The crystal and molecular structures of (diethylenetriamino)copper(II) nitrate

R. Allmann, M. Krestl
Institute of Mineralogy, University of Marburg, Marburg 3550 (F.R.G.)

C. Bolos, G. Manoussakis
Department of Inorganic Chemistry, University of Salonica, Salonica 54006 (Greece)

and **G. St. Nikolov***
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040 (Bulgaria)

(Received February 2, 1990; revised April 18, 1990)

Abstract

The blue needle-like $(H_2NCH_2CH_2NHCH_2CH_2NH_2)Cu(NO_3)_2$ or $Cu(dien)(NO_3)_2$ for short was studied by X-ray diffraction, magnetic measurements, infrared and electronic spectra, and electric conductivity. It crystallizes in the space group *Pmnb* with $Z=4$ and $a=9.050(4)$, $b=9.066(4)$, $c=12.944(4)$ Å, $V=1062.0$ Å^3 and $D_x=1.818$ g cm^{-3}. The symmetry plane contains the Cu atom, one NO_3^- group (asymmetric bidentate and bridging, Cu–O1 = 2.13 Å, Cu–O2 = 2.56 Å), the dien NH group (Cu–N = 1.99 Å) and an intermolecular contact with the neighbouring bridging NO_3^- group (Cu–O2″ = 2.29 Å). The two terminal NH_2 groups provide almost linear (∢N–Cu–N′ = 169°) out-of-plane Cu–N bonds (1.994 Å long). Viewed down the intermolecular contact, parallel to the symmetry plane, Cu is five-coordinate in a distorted square pyramidal (with O2″ in the apical position) arrangement or a distorted trigonal pyramid with N, N′ apical contacts. The second (uncoordinated) NO_3^- group is hydrogen bonded to dien. Magnetic and solid state spectral data are in agreement with this molecular structure. Solution spectra, however, and electric conductivity data indicate a monomeric $Cu(dien)(NO_3)^+$ unit with a four-coordinate Cu atom.

Introduction

The diethylenetriamine (dien) ligand is known to form two fused five-membered rings with metal ions [1]. The compound $Cu(dien)_2(NO_3)_2$ is known to have a tetragonally distorted octahedral $[Cu(dien)_2]^{2+}$ unit with C_2 symmetry and uncoordinated NO_3^- groups [1a]. The mono-dien Cu(II) complex exhibits an ESR spectrum of a rhombically distorted axial unit [2]. The $Cu(dien)(formiate)_2$ complex [1b] is square pyramidal and its space group is *Pnam*. The cations $[Cu(dien)L]^{2+}$ display a very broad band in the visible spectra at 580–620 nm (17.2–16.1 kK) [1-5] that is pressure dependent [5] and composite. The nitrate ligand in such Cu complexes can function as a uni- or bidentate unit and it often bridges two metal ions [6, 7].

The five-coordinate Cu- and Ni-dien complexes have been reviewed extensively as to their molecular structures (see, for example, ref. 8) and the possible sources of electronic origin that may contribute to the observed structural distortions [9, 10]**.

We report here the molecular and crystal structures of $Cu(dien)(NO_3)_2$ and some physical properties of its crystals and solutions. This compound was prepared in order to assess the possible manifestations of the Jahn–Teller effect in multidentate Cu(II) complexes. It is expected that the rigidity of the dien ligand would hinder the free distortion of the complex subject only to the Jahn–Teller forces thus restricting the number of possible geometries.

Experimental

Preparation of spectroscopic measurements

The preparation of $Cu(dien)(NO_3)_2$ followed the procedure described elsewhere [11] and was used

---

*Author to whom correspondence should be addressed.

**Symmetry coordinates and force constants in ref. 10b are not correct. AOM calculations on geometry conversions should be viewed with caution.

0020-1693/90/$3.50

in the preparation of the Ni(dien)X_2 compound. Benzaldehyde 2.1 ml (20 mmol) was mixed with 1 ml (10 mmol) of diethylenetriamine and the resulting mixture was dissolved in methanol (50 ml). The role of benzaldehyde was discussed previously [11]. Copper nitrate trihydrate 2.416 g (10 mmol) was added to this solution and the mixture was refluxed for 1 h. After cooling for 12 h to room temperature, blue needles separated from the solution. They were isolated by filtration and dried under vacuum. Yield 62%. *Anal.* Calc. for $C_{14}H_{13}N_5O_6Cu$: C, 16.52; H, 4.47; N, 24.09; Cu, 21.87.Found: C, 16.43%; H, 4.60; N, 24.01; Cu, 22.01%. The microanalyses of C, H and N were carried out with a Perkin-Elmer 240 elemental analyser. Copper was determined by atomic absorption spectrometry. The electronic spectrum was recorded on a Perkin-Elmer Hitachi 200 spectrophotometer. Molar conductivities were measured with an Industrial Instruments Incl. RC 216B conductivity bridge. The magnetic moment was measured at room temperature with a Gouy balance using Hg-[Co(SCN)$_4$] as calibrant. The infrared spectra were recorded in the 250–4000 cm^{-1} region with a Perkin-Elmer 467 spectrophotometer.

X-ray structure determination

A crystal 0.2×0.3×0.9 mm was enclosed in a glass capillary and was measured on a Stoe 4-circle diffractometer at the Institute of Mineralogy, University of Marburg, using Mo Kα ratiation up to $\theta_{max}=23°$ (graphite monochromator, scan width in $\theta=1.6°$, 40 s per reflex+2×5 s for background). The substance crystallizes in space group *Pmnb* with $a=9.050(4)$, $b=9.066(4)$, $c=12.944(4)$ Å, $V=1062.0$ Å^3 and $D_x=1.818$ g cm^{-3}.

The group *P*2$_1$*nb* was adopted at first as preliminary space group. Among the 743 independent reflections, 75 were less than $F_{min}=2\sigma(F)$. The positions of the Cu and O atoms were found by 201 strong reflections ($E_{min}=1.202$). Two subsequent difference Fourier syntheses revealed the positions of all the non-hydrogen atoms which were refined isotropically until $R=7.93\%$, $R_w=8.42\%$. The positions of the H atoms were calculated and the subsequent anisotropic refinement of the non-hydrogen atoms yielded $R=3.74\%$, $R_w=3.74\%$ using unit weighting factors.

The strong correlation among the corresponding atomic parameters indicated the presence of a mirror plane, i.e. the preliminary space group *P*2$_1$*nb* had to be replaced by *Pmnb*. After fixing this plane at $x=1/4$ and averaging the y and z parameters of the symmetry related atoms, the refinement of the structure was continued in the centrosymmetric space group. A damping factor of 0.8 was adopted at this stage and $R=5.99\%$ was obtained in two refinements with non-hydrogen atoms anisotropic and hydrogen atoms fixed. After introducing individual weighting factors for the reflections, $R=3.81\%$ and $R_w=4.48\%$ were obtained for 668 observed reflections. The corresponding values for all the 743 reflections were $R=4.52\%$ and $R_w=5.43\%$. Table 1 lists the final atomic parameters. The bond lengths and bond angles are collected in Tables 2 and 3, respectively. Some torsional angles and the hydrogen bond configurations are given in Table 4.

Results and discussion

Figure 1 shows the molecular unit in the *x*–*y* plane with two neighbouring NO_3 groups of the non-bonded (to Cu) type. The Cu atoms are five-coordinate: equatorially (in the mirror plane) Cu is bonded to the middle dien nitrogen atom (Cu–N4 = 1.99 Å) and to two oxygen atoms of the bonded (bridging and bidentate) NO_3 groups (Cu–O1 = 2.13 Å and Cu–O2″ = 2.29 Å). Additionally there is a very weak Cu–O bond with one of the NO_3 groups (Cu–O2 = 2.56 Å). The two terminal dien nitrogen atoms are bonded axially to Cu (2×Cu–N1 = 1.994 Å, ∢N1–Cu–N1′ = 168.8°), thus completing a slightly distorted trigonal bipyramidal arrangement around Cu with the dien ligand in a meridional position.

Two hydrogen bonds can be clearly seen in Fig. 1: H11 to O5 (2.50 Å) of the free NO_3 group and a bifurcated bridge at H4 bonded to O5 and O5′ (H...O = 2.58 Å).

Figure 2 shows the molecular chain in the *y* direction, the molecule being projected approximately in the *yz* plane. Two oxygen atoms of the next layer are denoted by ^{III} and ^{IV}, respectively to designate the NH...O bridge.

The free uncoordinated NO_3 group lies with N3 and O4 in the mirror plane. The O5 atoms could neutralize part of their negative charge by approximate orientation with respect to the H-bond bridges. The atom O4 does not form such bridges and this is manifested in a strong anisotropic vibration.

The Cu environment can be alternatively described as a square pyramid with O2″ at the apex (compare with Fig. 1), or as a distorted trigonal bypyramid with N1 and N1′ at the apices.

The compound can be thus formulated as $[Cu(dien)(NO_3)]^+(NO_3)^-$. This formula is consistent with electric conductivity measurements indicating the presence of a 1:1 electrolyte (*vide infra*).

As compared with the molecular structure of $Cu(dien)_2(NO_3)_2$ [1] there are a number of prominent differences. In the bis-dien compound, Cu is six-coordinate while in the mono-dien compound, Cu is five-coordinate (plus one weaker bond). Obviously,

TABLE 1. Atomic parameters ($\times 10^4$) for $C_4H_{13}N_3Cu \cdot 2NO_3$. The *uik* values ($Å^2 \times 10^3$) refer to the expression $\exp(-2\pi^2(u_{11}a^{*2}h^2 + \ldots + 2u_{23}b^*c^*kl))$

Atom	x	y	z	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}	$\bar{\sigma}(u)$
Cu	¼	3058(1)	3151(1)	27	23	29	27	0	0	0
N1	307(4)	2897(3)	3250(3)	34	25	52	−2	−3	5	2
C2	−95(5)	2429(5)	4299(3)	35	46	49	−2	10	−7	2
C3	1123(5)	1497(5)	4720(4)	68	46	23	13	10	−8	2
N4	¼	2297(5)	4600(4)	41	20	35	−1	0	0	2
O1	¼	2654(4)	1535(3)	60	14	32	−3	0	0	2
N2	¼	1284(5)	1448(4)	30	16	34	−5	0	0	2
O2	¼	509(4)	2266(3)	52	15	32	4	0	0	2
O3	¼	704(4)	601(3)	73	27	33	−4	0	0	2
N3	¼	4352(6)	7005(4)	44	38	36	4	0	0	2
O4	¼	5071(8)	7812(5)	102	124	64	−51	0	0	3
O5	1351(3)	4043(4)	6581(3)	39	52	59	4	−7	−3	1
H11	39(14)	3613(14)	3031(13)	46						
H12	252(14)	2231(14)	2875(13)	35						
H21	−230(14)	3342(14)	4690(13)	46						
H22	−1165(14)	1888(14)	4238(14)	55						
H31	1261(14)	552(14)	4320(13)	51						
H32	1016(14)	1360(14)	5287(13)	40						
H4	¼	2864(14)	4964(14)	38						

TABLE 2. Internuclear distances (Å) (Riding model) for $C_4H_{13}N_3Cu(2NO_3)$; the ranges are given for CH and NH bond lengths as well as their averages

Cu-N1	1.994(4)	2.000	(2×)
Cu-N4	1.999(5)	2.001	
Cu-O1	2.123(4)	2.130	
Cu-O2′	2.287(3)	2.293	
Cu-O2	2.579(4)	2.584	
(Cu-O3′	2.893(4)	-)	
N1-C2	1.468(6)	1.447	
C2-C3	1.492(6)	1.493	
C3-N4	1.450(5)	1.461	
N2-O1	1.248(6)	1.258	
N2-O2	1.270(6)	1.282	
N2-O3	1.216(7)	1.237	
Average	1.245	1.259	
N3-O4	1.232(8)	1.303	(2×)
N3-O5	1.240(4)	1.254	
Average	1.237	1.270	
CH	0.750–1.089	av. (4)	0.956
NH	0.697–0.776	av. (3)	0.741

TABLE 3. Bond angles (°) for $C_4H_{13}N_3Cu(2NO_3)$

N4–Cu–O1	149.8(2)	
N4–Cu–O2′	123.8(1)	
O1–Cu–O2	53.7(1)	
O1–Cu–O2′	86.3(3)	
N1–Cu–N4	85.1(1)	(2×)
N1–Cu–O1	92.9(1)	(2×)
N1–Cu–O2′	95.0(1)	(2×)
N1–Cu–N1′	168.8(1)	
O2′–Cu–O3′	47.6(1)	
Cu–N1–C2	109.1(3)	
Cu–N4–C3	105.9(2)	
Cu–O1–N2	105.1(3)	
N1–C2–C3	108.6(4)	
C2–C3–N4	108.2(3)	
C3–N4–C3′	118.5(3)	
O1–N2–O2	118.4(4)	
O1–N2–O3	120.8(4)	
O2–N2–O3	120.9(4)	
O4–N3–O5	119.7(2)	(2×)
O5–N3–O5′	120.6(2)	

the lack of one dien molecule in the coordination compound cannot be compensated by one additional NO_3 group, although the latter plays the role of a (highly asymmetric, 2.13 and 2.53 Å) bidentate ligand. The molecular structure is somewhat similar to Cu(dien) (formiate)$_2$ [1b] although the space groups are different, but the molecular plane persists. In our compound the more weakly bonded oxygen atom is also bridging and this explains the longer Cu–O2″ bond length. The bridging is such that the planar meridional CuN_3 units (with symmetrical Cu–dien rings, see ref. 12) are knitted together by NO_3^- groups in a chain structure within the symmetry plane.

The three CuN bond lengths in the studied compound are shorter (1.99 Å) as compared with those lengths in the symmetry plane of the tetragonal bis-dien Cu compound (2.22 Å [1]) but they compare well with the axial CuN bond lengths (2.01 Å [1a]) in the same bis-dien compound or with the basal

TABLE 4. Some torsional angles of $C_4H_{13}N_3Cu(2NO_3)$

Cu–N1–C2–C3	−30.2(4)
N1–C2–C3–N4	51.9(4)
C2–C3–N4–Cu	−46.9(4)
C3–N4–Cu–N1	24.0(3)
N4–Cu–N1–C3	−14.0(3)
C2–C3–N4–C3′	−165.5(4)
O1–Cu–N1–C2	153.5(3)
Cu–N1–C2–C3	−30.2(4)

Hydrogen bridges

Atoms	Angle (°)	H...O distance (Å)
N4–H4...O5 (2×)	148.4(7)	2.585(15)
N1–H11...$O5^{III}$	145.0(12)	2.502(10)
N1–H12...$O5^{IV}$	145.3(9)	2.478(14)

Meaning of the indices for the symmetry equivalent atoms: ′: $\frac{1}{2}-x, y, z$; ″: $x, \frac{1}{2}+y, \frac{1}{2}-z$; ^{III}: $-x, 1-y, 1-z$; ^{IV}: $-x, \frac{1}{2}-y, z-\frac{1}{2}$.

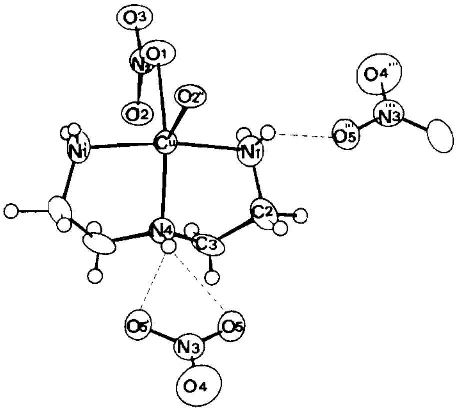

Fig. 1. ORTEP projection of the $Cu(dien)(NO_3)_2$ unit viewed parallel to the symmetry plane O1CuN4 with two ionic NO_3 groups interacting with the dien nitrogen atoms. The unit is in the *xy* plane.

Cu–N bonds in the Cu(dien)(formiate) unit [1b]. The dien ligand shows little variations in the $Cu(dien)^{2+}$ and $Cu(dien)_2{}^{2+}$ units though it is somewhat more relaxed (longer CN and CC bonds) in the second unit. The strain in the chelate rings is felt by inner ring chelate or bite angles: the strain is less in the mono-dien compound (NCuC angles closer to 90°, *c.* 85°) than in the bis-dien compound (*c.* 82° [1]). All three dien nitrogen atoms are involved in hydrogen bridges.

A closer inspection of Figs. 1 and 2 reveals that the distortion away from a regular trigonal bipyramid (tpy) D_{3h} consists in our compound in closing the equatorial OCuO angle and correspondingly opening the equatorial OCuN angles with N being the middle dien nitrogen atom. Such a distortion was called inappropriately 'reverse' [10a] implying that it is opposite to that expected to occur along the $D_{3h}(\text{tpy}) \rightarrow C_{4v}$ (spy) conversion pathway. Alternatively, this distortion may be termed as equatorially squashed tpy or tilted spy.

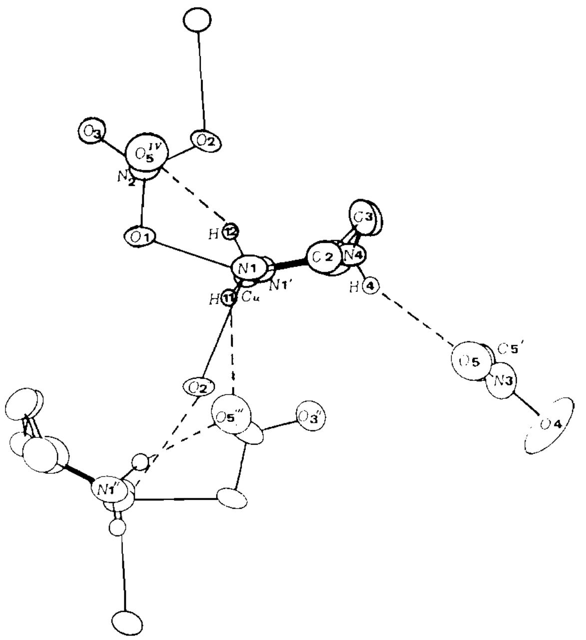

Fig. 2. ORTEP projection of the molecular chain in the *y* direction. The molecular units are projected approximately in the *yz* plane. The two formula units are interconnected with a bridging NO_3 group.

As already noted, the meridional angles involving the dien unit are close to 90°. The meridional position of the dien ligand is consistent with that predicted by the low (*c.* 1.4) normalized bite distance [13]. There are, however, several ways to explain the closing of the equatorial OCuO angle. It could be due to restrictions imposed by increased non-bonded (interligand) repulsion in the equatorial plane or alternatively to electronic factors. A rough estimate of the non-bonded repulsion in the tpy equatorial plane with fixed dien geometry (bond lengths and valence angles as listed in Tables 2 and 3) and variable equatorial OCuO angle produced minimum repulsion energy for $\sphericalangle\text{OCuO} \sim 108°$, much higher than the experimental 85°. This is strong evidence that the electronic factors may be important. The resulting CuN_3O_2 geometry may be vibronically stabilized [14].

The pseudo Jahn–Teller effect in D_{3h} was examined by Bacci [9] and Reinen *et al.* [10a, b]. The observed $D_{3h} \rightarrow C_{2v}$ distortion (the $D_{3h} \rightarrow C_{4v}$ conversion being forbidden by symmetry) could be viewed as a product of the e′ vibrations that are pseudo Jahn–Teller active. One of these vibrations closes the OCuO angle and mixes the $^2A_1$ ground state with the first excited $^2E'$ state, referred to D_{3h} geometry. The e′

modes for ML_5 in D_{3h} are three in number and an intricate nuclear motion in the $3\times2=6$ fold e′ space is involved in coupling the electronic and nuclear motions. As a result of this the symmetry is lowered and the ultimate geometry acquired can be found by the minimax principle put forward by Liehr [15]. It states that the distortion away from the highest possible symmetry should be minimal and the new geometry should possess maximum symmetry. In our case, the free CuN_3O_2 unit of initial symmetry D_{3h} should distort to C_{2v} where a totally symmetric mode is produced for the first time by an e′ mode. However, because of the rigid dien structure, the symmetry degrades further down to C_2 or C_s, in full agreement with the possible sites for the *Pnmb* space group, namely $4C_{2v}(2)$, $3C_2(4)$, $C_s(4)$, where the numbers in parentheses indicate the atoms that can be allocated in these sites.

There is another source of distortion factors. As seen from Fig. 2 the dien molecule is coordinated in a *syn* conformation, both ethylene fragments being above the N1–N4–N1′ plane. Since this conformation is expected to be less favoured as to strain energy [12], its existence in the present case may be related to the position of the free NO_3 group and/or to the intensive H-bond network. The two ethylene fragments jointly push the oxygen atom further away and produce unequal NCuO angles in the equatorial plane.

Electronic spectra

The electronic spectrum of $Cu(dien)(NO_3)_2$ in CH_3OH solutions shows two bands at 251 nm (39.8 kK) (log $\epsilon=3.8$) and 615 nm (16.3 kK) (log $\epsilon=2.15$). The 16.3 kK band gives rise to the intense blue colour of the compound. It is very broad and possibly represents a spectral envelop covering several d–d transitions [5]. The 39.8 kK band appears as a shoulder on the unshifted 206 nm (48.5 kK) dien band. The solid state reflection spectra show the same broad structureless band at 16.3 kK. Nujol suspensions of the studied compound revealed a very weak band at 4.85 kK (2060 nm) in the near IR region. This band is located very near to the Nujol overtone band. Hence it is probably due to the presence of the ethylene groups, being an overtone vibration of the CH_2 groups.

Detailed studies on the piezochromism of $Cu(dien)L_2X_2\cdot nH_2O$ (L = 2,2′-dipyridylamine, $n=1$ or 2) [12] have shown a very broad band at about 14 kK that could be resolved into three components with increasing pressure. Our 16 kK band, treated in a Gaussian band deconvolution, displayed three components at about 13, 16 and 18 kK. This three-band pattern is consistent with a spectral assignment of the d–d bands in C_{2v} symmetry of the CuN_3O_2 chromophore. The symmetry lowering down to C_{2v} splits the E′ and E″ states in D_{3h}. The four new states produced by this symmetry lowering give rise to three bands since the transition to one of them ($^2A_2$) is symmetry forbidden.

Infrared spectra

In the infrared spectrum of the free dien molecule the 3360 and 3295 cm^{-1} bands could be assigned to primary and secondary amine groups, respectively. They are shifted upon coordination to lower wavenumbers by 80 and 74 cm^{-1}. These shifts are strong evidence that the ligand is coordinated in a tridentate mode.

The 735, 810 and 1320 cm^{-1} bands as well as the 820 and 1360 cm^{-1} bands point to unidentate and ionic nitrate groups, respectively [6, 7]. The combination band at 1700 cm^{-1} is split into a doublet (20 cm^{-1} apart) and this splitting is on the borderline between the uni- and bidentate NO_3 modes, indicating [6] that the second NO_3 group could be both bridging and/or bidentate, in full agreement with the reported molecular structure (*vide supra*). The absence of a 930 cm^{-1} band in the recorded spectrum is taken as evidence for the symmetric (*syn*) dien conformation, as first suggested by Hathaway *et al.* [12a]. Thus, our results seem to support the suggestion [12a] that this band could be used as a diagnostic tool for the dien conformation.

Conductivity measurements and magnetic moment

The molar conductivities measured in 1 mmol methanol and aqueous solutions were 156 and 217 mho cm^2 mol^{-1}, respectively. These values are higher than those expected for a 1:1 electrolyte (80–115 in CH_3OH and 118–31 mho cm^2 mol^{-1} in H_2O) and somewhat lower than those for a 1:2 electrolyte (160–220 in CH_3OH and 235–73 mho cm^2 mol^{-1} in H_2O) [16]. The higher conductivity data can be explained in terms of partial dissociation of the complex cation, taking place in the solution

$$[Cu(dien)(NO_3)]^+ \rightleftharpoons [Cu(dien)]^{2+} + NO_3^-$$

the equilibrium being shifted considerably to the right.

The magnetic moment at room temperature was found to be 1.85 BM consistent with monomeric copper(II) units.

Conclusions

X-ray diffraction data and spectral data indicate the presence of five-coordinate Cu(II) units with a tridentate dien ligand and two types of NO_3 groups. The molecular structure can be considered either as a trigonal bipyramid with the dien ligand in a meridional position, or a square pyramid with an apical oxygen atom and the dien ligand forming part of the base. Conductivity measurements and solution spectra, however, suggest that a four-coordinate unit $[Cu(dien)(NO_3)]^+$ with a weakly bonded nitrate group may be present, the nitrate group being partially dissociated in the solution.

Supplementary material

A Table with observed and calculated structure factors for $C_4H_{13}N_3Cu \cdot 2NO_3$ (5 pages) can be obtained upon request from one of the authors (G.S.N.).

Acknowledgements

One of us (G.S.N.) gratefully acknowledges partial financial support through grant no. 152 of the Bulgarian Council for Science as well as the hospitality of the University of Thessaloniki during his stay in 1986.

References

1 (a) F. S. Stephens, *J. Chem. Soc. A,* (1969) 883; (b) G. Davey and F. S. Stephens, *J. Chem. Soc. A,* (1971) 103.

2 S. Siddiqui and R. E. Shepherd, *Inorg. Chem., 25* (1986) 3869.

3 H. Gampp, H. Sigel and A. D. Zuberbühler, *Inorg. Chem., 21* (1982) 1190.

4 W. Mori, T. Sakurai, A. Nakahara and Y. Nako, *Inorg. Chim. Acta, 132* (1987) 247.

5 K. L. Bray and H. G. Drickamer, *J. Phys. Chem., 93* (1989) 7604.

6 A. B. P. Lever, E. Montovani and B. S. Ramaswamy, *Can. J. Chem., 49* (1971) 1957.

7 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley-Interscience, New York, 3rd edn., 1978.

8 (a) B. J. Hathaway, *Coord. Chem. Rev., 5* (1970) 143; (b) R. R. Holmes, *Prog. Inorg. Chem., 32* (1984) 120.

9 M. Bacci, *Chem. Phys., 104* (1986) 191.

10 (a) M. I. Arriortua, J. L. Mesa, T. Rojo, T. Debaerdemaeker, D. Beltran-Porter, H. Stratemeier and D. Reinen, *Inorg. Chem., 27* (1988) 2976; (b) D. Reinen and M. A. Atanasov, *Chem. Phys., 136* (1989) 27.

11 (a) I. Bertini, D. L. Johnson and W. De W. Horrocks, *Inorg. Chim. Acta, 4* (1970) 79; *Inorg. Chem., 9* (1970) 698.

12 (a) N. J. Ray, L. Hullett, R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.,* (1981) 1466; (b) A. R. Gainsford and D. A. House, *Inorg. Chim. Acta, 3* (1969) 367.

13 (a) D. Kepert, *Inorganic Stereochemistry,* Springer, Berlin 1982, Ch. 5; (b) R. D. Hancock, *Prog. Inorg. Chem., 37* (1989) 187.

14 R. Engelman, *The Jahn–Teller Effect in Molecules and Crystals,* Wiley-Interscience, New York, 1972.

15 A. D. Liehr, *J. Phys. Chem., 67* (1963) 389; A. Ceulemans, D. Bayens and L. G. Vanquickenborne, *J. Am. Chem. Soc., 106* (1984) 5824.

16 W. J. Geary, *Coord. Chem. Rev., 7* (1971) 21.