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$[Cu(phdpa)Cl]^+ (phdpa = bis(2-pyridylmethyl)aniline):$ a moiety of unusual stability in some 1:1 Cu(II) complexes of phdpa. Synthesis and X-ray crystal structures of [Cu(phdpa)Cl₂] and [Cu₂(phdpa)₂Cl₃]PF₆·0.5MeOH

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Abstract

1:1 copper(II) complexes of bis(dipyridylmethyl)aniline (phdpa) of various kinds, with chloride and PF_6^- as anions, were synthesized and characterized by elemental analysis, IR spectroscopy and X-ray structure crystallography. The crystal structures of [Cu(phdpa)Cl₂] (I) and [Cu₂(phdpa)₂Cl₃]PF₆·0.5MeOH (II) showed that the metal atoms are five-coordinated and that the structures are also stabilized by a triple intramolecular hydrogen-bond system. The resulting unusual stability of the [Cu(phdpa)Cl]⁺ moiety influences the exchange properties with PF_6^- of compound I, which gave complexes where the cationic group is maintained also under drastic reaction conditions.

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1. Introduction

Polydentate ligands with nitrogen donor atoms are largely employed in mimicking the proteic environment of the copper in models of biological interest, in particular of enzymes with a type 2 copper site, whose coordination environment is provided by nitrogen atoms of the protein, plus one or more exogeneous ligands. It is of current interest to correlate the flexibility of the model ligand and its sterical hindrance with the geometry of the complex. The copper(II) ion, owing to the well known 'plasticity' of the coordination sphere, forms complexes of co-ordination number 4–6, with a variety of irregular geometries [1], both the anions and the solvent playing often a vital role on the stoichiometry and stereochemistry of the complexes [2].

In mononuclear complexes, linear 3N tridentate ligands with a central amine, can complex the metal atom with one or two molecules and in the latter case three potential geometric isomers are possible: *meridional* (a), *trans-facial* (b) and *cis-facial* (c)

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While with the archetype dietylentriamine all the $[Cu(dien)_2](NO_3)_2$ known complexes, [3], $[Cu(dien)_2]Br_2 \cdot H_2O$ [4], $[Cu(dien)_2]Cl_2 \cdot H_2O$ [5] and $[Cu(diene)_2]Cl(ClO_4)$ [5], form octahedral complexes *meridionally* coordinated, when aromatic heterocycles are present as substituents of the amine, fac- as well mer-coordination have been observed. A popular ligand, the dipicolyl-amine (dipica), gave two [Cu(dipi $ca)_2$ (ClO₄)₂ isomers, one with a *cis-fac* and the other with a mixed *trans-fac* and square-pyramidal structure, the latter comprising discrete hexacoordinate and pentacoordinate cations (the alifatic nitrogen of the bidentate dipica defining the axial position in the fivecoordination). The formation of the geometric isomers depends on the solvent used and on the sequence of addition of the reagents [6]. The $[Cu(dipica)_2](BF_4)_2$ presents trans-fac hexacoordinated and pentacoordinated cations within the same unit cell [7].

The copper organizes a square pyramidal geometry also in the complexes with dipica and other bidentate ligand as picolinate [2] or L-phenylalaninate [8]. The dipica shows a *mer*-coordination to the copper ion in the first compound and a fac-coordination in the second one. On the contrary in the $[Cu(dipica)(phen)](ClO_4)_2$ complex [9] a distorted trigonal bipyramidal geometry is observed, with the pyridine moieties of the dipica ligand occupying two sites of the equatorial plane and the amine nitrogen one of the axial sites. In another complex with a copper/ligand ratio of 1:1, that is $[Cu(dipica)(NO_3)_2]$ [10], in which only inorganic anions are present as supplementary ligands, the dipica bonds in a tridentate planar conformation, where the pyridine nitrogens occupy the axial positions and the alifatic nitrogen lies on the basal plane of a trigonal bipyramidal arrangement. The dipica ligand gives also the puzzling structure [Cu(TPA)Cl] [Cu(dipica)Cl][ClO₄]₂ (TPA = tris(pyridylmethyl)amine) [11], which contains two copper(II) complexes with different ligands in a single crystal: the cation with the dipica shows a square planar structure, with three coordinated N atoms and the last position occupied by the chloride.

Here we report on a series of Cu(II) complexes with a dipica derivative, the N,N-bis(2-pyridylmethyl)aniline (phdpa), a new ligand first prepared two years ago by Hazell and coworkers by nucleophilic substitution of 2-

picolylchloride with aniline in a two phases (water/ methylene chloride) system [12]. These complexes, compared with those of the unsubstituted dipicolylamine, show some interesting structural



characteristics, confirming that also the introduction of a substituent in a position not directly source of steric hindrance can largely influence the formation of complexes. Only 1:1 complexes were isolated with phdpa in the presence of chloride anions; one of these was a new kind of dimer, with an unusual single and nearly linear chloride bridge.

2. Experimental

2.1. Generalities

Reagents and solvents were used as received from commercial sources. The picolyl chloride hydrochloride was a technical Aldrich reagent (98%).

The visible spectra were registered on a Perkin–Elmer 124 spectrophotometer, in the 370–800 nm range, in methanol solutions. IR spectra ($4000-200 \text{ cm}^{-1}$) were recorded on Perkin–Elmer 983G and a P.E. System 2000 spectrometers as KBr pellets or as nujol mulls between polythene plates for the far IR region. The frequencies reported in Section 2 are relative to the main absorptions in the 2000–400 cm⁻¹ range. A Crison micro CM 2200 apparatus, with temperature compensation, was used for the conductivity measurements, which were performed on methanol solutions.

2.2. Syntheses

2.2.1. phdpa

The ligand was prepared following the method described in the literature [12]. The off white needles

obtained presented a m.p. 112-113 °C. IR (cm⁻¹): shs, 1590 s, 1573 mw; 1505 s, 1464 s,br, 1435 m, 1418 w; 1377, 1353 ms; 1276, 1254 w; 1224 m, 1191 w; 1177 ms; 1091, 1060, 1047, 1026 w; 992 m, 968 w, 952 m; 893, 873 w; 809 w,br; 767, 758, 750 s,727 mw; 694, 667 mw; 615 mw; 546 w, 516 mw; 469 w; 408 mw. The NMR data were in agreement with those previously reported.

2.2.2. $[Cu(phdpa)Cl_2](I)$

A solution of 0.100 g (0.59 mmol) of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ in 3 ml of water was added dropwise to 0.138 g of phdpa (0.50 mmol) dissolved in the minimum amount of methanol. The needles deposited after some hours were filtered off, washed with acetone and dried in vacuo. The crystals obtained were directly suitable for X-ray diffraction. Further product was recovered from the concentration of the filtrate at about a third of the original volume, for a total yield of 95.8%. Compound I is recrystallizable unchanged from acetonitrile. IR (cm⁻¹): 1605 s,sh, 1568 mw; 1495 s, 1477, 1463 ms, 1442, 1424 m; 1383 w; 1350 w; 1318 mw; 1284, 1280 m; 1250, 1231 w; 1182 m, 1150 w, 1130 m; 1099 m; 1052 m, 1029 m; 969, 946 w; 831, 817 w; 795 s,771 vs; 717 w; 692 s; 651 mw; 568, 546, 518 w; 464 w; 435 m.

Compound I is insoluble in ether, acetone, toluene and THF; sparingly soluble in acetonitrile and chloroform; fairly soluble in water and methanol.

2.2.3. $[Cu_2(phpda)_2Cl_3]PF_6 \cdot 0.5 MeOH (II)$

A total of 0.100 g (0.613 mmol) of solid NH_4PF_6 was added to a dark green solution obtained from 0.100 g (0.363 mmol) of phdpa and 0.100 g (0.587 mmol) of $CuCl_2 \cdot 2H_2O$ in 15 ml of methanol. Turquoise hexagonal platelets (II) of X-ray quality were obtained by resting; afterwards a powder of the same colour precipitated by fast concentration of the mother liquors. Yield 82.9%. A slow recrystallization in the air of the above product from methanol gave brilliant blue polyhedric crystals, with water as crystallization solvent. After an evident loss of solvent during the first stage of heating, the decomposition point is the same for the two forms, which also show the same pattern in the 2000– 400 cm⁻¹ range of the IR spectra.

IR (cm⁻¹): 1611 s,sh, 1574 w; 1495 m, 1482 mw, 1453, 1440 m; 1389, 1354, 1316 w; 1289 m; 1253 w,sh; 1165 mw; 1098 mw; 1053 mw, 1030 m; 973, 953 w; 899 w; 845 vs,br (vPF₆), 776 s,761 w; 720 w, 696 m, 650 mw; 558 s (δPF_6), 423 w.

The complex is insoluble in ether, toluene, THF and chloroform, soluble in acetone, methanol, acetonitrile and hot water.

2.2.4. $[Cu(phdpa)Cl]PF_6 \cdot H_2 O$ (III)

Solid NH_4PF_6 in large excess (0.100 g; 0.613 mmol) was added to a suspension of I (0.100 g; 0.244 mmol) in

Table 1

Crystal data and structure refinement parameters for ${\bf I}$ and ${\bf II}$

	I	II
Empirical formula	$C_{18}H_{17}Cl_2CuN_3$	$\begin{array}{c} C_{36}H_{34}Cl_3Cu_2F_6N_6P\cdot\\ 1/2CH_3OH \end{array}$
Formula weight	409.80	945.14
Diffractometer	CAD4	CAD4
Wavelength (Å)	1.54178 (Cu Kα)	1.54178 (Cu Ka)
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P 2_1/n$	$P2_1/n$
Unit cell dimensions ^a		
a (Å)	14.676(5)	11.668(5)
b (Å)	14.127(5)	14.408(5)
c (Å)	8.398(5)	23.851(5)
α (°)	90	90
β (°)	78.40(2)	101.75(2)
γ (°)	90	90
V (Å ³)	1706(1)	3926(2)
Ζ	4	4
$D_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.596	1.599
F(000)	836	1916
Linear absorption coeffi-	4.71	4.180
cient (mm^{-1})		
2θ Range (°)	4.39-69.99	3.60-65.02
Reflections measured	3437	6587
Unique data/restraints/	3218/0/220	6443/ 0/515
Observed reflections	2977	2900
Final R indices ^b	$R_{\rm r} = 0.0335$	$R_{\rm r} = 0.0535$
i mai i maiees	$R_1 = 0.0555,$ $w R_2 = 0.0916$	$R_1 = 0.0555$, $wR_2 = 0.1336$
Goodness-of-fit ^c	0.745	0.727
Highest neak deenest	0.749 0.470 and -0.453	0.436 and -0.512
hole in final difference map (e Å ⁻³)	0.170 and 0.455	0.150 and 0.512

^a Unit cell dimensions were obtained by least-squares analysis of the setting angles of 30 reflections found in a random search on the reciprocal space.

^b $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}.$ ^c Goodness-of-fit = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* the number of parameters.

acetonitrile (5 ml) and the mixture was refluxed for 1 h under stirring. The reagent complex solubilized, giving a dark blue–green solution, while a white powder began to form after a few minutes. At the end of the reaction the white precipitate (NH₄Cl; 12.5 mg; 0.24 mmol) was filtered off, the filtrate evaporated to dryness and the solid washed with water to remove the NH₄PF₆ excess. The residue (yield 95.2%) recrystallized from acetone and ether gave blue–violet rods (**III**) and, from acetonitrile and ether, green–blue needles, which rapidly changed to a blue colour in the air, with loss of transparence.

IR (cm⁻¹): 1613 ms, 1574 w; 1494 m, 1484 mw, 1453 m, 1443 mw; 1385 w; 1352 w; 1313 w, 1287 m; 1160 w; 1091 w, 1057 m, 1032 m; 978, 960 w; 842 vs (vPF₆); 777 ms; 741, 721 w; 694 m; 651 w; 558 s (δ PF₆); 426 w.

Table 2	
Characteristics of the Cu(II)(phdpa) complexes	

Complex	Colour	dec. p (°C)	Elemental analysis ^a (%)		Conductivity ^b (Σ^{-1} cm ² mol ⁻¹)		
			С	Н	Cu	Ν	
[Cu(phdpa)Cl ₂]	green	186-187 (red)	52.6 (52.75)	4.1 (4.18)	15.5 (15.51)	10.1 (10.25)	81.8
$[Cu_2(phdpa)_2Cl_3]PF_6 \cdot 0.5 MeOH$	turquoise	196–196.3 (red)	46.3 (46.39)	3.8 (3.85)	13.5 (13.68)	8.9 (8.89)	185.4
$[Cu(phdpa)]Cl](PF_6) \cdot H_2O$	blue-vio- let	212.5-213	40.3 (40.23)	3.0 (3.56)	11.8 (11.83)	7.7 (7.82)	100.1

^a The calculated data are given in brackets.

^b In methanol.

The complex is insoluble in ether, toluene, chloroform, sparingly soluble in water, soluble in THF and methanol and very soluble in acetone and acetonitrile.

2.3. X-ray data collection and structure determination of I and II

Intensity data and cell parameters were recorded at room temperature using Cu K α graphite monochromated radiation. The unit cell parameters were obtained by least-squares fit of 42 (I) and 31 (II) $I(\theta \chi \phi)_{hkl}$ reflections in the range $30 \le \theta \le 44^\circ$ (I) and $24 \le \theta \le 34^\circ$ (II).

The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analysis are reported in Table 1. The intensities were calculated from the analysis of the $\omega/2\theta$ diffraction profiles and were corrected for Lorentz and polarization effects. The data were corrected for absorption using ABSORB [13]; maximum and minimum values for the transmission coefficient were 1.000 and 0.819 (I) and 1.000 and 0.219 (II).

Both the structures were solved by direct methods using the SIR-92 program [14]. The E-maps revealed almost all the non-hydrogen atoms of the complexes. The remaining atoms were located by successive cycles of Fourier ΔF maps and refined by full-matrix leastsquares procedures (based on F_0^2), using SHELX-97 [15] with anisotropic atomic displacements for all nonhydrogen atoms. For each complex the hydrogen atoms were added to the corresponding C atoms in the 'riding' model and refined with isotropic atomic displacements. The weighting schemes used in the last cycle of refinements were $w = 1/[\sigma^2 F_o^2 + (0.0761P)^2 + 2.3819P]$ where $P = (F_o^2 + 2F_c^2)/3$ for compound I and $w = 1/[\sigma^2 F_o^2 +$ $(0.0981P)^2$] where $P = (F_o^2 + 2F_c^2)/3$ for compound II. Molecular geometry calculations were carried out using the PARST-97 program [16]. Drawings were made utilizing the ORTEP program in the WinGX suite [17]. All calculations were carried out on DIGITAL Alpha Station 255 computer.

3. Results and discussion

3.1. Synthesis

The analytical data and some of the physicochemical characteristics of the complexes are shown in Table 2. The complex obtained most easily is the [Cu(phdpa)Cl₂] (I), the only isolated for Cu:L ratios in the range $2:1^{1}-1:2$. In methanol the chloride can be partially substituted by PF_{6}^{-} with formation of a dimeric complex with the same Cu:L ratio, [Cu₂(phdpa)₂Cl₃]PF₆ (II). In acetonitrile the NH₄Cl, co-product of the substitution reaction with NH₄PF₆, is less soluble than in methanol and its precipitation shifts the substitution equilibrium a little more to the right; exactly one chloride is substituted for each copper, with formation of Cu(phdpa)ClPF₆. Anyway, the complete exchange of chloride with PF_{6}^{-} was not achieved, also after heating at reflux for some hours and in the presence of a large PF_{6} excess.

Copper(II) complexes of 1:2 stoicheiometry were not obtained in the presence of chloride or PF_6^- anions, also by adding the copper salt to an excess of ligand. As said, by using $CuCl_2 \cdot 2H_2O$ and ligand in a 1:2 ratio, the complexes isolated in methanol were **I**, or **II** after addition of $NH_4PF_6^-$ (in the latter case some (phdpa) PF_6^- was also recovered from the mother liquors). In acetonitrile the addition of NH_4PF_6 caused at first precipitation of NH_4Cl , in equimolecular amount with copper, then dilution with diethyl ether gave white microcrystals of (phdpa) PF_6 . A further addition of ether to the filtered solution furnished a mixture of crystals of various blue–green colours, which seem to be the same complex $Cu(phdpa)CIPF_6$, with

¹ At first, in presence of copper excess, we thought to have also isolated an assumed $Cu_3(phdpa)_2Cl_6$ complex, but we recognized then that this product was [Cu(2-pirydylmethylaniline)Cl₂], deriving from a side-product due to an incomplete reaction of formation of the ligand. The two formulae have practically the same percentual composition, but the IR characteristics of the complex were incompatible with those of a phdpa derivative. Diffraction studies confirmed the true nature of the complex, wich is a monomer, with a square planar structure [18].

different solvation. On the contrary, a 1:2 complex $Cu(phdpa)_2(ClO_4)_2$ was prepared easily in methanol, by adding copper(II) perchlorate to the ligand [18]. $M(phdpa)_2(ClO_4)_2$, complexes are also known for nickel(II) and iron(II) [12].

In methanol I and III are 1:1 electrolytes. The conductivity of II could apparently be that of a 2:1 electrolyte, but this high value is due, more probably, to the following disproportion:

 $[Cu_2(phdpa)_2Cl_3]PF_6$ = [Cu(phdpa)Cl_2] + Cu(phdpa)ClPF_6

which changes the dimeric structure of the solid **II** to monomer moieties in solution, doubling the molar concentration. This suggestion is supported by the visible spectra (see later) and by the recover, in approximately equimolecular amounts, of **I** and **III** in tentative recrystallizations of the dimer from acetone.

3.2. Spectroscopic studies

3.2.1. IR spectra

The IR spectra of the above complexes in the 2000- 400 cm^{-1} region have mainly a function of fingerprints, the absorption bands being too numerous for a reasonably correct assignment. Anyway, they confirm the ionic character of the PF₆ group and the presence in the ligand of coordinated pyridyl rings (bending absorptions in the phdpa complexes at about 775 cm⁻¹; 780–770 cm^{-1} in dipyam [19] and 775–772 cm^{-1} in dipica [6] complexes). The pyridyl vibration should overlap the C-H oop bending of the phenyl substituent: in I there is a near absorption peak at 795 cm^{-1} (masked probably in **II** an **III** by the broad vPF_6 band), but this is a value very high for a monosubstituted benzene (usual absorption range 747–737 cm⁻¹ [20]), considering also that the C-C oop frequency of the phenyl is regular for all the complexes (about 694 cm⁻¹; foreseen 701–694 cm⁻¹ [20]).

In the 200–400 cm⁻¹ region the spectral patterns of $[Cu_2(phdpa)_2Cl_3]PF_6$ and $[Cu(phdpa)Cl]PF_6$ complexes show only subtle differences, except for the relative peak heights of PF_6^- and ligand. The spectra of the two compounds differ completely, however, in the far IR field, where only the frequencies of the δ (pyridyl ring) are similar (II, 423 cm⁻¹; III, 425 cm⁻¹). The v(Cu–N) (weak) is tentatively assigned to 350 cm⁻¹ in II and to 336 cm⁻¹ in III; for the v(Cu–Cl) frequencies possible attributions are 260 (terminal) and 196 (bridging) cm⁻¹ in II, but no suggestions at all can be advanced for III, where many bands of similar absorption intensity are present. In I the δ -pyridyl absorption should be at 435 cm⁻¹, the v(Cu–N) at 324 cm⁻¹ and the Cu–Cl stretchings, two in agreement with the different bonding distances of the chlorine atoms, at 259 and 210 cm⁻¹.



Fig. 1. ORTEP view of the molecular $[Cu(phdpa)Cl_2]$ complex (I), with the atomic numbering scheme (dotted lines indicate the hydrogen bonds).

Table 3		
Selected bond lengths (Å)	and bond angles (°)	for [Cu(phdpa)Cl ₂] (I)

Bond lengths			
Cu-Cl1	2.275(1)	C5-C6	1.506(5)
Cu-Cl2	2.366(1)	C6-N2	1.477(4)
Cu-N1	1.994(3)	N2-C13	1.452(4)
Cu-N2	2.212(3)	N2-C7	1.475(4)
Cu-N3	1.984(3)	C7-C8	1.496(4)
N1-C1	1.345(5)	N3-C8	1.356(4)
N1-C5	1.345(4)	N3-C12	1.336(4)
Bond angles			
Cl1-Cu-Cl2	123.95(4)	Cu-N1-C1	124.9(2)
Cl1-Cu-N2	127.56(7)	Cu-N1-C5	116.0(2)
N2-Cu-Cl2	108.47(7)	C1-N1-C5	119.1(3)
N1-Cu-Cl1	95.30(8)	Cu-N2-C6	103.8(2)
N1-Cu-Cl2	94.31(8)	Cu-N2-C7	98.2(2)
N1-Cu-N2	81.1(1)	Cu-N2-C13	112.0(2)
N3-Cu-Cl1	96.37(8)	Cu-N3-C8	114.2(2)
N3-Cu-Cl2	91.39(8)	Cu-N3-C12	126.1(2)
N3-Cu-N2	80.0(1)	C8-N3-C12	119.7(3)
N1-Cu-N3	161.2(1)	C5-C6-N2	112.3(3)
C8-C7-N2	109.0(3)	C6-N2-C7	113.4(3)
Relevant hydrogen b	onds		
$C18{-}H18{\cdots}N1$	3.377(5)	C18-H18-N1	132(1)
$H18 \cdots N1$	2.68(1)		
$C1-H1\cdots Cl1$	3.370(4)	C1-H1-Cl1	110(1)
H1···Cl1	2.94(1)		
$C12-H12\cdots Cl1$	3.370(4)	C12-H12-Cl1	112(1)
H12···Cl1	2.91(1)		
$C12{-}H12{\cdot}\cdot\cdot Cl1'$	3.529(3)	C12-H12-Cl1'	141(1)
H7···O3‴	2.76(1)		
$C11-H11\cdots Cl2''$	3.662(4)	C11-H11-Cl2"	144(1)
$H11 \cdot \cdot \cdot Cl2''$	2.87(1)		
C7-H7A-Cl1'''	3.627(4)	C7-H7A-Cl1‴	144(1)
H7A···Cl1‴	2.80(1)		

Symmetry codes: ' -x, 1-y, 2-z; "x, y, 1+z; "" 1/2-x, -1/2+y, 3/2-z.

3.2.2. Electronic spectra

The visible absorption spectra of **I**, **II** and **III** in methanol show the same pattern, with the maximum of a broad band centered at 695 nm, so that complex moieties of the same nature should be present in solution for all the three complexes. In agreement with this result, for theoretically equal molar concentrations of the compounds, the molar absorptivity of $[Cu_2(phd-pa)_2Cl_3]PF_6$ ($\varepsilon = 348 \text{ M}^{-1} \text{ cm}^{-1}$), is approximately equal to the sum of those of the other complexes (**I**, $\varepsilon = 200$; **III**, $\varepsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$) and hence the dimeric nature of **II** is destroyed in solution, as already suggested by its conductivity.

3.3. X-ray diffraction structures of I and II

The structure of I consists of discrete copper(II) neutral complexes (see Fig. 1) with the metal atom five-coordinated to three nitrogens from the terdentate phdpa and two chloride ions. Selected bond distances and angles are given in Table 3. The Cu-Cl1 bond distance (2.275(1) Å) is significantly shorter than the Cu–Cl2 one (2.336(1) Å) and the average Cu– N_{pyr} bond lenght [1.989(3) Å] is shorter than the Cu-N_{amine} one [2.212(3) Å]. The coordination geometry is intermediate between that of a trigonal bipyramid with the pyridine nitrogens occupying the axial sites and that of a distorted square pyramid with the terdentate phdpa ligand meridionally coordinated and the Cl2 atom defining the apical position. The complex is also stabilized by three intramolecular interactions. The N1 pyridine nitrogen is in fact involved in an intramolecular hydrogen bond with the adjacent C18-H18 ortho group of the aniline moiety, while the Cl1 acts as an acceptor atom in two intramolecular hydrogen bonds with the ortho C1-H1 and C12-H12 groups from the two pyridine rings of phdpa. Two nearly coplanar pseudo five-membered chelate rings and one pseudo six-membered chelate ring nearly orthogonal to the first two ones, are defined by these $C-H\cdots Cl$ and $C-H\cdots N$ intramolecular hydrogen bonds. Weak intermolecular C-H···Cl interactions, which do not include the C-H groups of the aniline moiety, determine the crystal packing.

When I reacts with NH₄PF₆, in methanol or water, only a partial substitution of the chloride with the PF₆⁻ is observed, which leads to the dimeric compound II, with the same Cu:L ratio. The crystal structure of II consists of $[Cu_2(phdpa)_2Cl_3]^+$ dinuclear cationic complexes, PF₆⁻ anions and methanol of crystallization. Selected bond distances and angles are given in Table 4. In the dinuclear complex (see Fig. 2) each copper(II) ion is fivecoordinated to three nitrogens from the terdentate phdpa and two chlorides in a distorted square pyramidal environment: the plane is defined by the nitrogens from the *meridionally* coordinated phdpa [the average Cu–

Table 4

Selected bond lengths (Å) and bond angles (°) for $[Cu_2(phd-pa)_2Cl_3]PF_6$.0.5MeOH (II)

Bond lengths			
Cu1-Cl1	2 235(2)	$Cu_2 - Cl_2$	2504(2)
Cu1 - C12	2.255(2)	$Cu_2 = Cl_2$	2.304(2) 2.244(2)
Cu1-N1	1 995(6)	Cu2 - N4	2.244(2)
Cul N2	2.000(5)	Cu2 N4	2.010(0)
Cul-N2	2.090(3) 1.072(6)	Cu2 = NS	2.080(3)
Cl = NS	1.975(0)	$Cu_2 = 100$	2.003(0)
CI = CO	1.48/(11) 1.402(8)	C19-C24	1.483(11)
CO-INZ	1.492(8)	C24-IN5	1.303(9)
N2-C13	1.468(9)	N5-C31	1.4/2(10)
N2-C/	1.46/(9)	N5-C25	1.4/4(10)
C/-C8	1.523(9)	C25-C26	1.516(9)
Bond angles			
N1-Cu1-N2	82.4(2)	N4-Cu2-N5	80.8(2)
N2-Cu1-N3	82.3(2)	N5-Cu2-N6	81.1(2)
N1-Cu1-Cl1	96.8(2)	N4-Cu2-Cl3	98.1(2)
N3-Cu1-Cl1	97.5(2)	N6-Cu2-Cl3	97.1(2)
Cl2-Cu1-Cl1	110.45(8)	Cl2-Cu2-Cl3	110.32(8)
Cl2-Cu1-N1	90.1(2)	Cl2-Cu2-N4	91.5(2)
Cl2-Cu1-N2	97.1(2)	Cl2-Cu2-N5	101.7(2)
Cl2-Cu1-N3	90.2(2)	Cl2-Cu2-N6	92.4(2)
N1-Cu1-N3	164.6(2)	N4-Cu2-N6	161.9(2)
N2-Cu1-Cl1	152.4(2)	N5-Cu2-Cl3	148.0(2)
Cu1-N1-C1	113 4(4)	$Cu_2 - N_4 - C_{19}$	114 6(4)
Cu1-N2-C6	104 0(4)	$Cu_2 - N_5 - C_{24}$	103 1(4)
Cu1 - N2 - C7	104 1(4)	$Cu_2 = N_5 = C_{25}$	105 9(4)
Cu1 - N2 - C13	112 5(4)	$Cu_2 = N_5 = C_{23}$	1113(4)
C6-N2-C7	112.3(1) 113.2(5)	$C_{24} = N_{5} = C_{25}$	113.0(5)
C_{1} C_{2} C_{1} C_{2} C_{3} C_{3}	113.2(5) 114.7(5)	Cu2 N6 C26	115.0(5) 115.5(5)
Cu1 = IN3 = Co	$150\ 00(0)$	Cu2-110-C20	115.5(5)
Cu1-Cl2-Cu2	139.90(9)		
Relevant hydrogen bon	ds		
C18-H18···NI	3.335(10)	C18-H18-N1	116(1)
H18···N1	2.82(1)		
$C5-H5\cdots Cl1$	3.314(9)	C5-H5-Cl1	119(1)
$H5 \cdot \cdot \cdot Cl1$	2.76(1)		
$C12-H12\cdots Cl1$	3.325(10)	C12-H12-Cl1	118(1)
$H12 \cdot \cdot \cdot Cl1$	2.78(1)		
$C32-H32 \cdot \cdot \cdot N4$	3.194(10)	C32-H32-N4	114(1)
$H32 \cdot \cdot \cdot N4$	2.70(1)		
C23-H23···Cl3	3.361(8)	C23-H23-Cl3	118(1)
H23···C13	2.82(1)		
C30-H30-Cl3	3.327(9)	C30-H30-Cl3	118(1)
H30···C13	2.79(1)		
$C3-H3\cdots Cl2'$	3.827(11)	C3-H3-Cl2'	150(1)
$H3 \cdot \cdot \cdot Cl2'$	2.99(1)		
$C3-H3\cdots Cl3'$	3.521(13)	C3-H3-Cl3'	122(1)
$H3 \cdot \cdot \cdot C13'$	2.94(1)		
$C10-H10\cdots Cl2''$	3.715(11)	C10-H10-Cl2"	155(1)
H10···Cl2"	2.85(1)		
$C27-H27\cdots Cl1''$	3.691(8)	C27-H27-Cl1"	156(1)
H27···Cl1″	2.82(1)		

Symmetry codes: (1-x, 1-y, 1-z; "1/2-x, -1/2+y, 1/2-z).

 N_{pyr} bond lengths, of 1.984(6) and 2.011(6) Å around Cu1 and Cu2, respectively, are almost similar to the relative Cu- N_{amine} bond distances of 2.090(5) and 2.086(5) Å] and by the more strongly bonded Cl1 and Cl3 chlorides [2.235(2) and 2.244(2) Å]. The apical position of both square pyramids is occupied by the Cl2 chlorine atom which thus acts as an unusual single



Fig. 2. ORTEP view of the $[Cu_2(phdpa)_2Cl_3]^+$ cations in II, with the atomic numbering scheme (dotted lines indicate the hydrogen bonds).

and nearly linear chloride bridge: the Cu1-Cl2 and Cu2-Cl2 bond distances are 2.568(2) and 2.504(2) Å, respectively, and the Cu1-Cl2-Cu2 bond angle is $159.9(1)^{\circ}$. The coordination sphere around each copper ion in **II** is quite similar to that observed in **I**. In fact one pyridine nitrogen (N1 and N4) is involved in an intramolecular C-H···N hydrogen bond with an adjacent ortho C-H group from the aniline moiety (C18-H18 and C32-H32) and each equatorial chloride atom (Cl1 and Cl3) acts as a two hydrogen bonds acceptor with respect to a pair of ortho C-H groups from pyridine rings (C5-H5, C12-H12 and C23-H23, C30-H30). Moreover the mutual arrangement of the coplanar pseudo five-membered and of the pseudo sixmembered chelate rings is very similar to that found in I. Thus, complex II can be considered as formed by two square pyramidal complexes of type I, related by a pseudo twofold axis passing through the bridging Cl2 atom at the apical positions. In II the electrostatic interactions between cationic complexes and anions predominate over the weak intermolecular Cl interactions with the adjacent C-H groups of the pyridine rings, making the ionic bond the driving force for the crystal packing.

The triple intramolecular hydrogen-bond system around each metal atom in I and II, although weak, represents the most striking feature of the structure of these compounds. This hydrogen bonding seems to play a key role in determining the stability of the [Cu(phdpa)Cl]⁺ moiety and probably influences the exchange properties of compound I with incoming $({\rm PF_6}^-$ ions), as well as with leaving ligands (chloride ions). In fact it can justify that in the reaction of I with NH₄PF₆ it is possible to obtain new compounds only through the substitution of the more weakly bonded chloride Cl2 with one PF_6^- ion (in CH₃CN) giving the compound III or with another [Cu(phdpa)Cl₂] molecular unit (in methanol or water) giving the cation complex II, while compounds with complete exchange of chloride with PF_6^- were never obtained.

Also the impossibility of obtaining copper(II) complexes with Cu:L ratio 1:2 in the presence of chloride ions seems due to the stability of the [Cu(phdpa)Cl] moiety, which could prevent the binding of a second tridentate phdpa ligand.

An unusual aspect of **II** concerns the single and nearly linear chloride bridge between two copper atoms. To our knowledge the only other dimeric copper complexes with a single chloride bridge are: $[Cu_2(tet b)_2Cl]^{3+}$ (tetb = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclodecane) [21], which contains a tetra-amino macro- $[Cu_2(py2)_2Cl_3]^+$ cvclic ligand. (py2 = bis(2-(2pyridyl)ethylamine) [22] containing a nitrogen tridentate ligand similar to dipica and $[Cu_2(bzpy)_2Cl_3]^+$ (bzpy = benzyl(2-pyridylmethyl)amine) [23], with a N₃ tridentate ligating group similar to phdpa. Of these three compounds only the latter shows two crystallographically independent copper(II) ions [Cu-Cl = 2.639(1)] and 2.695(1) Å, Cu-Cl-Cu = $136.9(1)^{\circ}$], while, in the first two, the metals are related by a twofold axis passing through the chloride bridge (Cu-Cl = 2.501(4) Å, Cu- $Cl-Cu = 174.2(6)^{\circ}$ for $[Cu_2(tet b)_2Cl]^{3+}$ and Cu-Cl =2.549 Å, Cu–Cl–Cu = $178.0(1)^{\circ}$ for $[Cu_2(py2)_2Cl_3]^+$).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 176390 (I) and 176391 (II). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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