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Halide ion inclusion into a dicopper(II) bistren cryptate containing 'active' 2,5-dimethylfuran spacers: The origin of the bright yellow colour

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1. Introduction

Anion recognition is a topic of current interest in supramolecular chemistry [1]. Recognition refers to the selective interaction of the host system – the receptor – with the anion – the guest. Selectivity mainly depends upon (i) the energy of the interaction and (ii) the match of the geometrical features of the receptor with those of the anion. The major part of the anion receptors described during the last two decades operated through electrostatic interactions (which include hydrogen bonding). Due to the intrinsic weakness of these interactions, formation of stable complexes requires a high level of preorganization of the receptor, which has to be designed taking into account the shape and the size of the anion. The highest level of preorganization is achieved with tridimensional systems, e.g. cages [2].



Indeed, one of the first deliberately designed receptors for anions was the hexa-ammonium ion derived from the bistren cryptand **1**, which is capable to include a variety of inorganic anions in

ABSTRACT

The inclusion of halide ions into a dicopper(II) bistren cryptate complex containing 2,5-dimethylfuran spacers has been investigated through spectrophotometric titration experiments in MeCN solution. X-ray diffraction studies on the 1:1 chloride inclusion complex have shown that the encapsulated halide ion and the furan oxygen atoms lie at an interacting distance. Such an interaction perturbs the energy of the halide-to-copper(II) charge transfer transition, which is shifted to the visible region. As a consequence, an intense yellow colour develops on halide inclusion. Such a colour change is not observed on chloride or bromide inclusion into the dicopper(II) bistren cryptate containing spacers which are not capable to interact with the encapsulated halide and do not perturb the charge transfer transition, e.g. 1,3-xylyl fragments.

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an acidic aqueous solution (pH \leq 5), to give stable 1:1 complexes [3]. Acidity is required in order to keep protonated the six secondary amine nitrogen atoms of the parent bistren cage and to provide the receptor a multi-positive charge. However, a positive charge can be more conveniently constituted by placing inside the cryptand two transition metal centres, e.g. Cu^{II} [4]. In particular, each metal goes to occupy a tren subunit, giving a complex species of trigonal bipyramidal geometry. When bound to the tren moiety, each Cu^{II} ion is coordinatively unsaturated and maintains one of the axial positions available to the coordination of the donor atom of a further ligand. As an example, the bistren cryptand **2**, in which the two tetramine subunits are linked by 1,3-xylyl spacers, is able to include, according to a cascade process, first two Cu^{II} ion, then an ambidentate ion X⁻, which bridges the two metal centres. to give the ternary dinuclear complex $[Cu_2^{ll}(2)X]^{3+}$ [5]. In particular, complexes with $X^- = N_3^-$ [6], NCO⁻ [6], HCO₃⁻ [7] have been isolated and structurally characterized through X-ray diffraction studies. Moreover, titration experiments in aqueous solution disclosed a nice and unprecedented geometrical selectivity in anion recognition. In particular, a peak diagram was observed when plotting log K of the inclusion equilibrium versus anion bite, i.e. the distance between two consecutive donor atoms of the anion [8]. The highest stability was observed with the N_3^- anion, which is capable of placing its terminal donor atoms in the axial positions of the two Cull(tren)²⁺ moieties of the dinuclear cryptate, without inducing any endoergonic rearrangement of the cage framework. Anions providing either a shorter (e.g. NO_3^{-}) or a longer bite length (e.g. NCS⁻) cause an unfavourable conformational reorganization of the cryptate skeleton, which is reflected in a drastic decrease of the inclusion constant (up to two orders of magnitude). Changing of the spacers linking the two tren subunits may change the recognition tendencies of the dimetallic cryptate. This behaviour is quite obvious when the length of the spacer is drastically modified. As an example, the dicopper(II) complex of cryptand 3 includes both aromatic and aliphatic dicarboxylates [9], and is tailor made for the encapsulation of the L-glutamate neurotransmitter (as well as of the glutarate ion, in which the two -COO⁻ groups are separated by the same number of carbon atoms: two [10]). However, drastic changes of anion recognition properties have been observed also when the nature of the spacer is changed, even if its geometrical feature are not seriously modified. This is the case of the dicopper(II) complex of cryptand 4, which contains 2,5-dimetylfuran spacers. The length of 2,5-dimethylfuran fragment is rather close to that of the 1,3-xylyl spacer; however, anion recognition properties of the $[Cu_2^{II}(4)]^{4+}$ complex are quite different from those of the $[Cu_2^{II}(\mathbf{2})]^{4+}$ analogue. In particular, the $[Cu_2^{II}(\mathbf{4})]^{4+}$ cryptate forms stable 1:1 inclusion complexes also with monoatomic anions like halides, which show an intense bright yellow colour [11]. Equilibrium studies in aqueous solution indicated the formation of the pertinent the $[Cu_2^{II}(\mathbf{4})X]^{3+}$ inclusion complex at pH ~ 5. On increasing pH, the halide was displaced from the cage by the OH⁻ ions, which formed a very stable emerald green complex, in which the hydroxide ion bridged the two metal centres, placed at an unusually short distance [12]. The strikingly different behaviour of the $[Cu_2^{II}(4)]^{4+}$ receptor with respect to $[Cu_2^{II}(2)]^{4+}$ was basically ascribed to a greater flexibility of the 2,5-dimethylfuran compared to 1,3-xylyl [13].

In this article, we intend to explore in detail the formation of the halide inclusion complexes of the $[Cu_1^{II}(4)]^{4+}$ receptor, with a special reference to the development of the intense yellow colour (of interest for the design of a colorimetric sensor for halides). In order to avoid the interference of the hydroxide ion, we have carried out equilibrium studies in anhydrous MeCN. The crystal and molecular structure of the chloride inclusion complex $[Cu_2^{II}(4)Cl]^{3+}$ has been determined and compared with that previously reported for the bromide analogue $[Cu_2^{II}(4)Br]^{3+}$ [11]. The surprisingly short dis-

tances between the halide ion and furan oxygen atoms is instrumental for interpreting the unique spectral features of the halide inclusion complexes.

2. Experimental

2.1. General procedures and materials

Cryptands **2** and **4** were prepared following described procedures [5,11]. In titration experiments, UV–Vis spectra were registered on a scanning Varian Cary 100 spectrophotometer. The cell holder was thermostatted at 25.0 °C, through circulating water. Tipically, aliquotes of a fresh tetrabutylammonium salt standard solution of the envisaged anion were added and the UV–Vis spectra of the samples were recorded. For chloride, the [Et₃Bn]Cl salt was used, All spectrophotometric titration curves were fitted with the HYPERQUAD program [14].

2.2. X-ray crystallographic studies

Synthetic single crystals of $[Cu_2^{II}(4)Cl]$ (ClO₄)₃ complex were of small dimension and of poor X-ray diffraction quality. Diffraction data were collected in the θ range 2–20° at ambient temperature by means of an Enraf-Nonius CAD4 four circle diffractometer, working with graphite-monochromatized Mo K α X-radiation (λ = 0.7107 Å). Intensities of reflections having θ greater than 20° were unobservable. Data reductions (including intensity integration, background, Lorentz and polarization corrections) were performed with the WinGX package [15]. Absorption effects were evaluated with the psi-scan method [16] and absorption correction was applied to the data (min./max. transmission factors were 0.562/0.915).

Crystal structure was solved by direct methods (SIR 97 [17]) and refined by full-matrix least-square procedures on F^2 using all reflections (SHELXL 97) [18]. However, the poor X-ray diffraction quality of the crystal prevented an anisotropic structure refinement for all non-hydrogen atoms. Therefore, only the two Cu^{II} centres and the Cl atoms were refined with unconstrained anisotropic

Table	1			

Crystal data i	for	investigated	crystal	S
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	$[Cu_2^{II}(\textbf{4})Cl] \ (ClO_4)_3$
Formula	C ₃₀ H ₄₈ Cl ₄ Cu ₂ N ₈ O ₁₅
Μ	1029.66
Colour	orange
Dimension (mm)	$0.35 \times 0.14 \times 0.07$
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
a (Å)	16.441(6)
b (Å)	9.969(5)
<i>c</i> (Å)	27.463(7)
β(°)	100.77(3)
$V(Å^3)$	4422.0(26)
Ζ	4
$\rho_{\rm calc} ({\rm g} {\rm cm}^{-3})$	1.547
F(000)	2120
μ Mo K α (mm ⁻¹)	1.275
Scan type	ω scans
θ Range (°)	2-20
Measured reflections	4210
Unique reflections	4090
R _{int}	0.1513
Strong data $[I_0 > 2\sigma(I_0)]$	1160
Refined parameters	327
R_1 , wR_2 (strong data)	0.1190, 0.2733
R_1 , wR_2 (all data)	0.3746, 0.3514
Goodness-of-fit	0.885
Maximum/minimum residuals (e Å ⁻³)	0.984/-0.843

atom displacement factors. The O atoms of the perchlorate counterions were treated as anisotropic species with U_{ij} components restrained to simulate an isotropic behaviour (ISOR instruction of SHELXL-97) and the C, N and O atoms forming the cryptand moiety were refined with isotropic atom displacement factors. All hydrogen atoms were placed at calculated positions with the appropriate AFIX instructions and refined using a riding model.

The slightly elevated R_1 and wR_2 agreement indexes measured for all reflections are due to the poor X-ray diffraction quality of the crystal, that shows only 28% of intensities with an $I/\sigma(I)$ ratio greater than 2 and an average $I/\sigma(I) = 2.52$. However, the final refined model does not exhibit any unacceptable chemical features and the obtained crystal structure is more than suitable for the aims of this study. Crystal data for studied crystal are shown in Table 1.

3. Results and discussion

3.1. The crystal and molecular structure of the $[Cu_2^{ll}(4)Cl]$ $({\it ClO}_4)_3$ complex salt

The X-ray crystallographic study showed that the crystal of the $[Cu_1^{II}(\mathbf{4})Cl]$ (ClO₄)₃ cryptate salt and that of the previously studied $[Cu_2^{II}(\mathbf{4})Br]$ (ClO₄)₃ cryptate salt [11] are isostructural. An ORTEP view of the $[Cu_2^{II}(\mathbf{4})Cl]^{3+}$ complex cation is displayed in Fig. 1, showing that the chloride anion is placed at the centre of the cage and bridges the two metal centres according to a collinear arrangement (Cu(1)-Cl(1)-Cu(2) angle = 179.1(5)°).

Selected geometrical features are reported in Table 2. Each Cu^{II} centre shows a trigonal-bipyramidal coordination geometry. The complex exhibits a C_{3h} molecular symmetry, with each metal centre slightly displaced from the best plane of the three secondary amine atoms (N₃) towards the chloride ion. Displacement from the N₃ plane is 0.17(1) Å for Cu(1) and 0.18(1) Å for Cu(2). The Cu^{II}...Cu^{II} distance (4.86(1) Å) is expectedly lower than that observed with the previously described $[Cu_2^{II}(4)Br]^{3+}$ complex (4.67(1) Å), due to the smaller size of the bridging halide ion. However, the difference of the Cu^{II}...Cu^{II} distances (0.19 Å) is distinctly smaller than the difference between the diameters of the two halide ions: 0.30 Å. Quite interestingly, the distances between the halide anion and the centroid of the furan rings are similar in the two dicopper(II) cryptates. In particular, pertinent values are in the range 3.25(2)–3.33(2) Å for $[Cu_2^{II}(4)Cl]^{3+}$ complex and



Fig. 1. ORTEP view of the $[Cu_2^{II}(4)Cl]^{3+}$ cationic cryptate (perchlorate counterions and hydrogen atoms have been omitted for clarity; ellipsoids are drawn at the 30% probability level). Only Cu and Cl atoms were refined with anisotropic atom displacement parameters, whereas isotropic displacement parameters were used for all remaining atoms.

Table 2

Selected bond distances (Å) and bond angles (°) involving the two Cu^{II} centres

Cu(1)-Cl(1)	2.337(9)	Cu(2)-Cl(1)	2.338(9)
Cu(1)-N(1)	2.007(24)	Cu(2)-N(4)	2.058(26)
Cu(1)-N(2)	2.029(22)	Cu(2)-N(3)	2.052(29)
Cu(1)-N(5)	2.073(18)	Cu(2)-N(6)	2.116(19)
Cu(1)–N(7)	2.089(23)	Cu(2)-N(8)	2.073(25)
Cl(1)-Cu(1)-N(2)	94.1(7)	Cl(1)-Cu(2)-N(3)	93.9(8)
Cl(1)-Cu(1)-N(5)	93.3(6)	Cl(1)-Cu(2)-N(6)	97.6(7)
Cl(1)-Cu(1)-N(7)	96.8(7)	Cl(1)-Cu(2)-N(8)	93.6(8)
N(1)-Cu(1)-N(2)	87.9(10)	N(4)-Cu(2)-N(3)	84.6(11)
N(1)-Cu(1)-N(5)	84.2(9)	N(4)-Cu(2)-N(6)	83.8(10)
N(1)-Cu(1)-N(7)	83.5(10)	N(4)-Cu(2)-N(8)	86.8(11)
N(2)-Cu(1)-N(5)	119.3(9)	N(3)-Cu(2)-N(6)	118.5(10)
N(2)-Cu(1)-N(7)	122.6(8)	N(3)-Cu(2)-N(8)	126.2(10)
N(5)-Cu(1)-N(7)	116.1(9)	N(6)-Cu(2)-N(8)	113.1(10)

3.28(1)–3.32(1) Å for the $[Cu_2^{II}(4)Br]^{3+}$ analogue. Quite significantly, these distances are markedly higher than the those between the halide anion and the proximate furan oxygen atoms. Actually, $O \cdots X$ distances range from 3.14(2) to 3.18(2) Å for the chloride inclusion complex and from 3.17(1) to 3.21(1) Å for the bromide analogue. These values are appreciably lower than the sum of the average van der Waals radii (1.75 + 1.52 = 3.27 Å for Cl···O; 1.85 + 1.52 = 3.37 Å for Br···O) [19]. This suggests the occurrence in both dimetallic complexes of a significant interaction between the furan oxygen atoms of the cage and the encapsulated halide anion. Such an evidence will be important for interpreting the unique spectral features of the $[Cu_2^{II}(4)CI]^{3+}$ and $[Cu_2^{II}(4)Br]^{3+}$ complexes (*vide infra*).

3.2. The behaviour of the $[Cu_2^{II}(4)]^{4+}$ complex in MeCN solution: chloride and bromide ion inclusion

Formation and stability of the $[Cu_2^{II}(4)]^{4+}$ complex in MeCN solution were investigated by carrying out spectrophotometric titration experiments. Fig. 2a shows the family of spectra obtained over the course of the titration of a solution 5.4 × 10⁻⁴ M of **4** with a standard solution of $Cu^{II}(CF_3SO_3)_2$.

On metal addition, well definite bands develop both in the UV and visible regions. High energy bands (300-400 nm) have an LMCT nature and refer to amine nitrogen atom to Cu^{II} charge transfer transitions. The broad band in the 600–900 nm interval (Fig. 2b) is the envelope of the d-d transitions pertinent to a d⁹ cation in a trigonal bipyramidal coordinative environment (each remaining axial position being probably occupied by a MeCN molecule). The titration profiles shown in Fig. 2c show a sharp discontinuity after the addition of 2 equiv. of Cu^{II}, which clearly indicates the formation of a stable complex of 1:2 ligand/metal ratio, whose formation constant is higher than 10^6 . It derives that solutions 10^{-3} – 10^{-4} M in **4** and 2×10^{-3} – 2×10^{-4} M in Cu^{II}(CF₃SO₃)₂ contain more than 99% of the $[Cu_2^{II}(4)]^{4+}$ complex. Thus, in anion recognition studies, solutions of the $[Cu_2^{II}(\mathbf{4})]^{4+}$ receptor have been safely prepared by dissolving in MeCN the bistren cryptand 4 and 2 equiv. of $Cu^{II}(CF_3SO_3)_2.$

Fig. 3a shows the complete family of spectra obtained over the course of the titration of an MeCN solution 5.3×10^{-4} M of $[Cu_2^{II}(4)]^{4+}$ with a standard MeCN solution of $[BnEt_3N]Cl$. On chloride addition the pale blue solution of the $[Cu_2^{II}(4)]^{4+}$ receptor begins to take a bright yellow colour, while drastic spectral changes are observed. In particular, an intense band centred at 410 nm develops up to more than 6000 M⁻¹ cm⁻¹, which is responsible for the intense yellow colour. Definite modifications are observed also in the d–d region of the spectrum (500–900 nm) (see Fig. 3b). The band centred at 410 nm results from a chloride-to-copper(II) charge transfer transition and is characterized by an



Fig. 2. (a) Spectra recorded over the course of the titration of a MeCN solution 5.4×10^{-4} M in **4**, with a standard solution of Cu^{II}(CF₃SO₃)₂. (b) d-d absorption bands. (c) Titration profiles at 370 and 750 nm.



Fig. 3. (a) Spectra recorded over the course of the titration of a MeCN solution 5.3×10^{-4} M in $[Cu_2^{II}(4)]^{4+}$, with a standard solution of $[BnEt_3N]Cl$. (b) d–d absorption bands. (c) Titration profiles at 440 and 650 nm.

energy much lower than observed in mononuclear complexes of type $[Cu^{II}(tren)CI]^+$, where the CI^- -to- Cu^{II} transition occurs at $\lambda \leq 350$ nm and overlaps with the amine-to- Cu^{II} transition (and the colour of the ternary complex is pale blue-green). Interesting pieces of information on the stoichiometry of the species which form in solution over the course of the titration experiment can be taken from the profiles displayed in Fig. 3b. It is observed that the CI^- -to- Cu^{II} CT band (filled triangles in Fig. 3c) increases until the addition of 1 equiv. of CI^- , then it decreases in intensity to disappear after the addition of 2 equiv. Discontinuity after the addition of 1 equiv. of chloride is observed also in the d–d region (see open triangles in Fig. 3c), suggesting the occurrence of drastic geometrical changes in the complex species present in solution. Moreover, a careful inspection of both titration profiles reported in Fig. 3 a indicates the existence of an inflection at 0.5 equiv.

The entire set of spectrophotometric titration data was analyzed with a non-linear least-squares procedure, using the HYPER-QUAD program [14]. Best fitting of titration data was obtained by assuming the occurrence of the following equilibria:

$$2[\operatorname{Cu}_{2}^{\mathrm{II}}(\mathbf{4})]^{4+} + \operatorname{Cl}^{-} \leftrightarrows \{[\operatorname{Cu}_{2}^{\mathrm{II}}(\mathbf{4})] \cdots \operatorname{Cl} \cdots [\operatorname{Cu}_{2}^{\mathrm{II}}(\mathbf{4})]\}^{7+}$$
(1)

$$\{[\mathbf{C}\mathbf{u}_{2}^{II}(\mathbf{4})]\cdots\mathbf{C}\mathbf{l}\cdots[\mathbf{C}\mathbf{u}_{2}^{II}(\mathbf{4})]\}^{7+}+\mathbf{C}\mathbf{l}^{-} \leftrightarrows 2[\mathbf{C}\mathbf{u}_{2}^{II}(\mathbf{4})]\mathbf{C}\mathbf{l}]^{3+}$$
(2)

$$[\mathsf{Cu}_2^{\mathrm{II}}(\mathbf{4})]\mathsf{Cl}]^{3+} + \mathsf{Cl}^- \leftrightarrows [\mathsf{Cu}_2^{\mathrm{II}}(\mathbf{4})]\mathsf{Cl}_2]^{2+} \tag{3}$$

Corresponding equilibrium constants are reported in Table 3 as $\log K$ values.

Fig. 4 shows the concentration profiles of the species which form over the course of the titration.

It can be noted that, on the very first additions of chloride, the complex species $\{[Cu_2^{II}(4)] \cdots Cl \cdots [Cu_2^{II}(4)]\}^{7+}$ forms, according to Eq. (1). In this species, which reaches its maximum concentration, ca. 30%, on addition of 0.5 equiv. of Cl⁻, the chloride ion is not included into the cage, but bridges two Cu^{II} ions of two distinct cryptate complexes. On further addition of chloride, the 1:1 complex $[Cu_2^{II}(4)]Cl]^{3+}$ appears as a major species. It is suggested that in this species the chloride ion is included into the cryptate and bridges the two Cu^{II} centres, as observed in the complex salt structurally investigated by X-ray diffraction studies. To the 1:1 inclusion complex the intense yellow colour corresponds, as indicated by the satisfactory superimposition of the absorbance profile of the Cl⁻-to-Cu^{II} charge transfer band (taken at 440 nm, open triangles in Fig. 4) with the concentration profile of the $[Cu_2^{ll}(4)]Cl]^{3+}$ species. The inclusion complex reaches its maximum concentration (more than 90%) on addition of 1 equiv. of Cl-. On further chloride

Table 3

 $\log K$ values for the equilibria occurring in a MeCN solution, at 25 °C with the systems $[Cu_1^{II}(4)]^{4+}/X^-$ (X = Cl, Br)

Equilibrium	Cl-	Br ⁻	Ι-
$2[Cu_2^{II}(4)]^{4+} + X^{-} \leftrightarrows \{[Cu_2^{II}(4)] \cdots X \cdots [Cu_2^{II}(4)]\}^{7+}$	13.2 ± 0.1	10.6 ± 0.1	4.46 ± 0.05
$\{[Cu_2^{II}(\boldsymbol{4})]\cdots X\cdots [Cu_2^{II}(\boldsymbol{4})]\}^{7+} + X^{-} \leftrightarrows 2[Cu_2^{II}(\boldsymbol{4})]X]^{3+}$	4.2 ± 0.1	2.8 ± 0.1	5.4 ± 0.1
$[Cu_2^{II}(4)]X]^{3+} + X^- \leftrightarrows [Cu_2^{II}(4)]X_2]^{2+}$	4.5 ± 0.1	4.0 ± 0.1	
$[Cu_2^{\mathrm{II}}(4)]^{4+} + X^- \leftrightarrows [Cu_2^{\mathrm{II}}(4)]X]^{3+}$	>6	>6	4.94 ± 0.03



Fig. 4. Concentration profiles of the complex species forming over the course of the spectrophotometric titration illustrated in Fig. 3. Profiles of the absorbances at 440 and 650 nm have been superimposed on the diagram.

addition, the concentration of the $[Cu_2^{II}(4)]Cl]^{3+}$ complex decreases and the yellow colour progressively vanishes, while the new species $[Cu_2^{II}(4)]Cl_2]^{2+}$ forms. It is suggested that in this complex two chloride ions are not included into the cage (a circumstance strongly disfavoured by electrostatic repulsions), but each anion should be coordinated to a Cu^{II} centre in a rather distorted mode. This may induce a rearrangement of the coordination sphere of each metal ion, which is signalled by a modification of the d–d absorption, as also indicated by the discontinuity of the titration profile on the d–d band (filled triangles in Fig. 4). On excess addition of chloride, the concentration of the $[Cu_2^{II}(4)]Cl_2]^{2+}$ complex tends to 100%, while the solution takes a pale blue-green colour. The development and the geometrical modifications of the three anion containing species over the course of the titration are pictorially illustrated in Fig. 5.

Thus, it appears that the intense yellow colour pertains specifically to the 1:1 inclusion complex $[Cu_2^{II}(4)]Cl]^{3+}$. The origin of this intense absorption at an unusually low energy has to be accounted for. It has been mentioned before that in typical $Cu^{II}(tetramine)Cl^+$ complexes the Cl^- -to- Cu^{II} charge transfer transition takes place in the UV region. However, it has been observed in the crystal structure of the $[Cu_2^{II}(4)]Cl]^{3+}$ complex that the distance between the encapsulated chlorine atom and the furan oxygen atom is well below the sum of average van der Waals radii, indicating interaction. It is now suggested that such an interaction raises the energy of the

 $p\pi$ level of chloride, which acquires an essentially antibonding character and from which the electron is excited to the d_{z^2} level of the metal. The energy of the transition, following Cl···O interaction, is therefore reduced, which makes the pertinent absorption band shift to the visible region. The Cl···O interaction cannot be established in the $\{[Cu_2^{II}(4)] \cdots X \cdots [Cu_2^{II}(4)]\}^{3+}$ species, where the bridging chloride ion is outside of the cage and far away from the furan oxygen atoms, and in the $[Cu_2^{II}(4)]Cl_2]^{2+}$ complex, in which the two coordinated anions, in order to minimize electrostatic repulsions, probably protrude outside of the cage. Thus, in the complexes $\{[Cu_2^{II}(4)] \cdots X \cdots [Cu_2^{II}(4)]\}^{3+}$ and $[Cu_2^{II}(4)]Cl_2]^{2+}$, the normal Cl⁻-to-Cu^{II} charge transfer transition takes place.

A completely analogous behaviour was observed with bromide. Fig. 6a shows the family of spectra taken over the course of the titration of an MeCN solution 5.3×10^{-4} M of $[Cu_2^{II}(4)]^{4+}$ with a standard MeCN solution of $[Bu_4N]Br$. Development and decrease of the absorption band associated to the Br⁻-to-Cu^{II} charge transfer transition are observed (see the absorbance profile in Fig. 6b). The same three bromide containing complex species ($\{[Cu_2^{II}(4)]\}^{-+}$, $[Cu_2^{II}(4)]Br]^{3+}$ and $[Cu_2^{II}(4)]Br_2]^{2+}$) formed in solution over the course of the titration. Log *K* values associated to the stepwise equilibria of type (1)–(3) are reported in Table 3. In all cases, log *K* values are lower than observed in the case of corresponding tendencies of bromide compared to chloride, generally observed in transition metal coordination chemistry. In Table 3, the log *K* values associated to the inclusion Eq. (4) are also compared.

$$\left[\mathsf{Cu}_{2}^{\mathrm{II}}(\mathbf{4})\right]^{4+} + \mathsf{X}^{-} \leftrightarrows \left[\mathsf{Cu}_{2}^{\mathrm{II}}(\mathbf{4})\right]\mathsf{X}\right]^{3+} \tag{4}$$

It is observed that inclusion of Cl⁻ is favoured by two orders of magnitude with respect to Br⁻, in agreement with what observed in an aqueous solution adjusted to pH = 5 [11]. In the present case, the halide-to-metal charge transfer band is shifted to 535 nm, which accounts for the intense egg-yellow colour. A nice superimposition of the absorbance profile (filled triangles in Fig. 6b) with the % concentration curve of the $[Cu_2^{II}(4)]Br]^{3+}$ inclusion complex is observed also in the present case. The establishing of a significant interaction between the encapsulated halide ion and the furan oxygen atoms, documented by the short low Br···O distance, crystallographically determined [11], has again to be invoked for justifying the low energy of the charge transfer band.

The question now is: does the intense yellow colour develop also on titration with chloride and bromide of dicopper(II) cryptates containing different spacers? Looking at the cryptate $[Cu_2^{II}(\mathbf{2})]^{4+}$, which possesses 1,3-xylyl spacers, the answer is not.



Fig. 5. Pictorial illustration of stepwise equilibria involving the three species: $\{[Cu_2^{II}(4)] \cdots [Cu_2^{II}(4)]\}^{7+}$, $[Cu_2^{II}(4)]X^{3+}$, $[Cu_2^{II}(4)]X_2]^{2+}$, which form over the course of the titration of a MeCN solution of $[Cu_2^{II}(4)]^{4+}$ with Cl^- . The largest sphere represents the halide ion.



Fig. 6. (a) Spectra recorded over the course of the titration of a MeCN solution 5.3×10^{-4} M in $[Cu_2^{II}(4)]^{4+}$, with a standard solution of $[Bu_4N]Br$. (b) Concentration profiles of the complex species forming over the course of the spectrophotometric titration experiment. The profiles of the absorbance at 460 nm has been superimposed on the diagram. On titration, the solution takes an egg-yellow colour.

In fact, on addition of either chloride or bromide, the pale blue solution of $[Cu_2^{II}(2)]^{4+}$ turns pale blue-green, a behaviour which can be accounted for by the spectrophotometric titration experiment. As an example, Fig. 7a displays the family of spectra taken over the course of the titration of an MeCN solution $5.02\times10^{-4}\,M$ of $[Cu_2^{II}(2)]^{4+}$ with a standard MeCN solution of $[Bu_4N]Br.$

The Br⁻-to-Cu^{II} charge transfer transition takes place at a much higher energy than observed for the furan containing cryptate and appears at 350–370 nm as a shoulder of the amine nitrogen-to-metal transition. The same three complex species observed for the $[Cu_2^{II}(4)]^{4+}$ receptor form over the course of the titration: $\{[Cu_2^{II}(2)]^{-1} \cdots [Cu_2^{II}(2)]\}^{7+}$, $[Cu_2^{II}(2)]Br]^{3+}$ and $[Cu_2^{II}(2)]Br_2]^{2+}$. The absorbance profile at 360 nm (filled triangles in Fig. 7c) does not show any inflection or discontinuity, but keeps increasing as far as the cryptate uptakes bromide ions. This indicates that the halide-to-copper(II) charge transfer transition is independent upon the environment, is not affected by the cage framework and, in particular, is not perturbed by the spacers. In fact, the 1,3-xylyl fragment cannot play any 'active' role.

3.3. Iodide ion interaction with dicopper(II) bistren cryptates and with a model $[Cu^{II}(tren)]^{2+}$ complex

Spectrophotometric titration of the $[Cu_2^{II}(\textbf{4})]^{4+}$ receptor with iodide gave different results. Fig. 8a shows the family of spectra obtained over the course of the titration of a MeCN solution 6.15×10^{-4} M in $[Cu_2^{II}(\textbf{4})]^{4+}$ with a standard solution of $[Bu_4N]I$.

On iodide addition, two rather intense bands develop around 400 nm. These bands have a halide ion-to-copper(II) charge transfer nature, but appear quite different from what observed on titration of $[Cu_2^{II}(4)]^{4+}$ receptor with chloride and bromide. First, they show two well distinct transitions, at 370 and 440 nm; second, they occur at an energy higher than expected; in fact, the X⁻-to-Cu^{II} transition has been observed at 415 nm for chloride and at 435 nm for bromide. Thus, in view of the higher reducing tendencies, such a band would be expected for iodide at 455 nm or more. Moreover, best fitting of spectrophotometric data was obtained by assuming the presence at the equilibrium of only two complex species: { $[Cu_2^{II}(4)] \cdots I \cdots [Cu_2^{II}(4)]^{7+}$ and $[Cu_2^{II}(4)I]^{3+}$, whose concentra-



Fig. 7. (a) Spectra recorded over the course of the titration of a MeCN solution 5.02×10^{-4} M in $[Cu_2^{II}(4)]^{4+}$, with a standard solution of $[Bu_4N]$ Br. (b) d-d spectrum. (c) Concentration profiles of the complex species forming over the course of the spectrophotometric titration experiment. The profiles of the absorbance at 360 nm has been superimposed on the diagram. On titration, the solution takes a pale blue-green colour.



Fig. 8. (a) Spectra recorded over the course of the titration of a MeCN solution 6.15×10^{-4} M in $[Cu_2^{II}(4)]^{4+}$, with a standard solution of $[Bu_4N]I$. (b) Portion of d–d spectra. (c) Lines: concentration profiles of the complex species forming over the course of the spectrophotometric titration experiment; symbols: absorbances at 440 and 700 nm (right vertical axes). On titration, the solution takes a canary-yellow colour.

tion profiles are shown in Fig. 8c. The 1:1 iodide inclusion complex $[Cu_2^{II}(4)I]^{3+}$ is poorly stable and its concentration reaches only ca. 80% even after the addition of a large excess of anion (up to 4 equiv.). The low stability of the 1:1 inclusion complex is quantitatively expressed by the constant associated to Eq. (4), which is 65-fold lower than observed for bromide and 6000-fold lower than for chloride. Notice that the complex of type $[Cu_2^{II}(4)I]_2^{2+}$ does not form, a behaviour which may be ascribed to the intrinsic weakness of the $Cu^{II}-I^-$ coordinative bond and to the difficulty experienced by the dimetallic cryptate to accommodate two rather large anions in a sterically constrained arrangement.

At this stage, it seemed useful to consider, for comparative purposes, the recognition tendencies of the $[Cu_2^{II}(2)]^{4+}$ cryptate toward the iodide ion. Fig. 9a displays the spectra taken over the course of the titration of an MeCN solution 5.00×10^{-4} M in $[Cu_2^{II}(2)]^{4+}$ with $[Bu_4N]I$. Results are very similar to those obtained with the $[Cu_2^{II}(4)]^{4+}$ receptor. In particular, (i) two rather intense bands centred at ca. 370 and 440 nm are observed; (ii) the same complex species are formed on iodide titration: $\{[Cu_2^{II}(2)] \cdots I \cdots [Cu_2^{II}(2)]\}^{7+}$ and $[Cu_2^{II}(2)I]^{3+}$; (iii) the 1:1 anion inclusion complex $[Cu_2^{II}(2)I]^{3+}$ is not particularly stable (the log *K* value for Eq. (4), 4.82 ± 0.04, is very close to that observed for the $[Cu_2^{II}(4)]^{4+}$ receptor) and on addi-

molar absorbance, M⁻¹ cm⁻¹

tion of 4 equiv. of I^- reaches ca. 80%; (iv) the complex of type $[Cu_2^{II}(\pmb{2})]X_2]^{2+}$ does not form.

The similarity of the results obtained for the two dinuclear cryptate complexes suggests that the spectral behaviour is not related to the cage structure, but rather depends on each separated Cu^{II}(tren)²⁺ subunit. This prompted us to investigate the binding tendencies towards iodide of the copper(II) complex of tren derivative **5**.





Fig. 9. (a) Spectra recorded over the course of the titration of a MeCN solution 5.00×10^{-4} M in $[Cu_2^{II}(2)]^{4+}$, with a standard solution of $[Bu_4N]I$. (b) Portion of d–d spectra. (c) Lines: concentration profiles of the complex species forming over the course of the spectrophotometric titration experiment; symbols: absorbances at 430 and 700 nm (right vertical axes). On titration, the solution takes a canary-yellow colour.



Fig. 10. (a) Spectra recorded over the course of the titration of a MeCN solution 3.15×10^{-4} M in $[Cu^{II}(5)]^{2+}$, with a standard solution of $[Bu_4N]I$. (b) Portion of d–d spectra. (c) Lines: concentration profiles of the complex species forming over the course of the spectrophotometric titration experiment; symbols: absorbances at 450 and 800 nm (right vertical axes). On titration, the solution takes a canary-yellow colour.

Fig. 10a shows the family of spectra obtained over the course of the titration of a MeCN solution 3.15×10^{-4} M of $[Cu^{II}(5)]^{2+}$ with a standard solution of $[Bu_4N]I$.

Noticeably, on iodide addition, two bands develop at 370 and 440 nm, as observed for the $[Cu_1^{II}(4)]^{4+}$ receptor, and, less evidently, with the $[Cu_2^{II}(2)]^{4+}$ cryptate. Two iodide containing species form over the course of the titration: the dimeric complex $\{[Cu^{II}(5)]\cdots I\cdots [Cu^{II}(5)]\}^{3+}$ and the five-coordinate complex $[Cu^{II}(5)I]^+$, whose concentration profiles are shown in Fig. 10c. Thus, in the case of iodide, any cryptate effect vanishes for the $[Cu_2^{II}(4)]^{4+}$ complex and the spectral response simply derives from each individual $Cu^{II}(tren)^{2+}$ fragment.

Moreover, an important feature to be pointed out is the high stability of the 1:1 complex $[Cu^{II}(5)I]^+$ in comparison with the 1:1 inclusion complexes $[Cu_2^{II}(\mathbf{2})I]^{3+}$ and $[Cu_2^{II}(\mathbf{4})I]^{4+}$. In particular, the constant associated to Eq. (4) $(\log K = 5.2 \pm 0.1)$ is slightly, still perceptibly higher than those associated to iodide inclusion into the two investigated cryptates (equilibria of type (4)). Thus, the following paradox is observed: anion binding to a single Cu^{II} cation, in the tren complex, is favoured with respect to the binding of two Cu^{II} centres prepositioned within the bistren cage. However, this apparent inconsistency can be accounted for by considering that the inclusion of the large I⁻ anion may induce a severe conformational rearrangement of the bistren cage, whose endergonicity more than compensates the advantage of making two distinct coordinative bonds. Moreover, it comes out that with iodide all the special features related to the presence of the 2,5-dimethylfuran spacers disappear. In particular, probably due to anion size and the associated conformational rearrangement of the cage, which may involve a change in the orientation of the furan spacer, any halide ion-furan oxygen atom interaction fades away, thus cancelling the unique spectral properties.

4. Conclusions

There exists a current interest in the development of colorimetric molecular sensors for anions [20]. Most of them are constituted by a specific receptor covalently linked to or integrated with an organic chromogenic subunit. This work has demonstrated that transition metal containing receptors can provide a powerful signal for communicating anion recognition, i.e. the colour change associated to the development of an anion-to-metal charge transfer band. In particular, we have shown that the dicopper(II) cryptate $[Cu_2^{II}(4)]^{4+}$ by means of its 'active' furan spacers allows specific recognition and colorimetric sensing of chloride and bromide ions. The concept of the 'active' spacers can be profitably exploited in the design of optical sensors for anions. Research work in this perspective is currently under way in our Laboratory.

5. Supplementay material

CCDC 678004 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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