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Coordination Fluxionality of Copper(II) with a Sterically Constrained Pyrazole-containing Chelating Ligand. Crystal and Molecular Structure at 298 K and 140 K of 1,6-Bis(3,5-dimethylpyrazol-1-yl)-2,5-dimethyl-2,5-diazahexane-bis(thiocyanato-*N*)copper(II), [$C_{18}H_{28}CuN_8S_2$]

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Abstract

The X-ray structure determinations of the compound Cu(debd)$(NCS)_2$ at 140 K and at 298 K showed at both temperatures a tetragonal crystal system with space group $P4_12_12$ ($Z = 4$) and a molecular C_2 symmetry. Cell dimensions are: $a = 9.577$, $c = 24.422$ Å and $V = 2240$ Å^3 at 140 K, and $a = 9.614$, $c = 24.854$ Å and $V = 2297$ Å^3 at 298 K. 1218 (140 K) and 1057 (298 K) reflections with $I > 1.96\ \sigma(I)$ were used for the solution to a final R_w value of 0.036 (140 K) and 0.032 (298 K). The copper(II) environment is roughly octahedral. The copper to nitrogen bonds vary with temperature: Cu–N(amine) = 2.242 Å (140 K) and 2.191 Å (298 K), Cu–N(pyrazole) = 2.099 Å (140 K) and 2.193 Å (298 K), and Cu–NCS = 2.060 Å (140 K) and 2.034 Å (298 K). The ESR spectra of the Cu(II)-doped isomorphous Zn(II) and Cd(II) compounds, which have been measured at ambient temperature, at 77 K, and at 3 K, clearly reflect the temperature dependence of the structure.

Introduction

In a regular octahedral coordination sphere the copper(II) ion would possess a degenerate ground state. The Jahn–Teller theorem [1] states that this degeneracy has to be removed through distortion of the coordination octahedron. The distortion is usually effected through vibronic coupling [2], leading to the now well-known 'Mexican hat'-shaped potential energy surface of the copper(II) coordination sphere. This property accounts for many peculiarities of six-coordinated copper(II) compounds, which have been the subject of many investigations during the last decades [3, 4]. High-symmetry Cu(II)L_6 or Cu(II)$(LL)_3$ compounds with an apparent regular six-coordinated structure at ambient temperatures show a distorted geometry at lower temperatures (usually below 150 K), as is seen from low-temperature crystal-structure determinations and temperature variable spectroscopic (ESR) investigations [6]. Due to its short interaction time, electronic spectra may indicate the presence of a dynamically distorted geometry, where crystal structure determinations and ESR spectra may indicate a time-averaged geometry of higher symmetry [7, 8].

Due to the lower symmetry in copper(II) compounds of the type $Cu(LL)_2X_2$ the ground state is split into two components, and the degeneracy is removed. However, when the splitting is small, the compounds are susceptible to a pseudo Jahn-Teller effect, which accounts for the plasticity effect of this type of copper(II) compounds [9].

Investigations on more complicated (tetradentate or hexadentate) ligands have hardly been reported, and it is as yet not clear whether ligand constraints prohibit plasticity phenomena. The ligand 1,6-bis(3′,5′-dimethylpyrazol-1′yl)-2,5-dimethyl-2,5-diazahexane (abbreviated debd) has been shown to impose an octahedral geometry on first row transition metals; the compound Ni(debd)$(N_3)_2$ has a symmetrical structure with the ligand occupying two apical and two equatorial positions and with two *cis*-coordinated azide ligands [10].

The Cu(debd)$(NCS)_2$ compound, having an octahedral CuN_6 chromophore, seemed a suitable subject for the investigation of possible temperature-dependent distortions. In this paper we present the crystal structure of Cu(debd)$(NCS)_2$ at two temperatures and the ESR results of the isomorphous Cu-doped Zn(debd)$(NCS)_2$ and Cd(debd)$(NCS)_2$.

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Experimental

Synthesis and Spectroscopic Measurements

The compounds were synthesised as reported before [10]. Cu-doped Zn(debd)(NCS)$_2$ and Cd(debd)(NCS)$_2$ were prepared in concentrations of 1, 5, and 10% Cu in the host lattice. Crystals of Cu(debd)(NCS)$_2$ could be obtained from an ethanolic solution of the ligand. ESR spectra of powder samples were measured on a Varian E-3 EPR spectrometer, using a 9.5 GHz microwave bridge, at ambient temperature at liquid nitrogen temperature and at liquid helium temperature. Q-band spectra (35 GHz) were measured on a Varian V 4500 instrument, using a V 4561 bridge, at liquid nitrogen temperature. Electronic spectra (2000–300 nm) were measured on a Perkin Elmer UV330 instrument, operating in the diffuse reflectance mode with MgO as a reference.

X-ray Methods and Structure Determination

Cu(debd)(NCS)$_2$ crystallizes in the tetragonal space group $P4_12_12$ (no. 92) with four molecules in the unit cell. X-ray intensity data were collected at ambient temperature (25 °C) and at −133 °C on a Syntex P2$_1$ four-circle diffractometer using a compact polyhedral crystal measuring approximately 0.24 × 0.16 × 0.32 mm. 1057 (at 298 K) and 1218 (at 140 K) reflections with $I > 1.96\sigma(I)$ were considered as being observed and were used for the structure determination.

The intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct multisolution methods (MULTAN) followed by difference Fourier syntheses and full-matrix least-squares refinements. All hydrogen atoms were located in the final ΔF synthesis. The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were refined isotropically. The data of the low temperature structure were used for the high temperature structure solution. Crystal data and details of measurement, structure solution and refinement are given in Table I.

The calculations were done on a Data General Eclipse S/200 using the Syntex EXTL program system. Scattering curves were taken from the International Tables [11]. Atomic coordinates of the non-hydrogen atoms are given in Table II. Hydrogen atom coordinates as well as a list of observed and calculated structure factors and the anisotropic temperature factors of the non-hydrogen atoms are available as supplementary material.

TABLE I. Crystal Data and Details of Measurement and Structure Solution of Cu(debd)(NCS)$_2$, $C_{18}H_{28}CuN_8S_2$

Molecular formula	$C_{28}H_{28}CuN_8S_2$	
Formula weight	533.17	
Temperature	140 K	298 K
Crystal system	tetragonal	
Space group	$P4_12_12$	
a (Å)	9.577(4)	9.614(5)
c (Å)	24.422(4)	24.854(8)
V (Å^3)	2240	2297
Z	4	
D_x (g cm^{-3})	1.44	
D_m(flotation) (g cm^{-3})	1.41	
Radiation	Mo Kα (λ = 0.71069 Å); monochromator	
μ(Mo Kα) (cm^{-1})	12.1	
Scan range	$4° < 2\theta < 54°$	
Scan mode	$\theta - 2\theta$ –scan	
Scan speed	6–30° min^{-1} (intensity-dependent)	2–30° min^{-1} (intensity-dependent)
Number of independent data collected	1501	1531
Number of observed data with $I > 1.96\sigma(I)$	1218	1057
Absorption correction	empirical (ψ-scan)	
Structure solution	direct methods (MULTAN)	coordinates from the low temperature solution
Number of variables	188	
Refinement	full-matrix least-squares	
Weighting scheme	$w = \{\sigma(F_o)^2 + (0.01\|F_o\|)^2\}^{-1}$, with $\sigma(F_o) = \sigma(I)/(2F_oL_p)$	
$R_1 = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.038	0.042
$R_2 = \{\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2\}^{1/2}$	0.036	0.032

TABLE II. Atomic Coordinates of Cu(debd)$(NCS)_2$, $C_{18}H_{28}CuN_8S_2$

	Low temperature measurement			High temperature measurement		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu	0.19749(5)	0.19749	0.0	0.19782(5)	0.19782	0.0
S(1)	0.64248(12)	0.29001(14)	0.08242(5)	0.63663(13)	0.28684(17)	0.08126(5)
N(1)	0.0807(4)	0.2959(5)	0.0616(1)	0.0785(4)	0.3000(5)	0.0639(1)
N(2)	0.0507(4)	0.2092(4)	0.1042(1)	0.0515(4)	0.2094(5)	0.1045(2)
N(3)	0.1237(4)	0.0170(4)	0.0508(1)	0.1265(4)	0.0233(4)	0.0495(1)
N(4)	0.3732(4)	0.2208(4)	0.0478(2)	0.3727(5)	0.2221(5)	0.0450(2)
C(1)	0.0168(5)	0.4156(5)	0.0741(2)	0.0121(6)	0.4164(6)	0.0777(2)
C(2)	−0.0518(5)	0.4047(5)	0.1238(2)	−0.0541(6)	0.3980(6)	0.1265(3)
C(3)	−0.0299(5)	0.2719(4)	0.1424(2)	−0.0294(6)	0.2677(5)	0.1430(2)
C(4)	0.1180(5)	0.0732(5)	0.1061(2)	0.1208(6)	0.0785(6)	0.1047(2)
C(5)	−0.0182(5)	−0.0205(5)	0.0310(2)	−0.0140(6)	−0.0139(6)	0.0300(2)
C(6)	0.4844(5)	0.2508(5)	0.0623(2)	0.4823(5)	0.2501(5)	0.0596(2)
C(7)	0.0209(7)	0.5406(6)	0.0369(2)	0.0124(13)	0.5413(9)	0.0426(4)
C(8)	−0.0776(7)	0.2001(7)	0.1929(2)	−0.0729(11)	0.1903(11)	0.1922(3)
C(9)	0.2168(6)	−0.1049(5)	0.0506(2)	0.2205(8)	−0.0956(7)	0.0489(3)

Results and Discussion

Structure Description

Bond lengths and angles of Cu(debd)$(NCS)_2$ are given in Table III. An ORTEP drawing of the Cu(debd)$(NCS)_2$ molecule with atomic designations is shown in Fig. 1. The Cu(debd)$(NCS)_2$ has the expected symmetrical *cis*-like structure as was previously observed for Ni(debd)$(N_3)_2$ [10] and Cd(debd)Cl_2 [12]. The ligand geometry is very similar to that found in the two related compounds, and does not change significantly upon going from 298 K to 140 K. Also the Cu–NCS distance does not significantly change upon lowering of the temperature, and its value (2.034 Å at 298 K and 2.060 Å at 140 K) is comparable with the distance of 2.04 Å found for the *cis*-coordinated isoselenocyanates in the octahedral [13] Cu(o-phenantroline)$_2$(NCSe)$_2$ and the Cu–N distance of 1.99 Å found in the pentacoordinated [14] Cu(bipy)(NCS)$^+$. The C–N and C–S distances and the Cu–N–C and N–C–S angles have the usual values [15]. Significant structural changes are observed in the other Cu–N distances (see below).

At 298 K, the molecule has exact C_2 symmetry. The coordination octahedron has two short Cu–NCS bonds (2.034 Å) and four significantly longer bonds of 2.19 Å. This *cis*-distorted octahedral structure can be compared with that of a well-studied series of Cu(bipy)$_2$(OXO)$^+$ and Cu(o-phen)$_2$(OXO)$^+$ compounds (OXO is a bidentate ligand) [7, 9, 16–19], which have a similar structure. Thermal parameters of the donor-atoms have been used as evidence of fluxional behavior [7, 19], but the Cu(debd)$(NCS)_2$ compound does not show large anisotropic thermal motions along coordination bond axes. So, these data give indications neither for a fluxional behaviour, nor for a deviation from strict C_2 symmetry.

Upon cooling to 140 K, no change in space group occurs. The molecule retains its C_2 symmetry. However, significant changes in the coordination geometry are observed. The Cu–N(pyrazole) bonds are shortened significantly by 0.094 Å to 2.099 Å. The Cu–N(tertiary amine) bonds are lengthened somewhat, by 0.051 Å to 2.242 Å. The Cu–NCS bonds show a small but significant lengthening of 0.036 Å to 2.060 Å. The shortening of the Cu–N(pyrazole) bonds is accompanied by an increase of the average in-plane bond lengths from 2.113 Å to 2.151 Å. The bond lengthening is not accompanied by changes in the coordination angles, which remain essentially the same. Analogous to the high temperature structure, the thermal parameters do not show unusually large anisotropy along the coordination bond axes.

Since there is no indication for fluxional behaviour either at 298 K or at 140 K, it can be concluded that the coordination geometry of Cu(debd)$(NCS)_2$ has genuine, static C_2 symmetry, but that the Cu–debd bond lengths show a strong temperature dependency.

Spectroscopic Properties

The NIR–Vis spectrum of Cu(debd)$(NCS)_2$ shows a single d–d transition at 13.1×10^3 cm^{-1}, which is in agreement with the distorted octahedral coordination [3]. An absorption of higher intensity at 25.4×10^3 cm^{-1} is ascribed to a Cu–NCS charge-transfer transition. The spectra of the Cu-doped Zn and Cd compounds show essentially the same features. As ESR spectra of copper(II) compounds are sensitive indicators of structural changes, the spectra of Cu(debd)$(NCS)_2$ and Cu-doped Zn(debd)$(NCS)_2$ and Cd(debd)$(NCS)_2$ have been studied at ambient tem-

TABLE III. Intramolecular Distances (A) and Angles (°) with Standard Deviations of Cu(debd)(NCS)$_2$, $C_{18}H_{28}CuN_8S_2$

	Low temperature	High temperature
Cu–N(1)	2.099(4)	2.193(4)
Cu–N(3)	2.242(4)	2.191(4)
Cu–N(4)	2.060(4)	2.034(4)
N(1)–C(1)	1.334(6)	1.334(7)
C(1)–C(2)	1.385(7)	1.382(8)
C(1)–C(7)	1.503(7)	1.485(11)
C(2)–C(3)	1.366(7)	1.340(8)
C(3)–C(8)	1.486(7)	1.491(10)
C(3)–N(2)	1.351(6)	1.355(7)
N(2)–N(1)	1.362(5)	1.359(6)
N(2)–C(4)	1.454(6)	1.424(8)
C(4)–N(3)	1.455(6)	1.472(6)
N(3)–C(9)	1.469(6)	1.457(8)
N(3)–C(5)	1.486(6)	1.479(7)
C(5)–C(5')	1.515(6)	1.492(6)
N(4)–C(6)	1.158(6)	1.147(7)
C(60–S(1)	1.635(5)	1.618(5)
N(1)–Cu–N(1')	173.2(1)	173.9(2)
N(1)–Cu–N(3)	77.4(1)	76.8(2)
N(1)–Cu–N(3')	97.3(1)	98.4(2)
N(1)–Cu–N(4)	88.9(2)	89.0(2)
N(1)–Cu–N(4')	95.6(2)	95.1(2)
N(3)–Cu–N(3')	79.6(1)	80.6(2)
N(3)–Cu–N(4)	91.6(2)	92.2(2)
N(3)–Cu–N(4')	167.8(2)	168.1(2)
N(4)–Cu–N(4')	98.3(2)	96.5(2)
Cu–N(1)–C(1)	142.6(3)	144.4(4)
Cu–N(1)–N(2)	112.7(3)	110.6(3)
C(1)–N(1)–N(2)	104.7(4)	104.8(4)
N(1)–C(1)–C(2)	110.7(4)	109.8(5)
N(1)–C(1)–C(7)	122.3(4)	121.8(6)
C(2)–C(1)–C(7)	127.0(5)	128.4(6)
C(1)–C(2)–C(3)	106.7(4)	107.9(5)
C(2)–C(3)–N(2)	105.9(4)	105.8(5)
C(2)–C(3)–C(8)	131.2(5)	132.0(6)
N(2)–C(3)–C(8)	122.9(4)	122.3(6)
C(3)–N(2)–N(1)	112.1(4)	111.7(4)
C(3)–N(2)–C(4)	129.0(4)	129.2(5)
N(1)–N(2)–C(4)	118.5(4)	118.7(4)
N(2)–C(4)–N(3)	108.6(4)	109.4(4)
C(4)–N(3)–C(5)	110.9(4)	111.0(4)
C(4)–N(3)–C(9)	108.7(4)	108.4(4)
C(4)–N(3)–Cu	103.9(3)	105.1(3)
C(5)–N(3)–C(9)	111.2(4)	111.9(4)
C(5)–N(3)–Cu	107.2(3)	106.7(4)
C(9)–N(3)–Cu	114.8(3)	113.7(4)
N(3)–C(5)–C(5')	109.6(4)	109.1(4)
Cu–N(4)–C(6)	161.9(4)	164.0(4)
N(4)–C(6)–S(1)	178.9(5)	178.7(5)

perature (295 K), at liquid nitrogen temperature (77 K) and at liquid helium temperature (3 K). The compounds Cu(debd)(NCS)$_2$, Zn(debd)(NCS)$_2$ and Cd(debd)(NCS)$_2$ are mutually isomorphous, as has been concluded on basis of the similarities of their IR spectra and their X-ray powder diffraction patterns [10]. It can therefore be concluded that the copper-coordination geometry is essentially the same in the pure compound Cu(debd)(NCS)$_2$ and in the Cu-doped Zn and Cd compounds. The similarities of their X-ray powder diffraction patterns suggest identical crystal packing forces. Furthermore, the spectroscopic properties (ESR) appear to be independent of the Cu-concentration up to 10% Cu-dope and independent of the host lattice (Zn or Cd). Therefore it seems reasonable to relate the data of the structure of Cu(debd)(NCS)$_2$ to the ESR spectra of the Cu-doped compounds. The pure Cu(debd)(NCS)$_2$ only shows one, broad, isotropic resonance centered around $g = 2.15$. Such a single line is quite common in magnetically undiluted compounds, which have their magnetic axes non-parallel. The spectra of the Cu-doped compounds yield more information. The structural change of the coordination octahedron is reflected in the temperature dependence of the ESR spectra (see Fig. 2). The compounds have a rhombic room temperature spectrum with one well-resolved resonance of $g_{\parallel} = 2.26$, $A_{\parallel} = 0.0175$ cm^{-1}. The other two resonances are poorly resolved and have g values of ~2.15 and ~2.05, with A values of *ca.* 0.005 cm^{-1}. The $g_{\parallel}$ remains essentially the same upon going to 77 K. The second g value (2.16) is split due to an increase of the A value to *ca.* 0.008 cm^{-1}, the third g value remains 2.06, with $A \sim 0.005$ cm^{-1}. The g values at 77 K have been confirmed to be 2.26, 2.16 and 2.06 respectively by taking a Q-band spectrum. Finally, upon cooling to 3 K, the $g_{\parallel}$ still remains 2.26, with $A_{\parallel} = 0.0175$ cm^{-1}. The second g value is shifted further upfield, towards *ca.* 2.09, the third g value becomes 2.03. The A values are *ca.* 0.005–0.01 cm^{-1}.

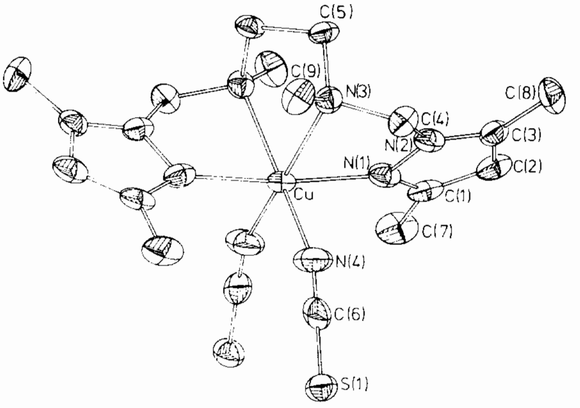

Fig. 1. Structure of the molecule with atomic numbering and 50% probability vibrational ellipsoids. For clarity the hydrogen atoms are omitted.

The temperature dependence is thus most clearly visualised through the centre g and A values, which are probably related to the character and strength of the Cu–N(pyrazole) bond.

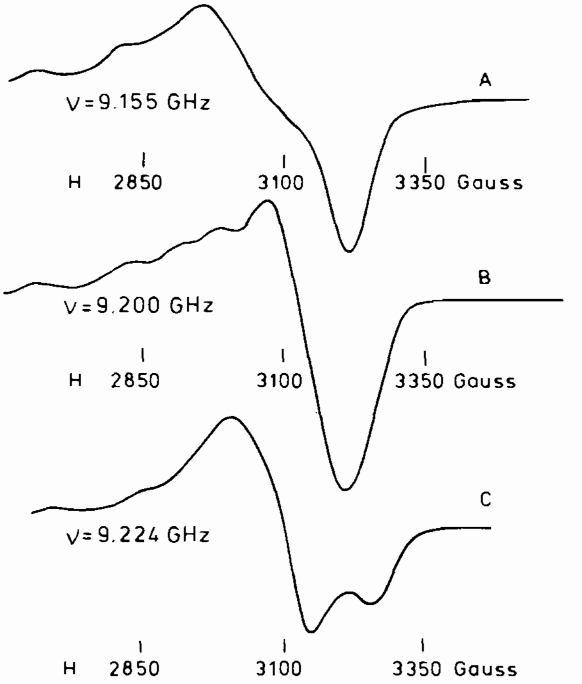

Fig. 2. ESR spectra of 5% Cu^{2+} in Zn(debd)$(NCS)_2$ at ambient temperature (A), 77 K (B) and at 3 K (C).

Conclusions

The structure of the compound Cu(debd)$(NCS)_2$ appears to be a compromise between the steric requirements of the ligand and the electronic demands of the Cu(II) ion, resulting in a temperature dependent structure. The Cu(chelate)$(NCS)_2$ chromophore does not seem to require an asymmetrically distorted structure. The temperature dependence of the structure is also reflected in the ESR spectra of the Cu-doped Zn(debd)$(NCS)_2$ and Cd(debd)$(NCS)_2$ compounds. Furthermore, the ESR data indicate that the structural changes do not stop at 140 K, but are continued to 77 K and, even more pronounced, on going to 3 K.

The debd ligand, although very small, shows that it is possible to impose a structure upon Cu(II) which is not electronically favourable, as shown by the structural change upon temperature variation.

Supplementary Material

The following are available on request from the authors: Table Suppl. 1, *F*(obs.) and *F*(calc.) at 293 K (7 pages); Table Suppl. 2, *F*(obs.) and *F*(calc.) at 140 K (4 pages); Table Suppl. 3, Hydrogen atom parameters (1 page); Table Suppl. 4, Anisotropic temperature factors (1 page).

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