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Crystal and Molecular Structure of μ-Propane-1,3-diamine Di[bis(propane-1,3-diamine)copper(II)] perchlorate Complex

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Abstract

The title compound, $[Cu_2(1,3\text{-pn})_5](ClO_4)_4$, crystallizes in the orthorhombic space group *Pbca* with $Z = 8$ formula units in a cell of dimensions: $a = 30.882(9)$, $b = 14.664(6)$, $c = 15.737(6)$ Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to $R = 0.082$ for 3156 counter data. It consists of discrete dinuclear $[Cu_2(1,3\text{-pn})_5]^{4+}$ cations and ClO_4^- anions. In the dinuclear cation two propane diamine molecules act as chelating to each copper atom in the basal plane; the fifth amine molecule in an extended form, with its nitrogen atoms located at the apices of two square-pyramides, bridges two copper atoms. Magnetic and spectroscopic data are also discussed.

Introduction

It is known that copper(II) ion and propane-1,3-diamine (hereafter abbreviated as 1,3-pn) form complexes with metal to ligand molar ratios of 1:2, the amine invariably acting as a chelating agent [1, 2].

On the other hand the less favourable entropy change in the formation of six-membered rings with respect to five-membered rings [3–6] suggests for propane-1,3-diamine the possibility of another kind of coordinative behavior.

In the framework of a systematic investigation on the coordinative abilities of propane-1,3-diamine, we report in this paper the synthesis and characterization by means of structural, spectroscopic and magnetic measurements of a compound having the unusual empirical formula, $Cu(1,3\text{-pn})_{2.5}(ClO_4)_2$.

Experimental

Preparation of the $Cu(1,3\text{-pn})_{2.5}(ClO_4)_2$ Complex

By mixing a methanolic solution containing the copper(II) salt and the amine in a metal to ligand molar ratio of 1:3, a crystalline blue compound was separated. *Anal.* Found: C, 20.22; H, 5.72; N, 5.59; Calcd. for $C_{7.5}H_{25}N_5O_8CuCl_2$: C, 20.10; H, 5.68; N, 5.60%.

Physical Measurements

The room temperature magnetic moment was measured by the Gouy method using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal Constants. The electronic reflectance spectrum of the solid compound was recorded at room temperature with a Varian 2300 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 180 Instrument as Nujol mull (partial decomposition of the compound was observed on mulling with KBr) in the 300–4000 cm^{-1} spectral range and as polythene pellets in the 100–500 cm^{-1} range. Nitrogen, carbon and hydrogen were analysed with a Carlo Erba Analyser Instrument Mod. 1106.

X-Ray Structure Determination

The unit cell dimensions were obtained by refining by least-squares methods the 2θ values of 15 high-angle reflections accurately measured on an on-line single-crystal automated Siemens AED diffractometer. Three-dimensional intensity data were collected at room temperature with a selected crystal mounted in a random orientation on the same diffractometer. Details specific of the X-ray data collection and processing are reported in Table I. The data were corrected for Lorentz and polarization effects, but not for absorption in view of the small absorption coefficient.

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TABLE I. Crystal Data.

molecular formula	$C_{15}H_{50}Cu_2Cl_4N_{10}O_{16}$
mol wt	895.5
a, Å	30.882(9)
b, Å	14.664(6)
c, Å	15.737(6)
V, Å^3	7127(4)
Z	8
d_{obs}, gcm^{-3}	1.69
d_{calc}, gcm^{-3}	1.67
crystal system	orthorhombic
space group	*Pbca*
crystal dimens., mm	0.45 × 0.49 × 0.67
radiation ($\bar{\lambda}$, Å)	Mo-K$_\alpha$ ($\bar{\lambda}$ = 0.71069)
2θ limits, deg.	3–25
temp., °C	20 ± 2
abs. coeff., cm^{-1}	15.0
F(000), electrons	3712
reflections collected	6954
unique data used (I) > 2σ(I)	3156
No of variables	384
R	0.082
R_w	0.085
scan type	ω–2θ
lowest speed (°min^{-1})	2.5
Max. scan width (°)	1.20
standards	1 every 50 reflections (no changes)

TABLE II. Fractional Atomic Coordinates × 10^4.

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Cu1	3216(1)	5678(1)	7242(1)	C13	14(6)	6808(14)	6172(13)
Cu2	601(1)	5994(1)	7555(1)	C14	300(7)	6521(16)	5538(14)
N1	3187(4)	4722(10)	8192(9)	C15	505(7)	5639(17)	5689(14)
N2	3620(4)	6434(9)	8014(9)	Cl1	601(1)	2179(3)	1216(3)
N3	3011(4)	4688(10)	6431(9)	Cl2	3078(1)	6100(3)	2278(3)
N4	3413(4)	6452(9)	6245(9)	Cl3	645(1)	5494(3)	2191(3)
N5	2556(4)	6304(8)	7375(7)	Cl4	1605(2)	7600(4)	388(3)
N6	1166(4)	6910(9)	7879(8)	O1	181(4)	1841(10)	1334(8)
N7	701(5)	4679(10)	7942(9)	O2	602(5)	2806(11)	567(11)
N8	306(5)	6228(10)	8683(9)	O3	879(5)	1479(12)	1029(10)
N9	209(6)	6975(10)	7014(10)	O4	726(6)	2539(14)	1975(12)
N10	826(5)	5669(10)	6366(8)	O5	3293(4)	5429(10)	1826(9)
C1	3173(7)	5052(16)	9062(12)	O6	2900(4)	6719(10)	1704(8)
C2	3555(8)	5569(15)	9330(13)	O7	2749(4)	5716(9)	2771(8)
C3	3596(7)	6508(16)	8897(14)	O8	3351(4)	6564(10)	2851(8)
C4	2788(6)	4931(14)	5619(11)	O9	317(5)	5932(10)	1710(9)
C5	3081(7)	5518(17)	5053(11)	O10	835(6)	6112(12)	2752(10)
C6	3168(7)	6462(16)	5411(13)	O11	958(5)	5142(10)	1612(9)
C7	2402(4)	6794(10)	8137(10)	O12	459(6)	4796(14)	2650(12)
C8	1967(4)	7215(10)	8019(9)	O13	1353(4)	7989(9)	–262(8)
C9	1596(4)	6530(9)	7965(10)	O14	1610(6)	6685(14)	24(12)

(continued on facing page)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C10	832(7)	4481(13)	8835(13)	O15	1385(6)	7304(13)	1071(11)
C11	554(6)	4850(15)	9450(11)	O16	2041(7)	7694(16)	325(15)
C12	539(6)	5881(14)	9460(11)				

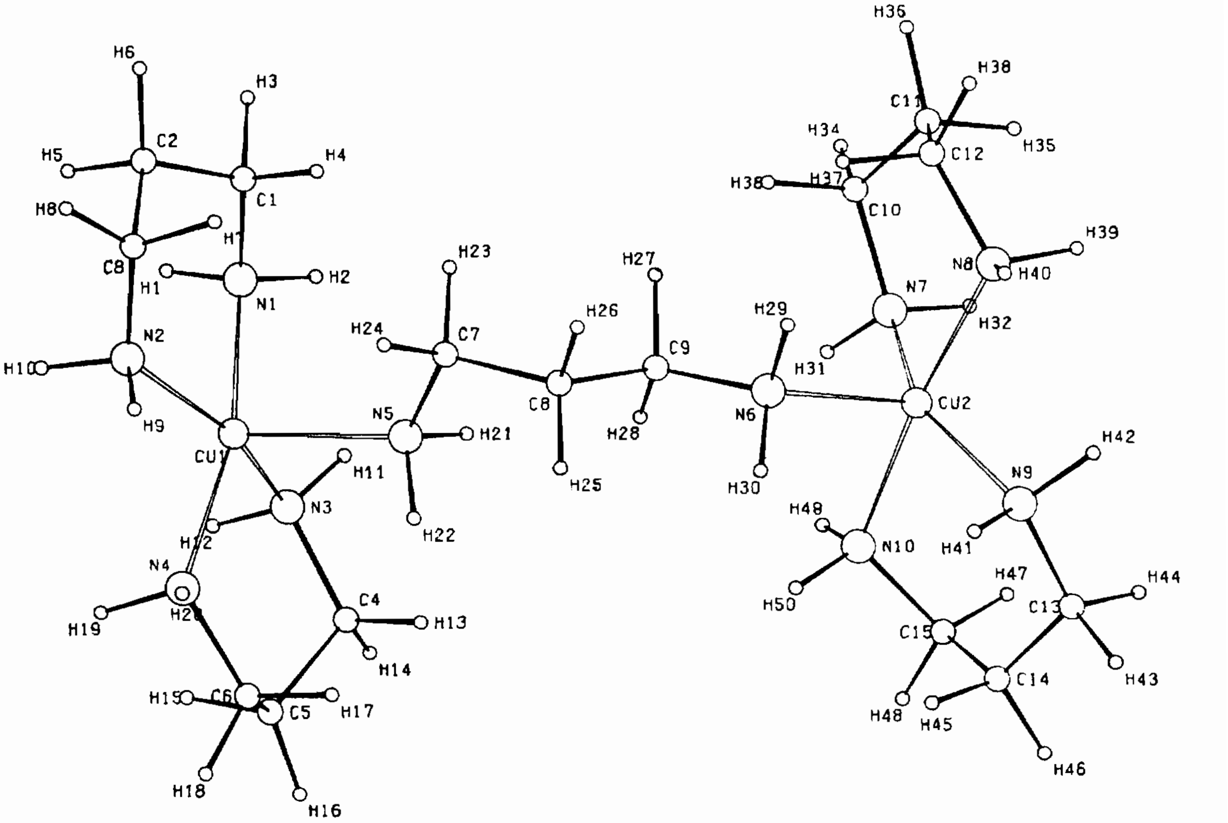

Fig. 1. Projection of the molecule along the *b* axis.

The structure was solved by localizing the copper atoms by Patterson and direct methods; the successive Fourier maps gave the positions of all non-hydrogen atoms. Refinement was by full-matrix least-squares with $w(|F_o| - |F_c|)^2$ being minimized with isotropic and anisotropic thermal parameters; the introduction of the hydrogen atoms as fixed contributors at the calculated positions led to convergence to $R = 0.082$ and $R_w = 0.085$. During the final refinement zero weight was assigned to 37 reflections, which may be affected by extinction or counting errors. The final atomic coordinates are quoted in Table II. The scattering factors were taken from International Tables [7]. Calculations were performed with the use of the CYBER 76 of the Centro di Calcolo dell'Italia Nord Orientale, Bologna, with the SHELX system of programs [8], and financial support from the University of Parma.

Results and Discussion

Description of the Structure

The structure consists of ClO_4^- anions and dinuclear complex $[Cu_2(1,3\text{-pn})_5]^{4+}$ cations in which each copper atom shows a square-pyramidal coordination (Fig. 1): two propane-1,3-diamine molecules act as chelating agents to each metal with their donor atoms in the basal plane; the fifth amine molecule in an extended form, with its nitrogen atoms located at the apices of the two pyramides, bridges two copper atoms.

In the structure it is worth remarking on the different coordinative behavior of propane-1,3-diamine present in chelating and extended form. This fact can be explained by considering: (a) the high flexibility of this molecule (Table VII); (b) the low coordinating ability of the ClO_4^- anions which are

TABLE III. Bond Distances (Å) with e.s.d.s in Parentheses.

Cu(1)–N(1)	2.05(1)	Cu(2)–N(6)	2.26(1)
Cu(1)–N(2)	2.06(1)	Cu(2)–N(7)	2.05(1)
Cu(1)–N(3)	2.03(1)	Cu(2)–N(8)	2.02(1)
Cu(1)–N(4)	2.03(1)	Cu(2)–N(9)	2.06(1)
Cu(1)–N(5)	2.25(1)	Cu(2)–N(10)	2.05(1)
N(1)–C(1)	1.45(2)	C(8)–C(9)	1.53(2)
C(1)–C(2)	1.46(3)	C(9)–N(6)	1.45(2)
C(2)–C(3)	1.54(3)	N(7)–C(10)	1.49(3)
C(3)–N(2)	1.40(3)	C(10)–C(11)	1.40(3)
N(3)–C(4)	1.49(2)	C(11)–C(12)	1.51(3)
C(4)–C(5)	1.53(3)	C(12)–N(8)	1.51(2)
C(5)–C(6)	1.52(3)	N(9)–C(13)	1.48(3)
C(6)–N(4)	1.52(2)	C(13)–C(14)	1.40(3)
N(5)–C(7)	1.48(2)	C(14)–C(15)	1.46(3)
C(7)–C(8)	1.49(2)	C(15)–N(10)	1.46(3)
Cl(1)–O(1)	1.40(1)	Cl(3)–O(9)	1.42(2)
Cl(1)–O(2)	1.37(2)	Cl(3)–O(10)	1.39(2)
Cl(1)–O(3)	1.37(2)	Cl(3)–O(11)	1.43(2)
Cl(1)–O(4)	1.36(2)	Cl(3)–O(12)	1.38(2)
Cl(2)–O(5)	1.38(1)	Cl(4)–O(13)	1.41(1)
Cl(2)–O(6)	1.39(1)	Cl(4)–O(14)	1.46(2)
Cl(2)–O(7)	1.40(1)	Cl(4)–O(15)	1.34(2)
Cl(2)–O(8)	1.41(1)	Cl(4)–O(16)	1.36(2)

practically uninvolved in the coordination; (c) packing requirements (Tables III, IV, V).

Also interesting is the presence of CuN$_5$ chromophore in a square pyramidal arrangement previously found in relatively few examples [9].

The bond distances between the metal ions and the nitrogen atoms in the two polyhedra show only small differences: Cu–N(basal) 2.02(1)–2.06(1) Å, Cu–N(apex) 2.25(1)–2.26(1) Å (Table III), these values being in agreement with those usually found in the literature [9–12]. Bond angles in the basal plane involving the adjacent nitrogen atoms approximate to the 90° ideal value [Cu(1): 87.5(6)–90.4(6)°; Cu(2): 88.1(6)–90.1(6)°] (Table IV), but the '*trans*' angles, planarity analyses (Table VI) and non-bonding N•••N contacts (Table V) show that the copper atoms lie out of the basal planes 0.323(3) and 0.315(3) Å, respectively for Cu(1) and Cu(2) toward the apical nitrogens.

The distortion of the coordination polyhedra is significantly greater for the Cu(2) atom: the nitrogen atoms in the basal plane of Cu(1) deviate only a little from planarity, whereas those involving Cu(2) show considerable displacements; a very weak interaction Cu(1)•••O(11) $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ = 2.99(2) Å at the sixth potentially bonding position

TABLE IV. Bond Angles (°) with e.s.d.s in Parentheses.

N(1)–Cu(1)–N(2)	88.0(6)	N(6)–Cu(2)–N(7)	112.1(6)
N(1)–Cu(1)–N(3)	87.5(6)	N(6)–Cu(2)–N(8)	92.8(5)
N(1)–Cu(1)–N(4)	163.4(5)	N(6)–Cu(2)–N(9)	97.6(5)
N(1)–Cu(1)–N(5)	99.9(5)	N(6)–Cu(2)–N(10)	94.7(5)
N(2)–Cu(1)–N(3)	160.2(5)	N(7)–Cu(2)–N(8)	88.1(6)
N(2)–Cu(1)–N(4)	88.5(5)	N(7)–Cu(2)–N(9)	150.3(7)
N(2)–Cu(1)–N(5)	105.9(5)	N(7)–Cu(2)–N(10)	90.1(6)
N(3)–Cu(1)–N(4)	90.4(6)	N(8)–Cu(2)–N(9)	88.8(6)
N(3)–Cu(1)–N(5)	93.9(5)	N(8)–Cu(2)–N(10)	172.4(6)
N(4)–Cu(1)–N(5)	96.6(5)	N(9)–Cu(2)–N(10)	89.1(6)
Cu(1)–N(1)–C(1)	117(1)	Cu(2)–N(6)–C(9)	120(1)
Cu(1)–N(2)–C(3)	127(1)	Cu(2)–N(7)–C(10)	120(1)
Cu(1)–N(3)–C(4)	121(1)	Cu(2)–N(8)–C(12)	116(1)
Cu(1)–N(4)–C(6)	122(1)	Cu(2)–N(9)–C(13)	120(1)
Cu(1)–N(5)–C(7)	125(1)	Cu(2)–N(10)–C(15)	116(1)
N(1)–C(1)–C(2)	115(2)	C(8)–C(9)–N(6)	116(1)
C(1)–C(2)–C(3)	114(2)	N(7)–C(10)–C(11)	114(2)
C(2)–C(3)–N(2)	112(2)	C(10)–C(11)–C(12)	114(2)
N(3)–C(4)–C(5)	111(1)	C(11)–C(12)–N(8)	110(2)
C(4)–C(5)–C(6)	114(2)	N(9)–C(13)–C(14)	116(2)
C(5)–C(6)–N(4)	114(2)	C(13)–C(14)–C(15)	115(2)
N(5)–C(7)–C(8)	113(1)	C(14)–C(15)–N(10)	113(2)
C(7)–C(8)–C(9)	114(1)		
O(1)–Cl(1)–O(2)	109.7(8)	O(5)–Cl(2)–O(6)	108.6(8)
O(1)–Cl(1)–O(3)	110.1(9)	O(5)–Cl(2)–O(7)	110.3(8)

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TABLE IV. *(continued)*

O(1)–Cl(1)–O(4)	106.5(9)	O(5)–Cl(2)–O(8)	112.6(7)
O(2)–Cl(1)–O(3)	109.9(9)	O(6)–Cl(2)–O(7)	109.6(7)
O(2)–Cl(1)–O(4)	113(1)	O(6)–Cl(2)–O(8)	109.6(8)
O(3)–Cl(1)–O(4)	107(1)	O(7)–Cl(2)–O(8)	105.9(7)
O(9)–Cl(3)–O(10)	110.1(9)	O(13)–Cl(4)–O(14)	95.3(9)
O(9)–Cl(3)–O(11)	107.8(8)	O(13)–Cl(4)–O(15)	115(1)
O(9)–Cl(3)–O(12)	108(1)	O(13)–Cl(4)–O(16)	117(1)
O(10)–Cl(3)–O(11)	110.7(9)	O(14)–Cl(4)–O(15)	91(1)
O(10)–Cl(3)–O(12)	109(1)	O(14)–Cl(4)–O(16)	93(1)
O(11)–Cl(3)–O(12)	110(1)	O(15)–Cl(4)–O(16)	126(1)

TABLE V. Non-Bonding Interatomic Distances (A) with e.s.d.s in Parentheses.

Cu(1)···Cu(2)	8.104		
N(1)···N(2)	2.86(2)	N(1)···N(5)	3.29(2)
N(1)···N(3)	2.82(2)	N(2)···N(5)	3.44(2)
N(2)···N(4)	2.86(2)	N(3)···N(5)	3.13(2)
N(3)···N(4)	2.88(2)	N(4)···N(5)	3.20(2)
N(7)···N(8)	2.83(2)	N(6)···N(7)	3.57(2)
N(7)···N(10)	2.90(2)	N(6)···N(8)	3.11(2)
N(8)···N(9)	2.86(2)	N(6)···N(9)	3.26(2)
N(9)···N(10)	2.89(2)	N(6)···N(10)	3.18(2)
Short intermolecular contacts (<3.5 A)			
Cu(1)···O(11^{i})	2.99(2)	C(9)···O(5^{i})	3.40(2)
N(1)···O(10^{i})	3.33(2)	C(9)···O(14^{iii})	3.25(2)
C(2)···O(3^{ii})	3.46(3)	N(6)···O(13^{iii})	3.38(2)
N(2)···O(4^{i})	3.00(2)	Cu(2)···O(12^{iv})	3.49(2)
N(2)···O(11^{i})	3.45(2)	N(7)···O(8^{i})	3.45(2)
N(2)···O(12^{i})	3.42(2)	N(7)···O(9^{iv})	3.31(2)
N(3)···O(7^{i})	3.21(2)	C(10)···O(8^{i})	3.33(2)
N(3)···O(11^{i})	3.21(2)	C(11)···O(2^{iii})	3.48(3)
N(3)···O(14^{i})	3.21(2)	C(11)···O(9^{iv})	3.45(2)
C(4)···O(14^{i})	3.15(3)	N(8)···O(1^{iv})	3.21(2)
C(5)···O(14^{i})	3.37(3)	N(8)···O(2^{iv})	3.36(2)
N(4)···O(2^{i})	3.40(2)	N(9)···O(1^{iv})	3.35(2)
N(4)···O(4^{i})	3.25(2)	N(9)···O(4^{iv})	3.37(3)
N(4)···O(11^{i})	3.09(2)	N(9)···O(12^{iv})	3.36(3)
N(5)···O(7^{i})	3.17(2)	C(3)···O(12^{iv})	3.33(3)
C(8)···O(13^{iii})	3.49(2)	N(10)···O(3^{v})	3.20(2)
C(8)···O(14^{iii})	3.43(2)	N(10)···O(5^{i})	3.24(2)

$i = \frac{1}{2} - x, 1 - y, \frac{1}{2} + z; ii = \frac{1}{2} - x, \frac{1}{2} + y, 1 + z; iii = x, y, 1 + z; iv = \bar{x}, 1 - y, 1 - z; v = x, \frac{1}{2} - y, \frac{1}{2} + z$

TABLE VI. Equations of Least-Squares Planes and Perpendicular Distances d (A) from these Planes; the Equations are in the Form: $m_1X + m_2Y + m_3Z = D$ (X, Y, Z are the Orthogonal Coordinates; the Starred Atoms are not included in the Planarity).

	d	
N(1)	−0.03(1)	$m_1 = 0.869(2)$
N(2)	0.03(1)	$m_2 = -0.460(4)$
N(3)	0.03(1)	$m_3 = -0.184(5)$
N(4)	−0.03(1)	$D = 3.03(7)$
Cu(1)*	−0.323(3)	
	d	
N(7)	0.18(2)	$m_1 = -0.839(3)$
N(8)	−0.18(2)	$m_2 = -0.476(5)$
N(9)	0.24(2)	$m_3 = -0.265(5)$
N(10)	−0.18(2)	$D = -8.57(6)$
Cu(2)*	−0.315(3)	

is also present. As results from the values of the torsion angles (Table VII), the four chelate rings show the usual 'chair' conformation with the minimum free energy; the structural parameters involving the ligands show no abnormal features: some large differences in bond distances [*e.g.* C(10)–C(11), C(13)–C(14)] are not significant considering their large e.s.d.'s, and the same can be said for some bond angles of ClO_4^- anions in agreement with the high thermal parameters or disorder of the atoms [O(13), O(14), O(15), O(16)] involved.

The crystal structure is packed by the weak hydrogen bonds: N(1)···O(7^{i}) = 3.03(2) Å; N(1)–H(2)···O(7^{i}) = 148°; N(1)–H(2)= 1.07(2) Å; ($i = \frac{1}{2} - x, 1 - y, \frac{1}{2} + z$), and by several short intermolecular contacts (Table III) involving the perchlorate oxygens.

Physical Results

The polycrystalline room temperature ESR spectrum of the compound ($g_1 = 2.058$, $g_2 = 2.099$, $g_3 = 2.205$) confirms an elongated stereochemistry for the copper(II) ion, consistent with the deter-

TABLE VII. Torsion Angles (°) Involving the Ligand Molecules.

a) In the chelate rings			
Cu(1)–N(1)–C(1)–C(2)	–62(2)	Cu(1)–N(3)–C(4)–C(5)	60(2)
N(1)–C(1)–C(2)–C(3)	70(2)	N(3)–C(4)–C(5)–C(6)	–68(2)
C(1)–C(2)–C(3)–N(2)	–59(2)	C(4)–C(5)–C(6)–N(4)	64(2)
C(2)–C(3)–N(2)–Cu(1)	49(2)	C(5)–C(6)–N(4)–Cu(1)	–51(2)
C(3)–N(2)–Cu(1)–N(1)	–36(2)	C(6)–N(4)–Cu(1)–N(3)	35(1)
N(2)–Cu(1)–N(1)–C(1)	38(1)	N(4)–Cu(1)–N(3)–C(4)	–40(1)
Cu(2)–N(7)–C(10)–C(11)	55(2)	Cu(2)–N(9)–C(13)–C(14)	–50(2)
N(7)–C(10)–C(11)–C(12)	–64(2)	N(9)–C(13)–C(14)–C(15)	64(3)
C(10)–C(11)–C(12)–N(8)	71(2)	C(13)–C(14)–C(15)–N(10)	–71(2)
C(11)–C(12)–N(8)–Cu(2)	–66(2)	C(14)–C(15)–N(10)–Cu(2)	63(2)
C(12)–N(8)–Cu(2)–N(7)	47(1)	C(15)–N(10)–Cu(2)–N(9)	–41(1)
N(8)–Cu(2)–N(7)–C(10)	–41(1)	N(10)–Cu(2)–N(9)–C(13)	35(1)
b) In the bridging ligand			
Cu(1)–N(5)–C(7)–C(8)	174(1)		
N(5)–C(7)–C(8)–C(9)	70(2)		
C(7)–C(8)–C(9)–N(6)	178(1)		
C(8)–C(9)–N(6)–Cu(2)	169(1)		

mined structure, as requested for the $d_{x^2-y^2}$ ground state [13]. No evidence of any type of exchange interaction between the two copper(II) atoms in the dinuclear unit is present, in agreement with the large copper–copper distances (8.04 Å).

The electronic reflectance spectrum of the complex has a band maximum at 16200 cm^{-1} and a shoulder at 12000 cm^{-1}. The d–d bands, at greater energy in $[Cu_2(1,3\text{-pn})_5]^{4+}$ than in $[Cu(NH_3)_5]^{2+}$ [9], agree with the higher distortion of the coordination polyhedra and the longer Cu–N (apical) bond lengths in the former than in the latter.

Differences between the IR spectra of $Cu_2(1,3\text{-pn})_5(ClO_4)_4$ and $Cu(1,3\text{-pn})_2(ClO_4)_2$ [1] mainly involve the N–H vibrations. Furthermore, typical bands of ionic perchlorate (1080 and 620 cm^{-1}) are also present.

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Supplementary Material

Lists of complete structure factors, thermal vibration parameters and atomic hydrogen parameters are available from the authors on request.

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