Metallacoronates

Structural Diversity of Alkaline Earth Centered Gold(I) Metallacoronates

Suelen Ferreira Sucena,[a][‡] Thu Thuy Pham,[b] Adelheid Hagenbach,[a] Chien Thang Pham,[b] and Ulrich Abram*[a]

Abstract: One-pot reactions of the catechol-scaffolding aroylbis(N,N-diethylthiourea) H₂Lcat with mixtures of alkaline earth nitrates M(NO₃)₂ (M²⁺ = Ca²⁺, Sr²⁺ or Ba²⁺) and (NEt₄)[AuCl₄] or [Et₃N][AuCl₄] as supporting base give rise to neutral trinuclear gold(I) [2]-metallacoronates with the composition of {M[Ni²⁺,Pt²⁺ or Cu²⁺]₂}⊂{M[Ni²⁺,Pt²⁺]₃(Au(I))} (2). In both 1 and 2, Au(I) ions are exclusively S-bonded with the organic ligands and adopt a virtually linear coordination fashion. Such metal-ligand binding is responsible for the formation of metallacoronands, which accommodate alkaline earth metal ions in their molecular voids, thereby resulting in host-guest coordination assemblies. The level of metal-ligand aggregation in the resulting assemblies is dependent on the denticity, size and flexibility of the centered building block of the aroylbis(N,N-diethylthiourea) ligands.

Introduction

The coordination chemistry of aroyl-N,N-dialkylthioureas is pioneered by the work of L. Beyer et al.[1] and attracted the interests of many other chemists during the last four decades. Most contributions in this field focus on the aroyl mono-HŁben and bis-thioureas H₂LPTH (Scheme 1), which are versatile chelators for most transition metal ions.[2–11] The structural chemistry of metal complexes with aroyl-N,N-dialkylthioureas is dominated by the monoanionic S,O-chelating fashion of aroylthiourea moieties (see Scheme 1). It is interesting that with the two S,O-chelating moieties in the symmetrical bipodal phthaloylbis(N,N-dialkylthioureas) m-/p-H₂LPTH and divalent metal ions such as Ni²⁺, Pt²⁺ or Cu²⁺, which prefer square-planar or pseudoplanar coordination spheres, multinuclear complexes are formed. The structures of the resulting multinuclear systems strongly depend on the relative positions of the substituted aroylthiourea groups. In particular, para-H₂LPTH ligands yield trinuclear compounds [M₂(p-LPTH-S₂O₂)] (M²⁺ = Ni²⁺, Pt²⁺) (I),[4,11–13] while meta substitution gives rise to binuclear complexes of the general formula [M₂(m-LPTH-S₂O₂)] (M²⁺ = Co²⁺, Ni²⁺, Cu²⁺, Pt²⁺, [Ptx₃]²⁺ for X = Cl, Br or I, [ReO(OMe)]²⁺) (II).[9–11,14–17] Although the obtained multinuclear complexes possess large central voids, these voids are empty and cannot accommodate any guest atoms or molecules due to the lack of donor atoms and, more seriously, the restricted effective space caused by the hydrogen atoms of the central phenyl rings pointing toward the centers.

Recently, the modification of m-H₂LPTH by the replacement of the phenylene ring by other spacers possessing potential donor atom(s) such as a disubstituted pyridine ring (H₂LPTH) or a catechol building block (H₄Lcat) brought about a new generation of ligands with bifunctional coordination sites each of which favorably binds to a particular type of metal ions. Such interesting structural features gave access to the synthesis of a large variety of trinuclear bimetallic complexes from simple one-pot reactions of the ligands and mixtures of two metal ions with different Pearson’s acidities.[18–20] In such self-assembling processes, the “soft” metal ions prefer bonding to the satellite aroylthiourea moieties, while the harder ions such as alkali, alkaline earth metal or lanthanide ions are directed to the central binding sites. As a result of this selective coordination, trinuclear, bimetallic systems could be recognized as host-guest compounds, for example the Zn(II) [2]-metallacoronate III or the Fe(III) [2]-metallacyclomet  IV (see Scheme 2),[19,21] where the “hard” guest ions are encapsulated in metallamacrocycles consisting of the ligands and the softer metal ions.

A number of studies show that such inclusion compounds with diverse compositions, structures and physicochemical properties can be rationally designed by self-assembly from a
mixture of metal ions and the ligands H$_2$L$_{\text{cat}}$ or H$_2$L$_{\text{py}}$.[18–20,22,23] To get deeper insight in the control of the self-assembling process, in this report, the utilization of the ligands H$_2$L$_{\text{cat}}$ and H$_2$L$_{\text{py}}$ as subunits for the construction of host–guest assemblies is continued.

Although the transition metal complexes of aroyl-$N,N$-dialkylthioureas have been extensively studied, surprisingly, their coordination compounds with thiophilic cations, such as Cu$^+$, Ag$^+$, Hg$^{2+}$ and Au$^+$, are not well-explored. A literature survey shows only a few reports on structures of aroylthiourea complexes with Cu$^+$,[24–27] Ag$^+$,[28–32] or Hg$^{2+}$ ions,[33–35] and only two descriptions of Au(I) complexes.[36,37] Because of the high thiophilicity of these ions, in all of their structurally characterized compounds, they are exclusively S-bonded to aroylthiourea ligands. This means, they essentially coordinate in the same way as unsubstituted thioureas and their derivatives.[38–47] Very recently, such flexible coordination fashion is also observed in inclusion complexes built from H$_2$L$_{\text{cat}}$, alkaline earth metal and Ag$^+$ or Hg$^{2+}$ ions.[20] In this context, we extend the research to the Au(I) host–guest coordination compounds based on the versatile H$_2$L$_{\text{cat}}$ and H$_2$L$_{\text{py}}$ ligands.

**Results and Discussion**

Reactions of H$_2$L$_{\text{cat}}$ (4 equiv.) with methanolic solutions containing mixtures of alkaline earth nitrates (1 equiv.) and the common Au(III) starting material (Et$_4$N)[AuCl$_4$] (2 equiv.) give rise to colorless solids with the chemical composition [M⊂[Au$_2$(L$_{\text{cat}}$)$_2$]] (1) (M$^{2+}$ = Ca$^{2+}$ (1a), Sr$^{2+}$ (1b) and Ba$^{2+}$ (1c)). The color of the products gives a good hint for the formation of Au(I) complexes from the reduction of (Et$_3$N)[AuCl$_4$] by H$_2$L$_{\text{cat}}$ as reducing agent.
This assumption is consistent with the fact that a large excess of $H_2L^\text{cat}$ must be provided to get a maximum yield. Furthermore, similar redox reactions were found in the literature, when Au(III) compounds were allowed to react with $N,N$-dialkyl-$N'$-benzoylthioureas of the type $HL^\text{ben}$[36,37,48]. Identical products are obtained from an alternative approach using $[Au(tht)Cl]$ as gold starting material with an exact stoichiometric ratio of the reactants (Scheme 3). With this second method, undesired side-reactions can be avoided and higher yields are obtained.

X-ray diffraction analyses were performed on single crystals obtained from the slow evaporation of $CH_2Cl_2/MeOH$, $CHCl_3/EtOH$ or $CH_2Cl_2/MeCN$ solution of 1a, 1b, or 1c. The structures of 1a and 1c are shown in Figure 1 and selected bond lengths, bond angles and intermetallic distances are given in Table 1. Due to an unsatisfactory crystal quality of 1b, the derived crystallographic data are not suitable to discuss in detail bond lengths and angles, but are sufficient to invoke the general structural features of the complex. Structural details of this compound are given in the Supporting Information together with its molecular structure (Figure S2.3).

Structural analyses indicate neutral trinuclear host–guest compounds with the composition $\{M \subset [Au(L^\text{cat})]_2\}$ ($M=Ca^{2+}$, $Sr^{2+}$ or $Ba^{2+}$). In all structures, the Au$^+$ ions are exclusively bonded to two soft S donor atoms of two deprotonated $[L^\text{cat}]^-$ ligands. This behaviour is not surprising with regard to the high thiophilicity of Au(I) ions. The Au–S bond lengths vary from 2.290(3) to 2.294(2) Å and are slightly shorter than those found in a Au(I) complex with the $m$-$H_2L^\text{pth}$ ligand.[37] The minor deviations of the S–Au–S bond angles (Table 1) from 180° point out the linear coordination mode of the Au centers. The linkage between two Au$^+$ ions and two S-bonded arylthioureaato ligands ($L^\text{cat}$)$^2$- leads to a (2)-metallacoronand $[Au_2(L^\text{cat},xS)]^2$- unit, which can capture guest alkaline earth metal ions $M^{2+}$ in their central cavities by interactions with all oxygen donors of the ligand backbones. The shorter $M$–Ocarbonyl distances compared to $M$–Oether ones indicate that more negative charge is located on the carbonyl O atoms than on the ether O atoms. A comparison between the structures of the three (2)-metallacoronates reveals significant differences in (i) their metal–metal distances, (ii) the coordination environment of the host ions and (iii) the conformation of the ligand skeletons. Specifically, the smaller ions $Ca^{2+}$ and $Sr^{2+}$ are eight-coordinate and adopt snub-diphenoidal coordination polyhedra,[49] while one additional coordinating acetonitrile molecule is responsible for the coordination number nine of the $Ba^{2+}$ ion with a “hulla-hop” coordination geometry (Figure 1b).[50,51] Furthermore, the deviation of the (S)-$NET_2$ moieties in opposite directions from the mean plan of the ligands causes a twisted conformation, which in turn produces the helical $Ca^{2+}$- or $Sr^{2+}$-binding complexes with dihedral angles between two mean plans of the ligands of 78.01(2)° and 76.32(2)° respectively (Figure S2.2 and S2.4). A similar deviation but in the same direction brings about the untwisted conformation, which induces a larger void, thereby resulting in a $Ba^{2+}$ inclusion compound with a narrow dihedral...
Table 1. Selected bond lengths, intermetallic distances [Å] and angles [°] in 1a and 1c.[a]

|       | 1a                  | 1c                  |
|-------|---------------------|---------------------|
| Au–S10 | 2.2902(7)           | Au1–S10             |
| Au–S20 | 2.2937(7)           | Au1–S40             |
| Ca–O10 | 2.529(2)            | Ba–O10              |
| Ca–O11 | 2.336(2)            | Ba–O11              |
| Ca–O20 | 2.505(2)            | Ba–O20              |
| Ca–O21 | 2.299(2)            | Ba–O21              |
| Au–Au | 9.5003(3)           | Au1–Au2             |
| Au–Ca | 4.9048(1)           | Au1–Ba              |
| O11–C11 | 1.256(3)          | O11–C11             |
| N10–C11 | 1.318(3)          | N10–C11             |
| N10–C12 | 1.342(3)          | N10–C12             |
| O11–C12 | 1.330(3)          | N11–C12             |
| S10–C12 | 1.756(3)          | S10–C12             |
| O21–C21 | 1.250(3)          | O21–C21             |
| N20–C21 | 1.318(3)          | N20–C21             |
| N20–C22 | 1.361(3)          | N20–C22             |
| N21–C22 | 1.321(3)          | N21–C22             |
| S20–C22 | 1.741(3)          | S20–C22             |
| S10–Au–S20 | 176.47(2)  | S10–Au1–S40         |

[a] Symmetry operations used to generate equivalent atoms: i = x + 1, y, –z + 3/2.

In addition to the X-ray structural analyses, the bonding situation of the host–guest assemblies was characterized by spectroscopic methods. In the IR spectra of the complexes, strong bands in the region between 1570 and 1590 cm⁻¹ can be assigned to the νC=O stretches. This corresponds to bathochromic shifts in the range of 70 cm⁻¹ to 90 cm⁻¹ with regard to the uncoordinated ligand. In comparison with the common values of approximately 150 cm⁻¹ for chelating aroylthioureas,[18,19,52] the shift is modest and confirms that the C-O bonds possess a higher degree of electron density on sulfur atoms of the coordinated aroylthioureas.
more double bond character in the anionic S-bonded aroylthio-ureato ligands. The existence of the ligands in their deprotonated form \([L^{cat}]^2-\) is confirmed by the disappearance of the \(\nu_{NH}\) stretches in the region above 3100 cm\(^{-1}\) in the IR spectra as well as by the absence of the signal corresponding to the NH protons in their \(^1H\) NMR spectra. It is interesting that the splitting patterns of the methylene protons of the OCH\(_2\) and NCH\(_2\) groups illustrate the varying rigidity of the organic framework in the resulting complexes. In the \(^1H\) NMR spectra of 1b and 1c (Figure S1.9 and S1.12), the signals assigned to OCH\(_2\) and NCH\(_2\) protons resemble the corresponding resonances in the \(^1H\) NMR spectrum of the ligand. Particularly, the signal belonging to the OCH\(_2\) protons appears as a broad singlet at about 4.9 ppm and the resonances of the NCH\(_2\) protons are detected in the range 3.0–4.0 ppm as two broad signals or two quartets for 1b and 1c respectively. In contrast to the simple pattern described above, the \(^1H\) NMR spectrum of 1a reveals two singlets around 4.8 ppm with the typical geminal spin-spin coupling constants of 13.0–13.5 Hz for OCH\(_2\) protons and three sextets in the range 3.2–3.7 ppm with ABX\(_3\) splitting patterns, where \(J_{AB}\) (ca. 14.0 Hz) is approximately twice of \(J_{AX}\) (ca. 7.0 Hz), for NCH\(_2\) protons (Figure S1.6). The more delicate fine structures of the signals associated with the methylene protons in 1a is a strong evidence for the significant increase of the rotation barrier around the O-CH\(_2\) and C(S)-NET\(_2\) bonds, in other words of the rigidity of the organic backbones, due to accommodating the smaller Ca\(^{2+}\) guest ion. Despite of the complication of the \(^1H\) NMR spectra, the corresponding \(^{13}C\) NMR spectra (Figure S1.7, S1.10 and S1.13) are straightforward because of an only small influence of the hindered rotation around the C(S)-NET\(_2\) bonds. Therefore, the resonances of the CH\(_3\) and CH\(_2\) carbon atoms of the NET\(_2\) groups appear as two separate signals in the upfield region from 10 ppm to 50 ppm. The signals belonging to the OCH\(_2\) carbon atoms are found around 72 ppm, while those of the aromatic carbon atoms are in the range of 110 ppm to 150 ppm. The weak signals at approximately 180 ppm and 170 ppm are attributed to the resonances of C=O and C=S carbon atoms, respectively.

With the aim of constructing the similar Au(I)-metallacoronates 2 derived from the pyridine-centered ligand \(H_2L^{py}\), the same synthetic route was applied for reactions between \(H_2L^{py}\) and mixtures of [Au(tht)Cl] and alkaline earth nitrates \(M(NO_3)_2\) (M\(^{2+}\) = Ca\(^{2+}\), Sr\(^{2+}\) or Ba\(^{2+}\)) (Scheme 4). Such reactions result in analytically pure, neutral products, which deposit from the methanolic reaction mixtures in good yields. Assuming that \(H_2L^{py}\) could perform the same coordination mode as \(H_2L^{cat}\), the obtained products should have the compositions of \([M \subset [Au_2(L^{py})_2]]\), which would resemble those of the preceding compounds. The assumption was (preliminarily) supported by the elemental analyses as well as mass spectroscopic studies with the appearance of signals matching the expected fragments \([M \subset [Au_2(L^{py})_2]] + Na^+\) in the ESI\(^+\) mass spectra of the complexes. However, the same mass spectra show signals with higher m/z values, which could be explained by a cluster ion formation in the matrix, but may also indicate that the inclusion compounds formed with the pyridine-based thiourea derivative have a higher nuclearity.

The question could be answered by the determination of the crystal structures of the compounds 2. The structures clearly confirm the formation of larger aggregates with the general composition of \([2M \subset [Au_2(L^{py}-\kappa-S)]_4]_2\). The products possess the same metal-to-ligand ratio, but a higher nuclearity than the inclusion compounds of type 1. Figure 2 presents the structures of the Ca\(^{2+}\)– (2a), Sr\(^{2+}\)– (2b) and Ba\(^{2+}\)– (2c) containing complexes. Selected bonding parameters are listed in Table 2.
The hexanuclear coordination assemblies 2M⊂[Au4(Lpy)5-Sx3]4− result from the encapsulation of alkaline earth metal ions M2+ in the void of metallacorands consisting of four Au(I) ions and four deprotonated ligands Lpy}. The gold ions are exclusively bonded by the sulfur atoms of the organic ligands in a virtually linear fashion. The lower degree of π-electron delocalization in the deprotonated S-bonded aroylthiourea moieties is confirmed by the corresponding C-S, C-O and C-N bond lengths (Table S2.1 to S2.3). The pyridinedicarboxamide moieties serve as planar tridentate ligand systems and coordinate the guest M2+ ions through their ONO donor sets. Furthermore, small coordinating solvent molecules saturate the coordination spheres of such divalent ions. In the isostructural compounds 2a and 2b, each alkaline earth metal ion is coordinated by two pyridinedicarboxamide moieties, methanol and/or water molecules. This leads to the coordination number of eight with a biaugmented "muffin-shape" coordination polyhedron by directional intermolecular interactions with two pyridinedicarboxamide groups, one bridging carbonyl oxygen atom, one bridging water molecule and one sulfur atom with a Ba-S(40) distance of 3.536(3) Å.[50,51]

Table 2. Selected bond lengths, intermetallic distances [Å] and angles [°] in the inclusion compounds of type 2

|     | 2a                                      | 2b                                      | 2c                                      |
|-----|-----------------------------------------|-----------------------------------------|-----------------------------------------|
| Au1−S10/Au1−S110 | 2.280(2)/2.275(2) | 2.270(4)/2.269(4) | Au1−S10 | 2.277(4) |
| Au2−S80/Au2−S40 | 2.273(2)/2.283(2) | 2.302(3)/2.275(3) | Au2−S20 | 2.285(3) |
| Au3−S40/Au3−S100 | 2.248(5)/2.435(5) | 2.561(8)/2.539(9) | Au2−S50 | 2.273(2) |
| Au4−S40/Au4−S50 | 2.528(4)/2.586(5) | 2.621(8)/2.651(9) | Ba−Au1 | 4.0857(8) |
| M1−Au1/M2−Au4 | 5.088(2)/4.987(2) | 5.161(2)/5.077(2) | Ba−Au2 | 5.3444(9) |
| M1−Au2/M2−Au2 | 5.082(1)/5.193(2) | 5.166(2)/5.062(2) | Ba−Au3 | 6.3258(7) |
| M1−Au3/M2−Au3 | 5.104(2)/5.021(2) | 5.084(1)/5.248(1) | Ba−Au1 | 4.4299(1) |
| M1−M2 | 5.118(3) | 5.076(2) | Ba−Ba | 2.7821(7) |
| M1−O1/M2−O70 | 2.406(5)/2.435(5) | 2.561(8)/2.539(9) | Ba−01 | 2.7377(7) |
| M1−O20/M2−O80 | 2.538(4)/2.586(5) | 2.621(8)/2.651(9) | Ba−040 | 2.8546(6) |
| M1−O100/M2−O40 | 2.522(5)/2.586(5) | 2.621(8)/2.651(9) | Ba−050 | 2.790(9) |
| M1−O110/M2−O50 | 2.445(4)/2.413(5) | 2.610(9)/2.564(9) | Ba−N01 | 2.918(7) |
| M1−N01/M2−N61 | 2.490(6)/2.506(7) | 2.631(7)/2.641(7) | Ba−N01 | 2.918(7) |
| M1−N91/M2−N31 | 2.489(5)/2.490(6) | 2.641(7)/2.651(5) | Ba−N01 | 2.856(9) |
| M1−O120/M2−O150 | 2.405(5)/2.397(5) | 2.5468(5)/2.55(1) | Ba−040 | 2.7776(7) |
| M1−O130/M2−O140 | 2.404(5)/2.391(5) | 2.5429(9)/2.542(9) | Ba−060 | 2.8967(7) |
| S10−Au1−S110/S70−Au4−S50 | 173.26(2)/174.52(8) | 173.1(2)/174.3(2) | S10−Au1−S40 | 5.0857(8) |
| S20−Au1−S110/S70−Au4−S50 | 173.26(2)/174.52(8) | 173.1(2)/174.3(2) | S20−Au1−S40 | 5.3444(9) |
| S20−Au2−S110/S70−Au4−S50 | 173.26(2)/174.52(8) | 173.1(2)/174.3(2) | S20−Au2−S40 | 6.3258(7) |

[a] Symmetry operations used to generate equivalent atoms: [−x+3/2, y, −z+3/2].

Spectroscopic studies on 2 are in good agreement with the conclusion drawn from the solid-state structures. The IR spectra of the resulting [4]-metallacoronates 2 are quite similar to those of the previously discussed [2]-metallacoronates 1. The absence of νas(C=O) bands in the region above 3100 cm−1 indicates the double deprotonation of H2Lpy during the complex formation. In addition, the modest bathochromic shifts of the NH bands in the region above 3100 cm−1 indicates the coordination number of eight with a biaugmented "muffin-shape" coordination polyhedron by directional intermolecular interactions with two pyridinedicarboxamide groups, one bridging carbonyl oxygen atom, one bridging water molecule and one sulfur atom with a Ba-S(40) distance of 3.536(3) Å.[50,51]

The 1H NMR spectra of 2 confirm the deprotonation of the ligands through the disappearance of the NH signal, which appears in the spectrum of the non-coordinated ligand around 9.0 ppm. In all spectra, the resonances in the range of 7.5–8.0 ppm are attributed to protons of disubstituted pyridine rings, while broad signals at 1.15 ppm and around 3.6 ppm are assigned to the CH3 and CH2 protons respectively. This NMR line broadening is a clear sign for the hindered rotation of the -NEt3 group in the Et3N-C(S)- fragment. Such effect is also detected in the 13C NMR spectra by the splitting patterns of resonances of the carbon atoms appearing in the range of 120 ppm to 160 ppm. The weak signals at approximately 180 ppm and 170 ppm are assigned to the resonances of C=O and C=S carbon atoms, respectively. In comparison with the simple NMR pattern of 2b and 2c, the fine-structures of spectral lines corresponding to ortho-H of pyridine ring, CH3 and CH2 protons in the 1H NMR spectrum of 2a (Figure S1.19) as well as the two sets of signals with the 1:1 ratio in the 13C NMR spectrum of 2a (Figure S1.20) demonstrate the magnetic nonequivalence of the two halves of each [Lpy]2− anion in solution. This phenomenon reflects a significant increase of the rigidity of the organic skeleton in 2a due to the coordination of the guest Ca2+ ion. Such bonding characteristics have also been observed in 1a. The results of the structure analysis also shed light on the ESI mass spectra of 2. The appearance of the expected peaks ascribed to the molecular ion of the cyclic tetrameric complexes, namely [2a + Na]+, [2b + H]+ and [2c + Na]+, confirms their compositions. The fragments related to the “dimers” [M⊂[Au4(Lpy)5−X3]]+ result from the fragmentation of the molecular ions.

A comparison of the compositions and structures of the self-assembled inclusion compounds 1 and 2 demonstrates that due to its lower denticity, size and flexibility, the ligand H2Lpy forms larger metallamacrocycles than the corresponding catechol-based ligand. Particularly, the higher flexibility of H2Lpy due to its aliphatic backbone may enable this compound to provide the lone pairs of the donor atoms in positions for a

DOI: 10.1002/ ejic.202000770
more efficient coordination of the large alkaline earth ions, which in return gives the cations more influence to act as templates during the self-assembly of the multi-metallic compounds. More experiments with other metal ions are in preparation to shed more light to this points.

Conclusions

Two series of Au(I) metallacarboranes encapsulating alkaline earth metal ions have been prepared by one-pot reactions using catechol- and pyridine-scaffolding arylbis(N,N-diyethylthioureas). The almost linear coordination of S-bonded Au(I) centers with such ligands produces two types of products: (i) the (2)-metallacarborands \([\text{Au}_2(L_{\text{cat}}^2)_2]^{2-}\) and (ii) the (4)-metallacarborands \([\text{Au}_4(L_{\text{py}})^4]^{4-}\). The central voids of the obtained metallacycles capture one and two alkaline earth metal ions, respectively. The denticity, size and flexibility of the central spacers exert considerable influence on the level of metal-ligand aggregation, and, thus, the compositions and structures of the resulting host-guest coordination assemblies.

Experimental Section

Materials. All chemicals used in this study were reagent grade and used without further purification. Solvents were dried and used freshly distilled unless otherwise stated. \([\text{Au(tht)}] \text{Cl}_2\) was prepared by the standard procedure.[53] The ligands were synthesized according to the procedures recently reported[19]

Physical measurements. IR spectra were measured as KBr pellets from slow diffusion of MeOH into the solutions of complexes in CH2Cl2.

All chemical shifts (δ ppm) and coupling constants (J Hz) are given as Supporting Information. ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technology) mass spectrometer. All MS results are given in the form: Calcd. for \(\text{C}_m\text{H}_n\text{O}_p\text{N}_q\text{S}_r\text{Au}_s\text{M}_t\) ppm: 183.3 (C=O); 168.9 (C=S); 146.2, 121.8, 112.0 (Ph); 71.2 (OCH2); 47.0, 46.1 (NCH2); 1.24 (t, \(J = 7.0\) Hz, 12H, CH3). Single crystals for X-ray analysis were grown from CH3Cl2/MeOH.

[2M] = [\text{Au}_2(L_{\text{py}}^2\cdot\text{M}_2\text{O}_4\cdot\text{S}_2\text{H}_2\text{O})]: C, 38.0; H, 3.7; N, 8.2; S, 9.3 %; found C, 38.0; H, 3.6; N, 8.3; S, 9.4 %. IR (KBr, cm–1): 1834 (w), 1757 (s), 1665 (w), 1602 (w), 1584 (m), 1559 (s), 1536 (s), 1438 (m), 1331 (m), 1211 (w), 1171 (w), 1032 (m), 988 (s), 950 (s), 858 (w), 820 (m), 715 (s), 662 (m), 567 (m).\n
M = Ca\(^2+\), Sr\(^2+\), Ba\(^2+\)

| Complex | Method | Yield | Elemental Analysis | IR (KBr, cm–1) |
|---|---|---|---|---|
| \([\text{Au}_2(L_{\text{cat}}^2\cdot\text{x}_2\text{S}_2]\cdot\text{M}_2\cdot\text{O}_4\cdot\text{S}_2\text{H}_2\text{O})\] | Method 1 | 27% | C, 34.6; H, 3.7; N, 8.5; S, 9.3 %; found C, 34.6; H, 3.8; N, 8.5; S, 9.3 %. | 1834 (w), 1757 (s), 1665 (w), 1602 (w), 1584 (m), 1559 (s), 1536 (s), 1438 (m), 1331 (m), 1211 (w), 1171 (w), 1032 (m), 988 (s), 950 (s), 858 (w), 820 (m), 715 (s), 662 (m), 567 (m). |
| \([\text{Au}_2(L_{\text{py}}^2\cdot\text{M}_2\text{O}_4\cdot\text{S}_2\text{H}_2\text{O})]\) | Method 2 | 34% | C, 34.6; H, 3.7; N, 8.5; S, 9.3 %; found C, 34.6; H, 3.8; N, 8.5; S, 9.3 %. | 1834 (w), 1757 (s), 1665 (w), 1602 (w), 1584 (m), 1559 (s), 1536 (s), 1438 (m), 1331 (m), 1211 (w), 1171 (w), 1032 (m), 988 (s), 950 (s), 858 (w), 820 (m), 715 (s), 662 (m), 567 (m). |

ESI+ MS (m/z): 4347 (M+Na)+. Mass Spectra: For all complexes, the calcd. and found masses are given in the Supporting Information.
(s), 1315 (w), 1244 (s), 1122 (m), 1076 (w), 1008 (w), 906 (w), 841 (w), 748 (m), 678 (w), 654 (w), 480 (w), 420 (w). $^1$H NMR (CDCl$_3$, ppm): 7.98 (br, 2H, Py); 7.72 (t, J = 7.5 Hz, 1H, Py); 3.62–3.41 (br, 8H, CH$_2$); 1.09 (br, 12H, CH$_3$). $^{13}$C{1H} NMR (CDCl$_3$, ppm): 181.4 (C=O); 168.7 (C=S); 154.4, 137.4, 126.3 (Py); 46.4, 45.8 (CH$_2$); 13.0, 12.9 (CH$_3$). ESI$^+$ MS (m/z): 2537.2070, 14 %, [$(\text{Au}_4\text{Lpy})^+\text{H}^+\text{Na}^+]$ (calcd. 2537.2025); 1946.1044, 18 %, [$(\text{Au}_4\text{Lpy})^+\text{H}^+\text{Na}^+]$ (calcd. 1946.0998); 1860.2139, 13 %, [$(\text{Sr}_2\text{Lpy})^+\text{H}^+\text{Na}^+]$ + 2H$_2$O] (calcd. 1860.2089); 1291.0909, 17 %, [$(\text{Sr}_2\text{Lpy})^+\text{H}^+]$ + Na$^+$] (calcd. 1291.0871); 1269.1111, 20 %, [$(\text{Ca}_2\text{Lpy})^+\text{H}^+]$ + 2H$_2$O] (calcd. 1269.1052); 1243.1530; 1221.1660, 23 %, [$(\text{K}_2\text{Lpy})^+\text{H}^+]$ (calcd. 1221.1711); 592.1146, 100 %, [$(\text{Au}_5\text{Lpy})^+\text{H}^+]$ (calcd. 592.1115).

Table 3. Crystal data and details of the structure determinations.

| Formula | $\text{Ca}_2\text{H}_6\text{O}_3\text{N}_3\text{S}_5\text{Au}_4\text{Ca}$ | $\text{MeCN}_2\text{Ba}_2\cdot \text{MeCN}_2$ | $\text{MeOH}_2\text{H}_2\text{O}_2\text{Ca}_2\cdot \text{MeCN}_2\text{Cl}_2\text{H}_2\text{Cl}_2\text{MeOH}$ | $\text{MeOH}_2\text{H}_2\text{O}_2\text{Sr}_2\cdot \text{MeCN}_2\text{Cl}_2\text{H}_2\text{Cl}_2\text{MeOH}$ | $\text{MeOH}_2\text{H}_2\text{O}_2\text{Ba}_2\cdot \text{MeCN}_2\text{Cl}_2\text{H}_2\text{Cl}_2\text{MeOH}$ |
| --- | --- | --- | --- | --- | --- |
| Mw | 1339.18 | 1518.55 | 2659.1751 | 2046.0917 | 2694.36 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| $a/$Å | 23.2665(9) | 22.6724(16) | 34.6343(5) | 34.6343(5) | 34.6343(5) |
| $b/$Å | 14.7403(5) | 12.7544(19) | 14.6633(19) | 14.6633(19) | 14.6633(19) |
| $c/$Å | 15.2530(5) | 20.1143(16) | 26.176(6) | 26.176(6) | 26.176(6) |
| $\alpha$ | 90 | 90 | 90 | 90 | 90 |
| $\beta$ | 111.742(1) | 112.704(2) | 128.923(3) | 128.923(3) | 128.923(3) |
| $\gamma$ | 90 | 90 | 90 | 90 | 90 |
| V/$\text{Å}^3$ | 4859.03(3) | 5365.87(7) | 10341(3) | 10341(3) | 10341(3) |
| Space group | C2/c | P2/c | P2/c | P2/c | P2/c |
| Z | 4 | 4 | 4 | 4 | 4 |
| $D_x$/g·cm$^{-3}$ | 1.381 | 1.880 | 1.710 | 1.698 | 1.750 |
| $\mu$/mm$^{-1}$ | 6.366 | 6.394 | 6.006 | 6.772 | 6.208 |
| No. reflect. | 48563 | 54614 | 116408 | 277277 | 43038 |
| No. indep. | 6057 | 13230 | 23396 | 25243 | 9801 |
| $R_F$ | 0.0485 | 0.0754 | 0.0279 | 0.0831 | 0.0849 |
| No. param. | 289 | 632 | 1120 | 922 | 619 |
| $R_w$/F$_{\text{calc}}$ | 0.0219/0.0432 | 0.0413/0.0629 | 0.0251/0.0603 | 0.0420/0.0991 | 0.0544/0.1386 |
| GOF | 1.047 | 1.051 | 1.038 | 1.112 | 1.068 |
| CCDC | 1950399 | 1950400 | 2021266 | 2021267 | 2021268 |

X-ray Crystallography. The intensities for the X-ray determinations of $\{\text{Ca} \subset \{\text{MeCN}_2\text{Ba}_2\cdot \text{MeCN}_2\}\}$ and $(\text{MeCN})\text{Ba}_2\subset \{\text{Au}_2\text{Lpy}^-\cdot \text{MeCN}\}$ were collected on a Bruker D8 QUEST CMOS instrument at 100 K with Mo $\lambda$ radiation ($\lambda$ = 0.71073 Å) using a TRIUMPH monochromator, while the corresponding data for $\{\text{Ca} \subset \{\text{MeCN}_2\text{Ba}_2\cdot \text{MeCN}_2\}\}$·1.5H$_2$O were collected on a STOE IPDS 2T instrument at 100 K using Mo $\lambda$ radiation with a graphite monochromator. Standard procedures were applied for data reduction and absorption correction. Structure solutions and refinements were performed with the SHELXT and SHELXL 2014/7 programs included in the WinGX program package$^{54-56}$. The structure of $\{\text{MeOH}_2\text{H}_2\text{O}_2\text{Sr}_2\subset \{\text{Au}_2\text{Lpy}^-\cdot \text{MeCN}\}\}$·MeOH·1.5H$_2$O was refined as a two-component twin. The final refinement was performed using HKLF 5 with reflection data prepared using TwinRotMat of PLATON program.$^{57}$ Hydrogen atoms were calculated for idealized positions and treated with the “riding model” option of SHELXL. More details on data collections and structure calculations are contained in Table 3. The representation of molecular structures was done using the program DIAMOND.$^{58}$ Since ball and stick presentations of the molecules are used in all of the Figures of this paper for reason of clarity, ellipsoid representations of all compounds are contained in the Supporting Information. Stereochemical analysis of the coordination spheres of the guest alkali metal ions are performed by the program SHAPE 2.1.$^{59}$ More details about the compounds are contained in the Supporting Information.

Deposition Numbers 1950399, 1950400, 2021266 and 2021268 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structure Services www.ccdc.cam.ac.uk/structures.

Acknowledgments

SFS is grateful for a “Science without Borders” fellowship of the Brazilian Council for Scientific and Technological Development (CNPq), under project number 99999.009533/2013-03. CTP gratefully acknowledges financial support from the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.03-2017.322. UA thanks the Dahlem Research School (DRS, FU Berlin) for financial support. We also gratefully acknowledge the assistance of the Core
