Inorganica Chimica Acta, 187 (1991) 167–174

Tetranuclear copper(II) complexes with polydentate hydrazone ligands: synthesis and X-ray structure

Alex Bonardi, Sandra Ianelli, Corrado Pelizzi, Giancarlo Pelizzi*

Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, viale delle Scienze, 43100 Parma (Italy)

and Costantino Solinas

Istituto di Chimica Biologica, via Muroni 23/a, 07100 Sassari (Italy)

(Received April 23, 1991)

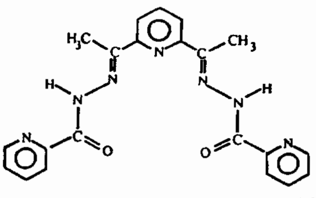
Abstract

The synthesis and X-ray crystal structure of two copper(II) complexes, $[Cu_2(dappc)(OH_2)_3]_2[Cu_2(dappc)(OH_2)_2(ClO_4)]_2(ClO_4)_6 \cdot 2H_2O$ (**I**) (H_2dappc = 2,6-diacetylpyridine bis(2-pyridinecarbonylhydrazone)) and $[Cu_2(dapip')Br]_2 \cdot 2H_2O$, (**II**) ($H_3dapip'$ = 2,6-diacetylpyridine 2-pyridinecarbonylhydrazone 2-(2'-pyridine carbonylhydrazono)phenylacetohydrazone) are reported. The interest of both structures pertains mainly to their tetranuclear nature with dimeric units related by an imposed center of symmetry. The structure of compound **I** is built up from two different complex cations, ClO_4^- anions and uncoordinated H_2O molecules, while that of compound **II** consists of neutral complex molecules and solvating H_2O molecules. During the formation of the latter complex the original H_4dapip ligand (H_4dapip = 2,6-diacetylpyridine bis[2-(2'-pyridinecarbonylhydrazono)phenylacetohydrazone] has undergone a modification through a hydrolysis process, resulting in partial cleavage of one arm to give H_3dapip'.

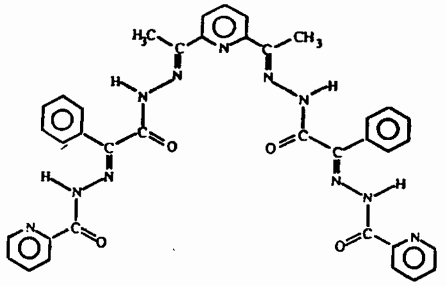
Introduction

The synthesis of new polyfunctional ligands and the investigation of their coordinating properties in metal complexes has been a continuing subject of study in this laboratory. In particular, our attention has been mainly attracted by 2,6-diacetylpyridine bis(acylhydrazones), whose interest as ligands is due to their versatility as chelating agents towards different metal ions, as evidenced by previous investigations [1–3].

Within this context we have synthesized two copper(II) complexes obtained from the reaction of 2,6-diacetylpyridine bis(acylhydrazones), namely H_2dappc and H_4dapip, with copper perchlorate and copper bromide, respectively.



2,6-Diacetylpyridine bis(2-pyridinecarbonylhydrazone) (H_2dappc)



2,6-Diacetylpyridine bis[2-(2'-pyridinecarbonylhydrazono)phenylacetohydrazone] (H_4dapip)

In this paper we show conclusively, by X-ray crystallography, the identity and structures of the two compounds, both tetranuclear with dimeric units related by an imposed center of symmetry: $[Cu_2(dappc)(OH_2)_3]_2[Cu_2(dappc)(OH_2)_2(ClO_4)]_2(ClO_4)_6 \cdot 2H_2O$ (**I**) and $[Cu_2(dapip')Br]_2 \cdot 2H_2O$ (**II**). For **II** this study has established that during the formation of the compound the original H_4dapip ligand has undergone a modification through a hy-

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*Author to whom correspondence should be addressed.

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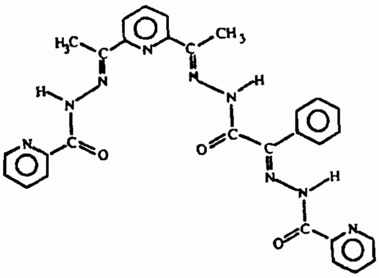
drolysis process which has caused the partial cleavage of one arm.



2,6-Diacetylpyridine 2-pyridinecarbonylhydrazone 2-(2′-pyridinecarbonylhydrazono)phenylacetohydrazone (H_3dapip′)

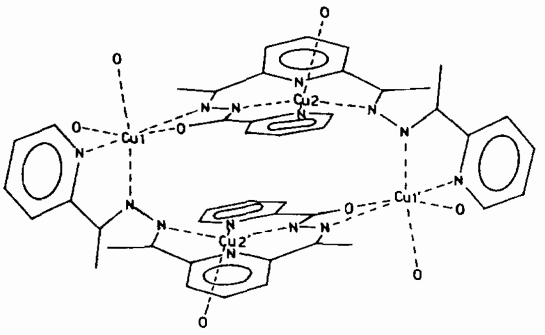
Experimental

Preparations

Organic solvents were purified using published procedures [4]. Copper bromide was commercially available (Fluka). Copper perchlorate heptahydrate was prepared by reacting copper carbonate with perchloric acid in aqueous solution. H_2dappc was prepared by treating 2,6-diaceytlpyridine with 2-pyridinecarbonylhydrazide, as previously described [5]. H_4dapip was obtained from a three-step process involving 2-pyridine-carbonylhydrazide, methyl benzoylformiate, hydrazine hydrate and 2,6-diacetylpyridine [6].

$[Cu_2(dappc)(OH_2)_3]_2[Cu_2(dappc)(OH_2)_2(ClO_4)]_2(ClO_4)_6 \cdot 2H_2O$ (I)

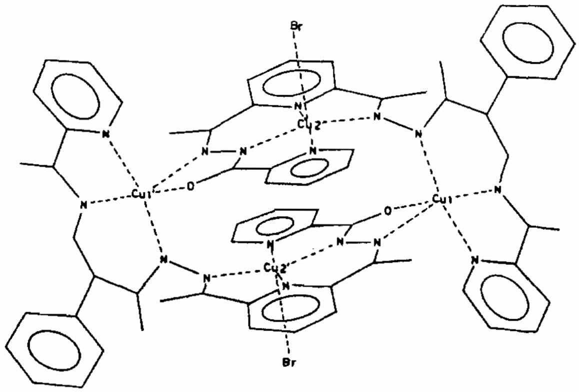
To a hot ethanol/chloroform (2:1 vol./vol.) solution of H_2dappc (0.5 g, 1.25×10^{-3} mol) an ethanol solution of copper(II) perchlorate heptahydrate (0.97 g, 2.49×10^{-3} mol) was added at room temperature. The solution was then refluxed for 1 h and allowed to stand. Bottle green crystals were obtained after some days by slow evaporation of the solvents.



I

$[Cu_2(dapip')Br]_2 \cdot 2H_2O$ (II)

To a hot methanol solution of copper(II) bromide (0.2 g, 9.0×10^{-4} mol) a methanol solution of H_4dapip (0.31 g, 4.5×10^{-4} mol) was added and the resulting solution was refluxed for c. 3 h. After cooling at room temperature the orange-brown solution was filtered and allowed to stand. By slow evaporation of the solvent a red crystalline product was isolated.



II

Measurements

Elemental C, H and N analyses were carried out on a Perkin-Elmer model 240 automatic equipment. IR spectra (4000–200 cm^{-1}) for KBr disks were recorded on a Perkin-Elmer model 283 B spectrophotometer.

Crystallographic structural analysis

All the X-ray diffraction experiments were made at room temperature using a Siemens AED single-crystal diffractometer equipped with an IBM PS2/30 personal computer. The results from automatic peak search, centering, and indexing procedures were consistent with a triclinic lattice in the case of **I** and with a monoclinic lattice in the case of **II**. For **I** a cell reduction program failed to show the presence of a higher symmetry cell and the choice of the centric space group $P\bar{1}$ was justified by the intensity distribution statistics and successful refinement of the structure. For **II** the systematic absences observed during the data collection, $h0l$, $h+l$ odd and $0k0$, k odd, identified the space group as $P2_1/n$, a non-standard setting of C_{2h}^5, No. 14 (equivalent positions: $\pm x, y, z$; $\pm \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$). The unit cell parameters, determined from a least-squares refinement of the setting angles of 25 strong reflections accurately centered are listed in Table 1 together with some details concerning the data collection and structure analysis. The intensity of a standard reflection, measured periodically to assess possible crystal decomposition or loss of alignment, showed only random

TABLE 1. Experimental data for the crystallographic analyses

Compound	**I**	**II**
Formula	$C_{84}H_{92}Cl_8Cu_8N_{28}O_{52}$	$C_{58}H_{48}Br_2Cu_4N_{18}O_8$
Molecular weight	3117.80	1539.13
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	12.436(6)	14.433(7)
b (Å)	14.642(6)	15.491(8)
c (Å)	17.736(8)	13.889(6)
α (°)	100.69(5)	90
β (°)	99.70(5)	103.94(2)
γ (°)	66.30(3)	90
V (Å^3)	2890(2)	3014(2)
Z	1	2
D_c (g cm^{-3})	1.792	1.696
$F(000)$	1576	1544
μ(Cu Kα) (cm^{-1})	42.20	37.13
Crystal size (mm)	0.06×0.22×0.51	0.20×0.30×0.45
Absorption correction (min., max.)	0.8287, 1.2644	0.8770, 1.2228
Extinction correction (min., max.)	0.9814, 1.2827	0.9081, 1.1120
θ range (°)	3–65	3–60
Collection region	$+h\pm k\pm l$	$\pm h+k+l$
No. measured reflections	9539	4881
Condition for observed reflections	$I>3\sigma(I)$	$I>2.5\sigma(I)$
No. reflections used in the refinement	6953	1759
Min., max. height in final ΔF map (e Å^{-3})	−0.40, +0.46	−0.53, +0.97
No. refined parameters	795	260
R, $\Sigma\lvert F_o-F_c\rvert/\Sigma F_o$	0.0742	0.0629
R_w, $\Sigma\lvert F_o-F_c\rvert w^{1/2}/\Sigma F_o w^{1/2}$	0.0810	0.0671
k, g ($w=k/[\sigma^2(F_o)+gF_o^2]$	7.2255, 0.000536	0.4950, 0.005153

Features common to both determinations include the use of Cu Kα radiation ($\lambda=1.54178$ Å) and the θ–2θ scan mode.

statistical fluctuations for either compound. Peak profile analyses were performed with a local modification of the Lehmann and Larsen method [7] and the intensities were converted to relative structure amplitudes by routine procedures. In each case, the empirical method of Walker and Stuart [8] was applied during the refinement to account for absorption effects. Both structures were solved by a combination of direct method and difference Fourier techniques and refined by least-squares procedures based upon F until convergence. The quantity minimized was $\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2$, in which a weighting scheme of the type $w=k/[\sigma^2(F_o)+gF_o^2]$ was used during the final stages. A disordered situation occurs in two of the perchlorate anions in **I**. The oxygen atoms of one of these (C12, O14–O17) were found disordered over two sites with a 0.7/0.3 occupancy ratio, while the best resolution of the other ion (C14, O22–O25) had two O atoms of unity occupancy and four O atoms with a 0.5/0.5 occupancy ratio. Except for the oxygen atoms of the disordered perchlorates, which were refined isotropically, all the atoms in **I** were assigned anisotropic thermal parameters. In **II**, due to the limited amount of observed data, only the atoms heavier than carbon with the exception of the uncoordinated water molecules (both were given a half atomic multiplicity) were refined anisotropically. No allowance was made for H-atom contributions in the calculations of either compound. Complex atom scattering factors were employed and corrections for both the real and imaginary components were included [9]. All calculations were performed on a GOULD 6040 computer by using the programs SHELX 76 [10], PARST [11] and ORTEP [12]. The final atomic parameters for the two compounds are given in Tables 2 and 3. Selected bond distances and angles are in Tables 4, 5 and 6. See also 'Supplementary material'.

Results and discussion

The structure of compound **I** is built up from complex cations of formulae $[Cu_2(dappc)(OH_2)_3]_2^{4+}$ and $[Cu_2(dappc)(OH_2)_2(ClO_4)]_2^{2+}$, ClO_4^- anions and uncoordinated H_2O molecules, while that of compound **II** consists of neutral units of formula $[Cu_2(dapip')Br]_2$ and solvating H_2O molecules. In both compounds two metal atoms for one hydrazone molecule are present and the ligand is deprotonated (bideprotonated in **I** and trideprotonated in **II**). A

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2) of **I** (one third trace of the diagonalized matrix) with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}
Cu1	−1634.7(9)	8233.0(7)	5452.1(6)	3.47(3)
Cu2	927.2(8)	5391.8(7)	4455.4(6)	2.89(3)
Cu3	1085.1(8)	7036.1(7)	1431.6(6)	3.32(3)
Cu4	−1943.1(8)	5502.5(7)	140.2(6)	3.35(3)
Cl1	2882(2)	7455(2)	3197(1)	4.65(7)
Cl2	3634(2)	1508(2)	8116(2)	5.67(7)
Cl3	3855(2)	2933(2)	3061(1)	4.76(7)
Cl4	8132(2)	1540(2)	1961(2)	5.95(9)
O1	44(5)	7890(4)	3592(3)	4.93(20)
O2	601(4)	2723(3)	3807(3)	3.42(16)
O3	−3006(4)	8748(4)	6055(3)	4.45(19)
O4	−880(6)	9409(4)	6337(4)	6.17(24)
O5	1779(6)	5504(4)	3484(4)	6.08(26)
O6	−4048(5)	3850(5)	−364(4)	5.33(22)
O7	775(4)	5873(4)	1564(3)	3.78(17)
O8	−148(4)	8017(4)	2097(3)	3.98(17)
O9	2294(5)	6840(4)	2732(3)	4.83(21)
O10	3140(6)	7232(6)	3958(4)	6.65(27)
O11	3965(6)	7227(6)	2870(4)	7.47(32)
O12	2145(7)	8477(5)	3189(5)	9.43(36)
O13	−3511(5)	5805(5)	891(4)	5.45(24)
O14	2398(12)	2005(11)	8031(8)	9.68(34)
O15	3952(11)	2155(10)	8710(8)	8.64(30)
O16	4137(20)	581(18)	8277(16)	15.81(66)
O17	3848(11)	1514(10)	7359(7)	8.56(29)
O18	2836(8)	2701(8)	3073(6)	10.67(49)
O19	4217(7)	3134(7)	3867(4)	8.42(41)
O20	4788(10)	2220(8)	2713(6)	15.98(57)
O21	3468(6)	3797(5)	2694(4)	6.18(26)
O22	7704(11)	829(10)	1921(7)	13.79(36)
O23	9277(9)	1403(7)	2311(6)	10.07(25)
O24	7833(22)	1864(20)	1301(15)	11.85(61)
O25	7401(16)	2285(14)	2506(11)	9.05(43)
O26	3981(7)	9410(5)	3254(6)	8.99(36)
O14′	2705(19)	1234(17)	8262(13)	5.82(45)
O15′	4193(27)	2284(23)	8217(19)	8.95(73)
O16′	4328(34)	660(30)	7645(25)	11.24(95)
O17′	4343(56)	1137(55)	8884(40)	20.09(208)
O24′	8604(20)	1114(18)	1190(13)	11.07(57)
O25′	7501(14)	2541(12)	1878(10)	7.47(35)
N1	−2397(5)	9232(4)	4690(4)	3.37(19)
N2	−444(4)	7708(4)	4729(3)	2.86(18)
N3	611(5)	6856(4)	4819(4)	3.11(18)
N4	2348(4)	5245(4)	5187(3)	3.00(18)
N5	2029(5)	3262(4)	4847(4)	3.20(19)
N6	1295(4)	3997(4)	4459(3)	3.01(18)
N7	−456(5)	5331(4)	3677(3)	3.50(20)
N8	−1628(5)	1922(4)	−1260(4)	3.54(21)
N9	−2493(5)	3843(4)	−913(4)	3.48(20)
N10	−2809(5)	4880(4)	−700(4)	3.56(20)
N11	−2885(5)	6689(4)	−376(4)	3.32(19)
N12	−835(5)	7044(4)	602(4)	3.36(20)
N13	−886(5)	6131(4)	663(4)	3.28(19)
N14	−916(5)	4405(4)	766(4)	3.31(19)
C1	−3414(6)	10025(6)	4711(5)	4.39(28)
C2	−3831(7)	10657(6)	4174(5)	4.51(28)
C3	−3161(7)	10508(5)	3566(5)	4.34(27)
C4	−2088(7)	9680(5)	3523(5)	4.12(26)
C5	−1758(6)	9066(5)	4102(5)	3.37(23)
C6	−611(6)	8156(5)	4120(5)	3.43(24)
C7	1510(6)	7027(5)	5187(4)	3.37(23)
C8	1563(7)	8034(6)	5452(6)	4.89(31)
C9	2529(6)	6114(5)	5387(5)	3.56(24)
C10	3597(7)	6145(6)	5759(5)	4.73(30)
C11	4483(8)	5246(7)	5963(7)	6.42(38)
C12	4257(7)	4379(6)	5809(6)	4.97(30)
C13	3191(6)	4388(5)	5405(4)	3.50(24)
C14	2964(6)	3445(5)	5263(4)	3.37(23)
C15	3878(7)	2561(6)	5665(5)	4.60(28)
C16	505(6)	3616(5)	3945(4)	3.06(22)
C17	−468(6)	4387(5)	3515(4)	2.89(21)
C18	−1286(6)	4122(6)	3013(4)	3.81(26)
C19	−2164(7)	4894(7)	2610(5)	4.78(31)
C20	−2131(7)	5848(6)	2739(5)	4.66(29)
C21	−1279(7)	6039(6)	3297(5)	5.02(30)
C22	−1147(7)	937(6)	−1478(6)	4.85(31)
C23	−1678(9)	287(7)	−1432(7)	6.76(42)
C24	−2776(9)	696(8)	−1115(8)	7.20(46)
C25	−3249(7)	1719(7)	−848(7)	5.91(37)
C26	−2663(6)	2306(6)	−945(5)	3.85(26)
C27	−3155(6)	3428(6)	−704(5)	4.09(27)
C28	−3721(6)	5503(6)	−1047(4)	3.74(26)
C29	−4587(7)	5235(7)	−1655(5)	4.70(31)
C30	−3842(6)	6575(6)	−813(4)	3.69(25)
C31	−4810(7)	7395(7)	−1063(5)	4.80(30)
C32	−4750(8)	8332(7)	−880(6)	5.79(35)
C33	−3748(7)	8448(6)	−440(5)	4.75(30)
C34	−2814(6)	7598(6)	−203(4)	3.75(26)
C35	−1720(7)	7694(6)	227(5)	3.80(26)
C36	−1553(8)	8679(6)	229(6)	5.22(33)
C37	−16(6)	5614(5)	1162(4)	3.17(23)
C38	−37(5)	4617(5)	1225(4)	3.10(23)
C39	805(6)	3980(6)	1687(5)	3.70(26)
C40	723(7)	3057(6)	1707(5)	4.35(29)
C41	−212(7)	2829(6)	1251(5)	4.14(28)
C42	−1003(7)	3523(6)	814(5)	4.03(28)

striking feature of the structure of compound **I** is the presence in the asymmetric unit of two distinct complex cationic entities which differ only in the nature of one of the coligands (water or perchlorate). Both these cations as well as the neutral molecule in **II** contain two kinds of crystallographically and chemically independent copper atoms linked by N–N bridges. Bridging also involves one more centrosymmetrically related unit to give a tetranuclear system as shown in the drawings of Figs. 1 and 2. As a consequence of the N–N bridging linkage, in both compounds an inner 12-membered Cu–N–N–Cu–N–N–Cu–N–N–Cu–N–N ring system is formed.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2) of **II** (one third trace of the diagonalized matrix) with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}
Cu1	1135(2)	1288(2)	−2084(2)	3.79(7)
Cu2	781(1)	1002(1)	857(2)	3.20(6)
Br	1076(2)	2125(1)	2298(2)	5.84(7)
O1	697(10)	2803(10)	−4485(10)	7.92(55)
O2	2053(9)	3144(8)	−3(8)	6.87(46)
O3	−1546(7)	−172(7)	1390(7)	3.92(33)
N1	1142(8)	754(8)	−3455(9)	3.48(40)
N2	1038(9)	2339(9)	−2841(10)	4.39(47)
N3	970(9)	3149(10)	−2569(10)	4.40(46)
N4	1388(8)	1960(8)	−835(8)	3.45(39)
N5	1655(8)	1481(8)	72(8)	3.39(39)
N6	1950(8)	326(7)	1464(8)	3.10(36)
N7	272(8)	−581(8)	1949(8)	2.92(35)
N8	20(8)	132(8)	1344(9)	3.56(40)
N9	−508(8)	1455(7)	190(8)	3.19(37)
C1	1249(14)	−60(14)	−3588(15)	6.24(47)
C2	1328(14)	−369(14)	−4545(15)	7.01(52)
C3	1215(16)	278(16)	−5306(17)	7.77(56)
C4	1066(13)	1118(13)	−5141(14)	5.93(45)
C5	1027(12)	1301(12)	−4105(13)	4.88(39)
C6	910(14)	2220(14)	−3849(16)	6.05(47)
C7	1217(11)	3357(11)	−1670(12)	3.96(34)
C8	1202(11)	4317(11)	−1475(12)	4.53(38)
C9	1331(15)	4860(15)	−2250(16)	7.42(55)
C10	1301(15)	5798(15)	−2110(16)	7.35(53)
C11	1123(15)	6143(14)	−1225(16)	7.11(52)
C12	983(14)	5609(15)	−482(15)	7.07(52)
C13	1029(13)	4662(14)	−629(14)	6.25(47)
C14	1601(12)	2799(12)	−762(12)	4.33(36)
C15	2533(11)	1279(10)	385(11)	3.59(31)
C16	3351(12)	1535(11)	−73(12)	4.62(38)
C17	2727(11)	677(10)	1259(11)	3.63(33)
C18	3661(12)	495(11)	1797(12)	4.60(38)
C19	3749(12)	−145(12)	2524(13)	5.19(42)
C20	2935(12)	−539(11)	2726(12)	4.54(37)
C21	2023(10)	−278(10)	2142(11)	3.33(32)
C22	1172(10)	−737(10)	2326(11)	3.30(31)
C23	1365(12)	−1560(11)	2977(12)	4.65(38)
C24	−917(11)	268(10)	1119(11)	3.39(32)
C25	−1222(10)	1030(10)	468(10)	3.11(30)
C26	−2201(11)	1277(10)	177(11)	3.95(34)
C27	−2429(12)	1984(11)	−481(12)	4.44(36)
C28	−1712(12)	2421(11)	−775(12)	4.46(37)
C29	−721(12)	2148(11)	−420(12)	4.36(36)
O4	542(23)	4482(22)	5027(25)	10.56(96)
O5	−758(25)	2294(23)	3354(28)	11.41(105)

TABLE 4. Selected bond distances (Å) of **I**

Cu(1)–O(2^{i})	2.001(5)	Cu(3)–O(7)	1.952(6)
Cu(1)–O(3)	1.975(6)	Cu(3)–O(8)	2.005(5)
Cu(1)–O(4)	2.472(7)	Cu(3)–N(8^{ii})	1.987(8)
Cu(1)–N(1)	2.013(6)	Cu(3)–N(9^{ii})	1.965(6)
Cu(1)–N(2)	1.946(6)	Cu(3)–N(12)	2.582(6)
Cu(1)–N(5^{i})	2.424(7)	Cu(3)–O(9)	2.529(6)
Cu(2)–O(5)	2.231(8)	Cu(4)–O(13)	2.394(7)
Cu(2)–N(3)	2.016(6)	Cu(4)–N(10)	1.988(6)
Cu(2)–N(4)	1.969(5)	Cu(4)–N(11)	1.955(6)
Cu(2)–N(6)	1.929(6)	Cu(4)–N(13)	1.918(7)
Cu(2)–N(7)	2.037(6)	Cu(4)–N(14)	1.995(6)
O(1)–C(6)	1.249(10)	O(6)–C(27)	1.231(10)
O(2)–C(16)	1.245(9)	O(7)–C(37)	1.258(9)
N(2)–N(3)	1.411(6)	N(9)–N(10)	1.399(9)
N(2)–C(6)	1.310(11)	N(9)–C(27)	1.332(13)
N(3)–C(7)	1.286(10)	N(10)–C(28)	1.281(8)
N(5)–N(6)	1.383(7)	N(12)–N(13)	1.389(10)
N(5)–C(14)	1.293(10)	N(12)–C(35)	1.305(9)
N(6)–C(16)	1.358(9)	N(13)–C(37)	1.340(8)
C(5)–C(6)	1.512(8)	C(26)–C(27)	1.508(11)
C(7)–C(9)	1.477(8)	C(28)–C(30)	1.500(12)
C(13)–C(14)	1.486(12)	C(34)–C(35)	1.490(12)
C(16)–C(17)	1.493(9)	C(37)–C(38)	1.494(12)
		Cl(1)–O(9)	1.440(7)
		Cl(1)–O(10)	1.402(8)
		Cl(1)–O(11)	1.447(8)
		Cl(1)–O(12)	1.407(7)

$i = -x, 1-y, 1-z$; $ii = -x, 1-y, -z$.

Inside this system the distances between metal atoms are: **I** Cu1···Cu2 4.370(3), Cu1···Cu2^{i} 5.049(3), Cu2···Cu2^{i} 3.849(2); Cu3···Cu4 5.143(3), Cu3···Cu4^{ii} 4.086(3), Cu4···Cu4^{ii} 4.538(2) Å; **II** Cu1···Cu2 4.260(4), Cu1···Cu2^{i} 5.040(4), Cu2···Cu2^{i} 4.219(3) Å. With only one exception, the Cu–N–N–Cu torsion angles deviate only a few degrees from either 90 or 180°. There are only two other examples of copper(II) complexes in the Cambridge Structural Database System which exhibit the same sequence, namely $[Cu_2(dappc)Cl_2]_2 \cdot 2H_2O$ [13] and $[Cu(\mu\text{-ppt})(H_2O)]_4(NO_3)_4 \cdot 12H_2O$ [14]. Owing to the presence of the two cationic units there are four structurally distinct copper atoms in the asymmetric unit of **I**, but only two different coordination environments: that about Cu1 and Cu3 and that about Cu2 and Cu4. The former is square planar with respect to two N atoms from a dappc molecule and two O atoms, one from a centrosymmetrically related dappc and one from a H_2O molecule. The four donors are approximately coplanar, the maximum deviation being 0.14 (Cu1) and 0.06 (Cu3) Å. In each case coordination is completed to elongated octahedral by two longer interactions involving a N atom from the same adjacent ligand, and an O atom from a H_2O molecule in the case of Cu1 and from a ClO_4 ion in the case of Cu3, which are *trans* with respect to the square. The coordination geometry of Cu2 and Cu4 is essentially five-coordinate square-pyramidal in which the apical position is occupied by an O atom of a H_2O molecule, with four N atoms from dappc at the corners of a slightly tetrahedrally distorted square. The deviations of the four basal donors from their mean plane are within 0.15 (Cu2) and 0.17 Å (Cu4) with the copper atom displaced

TABLE 5. Selected bond angles (°) of I

N(1)–Cu(1)–N(5^{i})	115.1(3)	N(9^{ii})–Cu(3)–O(9)	90.6(3)
N(1)–Cu(1)–N(2)	80.4(3)	N(9^{ii})–Cu(3)–N(12)	111.8(3)
O(4)–Cu(1)–N(5^{i})	152.6(3)	N(8^{ii})–Cu(3)–O(9)	91.5(3)
O(4)–Cu(1)–N(2)	99.2(3)	N(8^{ii})–Cu(3)–N(12)	114.7(3)
O(4)–Cu(1)–N(1)	91.4(3)	N(8^{ii})–Cu(3)–N(9^{ii})	81.1(3)
O(3)–Cu(1)–N(5^{i})	83.4(3)	O(8)–Cu(3)–O(9)	81.0(3)
O(3)–Cu(1)–N(2)	171.7(3)	O(8)–Cu(3)–N(12)	78.4(3)
O(3)–Cu(1)–N(1)	94.8(3)	O(8)–Cu(3)–N(9^{ii})	169.6(3)
O(3)–Cu(1)–O(4)	87.6(3)	O(8)–Cu(3)–N(8^{ii})	93.2(3)
O(2^{i})–Cu(1)–N(5^{i})	72.5(3)	O(7)–Cu(3)–O(9)	86.6(3)
O(2^{i})–Cu(1)–N(2)	91.9(3)	O(7)–Cu(3)–N(12)	70.0(3)
O(2^{i})–Cu(1)–N(1)	169.2(3)	O(7)–Cu(3)–N(9^{ii})	90.9(3)
O(2^{i})–Cu(1)–O(4)	82.3(3)	O(7)–Cu(3)–N(8^{ii})	171.7(4)
O(2^{i})–Cu(1)–O(3)	93.7(3)	O(7)–Cu(3)–O(8)	94.5(3)
N(6)–Cu(2)–N(7)	82.2(3)	N(13)–Cu(4)–N(14)	82.6(3)
N(4)–Cu(2)–N(7)	172.0(4)	N(11)–Cu(4)–N(14)	172.9(3)
N(4)–Cu(2)–N(6)	90.0(3)	N(11)–Cu(4)–N(13)	90.9(3)
N(3)–Cu(2)–N(7)	107.3(3)	N(10)–Cu(4)–N(14)	105.6(3)
N(3)–Cu(2)–N(6)	161.3(3)	N(10)–Cu(4)–N(13)	161.0(3)
N(3)–Cu(2)–N(4)	80.7(3)	N(10)–Cu(4)–N(11)	81.4(3)
O(5)–Cu(2)–N(7)	88.1(3)	O(13)–Cu(4)–N(14)	88.2(3)
O(5)–Cu(2)–N(6)	108.6(3)	O(13)–Cu(4)–N(13)	111.8(3)
O(5)–Cu(2)–N(4)	92.6(3)	O(13)–Cu(4)–N(11)	91.6(3)
O(5)–Cu(2)–N(3)	88.1(3)	O(13)–Cu(4)–N(10)	86.0(3)
Cu(1^{i})–O(2)–C(16)	118.9(5)	Cu(3)–O(7)–C(37)	124.1(6)
Cu(1)–N(1)–C(5)	113.9(5)	Cu(3^{ii})–N(8)–C(26)	113.6(6)
Cu(1)–N(1)–C(1)	128.3(6)	Cu(3^{ii})–N(8)–C(22)	127.3(7)
Cu(1)–N(2)–C(6)	119.5(6)	Cu(3^{ii})–N(9)–C(27)	118.6(6)
Cu(1)–N(2)–N(3)	123.6(5)	Cu(3^{ii})–N(9)–N(10)	124.1(6)
Cu(2)–N(3)–N(2)	129.4(5)	Cu(4)–N(10)–N(9)	124.7(5)
Cu(2)–N(3)–C(7)	114.4(6)	Cu(4)–N(10)–C(28)	115.1(6)
Cu(2)–N(4)–C(13)	127.6(6)	Cu(4)–N(11)–C(34)	126.6(6)
Cu(2)–N(4)–C(9)	112.5(5)	Cu(4)–N(11)–C(30)	110.8(6)
Cu(1^{i})–N(5)–C(14)	132.4(6)	Cu(3)–N(12)–C(35)	135.8(6)
Cu(1^{i})–N(5)–N(6)	106.9(5)	Cu(3)–N(12)–N(13)	104.9(5)
Cu(2)–N(6)–N(5)	131.1(5)	Cu(4)–N(13)–N(12)	130.9(5)
Cu(2)–N(6)–C(16)	116.7(5)	Cu(4)–N(13)–C(37)	116.9(6)
Cu(2)–N(7)–C(21)	130.2(6)	Cu(4)–N(14)–C(42)	129.8(6)
Cu(2)–N(7)–C(17)	112.3(5)	Cu(4)–N(14)–C(38)	112.9(5)
		Cu(3)–O(9)–Cl(1)	130.6(4)
		O(9)–Cl(1)–O(10)	109.9(5)
		O(9)–Cl(1)–O(11)	107.5(5)
		O(9)–Cl(1)–O(12)	109.5(5)
		O(10)–Cl(1)–O(11)	109.8(5)
		O(10)–Cl(1)–O(12)	109.4(5)
		O(11)–Cl(1)–O(12)	110.7(6)

i = $-x$, $1-y$, $1-z$; ii = $-x$, $1-y$, $-z$.

in each case by 0.13 Å toward the apical site. This study confirms the remarkable versatility of H_2dappc for binding metal ions. In fact, the ligand has been found to act as neutral pentadentate in Mn(H_2dappc)$Cl_2 \cdot 5H_2O$ [15] and in [Co(H_2dappc)$(OH_2)_2$]$Cl_2 \cdot 3H_2O$ [16], as anionic pentadentate in [Mn(dappc)$(OH_2)_2 \cdot 7H_2O$ [17], and as anionic octadentate in the above-mentioned [Cu_2(dappc)Cl_2]$_2 \cdot 2H_2O$ [13] and now in the title compound. The latter structure is closely related to the present one as far as the occurrence of tetranuclear systems, and

TABLE 6. Selected bond distances (Å) and angles (°) of II

Cu(1)–N(1)	2.078(13)	C(5)–C(6)	1.49(3)	N(4)–N(5)	1.43(2)
Cu(1)–N(2)	1.925(14)	C(6)–O(1)	1.25(2)	N(5)–C(15)	1.28(2)
Cu(1)–N(4)	1.980(12)	C(6)–N(2)	1.38(3)	C(15)–C(17)	1.50(2)
Cu(1)–O(3^{i})	1.999(10)	N(2)–N(3)	1.32(2)	C(21)–C(22)	1.49(2)
Cu(1)–N(7^{i})	2.354(12)	N(3)–C(7)	1.26(2)	C(22)–N(7)	1.30(2)
Cu(2)–Br	2.608(3)	C(7)–C(8)	1.51(2)	N(7)–N(8)	1.38(2)
Cu(2)–N(5)	1.999(13)	C(7)–C(14)	1.52(2)	N(8)–C(24)	1.33(2)
Cu(2)–N(6)	1.992(11)	C(14)–O(2)	1.22(2)	C(24)–O(3)	1.26(2)
Cu(2)–N(8)	1.958(13)	C(14)–N(4)	1.33(2)	C(24)–C(25)	1.49(2)
Cu(2)–N(9)	1.995(11)				

N(1)–Cu(1)–N(2)	81.5(5)	N(5)–Cu(2)–N(6)	81.0(5)
N(1)–Cu(1)–N(4)	166.2(5)	N(5)–Cu(2)–N(8)	157.5(5)
N(1)–Cu(1)–O(3^{i})	91.8(5)	N(5)–Cu(2)–N(9)	104.9(5)
N(2)–Cu(1)–N(4)	90.5(6)	N(6)–Cu(2)–N(8)	88.9(5)
N(2)–Cu(1)–O(3^{i})	165.7(5)	N(6)–Cu(2)–N(9)	168.9(5)
N(4)–Cu(1)–O(3^{i})	93.5(5)	N(8)–Cu(2)–N(9)	82.3(5)
N(1)–Cu(1)–N(7^{i})	94.7(5)	N(5)–Cu(2)–Br	99.4(4)
N(2)–Cu(1)–N(7^{i})	119.2(5)	N(6)–Cu(2)–Br	93.5(3)
N(4)–Cu(1)–N(7^{i})	99.0(5)	N(8)–Cu(2)–Br	101.3(4)
O(3^{i})–Cu(1)–N(7^{i})	73.8(4)	N(9)–Cu(2)–Br	94.8(4)
Cu(1)–N(1)–C(1)	123(1)	Cu(2)–N(5)–C(15)	115(1)
Cu(1)–N(1)–C(5)	112(1)	Cu(2)–N(6)–C(17)	111(1)
Cu(1)–N(2)–C(6)	115(1)	Cu(2)–N(6)–C(21)	126(1)
Cu(1)–N(2)–N(3)	130(1)	Cu(1^{i})–N(7)–N(8)	108(1)
N(2)–N(3)–C(7)	120(2)	Cu(1^{i})–N(7)–C(22)	133(1)
Cu(1)–N(4)–C(14)	125(1)	Cu(2)–N(8)–N(7)	132(1)
Cu(1)–N(4)–N(5)	117(1)	Cu(2)–N(8)–C(24)	116(1)
Cu(2)–N(5)–N(4)	127(1)	Cu(1^{i})–O(3)–C(24)	117(1)

i = $-x$, $-y$, $-z$.

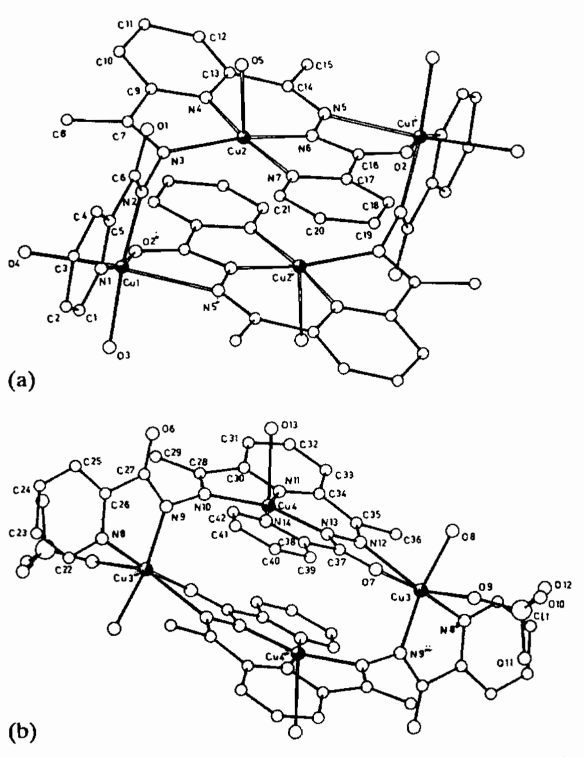


Fig. 1. A perspective view of: (a) the [Cu_2(dappc)$(OH_2)_3$]$_2^{4+}$ cation and (b) the [Cu_2(dappc)$(OH_2)_2(ClO_4)$]$_2^{2+}$ cation of compound I.

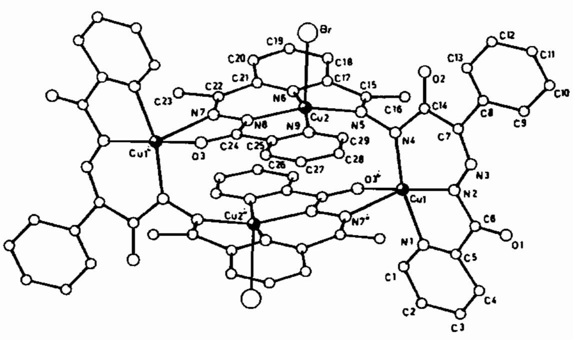


Fig. 2. A perspective view of compound **II**.

the conformation and the ligand behaviour of the hydrazone are concerned, but is significantly different as regards the nature of the complex (neutral units are present) and the geometry of the coordination polyhedra (the independent copper atoms are both five coordinated in a distorted square-pyramidal arrangement). As regards the planarity, the dappc ligand in both complex cations can be described in terms of three portions: the central pyridine ring (N4· · ·C13 and N11· · ·C34), which is planar within experimental error, and the two side arms, which, rather surprisingly, are in a very different situation, probably due to different coordinative interactions. In fact, while all of the atoms of the arm having the carbonyl O atom (O2 and O7) involved in the coordination to metal are located within 0.09 Å of their common plane, the atoms of the other arm show very large deviations from planarity: 10 out of the 12 atoms, i.e. those of the hydrazonic chain, are close to being coplanar, while the remaining two atoms are completely out of this plane, being displaced by *c*. 1.1 Å (C7 and C28) and 2.4 (C8 and C29) Å in the same direction. Although the H atoms were not found, an analysis of the closest interatomic contacts between complex cations, perchlorate anions and solvating water molecules reveals the existence of an extended hydrogen bonding network in the crystal lattice, with all the six waters present in the structure, five coordinated and one uncoordinated, involved as donors.

The IR spectrum of the complex shows a pattern very similar to that observed in the spectrum of $[Cu_2(dappc)Cl_2]_2 \cdot 2H_2O$ [13] with the exception of three strong bands at 1140, 1113 and 1085 cm^{-1} due to the perchlorate ion.

In the structure of compound **II** there are two different coordination polyhedra in both of which the copper atom has a slightly distorted square-pyramidal five-coordination geometry. In the Cu1 environment the basal plane of the pyramid is made up of three N atoms from dapip′ and an O atom from a symmetry-related ligand, while a N atom from the same adjacent ligand is at the apex. The atoms at the base of the pyramid are strictly coplanar with Cu1 displaced by 0.22 Å from the plane, toward the apical donor. In the Cu2 environment four N atoms from dapip′ span the basal corners of the pyramid, the summit of which is occupied by a Br atom. The deviations of the basal atoms from the least-squares plane are within ±0.12 Å, so indicating some tetrahedral distortion. The deviation of Cu2 from this plane is 0.24 Å, toward the apical site. The basal Cu–N bond distances range from 1.925 to 2.078 Å, with an average of 1.991 Å, only slightly longer than the 1.976 Å found in **I**. All these bonds are in the expected range for five-coordinated square-pyramidal copper(II) complexes [18–20]. The apical Cu–N distance of 2.354(12) Å is significantly longer by 0.1–0.2 Å than the corresponding distance usually quoted in the literature [18, 21]. Nevertheless, similar long distances have been previously observed in some cases, e.g. 2.357(4) Å in $Cu(IBO)_2Cl_2$ [22] and 2.401(6) Å in $[Cu_2(dappc)Cl_2]_2 \cdot 2H_2O$ [13]. Concerning the Cu2 environment, a bibliographic search carried out by means of the Cambridge Structural Database System gave only five examples of five-coordinated square-pyramidal copper(II) complexes having four N atoms in the equatorial positions and a Br ion at the apex [23–27]. The Cu–N and Cu–Br distances found in these compounds vary between 1.94–2.11 Å and 2.546–2.888 Å, respectively, the average being 2.04 and 2.728 Å, somewhat longer than the corresponding values of 1.99 and 2.608 Å found here. Since there is not structural study of a metal complex of H_4dapip, no direct comparison for ligand geometry is possible. However, mention can be made of the H_3L' ligand in $[Zn(H_3L')(OH_2)_2](ClO_4)_2 \cdot 1.5H_2O$ [3], during the formation of which a hydrolysis process has caused, as in the title compound, the partial cleavage of one arm of the original ligand. In this ligand, as compared to dapip′, two amino groups replace the two terminal 2-pyridyl moieties and bonded to the carbon atom located in the middle of the long arm there is a methyl group instead of a phenyl ring. The dapip′ ligand uses nine of its twelve potential donors in the coordination and is arranged to form three CuNCCN and one CuOCNN five-membered rings and two CuNNCCN six-membered rings, all of which are approximately planar, the greatest deviation from the least-squares for each ring being in the range 0.05–0.20 Å. The hydrazone molecule can be described as having three more or less planar parts: the strictly planar central pyridine ring N6· · ·C21, the 12-atom short side arm (N9 through C23), whose atoms describe a plane to within 0.09 Å and the 23-long side arm (N1 through C16), which is fully non-planar, as it shows deviations from the plane of best fit up to 1.8 Å for the methyl carbon C16. The two side arms are twisted by 11.4(3) (short arm) and 83.4(4)° (long arm) out of the central ring.

The absence of experimental H-atom positions precludes detailed discussion of any hydrogen bonding interactions; nevertheless, some close contacts involving the uncoordinated water molecules are certainly indicative of hydrogen bonding.

Even if a comparison of the IR spectrum of complex **II** with that of free H_4dapip is not very significant owing to the modification undergone by the original ligand, the assignments of the main vibrational bands agree well with the deprotonated nature of H_3dapip′ and the presence of coordinated (1628 cm^{-1}) and uncoordinated (1641 cm^{-1}) carbonyl groups.

Supplementary material

Thermal parameters, observed and calculated structure factors and a complete listing of bond distance and bond angle data are available from the authors on request.

Acknowledgements

The financial support of the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), 40%, is gratefully acknowledged. We thank Mr Andrea Cantoni and Mr Gianfranco Pasquinelli for their valuable technical assistance.

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