

Anion Binding

Synthesis, Coordination Chemistry and Anion Binding by a Cyanophenyl-Substituted 2-Pyridinyurea

Tristen Moyaert,^[a] Zachary W. Schroeder,^[a] and Louise N. Dawe*^[a]

Abstract: The design and synthesis of urea-based systems suitable for selective anion recognition has demonstrated potential for environmental remediation. These systems act as a double hydrogen-bond donor to anion acceptors, however, the availability of the carbonyl group to also act as a hydrogen-bond acceptor has posed as an optimization challenge. One approach to address this obstacle is to design preorganized coordination complexes that decrease the accessibility of the carbonyl group, yet are still capable of anionic hydrogen bonding by secondary

coordination. Herein, a new 2-pyridinyurea ligand, *N*-(3-cyanophenyl)-*N'*-pyridin-2-ylurea (**L1**), and its transition metal complexes, [(**L1**)₂Ni(CH₃OH)₂](NO₃)₂, [(**L1**)₂Co(CH₃OH)₂](NO₃)₂, [(**L1**)₂Ni(H₂O)₂](NO₃)₂ and [(**L1**)₂Cu(ClO₄)₂]_n are reported. Subtle changes in metal-to-ligand ratio and solvent conditions yielded dramatically different anion-binding motifs for two Ni²⁺ complexes, while bis-metal coordination of a perchlorate anion in the Cu²⁺ complex resulted in hydrogen bonding with the weakest available ligand acceptor.

Introduction

With increasing attention to the environmental implications of anions (for example, nitrates and phosphates), significant efforts have surrounded the synthesis of systems suitable for anion recognition.^[1] The propensity for urea amines to hydrogen-bond to anions is well-known^[2–4] and many systems have been designed to utilize this capacity. One limitation, however, in designing new urea-based anion receptors is the availability of the carbonyl group to also act as a hydrogen-bond acceptor.^[1] A possible strategy to overcome this challenge is to design a pre-organized system that decreases the accessibility of the carbonyl group, by metal coordination, yet still leaves the N–H functionality available for secondary coordination.^[5]

While there exists many examples of metal–urea coordination complexes,^[6–8] until recently, the coordination chemistry of 2-pyridinyureas remained relatively unexplored.^[9–13] In addition to their ability to coordinate metal cations, 2-pyridinyurea-based ligands also have the potential to engage in a variety of hydrogen bonding interactions (Figure 1), which has been explored in the past for applications as a model for metal-linked and hydrogen bonded base pairs,^[10] or as catalysts for the mild (H₂O₂) oxidation of alkanes.^[11] More recently, a report by Steed and colleagues^[14] on the Cu²⁺ complexes of *N*-[3-(methylsulfanyl)phenyl]-*N'*-pyridin-2-ylurea points to the implications for hydrogen bonding interactions to metal-coordinated anions in the extraction of halometalates in mining processes. Current

commercial extractants (phenolic oximes^[15]) exhibit the same coordination motif as 2-pyridinyureas, and extension/elaboration of the terminal, non-pyridyl moiety, presents opportunities for tuning solubility of the ligand and metal complexes. In all reported complexes by Steed,^[14] the anions were simultaneously bound to the metal cation and also engaged in hydrogen bonding with the ligand amine groups, which functioned as a double hydrogen-bond donor to either one (Cl[–] or Br[–]), or two acceptors (NO₃[–] or CF₃SO₃[–]) on the same anion.

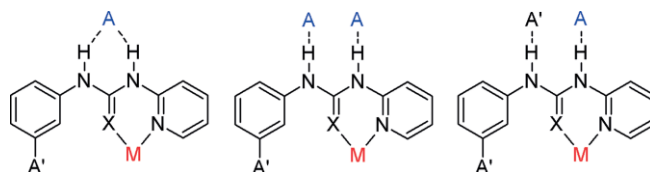


Figure 1. Simple (thio)urea ligands with diverse potential; possible metal (M) coordination and hydrogen-bond donor (to acceptor, A) capacities shown. **L1**: X = O, A' = CN; **L2**:^[17] X = S, A' = OCH₃.

We have recently synthesized and characterized several multifunctional (thio)urea based-ligands (Figure 1) which have applications in this area. Herein, the Ni²⁺, Co²⁺ and Cu²⁺ coordination complexes with *N*-(3-cyanophenyl)-*N'*-pyridin-2-ylurea (**L1**) are reported. Hydrogen bond parameters for common neutral functional groups have been previously reported by Hunter,^[16] which included the acceptor constant (β) of 4.7 for nitrile and 8.3 for amide and urea (where a larger value indicates greater hydrogen bond strength.) In each case presented here, the ligand carbonyl group is coordinated to a metal cation, leaving only the weaker nitrile hydrogen-bond acceptor, or anions, to fulfil the hydrogen-bond donor capacity of the ligand. Non-covalent interactions between the metal cations, **L1**, and anions are characterized, with a view to future advantageous applica-

[a] Department of Chemistry and Biochemistry, Faculty of Science, Wilfrid Laurier University, 75 University Ave. W., Waterloo, ON, N2L 3C5, Canada
E-mail: ldawe@wlu.ca
<https://www.wlu.ca/academics/faculties/faculty-of-science/faculty-profiles/louise-n-dawe/index.html>

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tions of the ligand's weakest hydrogen-bond acceptor (e.g. as an anchor for surface attachment.)

Results and Discussion

Supramolecular Chemistry of the Complexes of N-(3-Cyanophenyl)-N'-pyridin-2-ylurea (L1)

Reaction of **L1** and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in a one-to-one mol ratio in methanol yielded isostructural complexes $[(\text{L1})_2\text{Ni}(\text{CH}_3\text{OH})_2](\text{NO}_3)_2$ (**1**; Figure 2) and $[(\text{L1})_2\text{Co}(\text{CH}_3\text{OH})_2](\text{NO}_3)_2$ (**2**), respectively (**2** is reported in the Supplemental Information.) **1** crystallized in the triclinic space group $P\bar{1}$ with half of the complex contained in the asymmetric unit ($Z' = 0.5$). The molecular structure consists of one six-coordinate metal cation (Ni^{2+} in **1**; Co^{2+} in **2**) in an approximately octahedral environment (Table 1), with two molecules of **L1** coordinated by the pyridyl nitrogen atom (N1) and the urea oxygen atom (O1), in the equatorial plane, and axial positions occupied by solvent methanol molecules (via O2.) The metal cation is situated on an inversion center, and so O1 and N1 are *trans* to their symmetry related equivalents in the equatorial plane.

Table 1. Selected geometric parameters for complex **1** [Å [°]].^[a]

Ni1–O1 ⁱⁱ	2.0150 (12)	Ni1–O2	2.1048 (12)
Ni1–O1	2.0150 (12)	Ni1–N1	2.0598 (14)
Ni1–O2 ⁱⁱ	2.1048 (12)	Ni1–N1 ⁱⁱ	2.0597 (14)
O1 ⁱⁱ –Ni1–O1	180.0	O1–Ni1–N1 ⁱⁱ	92.85 (5)
O1–Ni1–O2	89.52 (5)	O2 ⁱ –Ni1–O2	180.0
O1–Ni1–O2 ⁱⁱ	90.48 (5)	N1–Ni1–O2 ⁱⁱ	88.80 (5)
O1 ⁱⁱ –Ni1–O2	90.48 (5)	N1 ⁱ –Ni1–O2 ⁱⁱ	91.20 (5)
O1 ⁱⁱ –Ni1–O2 ⁱⁱ	89.52 (5)	N1–Ni1–O2	91.20 (5)
O1 ⁱⁱ –Ni1–N1 ⁱⁱ	87.15 (5)	N1 ⁱⁱ –Ni1–O2	88.80 (5)
O1–Ni1–N1	87.15 (5)	N1 ⁱⁱ –Ni1–N1	180.0
O1 ⁱⁱ –Ni1–N1	92.85 (5)		

[a] Symmetry code(s): (ii) $-x + 1, -y + 1, -z + 1$.

Each ligand is in its neutral state, and charge balance is established by the presence of one nitrate anion in the asymmetric unit (that is, two nitrate anions per formula unit.) Examination of the expanded structure shows that this nitrate anion is

involved in hydrogen bonding to both **L1** via the amine functionalities in an $R_2^2(8)$ (graph set) motif, and also to the metal-coordinated methanolic proton in a simple $D_1^1(2)$ motif (Figure 3.) These combined ligand-anion interactions lead to extended 1D chains in the crystal lattice, with each nitrate accepting three hydrogen bonds (Table 2.) The same interactions and packing motif are also present for **2** (see Supplemental Information.)

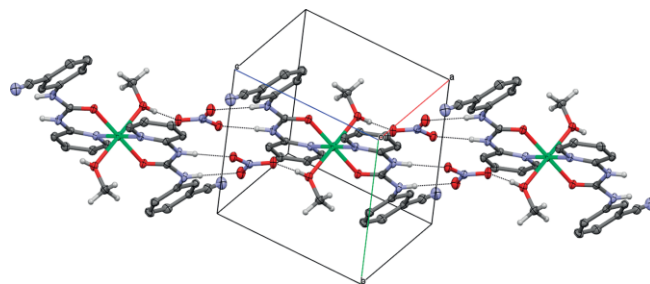


Figure 3. Hydrogen-bonded chains with base vector $[1\ 0\ -1]$ in complex **1**, via a combined $R_2^2(8)$ and simple $D_1^1(2)$ motif.

Table 2. Selected hydrogen-bond parameters for complex **1**.^[a]

D–H...A	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A [°]
O2–H2A...O3	0.816 (16)	1.888 (17)	2.6968 (18)	171 (2)
N2–H2...O5 ⁱ	0.82 (2)	1.99 (2)	2.8096 (19)	172 (2)
N3–H3...O4 ⁱ	0.81 (2)	2.10 (2)	2.906 (2)	173 (2)

[a] Symmetry code(s): (i) $x + 1, y, z - 1$.

In contrast to the one-to-one reaction of **L1** and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol to yield **1**, reaction of **L1** with 1.5 mol equivalents of Ni^{2+} in a mixed methanol/acetonitrile solvent system yielded, $[(\text{L1})_2\text{Ni}(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (**3**), which crystallized in the monoclinic space group $P2_1/n$ with one molecule fully contained in the asymmetric unit ($Z' = 1$.) Similar to **1**, the Ni^{2+} cation is in an approximately octahedral environment (Table 3), with two molecules of **L1** coordinated by the pyridyl nitrogen atoms (N1 and N5) and the urea oxygen atoms (O1 and O2), in the equatorial plane, however, the axial positions are now occupied by solvent water molecules (O3 and O4.)

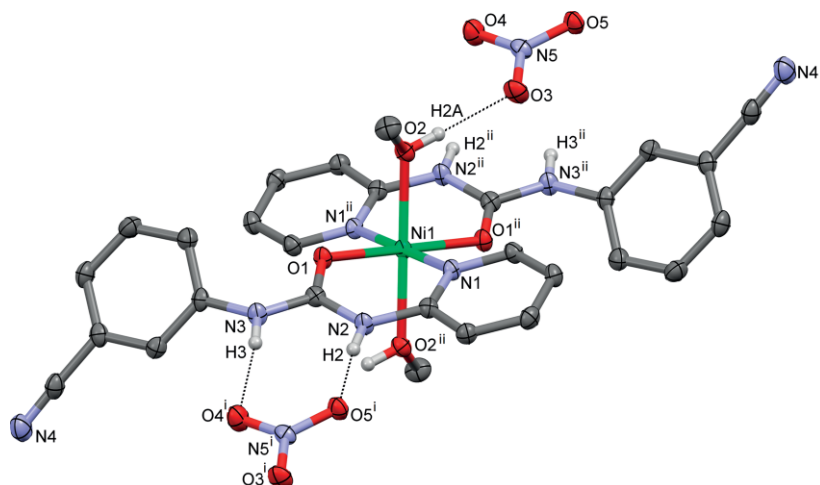


Figure 2. Complex **1** shown with 50 % displacement ellipsoids. Hydrogen bonds indicated as dashed lines. H-atoms, except those involved in hydrogen bonding, omitted for clarity. Symmetry codes: (i) $x + 1, y, z - 1$; (ii) $-x + 1, -y + 1, -z + 1$.

While the metal cation is not situated on a symmetry site, **L1** has again adopted an inverted (*trans*) orientation about the equatorial plane.

Table 3. Selected geometric parameters for complex **3** [Å [°]].

Ni1–O1	2.022 (3)	Ni1–O4	2.063 (4)
Ni1–O2	2.024 (3)	Ni1–N1	2.087 (4)
Ni1–O3	2.044 (4)	Ni1–N5	2.083 (4)
O1–Ni1–O2	178.05 (13)	O2–Ni1–N5	87.80 (13)
O1–Ni1–O3	90.66 (16)	O3–Ni1–O4	177.89 (16)
O1–Ni1–O4	91.14 (14)	O3–Ni1–N1	91.25 (15)
O1–Ni1–N1	87.47 (13)	O3–Ni1–N5	89.52 (15)
O1–Ni1–N5	91.89 (13)	O4–Ni1–N1	89.92 (15)
O2–Ni1–O3	87.42 (16)	O4–Ni1–N5	89.33 (15)
O2–Ni1–O4	90.77 (14)	N5–Ni1–N1	179.00 (15)
O2–Ni1–N1	92.87 (13)		

Each ligand is again in its neutral state, and charge balance is established by the presence two independent nitrate anions in the asymmetric unit. Each nitrate is involved in hydrogen bonding to **L1** via the amine functionalities in an $R_2^2(8)$ motif (Figure 4), but now, each water molecule also acts as a double hydrogen-bond donor to the nitrate anions, leading to the formation of chains parallel to the crystallographic a-axis, resulting from an $R_4^4(12)$ motif (Figure 5a.) Therefore, in total, each nitrate

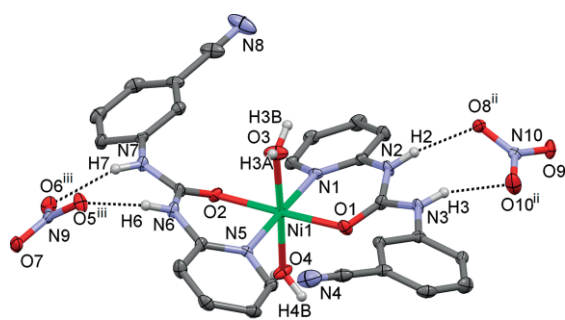


Figure 4. Complex **3** shown with 50 % displacement ellipsoids. Hydrogen bonding, indicated as dashed lines. H-atoms, except those on water and nitrogen, omitted for clarity. Symmetry codes: (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.

is involved in four significant hydrogen bonds (Table 4), with interactions via the amine functionalities propagating parallel to the crystallographic b-axis, and orthogonally to those involving water (Figure 5b.)

Table 4. Selected hydrogen-bond parameters for complex **3**.^[a]

<i>D</i> –H... <i>A</i>	<i>D</i> –H [Å]	H... <i>A</i> [Å]	<i>D</i> ... <i>A</i> [Å]	<i>D</i> –H... <i>A</i> [°]
O3–H3A...O5	0.88 (4)	1.84 (4)	2.699 (5)	165 (6)
O3–H3B...O8	0.88 (4)	1.87 (4)	2.735 (5)	169 (6)
O4–H4A...O9 ⁱ	0.88 (4)	1.95 (4)	2.787 (5)	159 (6)
O4–H4B...O7 ⁱ	0.87 (4)	1.93 (4)	2.774 (5)	162 (7)
N2–H2...O8 ⁱⁱ	0.86 (3)	2.01 (3)	2.835 (5)	160 (6)
N3–H3...O10 ⁱⁱ	0.86 (3)	2.12 (3)	2.932 (5)	159 (6)
N6–H6...O5 ⁱⁱⁱ	0.87 (3)	2.00 (3)	2.860 (5)	172 (6)
N7–H7...O6 ⁱⁱⁱ	0.87 (3)	2.18 (3)	3.003 (5)	157 (5)

[a] Symmetry code(s): (i) $x + 1, y, z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.

Reaction of **L1** with two molar equivalents of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in ethanol yielded $[(\text{L1})_2\text{Cu}(\text{ClO}_4)_2]_n$ (**4**), which crystallized in the monoclinic space group $P2_1/c$, with one molecule fully contained in the asymmetric unit ($Z' = 1$.) In the molecular structure Cu^{2+} is five-coordinate in a distorted square pyramidal environment (Table 5; $\tau = 0.14$),^[18] with two molecules of **L1** coordinated by the pyridyl nitrogen atoms (N1 and N5) and the urea oxygen atoms (O1 and O2), in the equatorial plane, and the

Table 5. Selected geometric parameters for complex **4** [Å [°]].^[a]

Cu1–O1	1.9382 (14)	Cu1–N5	1.9771 (18)
Cu1–O2	1.9367 (15)	Cu1–O3	2.4519 (18)
Cu1–N1	1.9804 (18)	Cu1–O4 ⁱⁱⁱ	2.6104 (19)
O1–Cu1–N1	89.92 (7)	O2–Cu1–O4 ⁱⁱⁱ	87.08 (6)
O1–Cu1–N5	90.25 (7)	N1–Cu1–O3	82.71 (7)
O1–Cu1–O3	88.30 (6)	N1–Cu1–O4 ⁱⁱⁱ	84.06 (7)
O1–Cu1–O4 ⁱⁱⁱ	81.69 (6)	N5–Cu1–N1	176.95 (8)
O2–Cu1–O1	168.52 (7)	N5–Cu1–O3	94.24 (7)
O2–Cu1–N1	91.26 (7)	N5–Cu1–O4 ⁱⁱⁱ	98.98 (6)
O2–Cu1–N5	89.18 (7)	O3–Cu1–O4 ⁱⁱⁱ	163.41 (6)
O2–Cu1–O3	103.17 (6)		

[a] Symmetry code(s): (iii) $x, y + 1, z$.

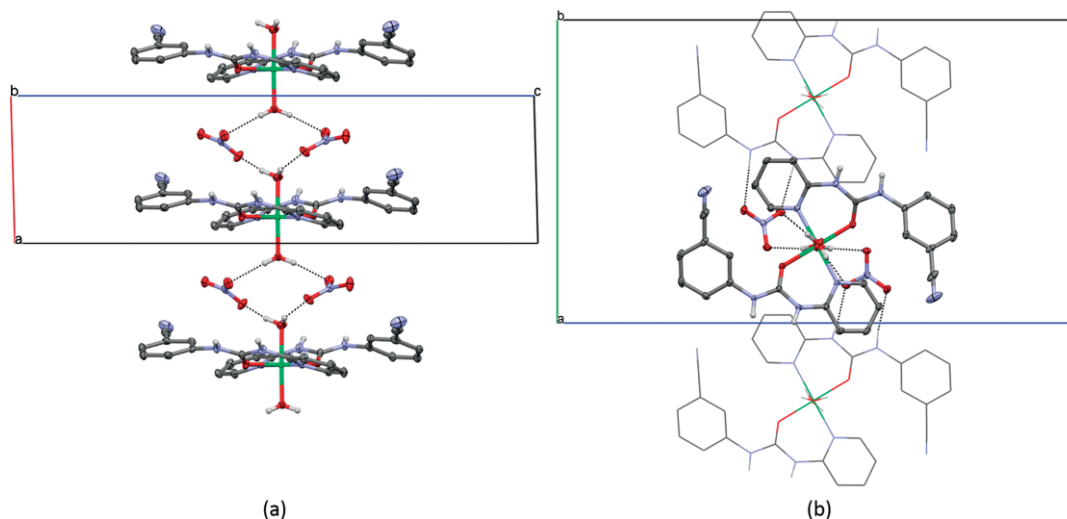


Figure 5. (a) Hydrogen-bonded chains in complex **3**, exhibiting an $R_4^4(12)$ motif, parallel to the crystallographic a-axis. (b) Alternate view to show hydrogen bonding between chains in (a), parallel to the crystallographic b-axis, via an $R_2^2(8)$ motif, forming a hydrogen bonded plane in (0 0 1).

axial position occupied by a perchlorate anion via O3 (Figure 6.) As in complexes **1–3**, **L1** is coordinated in a *trans*-fashion in the equatorial plane, and is in a neutral state.

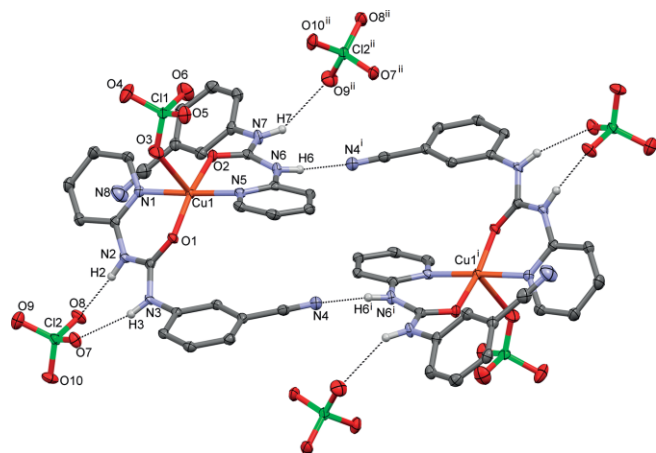


Figure 6. Expanded view of complex **4** shown with 50 % displacement ellipsoids; H-atoms, except those involved in hydrogen bonding (dashed lines), omitted for clarity. Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, -y + 3/2, z - 1/2$. The expected $R_2^2(8)$ motif is present, however, the complexes assemble into dimers via an $R_2^2(26)$ association.

For charge balance, a second unique perchlorate anion is present in the asymmetric unit, and makes three hydrogen bonds to the amine functionalities (Table 6.) Two of these

Table 6. Selected hydrogen-bond parameters for complex **4**.^[a]

D–H...A	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A [°]
N2–H2...O8	0.844 (17)	2.020 (17)	2.857 (2)	172 (2)
N3–H3...O7	0.831 (17)	2.148 (18)	2.964 (2)	167 (2)
N6–H6...N4 ⁱ	0.852 (17)	2.062 (18)	2.909 (3)	172 (2)
N7–H7...O9 ⁱⁱ	0.857 (17)	2.39 (2)	3.166 (3)	151 (2)

[a] Symmetry code(s): (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, -y + 3/2, z - 1/2$.

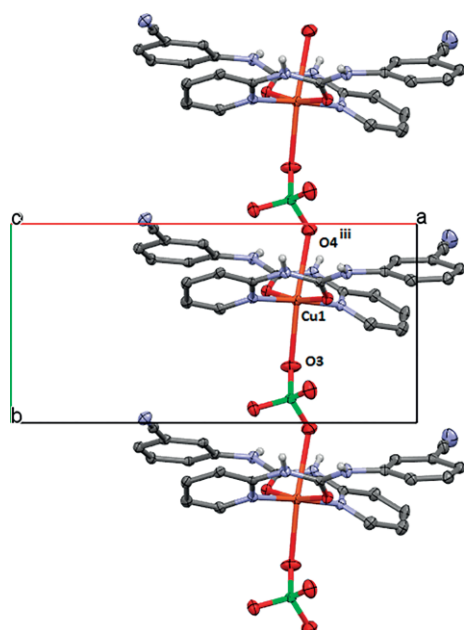


Figure 7. Complex **4** showing infinite chains parallel to the crystallographic *b*-axis. Symmetry code: (iii) $x, y + 1, z$.

bonds result in an $R_2^2(8)$ motif (N2–H2...O8; N3–H3...O7), while the third is a simple $D_1^1(2)$ interaction with a single amine functionality on a second different ligand (N7–H7...O9ⁱⁱ). Unlike in complexes **1–3**, the fourth unique ligand amine group is involved in a donor-acceptor relationship with a nitrile on a different symmetry related molecule (N6–H6...N4ⁱ), resulting in a dimer-like association between pairs of complexes in an extended $R_2^2(26)$ motif (Figure 6.)

Each Cu^{2+} cation is involved in one additional, long axial interaction with another perchlorate oxygen atom, which is already coordinated to a symmetry related molecule [Cu1–O4ⁱⁱⁱ; 2.6104(19) Å], (iii) = $x, y + 1, z$. These interactions result in an infinite chain parallel to the crystallographic *b*-axis (Figure 7.)

Hydrogen Bond Capacity and Anion Interactions

Interpreting the nature of hydrogen bond interactions is non-trivial, however, in the four reported complexes the number of available donor sites and hydrogen-bond acceptor strength appears to factor significantly. Varying the ligand-to-metal salt ratio, and the reaction solvent in the synthesis of **1** and **3** resulted in axial sites on the metal changing from single (methanol) to double (water) hydrogen-bond donors. In the case of **1**, the hydrogen bond-donor capacity of the charge neutral unit, with one methanol and one double-hydrogen-bond donor (**L1**) matched perfectly with the hydrogen-bond acceptor capacity of the nitrate anion, and the resulting hydrogen bond motif propagated in a single dimension. In the case of methanol replaced by water (**3**), the donor capacity increased by one, and resulted in nitrate accepting one additional hydrogen bond, and propagating these interactions in two dimensions.

Another, unused, hydrogen-bond acceptor was available in complexes **1–3**; that is, the uncoordinated nitrile group on **L1**. Hunter reported^[16] hydrogen bond parameters for common neutral functional groups, which included the acceptor constant (β) of 4.7 for nitrile. More recently, Hunter and colleagues^[19] undertook an examination of hydrogen-bond acceptor constants for anions, and reported values of 10.7 and 8.4 for nitrate and perchlorate, respectively (where larger β values represent greater hydrogen bond strength.) The preference for filling the hydrogen donor capacity with nitrate acceptors for **1–3** can be reasoned in this context. For **4**, however, competing forces, including the bridging metal coordination of one perchlorate anion, and the steric implications of the remaining single perchlorate anion to act as a fourfold hydrogen-bond acceptor, led to a different hydrogen bonding motif, and incorporation of the weaker available nitrile acceptor.

Conclusions

A new 2-pyridinylurea with capacity for simultaneous metal and anion binding has been synthesized, and its metal complexes with nitrate salts of Ni^{2+} and Co^{2+} have been reported. In these cases, the hydrogen-bond-donor capacity of the ligand is fulfilled by nitrate acceptors. In the case of the reported complex with the perchlorate salt of Cu^{2+} , however, axial coordination sites of the metal were occupied by one anion, and not solvent

(as was the case in the other complexes), effectively reducing the availability of anions as hydrogen-bond acceptors, and introducing the weaker accepting nitrile group into this role. Future work on these systems will examine anion selectivity, and the possibility of using the nitrile group to coordinate free heterometallic cations, or to those on surfaces.

Experimental Section

Synthesis

***N*-(3-Cyanophenyl)-*N'*-pyridin-2-ylurea (L1):** 3-Cyanophenyl isocyanate (5.811 g, 40.32 mmol) and 2-aminopyridine (3.852 g, 40.93 mmol) were combined in pyridine (125 mL) to give a clear yellow solution upon heating. This was refluxed for 12 h. Upon cooling to room temperature, a white solid formed, and was collected by suction filtration. Water (50 mL) was added to the filtrate to yield a second crop of white solid, which was again collected by suction filtration, and combined with the first. Recrystallization from ethanol (400 mL) yielded *N*-(3-cyanophenyl)-*N'*-pyridin-2-ylurea (7.160 g, 30.05 mmol; 74.5 % yield.) m.p. 194.5–195.5 °C. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C): δ = 10.88 (s, 1 H), 9.57 (s, 1 H), 8.27 (d, *J* = 4.9 Hz, 1 H), 8.04 (s, 1 H), 7.74 (m, *J* = 2.3 Hz, 2 H), 7.45 (dd, *J* = 17.2, 8.0 Hz, 3 H), 7.00 (m, 1 H) ppm. ¹³C NMR (100 MHz, [D₆]DMSO, 25 °C): δ = 157.72, 157.37, 152.07, 145.10, 143.86, 135.42, 131.15, 128.66, 126.64, 123.94, 122.96, 117.19, 116.88 ppm. HRMS [EI-(+)] calculated for C₁₃H₁₀N₄O ([M + H]⁺) 239.0927, found 239.0925.

[(L1)₂Ni(CH₃OH)₂](NO₃)₂ (1): Compound L1 (0.050 g, 0.21 mmol) and Ni(NO₃)₂·6H₂O (0.060 g, 0.21 mmol) were separately dissolved in methanol (5 mL). The solution of Ni(NO₃)₂ was added dropwise to the solution of L1. The resulting clear blue solution was stirred vigorously with heating (≈ 60 °C) for 20 min. This was filtered and left for slow evaporation. Blue, prismatic crystals grew from the filtrate over the course of six weeks. These analytically pure crystals (34.9 mg, 0.0483 mmol, 46 % yield) were harvested and analyzed via small molecule X-ray diffraction, and elemental analysis. [(C₁₃H₁₀N₄O)₂Ni(CH₃OH)₂](NO₃)₂ (723.28): C, 46.50; H, 3.90; N, 19.37; found C, 46.19; H, 3.96; N, 19.40.

[(L1)₂Co(CH₃OH)₂](NO₃)₂ (2): Compound L1 (0.050 g, 0.21 mmol) and Co(NO₃)₂·6H₂O (0.060 g, 0.21 mmol) were separately dissolved in 5 mL of methanol. The solution of Co(NO₃)₂ was added dropwise to the solution of L1. The resulting clear red solution was stirred vigorously with heating (≈ 60 °C) for 20 min. This was filtered and left for slow evaporation. Pink, prismatic crystals grew from the filtrate over the course of six weeks. These analytically pure crystals (38.9 mg, 0.0525 mmol, 50 % yield) were harvested and analyzed via small molecule X-ray diffraction, and elemental analysis. [(C₁₃H₁₀N₄O)₂Co(CH₃OH)₂](NO₃)₂·H₂O (741.53): calcd. C 45.35, H 4.08, N 18.89; found C 45.69, H 3.98, N 18.93.

[(L1)₂Ni(H₂O)₂](NO₃)₂ (3): Compound L1 (0.062 g, 0.26 mmol) and Ni(NO₃)₂·6H₂O (0.115 g, 0.40 mmol) were separately dissolved in 1:1 (v/v) methanol/acetonitrile (5 mL). The solution of Ni(NO₃)₂ was added dropwise to the solution of L1. The resulting clear blue solution was stirred vigorously with heating (≈ 60 °C) for 15 min. This

Table 7. Crystal data and structure refinement.

Identification code	1	2	3	4
Empirical formula	C ₂₈ H ₂₈ N ₁₀ NiO ₁₀	C ₂₈ H ₂₈ CoN ₁₀ O ₁₀	C ₂₆ H ₂₄ N ₁₀ NiO ₁₀	C ₂₆ H ₂₀ Cl ₂ CuN ₈ O ₁₀
Formula weight	723.31	723.53	695.26	738.94
Temperature /K	110(2)	110(2)	110(2)	110(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>c</i>
<i>a</i> /Å	8.9169(2)	8.9287(2)	7.5805(2)	14.7204(19)
<i>b</i> /Å	9.6067(2)	9.5805(2)	14.9276(3)	7.2027(11)
<i>c</i> /Å	9.7083(2)	9.7950(2)	25.4714(5)	27.430(4)
α /°	82.157(2)	82.0200(10)	90	90
β /°	73.460(2)	73.8600(10)	88.558(2)	92.731(5)
γ /°	76.024(2)	75.845(2)	90	90
Volume /Å ³	771.57(3)	778.16(3)	2881.40(11)	2905.0(7)
<i>Z</i>	1	1	4	4
ρ_{calc} /g cm ⁻³	1.557	1.544	1.603	1.690
μ /mm ⁻¹	1.564	0.626	0.750	3.404
<i>F</i> (000)	374.0	373.0	1432.0	1500.0
Crystal size /mm ³	0.273 × 0.204 × 0.134	0.319 × 0.311 × 0.067	0.381 × 0.336 × 0.243	0.224 × 0.169 × 0.166
Radiation	Cu-K α (λ = 1.54184)	Mo-K α (λ = 0.71073)	Mo-K α (λ = 0.71073)	Cu-K α (λ = 1.54178)
2 θ range for data collection /°	9.512 to 132.304	4.342 to 51.352	4.204 to 51.364	6.01 to 132.588
Index ranges	-10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 9, -11 ≤ <i>l</i> ≤ 11	-10 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -11 ≤ <i>l</i> ≤ 11	-9 ≤ <i>h</i> ≤ 9, -18 ≤ <i>k</i> ≤ 18, -30 ≤ <i>l</i> ≤ 31	-17 ≤ <i>h</i> ≤ 15, -8 ≤ <i>k</i> ≤ 8, -32 ≤ <i>l</i> ≤ 31
Reflections collected	21621	40342	10973	40887
Independent reflections	2622 [2529 with <i>I</i> > 2 σ (<i>I</i>); <i>R</i> _{int} = 0.0406]	2946 [2939 with <i>I</i> > 2 σ (<i>I</i>); <i>R</i> _{int} = 0.0315]	10973 [10956 with <i>I</i> > 2 σ (<i>I</i>); <i>R</i> _{sigma} = 0.047]	4966 [4419 with <i>I</i> > 2 σ (<i>I</i>); <i>R</i> _{int} = 0.0402]
Data/restraints/parameters	2622/2/236	2946/1/236	10973/10/456	4966/4/440
Goodness-of-fit on <i>F</i> ²	1.078	1.148	1.296	1.038
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0317, <i>wR</i> ₂ = 0.0807	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0682	<i>R</i> ₁ = 0.0619, <i>wR</i> ₂ = 0.1904	<i>R</i> ₁ = 0.0307, <i>wR</i> ₂ = 0.0800
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0682	<i>R</i> ₁ = 0.0624, <i>wR</i> ₂ = 0.1918	<i>R</i> ₁ = 0.0352, <i>wR</i> ₂ = 0.0825
Largest diff. peak/hole /e Å ⁻³	0.29/-0.28	0.25/-0.36	0.67/-1.07	0.59/-0.41
CCDC #	1580008	1580010	1580009	1580011

was filtered and left for slow evaporation. Blue, prismatic crystals grew from the filtrate over the course of six weeks. These analytically pure crystals (40.6 mg, 0.0584 mmol, 45 % yield) were harvested and analyzed via small molecule X-ray diffraction, and elemental analysis. $[(C_{13}H_{10}N_4O)_2Ni(H_2O)_2](NO_3)_2$ (695.22): calcd. C 44.92, H 3.48, N, 20.15; found C 45.01, H 3.50, N 20.06.

$[(L1)_2Cu(ClO_4)_2]_n$ (4): L1 (0.050 g, 0.21 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.160 g, 0.43 mmol; *Caution! Perchlorates are explosive and must be handled with care!*) were separately dissolved in ethanol (8 mL). The solution of $Cu(ClO_4)_2$ was added dropwise to the solution of L1. The resulting clear blue-green solution was stirred vigorously with heating ($\approx 60^\circ C$) for 20 min. This was filtered and left for slow evaporation. Blue, prismatic crystals grew from the filtrate over the course of six weeks. These analytically pure crystals (13.4 mg, 0.0181 mmol, 17 % yield) were harvested and analyzed via small molecule X-ray diffraction, and elemental analysis. $[(C_{13}H_{10}N_4O)_2Cu(ClO_4)_2]$ (738.34): C 42.26, H₂7.73, N 15.16; found C 42.30, H 2.82, N 15.16.

X-ray Experimental: Single crystals of **1–4** were selected and collected on a Bruker APEX-II CCD diffractometer. Crystals were kept at 110(2) K during data collection. Using Olex2,^[20] the structures were solved with the ShelXT^[21] structure solution program using intrinsic phasing and refined with the ShelXL^[22] refinement package using least-squares minimisation. The selected crystal of **3** was a two component twin that was initially solved and refined using the single component reflection file. The final refinement was done with both integrated components and a batch scale factor of 0.4112(16). For all structures, N–H and O–H hydrogen atoms were introduced in difference map positions, and refined isotropically with distance restraints and their associated default standard uncertainties. All other H-atoms were introduced in calculated positions and refined on a riding model. Non-hydrogen atoms were refined anisotropically. See Table 7 for crystal data and structure refinement information.

CCDC 1580008 (for **1**), 1580009 (for **3**), 1580010 (for **2**), and 1580011 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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