seen from Table 6 that:

(i) There are bands in the experimental spectrum which are present in the calculated spectrum of both the linear and omega isomers, while other bands are typical for a given isomer. This finding suggests that the experimental spectrum is probably that of a mixture of several structural isomers.

(ii) The region most sensitive to the dien geometry is 800–950 cm^{-1}.

(iii) The 460, 798, 874 cm^{-1} bands should be attributed to the linear geometry and the 920 cm^{-1} band to dien in the omega isomer.

(iv) The bands at 650–700 cm^{-1} were absent in the calculated spectra. As seen from Table 4 these are exactly the NH_2-wagging, rocking and twisting motions. Since these motions are related to the N atoms, which have one lone pair, obviously MOPAC cannot reproduce them.

TABLE 6. Experimental and calculated (MOPAC) frequencies of dien (200–1500 cm^{-1})

Experimental	Linear (LIN)	Omega (ω)
1458s	1447, 1460, 1455, 1457	1440, 1444, 1447, 1455
1360m	1352, 1365, 1372, 1384	1356, 1368, 1399, 1402
1300m	1300, 1313, 1316	1337
1250w	1262, 1271	1263
1210w	1234, 1243	1219, 1224
1127s	1129, 1167, 1183	1101, 1145, 1161, 1184
1060m	1060, 1084	1067
1030m	1044	995, 1006
920m*		914, 928*
874m*	882*	
848m	829	823
798m*	800*	
770m		
735w		[a]
650m		
546w	541	541, 548
460w*	492*	
360w	347	363
300w	317	337
290vw		
		245
		225
	190	

Starred items: diagnostic. [a]Vibrations involving NH-wagging, rocking and twisting are shifted very high, not observed here (see text).

3.3. MOPAC calculation of the coordinated dien vibrational spectrum

Table 7 shows the calculated vibrational spectrum of the dien ligand in the studied complexes. The bands related to L (Cl^-, Br^-, NO_3^-, ClO_4^-) have been detected. It is readily seen from this Table that two bands are typical for the *mer* conformation, namely 920 and 840 cm^{-1}. The first band (920 cm^{-1}), assigned to CH_2-rocking (see Table 4), is close to the 934 cm^{-1} band of the *fac* conformation, although typically the *mer* conformation suggests a doublet (918, 940 cm^{-1}) while the *fac* predicts one band (934 cm^{-1}). In fact it was the 933 cm^{-1} band which was suggested as diagnostic for *fac* coordination [23]. Compared with the experimental spectrum of coordinated dien it is seen that the free dien 920 cm^{-1} band is shifted to higher frequencies (973–989 cm^{-1}) where a band is predicted

TABLE 7. Experimental and calculated (MOPAC) frequencies of the coordinated dien (200–1500 cm^{-1})

Experimental		calculated	
dien (free)	dien (coordinated)	*mer*	*fac*
1458s	1443–55	1442, 1447, 1454, 1460, 1470	1414, 1441–58
1360m	1330–58	1343, 1348, 1362, 1383, 1402	1372
1300m	1290–92	1308	1286, 1310
1250w	1249–65	1243, 1262	1241, 1254, 1258
1210w		1213, 1197	1198
1127s	1146–53	1144, 1168	1113, 1140
1060m	1084	1073, 1096	1058, 1092
1030m	1030–34	1006	1022
920m	973–980	918, 940, 987	934, 989?
874m	895–900		890
848m	840	822	
798m			
770m			
735w			728
650m	633–50		
546w	517–65	522,546	553
460w	476–88		489
360w	380–97	359, 366	385
300w	293–312		313
290vw	231–57	243	257

for both *mer* and *fac* conformations. Hence this band should be treated with caution as a *mer–fac* diagnostic tool.

The 848 cm^{-1} free dien band assigned to ν(C–C) with a high percentage of δ(CCH) (see Table 4) stays almost unshifted (840 cm^{-1}) and is predicted to appear only with the *mer* conformer. Consequently this band may be used as a diagnostic tool.

The 735 (NH-rocking) and 874 (δ(CCH)) cm^{-1} bands can be used to diagnose the presence of *fac* coordinated dien, they both comprise CN-torsion. Unfortunately a detailed IR spectrum of a *fac* coordinated dien is not available.

It can be thus concluded that all the studied compounds contain dien in the *mer* position.

The IR spectra of the studied compounds and their assignments, compared with the free ligand spectrum are given in Table 8.

3.4. IR spectra of the L ions (NO_3^-, ClO_4^-, Cl^-, Br^-)

Three bands due to the unidentate NO_3^- group vibrations have been observed (1037(w), 810(m) and 740(w) cm^{-1}) in the [Cu(dien)(NO_3)](NO_3) spectrum. A combination band, ($\nu_1+\nu_4$), very weak and split by 15 cm^{-1} was observed at 1750 cm^{-1}, proving the unidentate coordination of (NO_3^-) [33, 34]. The very strong band at 1385 and that at 825 cm^{-1} points to the presence of a free uncoordinated (NO_3^-) group in the complex, which was proved by X-ray data [12].

The totally symmetric mode ν_1 (ClO_4^-) is theoretically forbidden in T_d symmetry [35, 36]. In the [Cu(dien)(ClO_4)](ClO_4) IR spectrum it appears as a very weak absorption at 970 cm^{-1}, indicating a small distortion.

The symmetric band, ν_2 (e symmetry), only Raman active in T_d symmetry, appears also with a weak intensity at 460 cm^{-1}. The other two vibrational modes ν_3 and ν_4 (t_2 symmetry, IR and Raman active) were detected in our study split into two components: ν_3 at 1092 and 1112 and ν_4 at 626 and 635 cm^{-1}. The number of detected bands (6 when the splittings are taken into account) is in agreement with the predicted C_{3v} symmetry for unidentate ('semi-coordinate') perchlorate group [35–37].

A comparison between the [Cu(dien)(NO_3)](NO_3) and [Cu(dien)(ClO_4)](ClO_4) spectra shows that they are similar with a few exceptions due to the different NO_3^- and ClO_4^- group vibrations. Thus, the IR spectra give evidence for a similar type of coordination of the NO_3^- and ClO_4^- groups to the copper ion which should be five-coordinate. The spectra of [Cu(dien)Cl_2] and [Cu(dien)Br_2] show similar behavior in the entire studied region including the far-IR.

The Cu–N vibrations give rise to the bands at 450 and 340–350 cm^{-1}. The Cu–O stretching modes should appear in the [Cu(dien)(NO_3)](NO_3) and [Cu(dien)(ClO_4)](ClO_4) spectra only. Our comparative study shows that these bands could not be detected. Probably if present, they are very weak and/or over-

TABLE 8. Experimental frequencies of diethylenetriamine (D) and Cu(D)L_2, ($L = NO_3^-$, Br^-, Cl^-, ClO_4^-), (ν, cm^{-1})

Dien (D)[a]	Cu(D)$(NO_3)_2$[b] (1)	Cu(D)Br_2[b] (2)	Cu(D)Cl_2[b] (3)	Cu(D)$(ClO_4)_2$[b] (4)	Assignment
3360s					NH_2-stretching
3280s	3283m	3279s	3279s	3291m	
	3252m	3233vs	3237vs	3244m	
	3163m	3136s	3140s	3136m	
2929vs	2963w	2940m	2947m	2955w	CH_2-stretching
2860vs	2882w	2882m	2882m	2886w	
	1750vw				$\nu_1 + \nu_4$ (NO_3^-)
1599s	1605w	1574s	1585s	1589w	NH_2-deformation
	1481m	1470m	1474m	1466m	CH_2-deformation
1458s	1443m	1447m	1450m	1455m	
	1358vs				ν_3 (NO_3^-)
	overlapped	1380m	1380m	1390m	CH_2-wagging
1360m	1358m	1350m	1350m	1330m	
1300m	1290w	1292w	1290w		
1250w	1254w	1249w	1254w	1265vw	CH_2-twisting
1210w					
1127s	1153m	1146m	1150m	1146sh	NH-wagging + CN-stretching
				1112m	ν_3 (ClO_4^-)
				1092vs	
1060m	1084w	1084vs	1084vs	overlapped	CN-stretching
	1050vw	1048w	1049w	overlapped	CN-stretching
1030m	1034w	1030m	1030m	1030sh	CN-stretching
	1037w				ν_1 (NO_3^-)
920m	980w	999m	1000m	973sh	CH_2-rocking
				970w	ν_1 (ClO_4^-)
874m	900vw	900w	900w	895vw	CH_2-rocking
848m	840vw	840w	840vw	840vw	CC-CN-stretching
	825vw				ν_2 (NO_3^-)
	810m				ν (NO_3^-) unidentate
798m					CH_2-rocking
770m					NH_2-wagging
735w	740w				ν_4 (NO_3^-) + NH-rocking
650w	640m	633m	630w	650w	NH_2-twisting
				635s	ν_4 (ClO_4^-)
				626s	
546w	546m	517m	531w	565w	NH_2-rocking(t-CN)
460w	476w	488w	488s	488m	NCC skeletal
				460w	ν_2 (ClO_4^-) + NCC-skeletal
	467m	445s	453s	455m	Cu–N-stretching
360w	397m	388m	380w	382m	NCC-skeletal
	351m	346w	346m	348m	Cu–N-stretching
		335m	338m		Cu–X-stretching
	324m	322vw	322w	328w	N–Cu–N-deformation
300m	293m	312m	312w	301w	CNC-skeletal
290w	247m	239m	257s	231w	CC-torsion
		217m	219m		X–Cu–X-deformation
161[c]	185s	184m	185m	174m	NCC-skeletal
144[c]	147w	153m	153m	154sh	
	129w	124m	130m	127w	N–Cu–N-deformation
	116w	116w	114w	108w	Cu–N–C-deformation
	94w	97w	96w	95w	CN- + CC-torsion
77[c]	81w	74w	78w	80w	
64w		63w	64w		

s = strong, m = medium, w = weak, vw = very weak, vs = very strong, sh = shoulder, ν = stretching, δ = deformation, t = torsion. [a]From refs. 29 and 32. [b]This work. [c]Calculated values from Table 4.

lapped by other vibrations in this region. The δ(N–Cu–N) deformation modes give rise to the bands at 324 and 130 cm^{-1}. These bands were detected in all the studied complexes. The Cu–X ($X=Br^-$, Cl^-) and X–Cu–X vibrational modes have been assigned to the bands at 335, 338 and 217, 219 cm^{-1}, respectively. These bands did not appear in both $[Cu(dien)(NO_3)](NO_3)$ and $[Cu(dien)(ClO_4)](ClO_4)$ spectra and this finding makes their assignment more certain. The other bands below 400 cm^{-1} were assigned according to the PED values to the dien vibrational modes (see Table 4). The bands which appeared near 161 and 144 cm^{-1} in all the studied spectra have been assigned to NCC skeletal. The CNC deformation was found near 300 cm^{-1}.

Conclusions

In general the ligand IR spectra of the studied complexes are similar as to the spectral region attributed to dien vibrations. They are typical for the meridionally coordinate dien complexes. The 933 cm^{-1} band which was found to be characteristic for facial conformation of dien was not observed in the spectra of the studied complexes, which is also evidence that all adopt the *mer* conformation of the dien ligand.

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