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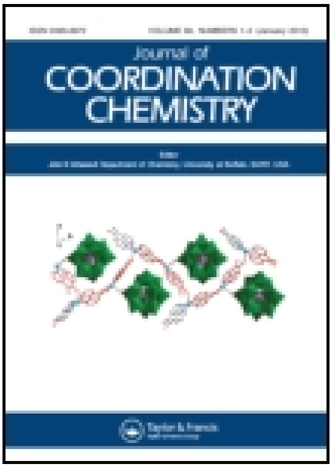

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# Synthesis and crystal structure of a triple-decker $Cu^{II}_3Tl^{I}_2$ complex: first example of a thallium(I) system in the imino-phenolate Schiff base ligand family

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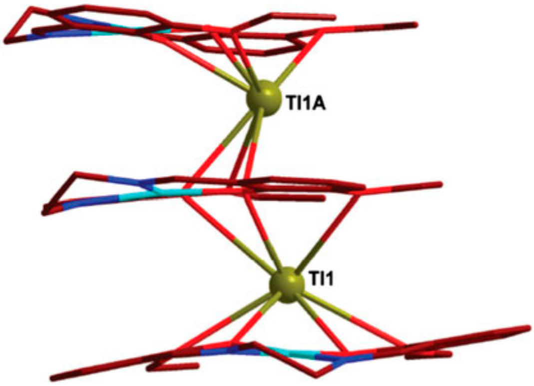

Synthesis and crystal structure of $[(Cu^{II}L)_3Tl^{I}_2](NO_3)_2$ is described, where $H_2L = N,N'$-ethylenebis(3-ethoxysalicylaldimine). This is a sandwich, triple-decker system and the sole $Tl^{I}$ complex derived from an iminophenolate ligand.

This report deals with the synthesis, characterization, and crystal structure of a heteropentanuclear $Cu^{II}_3Tl^{I}_2$ compound $[(Cu^{II}L)_3Tl^{I}_2](NO_3)_2$ (**1**), where $H_2L=N,N'$-ethylenebis(3-ethoxysalicylaldimine). This compound crystallizes in the monoclinic crystal system within space group *C2/c*. Each of the two symmetry related thallium(I) centers is located between a terminal and a common, central $[Cu^{II}L]$ by forming bonds with four phenoxo and three ethoxy oxygens. The three $[Cu^{II}L]$ moieties are parallel and hence **1** is a triple-decker system. Neighboring triple-decker moieties are interlinked by $\pi\cdots\pi$ stacking interaction and weak hydrogen bonds to generate 3-D self-assembly in **1**. Salient features in the composition and structure of the title compound are discussed; the title compound is the first example of a thallium(I) system in imino-phenolate Schiff base family.

*Keywords*: Triple-decker; Thallium(I); Heterometallic; Compartmental ligand; Iminophenolate ligand

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## 1. Introduction

Thallium is called the "duckbill platypus among elements" [1, 2] because of its similarity with elements from various parts of the periodic table, such as alkali metals, lead, mercury, and silver [3–7]. Due to the well-known Inert pair effect, this element prefers +1 to +3 oxidation state. Thallium in its monovalent state shows the best similarity with potassium(I) because of the similarity in their ionic radii (1.64 Å for $Tl^{I}$ *versus* 1.55 Å for $K^{I}$) six coordination and dehydration energy (80 kcal $M^{-1}$ for $K^{I}$ *versus* 82 kcal $M^{-1}$ for $Tl^{I}$) [2, 5, 7]. However, while some simple salts of the two monovalent cations behave isotypically [2, 4], coordination compounds including organometallic systems of the two cations are seldom isostructural [2]. The reason behind this is the difference in their coordination numbers; high coordination numbers are favorable for $K^{I}$ while $Tl^{I}$ favors low coordination numbers, this in turn, is associated with the relativistically contracted valence shell and the stereochemically active $6s^2$ lone pair of electrons in the latter [2, 8]. From a structural point of view, $Tl^{I}$ systems are interesting because, in addition to bonds with ligands, this cation can form secondary interactions like Tl···Tl (thallophilic), Tl···C, Tl···π, and Tl···H [8–12]. As a result, there has been much interest in exploring the structural aspects of thallium(I) compounds, including coordination polymers and self-assembled supramolecules [2, 5, 8–17]. Understanding and prediction of the structure of a metal/ligand combination with high certainty is quite difficult for main group metals in low oxidation states (e.g. $Tl^{I}$) which have lone pairs of electrons [8–10]. All in all, further exploration of $Tl^{I}$ systems seems appropriate.

Acyclic Schiff base ligands obtained on condensation of salicylaldehyde or substituted salicylaldehyde with a diamine constitute a major class of ligands in the broad area of coordination chemistry; more than 2,500 crystals of metal complexes derived from such ligands have been reported, including mononuclear, dinuclear, oligonuclear clusters, and polymeric systems [18]. If we look into the metal ions present in these complexes, they are of the following: 2nd period: Li; 3rd period: Na, Mg, Al; 4th period: all from K to Ga; 5th period: all from Rb to Sn; 6th period: all from Cs to Bi including the lanthanides, except Ta and Tl (and Pm); 7th period: Th and U. Clearly, out of the possible and available metal ions, all but Ta and Tl are present in the acyclic Schiff base ligands which we discuss here. It is thus relevant to explore Tl (or Ta) systems in association with this major class of ligands. It is worth mentioning also that there is no $Tl^{I}$ complex in any type of iminophenolate Schiff base, acyclic, or macrocyclic [18].

We have been exploring the structural diversity of coordination compounds derived from 3-ethoxysalicylaldehyde-diamine acyclic Schiff base ligands, $H_2L^{OEt}$ (which belong to the above mentioned general class) [19–38]. Reactions of the mononuclear compounds $[Cu^{II}L^{OEt}\subset(H_2O)]$ or $[Ni^{II}L^{OEt}\subset(H_2O)]$ have been carried out with metal ions from various parts of the periodic table, such as alkali metal ions ($Li^{I}$, $Na^{I}$, $K^{I}$, $Rb^{I}$, $Cs^{I}$) [19–23], alkaline earth metal ions ($Mg^{II}$, $Ca^{II}$, $Ba^{II}$; $Sr^{II}$ attempted but could not be isolated) [20–22, 24], 3d metal ions ($Cu^{II}$, $Ni^{II}$, $Co^{II}$, $Fe^{II}$, $Mn^{II}$) [25–29], $d^{10}$ metal ions ($Zn^{II}$, $Cd^{II}$, $Hg^{II}$, $Ag^{I}$) [30], 4f metal ion ($Ce^{III}$-$Yb^{III}$ except $Pm^{III}$) [31, 32], 5f metal ion ($U^{VI}$) [24, 33, 34], and p-block metal ions ($Pb^{II}$, $Bi^{III}$) [21, 22, 24]. The products obtained from these are discrete systems in some cases, but interesting examples of two-component and even three-component co-crystals were found in other cases. Some of the systems have sandwich topology: double-decker [21, 22], both double-decker and triple-decker [19, 20] and even quadruple-decker [20]. With the aim to stabilize a 3d-thallium(I) system derived from $H_2L^{OEt}$ and also to stabilize the first example of a $Tl^{I}$ complex in any type of iminophenolate Schiff base ligand environment, we have reacted $[Cu^{II}L\subset(H_2O)]$ with $Tl^{I}NO_3$, where $H_2L$=*N*,*N′*-ethylenebis(3-ethoxysalicylaldimine) (scheme 1). Herein, we report the synthesis, characterization, and crystal structure of the product obtained.

## 2. Experimental

### 2.1. *Materials and physical methods*

All the reagents and solvents were purchased from commercial sources and used as received. $[Cu^{II}L\subset(H_2O)]$ was prepared by the reported method [25]. Elemental (C, H, and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded from 400 to 4000 $cm^{-1}$ on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks.

### 2.2. *Synthesis of* $[(Cu^{II}L)_3Tl^{I}_2](NO_3)_2$ *(1)*

Finely powdered thallium(I) nitrate (0.133 g, 0.5 mM) was added to a suspension of $[Cu^{II}L\subset(H_2O)]$ (0.218 g, 0.5 mM) in acetone (15 mL). After 10 min stirring, the red solution was filtered to remove suspended particles and the filtrate was kept at room temperature and allowed to evaporate slowly. After a few days, a red crystalline compound containing diffraction quality single crystals deposited, was collected by filtration and washed with cold acetone. Yield: 0.192 g (65%; in terms of $Cu^{II}$). Anal. Calcd for $C_{60}H_{66}N_8O_{18}Cu_3Tl_2$: C, 40.34; H, 3.72; N, 6.27. Found: C, 40.56; H, 3.58; N, 6.45. IR ($cm^{-1}$, KBr): *ν*(C=N), 1632vs; *ν*(nitrate), 1390s, 1297s.

Table 1. Crystallographic data for **1**.

| | |
|---|---|
| Empirical formula | $C_{60}H_{66}N_8O_{18}Cu_3Tl_2$ |
| Formula weight | 1786.57 |
| Crystal color | Red |
| Crystal system | Monoclinic |
| Space group | *C2/c* |
| *a* (Å) | 19.9172(9) |
| *b* (Å) | 13.2276(6) |
| *c* (Å) | 23.8088(11) |
| $\beta$ (°) | 101.4970(10) |
| $V$ (Å$^3$) | 6146.7(5) |
| *Z* | 4 |
| *T* (K) | 120(2) |
| $2\theta$ | 3.50–52.74 |
| $\mu$ (Mo Kα) ($mm^{-1}$) | 6.326 |
| $\rho_{Calcd}$ ($g\,cm^{-3}$) | 1.931 |
| *F* (0 0 0) | 3500 |
| Absorption-correction | Multi-scan |
| Index ranges | $-24 \le h \le 24$<br>$-16 \le k \le 16$<br>$-29 \le l \le 29$ |
| Reflections collected | 29699 |
| Independent reflections ($R_{int}$) | 6278 (0.0762) |
| $R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$] | 0.0366/0.0702 |
| $R_1{}^a/wR_2{}^b$ [for all $F_o{}^2$] | 0.0579/0.0761 |

$^aR_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$.
$^bwR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

### 2.3. *Crystal structure determination of $[(Cu^{II}L)_3Tl^{I}{}_2](NO_3)_2$ (1)*

The crystallographic data of **1** are listed in table 1. X-ray diffraction data were collected at 120 K using graphite-monochromated Mo-$K\alpha$ (0.71073 Å) radiation. Data were collected on a Bruker SMART 1 K CCD diffractometer and processed using SAINT [39]. The structure was solved by direct methods in SHELXS-97 and refined by full-matrix least-squares on $F^2$ using SHELXL-97 [40]. The structure crystallized in the monoclinic space group $C2/c$ with $Z' = 0.5$. All hydrogens were positioned geometrically (aromatic C–H 0.95 Å, ethyl C–H 0.99 Å and methyl C–H 0.98 Å) and refined using a riding model with isotropic displacement parameters fixed at $U_{\mathrm{iso}}(\mathrm{H})$ = 1.2 times $U_{\mathrm{eq}}$ of the parent carbon for the aromatic and ethyl hydrogens and $U_{\mathrm{iso}}(\mathrm{H})$ = 1.5 times $U_{\mathrm{eq}}$ of the parent carbon for the methyl hydrogens. The final refinement converged to $R_1$ ($I > 2\sigma(I)$) value 0.0366.

## 3. Results and discussion

### 3.1. *Description of crystal structure of $[(Cu^{II}L)_3Tl^{I}{}_2](NO_3)_2$ (1)*

The structure of **1** consists of the heteropentanuclear triple-decker $[(Cu^{II}L)_3Tl^{I}{}_2]^{2+}$ cation and two nitrates. The structure of $[(Cu^{II}L)_3Tl^{I}{}_2]^{2+}$ is shown in figures 1 and 2, the latter of which demonstrates the triple-decker topology more clearly. One half of the structure of **1** is symmetry related to the other half through a twofold rotation. Each of the two symmetry related thallium(I) ions, Tl1 and Tl1A (where A = 1 − $x$, $y$, 0.5 − $z$), is linked with a pair of $[Cu^{II}L]$ moieties. The Tl1 center is coordinated to all four oxygens (O1, O2, O3, and O4) of one terminal $[Cu^{II}L]$ and two phenoxo (O6 and O6A, where A = 1 − $x$, $y$, 0.5 − $z$) and one ethoxy (O5) oxygen of the central $[Cu^{II}L]$ moiety. The thallium(I) is seven-coordinate and the two metal centers in both the Cu⋯Tl pairs, Cu1⋯Tl1 and Cu2⋯Tl1, are diphenoxo-bridged. The N(imine)$_2$O(phenoxo)$_2$ and also the O(phenoxo)$_2$O(ethoxy)$_2$ of the

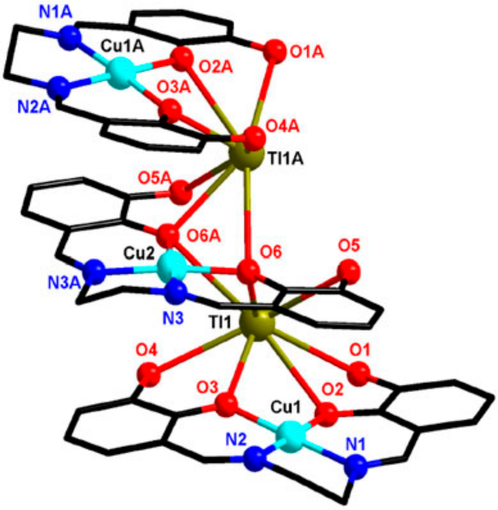


Figure 1. Crystal structure of $[(Cu^{II}L)_3Tl^{I}{}_2](NO_3)_2$ (**1**). Carbons of the ethoxy moieties and all hydrogens are omitted. Symmetry code: A, 1 − $x$, $y$, 0.5 − $z$.

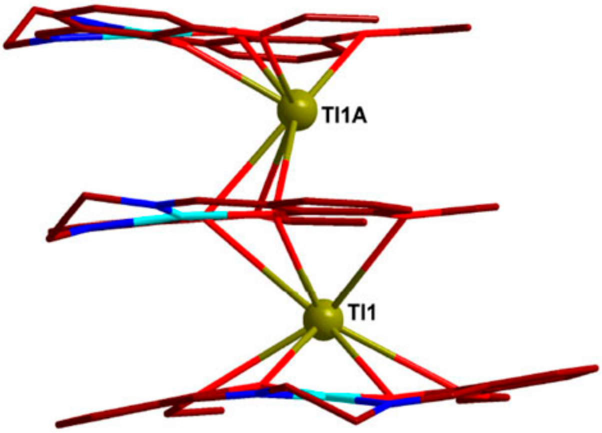
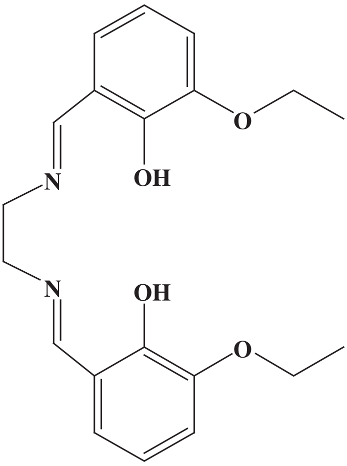


Figure 2. Crystal structure of $[(Cu^{II}L)_3Tl^{I}_2](NO_3)_2$ (**1**), showing its triple-decker topology. All hydrogens are omitted. Symmetry code: A, 1 – *x*, *y*, 0.5 – *z*.



Scheme 1. Chemical structure of $H_2L$.

[Cu1L] and [Cu2L] fragments are almost planar as evidenced by the average deviation, <0.1 Å, of the constituent atoms from the corresponding least-squares $N_2O_2$ or $O_4$ planes. The dihedral angles between the least-squares $N_2O_2/O_4$/aromatic $C_6$ planes of [Cu1L] and the corresponding least-squares plane of [Cu2L] are less than 15°, indicating that [Cu1L] and [Cu2L] may be considered parallel. The distances between Tl1 and least-squares O1O2O3O4 plane of [Cu1L] and O5O5AO6O6A (where A = 1 – *x*, *y*, 0.5 – *z*) plane of [Cu2L] are, respectively, 1.42 and 1.97 Å. So, each of the two symmetry related thallium(I) centers, Tl1 and Tl1A, are sandwiched in between two [CuL] moieties, resulting in an overall triple-decker topology.

As listed in table 2, the Cu–O(phenoxo) bond distances for Cu1 and Cu2 are slightly shorter than the Cu–N(imine) bond distances. The *transoid* angles (177.59(18)° and

Table 2. Bond lengths (Å) and angles (°) in the coordination environments of copper(II) and thallium(I) centres in **1**. Symmetry code: A, $1-x$, $y$, $0.5-z$.

| | | | |
|---|---|---|---|
| Cu1–N1 | 1.924(5) | N1–Cu1–O3 | 177.59(18) |
| Cu1–N2 | 1.926(4) | N2–Cu1–O2 | 179.37(19) |
| Cu1–O2 | 1.898(4) | N1–Cu1–N2 | 85.77(19) |
| Cu1–O3 | 1.906(4) | N1–Cu1–O2 | 94.21(17) |
| | | N2–Cu1–O3 | 93.15(17) |
| | | O2–Cu1–O3 | 86.84(15) |
| Cu2–N3 | 1.923(5) | N3–Cu2–O6A | 174.49(18) |
| Cu2–O6 | 1.900(4) | N3–Cu2–O6 | 94.59(18) |
| | | N3–Cu2–N3A | 85.1(3) |
| | | O6–Cu2–O6A | 86.2(2) |
| Tl1–O1 | 3.187(4) | O1–Tl1–O2 | 50.93(9) |
| Tl1–O2 | 2.815(4) | O1–Tl1–O3 | 104.86(10) |
| Tl1–O3 | 2.576(4) | O1–Tl1–O4 | 123.06(10) |
| Tl1–O4 | 2.924(4) | O1–Tl1–O5 | 80.61(10) |
| Tl1–O5 | 3.027(4) | O1–Tl1–O6 | 132.14(10) |
| Tl1–O6 | 2.744(4) | O1–Tl1–O6A | 161.29(9) |
| Tl1–O6A | 3.118(4) | O2–Tl1–O3 | 57.83(11) |
| | | O2–Tl1–O4 | 103.92(11) |
| Cu1···Tl1 | 3.609 | O2–Tl1–O5 | 72.84(10) |
| Cu2···Tl1 | 3.678 | O2–Tl1–O6 | 98.34(11) |
| Cu1–O2–Tl1 | 98.04(14) | O2–Tl1–O6A | 145.60(10) |
| Cu1–O3–Tl1 | 106.28(15) | O3–Tl1–O4 | 55.75(11) |
| Cu2–O6–Tl1 | 103.26(14) | O3–Tl1–O5 | 99.88(11) |
| Cu2–O6A–Tl1 | 90.96(13) | O3–Tl1–O6 | 75.33(11) |
| | | O3–Tl1–O6A | 93.84(10) |
| | | O4–Tl1–O5 | 147.82(10) |
| | | O4–Tl1–O6 | 97.12(11) |
| | | O4–Tl1–O6A | 68.21(10) |
| | | O5–Tl1–O6 | 53.17(10) |
| | | O5–Tl1–O6A | 96.00(10) |
| | | O6–Tl1–O6A | 52.13(13) |

179.37(19)° for Cu1 and 174.49(18)° for Cu2), the ranges of the *cisoid* angles (85.77(19)°–94.21(17)° for Cu1 and 85.1(3)°–94.59(18)° for Cu2) along with no displacement (for Cu2) or only slight displacement (0.023 Å for Cu1) of the metal ions and deviation (<0.1 Å) of the constituent atoms from the corresponding least-squares $N_2O_2$ plane indicate that the coordination geometry of both Cu1 and Cu2 are slightly distorted square planar.

The bond distances and angles in the coordination environment of $Tl^I$ are also listed in table 2. The Tl–O(phenoxo) bond distances involving the four phenoxo oxygens O2, O3, O6, and O6A are, respectively, 2.815(4), 2.576(4), 2.744(4), and 3.118(4) Å, while the Tl–O(ethoxy) bond distances involving the three ethoxy oxygens O1, O4, and O5 are, respectively, 3.187(4), 2.924(4), and 3.027(4) Å. The Tl–O(phenoxo) (2.576(4)–3.118(4) Å) and Tl–O(ethoxy) (2.924(4)–3.187(4) Å) bond distances in **1** lie in ranges of Tl–O (phenoxo) (2.372–3.220 Å) [9, 10, 14–18, 41] and Tl–O(ether) (2.564–3.341 Å) [15, 17, 18] bond distances observed in previously reported thallium(I) compounds. The coordination of O5A with Tl1 is not considered because of much longer separation, 3.783 Å. The O–Tl–O bond angles vary between 50.93(9)° and 145.60(10)°. The Cu1–O2–Tl1, Cu1–O3–Tl1, Cu2–O6–Tl1, and Cu2–O6A–Tl1 phenoxo bridge angles are 98.04(14)°, 106.28(15)°, 103.26(14)°, and 90.96(13)°, respectively, while the Cu1···Tl1 and Cu2···Tl1 distances are 3.609 and 3.678 Å, respectively.

There exist four weak CH···O hydrogen bonds (figure S1 , see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.879122) and one $\pi \cdots \pi$ stacking interaction (figure S2) in **1**. The four CH···O hydrogen bonds, involving nitrate oxygens and CH=N/aromatic/$NCH_2CH_2N$ moieties, interlink the triple-decker complex units to generate a 2-D sheet in the crystallographic *ab* plane (figure S1). The $\pi\cdots\pi$ stacking interaction interlinks the triple-decker units to generate a 1-D topology along the crystallographic *c* axis. Therefore, the overall supramolecular structure of **1** is 3-D, which may be considered as the interlinking of the 2-D sheets (as in figure S1) by the 1-D chains (as in figure S2). The geometries of the hydrogen bonds are listed in table S1. For $\pi\cdots\pi$ stacking interaction, centroid···centroid distance, offset distance and dihedral angle between the two corresponding aromatic rings are, 3.703 Å, 1.552 Å, and 3.14°, respectively.

### 3.2. *Comparison of 1 with related systems*

Previously, a few (*ca*. 25) phenoxo-bridged homometallic [9, 10, 16–18, 41] and a few (*ca*. five) heterometallic [14, 15, 18] compounds of thallium(I) have been reported. The homometallic thallium(I) compounds are dinuclear, tetranuclear, or polymeric. The heterometallic compounds are trinuclear $Tl^ICu^{II}Tl^I/Tl^INi^{II}Tl^I$, hexanuclear $Cu^{II}_2Tl^I_4$, or polymeric $\{Cu^{II}Tl^I_2\}_n$. Unlike **1**, none of these homo/heteronuclear systems are derived from Schiff base ligands but phenolic moieties in these compounds are mostly fluorinated phenol; hexafluorophenol, 3,5-bis(trifluoromethyl)phenol, or 2,3,5-tris(trifluoromethyl)phenol. Also, unlike **1**, none of the previously reported structures are sandwich systems. There are two mononuclear thallium(III) systems derived from iminophenolate ligands [42, 43]. One of those was derived from an iminophenolate cryptand host, which is the [3 + 2] condensation product of 4-methyl-2,6-diformylphenol and tris(aminoethylamine) [42], while the second is derived from a tripodal ligand, which is the [3 + 1] condensation product of 5-bromosalicylaldehyde and tris(aminoethylamine) [43].

As mentioned above, there is a possibility for similarity between $K^I$ and $Tl^I$ compounds. Previously, three copper(II)–potassium(I) compounds derived from $H_2L$ have been reported [19, 20]. One, $[Cu^{II}LK^I(\mu\text{-}PF_6)]_n$ (**I**) [20], of these is a dinuclear-based 1-D system, while the other two, $[\{(Cu^{II}L)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**II**) [19] and $[\{(Cu^{II}L)_2K^I\}(ClO_4)]\cdot[\{(Cu^{II}L)_3K^I_2(\mu\text{-}ClO_4)\}(ClO_4)]$ (**III**) [20], are cocrystals of a double-decker $Cu^{II}_2K^I$ and a triple-decker $Cu^{II}_3K^I_2$ moieties. So, the types of copper(II)–potassium (I) and copper(II)–thallium(I) systems derived from $H_2L$ are different, except that both $K^I$ (in **II** and **III**) and $Tl^I$ (in **1**) stabilize triple-decker $Cu^{II}_3M^I_2$ (M = K, Tl) moiety. The coordination number of both of $K^I$ in the triple-decker moiety in **II** and **III** and $Tl^I$ in **1** is seven, but the coordination sites are not occupied by equivalent sets of ligands; while $Tl^I$ is coordinated with four phenoxo and three ethoxy oxygens, $K^I$ is coordinated with four phenoxo, two ethoxy and one bridging nitrate (**II**)/perchlorate (**III**) oxygen. Comparison of some structural parameters in the coordination environment of $Tl^I$ in **1** and $K^I$ in the triple-decker moiety in **II**/**III** (table 3) reveals that some are similar while others are significantly different.

The $O(phenoxo)_2O(ethoxy)_2$ compartment of mononuclear copper(II)/nickel(II) complexes derived from 3-ethoxysalicylaldehyde-diamine ligands can interact with various metal ions. It is also known that this compartment can interact with water [25, 27], aquated proton [36], ammonium ion [21], and diprotonated diamines [37]. Therefore, in terms of interaction with various moieties, this $O_4$ compartment resembles the $O_n$ cage of crown ethers [15, 18]. On the other hand, while $Tl^I\cdots O_n$ (crown ethers) interactions are also known [15, 18], the title compound demonstrates that $Tl^I$ can interact with the $O_4$ compartment of 3-ethoxysalicylaldehyde-diamine ligands.

Table 3. Comparison of some structural parameters in the coordination environment of copper(II)–potassium(I)/thallium(I) compounds derived from $H_2L$ (distances in Å and angles in °).

| Compound/moiety | M–O (phenoxo) | M–O (ethoxy) | Cu–O–M | O–M–O | Cu···M | Ref. |
|---|---|---|---|---|---|---|
| $[(Cu^{II}L)_3Tl^{I}{}_2](NO_3)_2$ (**1**) | 2.57–3.12 | 2.92–3.19 | 91.0–106.3 | 50.9–161.3 | 3.61–3.68 | |
| Triple-decker in $[\{(Cu^{II}L)_2K^{I}\}(NO_3)]\cdot[\{(Cu^{II}L)_3K^{I}{}_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**II**) | 2.73–2.80 | 2.86–2.97 | 103.0–110.0 | 52.8–172.0 | 3.70–3.91 | [19] |
| Triple-decker in $[\{(Cu^{II}L)_2K^{I}\}(ClO_4)]\cdot[\{(Cu^{II}L)_3K^{I}{}_2(\mu\text{-}ClO_4)\}(ClO_4)]$ (**III**) | 2.72–2.85 | 2.73–3.11 | 99.7–107.9 | 51.1–170.1 | 3.68–3.82 | [20] |

## 4. Conclusion

The structural diversity of 3-ethoxysalicylaldehyde-diamine ligands has been further enriched and the similarity of the $O_n$ cage of crown ethers and the $O_4$ compartment of 3-ethoxysalicylaldehyde-diamine ligands has been further explored due to the isolation of the 3d–$Tl^{I}$ compound $[(Cu^{II}L)_3Tl^{I}{}_2](NO_3)_2$ (**1**). The title compound is the sole example of a $Tl^{I}$ system in imino-phenolate acyclic or macrocyclic ligands; as there are a few thousands crystal structures of macrocyclic/acyclic imono-phenolate complexes of other metal ions, a rare example of a thallium compound (next to only two $Tl^{III}$ compounds) and first example of a $Tl^{I}$ system in this family of thousands of members deserves importance.

It is also worth mentioning that the present study is ongoing exploration of structures and properties of homo/heterometallic complexes derived from compartmental ligands [44–46].

## Supplementary material

Crystallographic data in cif format, figures S1 and S2 and table S1. Crystallographic information is available (CCDC reference number: 823431 for **1**) from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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