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Metal Complexes of 3-Thiophene Carboxamides Containing a Pyridine Ring

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Abstract

Complexes of Zn(II), Cu(II) and Co(II) with either N-(2-methylpyridyl)-3-thienyl-alkyl-carboxamide or N-(2-pyridyl)-3-thienylalkyl-carboxamide groups have been prepared and characterized. Crystal structures of ten new complexes are reported and discussed. N-(2-Methylpyridyl)-3-thienyl-alkyl-carboxamide exhibits both uni- and bidentate behavior. With all ligands, bidentate complexation is through the carbonyl oxygen and pyridine nitrogen atoms (O, N) and the amide nitrogen atom remains protonated. The electrochemical behavior and the infrared spectra of selected complexes are discussed.

Keywords

copper; zinc; cobalt; complexes; crystal structures; infrared; synthesis; visible spectroscopy; electrochemistry

1. Introduction

Recently there has been renewed interest in the use of pyridine carboxamide complexes, especially those of copper, as therapeutic agents. Copper(II) complexes of the ligand N2-(2-pyridylmethyl)-2-pyridinecarboxamide have been investigated as HIV-1 protease inhibitors [1–3]. Transition metal complexes of an isonicotinamido-based ligand have been examined for antitumor activity [4] while two new pyridine carboxamide ligands and their copper complexes have been evaluated as bleomycin models [5]. Models of nitrile hydratase involving pyridine-amide compounds have been extensively studied by Mascharak and co-workers [6]. Complexes of pyridine-containing amides incorporating the thiophene group combine the properties of the compounds above with the pharmaceutically important thiophene ring and are likely to be of great interest. Antibacterial activity [7–9] and antifungal activity [10,11] have been reported for metal complexes containing thiophene as a non-coordinating group.

Lately there has also been interest in the self-assembly of metal complexes through amide functionality, especially those with an associated pyridine moiety [12,13]. The hydrogen-bonding properties of these species can be controlled by placement of donors and acceptors within the molecule [14]. Our syntheses of the ligands involved in this work have been reported

Supplementary material

Crystallographic data for the structural analyses of **1–11** have been deposited with the Cambridge Crystallographic Data Center, CCDC (2) 262976, (**1, 3–11**) 626468–626477. Copies of the data may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk).

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in an earlier paper [15] along with the preparation of a copper complex in which N-(2-pyridylmethyl)-3-thienyl-carboxamide acts as a bidentate ligand, **4**.

In this paper we report the synthesis and structures of ten new complexes containing the N-(2-methylpyridyl)-3-thienyl-alkyl-carboxamide and N-(2-pyridyl)-3-thienyl-alkyl-carboxamide groups and additional properties of **4**. The ligands are shown in Scheme 1.

2. Results and Discussion

Synthesis and Characterization

All of the metal complexes (**1–11**) were easily prepared by mixing methanol or ethanol solutions of the ligands and metal salts (perchlorate, chloride or hexafluorophosphate) and allowing crystallization to occur over a period of days. The stoichiometry was held at 1:1 ligand to metal so that the more soluble metal salts would remain in solution allowing easy separation of the products. In some cases, where the anion of the metal salt (chloride) was allowed to compete with the ligand, 1:1 ligand to metal complexes were formed (**9**, **10**). In all other cases save one, 2:1 ligand to metal complexes resulted in which the ligand was bidentate. The copper chloride complex formed with N-(2-pyridylmethyl)-3-thienyl-carboxamide (**5**) contains one bidentate ligand and one unidentate ligand along with two chloro ligands. The structures were based on either a tetragonally distorted octahedral or distorted square pyramidal geometry except for the cobalt complex (**10**) which was based on a tetrahedral geometry.

The compounds investigated by infrared spectroscopy, table 1, exhibit an NH stretching mode in the range of 3236–3375 cm^{-1} indicating that the amide nitrogen atom is not involved in coordination of the metal ion (data for **4** from a previous publication [15] are included for comparison). Compared to the free ligands, the amide I band is lowered about 40 cm^{-1} which is consistent with coordination by the carbonyl oxygen atom [16–18]. In **5**, two amide I bands are observed, one for the unidentate ligand and the other for coordinated oxygen in the bidentate ligand. The pyridine deformation in the free ligands at 612–619 cm^{-1} is raised to 621–626 cm^{-1} in the complexes consistent with coordination by the nitrogen atom of the pyridine ring [19,20]. The out-of-plane vibration of the thiophene ring (768 cm^{-1}), which is diagnostic of 3-substitution [21], is relatively unshifted in three of the compounds (**5**, **7**, **10**) which indicates the expected non-coordination of the thiophene ring although it has been observed in imines [22,23] and tridentate systems [24]. In **9**, this band is shifted to 791 cm^{-1} which may be due to the presence of lattice water which is observed in the IR spectrum and appears in the crystal structure in the vicinity of the thiophene ring.

In some cases, lattice solvent (methanol) appears in the crystals collected for x-ray analysis but is either absent or replaced by water in the samples taken for elemental analysis. For those samples in which methanol is bound to the metal, the methanol remains during the analytical procedure. The calculated compositions and the experimental results reflect these cases.

Electronic spectra for the copper complexes **1**, **4**, **6**, and **7** all showed a broad band near 677 nm (shifted from copper perchlorate near 836 nm) with intensities in the range of those for d-d transitions ($^2B_1 \rightarrow ^2E$) and characteristic of $\text{CuN}_2\text{O}_2(\text{O})$ in a tetragonally distorted ligand field [25]. The spectra of **6** and **7** were essentially identical showing that changing the anion (ClO_4^- and PF_6^-) had no effect. Compounds **5** and **9** exhibit bands at higher wavelengths (796 and 811 nm) consistent with the binding of weak field chloro ligands in these complexes. The structure of **11** is similar to those of **1**, **4**, **6**, and **7**, except that the ligand's amide nitrogen atom is bound directly to the pyridine ring; λ_{max} is about 15 nm lower and has about half the intensity.

Crystallography

X-ray crystal structures, obtained for all of the compounds reported here, demonstrate varied binding modes for the ligands. Interestingly, the bonding occurs through only the amide carbonyl group and the nitrogen on the pyridine ring; no evidence for bonding through the amide nitrogen atom was observed to occur in neutral solution although there are many examples of this mode of bonding for deprotonated amides [16,26–29]. Selected crystallographic data, bond distances, bond angles, and hydrogen bonds/contacts are presented in Tables 2–5. The metal complexes constitute three distinct groups: (1.) Cu(II) complexes with either perchlorate or hexafluorophosphate counterions, (2) Cu(II) and Co(II) complexes with the chloride counterion, and (3) Zn(II) complexes with the perchlorate counterion. The structures are shown in Figures 1–4 and selected packing diagrams in Figure 5.

The first group contains complexes **1**, **4**, **6**, **7**, and **11**. A distinctive characteristic of these complexes is that the carbonyl bond distances in the bound ligands have increased, by as much as +0.04 Å, and the amide bond distances have decreased by as much as –0.04 Å. Bond distances for the donor-metal atoms are similar to those in the copper (II) complexes reported by Lapouyade [30], Lebon [1,31], and Choi [32]. Complexes **1**, **6**, and **7** are distorted square pyramidal with two bidentate ligands bonded N,O in the equatorial positions of the metal with the N atoms *trans*- to each other and one solvent molecule (water or methanol) coordinated in the axial position. Complex **4** shows tetragonally-elongated octahedral coordination with the perchlorate anions oriented in the axial positions, while **11** is also 6-coordinate with two methanol molecules occupying the axial positions with the metal on an inversion center. The (O, N) bite angle in **11** (89.46(6)°) is smaller than that for the other copper (II) complexes in this group [low = 91.86(15)°; high = 94.7(2)°] owing to the smaller ring formed by the ligand, **L4**, which has no spacer between the amide function and the pyridine ring. The copper (II) complex Cu(DMABA-MP)₂(ClO₄)₂·3H₂O, which has a similar ring size displays a comparable bite angle (89.17(6)°) [31]. Complexes **4**, **6**, **7**, and **11** exhibit hydrogen-bonding between the amide protons and one oxygen atom of a perchlorate anion (or fluorine atoms of a hexafluorophosphate anion in the case of **7**) while **1** shows hydrogen bonding between the amide protons and adjacent methanol molecules in the lattice. In **4**, the copper perchlorate distance, 2.727(7) Å, is near the range of those which Procter [33] identified as “semi-coordinated” anions (2.5–2.6 Å); the slight distortion in the perchlorate ion would support this interpretation; however, the perchlorate ion is disordered in the crystal. Other workers have found that “semi-coordination” for perchlorate occurs at 2.695(1) and 2.807(1) Å for similar geometry in a trinuclear copper complex [34] and at 2.82 Å for a tetragonal amine complex [35]. The Cu–O separation in **4** is longer than those found for some five-coordinate amide complexes with perchlorate in the apical position (2.443(3) and 2.528(6) Å) [36,37] but the longer metal-anion distance would be consistent with the presence of two perchlorate anions in the tetragonally-elongated coordination sphere. There is no hydrogen-bonding between the copper complex units in the lattice.

In the second group, compounds **5**, **9**, and **10** are Cu(II) complexes or a Co(II) complex in which the chloride ion can either bond to the metal center, competing with the bidentate ligand, or function as a counterion to the charged complex. Complex **5** is a 2:1 ligand-to-metal structure with one ligand bound by the carbonyl oxygen in the equatorial plane and by the pyridine nitrogen in the axial position resulting in a large bite angle of 95.35(7)°, while the other ligand is bound only by the pyridine nitrogen in the other axial position. The metal coordination sphere is completed by two chloride ions directly bound in the equatorial positions. The bound carbonyl group has a bond distance of 1.234(3) Å similar to that of 1.223(3) Å for the unbound carbonyl group in the other ligand. These values do not vary greatly from those for the free ligand [15] owing perhaps to donation of electron-density to the metal by the electron-rich, directly coordinating chloride ligands (2.3179(7), 2.3327(7) Å) which would decrease the

metal-oxygen interaction. The metal center-donor atom bond distances are similar to those reported for other related Cu(II)-amide or amine structures [1,30,38,39].

Complexes **9** and **10** are 1:1 ligand to metal complexes in which the ligands are bidentate. In addition, complex **9** has methanol (1.916(3) Å), water (2.270(1) Å) and one chlorine atom (2.2650(5) Å) bound directly to the metal. A chloride anion, which balances the overall 1+ charge on the complex, undergoes very weak hydrogen-bonding with the amide N-H group, the bound water molecule, and the lattice water molecule. The ligand C-O bond distance has increased to 1.257(2) Å over that of the free ligand, 1.235(4) Å [15]. The overall geometry of **9** is distorted square pyramidal with an O1-Cu-Cl1 angle of 161.49(4)° and an O2-Cu-N2 angle of 176.02(6)°. The Cu-O (metal-water) bond distance of is close to that found in other complexes [1,31,40]. Complex **10**, which is the only cobalt (II) complex in the set, has tetrahedral geometry with one bidentate ligand and two directly bound chloride anions (2.2340(7) and 2.500(7) Å). The C-O bond distance is elongated to 1.258(3) Å and the ligand bite angle is 102.11(7)°, the largest of any of the complexes, consistent with the tetrahedral geometry. The Co-O, CoN, and Co-Cl bond distances in **10** (1.963(2) Å, 2.044(2) Å, 2.340(7) Å and 2.2500(7) Å, respectively) are comparable to those reported for the tetrahedral complex [CoCl₂(NITMepy)] [41].

An important aspect of the hydrogen-bonding in these complexes occurs between the amide proton of one complex and one of the bound chlorine atoms of an adjacent complex (**5**, two-dimensional chains and **10**, one-dimensional chains) which plays a large role in aligning the lattice structure. In the case of **9**, the hydrogen-bonding is more complex involving bound and free chlorine, bound and free water and bound methanol with free chloride which results in a more open layer structure.

The third group of complexes, **2**, **3**, and **8**, are all Zn (II) species with 2:1 ligand-to-metal ratios charge-balanced by non-bonding perchlorate anions. Complex **2** has a tetragonally-distorted octahedral metal center with two water molecules in the axial positions. The metal environments in complexes **3** and **8** are distorted square pyramidal with a lone water molecule in the apical position. The C-O and amide bond distances in all three Zn(II) complexes change very little when compared with their respective free ligands [15], although complex **3** shows a more profound change in bond lengths [C-O bond: 1.257(7) Å, C-N bond: 1.326(5) Å for the chelated ligand versus 1.236(3) Å and 1.450(3) Å for the free ligand]. The bite angles for all three Zn(II) complexes are similar to the Cu(II) complexes with either perchlorate or hexafluorophosphate anions ranging from 91.73(6)° to 93.73(10)°. All three Zn(II) complexes have donor-metal bond lengths, bite angles, and structures similar to the zinc complexes reported by Vahrenkamp [42] and Beauchamp [43].

Upon complexation with metal ion, the angle between the plane of the thiophene ring and the pyridine ring exhibits significant differences when compared with the free ligand values. When the coordinating ligand has a methylene group between the thiophene ring and the carbonyl function of the amide group (L₂), the angle is considerably smaller (**3**, 8.68 ° and 15.7 °; **4**, 15.87 °; **5**, 34.09° (bidentate) and 14.9 ° (unidentate) than those observed for the free ligand, 74.31°, 74.56°. [15]). When the ligand has either no spacer (L₁) between the amide group or a C₂H₂ unit (L₃), this angle (**2**, 65.37°; **8**, 65.37°; **7**, 69.01°; **9**, 69.84°; **6**, 70.97°; **1**, 67.43 ° and 71.04°) approaches that observed for the free ligands L₁, 80.30° and L₃, 80.68° [15]). A similar result is observed for **10** (64.72 ° vs 80.68°). The proximity of the amide function to the pyridine ring in **11** introduces considerable rigidity in the ligand, resulting in the largest angle observed, 79.72°; no comparison with the free ligand, L₄, is possible since the crystal structure is not known.

Electrochemistry

The electrochemistry of complexes **2** and **3** was investigated using cyclic voltammetry. For **2** a large irreversible wave at 2.01 V, shown in Figure 5 (top), was ascribed to a ligand-centered oxidation; the current was linearly proportional to $v^{1/2}$ which implies no preceding chemical step. A similar wave at 1.98 V was observed for the parent ligand [15] and the small difference in E_p^a suggests that ligand may be liberated upon oxidation of the complex. A similar result has been reported in a different solvent for trans-bis(propanone,1-[2-hydroxyphenyl]-oximate) copper (II), another N, O ligand [44]. The cathodic portion of the scan revealed the presence of a wave with E_p^c at -0.40 V which was associated with reduction of the complex, $Cu(L)_2^{2+}/Cu(L)_2^+$; a quasi-reversible companion oxidation wave appears on the reverse scan near 0.29 V. Another process, ascribed to the reduction of $Cu(L)_2^+$, is observed as a broad wave beginning near -0.58 V and produces free copper which deposits on the electrode. A large, sharp, copper stripping peak appears near 0.150 V. At slower scan rates (20 mV s^{-1}) a nucleation loop characteristic of electrodeposition could be observed. These results show some similarity with those reported for the $Cu(tpy)_2^{2+}$ complex for which the free ligand is oxidized at 1.9 V. $Cu(tpy)_2^{2+}$ undergoes its first reduction at -0.2 V and its second at -0.9 V [45]. The neutral complex, $Cu(2)_2$, is, therefore, not stable under these conditions and releases the metal. It is likely that copper is also produced by disproportionation of $[Cu(2)_2]^+$ since small stripping peaks can still be observed when the cathodic scan is truncated at -0.45 V. No features which could be associated with $Cu(III)/Cu(II)$ processes were observed under these conditions indicating that the ligand does not stabilize $Cu(III)$. This result is reasonable given that the complex is a dication and would be expected to have a high oxidation potential for a metal-centered oxidation.

The cyclic voltammogram for the corresponding zinc complex, **3**, (Fig. 5 bottom) shows an irreversible, ligand-centered, oxidation wave ($E_p^a = 2.02\text{ V}$), and, again, peak current was linearly proportional to $v^{1/2}$ indicating no preceding chemical step. A small shoulder on this wave could have been due to oxidation of the thiophene moiety of the ligand as has been observed for a series of similar ligands in our previous work [15]. A $[Zn(2)_2]^{2+}/Zn$ reduction beginning at -1.14 V resulted in a very pronounced nucleation loop for this process with a nucleation overpotential of 0.14 V. On the reverse scan, a sharp zinc stripping peak was observed ($E_p^a - 0.45\text{ V}$). Thus, the $Zn(2)_2$ neutral species is also not stable under these conditions.

3. Experimental

Materials

Acetonitrile (HPLC grade), tetrabutylammonium perchlorate, tetrabutylammonium hexafluorophosphate, copper (II) triflate, and zinc (II) triflate (Acros Organics) zinc (II) perchlorate hexahydrate (Sigma-Aldrich), copper (II) chloride dihydrate, cobalt (II) chloride hexahydrate (Baker), copper (II) perchlorate hexahydrate (Alfa Aesar), absolute ethanol (McCormick Distilling), chloroform- d_6 , acetone- d_6 , and DMSO- d_6 (Cambridge Isotope Labs) were obtained commercially. Other commercial materials used were polishing alumina (1.0, 0.3, and 0.05 micron mesh size) and polishing cloth (Buehler), ITO-glass electrodes (Donnelly), glassy carbon ($d = 1.5\text{ mm}$) and platinum ($d = 1\text{ mm}$) mini-electrodes (Cypress Systems), and silver and platinum wire (Sigma-Aldrich). The syntheses of N-(2-pyridylmethyl)-3-thienyl-carboxamide **L1**, N-(2-pyridylmethyl)-3-thenyl-carboxamide **L2**, N-(2-pyridylmethyl)-trans-3-(3-thienyl)-acrylamide **L3**, and N2-(2-pyridyl)-5-(3-thienyl)-methyl-carboxamide **L4** were described in a previous report [15].

Methods

Nuclear magnetic resonance (NMR) spectra were obtained on either a Bruker Avance DPX300 MHz FT-NMR with a 5 mm QNP probe or a Bruker Avance DRX500 FT-NMR with a 5 mm TBI probe and assignments were made by ^1H - ^1H COSY, ^1H - ^{13}C HMQC, and ^1H - ^{13}C HMBC NMR. IR transmittance spectra were obtained as KBr pellets using a Mattson Instruments 4020 Galaxy series II FT-IR spectrophotometer. UV-visible spectra were recorded on 10^{-5} – 10^{-4} samples in HPLC grade acetonitrile (10 mm quartz cell) on an HP 8453 diode array spectrophotometer. Elemental analyses were carried out by Atlantic Microlabs, Inc.

Single crystal X-ray diffraction data for complexes **2**, **3** and **4** were collected on a computer-controlled Bruker AXS P4 autodiffractometer; diffraction data for the remaining complexes were collected on a Bruker AXS APEX CCD system. All data were collected using omega scans with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). Structures were solved using “Direct Methods” techniques with the Bruker AXS SHELXTL-PC software package [46]. The resulting structural parameters have been refined to convergence using counter-weighted full-matrix least-squares on F^2 techniques. The structural models for all complexes except **3** and **4** incorporated anisotropic thermal parameters for all nonhydrogen atoms; the perchlorate anions in **3** and **4** were disordered and selected (minor occupancy) oxygen atoms of the anions were refined as isotropic atoms. Amide hydrogen atoms for all structures were located from difference Fourier maps and refined as independent isotropic atoms. For those compounds containing H_2O or MeOH coordinated to the metal center (**1**, **2**, **3**, **6**, **7**, **8**, **9** and **11**), hydrogen atoms on the coordinating solvent molecules were located and refined in all cases except compounds **1** (H_2O) and **6** (disordered MeOH) in which hydrogens could not be located from difference Fourier maps and were therefore not included in the structural models. For those compounds containing lattice H_2O or MeOH of crystallization (**1**, **3**, **5**, **6**, **7**, **8** and **9**), hydrogen atoms were located and refined for **7**, **8** and **9**, respectively; the others were not included in the structural models. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 - or sp^3 -hybridization of the carbon atoms) “riding” on their respective carbon atoms. In all of the structures reported except **2**, the 5-membered thiophene rings are disordered about the ring-C/exo-cyclic C bond and adopt one of two preferred orientations such that the S/CH group is distributed over two of the ring sites. Values of the occupancies for the S/CH distribution in the rings refined to final values of 75/25 (**1**), 96/4 and 91/9 (**3**), 67/33 (**4**), 87/13 (**5**), 56/44 (**6**), 59/41 (**7**), 54/46 (**8**), 86/14 (**9**), 76/24 (**10**) and 60/40 (**11**), respectively. A summary of crystal data and structure refinements for all structures is provided with a comparison of selected bond lengths and angles in Tables 2–5.

Electrochemical measurements were carried out using a Pine instrument model AFCBP 1 Bi-Potentiostat PC or an eDAQ model EA160 Potentiostat connected to an eDAQ e-corder model ED401 PC. The cell consisted of a single compartment (5 mL cylinder) with three-electrodes: (WE: GC disk (1.5 mm diam.) or Pt disk (1.0 mm diam.); CE: Pt coil; RE: Ag wire pseudoreference (calibrated against SCE). Acetonitrile (freshly distilled over CaH_2) was used as the solvent and was 0.2 M in electrolytic grade TBAClO_4 supporting electrolyte. The cell was cleaned in an aqua regia bath, rinsed with deionized water, and then dried at 125°C overnight before use. Prior to each experiment, the working electrode was polished using 1.0, 0.3, and finally 0.05 micron α -alumina paste, rinsed with deionized water, sonicated in an ultrasonic water bath, dried, and rinsed with the electrochemical solvent of the experiment. The electrolyte solution was then degassed with dry argon for 10 minutes and then scanned under an argon flow to obtain a baseline over the potential range of the experiment. The sample solution (5 mM) was similarly degassed and held under argon for each measurement.

Synthesis

Aquabis[N-(2-pyridylmethyl)-3-thienyl carboxamide]copper(II) perchlorate monohydrate (1)

The description of the preparation of **1** is typical for all of the other compounds except as noted. (**1**): A solution of **L**₁ in methanol (293 mg, 1.4 mmol) was added dropwise to a solution of copper(II) perchlorate hexahydrate in methanol (500 mg, 1.4 mmol), which produced a dark blue solution. Dark blue, cubic crystals of (**1**) formed several days later (0.14 mmol, 20%). Analysis calcd. % for C₂₂H₂₄Cl₂Cu N₄O₁₂S₂: C, 35.90%; H, 3.29%; N, 7.62%. Found: C, 35.69%; H, 3.22%; N, 7.46%. Visible spectrum (MeCN), λ, nm (log ε): 679 (1.91).

Diaqua[N-(2-pyridylmethyl)-3-thienyl carboxamide]zinc(II) perchlorate (2)—L₁

(87.3 mg, 0.4 mmol), zinc(II) perchlorate hexahydrate (149 mg, 0.4 mmol), methanol solvent. Pale white, orthogonal crystals of **2** (0.13 mmol, 65%). Analysis calcd. % for C₂₂H₂₄Cl₂Cu N₄O₁₂S₂: C, 35.86%; H, 3.28%; N, 7.60%. Found: C, 35.67%; H, 3.29%; N, 7.61%.

Aquabis[N-(2-pyridylmethyl)-3-thienyl carboxamide]zinc(II) perchlorate (3)—L₂

(88.5 mg, 0.4 mmol), zinc(II) perchlorate hexahydrate, (151 mg, 0.4 mmol), ethanol solvent. Pale white, orthogonal crystals of **3** (0.13 mmol, 65%). Analysis calcd. % for C₂₄H₂₆Cl₂N₄O₁₁S₂Zn: C, 38.59%; H, 3.51%; N, 7.50%. Found: C, 38.39%; H, 3.54%; N, 7.43%.

Bis[N-(2-pyridylmethyl)-3-thienyl carboxamide]copper(II) perchlorate (4)—L₂

(69.6 mg, 0.3 mmol), copper(II) perchlorate hexahydrate in ethanol (111.9 mg, 0.3 mmol), ethanol solvent. Dark blue, cubic crystals of **4** (0.11 mmol, 73%). Analysis calcd. % for C₂₄H₂₄Cl₂Cu N₄O₁₀S₂: C, 39.65%; H, 3.33%; N, 7.71%. Found: C, 39.71%; H, 3.34%; N, 7.74%. IR (KBr, cm⁻¹): 3292 s, 3111 m, 2933 w, 1606 s, 1571 m, 1446 m, 1325 w, 1120 s, 1080 s, 1054 s, 1042 m, 1030 m, 834 w, 773 m, 758 m, 624 s, 525 w. MS: Peaks at m/z = 626 [M-ClO₄]⁺, 526 [M-2ClO₄-H]⁺, 394 [M-ClO₄- (**2**)]⁺, 295 [M-2ClO₄-H- (**2**)]⁺. Visible spectrum (MeCN), λ, nm (log ε): 675 (1.83).

Dichlorobis[N-(2-pyridylmethyl)-3-thienyl carboxamide]copper(II) monohydrate (5)—L₂

(69.5 mg, 0.3 mmol), copper(II) chloride (40.6 mg, 0.3 mmol) methanol solvent. Green crystals of **5** (0.066 mmol, 44%). Analysis calcd. % for C₂₄H₂₄Cl₂Cu N₄O₃S₂: C, 46.72%; H, 4.25%; N, 9.08%. Found: C, 46.81%; H, 4.25%; N, 9.13%. IR (KBr, cm⁻¹): 3508 m, 3276 s, 3099 m, 2883 w, 2818 w, 1662 s, 1632 s, 1608 s, 1546 m, 1486 m, 1447 m, 1414 m, 1391 m, 1337 m, 1274 m, 1258 m, 1228 m, 1168 m, 1118 w, 1029 s, 950 w, 886 w, 770 s, 720 m, 626 m, 599 m, 507 w. Visible spectrum (MeCN), λ, nm (log ε): 796 (1.77).

Methanolbis[N-(2-pyridylmethyl)-trans-3-(3-thienyl) acrylamide]copper(II) perchlorate (6)—L₃

(49.4 mg, 0.2 mmol), copper(II) perchlorate hexahydrate (74.1 mg, 0.2 mmol) methanol solvent. Blue-green crystals of **6** (0.030 mmol, 30%). Analysis calcd. % for C₂₈H₂₈Cl₂Cu N₄O₁₁S₂: C, 41.41%; H, 3.60%; N, 7.15%. Found: C, 40.82%; H, 3.25%; N, 7.26%. Visible spectrum (MeCN), λ, nm (log ε): 677 (1.84).

Aquabis[N-(2-pyridylmethyl)-trans-3-(3-thienyl) acrylamide]copper(II) hexafluorophosphate (7)—L₃

(49.4 mg, 0.2 mmol), copper(II) perchlorate hexahydrate (74.1 mg, 0.2 mmol), methanol solvent. Green crystals formed in several days, which were collected and redissolved in a second vessel containing fresh methanol. Excess TBAPF₆ was added to the solution, and green crystals of **7** formed over several days. (0.030 mmol, 30%). IR (KBr, cm⁻¹): 3615 w, 3563 w, 3375 s, 3100 w, 2880 w, 1646 m, 1609 m, 1573 m, 1515 w, 1486 w, 1460 w, 1342 w, 1291 w, 1243 w, 1164 w, 1121 m, 1071 m, 841 s, 793 m, 621 m, 558 m, 433 w. Visible spectrum (MeCN), λ, nm (log ε): 677 (1.84).

Aquabis[N-2-(pyridylmethyl)-trans-3-(3-thienyl) acrylamide]zinc(II) perchlorate (8)—**L₃** (48.6 mg, 0.2 mmol), zinc(II) perchlorate hexahydrate (73.0 mg, 0.2 mmol), methanol solvent. White crystals of **8** (0.012 mmol, 12%). X-ray analysis showed the presence of two solvent molecules in the structure; these were lost during vacuum purification prior to analysis. Analysis calcd. % for C₂₆H₂₆Cl₂N₄O₁₁S₂Zn: C, 40.51%; H, 3.66%; N, 7.27%. Found: C, 39.83%; H, 3.65%; N, 7.00%.

Aquachloromethanol[N-2-(pyridylmethyl)-trans-3-(3-thienyl) acrylamide] copper(II) chloride monohydrate (9)—**L₃** (73.1 mg, 0.3 mmol), copper(II) chloride dihydrate (39.7 mg, 0.3 mmol), methanol solvent. Dark green crystals of **9** (0.091 mmol, 61%). Analysis calcd. % for C₁₄H₂₀Cl₂Cu N₂O₄S: C, 39.40%; H, 3.83%; N, 7.06%. Found: C, 40.78%; H, 3.48%; N, 7.22%. IR (KBr, cm⁻¹): 3441 s, 3203 s, 3081 m, 3053 m, 2812 w, 1647 s, 1607 s, 1583 m, 1550 s, 1513 m, 1484 m, 1440 m, 1345 m, 1291 m, 1242 m, 1157 w, 1074 w, 1009 w, 990 w, 924 w, 868 w, 791 m, 621 m, 593 w, 543 w, 435 w. Visible spectrum (MeCN), λ, nm (log ε): 811 (1.83).

Dichloro[N-2-(pyridylmethyl)-trans-3-(3-thienyl) acrylamide]cobalt(II) (10)—Cobalt(II) chloride hexahydrate (48.2 mg, 0.2 mmol) was added to a solution of **L₃** in acetonitrile (49.2 mg, 0.2 mmol) in a 50 mL round-bottom flask. The solution was boiled and then allowed to cool, whereupon dark purple-blue crystals of **10** formed after several days from slow evaporation of the solvent (0.087 mmol, 44% yield). Analysis calcd. % for C₁₃H₁₂Cl₂CoN₂OS: C, 41.73%; H, 3.23%; N, 7.49%. Found: C, 41.52%; H, 3.21%; N, 7.53%. IR (KBr, cm⁻¹): 3443 m, 3249 s, 3100 m, 3067 m, 2982 w, 2900 w, 1641 s, 1607 s, 1575 m, 1515 s, 1481 m, 1446 m, 1391 m, 1345 s, 1318 m, 1286 s, 1243 s, 1156 m, 1066 w, 1029 m, 977 m, 858 m, 776 s, 669 m, 622 m, 603 m, 548 m, 420 w.

Bis[N-2-(pyridyl)-3-thienyl carboxamide]copper(II) perchlorate monohydrate (11)—**L₄** (69.6 mg, 0.3 mmol), copper(II) perchlorate hexahydrate (111.9 mg, 0.3 mmol), methanol solvent. Dark blue, cubic crystals of **11** (0.08 mmol, 53%). Analysis calcd. % for C₂₂H₂₂Cl₂Cu N₄O₁₃S₂: C, 36.85%; H, 3.08%; N, 7.81%. Found: C, 36.87; H, 3.00; N, 7.85. Visible spectrum (MeCN), λ, nm (log ε): 661 (1.54).

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Figure 1. Thermal ellipsoid plot (probability level 50%) of **1**, **4**, **6** with the atom labelling scheme: **1** (top), **4** (center), **6** (bottom).

Figure 2.
Thermal ellipsoid plot (probability level 50%) of **5**, **9**, **10** with the atom labelling scheme: **5** (top), **9** (center), **10** (bottom).

Figure 3.
Thermal ellipsoid plot (probability level 50%) of **2**, **3**, **8** with the atom labelling scheme: **2** (top), **3** (center), **8** (bottom).

Figure 4. Thermal ellipsoid plot (probability level 50%) of **7** and **11** with the atom labelling scheme: **7** (top), **11** (bottom).

Figure 5. Ortep drawings of the packing in 5 (top), 9 (center), 10 (bottom)

Figure 5. Cyclic voltammograms of **2** (top) and **3** (bottom). WE, Pt (1 mm); CE, Pt spiral; RE, SCE. 0.005 M sample in 0.1 M TBAP/MeCN; v , 100 mV s⁻¹.

Figure 6.

Figure 6. Cyclic voltammograms of **2** (top) and **3** (bottom). WE, Pt (1 mm); CE, Pt spiral; RE, SCE. 0.005 M sample in 0.1 M TBAP/MeCN; v , 100 mV s⁻¹.

Scheme 1.
Ligands L1–L4

Table 1

Selected Infrared Stretching Frequencies (cm⁻¹)

Species	4	5	7	9	10	12	13
NH	3292	3276	3375	3249	3249	3275	3278
amide I	1606	1662, 1608	1609	1607	1607	1644	1654
amide II	1530	1546	1515	1513	1515	1560	1544
amide III	1325	1337, 1258	1291	1291	1318	1249	1278
C=C			1573	1583	1575		1614
pvr (def)	624	626, 599	621	621	622	612	619
thioph (o-o-p)	758	770, 720	(a.)	791	776	768	768
ClO ₄ ⁻	1120-1054						
PF ₆ ⁻			793				
OH (, b.c.)		3508	3615, 3563	3441, 3331			

(a.) obscured by PF6⁻

(b.) broad

(c.) OH from water and methanol

Crystallographic Data for 1–11.

Compound	1	2	3	4	5	6	7	8	9	10	11
Empirical formula	C24H30N4 O13S2Cl2Cu	C22H24N4 O13S2Cl2Zn	C24H26.5N4 O11.25S2Cl2Zn	C24H24N4 O10S2Cl2Cu	C24.5H26N4 O2.50S2Cl2Cu	C28H32N4 O12S2Cl2Cu	C28H34N4 O5F12P2S2Cu	C28H34N4 O13S2Cl2Zn	C14H20N2 O4S2Cl2Cu	Cl3H12N2 OSCl2Co	C24H28N4 O12S2Cl2Cu
Formula weight	781.08	736.84	751.38	727.03	615.05	815.14	924.19	834.98	446.82	374.14	763.06
Temperature	193(2) K	218(2) K	228(2)K	213(2)K	193(2) K	193(2) K	193(2) K	193(2) K	193(2) K	193(2) K	193(2) K
Crystal system, space group	Orthorhombic Pca2 ₁ (#29)	Monoclinic P2 ₁ /c (#14)	Triclinic P-1(#2)	Monoclinic P2 ₁ /n(#14)	Orthorhombic P2 ₂ -2 ₁ 2(#18)	Monoclinic P2 ₁ /c (#15)	Monoclinic C2/c (#15)	Monoclinic C2/c (#15)	Monoclinic P2 ₁ /n (#14)	Triclinic P-1(#2)	Monoclinic C2/c (#15)
Unit cell	15.977(1) Å a = 8.6990(7) Å b = 23.269(2) Å c = 108.152(8)° α = 82.15(1)° β = 75.88(1)° γ =	10.865(1) Å 9.139(1) Å 15.573(2) Å 108.152(8)°	9.358(2) Å 10.919(1) Å 16.038(2) Å 74.83(1)° 82.15(1)° 75.88(1)°	8.517(1) Å 9.837(1) Å 17.775(2) Å 100.36(1)°	17.459(1) Å 19.378(1) Å 7.6758(6) Å	16.235(7) Å 15.774(7) Å 15.745(7) Å 119.377(5)°	16.081(2) Å 16.311(2) Å 15.909(2) Å 118.683(2)°	16.348(1) Å 15.705(1) Å 15.910(1) Å 120.063(1)°	9.0525(9) Å 14.064(1) Å 14.905(1) Å 102.083(2)°	7.2301(8) Å 7.4986(8) Å 15.027(2) Å 81.188(2)° 77.606(2)° 72.440 (2)°	16.242(6) Å 13.044(5) Å 16.448(6) Å 116.449(5)°
Volume, Å ³	3233.9(5)	1469.5(3)	1529.4(4)	1464.9(3)	2596.9(3)	3514(3)	3660.9(7)	3535.2(4)	1855.5(3)	755.2(1)	3120(2)
Z, F(000)	4, 1604	2, 752	2, 769	2, 742	4, 1264	4, 1676	4, 1876	4, 1720	4, 916	2, 378	4, 1564
Densitv, g/cm ³ (calculated)	1.604	1.665	1.632	1.648	1.573	1.541	1.677	1.569	1.599	1.645	1.625
Absorption coefficient, mm ⁻¹	1.038	1.227	1.179	1.132	1.241	0.957	0.903	1.032	1.598	1.623	1.072
θ range for data collection	3.74 – 27.50°	2.62 – 27.50°	2.10 – 26.37°	2.33 – 26.37°	4.08 – 30.51°	3.92 – 27.48°	3.82 – 27.50°	1.95 – 28.22°	4.03 – 30.50°	3.80 – 29.57°	3.94 – 30.48°
Reflections collected	27084	4169	7374	3780	23605	14678	15760	10718	18190	7642	15382
Independent reflections(R (int))	7392 (0.048)	3230 (0.026)	6195 (0.030)	2837 (0.025)	7410 (0.044)	3919 (0.038)	4171 (0.031)	3994 (0.020)	5513 (0.042)	4087 (0.033)	4587 (0.047)
Data / parameters	7392 / 424	3230 / 208	6195 / 431	2837 / 204	7410 / 339	3919 / 280	4171 / 289	3994 / 244	5513 / 261	4087 / 186	4587 / 234
Goodness-of-fit	1.040	1.014	1.023	1.036	1.134	1.062	1.077	1.070	1.052	1.035	1.046
Final R indices [I>2sigma(I)]	R1 = 0.062 wR2 = 0.159	R1 = 0.047 wR2 = 0.094	R1 = 0.058 wR2 = 0.122	R1 = 0.079 wR2 = 0.215	R1 = 0.041 wR2 = 0.086	R1 = 0.046 wR2 = 0.130	R1 = 0.064 wR2 = 0.173	R1 = 0.039 wR2 = 0.110	R1 = 0.039 wR2 = 0.106	R1 = 0.042 wR2 = 0.102	R1 = 0.047 wR2 = 0.124
R indices (all data)	R1 = 0.076 wR2 = 0.171	R1 = 0.086 wR2 = 0.108	R1 = 0.102 wR2 = 0.142	R1 = 0.116 wR2 = 0.243	R1 = 0.046 wR2 = 0.088	R1 = 0.049 wR2 = 0.133	R1 = 0.075 wR2 = 0.181	R1 = 0.043 wR2 = 0.114	R1 = 0.042 wR2 = 0.109	R1 = 0.052 wR2 = 0.107	R1 = 0.053 wR2 = 0.129

TWIN/BASF and absolute structure parameters for **1** and **5** are 0.38(2) and 0.09(9), respectively.

All data were collected with MoKα radiation, wavelength 0.71073Å.

Table 3

Metal-Ligand Bond Distances (Å) 1–11

Bond*	1 (Cu)	2 (Zn)	3 (Zn)	4 (Cu)	5 (Cu)	6 (Cu)	7 (Cu)	8 (Zn)	9 (Cu)	10 (Co)	11 (Cu)
M(1)–O(1)	1.967(3)	2.075(2)	2.111(3)	1.957(4)	2.258(2)	1.984(2)	1.982(2)	2.119(1)	1.969(1)	1.963(2)	1.934(2)
M(1)–O(2)	1.977(3)		2.131(3)								
M(1)–N(1)	1.989(4)	2.184(3)	2.019(4)	2.007(7)	2.002(2)	1.991(2)	1.996(3)	2.042(2)	1.995(1)	2.044(2)	2.039(2)
M(1)–N(2)	2.004(4)		2.037(4)		2.003(2)						
M(1)–O(water)	2.177(4)	2.131(3)	1.969(4)				2.217(4)	1.985(2)	2.270(1)		
M(1)–O(MeOH)						2.261(3)			1.963(1)		2.401(2)
M(1)–Cl(1)					2.3179(7)				2.2650(5)	2.2340(7)	
M(1)–Cl(2)					2.3327(7)					2.2500(7)	
M(1)...O(ClO4)				2.727(7)							

* O(1) and N(1) are from ligand 1 and O(2) and N(2) are from ligand 2 when 2 crystallographically independent ligands are present in the metal coordination sphere.

Table 4

Metal-Ligand Bond Angles (°) 1–11

Bond Angle/deg	1 (Cu)	2 (Zn)	3 (Zn)	4 (Cu)	5 (Cu)	6 (Cu)	7 (Cu)	8 (Zn)	9 (Cu)	10 (Co)	11 (Cu)
O(1)-M(1)-O(2)	171.6(1)	180.0(1)	169.4(1)	180(–)		173.0(1)	173.4 (2)	176.10 (8)			180(–)
O(1)-M(1)-N(1)	93.0(2)	93.7(1)	92.8(2)	94.7(2)	95.35(7)	92.66(8)	92.6(1)	91.73 (6)	91.51(5)	102.11 (7)	89.46(6)
O(2)-M(1)-N(1)	88.2(2)	86.3(1)	92.6(1)				88.4(1)	89.33 (6)			90.54(6)
O(1)-M(1)-N(2)	89.7(2)		91.2(1)	85.3(2)	94.67(7)	88.29(8)					
O(2)-M(1)-N(2)	91.9(2)		91.7(1)								
N(1)-M(1)-N(2)	160.7(1)	180.0(2)	133.1(2)	180(–)	169.88 (8)	164.3(1)	162.6 (2)	148.20 (9)			180(–)
O(1)-M(1)-O(water1)	85.6(2)	94.0(1)	86.7(2)	92.0(3) **		86.72(8)	88.05 (4)	89.42 (5)			
O(1)-M(1)-O(water2)				88.0(3) **							
O(2)-M(1)-O(water1)	86.0(2)	86.0(1)	82.9(2)								
O(2)-M(1)-O(water2)											
N(1)-M(1)-O(water1)	99.6(2)	93.2(1)	112.9(2)	102.2(3) **		98.68(8)	105.90 (5)	95.50 (6)			
N(1)-M(1)-O(water2)				77.8(3) **							
N(2)-M(1)-O(water2)											
O(water1)-M(1)-O(water2)		180.0(2)		180(–) **					92.10(4)	107.40 (6)	
N(1)-M(1)-Cl(1)					92.27(6)						
N(2)-M(1)-Cl(1)					88.50(6)					109.23 (5)	
N(1)-M(1)-Cl(2)					88.76(6)						
N(2)-M(1)-Cl(2)					87.03(6)						
O(1)-M(1)-Cl(1)					94.05(5)				161.49 (4)	111.97 (5)	
O(1)-M(1)-Cl(2)					106.15 (5)					111.99 (6)	
Cl(1)-M(1)-Cl(2)					159.60 (3)					113.41 (3)	
O(water)-M(1)-Cl(1)									108.28 (4)		
O(1)-M(1)-O(MeOH)						86.50(5)			86.50(5)		92.93(6)
O(2)-M(1)-O(MeOH)											87.07(6)
N(1)-M(1)-O(MeOH)						97.83(5)			176.02 (6)		92.28(6)
N(2)-M(1)-O(MeOH)											87.72(6)
O(MeOH)-M(1)-O(MeOH)											180(–)
O(water)-M(1)-O(MeOH)									87.93(6)		
Cl(1)-M(1)-O(MeOH)									88.72(4)		
pvr ring-thio ring	67.43/71.04	65.37	8.68/15.67	15.87	34.09(b) 14.92 (unl)	70.97	69.01	65.37	69.84	64.72	79.72

* O(1) and N(1) are used to represent the carbonyl oxygen and pyridine nitrogen from ligand 1 and O(2) and N(2) are from ligand 2 when more than 1 ligand is present in the metal coordination sphere.

*** In compound 4, the 2 axial water oxygens are replaced by an oxygen of the perchlorate anions.

Table 5

Hydrogen Bonds and Contacts (Å) 1–11

Compound	D-H...A	d(D...A)	Symmetry**
1 (Cu)	N(2)-H(2N)...O(2S)	2.793(7)	
	N(4)-H(4N)...O(1S)	2.719(7)	
2 (Zn)	N(1)-H(1N)...O(3)	2.944(5)	$x, -y+1/2, z+1/2$
	O(2)-H(21)...O(5)	3.059(5)	
	O(2)-H(21)...O(3)	3.155(5)	
	O(2)-H(22)...O(4)	2.860(5)	$-x, -y+1, -z$
3 (Zn)	N(1A)-H(1NA)...O(11)	2.79(2)	
	N(1A)-H(1NA)...O(9)	3.122(8)	
	N(1A)-H(1NA)...O(8')	2.92(3)	
	N(1B)-H(1NB)...O(3)	2.825(5)	
	O(21)-H(21)...O(8)	2.685(7)	
	O(21)-H(21)...O(9')	2.87(2)	
4 (Cu)	O(21)-H(22)...O(6)	2.789(6)	
	N(1)-H(1N)...O(5)	2.93(1)	
	N(1)-H(1N)...O(3')	3.24(4)	
	N(1)-H(3N)...Cl	3.249(2)	
5 (Cu)	N(1)-H(1N)...O(2)	2.844(3)	
	N(1)-H(3N)...Cl	3.249(2)	
6 (Cu)	N(1)-H(1N)...O(2)	2.888(4)	
	N(1)-H(1N)...O(4')	3.00(2)	
	N(1)-H(1N)...O(3')	3.30(2)	
	N(1)-H(1N)...F(5)	2.89(1)	$1/2-x, 1/2-y, 1-z$
7 (Cu)*	N(1)-H(1N)...F(4')	2.98(1)	$1/2-x, 1/2-y, 1-z$
	N(1)-H(1N)...F(1)	3.151(7)	$1/2-x, 1/2-y, 1-z$
	O(2)-H(2O)...O(3)	2.744(5)	
	O(2)-H(2O)...O(3)	2.666(3)	$x-1/2, 1/2-y, -1/2+z$
8 (Zn)	O(3)-H(3O)...O(5)	2.892(3)	
	O(3)-H(3O)...O(6)	3.394(4)	
	N(1)-H(1N)...O(4)	2.918(3)	
	O(2)-H(2O)...O(4)	2.630(2)	$x+1/2, -y+3/2, z-1/2$
9 (Cu)	O(3)-H(31)...Cl(2)	3.237(2)	
	O(3)-H(32)...Cl(1)	3.212(2)	$1-x, 1-y, -z$
	O(4)-H(41)...Cl(2)	3.184(2)	$x-1, y, z$
	O(4)-H(42)...Cl(2)	3.152(2)	$1-x, 1-y, 1-z$
	N(1)-H(1N)...Cl(2)	3.210(2)	$x-1, y, z$
	N(1)-H(1N)...Cl(2)	3.245(2)	$x, -1+y, z$
10 (Co)	N(1)-H(1N)...Cl(2)	3.245(2)	$x, -1+y, z$
11 (Cu)	O(2)-H(2O)...O(4)	2.889(3)	$-x+1/2, y+1/2, -z+1/2$
	N(2)-H(2N)...O(3)	2.932(3)	$x+1/2, -y-1/2, z+1/2$

* HF contacts omitted in 7

** Symmetry operation required to generate coordinates for acceptor atoms.