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Homobinuclear sulfato-bridged and mononuclear nitrato complexes of Cu(II) with thiophen-2-yl-dipicolylamine; structure and anion-dependent absorption spectra

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ABSTRACT

A new ligand, bispyridin-2-ylmethyl-thiophen-2-ylmethylamine, 2ThDPA (**1**), was synthesized and its complexes of Cu(II) were isolated. When $Cu(NO_3)_2$ was used as the metal source, a mononuclear complex with the formula $[Cu(\mathbf{1})(NO_3)_2]$, **2**, was isolated featuring both nitro groups coordinated bidentate to the Cu. **2** crystallizes in the monoclinic P21/c space group with a = 14.848, b = 8.212, c = 32.752 Å, β = 102.52° and V = 3898.3 $Å^3$. When $CuSO_4$ was used as the metal source, a homobinuclear sulfato-bridged complex was isolated with the formula $[Cu(\mathbf{1})SO_4]_2 \cdot CH_3CN$, **3**. **3** crystallizes in the monoclinic P21/n space group with a = 10.457, b = 17.035, c = 12.425 Å, β = 108.72° and V = 2096.17 $Å^3$. The structures of **2** and **3** are shown to be stabilized by an extended system of π–π stacking and hydrogen-bonding interactions. Comparison of the electronic absorption spectra of the ligand and complexes shows that complexation is maintained in solution and that the ligand absorption is attenuated in the complexes, depending on the counter-anion utilized.

Introduction

Copper's physiological presence, along with its interesting magnetic properties, has kept it as one of the most researched elements [1–5]. Di-(2-picolyl)amine (dpa) has shown to coordinate to various transition metals as a tridentate ligand through the amine nitrogen and two pyridine nitrogen atoms with over 2500 hits in the CCDC [6]. Recently, the incorporation of Cu(II) into dpa based molecules has been reported [1–3,7–11]. Zhu and co-workers [1] synthesized a copper-sensitive fluoroionophore by modifying stilbene with dpa. High sensitivity and selectivity toward Cu(II) and Cu(I) was observed by significant fluorescence quenching upon binding with copper ions, even in the presence of metal ions such as Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Sn^{2+}, and Zn^{2+}. Mikata et al. [10] studied dpa-based complexes of Cu(II) and investigated the factors affecting intramolecular ether-oxygen coordination in their solid state structures. These authors noticed that the anion of the starting material plays a crucial role in this intramolecular coordination as well as the overall coordination environment of the metal ion. Contrary to this, Kumar et al. [11] studied Cu(II) metalorganic frameworks and found no influence of the counter anion on the primary framework structure, even though hydrogen-bonding interactions were observed with the counter anion.

Our research group focuses on luminescent metal ion complexes for applications such as light-emitting diodes and sensors [12–15]. In the course of our work, we developed a new N_3S donor tripodal ligand with dpa and methylthiophen-3-yl as the third arm attached to the central amine nitrogen [16]. Solid-state structures of Cu(II) complexes with this tripodal ligand, the effect of the counter-anion, and the extensive hydrogen-bonding network present within the resulting molecules were reported. We were interested in how ligand conformation affects the structure of the compounds. Thus, we synthesized a similar tripodal ligand with methylthiophen-2-yl as the third arm. We report here its characterization and the isolation and structural and photophysical characterization of its Cu(II) complexes, as well as the effect of the counter-anion on the molecular structure and on the absorption properties.

Experimental

All commercially available reagents were of analytical grade and used as received. Solvents were dried by standard methods [17]. NMR spectra were recorded on a Varian 400 spectrometer with chemical shifts (δ, ppm) reported against tetramethylsilane. Absorption spectra were obtained on a Perkin-Elmer Lambda 35 spectrometer in 1 cm quartz cells at 25.0 ± 0.1 °C. Methanol solutions of the compounds were prepared at about 10^{-4} M.

Synthesis of bispyridin-2-ylmethylthiophen-2-ylmethylamine, 2ThDPA (1)

2-Thiophenemethanol (2.0 g, 18 mmol) in diethyl ether was added under inert atmosphere to a solution of PBr_3 (7.1 g, 26.3 mmol) in diethyl ether. The solution was stirred at room temperature for 30 min, after which H_2O was slowly added to quench

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the reaction. The organic layer was separated and then washed with brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to give 2-bromomethylthiophene as an almost colorless oil in 70% yield (2.16 g). This product in diethyl ether was added to a solution of N,N-dipicolylamine (2.4 g, 12 mmol) and triethylamine (4.8 g, 48 mmol) in diethyl ether at 0 °C. The reaction mixture was stirred at this temperature for 5 min and then at room temperature for 18 h. The resulting red solution was filtered and the solvent was removed under reduced pressure to yield a red oil. Purification by flash chromatography using 90:10 THF/CH_2Cl_2 as the elutent gave **1** as a red oil in 45% overall yield (2.29 g). ^1H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ 8.52 (d, $^3J = 4.8$ Hz, 2H), 7.67 (t, $^3J = 8.0$ Hz, 4H), 7.23 (d, $^3J = 4.8$ Hz, 1H), 7.15 (t, $^3J = 7.8$ Hz, 2H), 6.94 (d, $^3J = 5.2$ Hz, 2H), 3.90 (s, 2H), 3.85 (s, 4H). λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 233 (13,000), 262 (8560).

Synthesis of the metal complexes

$[Cu(2ThDPA)](NO_3)_2$ (**2**). $Cu(NO_3)_2$ (0.16 g, 8.5 mmol) in MeOH was added to a solution of **1** (250 mg, 8.5 mmol) in MeOH. The dark blue solution was filtered after 30 min and the solvent removed under reduced pressure to yield a light blue powder (190 mg) in 52% yield. X-ray quality crystals formed by vapor diffusion of Et_2O into a solution of **2** in MeCN within 1 day. λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 261 (11,400), 305 (4430), 663 (100).

$[Cu(2ThDPA)](SO_4)]_2 \cdot CH_3CN$ (**3**). $CuSO_4$ (42 mg, 1.7 mmol) in MeOH was added to a solution of **1** (50 mg, 1.7 mmol) in MeOH. Slow solvent evaporation of the dark blue solution yielded blue crystals of **3** in 47% (45 mg) yield. X-ray quality crystals were grown by vapor diffusion of Et_2O into a solution of **3** in MeCN within 1 day. λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 237 (29,100), 260 (25,000), 283 (3010), 666 (243).

X-ray crystallographic characterization

Crystal data, data collection, and refinement details for compounds **2** and **3** are given in Table 1. Selected bond lengths and angles for these complexes as well as selected hydrogen bond distances are given in Tables 2 and 3. Suitable crystals were mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device, using graphite-monochromated Mo-*Kα* radiation ($\lambda = 0.71073$ Å). Data were measured using a strategy combining ω and ϕ scans of 0.3° per frame and an acquisition time of 10 or 20 s per frame. Multiscan absorption corrections were applied. Cell parameters were retrieved using SMART [18] software and refined using SAINTplus [19] software. Absorption corrections were applied using SADABS [20]. The structures were solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL [21] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically, and their parameters constrained to the parent site.

Table 1
Details of the X-ray crystallographic characterization of compounds 2–3.

Complex	2	3
CCDC no.	805496	805497
Formula	$C_{34}H_{34}Cu_2N_{10}O_{12}S_2$	$C_{19}H_{20}CuN_4O_4S_2$
M/g mol^{-1}	965.91	496.05
Crystal system	Monoclinic	Monoclinic
a/Å	14.8479(4)	10.4569(2)
b/Å	8.2115(2)	17.0349(2)
c/Å	32.7523(9)	12.4247(2)
α/deg	90	90
β/deg	102.519(2)	108.7190(10)
γ/deg	90	90
V/$Å^3$	3898.33	2096.17
T/K	100(2)	100(2)
Z	4	4
D_c/g cm^{-1}	1.646	1.572
μ(Mo − Kα)/mm^{-1}	1.275	1.275
Independent reflections, R_{int} [$F_o \geq 4\sigma(F_o)$]	7475, 0.1569	9518, 0.0449
Reflections collected	180,834	94,146
R_1, wR_2 [I>2σ(I)]	0.0683, 0.1288	0.0392, 0.0876
Data/restraints/parameters	7475/20/530	9518/0/272
GoF on F^2	1.023	0.945
Largest diff. peak and hole/e $Å^3$	0.808, −0.684	0.822, −0.822

Table 2
Selected bond lengths [Å] for 2.

Cu1–O1	2.202(5)	Cu2–O7	2.135(4)
Cu1–O2	2.862	Cu2–O9	2.824
Cu1–O4	2.084(4)	Cu2–O10	2.142(4)
Cu1–O5	2.653	Cu2–O11	2.616
Cu1–N1	1.947(5)	Cu2–N6	1.959(5)
Cu1–N2	2.082(5)	Cu2–N7	2.075(5)
Cu1–N3	1.948(5)	Cu2–N8	1.946(5)

Results and discussion

The ligand described here, bispyridin-2-ylmethylthiophen-2-ylmethylamine (2ThDPA), was synthesized as shown in Scheme 1. Bromination of 2-thiophenemethanol with PBr_3 in diethyl ether under inert atmosphere for 30 min yields 2-bromomethylthiophene. Stirring this compound with N,N-dipicolylamine in diethyl ether in the presence of triethylamine as base gives **1** in 45% overall yield.

Two different Cu(II) complexes with **1** were synthesized by stirring the ligand with the appropriate copper salt, as illustrated in Scheme 2. Reaction of **1** with the Cu(II) nitrate or sulfate yields the metal complexes **2** and **3,** respectively. X-ray quality crystals of each were grown by slow vapor diffusion of diethyl ether into a solution of MeCN containing the metal complex.

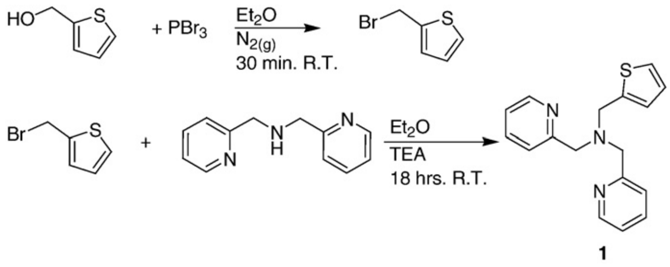
Complex **2** crystallizes in the monoclinic space group P2*1*/c. Crystallographic details for **2** are summarized in Table 1. The asymmetric unit contains two different molecules of **2**, which are rotated 127.1° from one another. Each Cu atom is coordinated by the three nitrogen atoms of dipicolyamine as well as two nitrate anions, as shown in Fig. 1. Both thiophene moieties are disordered, occupying two positions rotated by 180°, as is seen frequently with this ring [12–15,22,23]. Both nitrate anions display bidentate coordination, resulting in a coordination number of seven for the metal atoms. The coordination geometry around the central metal in both molecules is a distorted pentagonal bipyramid. For the molecule containing Cu1, the base of the pentagonal bipyramid is formed by the four oxygen atoms of the bidentate nitrate anions, O1, O2, O4, and O5, and the central amine nitrogen of the tripodal ligand, N2. The capping positions are occupied by the two pyridine nitrogen atoms, N1 and N3.

For the molecule containing Cu2 the base of the bipyramid is spanned by O7, O9, O10 and O11 from the bidentate nitrate anions, and N7 from the central amine of the tripodal ligand. The capping positions are occupied by the two pyridine nitrogen atoms, N6 and N8. The distances between the two Cu(II) and the ligating atoms are shown in Fig. 2 and summarized in Table 2. The Cu–N_{py} distances range from 1.946 to 1.959 Å, while the Cu–N_{amine} distances are

Table 3
Selected bond lengths (Å) for 3.

CuA–N1A	1.987
CuA–N2A	1.982
CuA–N3A	2.023
CuA–O1A	1.953
CuA–O1B	2.314
CuA–O2A	2.709
C18–H···O2*	2.257
C18–H···O4*	2.278

* Hydrogen bonding distance between acetonitrile and sulfato group (Fig. 7).



Scheme 1. Synthesis of 2ThDPA, **1**.

slightly longer at 2.075 and 2.082 Å. Each bidentate nitrate has one Cu–O longer than the other, the shorter distance in the range 2.083–2.202 Å and the longer in the range 2.616–2.862 Å. These rank among the longest reported Cu–O distances, however they are still within the sum of the van der Waals radii of the binding partners (2.92 Å) and are thus considered bonding interactions [6].

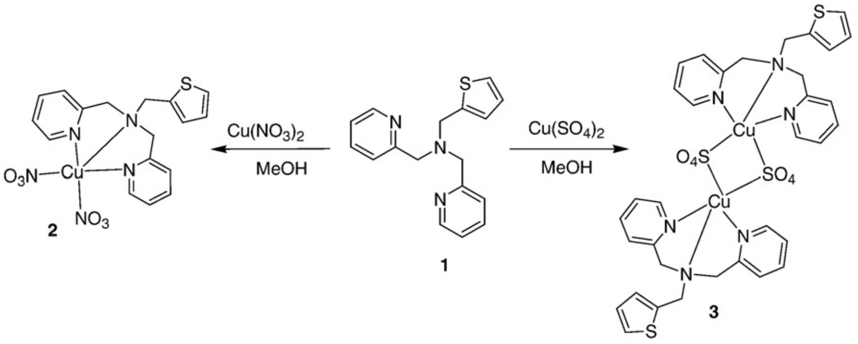
These distances are nearly identical to the previously reported structure [3ThDPACu(NO_3)$_2$], where 3ThDPA is the bispyridin-2-ylmethylthiophen-3-ylmethylamine ligand [16]. The previously reported complex displays two independent molecules in the asymmetric unit, as is the case in **2**. However, the nitrate anions display two different types of coordination. One molecule displays Cu bound to two bidentate coordinated nitrate anions and in the other molecule one nitrate is bidentate and the other is monodentate. The bidentate coordinated nitrate anions have one Cu–O bond longer than the other, with the shorter distances in the range 2.103 – 2.190 Å and the longer distances in the range 2.622–2.871 Å. The Cu–N_{amine} distances for the previously reported compound are 2.082 and 2.084 Å and the Cu–N_{py} distances are in the range 1.957 – 1.965 Å, slightly longer than the distances found for **2**.

There are seven other reported structures that feature copper coordinated to two nitrate anions and a tripodal dpa derivative ligand with non-coordinating arms on the central amine [7–10,24–26]. Only one of these features both nitrates coordinated bidentate [8]. This is however a Cu(III) complex, which also displays longer Cu–O distances in the range 2.126–2.538 Å. Frey et al [9]. reported a unique Cu(II) complex, in which three Cu(II) atoms coordinate in individual tridentate dpa pockets on a single ligand. One of the Cu(II) atoms is bound to two nitrate anions, one monodentate and one bidentate. The Cu(II)–O distances of the bidentate nitrate are 2.705 and 2.312 Å and 2.013 Å for the monodentate nitrate. Almesåker et al. [8] isolated a structure very similar to **2** with the dpa-based ligand *N*,*N*-4-tris(pyridine-2-ylmethyl)aniline (tmpa) and Cu(NO_3)$_3$ featuring bis-nitro-bidentate coordination. This complex has a similar pentagonal bipyramidal coordination geometry about the Cu center with a NO_4 base and capped by the two pyridine nitrogen atoms of dpa in the axial positions. The Cu–O bonds for these nitrates display short lengths of 2.126 and 2.356 Å, while the longer Cu–O bonds are 2.487 and 2.538 Å, significantly shorter than what is observed for **2**, as the longer Cu–O distances average 2.739 Å. Another key difference is that the longer Cu–O bond lengths are not across from one another as they are in **2**. Finally, the Cu–N_{py} distances are nearly identical to **2** at 1.948 and 1.958 Å, while the Cu–N_{amine} distance is slightly longer (2.180 Å vs. ~2.08 Å) due to the difference of the third arm attached to the amine moiety.

An extended network of π–π stacking interactions between pyridine and thiophene rings supports the packing structure. The centroid–centroid π–π stacking distance between two pyridine rings of adjacent molecules is 3.915 Å and the planes spanned by the rings intersect at 13.69°, as shown in Fig. 3. The π–π stacking distance between the centroids of the pyridine rings on the opposite side of the complex with the same ring of a second molecule within the unit cell is 3.681 Å and the planes of these rings intersect at an angle of 13.65°. Thiophene rings are involved in π–π stacking with the thiophene of neighboring molecules at a distance between centroids of 3.946 Å and with planes spanned by the thiophene rings intersecting at 8.54°. The previously reported structure with 3ThDPA also displays π–π stacking between the pyridine rings and thiophene rings. In this structure there are two different π–π interactions between the pyridine rings, showing distances of 2.6095 and 3.1613 Å and with the planes intersecting at 11.097 and 4.016°. The thiophene rings are separated by 3.5899 Å, and the planes intersect at 3.048°. These π–π stacking interactions are all at shorter distances and smaller intersecting angles than in **2**, indicating stronger π–π interactions.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$. Details of the crystallographic characterization are summarized in Table 1. Compound **3** is a homobinuclear complex, in which half of the molecule is generated by inversion. It displays the two Cu(II) ions connected by two bridging-bidentate sulfato anions, similar to the previously reported structure of [3ThDPACu(II)SO_4)]$_2$ [16]. A survey of the CCDC shows that to date only 5 reported examples of sulfate bridging between two Cu atoms are known [6]. Most other copper complexes display only monodentate sulfate coordination, making **3** as well as the recently described complex with 3ThDPA unique. In **3** each Cu(II) is additionally bound to a single ligand of **1** by the nitrogen atoms N1, N2, and N3 of the two pyridine rings and the tripodal amine. As in **2**, the thiophene does not coordinate to the Cu(II) atoms. This results in a distorted N_3O_3 octahedral geometry around the Cu (II), as shown in Fig. 4. The equatorial plane is comprised of the amine nitrogen atom, N3, and the three oxygen atoms from the two bridging sulfate anions. The axial positions of the octahedron are occupied by the pyridine nitrogen atoms N1 and N2.

The Cu–O and Cu–N bond lengths are summarized in Table 3 and are shown in Fig. 5. The Cu–N_{py} distances are in the range 1.982–1.987 Å and are shorter than the Cu–N_{amine} distance of 2.023 Å. The Cu–N_{py} distances of **3** are slightly longer than those in **2**, where as the Cu–N_{amine} bond length in **3** is shorter than that of **2**. This could be due to the fact that in **3** one of the sulfate oxygen atoms, more electronegative than nitrogen, is opposite from the N_{amine}. The Cu–N



Scheme 2. Synthesis of Cu(II) complexes **2** and **3**.

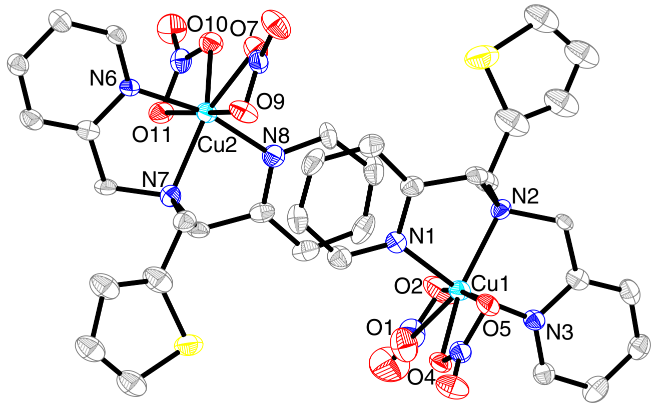


Fig. 1. Thermal ellipsoid plot of **2** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Only the thiophene ring with major occupancy in each ligand is displayed for clarity.

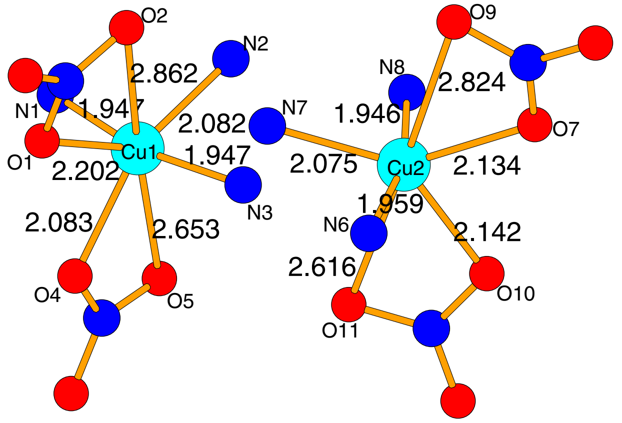


Fig. 2. Coordination environment around the two central Cu(II) atoms of **2**. Selected bond lengths are indicated in Å.

distances compare well with the previously reported Cu(II) complexes with 3ThDPA where the Cu–N_{py} distances are in the range 1.972–1.983 Å and the Cu–N_{amine} distances are slightly shorter in the range 2.013–2.016 Å.

Almesåker et al. [8] reported a $CuSO_4$ complex with tpma, [Cu(tpma)(μ-SO_4)], with a very similar coordination environment to **2**

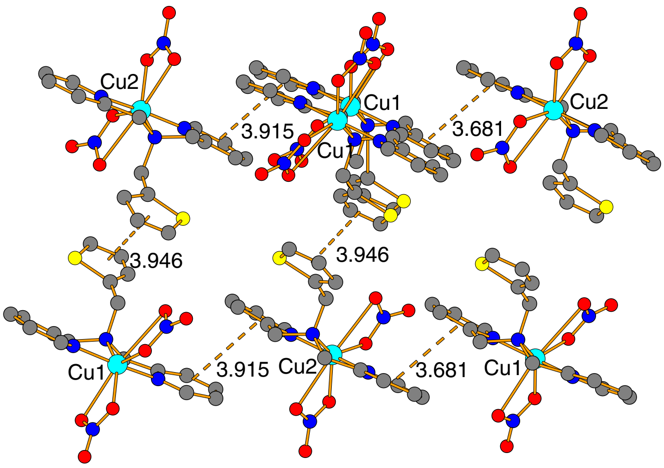


Fig. 3. Partial ball-and-stick diagram showing the π–π stacking interactions in **2**. Hydrogen atoms are omitted for clarity. Interplanar π–π distances (centroid–centroid) are indicated in Å.

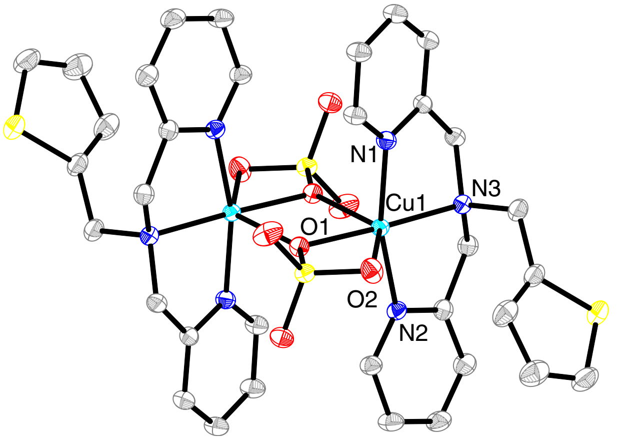


Fig. 4. Thermal ellipsoid plot of **3** with thermal ellipsoids at 50% probability**.** Hydrogen atoms and solvent molecule omitted for clarity.

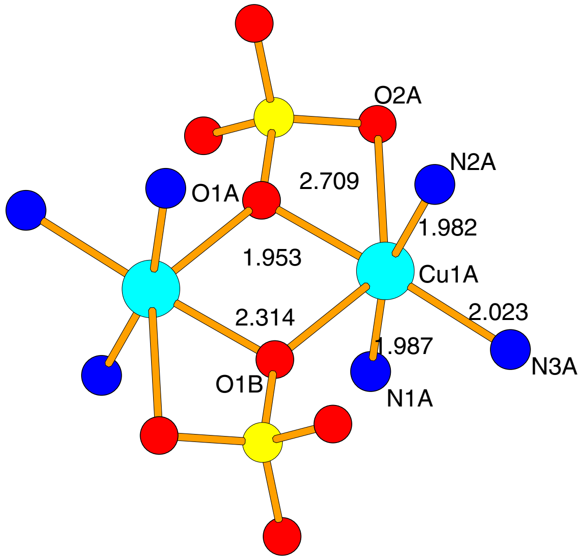


Fig. 5. Ball and stick diagram of **3** showing the distances (Å) of the coordination sphere around the Cu(II) center.

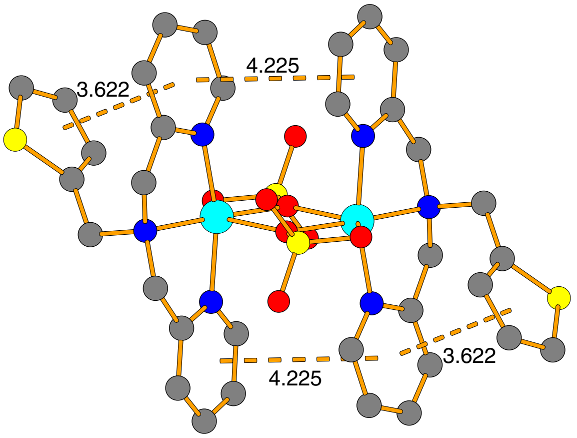


Fig. 6. Ball and stick diagram of **3** showing the π–π stacking interactions between the pyridine rings and thiophene. Centroid–centroid distances are indicated in Å. Hydrogen atoms have been omitted for clarity.

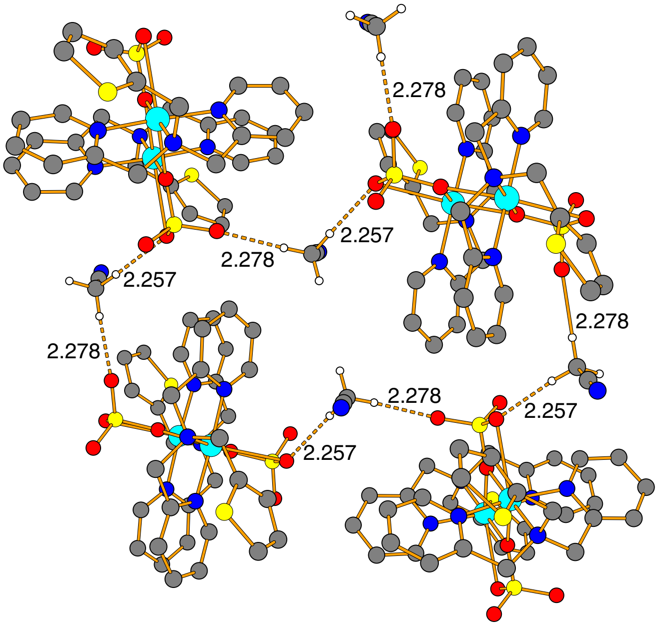


Fig. 7. Partial ball-and-stick packing diagram of **3** showing the H-bonding interactions between the acetonitrile and sulfato molecules. H-bonds shown in dashed lines with selected distances in Å. All hydrogen atoms not involved in hydrogen-bonding interactions were omitted for clarity.

and **3**. The complex, however, only displays monodentate sulfato bridging, resulting thus in 5-coordinate copper atoms. All of the bond lengths for [Cu(tpma)(μ-SO_4)] are longer than those observed for **3** in the range 1.957–2.888 Å for Cu–O and 1.996–2.029 Å for Cu–N.

3 also displays an extensive network of π–π stacking interactions, as seen in Fig. 6. The centroid–centroid distance between the pyridine rings is 4.225 Å with the planes spanned by the rings intersecting at an angle of 10.8°. This is much longer than similar interactions observed in the complexes with 3ThDPA, with centroid–centroid distances of 2.8193 and 3.7028 Å and an angle of intersection between the pyridine planes of 2.320 Å. A weak π–π stacking interaction is also present between one of the pyridine rings and the thiophene ring. The centroid–centroid distance is 3.622 Å with an angle of intersection of 26.1°. This angle is large considering π systems, but with a centroid–centroid distance of 3.6 Å it is considered a weak π-stacking interaction [27].

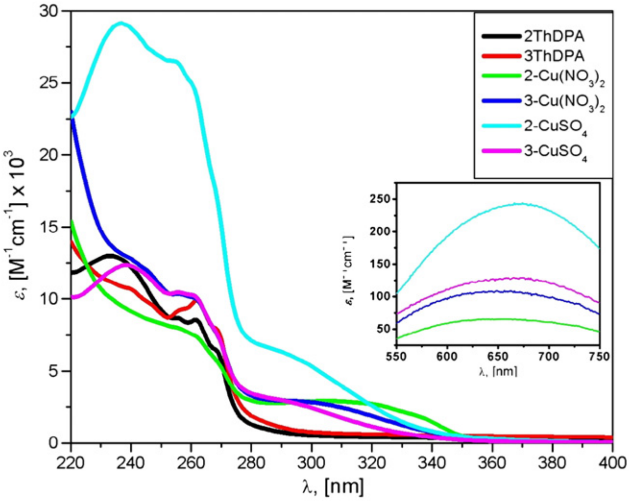


Fig. 8. Absorption spectra of **1** (2ThDPA), 3ThDPA, **2** [Cu(2ThDPA)$(NO_3)_2$] (2-Cu$(NO_3)_2$), [Cu(3ThDPA)$(NO_3)_2$] (3-Cu$(NO_3)_2$), **3** [Cu(2ThDPA)SO_4]$_2$ (2-$CuSO_4$), [Cu(3ThDPA)(SO_4)]$_2$ (3-$CuSO_4$) in methanol at ~[1.0×10^{-4} M]. Inset shows d–d transition in the range 550–750 nm.

Table 4
Electronic absorption spectroscopic data for ThDPA ligands and Cu(II) complexes.

	λ_{max} [nm[(ε [M^{-1} cm^{-1}])			
2ThDPA, **1**	233 (13,000)	262 (8560)		
3ThDPA	238 (10,800)	262 (9960)		
[Cu(2ThDPA)$(NO_3)_2$], **2**	–	261 (11,400)	305 (4430)	663 (100)
[Cu(3ThDPA)$(NO_3)_2$]	–	259 (10,100)	292 (2930)	656 (109)
[Cu(2ThDPA)(SO_4)]$_2$, **3**	237 (29,100)	260 (25,000)	283 (6800)	666 (244)
[Cu(3ThDPA)(SO_4)]$_2$	238 (12,400)	256 (10,500)	289 (3020)	658 (129)

One acetonitrile molecule crystallizes in the asymmetric unit of **3** and through two of its hydrogen atoms it is involved in hydrogen-bonding with the bridging sulfate anions, as shown in Fig. 7 and summarized in Table 3. At the same time, the bridging and the non-coordinated oxygen atoms of the sulfate anion are each interacting with a different acetonitrile molecule. The hydrogen-bond distance to the non-bonded oxygen atom is 2.278 Å and the bond distance to the bridging oxygen atom is slightly shorter at 2.257 Å.

Electronic absorption

UV/visible absorption spectra were obtained for both tripodal ligands 3ThDPA, which was previously reported [16], and 2ThDPA, as well as the Cu(II) complexes with nitrate and sulfate counter-anions. The spectra are shown in Fig. 8 and data are summarized in Table 4. Electron–donor–π–acceptor conjugated systems generally exhibit characteristic electronic absorption bands associated with π–π* intraligand charge transfer (ICT). Electronic or structural perturbations on the amine lone pair electrons influence the ICT properties and thus the electronic spectra, providing a useful signal transduction method for the design of chemosensors [1,28]. The ligands, 2ThDPA and 3ThDPA, exhibit absorption peaks at 233 and 262 nm, shown in the region common for dpa-substituted ligands [7,29,30]. These are assigned as the ligand–based ICT transitions. Both complexes with nitrate show almost complete disappearance of these bands, while they are still visible in the sulfate complexes. The metal complexes show the appearance of two new peaks, around 300 and 660 nm (Fig. 8 inset), with the latter assigned to a blue shift of the Cu d–d transition from $\lambda_{max} = 808$ nm for the hydrated Cu(II) ion [7,31]. These d–d transitions have very low ε values (100–243 M^{-1} cm^{-1}) compared to the ligand based π–π* ICT (8560–29,100 M^{-1} cm^{-1}). The d–d transition, however, does prove that complexation is maintained in solution by the >10-fold increase in ε when compared to $[Cu(H_2O)_6]^{2+}$ and the blue shift common for the exchange from O-donors to N-donors [31]. Kirin et al. [7] reported similar results with aromatic and aliphatic substituted dpa ligands, showing the d-d bands at ~650 nm ($\varepsilon = 100$–130 M^{-1} cm^{-1}) and the ligand based absorption at 240 nm for the aliphatic substituent and 252 nm for the aromatic and approximate ε values of 10,000 and 20,000 M^{-1} cm^{-1}, respectively.

Conclusion

A new dpa-based ligand with methylthiophen-2-yl and its complexes with Cu(II) were synthesized and characterized through X-ray crystallography and electronic absorption spectroscopy. The Cu(II) complexes display a similar coordination geometry to the previously reported Cu(II) complexes of 3ThDPA and structures which depend on the counter-anion utilized [16]. In the case of nitrate a mononuclear complex was formed with bidentate nitrate anions, resulting in a pentagonal bipyramidal coordination sphere around the copper atoms. In the case of the sulfate counter-anion, a homobinuclear sulfato bridged complex was formed, in which each sulfate is coordinated bidentate to one Cu(II) center while bridging to another Cu(II). The electronic absorption spectra revealed that these ligands possess intense π–π* transitions in the range 233–260 nm, which are partially quenched in the complexes. Additionally, the spectra of the complexes displayed a blue shifted d–d transition peak for Cu(II) at 660 nm, verifying thus complex formation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.02.028.

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