Inorg. Chem. **1995**, *34*, 4529−4535

Articles

{Cu^{II}[*N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)malondiamido(2−)]}: A Convenient Building Block for the Construction of Supramolecular Coordination Compounds Containing Exchangeable Peripheral Cu^{II} Cations

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Received February 24, 1995[⊗]

The ethylpyridino functionalized *N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridil)ethyl)malondiamide ligand **1b** has been prepared, its protonation and complexation properties (toward Cu^{II}) have been studied in aqueous solution, and the pertinent constants have been determined. The ligand is able to coordinate one Cu^{II} ion with the diamino−diamido binding unit, after the release of the two amido protons, thus forming complex **2**, which still presents a free, outward-pointing pyridine unit, capable of coordinating a second metal center. Two **2** units have been appended, through their pyridine nitrogen atom, to the kinetically inert *cis*-$Cl_2Pt^{II}<$ fragment. The obtained supramolecular species **3** is able to release the peripheral Cu^{II} ions when the pH of the solution becomes acidic and to re-form the original complex when basicity is restored (the pertinent complexation constants have been determined). This system thus represents the first example of a supramolecular coordination compound which contains exchangeable peripheral transition metal cations. The crystal and molecular structure of **2** has been determined, disclosing the formation of "head to tail" dimers in the solid state, with an unusual coordination geometry of the Cu^{II} ions. Single-crystal X-ray diffraction data were collected with the use of Mo Kα radiation: trigonal, space group $P\bar{3}$ with $a = b = 20.558(6)$ Å, $c = 7.562(3)$ Å, $V = 2768(2)$ Å^3, and $Z = 6$ ($R = 0.054$, $R_w = 0.058$). Finally, electrochemical studies revealed that both in the separate component and in the assembled system the Cu^{II} centers are reversibly oxidizable to Cu^{III}. In the supramolecular coordination compound, the two Cu^{II} centers weakly influence each other by means of electrostatic interactions.

Introduction

Multicomponent systems in which the subunits are metal complexes, assembled together by means of noncovalent interactions, can be defined as *supramolecular coordination compounds*[1] (SCC), in agreement with the general definition of *supramolecular species* put forward by Lehn.[2]

Systems of this kind can be obtained by means of a two-step synthetic strategy. In the first step, a ligand (L) is appended to a metal complex (X) to give the subunit L−X. The geometry of this subunit must be such that L cannot further bind the metal center in X but points its donor set outward, thus being able to coordinate another metal center. Accordingly, in the second step, one or more L−X subunits are coordinatively bound to a metal center M (which should be capable of forming kinetically inert complexes), thus giving the supramolecular coordination compound $[M(L-X)_n]$ (n = 1, 2, 3, ...).

A few examples of SCC of the $[M(L-X)_n]$ type have been reported in the literature, particularly if the X moiety is required to contain a *transition metal* center. In particular, one or three vinylferrocene moieties have been appended to bipyridine and one or three of the obtained L−X subunits assembled around a Ru^{II} center[3a,b] to give SCC which are able to undergo electrochemical polymerization to produce electrochromic polymers.[3a] Ferrocene has been also linked to a terpyridine ligand and two of the obtained molecules coordinated to Co^{II}, Fe^{II}, and Ru^{II} centers.[3c]

Moreover, a cyclam ring (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been linked to a bipyridine ligand and one or three of the resulting molecules coordinated, through the bipyridine nitrogen atoms, to a Ru^{II} center, generating systems which are capable of further binding transition metal cations.[4a−c] These SCC have shown the ability of quenching the fluorescence of the central $[Ru^{II}(bipy)_3]$ moiety, when selected transition metal cations are dropped in the peripheral cyclam ring(s).[4a]

We have extensively employed and developed this synthetic approach in some recent papers, with the aim of preparing multicenter-multielectron redox systems. Ferrocene and metallocyclam units have been appended to ligands such as

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[⊗] Abstract published in *Advance ACS Abstracts*, July 15, 1995.

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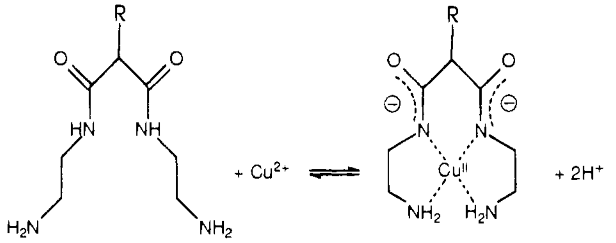
Scheme 1



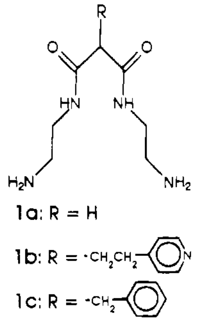
pyridine,[5,6] salicylic acid,[7] and triazacyclononane[8] and the obtained L−X components coordinatively bound to metal centers such as Pt^{II},[5,6] Ru^{II},[6] Fe^{III},[7] and Ni^{II}.[8] Moreover, in a recent paper,[9] we described an L−X component consisting of one phenanthroline (L) and one [Cu^{II}(azacyclam)] (X) subunit and the SCC obtained by coordination of two L−X around a Cu^{I} center.

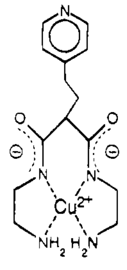
It is noticeable that only ferrocene or metallocyclam species have been used as metal complexes in the construction of the L−X components, most probably both for their rich electrochemical properties and for their stability and inertness.

On one side, inertness can be considered an advantage, as the X fragment remains intact under the action of external agents (solvent, acidity, additional ligands) and allows the use of severe synthetic conditions during the preparation of the [M(L−X)$_n$] compounds.

On the other hand, the drawback is that kinetic inertness prevents from exchanging the peripheral metal cations (*i.e.* those contained in X), and this precludes the possibility to impart to the [M(L−X)$_n$] supramolecular species useful properties such as sensing or transport ability toward transition metal cations.

In order to prepare [M(L−X)$_n$] SCC in which the peripheral cation can be released and uptaken in solution, under the variation of some bulk parameter, we appended the versatile *N,N'*-bis(2-aminoethyl)malondiamide binding unit (**1a**) to a pyridine ring, to give the ligand **1b**. It is well-known that both plain[10] and 2-substituted[11] *N,N'*-bis(2-aminoethyl)malondiamide ligands coordinate Cu^{II} with the release of the two protons on the amide nitrogen atoms. The process, which is described in Scheme 1, is pH dependent and the complexes are stable only in basic or slightly acidic solution. Moreover, the Cu^{II} complexes of these ligands present interesting redox properties, as they are easily and reversibly oxidized to Cu^{III} species.[11,12] When **1b** coordinates one Cu^{II} ion, according to Scheme 1, the obtained complex, **2**, still presents an outward-pointing free pyridine fragment, thus possessing all the features which are required for an L−X component. We have appended two of these L−X components to the kinetically inert *cis*-Cl$_2$Pt^{II}< fragment and obtained **3**, a water soluble SCC of the [M(L−X)$_2$] type, which is able to release and uptake Cu^{II} cations on variation of pH.





2

In this paper we describe the synthesis, electrochemistry, and solution behavior of both the separate L−X component and of the supramolecular species **3**. Moreover, the crystal and molecular structure of the L−X component (**2**) is reported.

Experimental Section

UV−visible spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer or on a Varian Cary 2300 spectrophotometer, and ^{1}H NMR spectra on a 300-MHz Bruker instrument; IR spectra were obtained on a Perkin-Elmer 1300 infrared spectrophotometer.

1,2-Diaminoethane (Fluka), diethyl malonate (Fluka), 4-vinylpyridine (Aldrich), and K$_2$PtCl$_4$ (Fluka) were used without further purification. 2-(2-Pyridin-4-ylethyl)malonic acid diethyl ester was synthesized from 4-vinylpyridine and diethylmalonate as described for related molecules.[13]

***N,N'*-Bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)malondiamide (1b).** 2-(2-Pyridin-4-ylethyl)malonic acid diethyl ester (1.2 g, 4.5 mmol) was syringed in 50 mL of freshly distilled 1,2-diaminoethane, under a dinitrogen atmosphere. The obtained clear solution was stirred for 7 days at room temperature under a dinitrogen atmosphere and avoiding exposure to light. After removal of the excess 1,2-diaminoethane on a rotary evaporator, a pale yellow oil was obtained, which solidified after treatment with 30 mL of diethyl ether. The white powdery product was filtered out, washed with diethyl ether, and used without further purification (yield: 42%). Anal. Calcd for $C_{14}H_{23}N_5O_2{\cdot}0.5H_2O$: C, 55.65; H, 7.94; N, 23.16. Found: C, 55.48; N, 23.09; H, 7.96. IR (Nujol mull): 3290 (N−H of amido groups), 1650 (C=O), 1595 (C−H of the pyridine ring) cm^{-1}. ^{1}H NMR: δ 8.45 (2H, d, H of pyridine), 7.45 (2H, t, CH$_2$N*H*CO), 7.12 (2H, d, H of pyridine), 3.31 (4H, m, CH$_2$C*H*$_2$NHCO), 3.03 (1H, t, COC*H*(R)CO), 2.85 (4H, t, CH$_2$C*H*$_2$NH$_2$), 2.64 (2H, t, pyC*H*$_2$), 2.19 (2H, q, pyCH$_2$C*H*$_2$CHR$_2$).

{Cu^{II} [*N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)malondiamido-(2−)]} (2). Ligand **1b** (0.5 g, 1.65 mmol) was dissolved in 10 mL of H$_2$O, and 3.0 mL of a 0.54 M aqueous solution of Cu(ClO$_4$)$_2$ was added dropwise, at room temperature. During the addition the pH was controlled and mantained between 9 and 10 with 0.1 M NaOH. Bright blue crystals precipitated from the pink-violet solution, which were filtered out, washed with 5 mL of ethanol, and dried under vacuum (yield: 91%). Anal. Calcd for $C_{14}H_{21}CuN_5O_2{\cdot}2H_2O$: C, 43.04; H, 6.40; N, 17.92. Found: C, 42.98; H, 6.43; N, 17.87.

Caution! Perchlorate salts are potentially explosive and should be handled with care. In particular, they should never be heated as solids.

***cis*-[Cl$_2$Pt^{II}{Cu^{II} [*N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)-malondiamido(2−)]}$_2$] (3).** The L−X component **2** (0.50 g, 1.28 mmol) was dissolved in 30 mL of H$_2$0, the pH adjusted to 8 with NaOH, and the volume brought to 60 mL with methanol. The obtained pink-violet solution was added dropwise to a 10 mL of water solution containing K$_2$PtCl$_4$ (0.58 mmol). The mixture was further magnetically stirred for 20 h at room temperature and then filtered to eliminate traces of a green-brown precipitate. An 80 mL volume of acetone was added to the clear pink solution, which immediately became cloudy. After 24 h, a pink oily substance deposited on the walls of the reaction vessel, leaving an almost colorless solution which was decanted and discarded. After the oil was layered with fresh acetone, a deep pink powder was obtained, which was filtered out and recrystallized in methanol (yield:

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Table 1. Crystallographic Data for Complex **2**

formula	$C_{14}H_{21}CuN_5O_2{\cdot}2H_2O$
cryst syst	trigonal
space group	$P\bar{3}$ (No. 147)
cell params at 295K^a	
a, Å	20.558(6)
c, Å	7.562(3)
V, Å^3	2768(2)
Z	6
D_{calcd} g cm^{-3}	1.407
$F(000)$	1230
mol wt	390.93
linear abs coeff, cm^{-1}	12.106
radiation	Mo Kα(0.7107 Å)
max δ/σ on last cycle	0.07
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.054
$R_w = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.058
GOF = $[\sum w\|\Delta F\|^2/(NO - NV)]^{1/2}$	3.03

^{a} Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centered reflections found in the $15.7 < \theta < 17.3°$ range of reciprocal space.

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Displacement Coefficients (Å^2 $\times$ 10^4) with Esd's in Parentheses for the Non-Hydrogen Atoms of $C_{14}H_{21}CuN_5O_2{\cdot}2H_2O$

	x/a	y/b	z/c	$U_{eq}{}^a$
Cu	870(1)	3182(1)	1598(1)	294(2)
N(1)	1775(3)	3613(3)	3227(7)	382(18)
C(2)	2373(4)	4319(4)	2432(10)	429(23)
C(3)	2357(4)	4237(4)	389(10)	445(24)
N(4)	1600(3)	3873(3)	−160(7)	321(17)
C(5)	1470(3)	3862(3)	−1888(9)	316(20)
C(6)	664(3)	3479(3)	−2568(9)	320(19)
C(7)	178(3)	2677(3)	−1939(9)	293(19)
N(8)	161(3)	2527(3)	−260(8)	351(17)
C(9)	−345(4)	1758(4)	313(9)	391(22)
C(10)	−474(4)	1782(4)	2316(10)	409(22)
N(11)	240(3)	2271(3)	3178(8)	417(19)
C(12)	272(4)	3923(4)	−2201(9)	341(20)
C(13)	725(4)	4737(4)	−2834(10)	392(22)
C(14)	318(4)	5183(4)	−2713(9)	341(20)
C(15)	701(4)	5931(4)	−3194(11)	468(25)
C(16)	348(4)	6350(4)	−3072(10)	467(24)
N(17)	−375(3)	6064(3)	−2540(8)	391(18)
C(18)	−737(4)	5339(4)	−2107(10)	431(24)
C(19)	−415(4)	4888(4)	−2171(10)	434(24)
O(1)	1985(3)	4164(3)	−3037(7)	436(16)
O(2)	−215(3)	2201(3)	−3096(6)	430(16)
O(1W)	0(0)	0(0)	1721(16)	828(33)
O(2W)	852(4)	1185(4)	3551(9)	824(20)
O(3W)	6667(0)	3333(0)	2189(24)	500(46)
O(4W)	5629(6)	2716(6)	3543(15)	565(30)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

20%). Anal. Calcd for $C_{28}H_{42}Cl_2Cu_2N_{10}O_4Pt{\cdot}2H_2O$: C, 33.25; H, 4.54; N, 13.84. Found: C, 33.29; H, 4.58; N, 13.76.

Crystal Structure Determination. A single crystal of **2**, of approximate dimensions 0.3 × 0.4 × 0.4 mm, suitable for X-ray diffraction, was sealed in a glass capillary. Crystal data and the most significant experimental details are given in Table 1. The atomic fractional coordinates for the non-hydrogen atoms are given in Table 2.

All X-ray measurements were performed at 295 K, using graphite-monochromatized Mo Kα radiation. For intensities and background, the profile measurement technique was used.[14]

The structure factors were obtained after the usual Lorentz and polarization corrections, and the absolute scale was obtained by the Wilson method.[15] The data were corrected for absorption using ABSORB.[16] The structure was solved by Patterson and direct methods using SHELX86[17] and refined by full-matrix least-squares methods using SHELX76[18] for a total of 128 parameters. The weighting Scheme $w = [\sigma^2(F_o)]^{-1}$ was used. Twelve solvent water molecules were found in the unit cell: two generated by the symmetry operations on O(1w) and six by O(2w), whereas O(3w) and O(4w), which represent the two alternative orientations (with occupancy factor of 0.5) of a disordered H_2O, generate one and three water molecules, respectively. This corresponds to a 1:2 stoichiometry between the copper mononuclear complex unit and the solvent water. Parameters refined were the overall scale factor, the atomic coordinates, the anisotropic atomic displacements for all the non-hydrogen atoms, and the isotropic ones for the solvent water molecules. The hydrogen atoms, except those of the water molecules, were placed in their calculated position with the geometrical constraint (X−H = 1.0 Å) and refined "riding" on their C or N atoms.

Anomalous scattering corrections were included in all structure factor calculations.[19a] Scattering factors for neutral atoms were taken from ref. 19b for the non-hydrogen atoms and from ref. 20 for hydrogen atoms. The geometrical calculations were obtained by PARST.[21] All the calculations have been performed on the Gould Encore91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Electrochemistry. Differential pulse voltammetry (DPV) measurements were performed in a conventional three-electrode cell with 0.1 M $NaClO_4$ as supporting electrolyte, using a PAR 273 potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. A saturated calomel electrode, connected to the cell through a salt bridge filled with NaCl solution, was used as the reference electrode. The working electrode was a graphite paste electrode.

Potentiometric titrations. Potentiometric titrations in the absence and in the presence of metal ions (as perchlorate salts) were carried out through an automatic system controlled by a personal computer and consisting of the following: (i) a Radiometer PHM84 research pH-meter, using a G202B radiometer glass electrode and an Ingold saturated NaCl calomel reference electrode, fitted in an Ingold cell system; (ii) a Radiometer ABU80 Autoburette; (iii) a Metrom thermostated cell; (iv) a HETO thermostat. The temperature was mantained at 25(±0.1) °C, and each titration was performed on a solution of 50 mL adjusted to a 0.1 M ionic strength with $NaClO_4$. Typical concentrations of the ligands and of the metal ions were in the $(0.5-1.0) \times 10^{-3}$ M range. Details of the experimental procedure have been described elsewhere.[22] The data were processed on a VAX11/870 computer, using the SUPERQUAD program package.[23]

Results and Discussion

1. Synthetic Strategy. The preparation of the pyridino-modified diamino−diamido ligand **1b** is straightforward. In the first step, a diethyl malonate moiety is appended to a pyridine ring in the 4-position, according to the well-established procedure for the synthesis of β-substituted pyridines,[13] starting from their vinyl derivatives. The obtained molecule is then reacted at room temperature with a large excess of 1,2-diaminoethane, to give **1b** in high yields.

Addition of $Cu(ClO_4)_2$ in basic aqueous solution affords the Cu^{II} complex **2** (*i.e.* the L−X component) which spontaneously precipitates in a pure crystalline form and with good yields.

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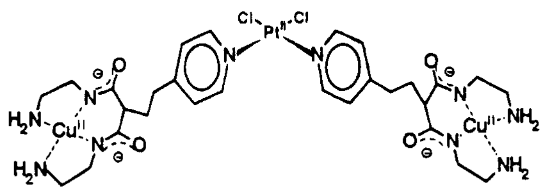
Table 3. Log K Values for Stepwise Protonation Equilibria[a]

compd	log K_1	log K_2	log K_3
1a[b]	9.01	8.66	
1b	9.13	8.41	5.47
1c[b]	9.07	8.35	
4-ethylpyridine[c]	6.06		

[a] Standard deviation = ±0.01 log units (measurements made in 0.1 M $NaClO_4$, $T = 25$°C). [b] Values taken from ref 27 (0.1 M $NaClO_4$, $T = 25$°C). [c] Reference 30 ($\mu = 0.1$; $T = 25$°C).

The preparation of the supramolecular species **3** *must* pass



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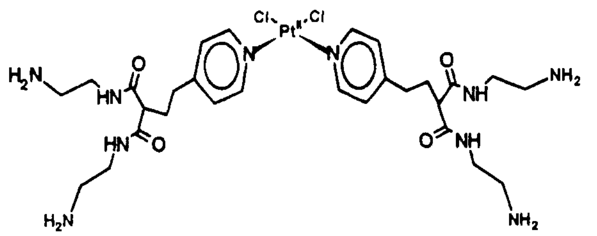

3*

through the preformed {Cu^{II} [*N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)malondiamido(2−)]} complex **2**, as it was not possible to first prepare the nonmetalated supramolecular ligand (*3**) and then react it with Cu^{II} to obtain **3**. As a matter of fact, direct reaction of K_2PtCl_4 with the pyridino-modified diamino−diamido ligand **1b** always produced unseparable mixtures of products, most probably polymeric, due to the competition of the primary amino groups with pyridine for the Cl^--substitution reaction at the platinum center.

On the other hand, room-temperature reaction in aqueous solution of the copper complex **2** with K_2PtCl_4, in a 2:1 molar ratio, easily produced the desired SCC **3** (the trans-effect driving the reaction to the *cis*-[$Pt^{II}(2)_2Cl_2$] complex[6]), with satisfactory yields, as coordination to Cu^{II} removes the primary amino groups from the competition with pyridine.

2. Solution Behavior of the L−X Component (2). Potentiometric titration experiments on solutions containing **1b** plus excess acid, allowed us to determine the pertinent protonation constants. **1b** binds three protons in three consecutive steps, the first two protons through the primary amine groups and the third through the pyridine nitrogen atom. Table 3 reports the log *K* values for **1b** and for the related molecules **1a,c** and 4-ethylpyridine. It can be seen by comparison that substitution of one H atom in the 6-position with a 2-(4-pyridyl)-ethyl group does not introduce a significant effect on the basicity constants of the primary amines. On the other hand, the basicity constant of the pyridine nitrogen atom of **1b** is lowered by ~0.5 log units, with respect to 4-ethylpyridine. This small variation could be ascribed to the presence of the protonated primary amine groups in the molecule, at the pH values at which protonation on pyridine starts to take place.

The coordinating tendencies of **1b** toward Cu^{II} has been studied by means of potentiometric titrations with standard base on aqueous solutions containing the ligand and $Cu(ClO_4)_2$ in equimolar amounts plus excess acid. **1b** behaves as its unsubstituted (**1a**) or benzyl-substituted (**1c**) analogues, as it releases the two protons on the amide nitrogens and forms a neutral complex with Cu^{II} (*i.e.* **2**), according to the equilibrium described in Scheme 1. This latter species is the only present in neutral or basic solutions. However, in more acidic conditions, complexes can form in which only one or no protons are released from the amide nitrogen atoms, in agreement with the already documented tendency[12] of tetraamino−dione ligands to form species of this kind.

Table 4. Logarithmic Formation Constants for the Complex Species in the System L/Cu^{II} (1:1 Molar Ratio)[a]

compd	L = **1a**[b]	L = **1b**[b]	L = **1c**[b]
CuL	7.20	7.61	
CuL_{-H}	1.03	1.35	1.62
CuL_{-2H}	−5.13[c]	−4.95[d]	−4.91[c]

[a] Column 1 indicates the degree of deprotonation. [b] Standard deviation = ±0.01 log units. [c] Values taken from ref 29. [d] In the case L = **1b**, CuL_{-2H} = complex **2**.

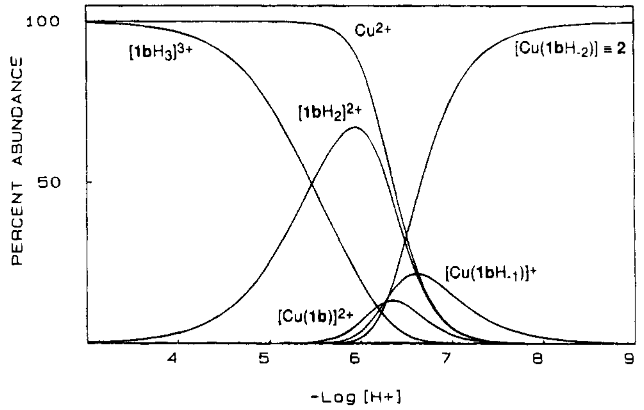

Figure 1. Distribution curves of the species present at the equilibrium in the system Cu^{II}/ligand **1b** with a 1:1 molar ratio. The species pertinent to each curve are indicated in the diagram.

Table 4 reports the log *K* values for the complexes with various degrees of deprotonation and, for comparison, those for the double deprotonated neutral complex of **1a,c**. In Figure 1, the distribution diagram for the possible species existing in an equimolar aqueous solution of **1b** and Cu^{II} is reported, from which it can be seen that (i) the nondeprotonated and monodeprotonated species exist only in a limited pH range and have an almost negligible weight in the species distribution and (ii) the double deprotonated complex **2** is the only species present in solution at pH ≥ 8. Moreover, it must be noted that under these conditions (1:1 molar ratio between Cu^{II} and ligand) no pyridine−metal cation interactions have been evidenced in the course of the potentiometric titration experiments, the appended pyridine behaving as a weak base which does not sense any metal.

The geometry of ligand **1b** guarantees by itself that, once the Cu^{II} ion is bound by the tetraamino−dione ligand, no contact is allowed between the pyridine nitrogen atom and the square planar Cu^{II} ion. In addition, the UV−vis spectra, recorded on solutions containing equimolar quantities of **1b** and Cu^{II} under conditions in which only **2** exists (*i.e.* pH > 8), show only one d−d band, centered at $\lambda = 520$ ($\epsilon = 70$ mol^{-1} dm^3 mL), which compares well with that found for the double deprotonated neutral Cu^{II} complexes of the related compounds **1a**[10] and **1c** ($\lambda_{max} = 516$ nm, $\epsilon = 63$ mol^{-1} dm^3 cm^{-1} and $\lambda_{max} = 520$ nm, $\epsilon = 65$ mol^{-1} dm^3 cm^{-1}, respectively), which exhibit square planar type coordination.[12] In addition, it must be mentioned that a series of cyclic tetramino−dione ligands, bearing an ethylpyridine group as in **1b**, but with the pyridine nitrogen atom in the correct position for further apical coordination, have

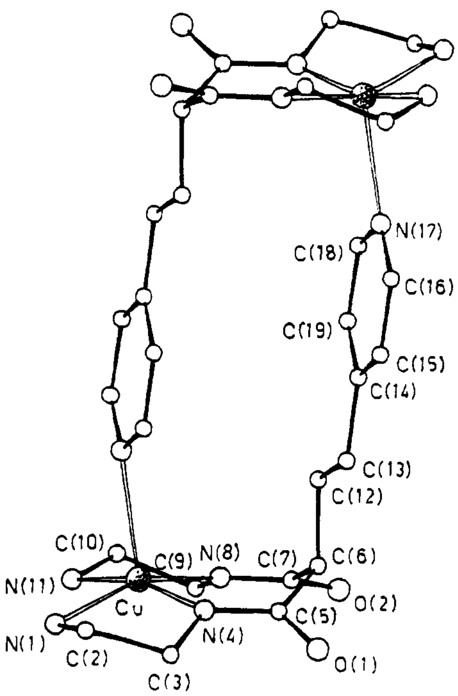

Figure 2. Perspective view of the centrosymmetric {Cu^{II} [*N,N'*-bis-(2-aminoethyl)-2-(2-(4-pyridyl)ethyl)malondiamido(2−)]}$_2$ (*i.e.* (**2**)$_2$) dinuclear complex with the atom numbering Scheme in the symmetry independent set.

Table 5. Relevant Bond Distances (Å) and Angles (deg) of the Complex $C_{14}H_{21}CuN_5O_2{\cdot}2H_2O$[a]

Cu−N(1)	2.029(5)	Cu−N(11)	2.046(5)
Cu−N(4)	1.976(5)	Cu−N(8)	1.987(5)
N(1)−C(2)	1.482(8)	Cu−N(17′)	2.350(7)
C(2)−C(3)	1.553(11)	C(7)−N(8)	1.303(9)
C(3)−N(4)	1.411(9)	C(7)−O(2)	1.259(7)
N(4)−C(5)	1.332(9)	N(8)−C(9)	1.458(8)
C(5)−C(6)	1.525(8)	C(9)−C(10)	1.543(10)
C(5)−O(1)	1.267(8)	C(10)−N(11)	1.454(8)
C(6)−C(7)	1.515(7)	C(12)−C(13)	1.529(10)
C(6)−C(12)	1.515(12)	C(13)−C(14)	1.522(14)
N(1)−Cu−N(4)	83.9(2)	N(4)−C(5)−O(1)	123.6(6)
N(1)−Cu−N(11)	93.9(2)	O(1)−C(5)−C(6)	116.6(6)
N(4)−Cu−N(8)	92.7(2)	C(5)−C(6)−C(7)	114.3(5)
N(8)−Cu−N(11)	83.0(2)	C(6)−C(7)−N(8)	119.2(6)
N(1)−Cu−N(17′)	97.6(2)	C(6)−C(7)−O(2)	116.5(5)
N(4)−Cu−N(17′)	98.8(2)	O(2)−C(7)−N(8)	124.2(6)
N(8)−Cu−N(17′)	104.4(2)	Cu−N(8)−C(7)	127.2(5)
N(11)−Cu−N(17′)	98.2(2)	Cu−N(8)−C(9)	114.1(4)
Cu−N(1)−C(2)	108.2(5)	C(7)−N(8)−C(9)	117.8(6)
N(1)−C(2)−C(3)	109.6(6)	N(8)−C(9)−C(10)	107.3(6)
C(2)−C(3)−N(4)	108.0(6)	C(9)−C(10)−N(11)	109.4(6)
C(3)−N(4)−Cu	115.0(5)	C(10)−N(11)−Cu	109.2(4)
C(5)−N(4)−Cu	125.0(4)	C(6)−C(12)−C(13)	112.7(6)
C(3)−N(4)−C(5)	117.2(6)	C(12)−C(13)−C(14)	115.0(6)
N(4)−C(5)−C(6)	119.8(6)		
Relevant Intermolecular Hydrogen Bonds			
N(1)−H(31)...O(2″)	3.00(1)	H(31)...O(2″)	2.01(1)
N(1)−H(31)−O(2″)	168(1)		
N(1)−H(32)...O(1‴)	2.99(1)	H(32)...O(2‴)	2.10(1)
N(1)−H(32)−O(1‴)	148(1)		
N(11)−H(131)...O(2‴)	2.95(1)	H(131)...O(2‴)	2.05(1)
N(11)−H(131)−O(2‴)	149(1)		
N(11)−H(132)...O2w	3.08(1)	H(132)...O2w	2.09(1)
N(11)−H(132)−O2w	167(1)		

[a] Equivalent positions: (′) $-x$, $1 - y$, $-z$; (″) y, $-x + y$, $-z$; (‴) x, y, $1 + z$.

shown *no tendency* of the pyridine moiety to interact with the encapsulated Cu^{II} ion.[24]

Finally, as demonstrated by the crystal and molecular structure (see next section and Figure 2), it has to be pointed out that, in the solid state, dimeric species are present, in which the pyridine group of one **2** unit coordinates the Cu^{II} ion of the other in an axial position. This gives reason for the unexpected deep blue color of the solid complex (λ_{max} = 590 nm in visible spectra recorded on powdered crystals spread on filter paper); as to better profit from pyridine axial coordination, the Cu^{II} ions are displaced from the N_4 equatorial plane, thus weakening the interactions with the diamino−diimido donor set. However, the hypothesis that even weak pyridine−Cu^{II} intermolecular interactions are mantained also in solution has to be discarded, as UV−vis spectra recorded at variable complex concentration ($5 \times 10^{-4} - 4 \times 10^{-2}$ M in 0.1 M $NaClO_4$, pH adjusted to 8 with NaOH) have not evidenced any change of the band position (λ_{max} = 520 nm, square planar coordination) or shape.

According to these results, the Cu^{II} complex **2** fulfills all the requirements which are needed for a L−X component, in so far as (i) it contains a well-defined and stable metal complex (at least in a delimited pH range) and (ii) it features a binding fragment which is by no means engaged in interactions with the already bound metal ion. In addition, the metal ion can be removed by variation of such a simple parameter as pH.

3. Crystal and Molecular Structure of the L−X Component 2. The crystal structure of complex **2** consists of centrosymmetric {Cu^{II} [*N,N'*-bis(2-aminoethyl)-2-(2-(4-pyridyl)-ethyl)malondiamido(2−)]}$_2$ (*i.e.* (**2**)$_2$) molecular complexes and crystallization water molecules. A perspective view of the dimeric molecule is shown in Figure 2. Selected bond distances and angles are given in Table 5.

In the dimeric complex, each dianion acts as a tetradentate tris(chelate) ligand, through the two amino (−NH_2) and the two imido (R−N^--CO) N atoms. The orientation of the (4-pyridyl)-ethyl moiety confers on each dianion a characteristic "cobra" conformation and allows the pyridine N atom to complete the coordination sphere of the centrosymmetric copper ion. Each Cu atom displays a distorted square pyramidal arrangement of the N_5 ligand donor set: two mutually *cis* N amino and two mutually *cis* N imido atoms are in the basal plane and the pyridine bridging nitrogen occupies the vertex of the pyramid at a distance [2.350(7) Å] quite in agreement with that usually found for the weak axial N donor (2.3−2.4 Å). The Cu−N(amino) and Cu−N(imido) bond lengths [2.038(5) (av) and 1.982(5) (av) Å, respectively] are as expected from the different electronic and hybridization states of the nitrogen atoms.[25] Also the values of the Cu−N(amino)−C [108.7(4)° (av)] and Cu−N(imido)−C [120.7(5)° (av)] bond angles agree with sp^3 and sp^2 hybridization states for the N atoms.

The roughly planar N_4 donor set is distorted toward a very flattened tetrahedron. The calculated displacements of the N atoms from the least-squares plane passing through them is 0.04-(1) Å for the N(1) and N(8) atoms and −0.04(1) Å for the N(4) and N(11) nitrogens. The metal center is displaced from the N_4 donor set least-squares plane by 0.34 Å toward the vertex of the pyramid.

The tetradentate tris(chelate) portion of each dianion is, as expected, markedly nonplanar, and the five-membered chelate rings adopt both *gauche* conformations while the six-membered chelate rings shows a *half-boat* conformation. The values of the torsion angles in the chelate rings suggest, at least for the

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(24) Kimura, E.; Koika, T.; Machida, R.; Nagai, R.; Kodama, M. *Inorg Chem.*, **1984**, *23*, 4181.

(25) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

tris-chelating complex moiety, a pseudosymmetry plane bisecting the N(1)−Cu−N(11), N(4)−Cu−N(8), and C(5)−C(6)−C(7) bond angles. In the six-membered chelate portion the C−N and the exocyclic C−O bond lengths indicate extensive conjugation for the involved imido moieties.

In the symmetry-independent mononuclear complex (**2**) the (4-pyridyl)ethyl fragment is almost orthogonal to the least-squares plane through N(1), N(4), C(5), C(7), N(8), and N(11) (the dihedral angle being 79.5(2)°) and the action of the inversion center, which builds the dimeric complex, brings the pyridine rings to interact with each other by "head to tail" type overlap, leaving an interplanar spacing between the pyridine moieties of 3.52 Å.

The dinuclear complexes are packed by intramolecular hydrogen bonds between N amino atoms, acting as donors, and acceptor O atoms from dianions or water molecules.

4. Solution Behavior of the SCC 3. Once dissolved in water, the SCC [*cis*-$Cl_2Pt^{II}(\mathbf{2})_2$], **3**, imparts to the solution the typical pink-violet color of square planar Cu^{II} diamino−diimido complexes, with a spectrum featuring only one band in the visible region, with $\lambda_{max} = 416$ nm ($\epsilon = 110$ dm^3 mol^{-1} cm^{-1}). The color is mantained at neutral or basic pH values, while it disappears on going to acidic conditions, in which the solution assumes the pale azure color of the Cu^{II} aqua ion. On going back to basic conditions, the pink-violet species is restored, indicating that is possible to go back and forth, on variation of pH, from the square planar dicopper supramolecular species **3** to the corresponding demetalated ligand *3** (partially or completely protonated on the primary amino groups).

The coordination behavior of **3** has been exhamined in more detail by means of potentiometric titrations with standard base on solution containing **3** plus excess acid. It has to be pointed out that, due to the impossibility to isolate the corresponding copper-free molecule (*i.e.* *3**), it has not been possible to directly measure the protonation constants of the four primary amino groups in **3**. However, considering the high flexibility of the system when no metal interacts with the tetramino−dione binding unit and the rather large distance between the two appended subunits, it seemed to us reasonable to assume that the two L−X components behave independently, at least when only protonation processes are taken into account. Moreover, the charge center of the Pt(II) ion is delocalized and spatially removed from the primary amino groups. According to this, the hypothesis that the relative protonation constants are very similar to those found in the separate component **1b** was put forward. In fact, a good fit has been found between the experimental and the calculated data when the protonation constants of the primary amines have been assumed to be identical to those of **1b**.[26] Under these conditions, a distribution of species has been found which features only two copper-containing complexes (see Figure 3 for distribution diagram).

The most abundant species is, as expected, **3**, *i.e.* the supramolecular complex in which the four amide protons have been released and two Cu^{II} ions uptaken. **3** represents the only species present in solution at pH > 7 and has a log *K* value of −13.76(0.04), corresponding to the equilibrium

$$3^* + 2Cu^{2+} = \mathbf{3} + 4H^+$$

It can be seen (see Table **4**) that the value for the formation of **3** is 3.8 log units lower than double of the log *K* value relative to the formation of the separate component **2**, which should be the correct value for comparison if the two diamino diamido subunits in **3** behave *independently* also in the complexation process. On the contrary, it is evident that the two complexed subunits *do interact*, disturbing each other and making the system less stable. This can be explained on the basis of the rigid square planar configuration that the diamino−diimido donor set must assume once complexed to a Cu^{II} ion, which raises the sterical demand of each subunit in the supramolecular system, thus lowering the overall formation constant.

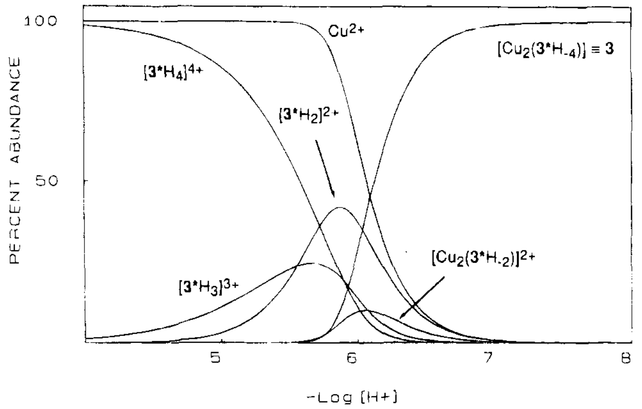

Figure 3. Distribution curves of the species present at the equilibrium in the system Cu^{II}/*3** (2:1 molar ratio). The species pertinent to each curve are indicated in the diagram.

As regards the other copper−containing species, which has a low weight in the distribution diagram, refinement of the potentiometric data has evidenced the release of two amide protons and the uptake of two copper ions, with respect to ligand *3**, with a log *K* value of −1.23(0.08) relative to the equilibrium

$$3^* + 2Cu^{2+} = [3^*_{(-2H)}Cu_2]^{2+} + 2H^+$$

As both a nondeprotonated and a monodeprotonated complex have been evidenced in the case of the separate component **1b**, two cases are possible in principle: (i) one subunit uptakes a copper ion forming a neutral complex, after the release of two protons, while the second subunit coordinates a copper ion with no proton release; (ii) both the subunits loose one proton and coordinate one copper ion.

The second possibility seems more likely if one takes into account the symmetry of the supramolecular system. Moreover, also the low formation constant of this species points in favor of this hypothesis, as, in the case of the separate component **1b**, the formation constants are 7.61 and 1.35, for the non-deprotonated and monodeprotonated species, respectively.

5. Redox Behavior. DPV studies were carried out both for the L−X component **2** and for the supramolecular complex **3** in aqueous solution, 0.1 M in $NaClO_4$, after adjusting the pH at 8, a value at which these complexes represents 100% of the species in solution (see the pertinent distribution diagrams). In the case of **2**, DPV measurements disclosed a one-electron reversible signal with an half-wave potential of 971 mV vs NHE, which corresponds to the oxidation of the Cu^{II} center to Cu^{III} and compares well with what found[27] for the complex with the unsubstituted ligand **1a** (941 mV vs NHE) and for that with the ligand bearing a benzyl group **1c** (981 mV vs NHE). In the case of the supramolecular complex **3**, only one oxidation wave was observed ($E_{1/2}$ = 951 mV vs NHE), corresponding to the two-electron oxidation of both the Cu^{II} centers, taking place at a potential well set in the range found for the related

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(26) Variation of the protonation constants in the range of ±0.4 log units with respect to those of **1b** neither improves the data fitting nor changes significantly the values of the formation constants for the copper-containing supramolecular species.

(27) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Poggi, A. *Supramolecular Chem.* **1994**, *3*, 115.

Cu^{II} diamino–diimido complexes. However, the DPV profile displayed a half-peak width of 105 mV, instead of the 90 mV value which is expected for a molecule containing two equivalent and independent (*i.e.* non-interacting) redox sites, undergoing a reversible electrochemical process.[28] This increase in the $\Delta E_{1/2}$ value in the case of **3** may be interpreted either as a partial irreversibility in the oxidation of two noninterfering Cu^{II} centers or, more likely, as an effect due to a weak electrostatic interaction between one already oxidized Cu^{III} and the second Cu^{II} center, which is able to sense the presence of the +1 charged proximate moiety. The latter hypothesis is supported by the results found in the complexation studies, which have demonstrated that the two L–X subunits **2**, once assembled in the supramolecular species **3**, sense each other.

Conclusions

This work has demonstrated that it is possible to build up supramolecular coordination compounds which are able to exchange the peripheral M^{n+} transition metal cations in aqueous solution, upon variation of a bulk parameter such as pH. In particular, complex **3** releases two Cu^{II} ions on going from basic to acidic conditions but the complex is regenerated if the pH value is raised again. This is due to the pH-dependant coordinative behavior of its L–X components (complex **2**), which are based on the properties of the versatile diamino–diamido binding unit (**1a**). In addition, the availability of straightforward synthetic routes to prepare functionalized derivatives of this latter moiety makes it a candidate for the construction of more sophisticated supramolecular devices, capable to recognize, sense, or transport transition metal cations.[29] Moreover, the study of the electrochemical and coordinative properties of the separated L–X component **2** has demonstrated that these are only slightly affected when two L–X are assembled in the molecule **3**, indicating weak (even if significant) interactions between the components in the supramolecular species. This allows one to design other SCC based on L–X components which feature an X fragment of the M^{2+} diamino diimido type and an L fragment of the pyridine (or polypyridine) type, thinking of the properties of the supramolecular species simply as a *sum* of those of its components.

Finally, X-ray diffraction studies on complex **2** have disclosed, in the solid state, an unusual coordination environment of the Cu^{II} cation, which is displaced from the plane of the N$_4$ coordinative set to interact in the axial position with the N atom of the pyridine moiety of a second complex, forming a "head to tail" dimeric species. This explains the blue color and the visible spectra of the solid (λ_{max} = 590 nm), which are quite unexpected for Cu^{II} complexes of the diamino–diimido type.

Supporting Information Available: Tables of the anisotropic and isotropic displacement parameters for the non-hydrogen atoms (Table SI), fractional coordinates and *U* values of the hydrogen atoms (Table SII), complete bond distances and angles (Table SIII), and a full presentation of the crystal data and experimental details (Table SIV) (5 pages). Ordering informations is given on any current masthead page.

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(29) Fabbrizzi, L.; Licchelli, M.; Pallavicini P.; Perotti, A.; Sacchi, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1975.

(30) Brown, H. C.; Mihm, R. X. *J. Am. Chem. Soc.* **1955**, *77*, 1723.