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Copper(I) Complexes with a Cu_4S_6- and CuS_4-Type Core Obtained from the Reaction of Copper(0) with $HN(SPPh_2)_2{\cdot}I_2$

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The copper(I) compounds $[Cu^I_4(L)_3]I_3$ (**1**) and $[Cu^I(HL)_2]$-$I_3{\cdot}CH_3CN$ (**2**) [HL = $HN(SPPh_2)_2$] have been obtained from the reaction of the adduct $HL{\cdot}I_2$ with copper(0) powder in diethyl ether solution. Compound **1** contains a tetrahedron of Cu atoms with three anionic L ligands coordinated to the coppers through the sulfur atoms to build a Cu_4S_6 core. The mean Cu–Cu and Cu–S bond lengths related to the Cu_4S_6 core in copper-loaded transcription factors CuAce1 and CuMac1, and in the model compound $[Cu_4(SPh)_6]^{2-}$, have been compared with those of the $[Cu_4(L)_3]^+$ cation, and the geometric volumes of the Cu_4 cores have been evaluated. The results suggest that the cation $[Cu_4(L)_3]^+$ is a possible structural model compound for the metal site in Ace1 and Mac1 transcription factors. In compound **2**, two neutral HL ligands bind a Cu^I ion in an *S*,*S′*-isobidentate chelating fashion to form a slightly distorted tetrahedral CuS_4 core. The ^{31}P NMR spectroscopic data of compound **1** are consistent with the maintenance of its structure in solution. Moreover, phosphorus variable-temperature measurements indicate a change from a two-spin coupled AB system at 0 °C to an A_2 spin system at 40 °C. The reaction of $[Cu_4(L)_3]^+$ with HI, monitored by ^{31}P NMR spectroscopy, leads to the protonation of the complexed ligands at the Cu_4 core and formation of the cation $[Cu_4(HL)_3]^{4+}$. The protonation reaction is reversible: increasing the amount of organic base 1,8-bis(dimethylamino)naphthalene (DMAN) regenerates the starting cation $[Cu_4(L)_3]^+$.

Introduction

The tetraphenyldithioimidodiphosphanic acid ligand HL, and its deprotonated derivative L, have been extensively used in coordination chemistry[1] since they feature a flexible SPNPS skeleton along with a large S···S bite that enables the formation of an unstressed six-membered, MSPNPS chelate ring with a great variety of metal ions.[1] A literature survey reveals that there have been some studies on the reaction of L with Cu^{II} salts, and these have led to the synthesis of complexes $[Cu^{I,II}_3L_4]$, $[Cu^I_3L_3]$, $[Cu^I_4L_3]$-$[Cu^ICl_2]{\cdot}CCl_4$[2a] and, more recently, $[Cu^I_4L_3][BF_4]$.[2b] Furthermore, the ability of L to form a tetrahedral CuS_4 core with the Cu^{II} ion has been used by Bereman et al.[3] to propose the complex $[Cu(L)_2]$ as a potential model for type-I Cu^{II} sites in metalloenzymes; unfortunately, the complex was not stable for more than a few days at room temperature, either in the solid state or in solution, due to autoreduction to Cu^I. Recently, Woollins et al. have described three other complexes of general stoichiometry $[Cu^I_3D_3]$ (D = $[N(SPiPr_2)_2]^-$, $[N(SPiPr_2)(SPPh_2)_2]^-$ and $[N\{SP(EtO)_2\}$-$\{SP(OPh_2)\}_2]^-$) obtained from the reaction of either Cu^{II} or Cu^I ions with the corresponding anionic ligand D.[4] The X-ray crystal structures of these complexes revealed that the molecules contain a six-membered $Cu^I_3S_3$ ring in their core, with each copper atom being tricoordinate in an approximately trigonal geometry resulting from the coordination of one terminal and two bridging S-donors.

The $Cu^I_xS_y$ cores[5] may be of interest as structural model compounds for the active-sites in copper(I)-containing enzymes and proteins, which are far less known or studied than the copper(II) analogues. For example, the $Cu^I_4S_6$ core is currently generating great interest since two copper-regulated transcription factors central to yeast copper homeostasis, Ace1 and Mac1, in *Saccharomyces cerevisiae*, have revealed the presence of a remarkably similar polycopper cluster in these two proteins.[6]

In this paper, we have delved into the synthesis of new copper complexes of HL and/or L using the well-tested route based on the iodine adduct of HL, $HL{\cdot}I_2$, as oxidising/complexing agent towards metal(0) powders. In fact,

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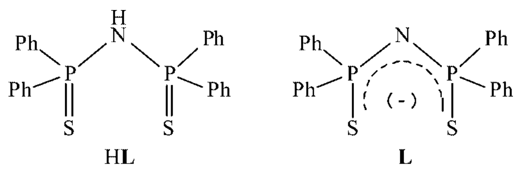
this kind of reaction has proved to be an interesting and promising synthetic route, as it has often led to the preparation of complexes with unusual stoichiometries and geometrical features.[7] The reaction between the $HL·I_2$ adduct and copper(0) powder has been investigated, and the X-ray crystal structures of complexes $[Cu_4(L)_3]I_3$ (**1**) and $[Cu(HL)_2]I_3·CH_3CN$ (**2**) are reported. The $Cu^I_4S_6$ core in complex **1** has been studied by solid-state ^{31}P NMR spectroscopy and solution variable-temperature NMR spectroscopy as well. The results, along with the structural data, suggest that $[Cu_4(L)_3]^+$ is a possible structural model compound for the metal site in Ace1 and Mac1 transcription factors. The reactivity of complex **1** to form the cationic complex $[Cu^I_4(HL)_3]^{4+}$ has also been evaluated as a dependence on the acid/base behaviour of the metal-complexed ligands L and HL (Scheme 1).



Scheme 1.

Results and Discussion

Syntheses and Crystal Structures of $[Cu^I_4(L)_3]I_3$ (1) and $[Cu^I(HL)_2]I_3·MeCN$ (2)

The reaction between the adduct $HL·I_2$ and Cu powder (1:1 molar ratio) was carried out in diethyl ether at room temperature for two days. During this time the dark-red colour of the mixture turned to pale-orange with separation of an orange powder. ^{31}P NMR spectroscopic analysis of the solution after two days indicated that the reaction was quantitative since no signal related to HL was detectable. The ^{31}P MAS NMR spectrum of the solid remaining after removal of the solvent revealed resonances at $\delta = 52.4$, 32.9, 31.4, 30.4, 28.9 and 26.6 ppm, which are indicative of the presence of metal-complexed ligands both in their protonated, HL, and deprotonated, L, forms. Resonances in two specific ranges of the spectrum, namely $\delta = 60$–50 and 40–20 ppm, can be considered highly diagnostic in identifying the species HL and L, respectively.[8] Treatment of the crude precipitate with $CHCl_3$ caused a partial dissolution of the solid; after slow evaporation of the solvent, orange crystals of stoichiometry $[Cu^I_4(L)_3]I_3$ (**1**) were isolated. The remaining crude precipitate was then dissolved in MeCN to produce orange crystals of $[Cu^I(HL)_2]I_3·MeCN$ (**2**) on slow evaporation of the solvent. From the ^{31}P MAS NMR resonances of compounds **1** and **2** it was possible to confirm that both copper complexes are present in the orange powder separated from the ethereal reaction solution. The separation of the two complexes is, therefore, attributable to their markedly different solubility in the solvents employed. The structure of the cation of **1** has been reported before as its $CuCl_2$ and BF_4 salts; however, it was re-determined, and is briefly reported here, to provide a solid basis for the interpretation of the ^{31}P NMR measurements.

Compound **1** consists of discrete $[Cu^I_4(L)_3]^+$ cations and I_3^- anions separated by normal van der Waals contacts. The molecular structure of the cation $[Cu^I_4(L)_3]^+$ is shown in Figure 1, while selected bond parameters are reported in Table 1. The cation consists of a tetrahedron of copper(I) atoms surrounded by three didentate L ligands coordinated to the copper atoms through the sulfur atoms. The arrangement of the ligands around the metal core resembles that found in $[Cu^I_4(L)_3]^+[CuCl_2]^-·CCl_4$ (**3**),[2a] i.e. it conforms to a pseudo-trigonal idealised symmetry, with the threefold symmetry axis passing through the unique Cu(4) and the mid-point of the three remaining copper atoms (Figure 1). One sulfur atom of each ligand binds the Cu(4) atom and one of the three remaining copper atoms [Cu(1), Cu(2) and Cu(3)], while the second sulfur atom binds a couple of copper atoms of the basal plane. Thus, each copper of the basal plane is coordinated by two S atoms of the same ligand and by the sulfur atom of a different ligand. The distances of the unique Cu(4) atom to the remaining copper atoms are, on average, slightly shorter than those found between the other couples of copper atoms (2.787 vs. 2.812 Å). These values compare well with those found in the analogous complex **3** (mean values of 2.777 vs. 2.806 Å), although significant variations in the single copper–copper distances are observed in the two compounds due to local packing effects associated with different counteranions and with the presence of a solvent molecule. In **3**, the Cu–S bond lengths involving the unique Cu(4) atoms are not significantly different from each other and range from 2.257 to 2.278 Å. This range is wider in **1** (2.256–2.291 Å), with the larger Cu–S bonds being those with Cu(4). Very small changes are observed in the P–S and P–N bonds of the two compounds,

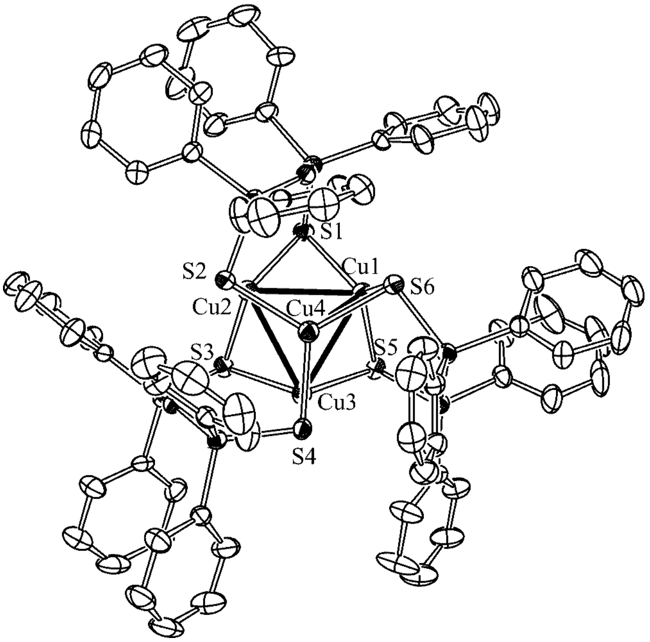


Figure 1. ORTEP drawing of the $[Cu_4(L)_3]^+$ complex cation of **1**. Thermal ellipsoids are drawn at 30% probability.

while a significant increase in the P–N–P angle occurs on passing from **1** to **3** (133.5° and 138.0°, respectively). The triiodide anion is slightly asymmetric and almost linear [174.60(2)°], and no I···I contacts between different anions are observed.

Table 1. Selected interatomic distances [Å] and angles [°] for compound **1**.

Cu(1)–Cu(2)	2.7679(8)	Cu(1)–Cu(4)	2.8033(8)
Cu(1)–Cu(3)	2.8370(9)	Cu(2)–Cu(4)	2.7994(8)
Cu(2)–Cu(3)	2.8306(8)	Cu(3)–Cu(4)	2.7578(8)
S(1)–Cu(2)	2.270(1)	S(1)–Cu(1)	2.280(1)
S(2)–Cu(2)	2.261(1)	S(2)–Cu(4)	2.285(1)
S(3)–Cu(3)	2.272(1)	S(3)–Cu(2)	2.283(1)
S(4)–Cu(3)	2.269(1)	S(4)–Cu(4)	2.291(1)
S(5)–Cu(1)	2.256(1)	S(5)–Cu(3)	2.280(1)
S(6)–Cu(1)	2.263(1)	S(6)–Cu(4)	2.291(1)
P(1)–S(1)	2.055(2)	P(2)–S(2)	2.043(2)
P(3)–S(3)	2.056(2)	P(4)–S(4)	2.058(2)
P(5)–S(5)	2.051(2)	P(6)–S(6)	2.052(2)
P(1)–N(1)	1.588(4)	P(2)–N(1)	1.593(4)
P(3)–N(2)	1.585(4)	P(4)–N(2)	1.593(4)
P(5)–N(3)	1.586(4)	P(6)–N(3)	1.585(4)
I(1)–I(2)	2.9436(9)	I(2)–I(3)	2.8911(8)
Cu(2)–Cu(1)–Cu(4)	60.32(2)	Cu(2)–Cu(1)–Cu(3)	60.65(2)
Cu(4)–Cu(1)–Cu(3)	58.54(2)	Cu(1)–Cu(2)–Cu(4)	60.46(2)
Cu(1)–Cu(2)–Cu(3)	60.88(2)	Cu(4)–Cu(2)–Cu(3)	58.66(2)
Cu(4)–Cu(3)–Cu(2)	60.11(2)	Cu(4)–Cu(3)–Cu(1)	60.12(2)
Cu(2)–Cu(3)–Cu(1)	58.47(2)	Cu(3)–Cu(4)–Cu(2)	61.24(2)
Cu(3)–Cu(4)–Cu(1)	61.34(2)	Cu(2)–Cu(4)–Cu(1)	59.21(2)
Cu(2)–S(1)–Cu(1)	74.92(4)	Cu(2)–S(2)–Cu(4)	76.00(4)
Cu(3)–S(3)–Cu(2)	76.82(4)	Cu(3)–S(4)–Cu(4)	74.40(4)
Cu(1)–S(5)–Cu(3)	77.40(4)	Cu(1)–S(6)–Cu(4)	75.97(4)
P(1)–N(1)–P(2)	133.5(2)	P(3)–N(2)–P(4)	134.2(2)
P(6)–N(3)–P(5)	132.9(2)	I(1)–I(2)–I(3)	174.60(2)

The molecular structure of [Cu^I(HL)$_2$]I$_3$·MeCN (**2**) is shown in Figure 2 and selected bond lengths and angles are collected in Table 2. In the complex cation [Cu^I(HL)$_2$]$^+$ the copper is coordinated by two neutral HL ligands in an *S*,*S′*-isobidentate chelating fashion, resulting in the formation of two six-membered CuS$_2$P$_2$N rings; the charge is balanced by a slightly asymmetric I$_3^-$ ion. One solvent molecule (MeCN) per formula unit is also present in the structure, giving rise to weak hydrogen bonding with an imido group [N(2)–H(N2)···N(3) = 2.925 Å; N(2)–H···N(3) = 166.63°]. The [Cu^I(HL)$_2$]$^+$ cation contains a slightly distorted tetrahedral CuS$_4$ core, with S–Cu–S angles ranging from 101.10(8)° to 117.92(8)°. The four Cu–S interatomic distances are slightly different and range from 2.338(2) [Cu(1)–S(3)] to 2.376 Å [Cu(1)–S(2)]. The CuSPNPS metallacycles display a pseudo-boat conformation with a P and an S atom of the ring acting as the stern and bow of the boat,

Table 2. Selected interatomic distances [Å] and angles [°] for compound **2**.

Cu(1)–S(1)	2.363(2)	Cu(1)–S(2)	2.376(2)
Cu(1)–S(3)	2.338(2)	Cu(1)–S(4)	2.352(2)
P(1)–S(1)	1.962(3)	P(2)–S(2)	1.959(3)
P(3)–S(3)	1.961(3)	P(4)–S(4)	1.963(3)
P(1)–N(1)	1.666(7)	P(2)–N(1)	1.689(6)
P(3)–N(2)	1.670(7)	P(4)–N(2)	1.675(7)
I(1)–I(2)	2.9486(9)	I(2)–I(3)	2.8786(9)
S(1)–Cu(1)–S(2)	112.96(8)	S(3)–Cu(1)–S(4)	112.62(8)
S(2)–Cu(1)–S(4)	101.10(8)	S(1)–Cu(1)–S(4)	117.92(8)
S(1)–Cu(1)–S(3)	101.40(8)	S(2)–Cu(1)–S(3)	111.22(9)
I(1)–I(2)–I(3)	175.52(3)		
P(1)–N(1)–P(2)	127.4(4)	P(3)–N(2)–P(4)	126.9(5)
N(1)–P(1)–C(1)	102.7(3)	N(1)–P(1)–C(7)	109.6(3)
C(1)–P(1)–C(7)	106.5(4)	N(1)–P(1)–S(1)	112.7(3)
C(1)–P(1)–S(1)	113.6(3)	C(7)–P(1)–S(1)	111.2(3)
N(1)–P(2)–S(2)	114.6(2)	N(2)–P(3)–S(3)	113.9(3)
N(2)–P(4)–S(4)	115.0(3)	P(1)–S(1)–Cu(1)	96.45(10)
P(2)–S(2)–Cu(1)	96.60(11)	P(3)–S(3)–Cu(1)	98.98(11)
P(4)–S(4)–Cu(1)	98.01(11)		

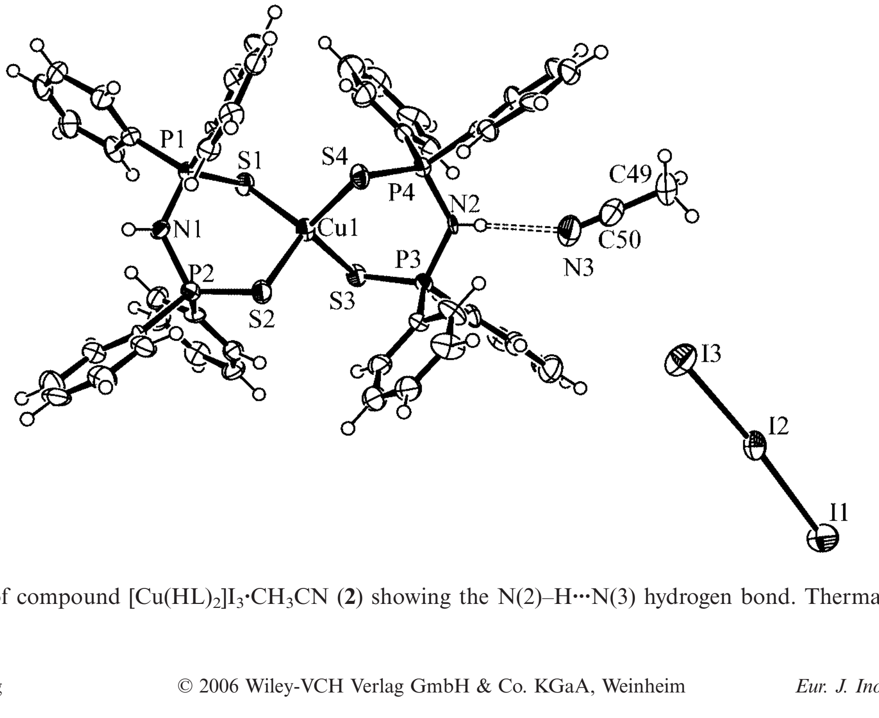


Figure 2. ORTEP plot of compound [Cu(HL)$_2$]I$_3$·CH$_3$CN (**2**) showing the N(2)–H···N(3) hydrogen bond. Thermal ellipsoids are drawn at 30% probability.

respectively. As a result of metal complexation, some degree of π-electron delocalisation over the $[Cu(SP)_2N]$ ring can be recognised from the slight increase in P–S bond lengths: from 1.937(1)–1.950(1) Å in the free ligand[9] to 1.959(3)–1.963(3) Å in **2**. Conversely, the P–N bond lengths remain substantially similar to those found in free HL [HL:[9] 1.672(2)–1.683(2) Å; **2**: 1.666(7)–1.689(6) Å].

Solution and Solid-State ^{31}P NMR Spectroscopy

The solid-state ^{31}P NMR spectrum of complex **1** shows resonances at δ = 32.9 (Δν½ = 168 Hz), 31.4 (Δν½ = 134 Hz), 30.4 (Δν½ = 159 Hz), 28.9 (Δν½ = 183 Hz) and 26.6 ppm (Δν½ = 213 Hz), indicative of different crystallographically independent phosphorus atoms in the complex. Conversely, complex **2** shows the presence of a single resonance at δ = 52.4 ppm with a spectral line-width of 410 Hz, suggesting that the phosphorus atoms in the asymmetric unit have a closely similar environment. The variable-temperature ^{31}P NMR spectra of **1** in $CHCl_3$ are shown in Figure 3. The spectrum recorded at 25 °C shows two distinct signals (δ = 28.5 and 28.1 ppm) with an intensity ratio of 1:1, also consistent with the maintenance of the solid structure in solution. (For $[\mathrm{Cu^I}_4\mathrm{L}_3][\mathrm{BF}_4]$ in CD_3CN, a single broad peak at δ = 27.05 ppm has been reported, although no temperature is given).[2b] As the temperature of the solution is lowered from 25 °C to 0 °C, the ^{31}P NMR spectra reveal two interesting spin-coupled doublets (AB system) with a $^2J_{P,P}$ coupling constant of 11.0 Hz; the spectrum at –40 °C shows that this coupling constant is temperature-invariant. The appearance of two spin-coupled doublets confirms that both phosphorus resonances are from the same complex molecule rather than from different isomers present in solution, and that the most likely explanation for this observation is the stabilisation of a conformer of the CuS_2P_2N rings. As the temperature of the solution is increased to 37.5 °C, the two well-separated resonances at δ = 28.5 and 28.1 ppm coalesce ($k_{\mathrm{coal}} = 126\ \mathrm{s}^{-1}$),[10] and at 40 °C, the highest temperature reached, the phosphorus atoms become equivalent and the spectrum degenerates to an A_2 system. At this point, a fast exchange process on the NMR timescale makes the four copper atoms equivalent. The dynamic process that averages the phosphorus NMR resonances seems to be non-dissociative, since the reaction of **1** with HL, or with the mixed sulfur/oxygen ligand $HN(SPPh_2)(OPPh_2)$, in the 25–40 °C ($CHCl_3$) range results in no ligand exchange. Moreover, the conductivity measured in $CHCl_3$ does not show changes in the range 25–40 °C.

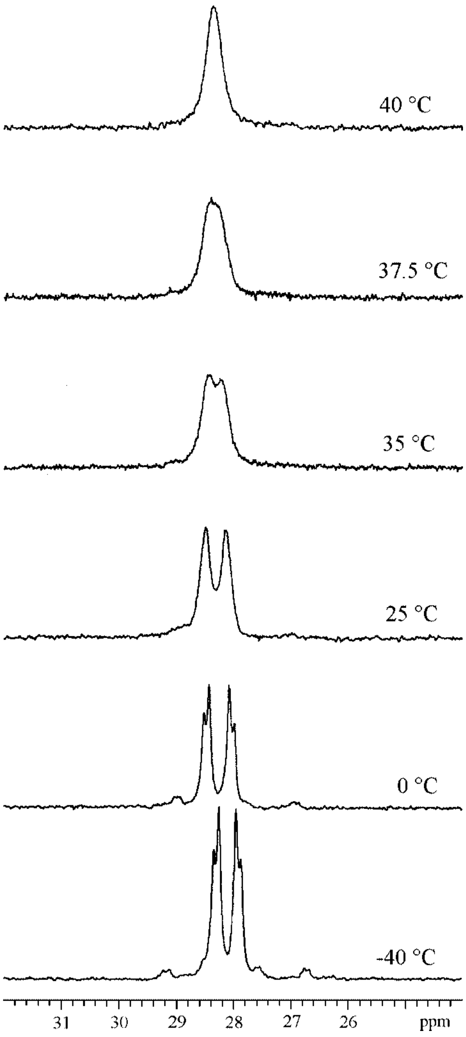


Figure 3. Variable-temperature ^{31}P NMR spectra of complex **1** (1.0×10^{-2} M, $CDCl_3$).

Reactivity of the $[Cu_4(L)_3]^+$ Cluster

Several studies have demonstrated that Cu activation of Ace1 and Mac1 involves formation of a tetracopper cluster within the Cu-regulatory domain. EXAFS data for CuAce1 and CuMac1[6b] suggests the presence of a distorted tetranuclear copper cluster; the Cu^I ions are trigonally coordinated with Cu–S distances of about 2.25 Å and a Cu–Cu distance of 2.7 and 2.9 Å when two different Cu···Cu interactions were considered (Table 3). In this context, the Cu_4S_6 core in the cation $[Cu_4(L)_3]^+$ might represent a useful model compound for the metal centres in CuAce1 and CuMac1, since the mean Cu–S and Cu–Cu bond lengths (Table 3) compare well with those reported for these clusters. Moreover, unlike the copper thiolate model compound[11] $[Cu_4(SPh)_6]^{2-}$, in which the Cu^I ions are chemically equivalent, the cation $[Cu_4(L)_3]^+$ contains two chemically different sets of Cu^I ions [Cu(1)/Cu(2)/Cu(3) and Cu(4), respectively] that might structurally better represent the distorted tetracopper cluster within the Cu-regulatory domain. Although the two ionic complexes $[Cu_4(L)_3]^+$ and $[Cu_4(SPh)_6]^{2-}$ feature the same Cu_4S_6 core type, a significant difference in the "volume" of the Cu_4 cages is calculated from the mean Cu···Cu bond lengths (Table 3). Interestingly, the Cu_4 volume in the CuAce1 and CuMac1 transcriptions factors proves to be intermediate between those found in the ionic model compounds. The possibility of the Cu_4 cluster expanding or contracting as a result of the nature of the ligands forming the Cu_4S_6 cores and of the charge transferred by the ligands upon it seems to be a peculiar characteristic of this species.

Table 3. Mean Cu–Cu and Cu–S bond lengths in selected copper complexes with a Cu_4S_6 core, and Cu_4 cluster volume.

Sample	Interaction	*N*[a]	Interatomic distances [Å]	Cu_4 volume[b] [Å^3]
CuAce1[c]	Cu····Cu	2	2.704(2)	2.50
	Cu····Cu	1	2.902(6)	
	Cu–S	3	2.251(1)	
CuMac1[c]	Cu····Cu	2	2.705(4)	2.50
	Cu····Cu	1	2.891(9)	
	Cu–S	3	2.251(2)	
1[d]	Cu····Cu[e]		2.8118(8)	2.60
	Cu····Cu[f]		2.7868(8)	
	Cu–S[g]	3	2.2751(1)	
$(Ph_4P)_2[Cu_4(SPh)_6]$[h]	Cu····Cu[i]	3	2.744(4)	2.43
	Cu–S[j]	3	2.261(6)	

[a] Number of Cu–Cu and Cu–S interactions of specified distance for each copper atom. [b] Calculated as geometrical volume of the Cu_4 tetrahedron. [c] Interatomic distances from EXAFS data analysis, ref.[6b] [d] This work. [e] Interatomic distance calculated as the mean of the Cu(1)–Cu(2), Cu(1)–Cu(3) and Cu(2)–Cu(3) bond lengths. [f] Interatomic distance calculated as the mean of the Cu(1)–Cu(4), Cu(2)–Cu(4) and Cu(3)–Cu(4) bond lengths. [g] Value calculated as the mean of all Cu–S bond lengths. [h] Data from ref.[11] [i] Value calculated as the mean value of all Cu–Cu bond lengths. [j] Value calculated as the mean value of all Cu–S bond lengths.

Dance et al.[5,6c] have reported on the stability of Cu^I tetracopper Cu_4S_6 clusters with small thiolate ligands and have shown that the clusters are held together by bridging thiolates and that the Cu···Cu bonding is a minor energetic factor in the stability of the clusters. In this regard, since both ligands L and HL can act as chelating agents towards a copper(I) ion, although a substantial difference in nucleophilicity is to be taken into account,[12] we thought of verifying the ability of the Cu_4 core to remain stable even if coordinated by a set of neutral HL ligands.

The treatment of **1** with the acid HI (55 wt.-% in water) in a mixture of MeCN and $CDCl_3$ (1:10 v:v) at 25 °C until a 1:2.8 molar ratio was reached resulted in a considerable change in the ^{31}P NMR spectrum of the complex (Figure 4a–d): the two distinct signals of **1** at δ = 28.5 and 28.1 ppm are lower in intensity, while a new signal at lowfield (δ = 52.9 ppm) increases with the amount of HI. The latter value is strongly indicative of the formation of a new complex with all the ligands in their *N*-protonated form; interestingly, no other resonances due to copper complexes bearing L and HL ligands at the same time were detected for any molar ratio of the reagents used. Values for the $\delta(PS)$ in the 60–50 ppm range have, in fact, been observed previously in the neutral complexes $[Pd(HL)I_2]$[13] [$\delta(PS)$ = 56.5 ppm (MeCN/$CHCl_3$, 1:1 v:v) and $[Hg(HL)I_2]$[14] [$\delta(PS)$ = 57.8 ppm, CH_2Cl_2]. To rule out that ligand protonation has caused the dismantling of the Cu_4 core, we also verified that the protonation reaction is reversible. The reaction of the acidic mixture with a strong base like 1,8-bis(dimethylamino)naphthalene (DMAN) causes the deprotonation of the coordinated ligands and the regeneration of the cation $[Cu_4(L)_3]^+$, as shown by the ^{31}P NMR peaks at δ = 28.5 and 28.1 ppm. (Figure 4, e and f). The overall reactions involving the protonation/deprotonation of the ligands in the cationic complexes $[Cu_4(L)_3]^+$ and $[Cu_4(HL)_3]^{4+}$ are summarised in Scheme 2.

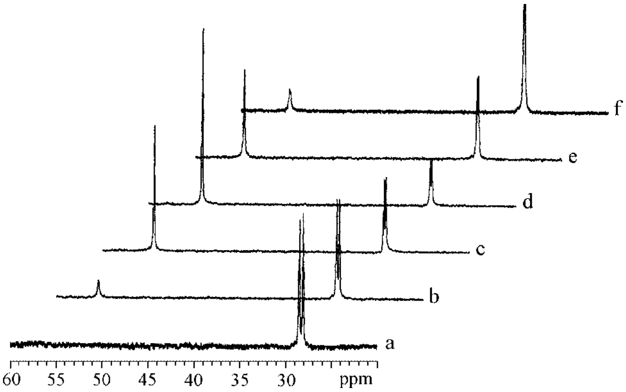
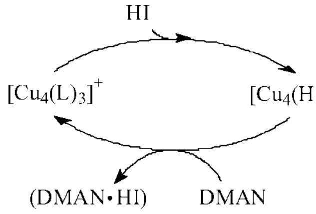


Figure 4. ^{31}P NMR spectra of (a) **1** (3.4×10^{-3} M); (b), (c), and (d) solution of **1** after the addition of HI to realise **1**/HI molar ratios of 1:1, 1:2 and 1:2.8, respectively; (e) the solution of (d) after addition of DMAN (**1**/HI/DMAN = 1:2.8:0.65); (f) the solution from (e) after addition of more DMAN (**1**/HI/DMAN, 1:2.8:1.3), all in MeCN/$CDCl_3$ (1:10 v:v) at 25 °C.



Scheme 2.

Although we were not able to isolate any solid compound from the reaction of **1** with HI, the reported results point to the ability of the Cu_4 cluster to be stabilised by neutral and anionic ligands.

Conclusions

The reaction of the adduct HL·I_2 with copper(0) powder under mild conditions affords complexes $[Cu^I_4(L)_3]I_3$ (**1**) and $[Cu^I(HL)_2]I_3$·CH_3CN (**2**). The latter compound represents a rare example of a structurally characterised complex of HL. To the best of our knowledge, only two other complexes are known in the literature, namely $[Hg(HL)I_2]$[14] and $[Ag(HL)_2BF_4]$[2b]. The copper(I) ion is coordinated by two neutral HL ligands in an *S,S′*-isobidentate chelating fashion to give a CuS_4 core. Compound **1** features a distorted tetrahedral Cu_4 cluster encapsulated by three bidentate anionic L ligands where only three of the four copper atoms of the Cu_4S_6 core are chemically equivalent. ^{31}P NMR variable-temperature measurements have confirmed that the solid structure is retained in solution and highlight a fast exchange process that makes all coppers equivalent (T_{coal} = 37.5 °C). Interestingly, the Cu_4S_6 core in the cation $[Cu^I_4(L)_3]^+$ might be considered as a new structural model compound for the distorted tetranuclear copper(I) cluster within the Cu-regulatory domain in proteins Ace1 and Mac1. Moreover, it constitutes a valid alternative to the higher symmetric Cu_4S_6 core found in the anionic copper thiolate compound $[Cu_4(SPh)_6]^{2-}$. A comparison of the "volume" of the Cu_4 cluster in **1** and in the anion $[Cu_4(SPh)_6]^{2-}$ reveals a significant difference that can be related to the different set and charge of the ligands complexing the Cu_4 unit. The stability of the Cu_4S_6 core in the species $[Cu_4(HL)_3]^{4+}$, obtained from the reaction of **1** with HI, was also established by ^{31}P NMR measurements. The expansion/contraction of the Cu_4 cluster may be important as regards the activation of Ace1 and Mac1 transcription factors. The electronic charge-modulation by cysteinyl residues at the metal sites in the proteins might reasonably act as a regulating device in building up, modifying or dismantling the Cu_4 cluster structural unit.[6b,15]

Experimental Section

Materials and Instrumentation: Reagents were used as purchased from Aldrich. Diethyl ether was distilled from over $LiAlH_4$ shortly before use. Hydroiodic acid: ACS reagent, 55 wt.-% in water. $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian Unity Inova 400 spectrometer operating at 161.9 MHz. The ^{31}P chemical shifts are referenced to an external standard of H_3PO_4 85% peak (δ = 0.0 ppm). Variable-temperature ^{31}P NMR spectroscopic data for compound **1** were collected for a 1.0×10^{-2} M solution in $CHCl_3$. ^{31}P MAS NMR spectra were calibrated indirectly through the H_3PO_4 85% peak (δ = 0.0 ppm). IR spectra were measured as KBr (4000–400 cm^{-1}) or polyethylene pellets (400–50 cm^{-1}) on a Bruker IFS 55 FT-IR spectrometer. FT-Raman spectra were measured as solid samples on a Bruker IFS 100 spectrometer. Conductometric measurements on compound **1** (1.0×10^{-3} M in $CHCl_3$) were carried out at 20, 30 and 40 °C.

Synthesis: Compound HL was prepared according to ref.[16] The adduct HL·I_2 was prepared in situ in freshly distilled Et_2O from equimolar amounts of HL and I_2.

$[Cu_4(L)_3]I_3$ (1): A mixture of HL (0.100 g, 0.222 mmol) and I_2 (0.0565 g, 0.223 mmol) in Et_2O (100 mL) was stirred at room temperature until complete dissolution of the reagents. Copper powder (submicron; 0.0141 g, 0.226 mmol) was then added while stirring and the mixture was allowed to react at room temperature for about 2 days. The resulting air-stable orange solid (149 mg) was isolated by suction filtration, then treated with 10 mL of $CHCl_3$ for 1 h. The mixture was filtered, and the resulting solution evaporated to dryness to give 0.100 g of **1** (5.05×10^{-2} mmol; yield 89%, based on metal). $C_{72}H_{60}Cu_4I_3N_3P_6S_6$ (1980.3): calcd. C 43.67, H 3.05, N 2.12, S 9.71; found C 44.0, H 3.1, N 2.0, S 9.6. FT-IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} br. m, 3118 br. m, 3054 m, 1587 w, 1572 w, 1479 s, 1436 w, 1288 ms, 1106 vs, 1026 w, 998 w, 900 s, 788 s, 735 vs, 721 ms, 687 s, 636 m, 613 ms, 551 vs, 528 ms, 495 m, 413 w. FT-Raman (500–50 cm^{-1}): $\tilde{\nu}$ = 114 cm^{-1}. ^{31}P NMR ($CHCl_3$, 25 °C): δ = 28.5 and 28.1 ppm.

$[Cu(HL)_2]I_3$·MeCN (2): A mixture of HL (0.100 g, 0.222 mmol) and I_2 (0.0565 g, 0.223 mmol) in Et_2O (100 mL) was stirred at room temperature until complete dissolution of the reagents. Copper powder (submicron; 0.0141 g, 0.226 mmol) was then added while stirring and the mixture was allowed to react at room temperature for about 2 days. The resulting air-stable orange solid was isolated by suction filtration, then treated with 10 mL of $CHCl_3$ for 1 h. The mixture was filtered, the separated solid compound washed with $CHCl_3$ and then dissolved in CH_3CN (5 mL); slow evaporation of the solution afforded orange crystals of **2** (0.030 g, 2.08×10^{-2} mmol; yield 10%, based on metal). $C_{50}H_{45}CuI_3N_3P_4S_4$ (1348.3): calcd. C 43.38, H 3.28, N 3.04, S 9.26; found C 43.5, H 3.2, N 3.1, S 9.0. FT-IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} br. vs, 3052 w, 1477 m, 1435 vs, 1385 m, 1205 vs, 1177 s, 1106 vs, 1026 w, 998 w, 913 w, 874 w, 743 m, 721 m, 693 vs, 550 vs, 531 m, 493 m, 414 w. FT-Raman (500–50 cm^{-1}): $\tilde{\nu}$ = 135 cm^{-1} (2.8), 112 (10), 79br (1.6) (relative intensities in parentheses, highest value: 10). ^{31}P NMR (MeCN): δ = 52.9 ppm.

X-ray Crystallography: Crystal data and details of the refinement for compounds **1** and **2** are reported in Table 4. Diffraction data were collected on a Bruker SMART CCD diffractometer at room temperature for compound **1** and at 120(2) K on a Bruker–Nonius area-detector diffractometer for compound **2**, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Cell parameters and orientation matrix were obtained from least-squares refinement of reflections measured in the range $2.23 < \theta < 22.41°$ for **1** and $2.91 < \theta < 27.48°$ for **2**. An absorption correction was applied using the SADABS routine[17] for **1** and the SORTAV algorithm[18] for **2**. The structures were solved by direct methods and refined on F^2 by using the SHELX[19] program implemented in the WinGX suite.[20] Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were included in the structure using the riding model.

Table 4. Crystal data and details of refinements for complexes **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{72}H_{60}Cu_4I_3N_3P_6S_6$	$C_{50}H_{45}CuI_3N_3P_4S_4$
Mol. wt.	1980.27	1348.25
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	14.139(1)	16.9869(5)
b [Å]	16.847(1)	17.0247(6)
c [Å]	32.955(2)	20.6025(7)
β [°]	98.24(1)	112.858(2)
V [Å^3]	7768.8(9)	5490.3(3)
Z	4	4
ρ_{calcd} [Mg m^{-3}]	1.693	1.675
μ(Mo-K_α) [mm^{-1}]	2.599	2.390
Transmission factors	0.714–1.000	0.9538–0.6730
Collected reflections	70186	65960
Unique refl. with $I > 2\sigma(I)$	10022	12392
Final R and wR_2 indices	0.0493–0.1291	0.0850–0.1054
Max. and min. final $\Delta\rho$	–1.244, 1.555	–0.802, 0.723

CCDC-271849 (for **1**) and -271850 (for **2**) contain 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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