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Anion binding by a copper(II) complex of a reinforced open-chain tetramine

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Abstract

The copper(II) complex of the reinforced tetramine **2** (1,3-propane-bis-[1-methyl-4-piperazine]) $[Cu^{II}(\mathbf{2})](ClO_4)_2$, exhibits a square-pyramidal geometry, with a perchlorate anion in the apical position. The $[Cu^{II}(\mathbf{2})]^{2+}$ species, in an MeCN solution, binds inorganic anions, to give five-coordinated complexes. Binding selectivity reflects the intensity of the metal–anion interaction, as shown by a satisfactory correlation with d–d spectral properties. Comparison with the anion binding tendencies of the square planar copper(II) complex of the plain tetramine **1** (*N,N′*-bis(-2-aminoethyl)-propane-1,3-diamine) discloses the inference of steric repulsive effects in the formation of the square-pyramidal adducts. ***To cite this article: M. Boiocchi et al., C. R. Chimie 8 (2005)***.

Résumé

Le complexe de cuivre **II** de la tétramine **2** renforcée, $[Cu^{II}\ (\mathbf{2})](ClO_4)_2$, montre une géométrie de plan carré pyramidal, avec un anion perchlorate en position sommitale. Les espèces $[Cu^{II}\ (\mathbf{2})]^{2+}$ avec un MeCN reliant les anions inorganiques pour donner des complexes de coordination 5. Cette liaison sélective met en évidence l'intensité de l'interaction métal–anion, comme le montre de manière satisfaisante la corrélation avec les propriétés spectrales d–d. La comparaison avec les dispositions liantes de l'anion du complexe de plan carré du cuivre **II** de la tétramine **1** montre l'influence des effets stériques répulsifs dans la formation des adduits de plan carré pyramidal. ***Pour citer cet article : M. Biocchi et al., C.R. Chimie 8 (2005)***.

Keywords: Polyamine ligands; Copper(II) complexes; Anion recognition; Halide ions

Mots clés: Ligands polyamines; Complexes du cuivre (II); Reconnaissance anionique; Ions halogénure

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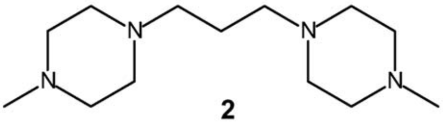
1. Introduction

Polyamine ligands form stable complexes with 3d metal ions. Stability increases with ligand's denticity due to the chelate effect [1]. In the case of copper(II), the highest binding affinity is observed with linear tetramines, which fulfil the stereochemical penchant of the metal of being four-coordinated, according to a square planar geometry [2]. Among linear tetramines, the greatest coordinating tendencies are shown by ligand **1** (*N,N′*-bis(-2-aminoethyl)-propane-1,3-diamine, currently named 2.3.2-tet, in view of the number of carbon atoms connecting the four amine groups), which possesses the right length to encompass the corners of the square [3]. Indeed, the crystal structure of the $[Cu^{II}(\mathbf{1})](ClO_4)_2$ complex salt indicates co-planar tetramine coordination, with the two perchlorate ions at a large distance along *z* axis [4].

1



2

We consider here the coordinating tendencies of the linear tetramine **2** (1,3-propane-bis-[1-methyl-4-piperazine]), which possesses the same 2.3.2 carbon skeleton as **1**, but in which each link between middle and terminal nitrogen atoms is *reinforced* by a further ethylenic chain. Due to the presence of a methyl substituent on each terminal nitrogen atom, ligand **2** possesses four tertiary amine groups, a feature that is expected to reduce its coordinating tendencies towards metal ions. The $[Cu^{II}(\mathbf{2})](ClO_4)_2$ complex salt was isolated as a crystalline solid and its molecular structure was determined. The binding affinity of the $[Cu^{II}(\mathbf{2})]^{2+}$ cation towards some selected inorganic anions in an MeCN solution was investigated and compared to that of the precursor complex $[Cu^{II}(\mathbf{1})]^{2+}$.

2. Results and discussion

2.1. Complex formation in solution

Binding of Cu^{II} by the reinforced tetramine **2** cannot be investigated in water through conventional pH-metric techniques (which typically involve the titration with standard base of a solution containing equimolar amounts of ligand and metal salt, plus excess of strong acid). In fact, precipitation of copper(II) hydroxide precedes complexation, indicating very low stability of the $[Cu^{II}(\mathbf{2})]^{2+}$ complex species. The low stability has to be ascribed to two distinct factors: (i) the presence of four tertiary amine nitrogen atoms; (ii) the presence of two piperazine rings in the ligand framework. In fact, in the uncomplexed ligand, the two piperazine subunits probably exist in the more stable *chair* conformation. When coordinating the metal ion, piperazine has to change to the less stable *boat* conformation, as shown by the crystallographic study (vide infra): the enthalpy of such a conformational change, in the gas phase, corresponds to 5.34 kcal mol^{-1} [5]. It has been shown that the aqueous Cu^{II} complex with the 3.2.3 tetramine containing a middle piperazine ring has a formation constant 9 log units lower than that of the corresponding complex with the plain 3.2.3 tetramine [6]. It is therefore reasonable that complexation by **2** is especially disfavoured and cannot compete with the hydroxide formation and precipitation. However, the $[Cu^{II}(\mathbf{2})]^{2+}$ complex forms in boiling *n*-butanol (i.e. in strict absence of water), from which can be precipitated as perchlorate salt. The $[Cu^{II}(\mathbf{2})](ClO_4)_2$ salt dissolves in MeCN as a stable species, but, when put in water, it decomposes with formation of the bluish precipitate of $Cu(OH)_2$.

2.2. The molecular structure of the $[Cu^{II}(\mathbf{2})]^{2+}$ complex

On slow diffusion of diethyl ether in an acetonitrile solution of $[Cu^{II}(\mathbf{2})](ClO_4)_2$, dark blue crystals suitable for X-ray diffraction studies were obtained. The structure of the metal complex is shown as an ORTEP plot in Fig. 1. Selected bond lengths and angles are listed in Table 1.

The Cu^{II} centre shows a *square-pyramidal* coordination geometry, with the oxygen atom of a perchlorate group occupying the axial position: the metal cen-

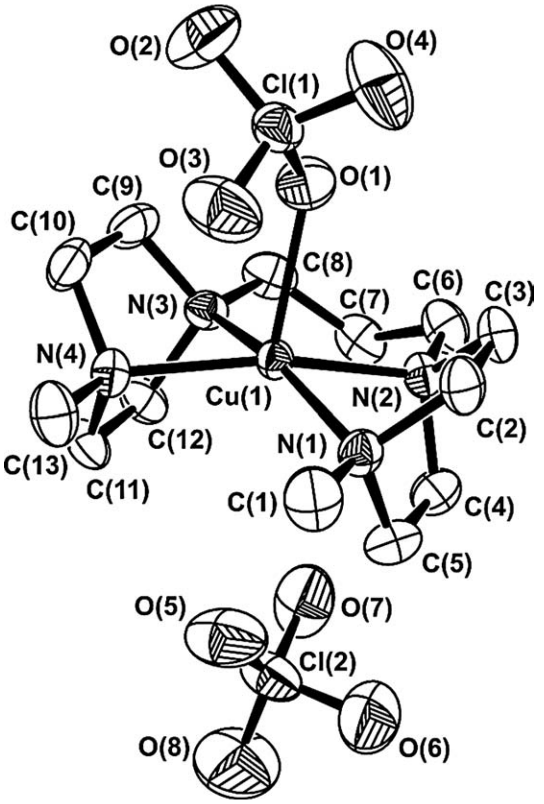


Fig. 1. An ORTEP view of $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$ (thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity): the Cu^{II} centre shows a *square-pyramidal* coordination, both piperazine rings are in the *boat* conformation, and the $[Cu^{II}(\mathbf{2})(ClO_4)]^{1+}$ moiety exhibits C_S symmetry (see text).

Table 1
Selected bond lengths (Å) and angles (°) for $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$

Cu(1)–N(1)	2.051(4)
Cu(1)–N(2)	2.030(4)
Cu(1)–N(3)	2.026(4)
Cu(1)–N(4)	2.064(4)
Cu(1)–O(1)	2.355(4)
N(1)–Cu(1)–N(2)	73.83(15)
N(1)–Cu(1)–N(3)	163.12(15)
N(1)–Cu(1)–N(4)	110.34(15)
N(2)–Cu(1)–N(3)	97.71(15)
N(2)–Cu(1)–N(4)	163.81(14)
N(3)–Cu(1)–N(4)	73.93(15)
O(1)–Cu(1)–N(1)	99.17(15)
O(1)–Cu(1)–N(2)	94.69(14)
O(1)–Cu(1)–N(3)	96.03(14)
O(1)–Cu(1)–N(4)	99.91(14)

tre lies above the N(1)–N(2)–N(3)–N(4) mean plane at a distance of 0.271(2) Å. The deviations of the four nitrogen atoms from the basal plane range between 0.005(2) and 0.006(2) Å. The Cu–N bond distances show values typically observed in copper(II) polyamine complexes: the distances to N(1) and N(4) atoms (bearing the terminal methyl groups) are only slightly longer than those observed to the middle nitrogen atoms N(2) and N(3), which are connected through a $–CH_2CH_2CH_2–$ chain. On the other hand, the axial Cu–O distance is especially short: this value is among the smallest observed for Cu^{II} complexes containing coordinated perchlorate anions and unequivocally characterises $Cu^{II}N_4O$ square-pyramidal geometries [7]. It has to be noted that in the parent $Cu^{II}(\mathbf{1})(ClO_4)_2$ complex salt, the copper centre shows an octahedrally distorted coordination geometry. In particular, the metal is co-planar with the basal nitrogen atoms (the deviation from the N_4 best plane being 0.03 Å) and the two axial Cu–O distances are 2.667 and 2.527 Å, i.e. in the range expected for octahedrally elongated copper(II) complexes. Thus, steric effects related to the presence of the piperazine rings seem to prevent the achievement of the most favoured co-planar coordination by the four amine nitrogen atoms in the $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$ complex and raise the copper centre above the N_4 plane. It has to be noted that in the corresponding perchlorate complex salt with the *N*,*N′*,*N″*,*N‴*-tetramethyl-cyclam derivative (Me_4cyclam), in spite of the presence of four tertiary amine nitrogen atoms, the Cu^{II} ion is co-planarly chelated by the macrocycle, according to an octahedrally elongated geometry: in particular, the axial Cu–O distances are both 2.72 Å [8]. In the $[Cu^{II}(\mathbf{2})(ClO_4)]^+$ complex, the two piperazine rings show very similar boat conformations, the puckering parameters being [9]: $q_2 = 0.870(4)$ Å, $q_3 = -0.013(5)$, $\Phi = -3.3(3)°$, $Q_T = 0.870(4)$ Å, $\theta = 90.8(3)°$, for the ring containing N(1) and N(2) atoms; $q_2 = 0.872(5)$ Å, $q_3 = -0.006(5)$, $\Phi = 3.0(4)°$, $Q_T = 0.872(5)$ Å, $\theta = 90.4(3)°$ for the other ring. The deviations from the C(2)–C(3)–C(4)–C(5) best planes are 0.025(3) for all the four C atoms, 0.739(6) Å for N(1), and 0.765(6) Å for N(2); those respect of the C(9)–C(10)–C(11)–C(12) best plane are 0.022(3) for the four C atoms, 0.760(6) Å for N(3), and 0.747(6) for N(4). The N–N vertex–vertex distances are 2.451(6) Å [N(1)–N(2)] and 2.460(6) Å [N(3)–N(4)].

The presence of two piperazine rings with *boat* conformation strongly reduces the N(1)–Cu(1)–N(2) and the N(3)–Cu(1)–N(4) bond angles (73.83° and 73.93°, respectively). Note that in the $Cu^{II}(\mathbf{1})(ClO4)_2$ complex, corresponding angles are 85.30° and 85.24°. The two piperazine boats also force the C(1), C(6), C(8), and C(13) atoms to lie in the N(1)–N(2)–N(3)–N(4) mean-plane (the deviations respect of the amine best plane are in the range 0.028(8)–0.051(7) Å). In this way, the $[Cu^{II}(\mathbf{2})(ClO_4)_1]^+$ moiety shows C_S symmetry because it results characterised by a non-crystallographic mirror plane normal to the N4 best plane and passing through the Cu(1), C(7), O(1), Cl(1), and O(3) atoms. This atomic arrangement, in which the two terminal methyl groups remain in the amine best plane, produces (probably due to steric effects) an anomalous increase of the N(1)–Cu(1)–N(4) bond angle with respect to the value observed in the $Cu^{II}(\mathbf{1})(ClO_4)_2$ complex (95.47°).

The hexa-atomic chelate ring adopts a *chair* conformation: N(2)–N(3)–C(6)–C(8) atoms are very co-planar [the deviations from the best plane are in the range 0.001(2)–0.002(3) Å], Cu(1) is placed at 0.309(6) Å above the best plane and C(7) 0.739(7) Å below.

2.3. Interaction with inorganic anions in MeCN solution

On dissolving the $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$ complex salt in MeCN, a blue solution is obtained, whose absorption spectrum shows a band centred at 552 nm ($\varepsilon = 430\ M^{-1}\ cm^{-1}$). It is hypothesised that the spectrum pertains to the $[Cu^{II}(\mathbf{2})(MeCN)]^{2+}$ chromophore, in which a solvent molecule has replaced the perchlorate ion in the axial position of the square pyramid, observed in the solid complex salt. In fact, ClO_4^- is a poorly coordinating anion, which cannot compete with the MeCN ligand, present in overwhelming amount in an acetonitrile solution. Moreover, addition even of a large excess of Bu_4NClO_4 to the solution did not induce any modification of the spectrum, thus confirming lack of metal complex–anion interaction. On the other hand, on addition of Bu_4NCl, the solution changed its colour from violet to blue, while significant variations were observed in the absorption spectrum.

Fig. 2 displays the family of spectra obtained on titrating an MeCN solution 1.0×10^{-3}M in $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$ with a standard MeCN solution of Bu_4NCl. In particular, on chloride addition, the intensity of the band at 552 nm decreases, while a new band forms and develops at 676 nm. A sharp isosbestic point, at 610 nm, indicates that two species are present at the equilibrium. Moreover, a plot of the absorbance at 676 nm vs. the added equivalent. of chloride shows a saturation profile, a plateau being reached after the addition of 1 equiv (limiting absorbance value: 380 M^{-1} cm^{-1}). All the above evidences indicate that the following equilibrium is established in solution:

$$[Cu^{II}(\mathbf{2})(MeCN)]^{2+} + Cl^- \rightleftharpoons [Cu^{II}(\mathbf{2})(Cl)]^+ + MeCN \qquad (1)$$

Moreover, a log*K* value of 5.87 ± 0.07 was calculated through non-linear least-squares fitting of the titration profile shown in the inset of Fig. 2 [10]. The same titration experiments were carried out with a variety of tetrabuthylammonium salts, which included: bromide, iodide, thiocyanate and nitrate. In all cases, a decrease of the intensity of the band at 552 nm was observed, while a new absorption band formed and developed at a longer wavelength. The value of λ_{max} of the developing band with the corresponding value of the limiting absorbance, ε, are reported in Table 2. In all cases, the absorbance vs. anion equiv. showed a saturation profile and indicated 1:1 stoichiometry. Thus, it is suggested that an anion complexation equilibrium similar to (1) takes place. The corresponding equilibrium constants, calculated through least-squares processing of the titration curve [10], are reported as log*K* in Table 2.

The observed sequence of anion affinity ($Cl^- > Br^- > I^- > NCS^- > NO_3^-$) does not parallel the sequence of the solvation terms. In fact, the smallest chloride ion, in view of the highest value of the charge/radius ration, should be highly solvated and the very endothermic desolvation term should disfavour its binding to Cu^{II}. On the contrary, binding affinity decreases with the decreasing anion charge density, *q*/*r* and solvation, Thus, binding affinity has to be rather related to another energy term, for instance the intensity of the metal–ligand (Cu^{II}–X) interaction. In particular, it is observed that anion binding to the $[Cu^{II}(\mathbf{2})(MeCN)]^{2+}$ complex induces a different red-shift of the d–d absorption band: the magnitude of the shift decreases along the series: $Cl^- > Br^- > I^- > NCS^- > NO_3^-$, thus paralleling the log*K* sequence.

In particular, log*K* and $\Delta\nu$ are linearly correlated, as shown in the plot in Fig. 3 ($\Delta\nu$ is the difference of ν_{max} values of the $[Cu^{II}(\mathbf{2})(MeCN)]^{2+}$ and $[Cu^{II}(\mathbf{2})(X)]^+$

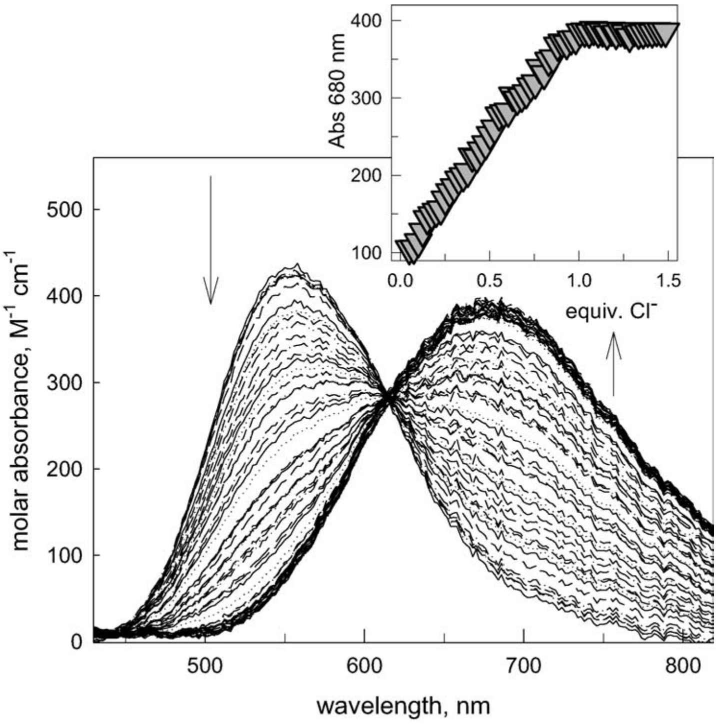


Fig. 2. Spectra recorded in the course of the titration of an MeCN solution of [Cu^{II}(**2**)(ClO$_4$)]ClO$_4$ with a standard solution of Bu$_4$NCl. The inset shows the change of the absorbance at 680 nm on addition of chloride equivalents.

complexes). The broad bands observed for the two square-pyramidal complexes [Cu^{II}(**2**)(MeCN)]$^{2+}$ and [Cu^{II}(**2**)(X)]$^+$ are the envelope of three transitions: $z^2 \rightarrow xz, yz$; $z^2 \rightarrow x^2 - y^2$; $z^2 \rightarrow xy$ [11,12]. In particular, one could assume that the maximum of the observed band coincides with the energy of the middle transition $z^2 \rightarrow x^2 - y^2$, which is related to the energy of the axial Cu^{II}–X interaction. Linear correlation indicates that log *K* strongly depends upon the energy of the metal–anion coordinative bond, while the observed sequence characterises the donor tendencies of X$^-$ as an apical ligand in a square-pyramidal complex.

Table 2
Data pertinent to the equilibrium: [Cu^{II}(**2**)(MeCN)]$^{2+}$ + X$^-$ ⇌ [Cu^{II}(**2**)(X)]$^+$ + MeCN, in an MeCN solution, at 25 °C. λ_{max} and ε (limiting molar absorbance) refer to the [Cu^{II}(**2**)(X)]$^+$ chromophore

X$^-$	log*K*	λ (nm)	ε (M^{-1} cm^{-1})
Cl$^-$	5.87 ± 0.07	676	380
Br$^-$	5.48 ± 0.03	670	400
I$^-$	5.18 ± 0.09	665	330
NCS$^-$	4.33 ± 0.03	638	390
NO$_3^-$	0.97 ± 0.05	572	350

For comparative purposes, we wanted to investigate the anion binding tendencies of the corresponding copper(II) complex with the parent tetramine 2.3.2-tet, **1**. Thus a red–violet MeCN solution of the

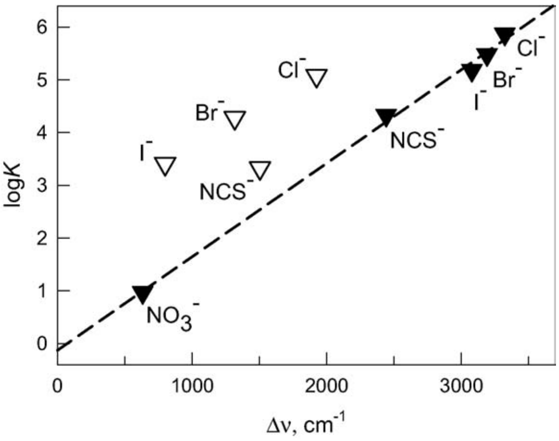


Fig. 3. Plot of log*K* values for the anion binding equilibrium to [Cu^{II}(**2**)]$^{2+}$ (filled triangles) and to to [Cu^{II}(**1**)]$^{2+}$ (open triangles) vs. Δ*v*. Δ*v* = v_{max}([Cu^{II}(L)(X)]$^+$) – v_{max}([Cu^{II}(L)]$^{2+}$), *L* = **1**, **2**.

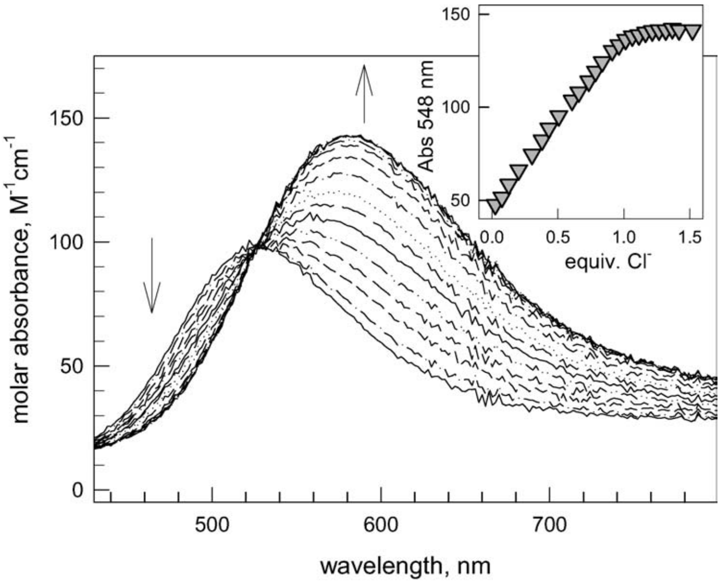


Fig. 4. Spectra recorded in the course of the titration of an MeCN solution of $[Cu^{II}(\mathbf{1})](ClO_4)_2$ with a standard solution of Bu_4NCl. The inset shows the change of the absorbance at 548 nm on addition of chloride equivalents.

$[Cu^{II}(\mathbf{1})](ClO_4)_2$ complex salt was titrated with the same tetrabutylammonium salts as $[Cu^{II}(\mathbf{2})(ClO_4)]ClO_4$. On chloride addition the colour of the solution turned blue. Fig. 4 shows the family of spectra taken during the titration. It is seen that the band of the $[Cu^{II}(\mathbf{1})]^{2+}$ complex, centred at 525 nm ($\varepsilon = 100\ M^{-1}\ cm^{-1}$), decreases, while a new band forms and develops at 584 nm, to reach a limiting value of molar absorbance $\varepsilon = 140\ M^{-1}\ cm^{-1}$ after the addition of 1 equiv. of chloride. The titration profile is shown in the inset.

Also in the present case, it is suggested the occurrence of an association equilibrium, as represented below:

$$[Cu^{II}(\mathbf{1})]^{2+} + Cl^- \leftrightarrows [Cu^{II}(\mathbf{1})(Cl)]^+ \qquad (2)$$

It is proposed that the $[Cu^{II}(\mathbf{1})]^{2+}$ complex maintains in solution the highly distorted octahedral (nearly square planar) geometry observed in the solid complex. The presence of a centre of symmetry in the complex accounts for the much lower value of the molar absorbance ($100\ M^{-1}\ cm^{-1}$), compared to the square-pyramidal complex $[Cu^{II}(\mathbf{2})(MeCN)]^{2+}$ ($\varepsilon = 430\ M^{-1}\ cm^{-1}$). On chloride addition, a five-coordinated species forms, to which a square-pyramidal geometry is tentatively assigned. However, it is believed that anion binding does not displace the Cu^{II} centre significantly above the N_4 plane. In fact, limiting molar absorbance does not increase too much ($\varepsilon = 140\ M^{-1}\ cm^{-1}$), which indicates only a moderate loss of symmetry (that would suggest that the metal centre is not displaced too much from the N_4 plane on anion coordination). In any case, substantial metal–anion axial interaction is established, as indicated by the distinct red shift of the band, λ_{max} moving from 552 nm to 584 nm.

Similar behaviour was observed on titration with bromide, iodide and thiocyanate salts. The association constants, calculated through non-linear least-squares fitting of the spectrophotometric titration profiles, are reported in Table 3, together with λ_{max} and ε values of the $[Cu^{II}(\mathbf{1})(X)]^+$ complex.

On the other hand, even addition of a large excess of $[Bu_4N]NO_3$ did not cause any spectral modification, indicating no anion interaction with the copper(II) tetramine complex. In Fig. 3, log *K* values are plotted vs. corresponding $\Delta\nu$ values (open triangles). It is seen that halide ions fit quite well a straight line parallel to that

Table 3
Data pertinent to the equilibrium: $[Cu^{II}(\mathbf{1})]^{2+} + X^- \rightleftharpoons [Cu^{II}(\mathbf{2})(X)]^+$, in an MeCN solution, at 25 °C. λ_{max} and ε (limiting molar absorbance) refer to the $[Cu^{II}(\mathbf{1})(X)]^+$ chromophore

X^-	log*K*	λ (nm)	ε ($M^{-1}\ cm^{-1}$)
Cl^-	5.08 ± 0.02	584	140
Br^-	4.28 ± 0.04	564	130
I^-	3.41 ± 0.01	548	81
NCS^-	3.33 ± 0.01	570	99

observed in the case of the reinforced tetramine complexes, while NCS^- does not correlate. We could tentatively assume that the 'bad' behaviour of the ambidentate thiocyanate ligand is related to its binding mode, which may differ when moving from complex $[Cu^{II}(\mathbf{2})(NCS)]^+$ to $[Cu^{II}(\mathbf{1})(NCS)]^+$.

Comparison of data in Fig. 3 suggests some considerations: (*i*) the energy of the axial coordinative interaction is the most important term determining the selective affinity of $[Cu^{II}(\mathbf{2})]^{2+}$ and $[Cu^{II}(\mathbf{1})]^{2+}$ complexes towards anions; (*ii*) axial binding seems stronger in the $[Cu^{II}(\mathbf{2})]^{2+}$ complex, which is pre-organised to five-coordination, as shown by the larger values of $\Delta\nu$. However, the $[Cu^{II}(\mathbf{1})]^{2+}$ complex is able to discriminate halide anions much better than the $[Cu^{II}(\mathbf{2})]^{2+}$ complex: this results by the significant difference of $\Delta\nu$ values, which reflects the varying intensity of the axial interaction; (*iii*) the 'straight line' of complex $[Cu^{II}(\mathbf{1})(X)]^+$ (for halides) lies ca. 2 log units above the straight line of the $[Cu^{II}(\mathbf{2})(X)]^+$ complex: the corresponding energy (ca. 3 kcal mol^{-1}) should reflect the steric repulsive effects which arise on anion coordination to the reinforced tetramine complex and which do not operate in the case of the complex with the plain tetramine **1**.

3. Conclusions

There exists a current interest on anion recognition and sensing, in view of the relevant role anions play in environmental sciences and biomedicine [13]. In most cases, recognition is based on electrostatic interactions, which are not especially strong and are adirectional. Coordinatively unsaturated metal complex can behave as more efficient receptors for anions, due to the higher intensity of the metal–ligand interactions and to their defined directionality. A convincing example in this sense has been shown by this investigation. In particular, we have demonstrated that a copper(II) tetramine complex can be a good receptor for inorganic anions, which give five-coordinated species. Anion binding tendencies can be enhanced by preorienting the metal centre to a square-pyramidal geometry. This goal has been achieved through the used of a sterically hindered tetramine like **2**.

4. Experimental section

4.1. 1,1′-(1,3-Propandiyl)bis-(4-methyl-piperazine) (2)

To a stirred solution of 1-methylpiperazine (5.00 g, 49.89 mmol) in acetonitrile (40 ml), K_2CO_3 (6.9 g, 49.9 mmol) and KI (in catalytic amount) were added. The solution was stirred at 60 °C and a solution of 1,3-dibromopropane (5.14 g, 25.84 mmol) in acetonitrile (10 ml) was added. The resulting mixture was stirred at 60 °C for 24 h and then the solvent was removed under *vacum*. The crude product was purified by liquid chromatography (Al_2O_3, $CH_2Cl_2/MeOH/NH_3$ 50:9:1, $R_f = 0.25$); yield 81%. MS (ESI): *m/z* 241.4 $[M^+H]^+$.

4.2. $[Cu(\mathbf{2})](ClO4)_2$

A solution of $Cu^{II}(ClO_4)_2{\cdot}6H_2O$ (2.5 mmol, 0.926 g) in butanol was added to a solution of the ligand **2** (2.5 mmol, 0.601 g) in butanol. The mixture was refluxed for 2 h, and a violet precipitate formed. The solid was filtered, washed with cold methanol and dried (94% yield). Diffusion of diethyl ether into the mother liquor gave crystals suitable for X-ray crystallography. Elemental analysis: Calculated for $C_{13}H_{28}N_4Cl_2CuO_8$: C, 31.05%, H, 5.61%, N, 11.14%. Found: C, 31.90%, H, 5.58%, N, 11.21%.

4.3. Crystal-structure analysis

An irregular dark-blue fragment of ~ 0.75 × 0.60 × 0.50 mm^3 was used for single-crystal X-ray diffraction study. Intensity data were collected at ambient temperature on a Enraf-Nonius four-circle diffractometer, working with graphite-monochromatised Mo*Kα* X-radiation (λ 0.71073 Å), in the 2θ range 4–52°. Crystal data for $C_{13}H_{28}Cl_2CuN_4O_8$ are: $M = 502.84$, monoclinic $P2_1/c$ (no. 14), $a = 8.767$ (6) Å, $b = 15.798(2)$ Å, $c = 15.179(6)$ Å, $\beta = 109.68(3)°$, $V = 1979.5(16)$ Å^3, $Z = 4$, $\rho_{calc} = 1.687$ g cm^{-3}, $\mu = 1.42$ mm^{-1}.

Data reduction (including intensity integration, background, Lorentz and polarisation corrections) was performed using the WinGX package [14]. Absorption effects were evaluated with the psi-scan method [15] and absorption correction was applied to the data (0.394 and 0.489 min. and max. transmission factors).

Crystal structure was solved by direct methods (SIR 97) [16] and refined by full-matrix least-square procedures on F^2 using all reflections (SHELXL 97) [17]. All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogens were placed at calculated positions using the appropriate AFIX instructions and refined using a riding model. Refinement of 253 parameters converged to final R values of 0.0521 for 3172 intense reflections $[I_O > 2\ \sigma(I_O)]$ and 0.0660 for all 3867 data. The weighted final wR_2 values were 0.1398 for intense reflections and 0.1498 for all data (GOF = 1.062).

5. Supplementary material available

Crystal structure details have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, and allocated the deposition number CCDC 237872. Data can be obtained by contacting the CCDC.

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