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Colorimetric response to anions by a “robust” copper(II) complex of a [9]aneN₃ pendant arm derivative: CN[−] and I[−] selective sensing†Marta Aguado Tetilla,^a M. Carla Aragoni,^b Massimiliano Arca,^b Claudia Caltagirone,^{*b} Carla Bazzicalupi,^c Andrea Bencini,^c Alessandra Garau,^b Francesco Isaia,^b Antonio Laguna,^a Vito Lippolis^{*b} and Valeria Meli^b

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The 1 : 1 complex [Cu(L)](BF₄)₂·MeCN (1) of the tetradentate ligand 1-(2-quinolinylmethyl)-1,4,7-triazacyclononane (L) selectively changes its colour in the presence of CN[−] in H₂O and MeCN (without undergoing decomplexation from the macrocyclic ligand). The same complex in MeCN assumes different colours in the presence of CN[−] or I[−].

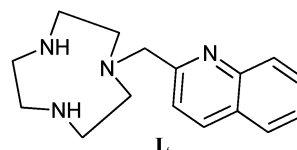
The design and development of artificial receptors able to recognise and sense selectively anionic species has become a prominent and active field of research within the realm of “supramolecular chemistry”.^{1–4} The intense research interest in this field is driven by the great demand for extremely sensitive and selective analytical tools for the detection and monitoring of anions, especially toxic ones such as CN[−], in biological, environmental, and industrial waste effluent samples. Applications can span from process control to environmental monitoring, food analysis and medical diagnosis, to give some examples.

There are different strategies for selectively binding anions at the molecular level, based either on noncovalent interactions (hydrogen bonding, π–π donor–acceptor, electrostatic, hydrophobic, hydrophilic) or on coordination-based metal–ligand interactions. If the receptor is designed to carry a chromophore, the binding event will hopefully be monitored by changes in colour or fluorescence intensity.^{1–4} Optical detection methods are largely preferred and sought as they are usually very sensitive, low cost, and easily performed in terms of equipment needed.^{5,6}

In aqueous conditions, anion receptors based on intrinsically weak noncovalent interactions can suffer from the competition

of H₂O for the anion. This problem is reduced with receptors based on the generally stronger metal–anion covalent interactions and this kind of receptors are, in principle, more suitable for anion recognition studies in this medium.^{1–6}

In particular, coordinatively unsaturated copper(II) complexes can be very useful for this purpose because they normally display an absorption in the visible region of the spectrum which can be tuned by strong binding of anionic species to the metal centre, thus offering the possibility of a selective colorimetric detection of anions even by naked eye.⁷ In our effort to develop new fluorescent sensors for metal ions, we have recently synthesised a new quinoline pendant arm derivative of [9]aneN₃, L, and we have studied its optical response in the presence of transition and post-transition metal ions.⁸ In particular L behaves as an efficient OFF–ON fluorescent chemosensor for zinc(II) in MeCN/H₂O 1 : 1 (v/v) and in pure H₂O at pH 7.0.



Because of the tetradentate nature of L, we thought that its 1 : 1 copper(II) complex, [Cu(L)](BF₄)₂·MeCN (1), easily obtainable as a blue powder from the reaction of L with Cu(BF₄)₂·xH₂O in 1 : 1 molar ratio in MeCN (see ESI†), would be coordinatively unsaturated and, therefore, ready to bind anionic species even in aqueous solution. We first confirmed in the solid state the unsaturated coordination sphere at the metal centre in 1 and, therefore, its ability to bind anionic species.

Indeed, we succeeded to grow dark blue single crystals of the compound [Cu(L)CN]BF₄·1/2H₂O from the reaction of 1 with ⁿBu₄NCN (1 : 1 molar ratio) in MeCN (see ESI†). In the complex cation [Cu(L)CN]⁺ (Fig. 1),† the anion is bound to the copper(II) centre, thus completing with the participation of the four nitrogen donors from L, a coordination environment around the metal ion that is intermediate between square-based pyramidal and trigonal bipyramidal. A similar coordination sphere at the copper(II) centre was also observed in the

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† Electronic supplementary information (ESI) available: Additional information as noted in the text including synthetic details for the preparation of the crystallographic characterized complexes, and X-ray crystallographic files. CCDC 796944 and 796945. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04500d

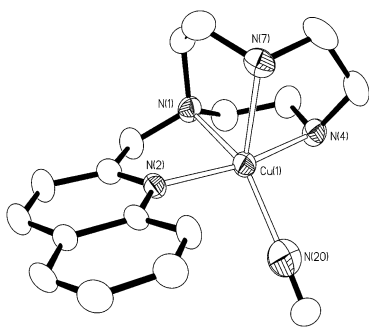


Fig. 1 ORTEP view of the complex cation $[\text{CuL}(\text{CN})]^+$ in $[\text{Cu}(\text{L})\text{CN}]\text{BF}_4 \cdot 1/2\text{H}_2\text{O}$. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at a 30% probability level. Cu(1)–N(1) 2.107(5), Cu(1)–N(4) 2.032(4), Cu(1)–N(7) 2.146(5), Cu(1)–N(2) 2.035(4), Cu(1)–N(20) 1.998(7) Å; N(1)–Cu(1)–N(2) 81.64(18), N(1)–Cu(1)–N(4) 83.78(18), N(1)–Cu(1)–N(7) 83.49(19), N(1)–Cu(1)–N(20) 144.5(2), N(2)–Cu(1)–N(4) 165.36(18), N(2)–Cu(1)–N(7) 96.66(18), N(2)–Cu(1)–N(20) 97.0(2), N(4)–Cu(1)–N(7) 82.85(18), N(4)–Cu(1)–N(20) 94.2(2), N(7)–Cu(1)–N(20) 131.6(2)°.

complex cation $[\text{Cu}(\text{L})\text{I}]^+$ (see ESI†, Fig. S1),‡ in the green compound $[\text{Cu}(\text{L})\text{I}]\text{I}$ obtained from the reaction of **1** with ${}^n\text{Bu}_4\text{NI}$ (1 : 2 molar ratio) in MeCN. Interestingly, in the unit cell, the two independent $[\text{Cu}(\text{L})\text{I}]^+$ cations interact *via* a soft–soft $\text{I} \cdots \text{I}$ long contact of 4.140(2) Å (see ESI†, Fig. S2).

On the basis of these results in the solid state, we tested the anion sensing ability of **1** towards F^- , Cl^- , Br^- , I^- , MeCO_2^- , PhCO_2^- , H_2PO_4^- , HSO_4^- , HCO_3^- , NO_3^- , N_3^- , CN^- and SCN^- *via* UV-Vis spectroscopy in MeCN and H_2O solutions (see ESI†). In MeCN a colour change was observed only upon addition of I^- or CN^- , while in H_2O only upon addition of CN^- . The UV-Vis spectrum of **1** in MeCN and H_2O shows a broad d–d absorption band at 600 nm ($\epsilon = 106 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 634 nm ($\epsilon = 78 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), respectively. In MeCN, upon addition to **1** of increasing amounts of I^- (Fig. 2), a progressive red-shift (up to 30 nm in the presence of 1 eq. of I^-) and increase in the absorbance of the d–d absorption band ($\epsilon = 330 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 630 nm) is observed, accompanied by the formation of a new band at 420 nm ($\epsilon = 1330 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

The titration profile at 420 nm (Fig. 2) indicates the formation of a stable 1 : 1 $\text{I}^-/\mathbf{1}$ complex, with an almost complete complexation of the anion when the 1 : 1 molar

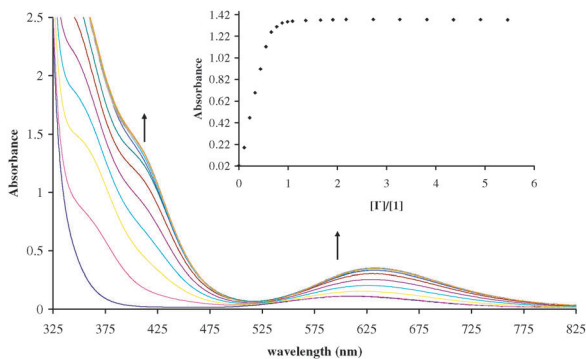


Fig. 2 Absorption changes of **1** ($1.00 \times 10^{-3} \text{ M}$) in MeCN upon addition of increasing amounts of ${}^n\text{Bu}_4\text{NI}$ (0.14 M). Inset: titration curve at 420 nm.

ratio is reached. Treatment of the spectra with the program Hypspec⁹ allows the determination of a constant of $4.8 \pm 0.1 \text{ log units}$ for the addition of I^- to **1**. Addition of I^- to an aqueous solution of **1** produces similar but much less marked spectral changes (see ESI†, Fig. S3). In fact, titration data treatment accounts for the formation of a 1 : 1 complex also in H_2O , but with a calculated stability constant of only $2.4 \pm 0.1 \text{ log units}$.⁹

Differently from I^- , addition of CN^- to **1** does not produce any significant spectral change for wavelengths lower than 450 nm both in MeCN and H_2O . Conversely, the d–d band is strongly affected by the presence of this anion in both solvents.

In H_2O , the d–d absorption band of **1** isospectically blue-shifts (Fig. 3) from 634 to 575 nm up to addition of two equivalents of CN^- and increases in the absorbance ($\epsilon = 133 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in the presence of 2 eq. of CN^-). The linear increase of the absorbance observed (see inset of Fig. 3) is in agreement with the simultaneous addition of two CN^- anions to the metal center to form a 2 : 1 $\text{CN}^-/\mathbf{1}$ complex; attempts to determine the formation constant of this complex failed due to its high value, which can only be estimated as higher than 10 log units.¹⁰

Addition of CN^- to **1** in MeCN solution produces a progressive blue-shift of the d–d absorption band of **1** and a slight increase of the absorbance up to a 1 : 1 $\text{CN}^-/\mathbf{1}$ molar ratio (in these conditions, $\lambda_{\text{MAX}} = 585 \text{ nm}$, $\epsilon = 144 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Further addition of CN^- gives rise to a more marked blue-shift of the band accompanied by a decrease of the absorbance up to a 2 : 1 $\text{CN}^-/\mathbf{1}$ molar ratio (in these conditions, $\lambda_{\text{MAX}} = 530 \text{ nm}$, $\epsilon = 80 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). These data strongly suggest the successive formation of stable 1 : 1 and 2 : 1 $\text{CN}^-/\mathbf{1}$ complexes (see ESI†, Fig. S4).¹⁰ However, as in aqueous solution, the high stability of the complexes prevents the determination of their formation constants and the formation constant of the 1 : 1 complex can be only estimated as higher than 7 log units.

Remarkably, the spectral changes described above correspond to naked-eye detectable solvent/anion dependent colorimetric responses. In fact, binding of I^- to **1** in MeCN with formation of a 1 : 1 complex is accompanied by a colour change of the solution from cyan to green; this colour is maintained for $\text{I}^-/\mathbf{1}$ molar ratios higher than 1 (Fig. 2 and 4).

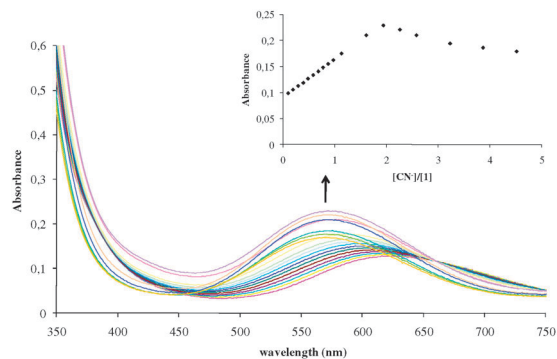


Fig. 3 Absorption changes of **1** ($1.72 \times 10^{-3} \text{ M}$) in H_2O upon addition of increasing amounts of ${}^n\text{Bu}_4\text{NCN}$ (0.14 M). Inset: titration curve at 575 nm.

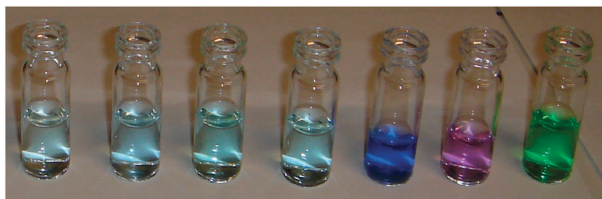


Fig. 4 Colour change of **1** (1.00×10^{-3} M) after addition of different anions in MeCN. From left to right: **1**, **1** + 1 eq. of F^- , **1** + 1 eq. of Cl^- , **1** + 1 eq. of Br^- , **1** + 1 eq. of CN^- , **1** + 2 eq. of CN^- , **1** + 1 eq. of I^- . Colour changes of **1** in MeCN in the presence of each anion considered are reported in Fig. S5 in the ESI.†

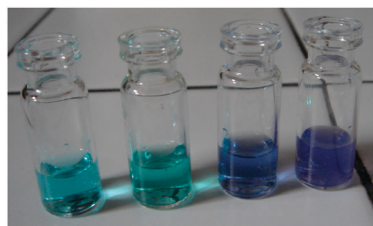


Fig. 5 Colour change of **1** (1.72×10^{-3} M) after addition of I^- and CN^- in H_2O . From left to right: **1**, **1** + 1 eq. of I^- , **1** + 1 eq. of CN^- , **1** + 2 eq. of CN^- .

Conversely, no naked-eye colour change of **1** is observed in aqueous solutions in the presence of I^- (Fig. 5).

In H_2O , a colour change of **1** is observed only in the presence of CN^- from cyan to dark blue and independently from the equivalents of this anion added (Fig. 3 and 5).

On the other hand, the formation of the two $CN^-/1$ complexes with different stoichiometries in MeCN is also evident to the naked eye (Fig. 4) with a colour change from cyan to dark blue (1 : 1 $CN^-/1$ complex) and from dark blue to pink (2 : 1 $CN^-/1$ complex). The pink coloration is maintained for $CN^-/1$ molar ratios higher than 2. Furthermore, upon addition of one equivalent of **1** to the pink solution of the 2 : 1 $CN^-/1$ complex, the dark blue colour of the 1 : 1 $CN^-/1$ complex is reversibly restored. No appreciable color changes of **1** are observed in the presence of the other anions considered in both solvents (see ESI†, Fig. S6 and S7).¹¹

During the preparation of this manuscript Hossain *et al.* reported a dinuclear complex of copper(II) with a hexaamino macrocycle able to recognise I^- in MeCN/ H_2O (3 : 1, v/v) through the same colour change we observed in MeCN.¹² In our case, instead, **1** in MeCN is able to selectively discriminate visually the presence of either I^- (in the absence of CN^-) or CN^- (also in the presence of I^-) among the other anions *via* different colour changes, representing a peculiar case of selective “double” (two sensed species) anion sensing by a metal complex. Furthermore, complex **1** in MeCN can also be in principle used to give a visual rough evaluation of the equivalents of CN^- present in solution, thanks to different colours observed in correspondence of the formation of the 1 : 1 and the 2 : 1 $CN^-/1$ complexes. A second peculiar property of **1** is represented by its ability to sense selectively CN^- in aqueous solution over the other anions tested, including I^- .

Therefore, in terms of its sensing properties, complex **1** could be considered a “solvent-based dual” sensor, because

it is able to sense CN^- selectively in two different media, with “double” response in acetonitrile because it can distinguish visually two different anions with different colours in this solvent (see ESI† for a further discussion).

However, to the best of our knowledge, the most important property of **1** is that it represents the first selective and structurally simple copper(II)-based optical sensor for CN^- whose response is determined by a shift of the metal-based d-d absorption upon binding of the anion to the metal centre, without a consequent decomplexation of the metal centre from the ligand.⁹ In the other optical sensors reported so far, the CN^- sensing mainly arises either from the removal of the copper(II) centre from the receptor complex as $[Cu(CN)_n]^{n-}$ species, or from irreversible reactions between CN^- and metal-free molecular indicators with formation of C-CN or B-CN bonds.^{13,14}

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Notes and references

† Crystal data were collected on an Oxford Diffraction Xcalibur3 diffractometer equipped with a CCD area detector and graphite monochromated Cu-K α radiation ($\lambda = 1.5418$ Å); standard procedures were followed. Crystal data for $[Cu(L)CN]BF_4 \cdot 1/2H_2O$: $C_{17}H_{23}BCuF_4N_5O_{0.5}$; $M = 455.75$, $T = 298$ K, triclinic, space group $P\bar{1}$, $a = 6.9541(6)$ Å, $b = 9.935(1)$ Å, $c = 14.552(1)$ Å, $\alpha = 84.396(8)^\circ$, $\beta = 80.834(8)^\circ$, $\gamma = 82.115(8)^\circ$, $V = 980.20(15)$ Å³, $\rho_c = 1.544$ g cm⁻³, $\mu = 1.166$ mm⁻¹, $Z = 2$, reflections collected: 5972, independent reflections: 3688, ($R_{int} = 0.0473$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0673$, $wR_2 = 0.1507$. Crystal data for $[Cu(L)]I$: $C_{16}H_{22}CuI_2N_4$; $M = 587.73$, $T = 298$ K, orthorhombic, space group $Pna2_1$, $a = 15.858(1)$ Å, $b = 7.8424(4)$ Å, $c = 31.456(2)$ Å, $V = 3912.0(4)$ Å³, $\rho_c = 1.996$ g cm⁻³, $\mu = 4.277$ mm⁻¹, $Z = 8$, reflections collected: 12965, independent reflections: 5506, ($R_{int} = 0.0889$), final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0509$, $wR_2 = 0.0975$.

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- The slight decrease (H_2O) or increase (MeCN) in the absorbance observed beyond the 2 : 1 $CN^-/1$ molar ratio (Fig. 3 and Fig. S4) might be indicative of other species forming in low percentage in the presence of excess CN^- , but we could not ascertain their nature.
- In competitive experiments in both MeCN and H_2O , the colour changes observed for **1** in the presence at the same time of 1 or 2 eq. of all anions considered were those corresponding to the formation of the 1 : 1 and/or 2 : 1 $CN^-/1$ complexes and did not change in time.
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