The crystal, molecular and electronic structures of copper(II) dipropylenetriamine thiocyanate nitrate*

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Abstract

The crystal and molecular structure of $Cu(dpta)(NCS)(NO_3)$ where dpta = dipropylenetriamine is reported. The blue compound which crystallizes in space group $P2_1/c$ with $Z = 4$ and $a = 9.571(2)$, $b = 10.453(2)$, $c = 13.620(3)$ Å, $\beta = 108.29(2)°$, $V = 1294(1)$ Å^3 gave 4313 reflections with $R_w = 0.068$. Cu(II) is four coordinate with three Cu–N contacts (2.017(6), 2.083(5) and 2.009(6) Å) from the tri-dentate dpta and one contact (2.005(6) Å) from the N-coordinated NCS group. The contact with an O atom from the NO_3 group is at >3.5 Å. The CuN_4 group is almost planar, slightly rhombically distorted, and Cu is out of the 4N plane, the amine nitrogens being tilted towards the NCS group. The dpta ligand is in a symmetric conformation (k,k') around the central Cu–N and the NCS group is linear but it is at 162° to the plane of the three dpta nitrogens. The observed molecular symmetry is explained by crowding of the CH_2 groups on the one side of the CuN_4 plane. This is consistent with electronic and ESR spectra and substantiated by MNDO and MM calculations. The red shift $(\Delta E \sim 400$ cm$^{-1})$ with the temperature observed in the electronic spectra and the polarizations can be explained in terms of dynamic Jahn–Teller coupling and displaced excited states.

Introduction

The chemistry of the copper(II) complexes with multidentate ligands is rather complicated [1]. The Cu ion is Jahn–Teller active in many symmetries and favours distorted geometries with lifted orbital degeneracy. The multidentate ligands can act as templates sharply reducing the possible geometric structures. Two complementary views have been put forward sofar. The first stipulates the predominance of the Jahn–Teller effect and interprets the observed geometries as due to vibronic coupling [1a]. The second view [2] takes into account the steric requirements coming from the ligand conformation and explains the observed geometry as due to the least strain in the coordinated ligand. Both factors must definitely contribute and the mo-

lecular geometry observed ultimately must be the compromise reached in their interplay. However, ligand rigidity decreases with increasing chelate ring size and the strain factor should become less important, the ligands being able to accommodate the Janh–Teller required distortions, and the vibronic forces should dominate the picture [3].

Copper(II) readily forms complexes with tridentate polyamine ligands [1–4]. In the bis(tridentate) Cu(II) complexes the two ligands take up facial arrangements with an overall pseudooctahedral symmetry. In the mono-tridentate Cu(II) complexes, however, the polyamine ligand prefers the meridional position and the resulting complex is either a trigonal bipyramid or planar, depending on the nature of the amine ligand and the additional ligands [5]. In order to assess the effect of the polyamine ligand length we have prepared and studied the copper(II) dipropylenetriamine complex which we want to compare with the already existing Cu(II) diethylenetriamine (dien) complexes.

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*This paper is dedicated to the memory of Professor Dr. G. Gliemann who died on Oct. 26, 1990.
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Experimental

Preparation procedure

The complex Cu(dpta)(NCS)(NO₃) was prepared as follows. Benzaldehyde 2.1 ml (20 mmol) was mixed with 1.41 (10 mmol) 1,5,9-tri-azanonane (dipropylenetriamine, dpta) and the resulting mixture was dissolved in methanol. Copper nitrate trihydrate 2.41 g (10 mmol) was added to this solution and the mixture was refluxed for 1 h. Cooling and slowly evaporating the solvent for 2–3 days produced an oily liquid but no solid. Thus, our attempts to isolate $Cu(dpta)(NO_3)_2$, similar to the already known $Cu(dien)(NO_3)_2$ [5], failed possibly because dpta, being larger than the dien ligand, leaves no room for the bulky NO_3^-. We resumed the preparation in a different manner. After refluxing for 1 h and cooling down to room temperature we added 0.76 g (10 mmol) of ammonium thiocyanate in 10 mmol methanol solution. Crystals started to form after 2 h of standing and the solid phase separation was complete after 5 h. The crystals were isolated by filtration and dried under vacuum. Yield 79% for Cu(H₂NCH₂-CH₂CH₂NHCH₂CH₂CH₂NH₂)(NCS)(NO₃). *Anal.* Calc. for one formula unit: Cu, 20.18; N, 22.25; C, 26.70; H, 5.44; S, 10.18; O, 15.25. Found: Cu, 19.87; N, 22.01; C, 26.7; H, 5.35%. C, H and N were analysed with a Perkin-Elmer 240 elemental analyser. Copper was determined by atomic absorption.

Physical measurements

The conductivity of the complex dissolved in methanol measured with a conductivity bridge was 86 mho⁻¹ cm² mol⁻¹ which is within the limits for a 1:1 electrolyte [6].

The magnetic moment measured with a Gouy balance Hg(NCS)₄ as calibrant was 1.73 BM which is consistent with monomeric copper. IR spectra were measured with a Bruker 113V IR spectrometer in KBr and polyethylene mulls down to 50 cm⁻¹.

The visible spectra were recorded with a spectrometer equipped with a polarizer. The experimental arrangement is described in detail elsewhere [7]. A 7 μm thick crystal was used to record the spectra with $E\|n_1$ and $E\perp n_1$ with n_1 lying in the (010) plane and a 16 μm thick crystal with $E\|n_2$ and $E\perp n_2$ with n_2 lying in the (101) plane. The crystals appeared blue in the first orientation and green in the second, thus strong dichroism was established. Taking into account the crystal axes and molecular axes orientation $E\|n_1$ is $E\|z$, $E\perp n_1$ is $E\perp y$, $E\|n_2$ is $E\perp z$, x and $E\perp n_2$ is $E\perp y$. Thus with the exception of $E\|n_2$, the remaining three crystal axes orientation can discern between the three molecular axes x, y, z. While in the second orientation (n_2) there was total extinction, in the first orientation (n_1) light was never totally extinguished. This implies that the crystal and molecular axes are not totally coincident.

X-ray measurements

A crystal with the size 90×90×150 μm was used to collect intensities of 4313 reflections on a Nonius-CAS4 using Mo Kα radiation (graphite monochromator in the incident beam) (23 °C). Within the limits $-14 < h < +14$, $0 < k < 15$, $0 < l < 20$ and $2 < \theta < 32.5°$ (($\sin \theta/\lambda)_{max} = 0.77$) 3953 unique reflections were obtained ($R_{int} = 0.04$) ($\omega/2\theta$ scan with 0.8 + 0.35. tg θ width, 60 s per reflection. Three control reflections showed a loss of intensity of 4.2% for which a linear correction was applied. Absorption was corrected using DIF ABS. The structure obtained from the direct methods was refined using 1951 reflexes with $I > |\sigma(I)|$, $w = 4I/\sigma^2(I)$, $S = 2.2$, $\Delta\rho = 1.4$ e Å⁻³, extinction coefficient = 3.9×10^{-9}.

ESR measurements

The ESR spectrum was recorded on a Varian instrument at 35 253 GHz frequency (Q-band) and 100 kHz modulation frequency using powdered samples and single crystals at 20 °C. The spectrum consists of three groups of signals giving for the g tensors 2.208, 2.085 and 2.047 or after correction $g_{\|} = 2.230$ and $g_{\perp} = 2.057$, values typical for rhombically distorted square planar Cu(II) complexes [8]. The signal does not vary with the orientation of the crystals and this implies that the g components are mixed. Thus, the molecular g components appear to be distinctly orthorhombic. The direction of the g axes seems to be controlled by the Cu–NCS bond in the distorted square planar arrangement (*vide infra*).

Theoretical treatments

Extended Hückel calculations were made with the program supplemented by Calzaferri et al. [9] for work with distance-dependent off-diagonal elements. The input parameters differ slightly from those used in earlier EH calculations on polyamine copper(II) complexes [10]. We preferred Calzaferri's parameters since they gave the correct dissociation limit (Cu²⁺ and neutral ligands) with increasing Cu–N bond length while the Tsipis parameters [10] gave negative Cu ions, i.e. electron redistribution upon dissociation was incorrect.

The molecular mechanics calculations were carried out with the MMX program employing standard parameters [11]. The MNDO calculations were made with Thiel's program adapted for PCs [12]. Angular overlap calculations with spin–orbit interaction were carried out with a Fortran program.

Results and discussion

The compound was found to crystallize in $P2_1/c$ (C_{2h}^5) space group with unit cell content $Z = 4$. The elementary cell is $a = 9.571(2)$, $b = 10.453(2)$, $c = 13.620(3)$ Å, $\beta = 108.29(2)°$ and $V = 1294(1)$ Å^3. The factor group is C_{2h} while the space group provides $4C_i(2)$ and $C_1(4)$ site symmetries [13].

The positional parameters and their estimated standard deviations are given in Table 1. The numbering of the atoms is shown in Fig. 1. The general displacement parameter expressions are given in Table 2. The bond lengths and valence angles are listed in Tables 3 and 4, respectively. Tables 5 and 6 provide information on the dihedral angles between planes and the equations of planes.

Molecular structure

It is readily seen from the X-ray determination that Cu is four-coordinate with four Cu–N bonds in a square planar arrangement. The only significant deviation is the Cu–N(imine) bond which is slightly longer than the Cu–NCS and the Cu–amine bonds. The valence angles are close to 90°, the value required for the square planar arrangement though the NCuN angles involving dpta nitrogens are significantly higher (93°, 94°) than 90° suggesting a faked displacement of the dpta nitrogens towards chelate ring opening (1). This displacement is favoured by the linear NCS group. In fact 1 seems to be a common structure of the dpta complexes which, due to the presence of six-membered
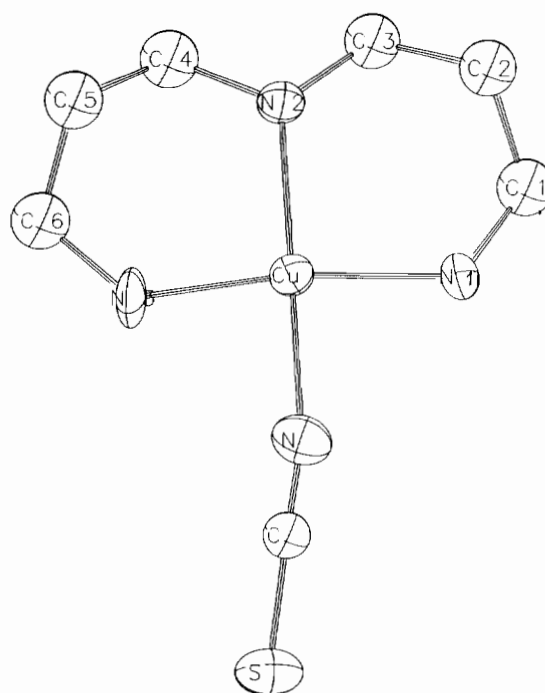

Fig. 1. The ORTEP projections of the atoms in a formula unit of Cu(dpta)(NCS)(NO$_3$) and the numbering of the atoms. Thermal ellipsoids at 296 K.

fused rings, tend to produce higher NMN angles than in the dien complexes (see for example refs. 14 and 15).
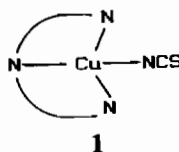

The two *trans* NCuN angles (162 and 169°) measured on one side of the 4N plane suggest that the almost square CuN$_4$ chromophore is distorted with the Cu atom below that plane. This finding may reflect the increased non-bonded atom repulsion produced by crowding of the CH$_2$ groups on the one side of the 4N plane. It can also possibly be the reason why the otherwise linear NCS ligand is out of the 4N plane and the Cu–N–C(S) angle is 162°.

Linearly N-coordinated NCS groups were found in many copper(II) thiocyanate complexes [14]. A striking feature is that the Cu–N–C angle deviates considerably (163° [15], 173° [14]) from 180°, a value required for best π-Cu–NCS bonding conditions. No satisfactory explanation has been put foward so far for the eluded Cu–NCS linearity. Possibly, non-bonded atom repulsion is reduced by positioning the CS group outside the CuN$_4$ plane with a non-linear Cu–NCS unit and this factor overrides the energy gain that may come with increasing the Cu–NCS bond order.

TABLE 1. Positional parameters ($\times 10^4$) and their e.s.d.s

Atoms	x	y	z	B (Å^2)^a
Cu	8222(1)	487(1)	3009(1)	2.39(2)
S	11414(4)	1961(3)	6242(2)	3.72(8)
O1	2468(7)	5793(7)	9018(5)	4.2(2)*
O2	3653(8)	7546(8)	9445(6)	4.9(2)*
O3	2527(9)	7119(8)	7858(6)	5.0(2)*
N	9690(10)	1329(8)	4222(6)	3.3(2)
N1	9866(8)	433(9)	2379(5)	2.7(2)
N2	6600(8)	−41(7)	1650(5)	2.6(2)
N3	6770(8)	1102(8)	3697(6)	3.1(2)
N4	2885(9)	6843(8)	8770(6)	3.3(2)
C	10390(10)	1580(10)	5063(7)	2.7(2)*
C1	9820(10)	−480(10)	1531(7)	3.9(2)*
C2	8330(10)	−370(10)	620(7)	3.7(2)*
C3	7080(10)	−930(10)	953(8)	3.6(3)*
C4	5220(10)	−580(10)	1821(7)	3.9(2)*
C5	4510(10)	360(10)	2336(8)	3.9(2)*
C6	5290(10)	520(10)	3486(8)	4.0(2)*

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as: $(4/3)[a^{*2}B(1,1) + b^{*2}B(2,2) + c^{*2}B(3,3) + a^*b^*(\cos \gamma)B(1,2) + a^*c^*(\cos \beta)B(1,3) + b^*c^*(\cos \alpha)B(2,3)]$.

TABLE 2. General displacement parameter expressions Us ($\times 10^4$)

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Cu	291(5)	311(6)	302(5)	−56(8)	89(4)	−37(7)
S	570(20)	370(20)	380(10)	−80(20)	0(10)	20(10)
N	540(60)	320(50)	380(50)	20(50)	100(40)	−30(40)
N1	320(40)	450(50)	300(40)	−40(50)	170(30)	−30(50)
N2	330(40)	320(50)	330(40)	−60(40)	90(40)	−100(40)
N3	370(40)	410(60)	560(50)	−120(40)	360(40)	−100(40)
N4	470(50)	400(60)	360(50)	40(50)	80(40)	30(40)

The form of the anisotropic displacement parameter is: $\exp[-0.25\{h^2 a^{*2} U(1,1)+k_2 b^{*2} U(2,2)+l^2 c^{*2} U(3,3)+2hla^* b^* U(1,2)+ 2hla^* c^* U(1,3)+2klb^* c^* U(2,3)\}]$, where a^*, b^*, c^* are reciprocal lattice constants.

TABLE 3. Bond distances (Å)

Cu–N	2.005(6)	N1–C1	1.488(9)
Cu–N1	2.017(6)	N2–C3	1.499(9)
Cu–N2	2.083(5)	N2–C4	1.517(9)
Cu–N3	2.009(6)	N3–C6	1.490(9)
S–C	1.646(7)	C1–C2	1.573(9)
O1–N4	1.250(7)	C2–C3	1.53(1)
O2–N4	1.225(7)	C4–C5	1.49(2)
O3–N4	1.217(6)	C5–C6	1.517(9)
N–C	1.160(7)		

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Bond angles (°)

N–Cu–N1	85.7(2)	Cu–N3–C6	122.5(4)
N–Cu–N2	169.3(2)	O1–N4–O2	119.4(6)
N–Cu–N3	83.3(2)	O1–N4–O3	118.3(6)
N1–Cu–N2	94.4(2)	O2–N4–O3	122.4(7)
N1–Cu–N3	162.5(2)	S–C–N	178.3(7)
N2–Cu–N3	93.9(2)	N1–C1–C2	111.4(6)
Cu–N–C	161.8(6)	C1–C2–C3	109.9(7)
Cu–N1–C1	120.8(4)	N2–C3–C2	112.5(7)
Cu–N2–C3	115.8(4)	N2–C4–C5	112.2(6)
Cu–N2–C4	113.8(5)	C4–C5–C6	114.2(6)
C3–N2–C4	108.9(5)	N3–C6–C5	112.0(6)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 5. Dihedral angles between planes

Plane number	Plane number	Dihedral angles
I	II	0.2±9.9
I	III	112.4±0.3
II	III	112.5±0.3

The planes I–III are defined in Table 6.

The nitrate group is planar and far away $(Cu–ONO_2 > 3.5$ Å$)$ from the copper atom so there is no bond between NO_3 and Cu. This is nicely reflected in the IR spectrum (Table 7) which points to ionic uncoordinated NO_3.

Molecular mechanics calculations

The results from the X-ray determinations are rather difficult to understand from the point of view of the least repulsion energy requirements and the interplay of electronic and nuclear repulsion factors. Four-co-ordinate tetrahedral Cu complexes which are those with the least interligand repulsion energy are known to distort by Jahn–Teller coupling and the resulting geometries produced by the ϵ-mode in T_d are with D_{2d} symmetry — compressed tetrahedra with LCuL angles ranging from 109.4° (regular tetrahedron) to 130° or higher for D_{2d} structures [16]. However, the trans NCuN angles in our case are about 162–169° — too high to be a distorted tetrahedral structure and much closer to the square planar values. In fact the high chelate NCuN angles 93–94° and the displacement of the two terminal NH_2 groups along the Cu–NCS axis may be interpreted as a result of the τ_2-mode of T_d trying to push the molecular structure towards C_{3v} symmetry [17] with the three dpta nitrogens occupying the equatorial positions and the N atom from the NCS group at the apical position of a trigonal pyramid with Cu out of the equatorial 3N plane. In view of the NCuN values, however, such a description is unrealistic. Hence the tetrahedral structure should be discarded as a basis for discussion. The square planar arrangement seems to be the only alternative left for discussion as a reference structure. The electronic spectra (vide infra) seem to support this assumption (Table 8).

The results from molecular mechanics calculations are presented in Table 9. It should be noted that the Cu–N contributions to the enthalpy of formation are not known and the MM results with regard to the Cu complexes should be viewed with caution only in a comparative way.

A closer inspection of Table 9 reveals several very interesting points.

There is a net difference in the steric behaviour of the two free ligands — dien and dpta. The longer dpta ligand, optimized by the MM calculations, produces the least energy structure to be linear, the two warped structures being some 20 kJ mol^{-1} higher in energy.

TABLE 6. Some equations of planes

Equations of planes	Atoms				χ^2
	A	B	C	D	
Cu, N1, N2, N3	−0.0070	0.9200	−0.3919	−0.9282	
I Cu(dpta)	(−0.0666	9.6167	−5.0381	−0.9282)	17525
Cu, N1, N2, N3, N	−0.0086	0.9187	−0.3948	−0.9476	
II Cu(dpta)(NCS)	(−0.0819	9.6038	−5.0683	−0.9476)	18081
N4, O1, O2, O3	0.8941	−0.4411	−0.0781	−4.9173	
III nitrate	(8.5573	−4.6105	−4.8307	−4.9173)	0.6

The equations are $Ax + By + Cz + D = 0$. First row shows the orthonormal equation of plane and the second row the crystallographic equation of plane.

TABLE 7. IR spectra of Cu(dpta)(NCS)(NO$_3$) (cm^{-1})

Frequency	Assignment
217s	δ(Cu–NH$_2$)
200m	δ(Cu–NCS)
340–360 doublet	ν_1(Cu–N)
400 doublet	ν_2(Cu–N)
435m	ν_3(Cu–N)
465 doublet	ν_4(Cu–N)
520s	ν(NCS)
645m	ν_4(NO$_3$) + δ_r(NH$_2$)
670m w	ν(CS)
1034m	ν_1(NO$_3$)
1096m	ν(C–C)
1132m	ρ_t(CH$_2$)
1169m	ρ_r(CH$_2$)
1250w	ρ_w(CH$_2$) + δ(HNH)
1281m sh	ρ_w(CH$_2$)
1344sh	ν_3(NO$_3$)
1390s	δ(CH)
1597m	δ(HNH)
2060–2112s doublet	ν(CNS)
2920–2943 triplet	ν_{sym}(CH$_2$)
3157s	ν_{asym}(CH$_2$)
3240s	ν_{sym}(NH$_2$)
3275s	ν_{sym}(NH$_2$)
3312s	ν_{asym}(NH$_2$)

500–4000 cm^{-1} in KBr mulls, 50–500 cm^{-1} in PE mulls ν, stretch; δ, bend; ρ, out-of plane; t, torsion, r, rock; w, wag; sh, shoulder.

Unlike dpta the shorter dien molecule warps into the puckered conformation with an energy gain of about 9 kJ mol^{-1}. The reason for this different steric behaviour is the strain energy variations which are different in size and sign for the two ligands. They closely match the variations in the heats of formations (see Table 9).

We shall now explore how this difference in the behaviour of the free ligands is reflected in the possible structures of the copper complexes. Before proceeding further we shall recall some conformations that have been discussed in the past for polyamine ligands [3]. Both ligands are known to occupy the meridional (mer)

position in complexes with coordination number less than 6. In fact since we are dealing with planar four-coordinate Cu, the fac conformers have to be ignored.

2 k,k   3 k,k'
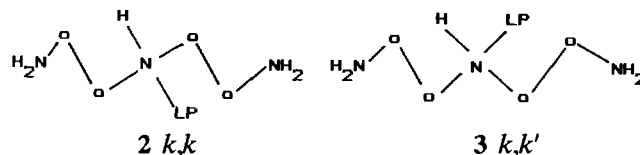
Structures 2 and 3 exhibit the k,k and k,k' conformers of the dien ligand and structures 4 and 5 give the corresponding conformers for dpta keeping the arrangements around the central N atom the same as in dien. LP stands for a lone pair. It should be noted that 4 is a very shallow minimum and readily slumps to a form where one of the (CH$_2$)$_3$NH$_2$ groups takes a position perpendicular to the first one, which is an arrangement that is appropriate for a facial coordination. The reason for this behaviour is the proximity of the imine LP to the amine LP in the k,k conformers.

The second point worth mentioning is the location of the two LPs at the NH$_2$ groups in the k,k' conformer. The energies listed in Table 9 refer to conformers with the two LPs in a non-eclipsed orientation with respect to the line connecting the two amine groups.

4 k,k   5 k,k'
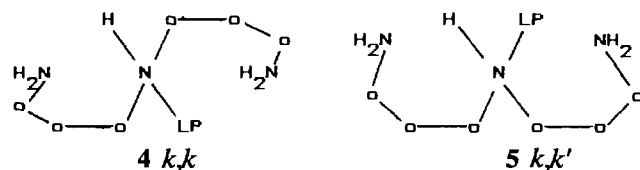
The two conformers 2, 3 and 4, 5 differ only slightly in energy. In fact the energy differences are very small (less than 4 kJ mol^{-1}) and the barrier to a rotation about the C–NH bond is about 12 kJ mol^{-1} for the free dpta.

The changes that must occur upon coordination are the following. The three LPs which are located as far apart as possible to reduce repulsion in the free ligand must point in the coordination compound to the central

TABLE 8. Single crystal polarized electronic spectra; energies in kK, 1 kK=1×10^3 cm^{-1}

| Transition energy		Polarization	ΔE	I/I_0	$(\nu/\nu_0)^2$	Assignment
10 K	295 K					
13.10(−)		z				$x^2-y^2\rightarrow xy$
13.50(33)	14.00	z	+0.5			
15.15(210)	14.75	y	+0.4	1.4	1.9	$x^2-y^2\rightarrow yz$
15.75(85)	15.25	z	+0.5	1.8	1.9	$x^2-y^2\rightarrow xz$
17.15(264)	16.80	x	+0.4	1.5	2.1	$x^2-y^2\rightarrow z^2$
17.40(58)	17.00	x	+0.4	1.7	2.1	

ΔE is the transition energy difference for the two temperatures; I/I_0 is the intensity ratio I_{295}/I_{10}; $(\nu/\nu_0)^2$ is the squared half-width ratio ν_{295}/ν_{10}; extinction coefficient, ϵ (l mol^{-1} cm^{-1}) is given in parentheses.

TABLE 9. Molecular mechanics calculations on the dien and dpta ligands and their copper(II) complexes; energies in kJ mol^{-1}

Compound	Conformation	MMX	Stretch	Bending	Van der Waals	Torsional	Dipole–dipole	ΔH_f	Strain energy
dien	linear	13.22	1.01	3.37	9.39	−2.57	1.64	−17.0	4.2
dien	k,k'	4.29	1.01	3.87	8.59	−9.34	0.00	−26.0	−2.5
dien	k,k	4.63	1.01	3.83	8.84	−9.47	0.00	−25.6	−2.1
dpta	linear	17.68	1.56	4.00	13.34	−2.61	0.93	−71.5	5.5
dpta	k,k'	38.51	1.85	8.84	14.81	12.63	−0.46	−50.9	26.1
dpta	k,k	35.98	1.77	7.74	12.58	13.97	−0.88	−53.4	23.6
Cu(dien)	k,k'	58.33	5.01	40.40	11.95	5.05	1.09	−74.9	51.3
Cu(dpta)	k,k'	82.87	1.64	25.04	15.70	35.56	4.04	−6.3	70.3

ΔH_f = enthalpy of formation. Cu–N contributions to the enthalpy are not known so that ΔH_f for the two Cu complexes should be viewed with caution.

atom. This doubles the strain (see Table 9). It is however readily seen that the only possible dpta conformation that can assume the meridional location is that of structure 6, which is viewed along the central N–Cu bond. The copper atom is overlayed by the central nitrogen.

6
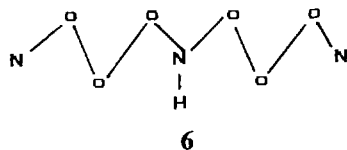
Structure 6 demonstrates that there should be crowding above the CuN$_3$ plane passing in 6 perpendicular to the sheet and through the three nitrogens. To avoid repulsion with the CH$_2$ groups the Cu atom should drop below that plane. To avoid crowding, the dpta molecule folds around the central Cu–N bond by closing the NCuN angle with the amine nitrogens.

It should be noted that for the dien complex such crowding cannot be present due to the lower (even) number of the CH$_2$ groups. The two CH$_2$ groups above and below the CuN$_3$ plane however are inequivalent due to the presence of the imine H atom.

Electronic structure calculation

MNDO calculations with full geometry optimization for dpta starting both from a linear molecule and from a puckered geometry yielded the k,k' conformer as the most stable with $\Delta H_f = -48.6$ kJ mol^{-1} and a dipole moment of 2.25 D. While the heat of formation agrees well with the MM value (−50.9 kJ mol^{-1}), the MNDO dipole moment is higher than the MM value (1.51 D). This reflects in general the abilities of the MNDO method to reproduce molecular properties [18].

The calculated (MNDO and MM) geometries are compared in Table 10 with the dpta geometry as found in M(dpta) complexes.

It is readily seen that the calculated bond lengths and valence angles for the free ligand agree very well with the experimental ones for the coordinated ligand giving credence to the claim that the van der Waals forces (non-bonded interaction) dominate the way the ligand is coordinated to the central atom. The experimental bond lengths are midway between those of MNDO and MM calculations but they are usually closer to the MNDO predicted values which is quite reasonable since both the electronic and non-bonded interactions are taken into account in this method.

TABLE 10. Calculated and experimental k,k'-dpta geometry (see structure 6)

Bond length (Å)	MNDO	MM	Exp.	Valence angle (°)	MNDO	MM	Exp.
C–NH$_2$	1.46	1.53	1.49	HNH	109.4?	108.9	a
C–C	1.54	1.66	1.50–7	NCC(amine)	111.9	103.2	111–2
C–NH	1.47	1.73	1.50–2	CCC	118.0	115.3	110–4
C–H	1.11–2	1.13	a	CCN(imine)	114.3	112.9	112
N–H(amine)	1.008	1.11	a	CNH(imine)	109.4	110.0	a
N–H(imine)	1.010	1.11					

Twist angle (°)	MNDO	MMX
HNCC	124.7	120.0
NCCC	83.8	82.4
CCCN	−69.8	−75.9
CCNH	−174.9	−163.2

^{a}not determined.

Since no parameters for copper are available in the MNDO method we have calculated by the extended Hückel method the electronic structures of both the free ligand and of the Cu(dpta)(NCS)$^+$ group. Geometry optimization was not attempted since EH is notorious in producing incorrect results as to absolute energy minima. In the EH calculations we have used the real geometry of the complex as determined by X-ray diffraction. The calculated electron transition energies (20.1, 20.6, 22.5 and 25.1 kK) were systematically higher by about 8 kK than the experimental ones and should be viewed only with respect to the relative d-orbital order. The charge on Cu is 0.155 a.u. (0.56 without charge iteration) and the highest occupied MO is composed predominantly of a $d_{x^2-y^2}$ and d_{z^2} mixture with

$$\Psi = 0.9992 d_{x^2-y^2} - 0.0391 d_{z^2}$$

for the highest occupied MO, renormalized to include only the two d-AO that may mix in D_{2h}. In the un-normalized MOs the copper d-AOs due to the low symmetry (C_s) are widely distributed, which substantiates the finding that the ESR signal is insensitive to crystal orientation and the small difference in the g_{xx} and g_{yy} tensor values. Using the formulas [8a]

$$\Delta g_x = -2\lambda k_x^2(a - \sqrt{3}b)^2/E_{yz}$$

$$\Delta g_y = -2\lambda k_y^2(a + \sqrt{3}b)^2/E_{xz}$$

$$\Delta g_z = -8\lambda k_z^2 a^2/E_{xy}$$

where $k_x^2 = k_y^2 = k_\perp^2 = 0.25$ and $k_z^2 = k_\parallel^2 = 0.49$ [8c], a and b are defined by the HOMO wave function and E_{yz}, E_{xz}, E_{xy} are the zero phonon transition energies (12.7, 14.8, 15.5 kK, see Table 8), $\lambda = -0.83$ kK. We

obtained $g_\perp = 2.02$ and $g_\parallel = 2.25$ in good agreement with the experimental g values (2.06 and 2.23). Calculations with more sophisticated formulas [8b] using the eigenvectors from the EH calculations reproduced the trend $g_\parallel > g_\perp$ but the absolute values were much lower thus exhibiting the impotency of the EH method to account for the finer details.

We shall now discuss the electronic spectra (Fig. 2). In Table 8 there are three groups of bands: 13, 15 and 17 kK, actually doublets. In fact as to the number and location of the bands this spectrum resembles very closely the spectrum of the planar CuCl$_4^{2-}$ unit (12.2, 14.0 and 16.5 kK) [19, 20], the transition energies being somewhat higher for our complex. The first striking feature of the Cu(dpta)(NCS)$^+$ spectrum is that the transition energies increase and the band intensities decrease with lowering temperature. The intensity decrease indicates a vibronic coupling mechanism to be operative in gaining intensity for the parity forbidden (in D_{4h}) d–d transitions [20]. The same red shift with increasing temperature was observed with the planar CuCl$_4^{2-}$ ion [21]. This shift was explained by double minima corresponding to two equivalent pseudotetrahedral coordination geometries in each excited state [21]. A case of hot bands was also observed for the centrosymmetric complexes [22]. Different lattice modes were supposed to be involved and the simple vibronic selection rules were thought to break down [23].

Before discussing the possible assignment two features should be examined. (i) The intensity ratio is low suggesting that low frequency vibrations may be involved [20]. (ii) The variation of the squared half-width ratio with the temperature suggests that the totally symmetric mode is about 400 cm^{-1}, which is very close to the transition energy difference at the two measured tem-
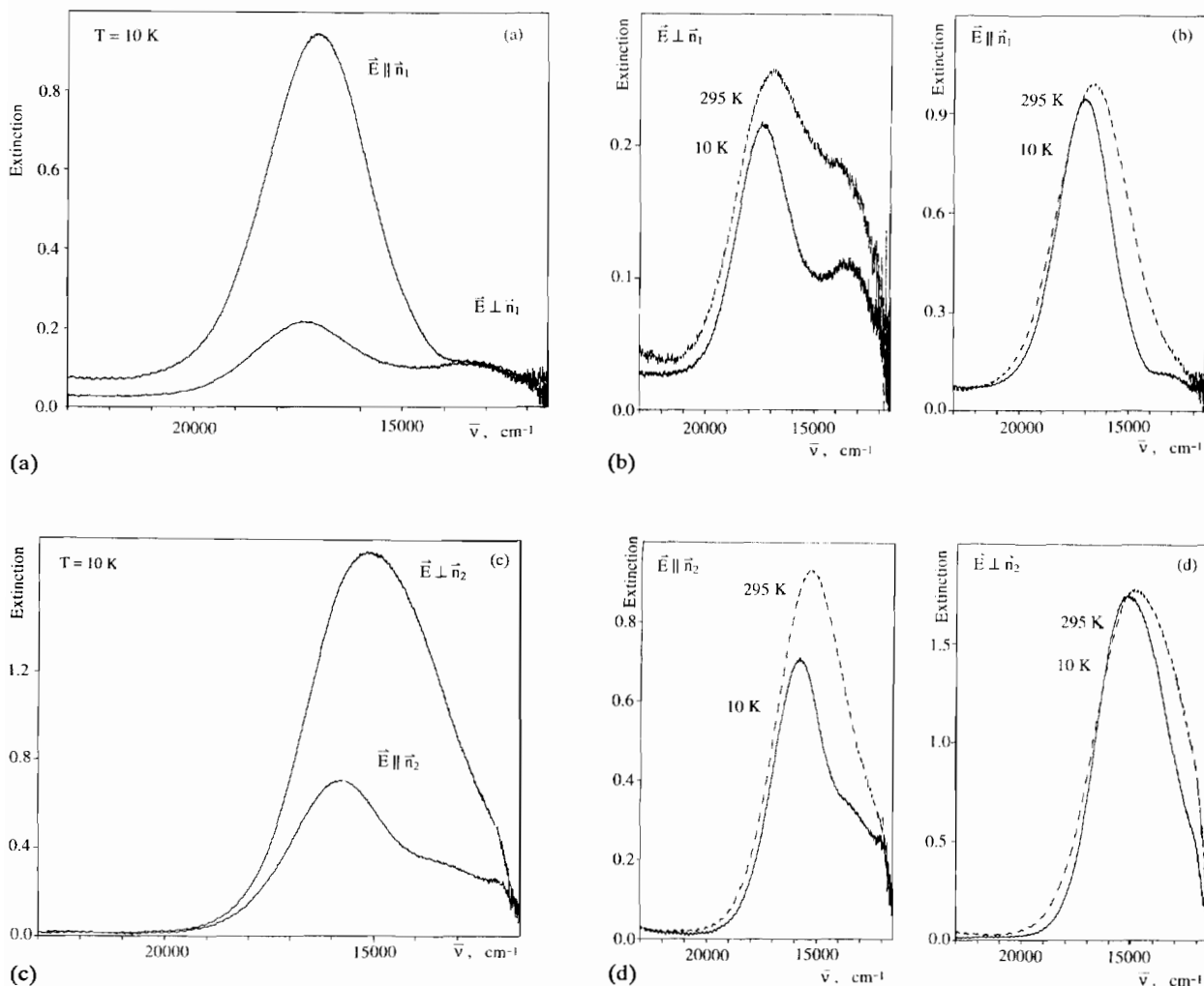
Fig. 2. Electronic spectra of Cu(dpta)(NCS)(NO$_3$) single crystals at 10 and 295 K recorded with polarized light. The n$_1$ ((a) and (b)) and n$_2$ ((c)) and (d)) orientations correspond to the electric vector lying in the (010) and (101) planes of the crystal, respectively.

peratures. It can thus be assumed that the red shift is due to excitation of the totally symmetric vibrations whereas the inducing vibration should be of low frequency.

It is seen that the polarizations of the higher energy components of the 13 and 17 kK bands are the same and this indicates that higher vibrational levels may be involved. Unlike these bands the ~15 kK components show different polarizations and may be interpreted as the e$_g$ level in D_{2h} split by lower symmetry and they could be assigned to transitions d$_{yz}$ and d$_{xz}$, although the order is not certain.

Summarizing the arguments discussed above we have collected in Table 11 a tentative assignment and the transitions energies calculated by the angular overlap model.

The experimental spectrum listed in Table 11 is that at 10 K. The transition energies are calculated by the AOM with $e_\sigma = 5.5$ kK and $e_\pi = 0$, spin orbit constant

TABLE 11. Electronic spectrum of Cu(dpta)(NCS)(NO$_3$) (in 10^3 cm^{-1})

Transition energies		Assignment D_{2h}	Allowing vibration	Displaced point group symmetry	δr (Å)
exp.	calc.				
13.1	10.7	$x^2-y^2 \rightarrow xy$	β_{2u}	C_{2v}	0.14
13.5		$+ \nu(\beta_{2u})$			
15.2	14.1	$x^2-y^2 \rightarrow yz$	β_{1u}	C_{2v}	
15.9	15.5	$x^2-y^2 \rightarrow xz$	β_{3u}	C_{2v}	
17.1	16.2	$x^2-y^2 \rightarrow z^2$	β_{3u}	C_{2v}	0.11
17.4		$+ \nu(\beta_{3u})$			

0.5 kK (60% reduction of the free ion value). The agreement between calculated and experimental energies may be improved if a slight non-vanishing π-contribution is included. The agreement is especially

poor for the 17.1 kK band but this seems to be a common feature for the $d_{x^2-y^2} \rightarrow d_z^2$ transition of planar CuL_4 complexes of approximately D_{4h} symmetry [24]. It is partly due to s–d mixing. The assignment is that resulting from the AOM calculations in agreement with the experimental polarizations. The allowing vibration is guessed from the experimental polarization and Table III in ref. 20 which provides the activation of the d–d transitions by an ungerade symmetry mode in D_{4h}. The corresponding rules for the D_{2h} group which explain the split of the d_{xd}, d_{yz} orbitals are given in Table 12. The displaced point group symmetry is that resulting when the atoms are displaced along the symmetry mode. The displacement (δr) is that of the potential energy minimum of the excited states, calculated with the formula of Yersin et al. [25] from the intensity ratio with parameters similar to those used in the $CuCl_4^{2-}$ spectral analysis [18] but with different reduced mass.

The band assignment in Table 11 supposes that the symmetry of the excited states differs from the ground state symmetry and that the excited states minima are strongly displaced (0.11–0.14 Å) with respect to the ground state minimum.

The lowest energy transition is $d_{x^2-y^2} \rightarrow d_{xy}$. It appears as a shoulder to the higher energy 15 kK band and shows vibrational structure. This structure is very complicated with several progressions of modes with less than 30 cm^{-1} energy. It is supposed that different lattice modes are involved as for the planar $CuCl_4^{2-}$ [23]. The resolution of our equipment is low (± 10 cm^{-1}), too low to permit further analysis especially below 12 kK. In addition the wavy line at about 20 kK is due to interferences that cannot be avoided when measuring thin crystals between quartz plates.

An alternative explanation of the observed spectrum can be invoked. It includes a double minimum ground state and dynamic pseudo-Jahn–Teller averaging at room temperature [26]. The molecule is frozen at low temperatures in the deeper minimum. This assumption explains the increased transition energies at the lower temperatures by decreasing the vibrational population. The mechanism was first proposed by Engelman [27]

but it was disputed by the transition energy variation with the temperature [20].

Obviously more work is needed to elicit the nature of the electronic spectra of centrosymmetric molecules.

Conclusions

Unlike the dien complex the studied $Cu(dpta)(NCS)(NO_3)$ complex illustrates the features of a planar four-coordinate Cu(II) ion. The small deviations from planarity could be explained fairly well by the conformation of the dpta ligand although vibronic factors, as evidence by the electronic spectra, cannot be ruled out.

Acknowledgements

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TABLE 12. Vibronic selection rules in D_{2h} symmetry

Inducing vibration	Polarization in		
	x	y	z
α_u	yz	xz	xy
β_{1u}	xz	yz	z^2
β_{2u}	xy	z^2	yz
β_{3u}	z^2	xy	xz

Transitions from hole in x^2-y^2 to the hole indicated in the Table. The ungerade vibrations for ML_4 in D_{2h} are $\alpha_u + \beta_{1u} + 2\beta_{2u} + 2\beta_{3u}$.

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