Inorganica Chimica Acta, 206 (1993) 201–208

Rotamers of the 1-phenylethylamine ligand in *trans*-bis(imidato)bis(1-phenylethylamine)copper(II) complexes, where imidato = 3,3-dimethylglutarimidato, hydantoinato and succinimidato ligands

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(Received July 16, 1992; revised December 3, 1992)

Abstract

Three [CuN_4] complexes, red *trans*-[Cu(3,3-dmgluim)$_2$(*R*-phenea)$_2$] (**1**), blue–violet *trans*-[Cu(hyd)$_2$(*R*-phenea)$_2$] (**2**) and blue *trans*-[Cu(succim)$_2$(*S*-phenea) (*R*-phenea)] (**3**) (3,3-dmgluim = 3,3-dimethylglutarimidato, hyd = hydantoinato, succim = succinimidato, phenea = 1-phenylethylamine), were prepared and their crystal structures were determined. Crystal data are as follows: **1** is monoclinic, space group $P2_1$, $a = 14.854(1)$, $b = 17.105(3)$, c-5.988(2) Å, $\beta = 91.65(1)°$, $U = 1520.8(5)$ Å^3, $Z = 2$, $R = 0.033$, and 2318 reflections; **2** is monoclinic, space group $P2_1$, $a = 19.946(2)$, $b = 6.035(1)$, $c = 10.025(1)$ Å, $\beta = 104.383(7)°$, $U = 1168.9(3)$ Å^3, $Z = 2$, $R = 0.035$, and 1864 reflections; **3** is triclinic, space group $P\bar{1}$, $a = 12.434(4)$, $b = 12.670(3)$, $c = 8.765(2)$ Å, $\alpha = 94.83(2)$, $\beta = 112.87(2)$ $\gamma = 73.15(2)°$, $U = 1219.9(6)$ Å^3, $Z = 2$, $R = 0.054$, and 3678 reflections. In **1** the coordination geometry is planar, and the specific intermolecular hydrogen bonds are formed along the *c* axis between H(NH_2) of phenea and O(CO) of the six-membered cyclic imidate. In **2** and **3** the coordination geometries are tetrahedrally distorted. The intramolecular hydrogen bonds are formed between H(NH_2) of phenea and O(CO) of the five-membered cyclic imidate. Three different staggered forms of and one eclipsed form of rotamers in the phenea ligands have been found.

Introduction

The transition metal complexes with various cyclic imidates have been widely studied [1]. The copper(II) imidate complexes with monodentate amine ligands, general formula [Cu(imidato)$_2$(amine)$_2$], are also interesting from the view of the physicochemical aspects [2]. They are red (pink) crystals [3]. Several X-ray structure determinations have been reported on them, and the results showed that all structures had a *trans*-planar 4N coordination [4]. Most of the red crystals are soluble in organic solvents like ethanol, forming deep blue solutions [2, 3]. The color change from red to deep blue has been studied extensively [2c, 3].

As a part of our structural studies of the effect of the asymmetric center on molecular structures [5], we tried to prepare the copper(II) imidate complexes with chiral primary amines and a pair of pink and blue crystals in these systems were obtained as follows: (1) 3,3-dimethylglutarimide and *R*-1-phenylethylamine (phenea) (reddish purple (red) crystals); (2) hydantoin and *R*-phenea (blue–violet crystals); (3) succinimide and racemic phenea (blue crystals) (Scheme 1)**. It is expected that the structure of these complexes will give valuable information about the color change in the solid state. In this paper we wish to report the results of the structure determinations of these three complexes.

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**The following combinations were also tried to obtain the diastereoisomer of copper(II) complexes. (1)′ 3,3-dmgluim and *racemic* phenea, (2)′ hyd and racemic phenea, (3)′ succim and *R*-phenea. (1)′ gave red crystals. *Anal* Found: C, 61.31; H, 7.28; N, 9.68%. Calc. for $C_{30}H_{42}N_4O_4Cu$: C, 61.47; H, 7.22; N, 9.50%. Monoclinic, $P2_1/n$, $a = 14.859(1)$, $b = 17.231(1)$, $c = 5.972(2)$ Å, $\beta = 92.43(1)°$, $V = 1527.2(5)$ Å^3, $Z = 2$, 1923 ref. and $R = 0.071$. Positional disorder was observed for the methyl carbon atom bounded to the carbon atoms of the chiral center of phenea. (2)′ and (3)′ gave only a blue oily product and we could not isolate pure material. [Cu(succim)$_2$(*R*-phenea)$_2$] in solution was very well investigated in ref. 2(c).

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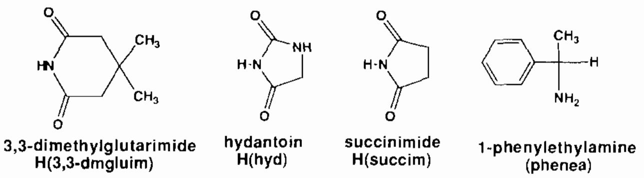

Scheme 1.

Experimental

Preparations

Complexes were prepared following Tschugaeff's method with slight modification [6].

[Cu(3,3-dmgluim)$_2$(R-phenea)$_2$] (1)

To a suspension containing 0.65 g (10 mmol) of copper powder and 3.0 g (21 mmol) of 3,3-dimethylglutarimide in 50 cm^3 of ethanol were added 3.4 g (28 mmol) of *R*-1-phenylethylamine. The mixture was stirred at room temperature for 6 h. The resulting red crystals were collected by filtration and recrystallized from hot ethanol. *Anal.* Found: C, 61.30; H, 7.19; N, 9.50. Calc. for $C_{30}H_{42}N_4O_4Cu$: C, 61.47; H, 7.22; N, 9.56%.

[Cu(hyd)$_2$(R-phenea)$_2$] (2)

To a suspension containing 0.65 g (10 mmol) of copper powder and 2.0 g (20 mmol) of hydantoin in 50 cm^3 of methanol were added 2.4 g (20 mmol) of *R*-1-phenylethylamine. The mixture was stirred at 40 °C for 2 h. The resulting blue–violet crystals were collected by filtration and recrystallized from hot methanol. *Anal.* Found: C, 52.38; H, 5.67; N, 16.44. Calc. for $C_{22}H_{28}N_6O_4Cu$: C, 52.42; H, 5.60; N, 16.67%.

[Cu(succim)$_2$(R-phenea)(S-phenea)] (3)

To a suspension containing 0.65 g (10 mmol) of copper powder and 2.0 g (20 mmol) of succinimide in 50 cm^3 of ethanol were added 2.4 g (20 mmol) of *racemic* 1-phenylethylamine. The mixture was stirred at room temperature for 2 h. The resulting blue crystals were collected by filtration and recrystallized from hot ethanol. *Anal.* Found: C, 57.33; H, 5.91; N, 11.32. Calc. for $C_{24}H_{30}N_4O_4Cu$: C, 57.41; H, 6.02; N, 11.16%.

Measurements

The diffuse reflectance spectra of the complexes **1–3** in the solid state were measured on a Hitachi U-3400 spectrophotometer.

X-ray structure determinations

Crystalls of compound **1–3** were mounted on a glass capillary with a covering of epoxy. The reflection data were collected by the ω–2θ scan technique on a Rigaku AFC-5 automated four-circle diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 1.54184$ Å). The unit cell dimensions were determined by a least-squares method using 25 reflections. Crystal data are summarized in

TABLE 1. Crystal data of compounds **1**, **2** and **3** with experimental conditions

	1	**2**	**3**
Formula	$H_{42}C_{30}N_4O_4Cu$	$H_{28}C_{22}N_6O_4Cu$	$H_{30}C_{24}N_4O_4Cu$
Formula weight	586.24	504.05	502.08
Crystal system	monoclinic	monoclinic	triclinic
Space group and Z	$P2_1$, 2	$P2_1$, 2	$P\bar{1}$, 2
a (Å)	14.854(1)	19.946(2)	12.434(4)
b (Å)	17.105(3)	6.035(1)	12.670(3)
c (Å)	5.988(2)	10.025(1)	8.765(2)
α (°)			94.83(2)
β (°)	91.65(1)	104.383(7)	112.87(2)
γ (°)			73.15(2)
V (Å^3)	1520.8(5)	1168.9(3)	1219.9(6)
D_m and D_x (g cm^{-3})	1.28, 1.28	1.43, 1.42	1.37, 1.36
Scan width (°)	$1.40 + 0.15 \tan\theta$	$1.50 + 0.15 \tan\theta$	$1.50 + 0.15 \tan\theta$
Scan speed (°min^{-1})	4.0	6.0	4.0
$2\theta_{max}$ (°)	120	120	125
Range of h, k and l	$-17 < h < 17$	$-22 < h < 22$	$-14 < h < 14$
	$0 < k < 19$	$0 < k < 7$	$-15 < k < 15$
	$0 < l < 7$	$0 < l < 11$	$0 < l < 10$
Observed reflections	2689	2125	4417
No. unique reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2318	1864	3678
No. variables	521	411	419
Final R	0.033	0.035	0.054
Final R_w	0.047	0.052	0.079

$R = \Sigma(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma\lvert F_o\rvert$, $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$ with $w = [\sigma c^2 + (0.015\lvert F_o\rvert)^2]^{-1}$.

TABLE 2. Fractional positional parameters ($\times 10^4$) for the non-hydrogen atoms of [Cu(3,3-dmgluim)$_2$(*R*-phenea)$_2$] (**1**), [Cu(hyd)$_2$(*R*-phenea)$_2$] (**2**) and [Cu(succim)$_2$(*R*-phenea)*S*-phenea)] (**3**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
1			
Cu	2532(0)	0(1)	2241(1)
N(G)A	1223(2)	231(2)	2030(5)
N(G)B	3815(2)	−296(2)	2478(5)
N(P)A	2279(2)	−792(2)	4746(6)
N(P)B	2731(2)	703(2)	−519(5)
O(GA)1	1463(2)	879(2)	5227(6)
O(GA)2	970(2)	−446(2)	−1131(6)
O(GB)1	3558(2)	−948(2)	−706(5)
O(GB)2	4078(2)	361(2)	5682(5)
C(GA)1	938(3)	706(2)	3660(7)
C(GA)2	−1(3)	1037(3)	3586(8)
C(GA)3	−682(3)	537(3)	2247(8)
C(GA)4	−225(3)	334(3)	45(8)
C(GA)5	685(2)	−1(3)	261(6)
C(GA)6	−883(3)	−215(3)	3540(10)
C(GA)7	−1545(4)	994(4)	1798(12)
C(GB)1	4072(3)	−807(2)	875(7)
C(GB)2	4971(3)	−1223(3)	1100(8)
C(GB)3	5666(3)	−780(3)	2521(8)
C(GB)4	5232(3)	−536(3)	4653(8)
C(GB)5	4335(3)	−113(2)	4321(6)
C(GB)6	5999(3)	−57(4)	1270(9)
C(GB)7	6476(4)	−1323(4)	3080(12)
C(PA)1	1992(3)	−1569(2)	3861(7)
C(PA)2	2762(3)	−2140(2)	3689(7)
C(PA)3	2870(4)	−2568(3)	1757(8)
C(PA)4	3534(4)	−3129(3)	1622(10)
C(PA)5	4109(4)	−3274(3)	3387(10)
C(PA)6	4021(4)	−2850(3)	5323(10)
C(PA)7	3353(3)	−2281(3)	5489(8)
C(PA)8	1247(3)	−1909(3)	5252(10)
C(PB)1	3000(3)	1538(3)	−435(8)
C(PB)2	2248(3)	2063(2)	346(7)
C(PB)3	2238(4)	2418(3)	2417(8)
C(PB)4	1563(5)	2936(3)	2964(10)
C(PB)5	884(4)	3094(3)	1478(11)
C(PB)6	869(4)	2729(4)	−561(10)
C(PB)7	1547(3)	2227(3)	−1135(8)
C(PB)8	3882(3)	1618(3)	944(12)
2			
Cu	2595(0)	0(2)	594(1)
N(HA)1	2327(2)	1364(7)	2216(3)
N(HA)2	2156(2)	1664(7)	4341(3)
N(HB)1	2790(2)	−1771(8)	−990(3)
N(HB)2	2928(2)	−2634(9)	−3085(4)
N(P)A	3517(2)	−992(9)	1799(4)
N(P)B	1776(2)	1451(8)	−674(3)
O(HA)1	1811(2)	4664(8)	1302(3)
O(HA)2	2756(1)	−1342(6)	3871(3)
O(HB)1	3226(3)	−4996(10)	172(4)
O(HB)2	2432(2)	673(6)	−2806(3)
C(HA)1	1997(2)	3358(9)	2236(4)
C(HA)2	1865(2)	3677(10)	3655(4)
C(HA)3	2437(2)	418(9)	3513(4)
C(HB)1	3069(3)	−3864(10)	−886(5)
C(HB)2	3210(3)	−4517(10)	−2237(6)
C(HB)3	2688(2)	−1117(9)	−2335(4)
C(PA)1	4143(3)	385(10)	1875(5)
C(PA)2	4786(2)	−633(9)	2803(5)
C(PA)3	5000(3)	−2770(10)	2535(5)
C(PA)4	5614(3)	−3593(13)	3326(8)
C(PA)5	6015(3)	−2450(18)	4368(7)
C(PA)6	5815(3)	−356(18)	4663(6)
C(PA)7	5194(3)	547(12)	3870(5)
C(PA)8	4251(3)	768(12)	456(6)
C(PB)1	1068(2)	484(10)	−892(4)
C(PB)2	526(2)	1819(8)	−1884(5)
C(PB)3	656(2)	2793(10)	−3054(5)
C(PB)4	148(3)	3904(10)	−3986(6)
C(PB)5	−513(3)	4092(11)	−3743(6)
C(PB)6	−645(2)	3180(12)	−2609(6)
C(PB)7	−134(2)	2051(10)	−1662(5)
C(PB)8	1057(3)	−1914(11)	−1386(7)
3			
Cu	3132(0)	1972(0)	1653(0)
N(S)A	1537(2)	1882(2)	−20(3)
N(S)B	4737(2)	1337(2)	3401(3)
N(P)A	3806(2)	2100(2)	−28(3)
N(P)B	2397(2)	2702(2)	3300(3)
O(SA)1	1090(2)	1058(2)	1808(3)
O(SA)2	1341(3)	2683(3)	−2404(3)
O(SB)1	5207(3)	−175(2)	1926(4)
O(SB)2	4869(2)	2599(2)	5458(3)
C(SA)1	825(3)	1421(2)	425(4)
C(SA)2	−349(3)	1434(3)	−1038(5)
C(SA)3	−280(4)	1999(4)	−2401(5)
C(SA)4	961(3)	2221(3)	−1656(4)
C(SB)1	5502(3)	387(3)	3139(5)
C(SB)2	6750(3)	148(3)	4523(5)
C(SB)3	6619(3)	1059(4)	5710(5)
C(SB)4	5323(3)	1762(3)	4879(4)
C(PA)1	4419(3)	2998(3)	301(4)
C(PA)2	5789(3)	2574(2)	1180(4)
C(PA)3	6482(3)	1657(3)	672(5)
C(PA)4	7744(4)	1361(3)	1439(6)
C(PA)5	8321(4)	1976(4)	2721(6)
C(PA)6	7643(4)	2873(4)	3216(5)
C(PA)7	6368(4)	3185(3)	2466(5)
C(PA)8	4086(4)	3625(3)	−1305(5)
C(PB)1	1462(3)	3780(2)	2712(4)
C(PB)2	2019(3)	4571(2)	2276(4)
C(PB)3	2924(3)	4959(3)	3471(5)
C(PB)4	3404(4)	5690(3)	3050(7)
C(PB)5	2967(4)	6040(3)	1402(7)
C(PB)6	2096(4)	5655(3)	226(6)
C(PB)7	1620(3)	4900(3)	645(5)
C(PB)8	898(4)	4249(3)	3991(5)

Table 1. Three standard reflections were recorded at regular intervals and they showed no significant decay throughout the data collection. The measurement intensities were corrected for Lorentz and polarization factors and for absorption.

All the structures were solved by direct methods. The remaining non-hydrogen atoms were found in

TABLE 3. Atomic deviations from the CuN_4 least-squares coordination planes

Atom	Deviation from P(1) (Å)	Atom	Deviation from P(2) (Å)	Atom	Deviation from P(3) (Å)
Cu	0.019	Cu	−0.001	Cu	−0.002
N(G)A	−0.018	N(HA)1	−0.132	N(S)A	−0.473
N(G)B	−0.022	N(HB)1	−0.160	N(S)B	−0.453
N(P)A	−0.090	N(P)A	0.199	N(P)A	0.562
N(P)B	−0.095	N(P)B	0.160	N(P)B	0.502

succeeding difference Fourier syntheses. Structures were refined by the block-diagonal least-squares procedure where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with $w=[\sigma c^2+(0.015|F_o|)^2]^{-1}$; σc is the standard deviation obtained from the counting statistics for each reflection. Hydrogen atoms were placed in calculated positions and were included in structure factor calculations in further refinement cycles. The details of the refinements with the final R and R_w values are also given in Table 1. The atomic scattering factors were taken from International Tables for X-ray Crystallography [7]. All the computations were carried out on a HITAC M680 computer at the Computer Center of the Institute for Molecular Science. The computer programs used were UNICS-III [8], MULTAN [9] and ORTEP [10].

The final atomic parameters for the non-hydrogen atoms for **1**–**3** are given in Table 2. The selected bond lengths and angles are given in the captions of Fig. 2 and deviations of atoms from the planes are listed in Table 3. See also 'Supplementary material'.

Results and discussion

UV–Vis spectra

The reflectance UV–Vis spectra of **1**–**3** are shown in Fig. 1. The reflectance spectrum of **1** shows a similar splitting pattern to that of the reported red complexes [2a]. The reflectance spectra of **2** and **3** differ from that of **1** and from other typical red complexes [2a]. The present X-ray structure analyses reveal that the CuN_4 coordination geometry around the copper atom in **1** (N–Cu–N(3,3-dmgluim) 176.6(2)° and N–Cu–N(phenea) 173.7(1)°) is nearly planar. In contrast, those in **2** and **3** are tetrahedrally distorted: in **2** (N–Cu–N(hyd) 171.8(2)° and N–Cu–N(phenea) 169.7(2)°) and in **3** (N–Cu–N(succim) 153.0(1)° and N–Cu–N(phenea) 149.1(1)°). Therefore, the blue–violet color of **2** and the blue color of **3** in solid state are attributable to the distortion around the copper atom*.

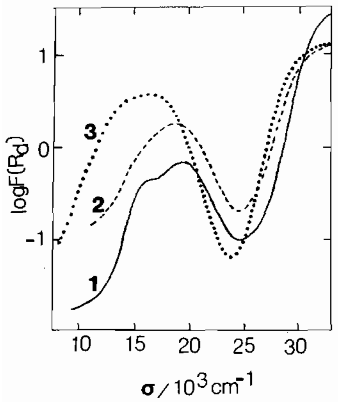

Fig. 1. The reflectance UV–Vis spectra of **1**–**3**. 1, $[Cu(3,3\text{-dmgluim})_2(R\text{-phenea})_2]$ (**1**) (——); 2, $[Cu(hyd)_2(R\text{-phenea})_2]$ (**2**) (– – –); 3, $[Cu(succim)_2(R\text{-phenea})(S\text{-phenea})]$ (**3**) (· · · · ·).

Description of the total coordination mode

The ORTEP diagrams of the molecular structures of **1**–**3** are shown in Fig. 2(a)–2(c). In all complexes, two phenea coordinate to the copper atom in *trans* position. In **1** and **2**, the absolute configuration of the coordinated phenea, *R*-form which was determined by the anomalous dispersion, was the same as that of the starting phenea molecule. The racemization reaction of phenea did not occur. It has been reported that imidate anion can coordinate to the metal ion in various fashions: as N-monodentate [4], N,O-chelate [11], N,O-bridge [1a, 1c, 12] and O-monodentate [13]. In the present system, the imidate anions coordinate to the copper atom only through their nitrogen atoms. The shortest distance in complexes **1**–**3** between the copper atoms and carbonyl oxygen atoms of the corresponding imidate groups is 2.854(4) (for **1**), 3.321(3) (for **2**) and 3.110(5) (for **3**) Å. Therefore, all complexes have a CuN_4 type coordination.

Molecular structure of [Cu(3,3-dmgluim)₂(R-phenea)₂] (1)

As shown in Table 3, the coordination geometry around the copper atom is almost planar, though dis-

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*The electronic absorption spectra in chloroform of typical $[Cu(succim)_2(amine)_2]$ complexes are reported in refs. 2(a) and 3, $\nu_{max}=15.0\times10^3$–16.3×10^3 cm^{-1} (0.002 M). Thus, the maxima of the reflectance spectrum of **3** are relatively close to the reported spectra in solution state in refs. 2(a) and 3.

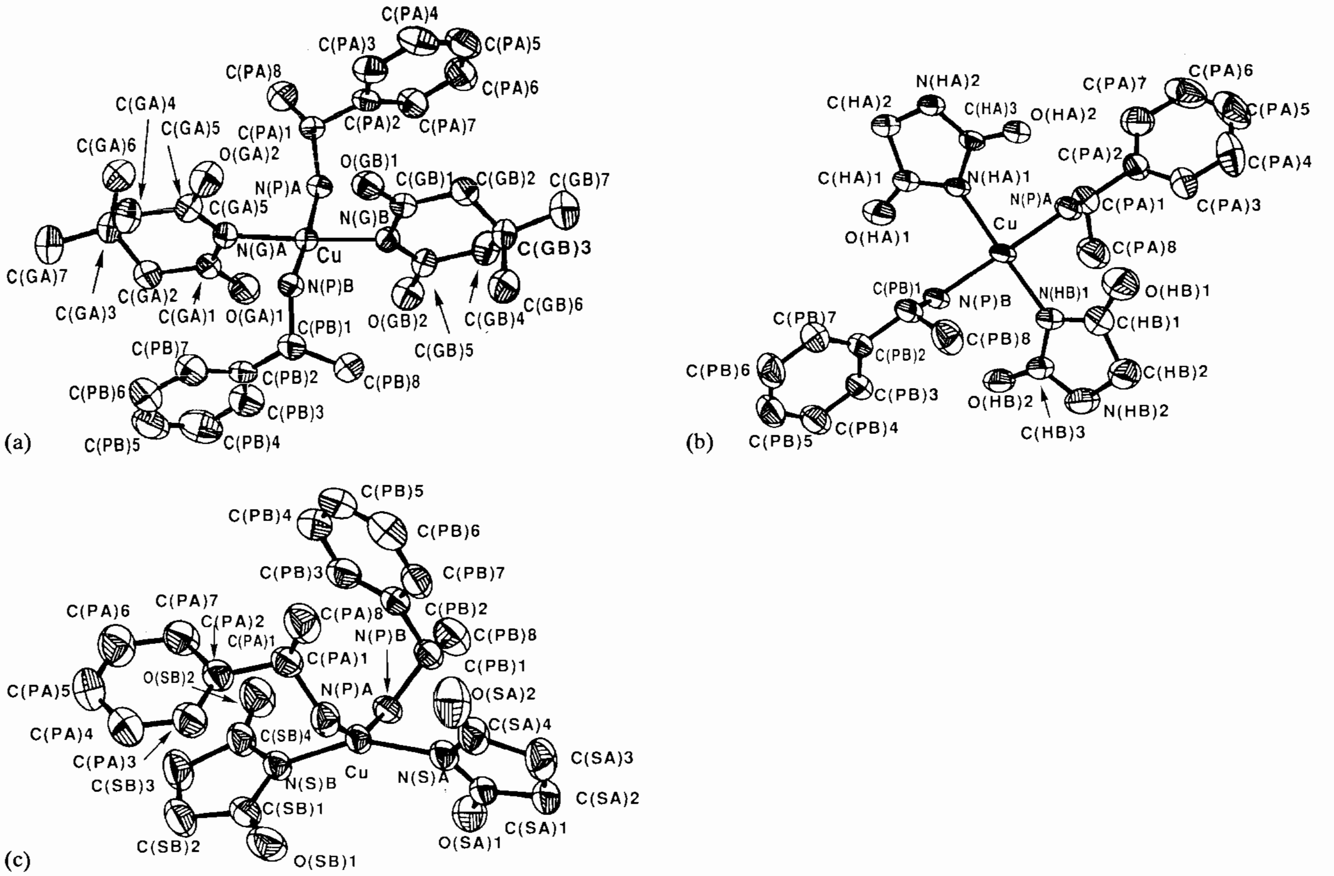

Fig. 2. (a) An ORTEP drawing of the molecular structure of [Cu(3,3-dmgluim)$_2$(*R*-phenea)$_2$] (**1**). Selected bond distances (Å) and angles (°) are as follows: Cu–N(G)A 1.985(3), Cu–N(G)B 1.973(4), Cu–N(P)A 2.064(3), Cu–N(P)B 2.072(4), N(G)A–Cu–N(G)B 176.6(2), N(G)A–Cu–N(P)A 88.8(1), N(G)A–Cu–N(P)B 89.8(1), N(G)B–Cu–N(P)A 88.6(1), N(G)B–Cu–N(P)B 92.7(1), N(P)A–Cu–N(P)B 173.7(1). (b) An ORTEP drawing of the molecular structure of [Cu(hyd)$_2$(*R*-phenea)$_2$] (**2**). Selected bond distances (Å) and angles (°) are as follows: Cu–N(HA)1 2.009(5), Cu–N(HB)1 2.031(5), Cu–N(P)A 2.025(5), Cu–N(P)B 2.005(5), N(HA)1–Cu–N(HB)1 171.8(2), N(HA)1–Cu–N(P)A 91.3(2), N(HA)1–Cu–N(P)B 89.8(2), N(HB)1–Cu–N(P)A 89.3(2), N(HB)1–Cu–N(P)B 91.1(2), N(P)A–Cu–N(P)B 169.7(2). (c) An ORTEP drawing of the molecular structure of [Cu(succim)$_2$(*R*-phenea) (*S*-phenea)] (**3**). Selected bond distances (Å) and angles (°) are as follows: Cu–N(S)A 1.984(3), Cu–N(S)B 1.970(3), Cu–N(P)A 1.995(3), Cu–N(P)B 2.021(3), N(S)A–Cu–N(S)B 153.0(1), N(S)A–Cu–N(P)A 94.3(1), N(S)A–Cu–N(P)B 92.7(1), N(S)B–Cu–N(P)A 94.3(1), N(S)B–Cu–N(P)B 92.9(1), N(P)A–Cu–N(P)B 149.1(1).

torted slightly from the planar to the pyramidal fashion. The copper atom is about 0.08 Å up from the N_4 mean plane. The bond angles of N(G)A–Cu–N(G)B and N(P)A–Cu–N(P)B are 176.6(2) and 173.7(1)°, respectively. The dihedral angle between the two 3,3-dmgluim C–N–C planes is 8°. All the non-hydrogen atoms in 3,3-dmgluim, except the quaternary carbon and the two methyl groups, are nearly coplanar. The dihedral angles between the CuN_4 least-squares mean plane and the C–N–C planes of 3,3-dmgluim are 72 and 73°, respectively. The intramolecular H(NH_2)...O(CO) hydrogen bonds are listed in Table 4.

Molecular structure of [Cu(hyd)$_2$(R-phenea)$_2$] (2)

As shown in Table 3, the coordination geometry around the copper atom is distorted from the planar to the flattened tetrahedral. The bond angles of N(P)A–Cu–N(P)B and N(HA)1–Cu–N(HB)1 are 169.7(2) and 171.8(2)°, respectively. The dihedral angles between the CuN_4 least-squares mean plane and the hyd C–N(Cu)–C planes are 36 and 37°, respectively, and those values are quite different from the reported value 49° in [Cu(5,5-diphenylhydantoinate)$_2$(ammine)$_2$] [4c]. The dihedral angle between two hyd C–N(Cu)–C planes is only 6°. Four intramolecular hydrogen bonds between the phenea NH_2 and carbonyl oxygen atoms of hyd are formed and their values are listed in Table 4.

Molecular structure of [Cu(succim)$_2$(R-phenea)(S-phenea)] (3)

In **3** the copper atom is located on the general position of space group $P\bar{1}$. In this complex, *R*- and *S*-phenea coordinate to one copper atom. As shown

TABLE 4. Possible intramolecular hydrogen bondings

D–H...A	D...A (Å)	D–H...A (°)
Complex **1**		
N(P)A–H(NPA)2...O(GA)2	3.122(5)	113(3)
N(P)A–H(NPA)1...O(GB)1	3.356(5)	109(3)
N(P)B–H(NPB)2...O(GA)1	3.284(5)	117(3)
N(P)B–H(NPB)1...O(GB)2	3.082(5)	113(3)
Complex **2**		
N(P)A–H(NPA)2...O(HA)2	2.869(5)	138(3)
N(P)A–H(NPA)1...O(HB)1	2.892(7)	139(3)
N(P)B–H(NPB)2...O(HA)1	2.761(6)	140(3)
N(P)B–H(NPB)1...O(HB)2	2.809(5)	146(3)
Complex **3**		
N(P)A–H(NPA)1...O(SA)2	2.875(4)	145(3)
N(P)A–H(NPA)2...O(SB)1	3.143(4)	124(3)
N(P)B–H(NPB)2...O(SA)1	2.922(4)	123(3)
N(P)B–H(NPB)1...O(SB)2	2.887(4)	143(3)

in Table 3, the coordination geometry around the copper atom is flattened tetrahedral. The bond angles of N(P)A–Cu–N(P)B and N(S)A–Cu–N(S)B are 149.1(1) and 153.0(1)°, respectively. In **3** the distortion around the copper atom is larger than that in **2**. The dihedral angles between the CuN_4 least-squares mean plane and the C–N–C planes of succim are 40 and 45°, respectively. The dihedral angle between two succim planes is 84°*. Intramolecular hydrogen bonds formed between the phenea NH_2 and carbonyl oxygen atoms of succim are listed in Table 4.

Description of the crystal structures

The intermolecular hydrogen bondings or cation–anion interactions are effective on the geometries of some monodentate copper(II) complexes in the crystalline state [14, 15]. For example in $[CuCl_4]^{2-}$, whose geometries vary from square-planar to tetrahedral, hydrogen bonding plays a critical role in determining the molecular geometries [14].

The crystal packings of **1**–**3** are shown in Fig. 3(a)–(c). The intermolecular hydrogen bondings of **1**–**3** are summarized in Table 5.

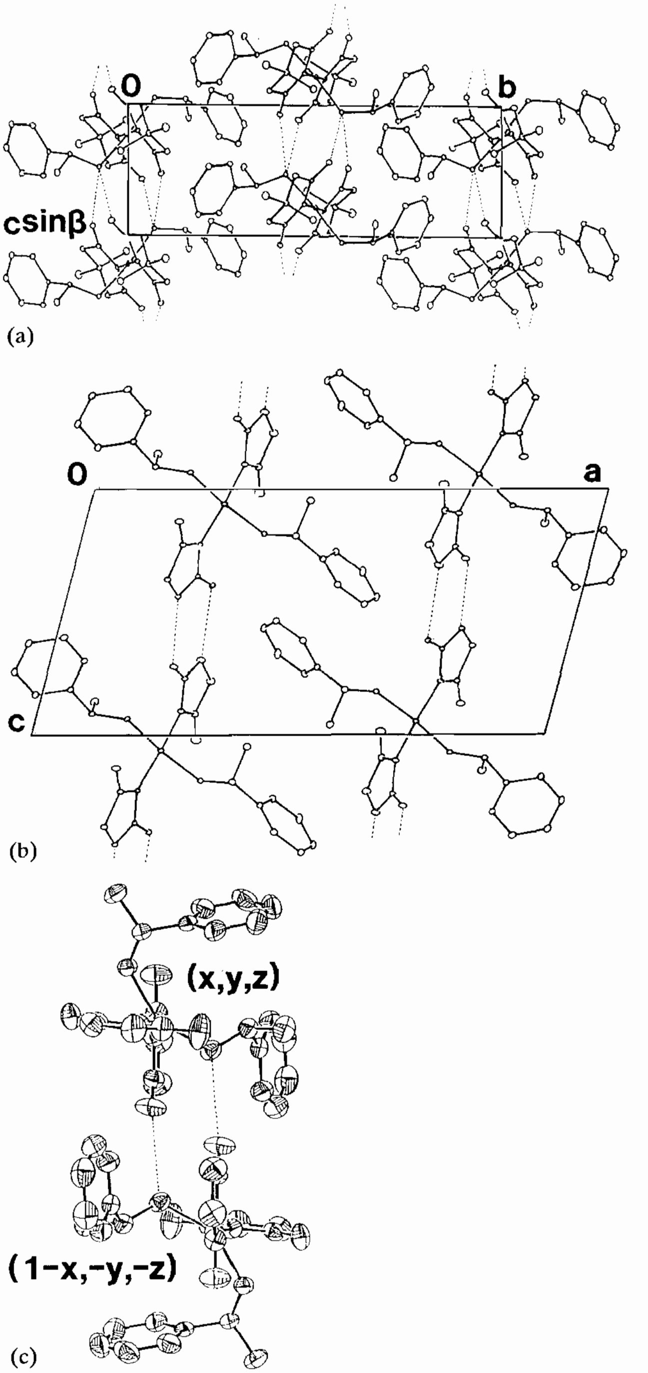

Fig. 3. Crystal structure of (a) $[Cu(3,3\text{-dmgluim})_2(R\text{-phenea})_2]$ (**1**) projected down the *a* axis; (b) $[Cu(hyd)_2(R\text{-phenea})_2]$ (**2**) projected down the *b* axis. (c) An ORTEP drawing of the hydrogen bonding unit of $[Cu(succim)_2(R\text{-phenea})(S\text{-phenea})]$ (*3*).

In **1** the specific intermolecular hydrogen bonds are formed between the molecules, whose symmetry relations are (*x*, *y*, *z*) and (*x*, *y*, 1+*z*) as shown in Fig. 3(a). These hydrogen bonds lead to the columnar packing along the *c* direction, and confine the axial positions of the copper atom in that column. Similar hydrogen bonding patterns are found in red *trans*-$[Cu(succim)_2(amine)_2]$ (amine = NH_3 and n-$PrNH_2$) [4a, b]. The planar geometries of the molecule **1** and other various red *trans*-$[Cu(imidate)_2(amine)_2]$ complexes may be stabilized effectively by the formation of those columnar structures. The contacts between these columns are of van der Waals character. The hydrogen bondings play a decisive role in determining the high degree of dihedral angles between the CuN_4 and the imidate planes of **1** (72 and 73°). In red *trans*-$[Cu(succim)_2$-

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*It may be pointed out that the almost perpendicular arrangement of two imidate groups in *trans* position can cause a 'propeller' chirality. The molecule **3** has such a pseudo 'propeller' chirality. The space group, however, indicates that enantiomeric pairs are present.

TABLE 5. Possible intermolecular hydrogen bondings

D–H...A (symmetry code)	D...A (Å)	D–H...A (°)
Complex **1**		
N(P)A–H(NPA)2...O(GA)2 (x, y, $z+1$)	3.241(5)	154(3)
N(P)A–H(NPA)1...O(GB)1 (x, y, $z+1$)	3.286(5)	154(3)
N(P)B–H(NPB)2...O(GA)1 (x, y, $x-1$)	3.139(5)	148(3)
N(P)B–H(NPB)1...O(GB)2 (x, y, $z-1$)	3.128(5)	154(3)
Complex **2**		
N(HA)2–H(NHA2)...O(HB)2 (x, y, $z+1$)	2.839(5)	154(3)
N(HB)2–H(NHB2)...O(HA)2 (x, y, $x-1$)	3.085(5)	163(3)
Complex **3**		
N(P)A–H(NPA)2...O(SB)1 ($1-x$, $-y$, $-z$)	3.064(5)	139(3)

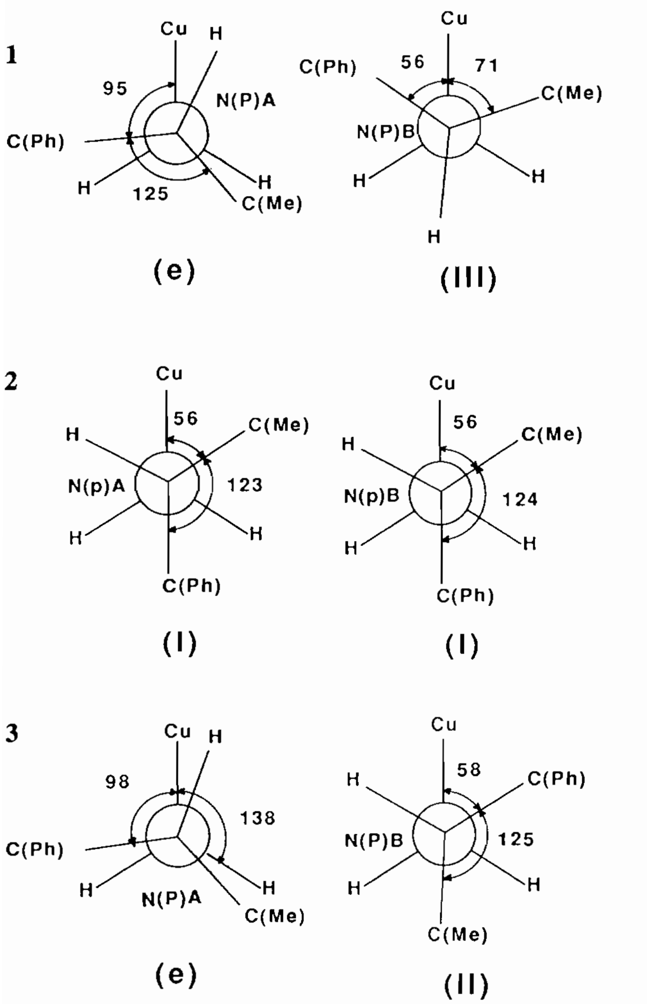

Fig. 4. The rotamers around N–C(chiral center) of phenea: (I) staggered-(I), (II) staggered-(II), (III) staggered-(III), (e) eclipsed form.

(amine)$_2$] (amine = NH_3 and n-$PrNH_2$), the corresponding dihedral angle is 73 and 83°, respectively [4a,b]. In **2**, as shown in Fig. 3(b), there are intermolecular hydrogen bonds between HN(hyd), namely H(NHA2) or H(NHB2), and adjacent carbonyl oxygen atoms. These hydrogen bondings have been found in [Cu(5,5-diphenylhydantoinate)$_2$(ammine)$_2$] [4c]. They probably prevent the complexes from building the columnar hydrogen bonds. In **3** between the hydrogen atoms of phenea NH_2 and the oxygen atom of the imidate carbonyl group belonging to the symmetry element ($1-x$, $-y$, $-z$), there are only two intermolecular hydrogen bonds. The small number of intermolecular hydrogen bonds suggests that the structure of **3** is affected not so strongly by 'packing effects'.

The conformational isomerism of phenea groups

The remarkable feature of the molecular structures of **1**–**3** is the presence of various rotamers of phenea. Newman projections around the N–C(chiral center) bonds in phenea of **1**–**3** are shown in Fig. 4. Three possible types of the staggered form appear: staggered-(I) for **2**, staggered-(II) for **3** and staggered-(III) for **1** [6a]. Staggered-(I) is of the opened form [5, 16], (II) and (III) are so-called closed forms [5, 16]. The eclipsed forms appear in **1** and **3**. Each eclipsed form also corresponds to the closed form. The Cu–N bond lengths suggest that the stability of the observed eclipsed forms in **1** and in **3** are quite comparable to those of the staggered forms. (Cu–N(P)A 2.064(3) versus Cu–N(P)B 2.072(4) Å for **1**, Cu–N(P)A 1.995(3) versus Cu–N(P)B 2.021(3) Å for 3).

In **1** the phenyl groups and imidate groups are close to each other. The phenyl and the imidate planes are almost parallel. These arrangements of the ligands may be attributable to the affinities between the quasi-aromatic character of the O–C–N–C–O moiety in 3,3-dmgluim and the aromatic character of the phenyl group of phenea. In **2** each phenyl group is inclined towards the outside of the CuN_4 mean plane. As mentioned in the crystal structure, HN(hyd)...O(CO) intermolecular hydrogen bonds are formed, and they possibly prohibit the phenyl group to incline inside onto the CuN_4 mean plane. In **3** two phenea groups are on the same side of the CuN_4 mean plane as shown in Fig. 4. One phenyl plane (PA group) is nearly parallel to one succim plane (SB group) and an aromatic...quasi-aromatic interaction is suggested.

Supplementary material

Tables of the positions of hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles (Table 6), the CuN_4 least-squares plane's parameters (Table 7) and observed and calculated structure factor amplitudes (69 pages) are available from the authors on request.

Acknowledgement

The present study was partly supported by Grant-in-Aid for Scientific Research No. 03640534 from the Ministry of Education, Science and Culture.

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