Copper(I)–Purine–Phosphine Complexes. Syntheses and Molecular Structures of [Cu$_2$(μ-HL)$_1$(μ-dppm)(η$^1$-dppm)$_2$] and {[Cu$_3$(μ$_3$-Cl)$_2$(μ-dppm)$_3$][Cu(HL)$_2$]} (H$_2$L$^1$ = 8-Mercaptothepophysline and H$_2$L$^2$ = 8-Ethyl-3-methylxanthine)

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The syntheses and molecular structures of two novel polynuclear copper(I)–purine–phosphine complexes are reported. The first one is a dinuclear [Cu$_2$(μ-HL)$_1$(μ-dppm)(η$^1$-dppm)$_2$] complex (H$_2$L$^1$ is 8-mercaptopthepophysline). The compound crystallizes in the triclinic system, space group P1, with cell constants a = 12.342(5) Å, b = 15.255(5) Å, c = 24.972(5) Å, α = 74.31(2)$^\circ$, β = 78.62(2)$^\circ$, γ = 72.51(2)$^\circ$, and Z = 2. The structure of this complex exhibits as the most important feature the simultaneous presence of η$^1$-terminal and η$^3$-bridging dppm ligands, which is first here described for a copper complex. This complex is also of interest because of its reversible photochromic behavior in the solid state. The second compound is an ionic {[Cu$_3$(μ$_3$-Cl)$_2$(μ-dppm)$_3$][Cu(HL)$_2$]} complex (H$_2$L$^2$ is 8-ethyl-3-methylxanthine), which crystallizes in the monoclinic system, space group P2$_1$/n, with cell constants a = 15.829(6) Å, b = 22.801(7) Å, c = 28.569(6) Å, β = 97.65(4)$^\circ$, and Z = 6. The structure of this complex consists of trinuclear copper(I) cations and mononuclear [Cu(purine)$_2$]$^-$ anions, exhibiting a linear stereochemistry. As far as we know, this compound represents the first example of a copper(I)–purine complex whose structure has been determined by X-ray crystallography.

Introduction

Copper(I)–phosphine complexes are well documented in the literature, in particular those corresponding to monophosphines. Even though the number of copper(I)–diphosphine complexes reported up to now is rather low, this number has been increasing in the last few years. The interest in these complexes arises from their catalytic, photochemical, and, in particular, cytotoxic and antitumor properties.

In view of the latter properties, the biological importance of the purine bases, and the possibility of Cu(I) binding to DNA bases, the study of copper(I)–purine–phosphine complexes is of interest. As a part of our studies on metal–purine complexes, we recently reported a trinuclear [Cu$_3$(η$^1$-purine)$_2$(dppm)$_3$] complex, in which the ligand 3-methyl-8-ethylxanthine showed a novel η$^5$-ligation mode in purified crystals. The structure of this complex consists of trinuclear copper(I) cations and mononuclear [Cu(purine)$_2$]$^-$ anions, exhibiting a linear stereochemistry. As far as we know, this compound represents the first example of a copper(I)–purine complex whose structure has been determined by X-ray crystallography.

Experimental Section

Preparations. The ligands 1,3-dimethyl-8-mercaptopthepophysline and 3-methyl-8-ethylxanthine were prepared as described in the literature.

[Cu(HL)$_1$]$_2$(μ-dppm)]$_2$(μ-dppm)] (I) was prepared by refluxing for 30 min in a 1:2 ratio, [Cu(HL)$_2$] and dppm in an ethanol/water mixture (5:1) under nitrogen atmosphere. After cooling, excess dppm was filtered off. From the resulting colorless solubility were collected white air-stable crystals, which were then dried under vacuum. Anal. Calcd for C$_9$H$_8$N$_8$O$_4$Cl$_2$P$_6$Cu: C, 58.62; H, 4.51; N, 6.01; Cu, 13.63. Found: C, 58.8; H, 4.1; N, 5.9; Cu, 13.3 (as CuO). The starting complex with empirical formula [Cu(Cl)(dppm)$_3$] was prepared by the procedure reported earlier.

[Cu$_3$(μ$_3$-Cl)$_2$(μ-dppm)$_3$][Cu(HL)$_2$]]$_2$(μ-dppm)] (II) was prepared by refluxing for 1 h in a 1:1 ratio, 3-methyl-8-ethylxanthine, previously monodoprotonated with KOH in water, and [Cu(Cl)(dppm)$_3$] in an ethanol/water mixture (20:1) under nitrogen atmosphere. After several days colorless crystals were collected and dried in vacuum. Anal. Calcd for C$_{30}$H$_{33}$N$_8$O$_4$Cu: C, 62.7; H, 4.7; N, 6.5; Cu, 7.4. Found: C, 62.1; H, 4.6; N, 6.6; Cu, 7.2 (as CuO).

[Cu$_3$(μ$_3$-Cl)$_2$(μ-dppm)$_3$][Cu(HL)$_2$]]$_2$(μ-dppm)] (II) was prepared by refluxing for 1 h in a 1:1 ratio, 3-methyl-8-ethylxanthine, previously monodoprotonated with KOH in water, and [Cu(Cl)(dppm)$_3$] in an ethanol/water mixture (20:1) under nitrogen atmosphere. After several days colorless crystals were collected and dried in vacuum. Anal. Calcd for C$_{30}$H$_{33}$N$_8$O$_4$Cu: C, 62.7; H, 4.7; N, 6.5; Cu, 7.4. Found: C, 62.1; H, 4.6; N, 6.6; Cu, 7.2 (as CuO).
were unsuccessful. Several crystals were tested, and the data were collected from the crystal having the better diffraction power.

**Crystal Data.** $C_{54}H_{60}N_8O_8P_4Cu_2$: MW = 1702.6, triclinic, space group $P1$, $a = 12.342(5)$ Å, $b = 15.255(5)$ Å, $c = 24.972(5)$ Å, $α = 74.31(2)^\circ$, $β = 78.62(2)^\circ$, $γ = 72.51(2)^\circ$, $V = 4282.6$ Å$^3$, $Z = 2$, $D_\text{c} = 1.320$ g cm$^{-3}$, $F(000) = 1764$, $μ(\text{Mo Kα}) = 0.71$ mm$^{-1}$; dimensions $0.19 \times 0.30 \times 0.60$ mm; maximum/minimum transmission factors 0.827/0.532; 9734 reflections (4326 with $I >$ 2σ($I$)); $R = 0.128$, and 1.80, respectively. $C_{54}H_{60}N_8O_8P_4Cu_2$: MW = 1864.5, monoclinic, space group $P2_1/n$, $a = 15.829(6)$ Å, $b = 22.801(7)$ Å, $c = 28.569(6)$ Å, $β = 97.654(6)$°, $V = 10219.2$ Å$^3$, $Z = 6$, $D_\text{c} = 1.818$ g cm$^{-3}$, $F(000) = 5748$, $μ(\text{Mo Kα}) = 1.52$ mm$^{-1}$; dimensions $0.23 \times 0.27 \times 0.15$ mm; maximum/minimum transmission factors 0.759/0.698; 6546 reflections (2326 with $I >$ 2σ($I$)); $R = 0.108$, 0.114, and 1.89, respectively. $C_{54}H_{60}N_8O_8P_4Cu_2$: MW = 1702.6, triclinic, space group $P1$, $α = 74.31(2)^\circ$, $β = 78.62(2)^\circ$, $γ = 72.51(2)^\circ$, $V = 4282.6$ Å$^3$, $Z = 2$, $D_\text{c} = 1.320$ g cm$^{-3}$, $F(000) = 1764$, $μ(\text{Mo Kα}) = 0.71$ mm$^{-1}$; dimensions $0.19 \times 0.30 \times 0.60$ mm; maximum/minimum transmission factors 0.827/0.532; 9734 reflections (4326 with $I >$ 2σ($I$)); $R = 0.128$, and 1.80, respectively.

**Data Collection and Structure Determination.** Single-crystal data collections were performed on a Siemens R3m/V diffractometer at 293 K using graphite-monochromatized Mo Kα ($λ = 0.710 69$ Å) radiation. The data were corrected for Lorentz and polarization effects and for absorption (empirical; based on azimuthal ψ scans). The structures were solved by the Patterson method and refined by Fourier synthesis using the SHELXTL PLUS program.$^{19}$ For I all non-hydrogen atoms were refined anisotropically while for 2 only the chloro, phosphorus, and copper atoms were so refined. In both cases, the phenyl rings were refined as rigid groups having isotropic temperature factors. Some of the phenyl rings exhibited a nonsystematic disorder, the remaining electron density peaks of -0.78, 1.16 (1) and -0.73, 2.14 e Å$^{-3}$ (2) being found in the vicinity of these phenyl rings. Hydrogen atoms were placed at their theoretical positions and not refined for 1 and ignored for 2.

**Results and Discussion**

8-Mercaptotheophylline reacts with CuSO$_4$·5H$_2$O in an ethanol/water mixture (4:1) to give, according to eq 1, the copper(I) complex [Cu(HL)$_2$], in which the ligand is present in monodeprotonated fashion.

$$\text{CuSO}_4 + 2\text{H}_2\text{L} \rightarrow [\text{Cu}(\text{HL})_2] + 1/2(\text{HL}_2^-) + \text{H}_2\text{SO}_4 \tag{1}$$

The complex is likely polymeric, with bridging thiolate groups between the copper atoms. Treatment of a suspension of [Cu(2-phenylthio)pyridine] in ethanol/water with dppm in a 2:1 molar ratio gives rise to a clear solution, from which the complex [Cu$_2$(2-phenylthio)pyridine)(μ-dppm)]$_2$ (I) can be isolated. It must be pointed out that all the attempts to obtain mixed H$_2$L$_1$—copper—dppm complexes from the reaction of the cationic complex [Cu$_2$(Cl)$_2$]$(\text{Cl})_2$ and (HL)$_2^-$ (prepared in situ from the free ligand and KOH) failed. However, with the oxopurine 3-methyl-8-ethyloxanthine, we succeeded in obtaining the complexes [Cu$_3$(L$_2^-$)]$(\text{Cl})_2$(dppm) and [(Cu$_2$(3-methyl-8-ethyloxanthine)]$_2$[Cu(2-phenylthio)pyridine)] (2), depending on the deprotonation degree of the purine ligand. Spectroscopic results and the X-ray structure characterization for the former were previously reported by us,$^{12}$ while a description of the main structural features of complexes 1 and 2 is reported below.

The structure of 1 consists of neutral discrete dinuclear [Cu$_2$-($\mu$-HL)$_2$($\mu$-dppm)]($\eta$$_2$-dppm)$_2$] molecules having a pseudo-$C_{2v}$ symmetry. Within the dinuclear entities, the copper atoms show distorted tetrahedral arrangements, both being similar but not identical Cu$_2$P$_x$S$_y$ chromophores. Two different perspective views of the molecule are given in Figure 1, together the atomic labeling scheme. Selected bond distances and angles are listed in Table 1.


captotheophyllinato complexes. The interaction with the purines by increasing the angles $\theta_3$ defined by the $P(1)$, $P(2)$, $Cu(1)$, and $Cu(2)$ atoms, decreasing with those found in the literature for copper(I) complexes with $\eta^1$-dppm coordination modes, such as $\eta^2$-chelate dppe ligand and the sulfur atom of the thiolate ligand. The latter coordination mode for copper(I) dimers seems to be favored over that shown by complex 1, as could be expected when the number of connecting carbons in the phosphine ligand backbone increases.

The $^{31}$P($^1$H) NMR spectrum of complex 1 shows the existence of a unique resonance at $-21.79$ ppm. Taking into account the solid-state molecular structure of 1, at least two signals are expected, for the coordinated and noncoordinated phosphorus atoms. This fact, which has previously been observed for analogous dicopper(I) complexes, implies dissociation of bridging phosphines and rapid exchange processes, the phosphorus atoms becoming effectively equivalent in solution.

On the other hand, the complex shows a change in color when exposed to sunlight for about 10 min, varying from white to violet in the solid state (Figure 2). This process is reversible, even though slower, going from violet to white when the complex is kept in absence of light for about 24 h. The mechanisms which could be responsible for the photochromic effect in the solid state are numerous. Among these, a redox process could be an effective mechanism. In our case, the nature
be described as a distorted trigonal bipyramid. Within this Cu3Cl3 core, the chlorine atoms occupy the axial vertices while the copper atoms lie on the equatorial positions. The Cu⋯Cu distances range from 2.996 to 3.097 Å, values which are slightly shorter than those found for [Cu3(μ3-Cl)(μ-μ-dppm)]Cl and [Cu3-(μ3-Cl)(μ-μ-L2)(μ-μ-dppm)]H2O.12,13 As for the μ3-Cl bridging coordination mode, Cl(1) bridges the three copper atoms with one short and two long bonds while Cl(2) bridges with one long and two short bonds. This asymmetrical μ3-bridging pattern is usual in this type of complex and has been justified on the basis of the steric hindrance of the chlorine atoms by the CH2 groups belonging to the dppm ligands.28 In good accordance with the solid structure of the trinuclear cations, the 31P[1H] NMR spectrum shows a single signal at −14.18 ppm, indicating the equivalence of all phosphorus atoms in solution.

The major structural feature of this complex lies in the anions. Both anions, which are chemically but not crystallographically equivalent, show a perfect linear geometry, the copper atoms lying on inversion centers, with Cu−N(7) bond lengths of 1.905 and 1.983 Å, which are well within the range of those found in the literature for two-nitrogen-coordinated complexes.29 This two-nitrogen coordination mode for copper(I) complexes is rather scarce. Even though several compounds have been reported, mainly as model compounds for metalloproteins29 and in supramolecular coordination chemistry,29 as far as we know, no other example of a copper-purine complex showing a linear stereochemistry coordination mode has been reported so far. It should be pointed out that, although the O(6) atoms are favorably oriented to interact with the metal ion similarly to those of other purine complexes described elsewhere,31 comparison of the Cu⋯O contact distances in our complex (longer than 3.35 Å) with those exhibiting weak copper-oxygen interactions (shorter than 2.9 Å) reveals that our complex does not exhibit any kind of bonding interaction. The remaining bond lengths and angles for both crystallographic purine bases do not significantly differ from those reported for purine complexes.9–12

Although crystallographically relevant, this complex is more significant from a chemical viewpoint. As was mentioned above, this complex was obtained similarly to the [Cu3(μ3-Cl)-
(μ-L2)(μ-μ-dppm)]H2O complex except that the ligand was monodeprotonated instead of dihydroxide.13 Thus, these two reactions show the great versatility of this ligand in the latter complex acts, by substituting one Cl atom from the starting [Cu3(μ3-Cl)(μ-μ-dppm)]+ cation, in a μ3-(N(1),O(2),O(2)) coordination mode, whereas for 2 the reaction involves the destruction of some trinuclear cations16 to yield [Cu(μ-L2)3]+, with monodentate coordination of the purine through the N(7).

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, and complete bond distances and angles (11 pages). Ordering information is given on any current masthead page.

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