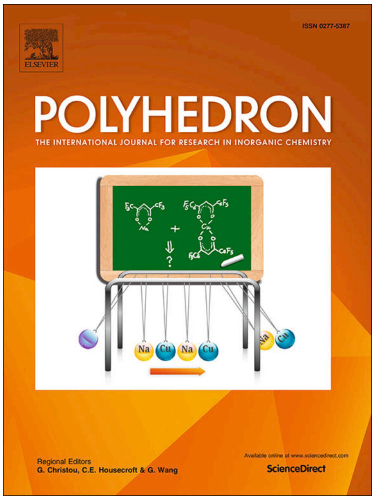

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Synthesis and Electronic Properties of Transition Metal Complexes Containing Sulfonamidoquinoline Ligands

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Abstract

The coordination chemistry of 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide has been expanded. Crystal structures of bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]cobalt(II) (**2**), diaqua-bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]nickel(II) (**3**), and bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]zinc(II) (**4**) containing this ligand in ML_2 stoichiometry were obtained. The nickel complex is isolated as a dihydrate. The degree of tetrahedrality for the four coordinate copper, cobalt, and zinc complexes was quantitatively compared by calculating the τ_4 geometric parameters. Zinc complex **4** was found to be the most tetrahedral, while copper complex **1-NO$_2$** deviated most from tetrahedral geometry. The magnetic moment calculated for **1-NO$_2$** showed inconsistencies when measured in solution and in the solid state. Only a Cu^{+2} center exists in solution, while a possible mixed spin state of Cu^{+2} and Cu^{+3} is proposed in the solid state. With a more electron releasing substituent on the ligand of the copper complex as seen in complex **1-Me**, this behavior is not observed and Cu^{+2} exists in solution and solid state. A reversible reduction at the same potential (-1.5 V vs. ferrocene) for both the ligand and the complex suggests possible redox activity of this class of ligand.

Keywords: Coordination complexes, Copper, magnetic moment, Quinoline sulfonamides, X-ray crystal structures

1. Introduction

8-Aminoquinoline (Figure 1) and its derivatives are versatile bidentate ligands in coordination chemistry. The luminescence of quinoline has been a subject of study.[1] This property extends to quinoline derivatives and their metal complexes, with zinc, cadmium, and mercury, exhibiting photoluminescence at room temperature.[2] Complexes of 8-aminoquinoline have also been prepared containing the lanthanides.[3] Additionally, complexation of this family of ligands with ruthenium forms an electroactive polymer.[4] In the preceding complexes, the amino group remains neutral upon coordination. 8-Aminoquinoline can serve as a building block for the synthesis of more complex ligands with increased functionality.

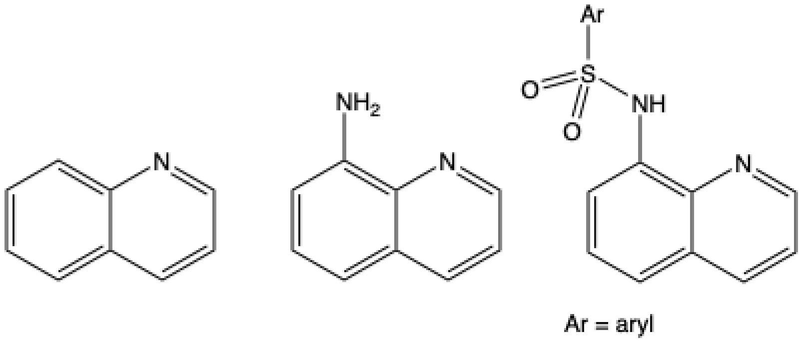


Figure 1. Structures of quinoline, 8-aminoquinoline, and aryl sulfonamide quinoline.

The addition of aryl sulfonyl moieties to 8-aminoquinoline (Figure 1) results in a class of monoanionic bidentate ligands with diverse properties. Complexes containing these ligands are of interest for their antifungal properties,[5],fluorescent properties, and role as sensors in biological systems.[6] Moreover, studies demonstrate the ability of these ligands to inhibit zinc(II) dependent metalloproteinases[7] and HIV-1 replication.[8] The ability of these complexes to form uniquely colored chelate precipitates based on the identity of the metal cation makes them useful for qualitative analysis of metals in solution.[9] Structurally similar ethylene linked pyridinesulfonamide ligands chelate to transition metals in a conformation comparable to the quinoline based ligands [10,11] and iridium complexes that possess this ligand catalyze the transfer hydrogenation of ketones and aldehydes.[12–14] Numerous coordination complexes containing sulfonamidoquinoline ligands have been reported in literature, along with their crystal structures. For example, copper[15,16] and manganese[17] complexes with tolyl, phenyl, and naphthyl substituted sulfonamidoquinoline ligands with L_2M formulas serve as DNA nuclease agents, that cleaveDNA by radical processes.[16,18] DNA cleavage is also observed in a copper(II) complex containing one sulfonamidoquinoline and one bipyridine ligand.[19] Nickel complexes containing the same derivatives of the sulfonamidoquinoline are also known.[20] Studies of the antiprotozoal effects of zinc and copper complexes with a wide range of sulfonamide derivatives were performed.[21,22] Additionally, crystal structures of copper and zinc complexes containing 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide are reported and these species exhibit chemical nuclease activity.[23–25] The reported copper complex has a distorted square planar geometry and was identified as a copper(II) complex by cyclic voltammetry and electron paramagnetic resonance.[25] Coordination complexes with these ligands are also applied in catalysis. For example, a palladium complex containing 3-nitro-*N*-(quinolin-8-yl)benzenesulfonamide catalyzes stereospecific allyl-aryl coupling reactions[26] and a ruthenium complex catalyzes transfer hydrogenation of acetophenone derivatives.[27]

As of yet, the redox activity of sulfonamidoquinoline ligands in transition metal complexes is not reported. There is increased interest in redox-active ligands for their use in catalysis. Additionally, improvements in X-ray crystallography and spectroscopic techniques have allowed for better electronic structural determinations of coordination complexes.[28] These aid in the identification of the presence of a radical-based ligand. Non-innocent ligands have been of interest in bioinorganic chemistry in reference to the single electron reactions that occur within enzymes.[29] Ligand-based redox activity is also observed in complexes that exhibit π-stacking in the solid state.[30] Non-innocent ligands play an important role as electron reservoirs in the catalytic cycle in certain organocatalysts.[31] Identification of these properties in sulfonamidoquinoline ligands would open up a new area of research including metal-catalyzed transformations.

We are interested in reevaluating the physical properties and solid-state structures of copper, zinc, and nickel complexes containing the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand. Here, we report X-ray structures for several coordination complexes containing the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand. The degree of tetrahedrality for the four coordinate copper (**1-NO$_2$**), cobalt (**2**), and zinc (**4**) complexes was quantitatively compared by calculating the τ_4 geometric parameters. Zinc complex **4** is the most tetrahedral, while copper complex **1-NO$_2$** was the most square planar. Based on magnetic susceptibility measurements performed on an Evans balance in the solid state, the copper complex possesses Cu^{+2} oxidation state. The Evans NMR method for the determination of magnetic moment in solution has confirmed the metal centers are in the +2 oxidation state. The structural evaluation of these complexes herein serves to aid in the continued investigation of the potential applications of these complexes.

2. Materials and Methods

2.1 General Methods

Unless otherwise noted, all reactions were performed under atmospheric conditions with solvents that were not dried or degassed. Microwave synthesis was performed on a Biotage+ Initiator Microwave Reactor set to high absorbance. All ^{1}H NMR spectra were obtained with a Bruker Biospin UltraShield 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts are reported in reference to residual $CHCl_3$ (δ 7.24 for ^{1}H) unless noted otherwise. X-ray diffraction was performed on a Bruker APEX II Single Crystal X-Ray Diffractometer with CCD detector at 100 K. Infrared spectra were obtained on a Perkin-Elmer Spectrum Two Fourier Transform Infrared Spectrometer. Mass susceptibility measurements were carried out on a Johnson Matthey Mark I Magnetic Susceptibility Balance. Cyclic voltammetry was performed with ferrocene as a reference. Elemental analyses were performed by Intertek Pharmaceutical Services of Whitehouse, NJ.

2.2 Materials

8-Aminoquinoline was obtained from TCI. 4-Toluenesulfonyl chloride, cobalt(II) acetate, and zinc(II) chloride were purchased from Acros Organics. 4-Nitrobenzenesulfonyl chloride and benzenesulfonyl chloride were purchased from Alfa Aesar. Copper(II) acetate, anhydrous nickel(II) chloride, nickel(II) chloride hexahydrate, methanol, and methylene chloride were purchased from Sigma Aldrich. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and dried over molecular sieves. All other reagents were used as purchased.

2.3 Synthesis of Sulfonamidoquinoline ligands

4-Methyl-*N*-(quinolin-8-yl)benzenesulfonamide, *N*-(quinolin-8-yl)benzenesulfonamide, and 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide were synthesized using a literature procedure.[7] The *p*-nitro substituted compound required recrystallization from methanol. The ^{1}H NMR and IR spectra obtained for each ligand were consistent with reported values.

2.4 Synthesis of bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]copper(II) (1-NO$_2$), bis[4-methyl-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]copper(II) (1-Me), and bis[*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]copper(II) (1-H)

All copper complexes were prepared by an adapted literature procedure.[15] In a 250 mL beaker, the sulfonamidoquinoline ligand was dissolved in boiling methanol (150 mL). Copper(II) acetate monohydrate was dissolved in methanol (30 mL) and added dropwise to the hot solution containing the ligand while stirring. The solution turned brown and was homogeneous. After several minutes, a brown precipitate formed. The solution was cooled and continued to stir for 3 h at 22 °C. The solution was filtered and the solid washed three times with methanol (5 mL). For complex **1-NO$_2$**, 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide (281 mg, 0.853 mmol) reacted with copper(II) acetate monohydrate (86 mg, 0.430 mmol) to yield a brown powder (281 mg, 0.390 mmol, 92%). Dark green X-ray quality crystals of **1-NO$_2$** were obtained by vapor diffusion of a dichloromethane saturated solution of **1-NO$_2$** with hexanes. Anal. Calcd for $C_{30}H_{20}N_6CuO_8S_2$: C, 50.03; H, 2.80; N,11.67. Found: C, 49.74; H, 2.79; N,11.74.

For complex **1-Me**, 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (302 mg, 1.01 mmol) reacted with copper(II) acetate monohydrate (102 mg, 0.509 mmol) to yield a brown powder (279 mg, 0.424 mmol, 83%). For complex **1-H**, *N*-(quinolin-8-yl)benzenesulfonamide (302 mg, 1.06 mmol) reacted with copper(II) acetate monohydrate (102 mg, 0.509 mmol) to yield a brown powder (310 mg, 0.492 mmol, 92%).

2.5 Synthesis of bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]cobalt(II) (2)

This complex was prepared by an adapted literature procedure.[15] 4-Nitro-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.455 mmol) was dissolved in boiling methanol (40 mL). Cobalt(II) acetate tetrahydrate (57 mg, 0.229 mmol) was dissolved in methanol (5 mL) and added dropwise to the hot ligand solution while stirring. A homogeneous red solution resulted and after several minutes, a red precipitate formed. The solution was heated to reduce the volume by half causing the product to precipitate. The solution was filtered and the precipitate was washed three times with methanol (5 mL). The complex was isolated as a red powder (118 mg, 0.165 mmol, 73%). Dark red X-ray quality crystals were obtained by vapor diffusion of a dichloromethane saturated solution of **2** with hexanes. Anal. Calcd for $C_{31}H_{22}N_6CoCl_2O_8S_2$: C, 46.51; H, 2.77; N, 10.50. Found: C, 47.00; H, 2.85; N, 10.43. The elemental analysis is consistent with one molecule of dichloromethane per complex which is consistent with the XRD determined unit cell of the sample submitted for elemental analysis.

2.6 Synthesis of diaqua-bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*] nickel(II) (3)

This complex was prepared by an adapted literature procedure.[20] 4-Nitro-*N*-(quinolin-8-yl)benzenesulfonamide (102 mg, 0.322 mmol) was dissolved of CH_2Cl_2 (50 mL). Triethylamine (89 µL, 0.644 mmol) was added to the solution while stirring. Nickel(II) chloride hexahydrate (37.2 mg, 0.156 mmol) was dissolved in methanol (5 mL) and added dropwise to the solution of the ligand while stirring. Crystals formed upon slow evaporation of the solution over several days. Redissolving the crystals in minimal dichloromethane and cooling in an ice bath for 5 min resulted in precipitation of the product. The powder form of the product was washed three times with methanol (5 mL) and collected via vacuum filtration. The complex was isolated as a pale green powder (74.2 mg, 0.0989 mmol, 64%). Anal. Calcd for $C_{30}H_{24}N_6NiO_{10}S_2$: C, 47.96; H, 3.22; N,11.19. Found: C, 47.93; H, 2.96; N,10.43.

2.7 Synthesis of bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]zinc(II) (4)

This complex was prepared by an adapted literature procedure.[32] 4-Nitro-*N*-(quinolin-8-yl)benzenesulfonamide (101 mg, 0.308 mmol) was dissolved in methanol (15 mL). 2 M NH_4OH (461 µL, 0.922 mmol) was added to the ligand solution. Zinc(II) chloride (22.3 mg, 0.164 mmol) was dissolved in methanol (1 mL) and added dropwise to the ligand solution while stirring resulting in a yellow solution. A yellow precipitate formed and was washed three times with methanol (5 mL) and then dissolved in a minimal amount of CH_2Cl_2 and crystallized via vapor diffusion with hexanes. (60.6 mg, 0.0839 mmol, 54.6%) Small pale yellow and colorless crystals formed and were characterized by single crystal X-ray diffraction. Colorless crystals were determined to be the uncoordinated ligand. Suitable elemental analysis could not be obtained after several sample submissions. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J = 4.68, 1.47 Hz, 1H), 8.46 (dd, J = 8.32, 1.49 Hz, 1H), 8.38 (dd, J = 6.96, 1.81 Hz, 2H), 8.20 (dd, J = 6.96, 1.83 Hz, 2H),7.63 (quartet, J = 4.33 Hz, 1H), 7.50 (d, J = 4.49 Hz, 2H), 7.45 (quartet, J = 4.40 Hz, 1H).

2.9 Evans Balance Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were repeated in triplicate for each sample. Equations to determine the effective magnetic moment (μ_{eff}) were obtained from literature.[33] Diamagnetic susceptibility of the sulfonamidoquinoline ligands and metal ions were estimated using the method described in the literature.[34]

2.10 Evans Method

An adapted literature procedure was performed.[35] The complex (7 mg) and tetramethylsilane (30 µL) were added to a 1 mL volumetric flask and diluted to volume with $CDCl_3$. 500 µL of this solution was pipetted into a coaxial tube which was then inserted into an NMR tube. Tetramethylsilane (30 µL) was added to a 1 mL volumetric flask and diluted to volume with $CDCl_3$. 500 µL of this solution was added to the NMR tube. Magnetic moments were determined by the degree the TMS peak shifted (Δv).

2.11 X-ray Crystallography

Single crystals were selected for analysis on a Bruker-AXS SMART Apex II X-ray diffractometer using Mo Kα radiation with a graphite monochromator. All samples were mounted using a MiTeGen MicroMount and NVH oil. Data were collected at 100°C. Unit cells were determined by taking 12 data frames, 0.5° ϕ, in three sections of the Ewald sphere. Full hemispheres were collected on each crystal and integrated using SAINT Plus. Data were corrected for absorption correction using SADABS. Structures were solved by the use of direct methods. Least squares refinement on F^2 was used for all reflections. Straightforward structure solution, refinement, and the calculations of measurements were accomplished with the SHELXTL package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized, theoretical positions. Hydrogens on the coordinated water on complex **3** were found from the electron density maps and refined using a free riding model.

2.12. Electrochemistry

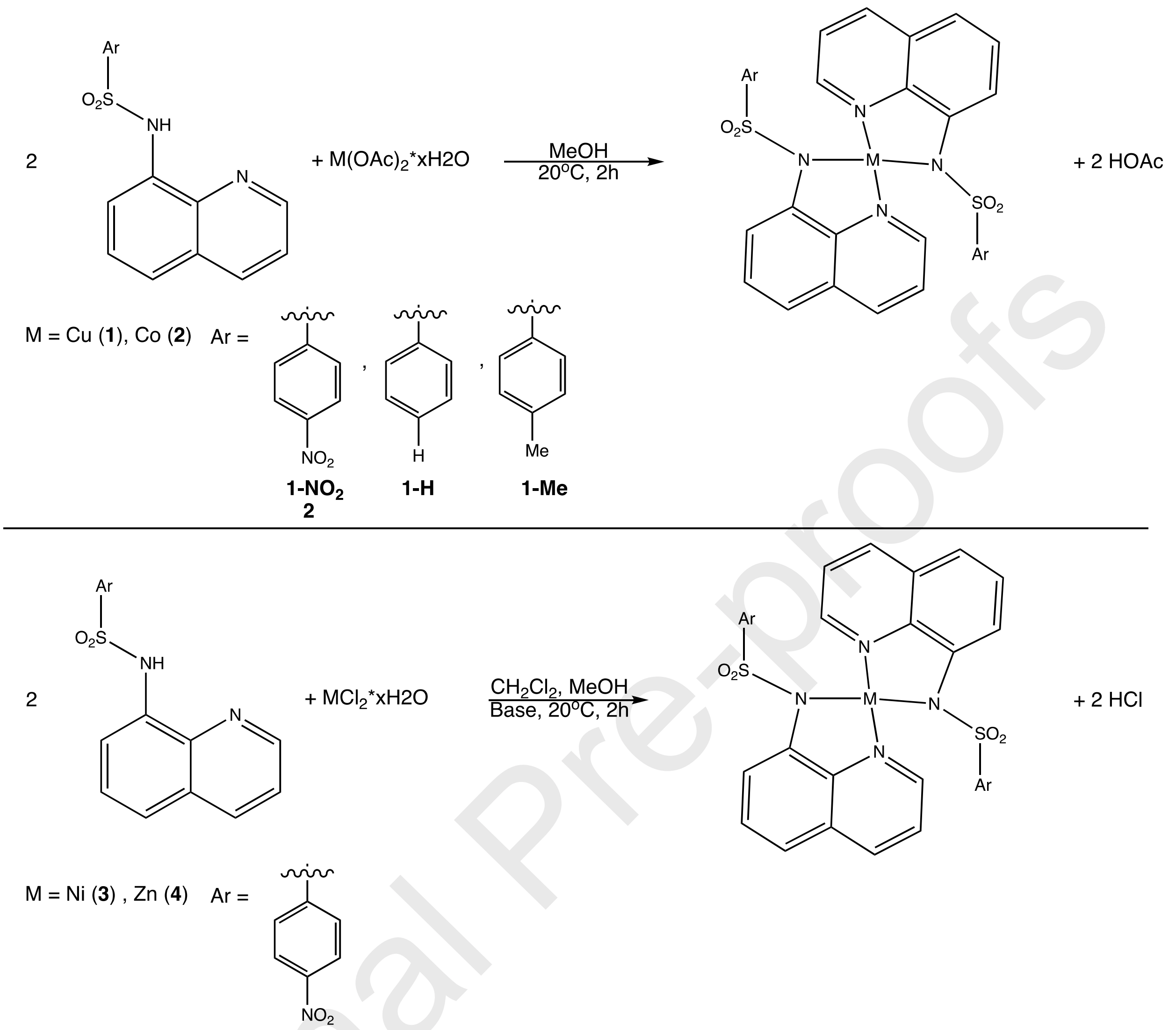
For the electrochemical experiments conducted on **1-NO$_2$**, a CH Instruments Model CHI260D potentiostat was used. The experiment was performed at room temperature (22 $\pm$ 1 °C) under an argon atmosphere at a scan rate of 100 mV/s using a glassy carbon working electrode (1.0 mm). This electrode was polished with 1.0 mm and 0.25 mm diamond paste and rinsed with methylene chloride before use. A non-aqueous Ag/AgCl electrode separated from the solution by a glass frit served as the reference electrode and the counter electrode was a platinum wire. Experiments were performed in dried DMF (10 mL)[36] with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Analyte concentrations were 1.0 mM. Ferrocene (FcH) was added as an internal standard giving a solution that was 0.1 mM in FcH after the initial electrochemical measurement. All reported data was background subtracted.

3. Results and Discussion

3.1 Synthesis of sulfonamidoquinoline ligands

All sulfonamidoquinoline ligands were prepared by reaction of 8-aminoquinoline with substituted aryl sulfonamides, using a microwave procedure.[7] The nitro-substituted ligand was recrystallized from methanol. ^{1}H NMR and IR spectral characterization of the ligands was consistent with previous reports.

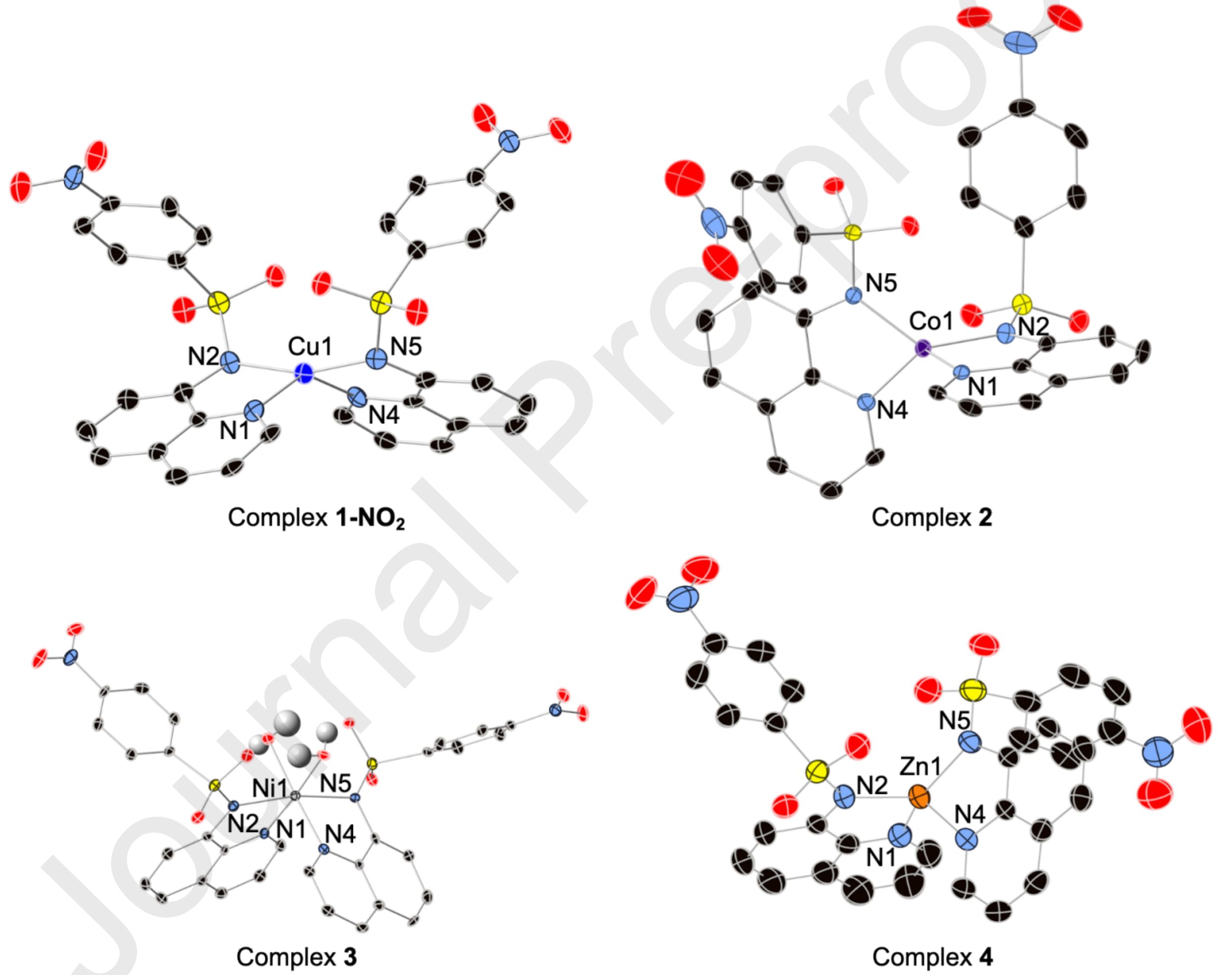
3.2 Synthesis and characterization of coordination complexes



Scheme 1. Synthesis of coordination complexes **1** - **4**.

The copper complexes **1** and cobalt complex **2** were synthesized from the metal acetates and the desired *N*-(quinolin-8-yl)benzenesulfonamide ligand in a methanol solution (Scheme 1). The copper complexes are known in the literature and the synthesized compounds are consistent with what has been reported.[16,25] Nickel complex **3** was synthesized from nickel chloride hydrate and two equivalents of the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand in CH_2Cl_2 in the presence of triethylamine. Complex **4** was synthesized from zinc chloride hydrate and two equivalents of the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand in methanol using NH_3OH as a base. Complexes **3** and **4** required base to deprotonate the ligand. The acetate anion served as the base for deprotonation to yield complexes **1** and **2**. All of the coordination complexes were synthesized in moderate to good yields (55-92%). Complexation of the ligand to the metal center was readily confirmed by the disappearance of the NH peak at ~3300 cm^{-1} for the free ligand in the infrared spectrum of the product.

X-ray quality crystals of **1-NO_2** and **2** were obtained from slow evaporation of the methanolic solution. X-ray crystal structures for complexes **1-NO_2** and **2** were collected at 100K, differing from the reported temperature of 299 K for the known species in the literature.[23] The structure of **1-NO$_2$** contained pseudo symmetry and a the literature solution was attempted in the monoclinic space groups, $C_{2/c}$ and C_{C}. In our low temperature analysis, the higher symmetry models diverged with multiple atoms becoming non-positive definite during anisotropic refinements, lower r-values (0.047, 0.050) and a poor goodness of fit (~0.7, ~0.6), respectively. The final space group for **1-NO$_2$** was assigned as triclinic, P_{-1} as the anisotropic refinement did not diverge, the goodness of fit was much closer to 1, but a slightly higher r-value (0.0526) was observed when compared to the literature report. Crystals of nickel complex **3** and zinc complex **4** were obtained by dissolving the complex in minimal dichloromethane followed by vapor diffusion in hexanes. Selected bond lengths (Å) and bond angles (°) for complexes **1-NO$_2$** and **2-4** are found in Table 1. X-ray diffraction parameters for complexes **1-NO$_2$** and **2-4** are found in Table 2. Crystal structures for complexes **1-NO$_2$** and **2-4** are shown in Figure 2.



Complex **1-NO$_2$**

Complex **2**

Complex **3**

Complex **4**

Figure 2. X-ray crystal structures of complexes **1-NO$_2$** – **4**. For complexes **3** and **4** dichloromethane solvent omitted for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°).

Complex **1-NO_2**		Complex **2**		Complex **3**		Complex **4**	
Bond Lengths							
Cu – N1	1.997(3)	Co – N1	2.043(3)	Ni – N1	2.052(3)	Zn – N1	2.049(3)
Cu – N2	1.953(3)	Co – N2	1.981(3)	Ni – N2	2.103(3)	Zn – N2	1.970(3)
Cu – N4	1.996(3)	Co – N4	2.032(3)	Ni – N4	2.071(3)	Zn – N4	2.032(3)
Cu – N5	1.955(3)	Co – N5	1.982(3)	Ni – N5	2.133(3)	Zn – N5	1.969(3)
Bond angles							
N1-Cu-N4	138.41(12)	N1-Co-N4 (α)	121.95(11)	N1-Ni-N4	92.90(12)	N1-Zn-N4	111.69(11)
N2-Cu-N5	162.57(12)	N2-Co-N5 (β)	130.10(12)	N2-Ni-N5	169.37(12)	N2-Zn-N5	129.15(12)

Table 2. Crystallography parameters for complexes **1-NO_2**, **2**, **3**, and **4**.

Complex	**1-NO_2**	**2**	**3**	**4**
Chemical formula	$C_{30}H_{20}N_6O_8S_2Cu$	$C_{30}H_{20}N_6O_8S_2Co$	$C_{31}H_{26}Cl_2N_6O_{10}S_2Ni$	$C_{31}H_{22}Cl_2N_6O_8S_2Zn$
Formula weight	720.18	715.58	836.30	806.93
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P-1	Pbca	$P2_12_12_1$	$P2_1/n$
a (Å)	10.886(7)	15.5950(10)	10.2413(13)	16.996(2)
b (Å)	10.900(7)	17.3877(11)	14.7107(18)	8.7489(10)
c (Å)	13.177(8)	22.1119(14)	22.500(3)	22.838(3)
α (°)	97.685(7)	90	90	90
β (°)	97.766(9)	90	90	105.239(2)
γ (°)	98.998(7)	90	90	90
V ($Å^3$)	1510.9(16)	5995.9(7)	3389.8(7)	3276.5(7)
Color and habit	Clear dark green block	Red plate	Clear pale green needle	Clear pale yellow block
Size	0.420x0.112x0.070	0.114x0.069x0.029	0.511x0.046x0.035	0.420x0.173x0.074
Z	2	8	4	4
T (K)	100(2)	100(2)	100(2)	296(2)
Radiation type	MoKα	MoKα	MoKα	MoKα
D_{calc} g cm^{-3}	1.583	1.585	1.639	1.636

μ (mm^{-1})	0.924	0.775	0.921	1.102
Final R indices [I > 2σ(I)]	R_1 = 0.0526 wR_2 = 0.1010	R_1 = 0.0393 wR_2 = 0.0742	R_1 = 0.0398 wR_2 = 0.0660	R_1 = 0.0410 wR_2 = 0.1094
R indices (all data)	R_1 = 0.1060 wR_2 = 0.1208	R_1 = 0.0833 wR_2 = 0.0906	R_1 = 0.0624 wR_2 = 0.0723	R_1 = 0.0495 wR_2 = 0.1148
Goodness-of-fit (GOF)	0.973	1.005	1.038	1.073

The coordination environment of the metal centers (Figure 3) varies with the identity of the metal center. Complexes **1-NO$_2$**, **2** and **4** are four coordinate complexes, whereas nickel complex **3** is octahedral. Complex **3** exhibits octahedral geometry due to the coordination of two water molecules at the nickel center. The zinc complex **4** reported here differs from a previously reported zinc complex which contains a coordinated water molecule. The structural parameters for the two molecules are similar.[24]

The steric influences around the octahedral nickel center in complex **3** increase the bond distance between the sulfonamido nitrogen and the metal center. For example, the Ni – N5 bond is approximately 0.15 Å longer than the equivalent Co – N11 bond (Table 1). This shows that the sulfonamido portion of the ligand is closer to the metal center in the 4-coordinate complexes. To examine the structural differences between the different coordination complexes, including complex **1-NO$_2$**, τ_4 parameters were calculated.[6] These parameters quantitatively characterize the geometry of four coordinate complexes on a spectrum ranging from perfectly square planar (τ = 0) to perfectly tetrahedral (τ = 1). Ligand-metal-ligand bond angles designated α and β (defined in Table 1) were used to calculate τ, and the results are found in Table 3. The angle between the cyclic nitrogens was designated α, and the angle between the sulfonamido nitrogens was designated β. The coordination chemistry at each metal center is evident from the polyhedral rendition for each complex, as depicted in Figure 3. Zn complex **4** possesses the most tetrahedral geometry while Cu complex **1-NO$_2$** is nearly square planar, whereas Ni complex **3** exhibits octahedral geometry.

Figure 3. Coordination environment for Co, Ni, Cu and Zn analogues.

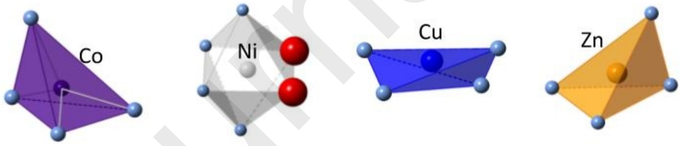


Table 3. τ_4 values for copper, cobalt and zinc complexes containing 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligands.

Complex	α	β	τ
1-NO$_2$	138.47°	162.66°	0.418
2	121.954°	130.08°	0.766
4	113.039°	128.310°	0.841

The τ_4 values show copper complex **1-NO$_2$** deviates the most from tetrahedrality with a τ value of 0.418. This is consistent with the observed distorted square planar geometry and is in line with reports for other copper complexes that possess substituted sulfonamidoquinoline ligands.[15] Zinc complex **4** exhibits nearly perfect tetrahedral geometry. Cobalt complex **2** lies between complexes **1-NO$_2$** and **4** in terms of tetrahedrality. A τ_4 value was not determined for nickel complex **3** due to its octahedral geometry; the nickel hydrate complex **3** is octahedral with two coordinated water molecules in *cis* configuration at the nickel center.

3.3 Magnetic susceptibility and cyclic voltammetry

The room temperature solid state magnetic moment of complexes **1-NO$_2$**, **1-Me**, **1-H**, and **4** were obtained using an Evans balance (Table 4). The values for copper complexes **1-Me** and **1-H** and cobalt species **2** correspond to the spin only magnetic moment for Cu^{2+} and Co^{2+}, respectively,[33] as expected for a complex containing two anionic ligands. A slightly higher value for the effective magnetic moment, when compared to the spin only magnetic moment expected for a Cu^{+2} metal center, was seen in copper complex **1-NO$_2$** containing the electron withdrawing *p*-nitro substituted sulfononamidoquinoline ligand. The effective magnetic moment of 2.37 BM for **1-NO$_2$** is in between one and two unpaired spins, which suggests potentially a mixture of two copper electronic states - Cu^{+2} and Cu^{+3}. This is not observed for **1-Me**, bearing an electron releasing substituent, in which the effective magnetic moment of 1.87 BM aligns with the spin only magnetic moment for on unpaired spin. The value for **1-H** is in between at 2.01 BM. To evaluate this further, the magnetic properties of the three copper complexes was also evaluated in the solution phase.

Table 4. μ_{eff} values obtained at 295 K.

Complex	μ_{eff} (BM)
1-NO$_2$	2.37
1-Me	1.87
1-H	2.01
2	3.04

Due to the higher than predicted μ_{eff} values, in the solid state, for the copper complex **1-NO$_2$**, the solution phase effective magnetic moment values were determined for all three copper derivatives for comparison. The Evans NMR method was employed to determine the solution phase effective magnetic moment for each of the copper complexes **1-NO$_2$**, **1-Me**, and **1-H** (Table 5). The oxidation state for copper in each complex, **1-NO$_2$**, **1-Me**, and **1H**, is consistent with Cu^{+2}. The calculated effective magnetic moment of all of the copper complexes now aligns quite well with the predicted spin-only μ_s values when in solution. A possible explanation for the variation of the μ_{eff} values in the solid state for complex **1-NO$_2$** is that the sulfonamidoquinoline ligands are non-innocent.

Table 5. μ_{eff} Values obtained at 300 K using the Evans NMR method for copper derivatives **1-NO$_2$**, **1-Me**, and **1H**.

Complex	μ_{eff} (BM)
1-NO$_2$	1.82
1-Me	1.76
1-H	1.81

The electrochemical properties of **1-NO$_2$** were then probed due to the variation in the effective magnetic moments observed in the solid state versus solution state. The redox potentials of complex **1-NO$_2$** and the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand were determined using cyclic voltammetry. Cyclic voltammetry data of complex **1-NO_2** has been previously reported in the literature.[25] However, the reduction potentials were collected using a limited sweep range. Upon expanding the sweep range, new interesting electrochemical features were found for the complex.

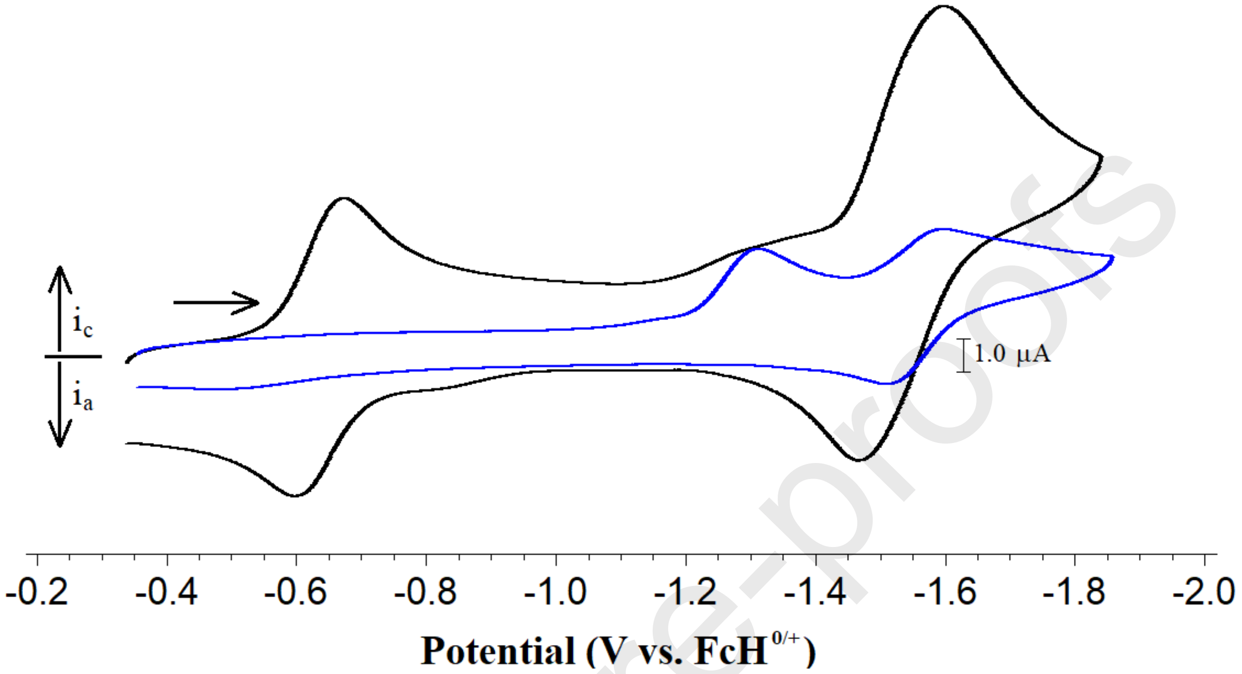


Figure 4. Overlay CV of 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand (black line) and complex **1-NO_2** (blue line) in DMF versus ferrocene. Scan rate is 100 mV/s, with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, data is not background subtracted.

Complex **1-NO_2** has two reversible reduction waves, one at -0.64 V and the other at -1.52 V. The additional reversible wave at -1.52 V versus FcH observed for **1-NO_2** (Figure 4) was not reported previously. This wave aligns with the reversible wave at -1.55 V observed in the CV of the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand. This supports the hypothesis that this ligand could be reversibly reduced allowing it to sustain an additional electron to become a radical, and thus be redox active.

Further examination of the packing of **1-NO_2** in the solid state also sheds some light on the possibility for redox activity for the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand. The **1-NO_2** complex exhibits π-stacking in the solid state (Figure 5), and this was also previously reported for **1-Me**.[23] Similar stacking has been seen before in complexes containing non-innocent ligands.[30] This interaction could allow stabilization of a radical on this type of ligand. Although the π-stacking is observed in the solid state for **1-NO_2** and **1-Me** only **1-NO_2** exhibits non-innocent behavior in the solid state. This is likely attributed to the presence of the electron withdrawing nitro group capable of aiding in stabilization of an additional electron at the ligand. In the case of **1-Me**, the electron releasing substituent would destabilize the ligand from supporting an additional electron.

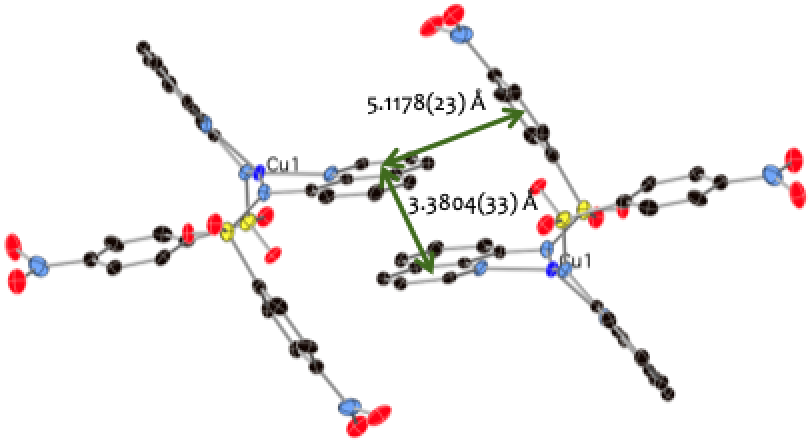


Figure 5. Pi-stacking observed in the solid state structure of **1-NO_2**.

4. Conclusion

4-Nitro-*N*-(quinolin-8-yl)benzenesulfonamide was synthesized by microwave reaction, and five coordination complexes containing this ligand were synthesized in good yields. Complexes **2-4** were characterized by IR spectroscopy, elemental analysis, and X-ray crystallography. The cobalt (**2**) and zinc (**4**) complexes were four coordinate, while the nickel hydrate complex **3** was octahedral with two coordinated water molecules in *cis* configuration. In the solid-state structure of the iron complex **7,** methanol and the sulfonyl oxygens on the ligand were coordinated to the metal center forming an octahedral bridged dimer. Upon extended exposure to air, the dimer converted to an extended chain structure. Magnetic susceptibility data confirms a +2 oxidation state for complexes **2-4**. A qualitative study of the structure of four coordinate complexes **1-NO_2**, **2**, and **4** (Cu, Co, Zn, respectively) was conducted by calculating the τ_4 parameters to assess the degree of tetrahedrality. The zinc complex **4** is nearly tetrahedral, while the copper complex **1-NO_2** has a distorted square planar structure. The magnetic moment of the copper complex **1-NO_2** was used to determine that the metal center is Cu^{+2} in solution. In the solid state, the effective magnetic moment of **1-NO_2** is in between the predicted values for one or two unpaired spins, suggesting a mixture of Cu^{+2} and Cu^{+3}. This suggests probable redox activity behavior of the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand. In addition, expansion of the sweep width used for the cyclic voltammetry measurements of complex **1-NO_2** showed the ligand could be reduced reversibly, providing support for non-innocent behavior. The highly electron withdrawing character of the nitro substituent on the ligand aids in stabilizing additional electrons at the ligand. Further studies to investigate the potential redox activity of the 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligand and its application in redox activity are future avenues to explore.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC <2064459> contains the supplementary crystallographic data for <bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]copper(II) **(1-NO$_2$)**>.

CCDC <2064457> contains the supplementary crystallographic data for <bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]cobalt(II) (**2**)>.

CCDC <2064458> contains the supplementary crystallographic data for <diaqua-bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]nickel(II) (**3**)>.

CCDC <2064455> contains the supplementary crystallographic data for <bis[4-nitro-*N*-(quinolin-8-yl)benzenesulfonamidato-κ^2*N,N'*]zinc(II) (**4**)>.

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Graphical Abstract:

Transition metal complexes with 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligands were prepared and characterized by X-ray crystallography. Magnetic studies of **1-NO$_2$** were reevaluated and show the complex to possess a Cu^{+2} metal center in solution and mixed Cu^{+2} and Cu^{+3} in the solid state. The electrochemistry of **1-NO$_2$** supports redox activity for this ligand.

Table 1. Selected bond lengths (Å) and bond angles (°).

Complex **1-NO$_2$**		Complex **2**		Complex **3**		Complex **4**	
Bond Lengths							
Cu – N1	1.997(3)	Co – N1	2.043(3)	Ni – N1	2.052(3)	Zn – N1	2.049(3)
Cu – N2	1.953(3)	Co – N2	1.981(3)	Ni – N2	2.103(3)	Zn – N2	1.970(3)
Cu – N4	1.996(3)	Co – N4	2.032(3)	Ni – N4	2.071(3)	Zn – N4	2.032(3)
Cu – N5	1.955(3)	Co – N5	1.982(3)	Ni – N5	2.133(3)	Zn – N5	1.969(3)
Bond angles							
N1-Cu-N4	138.41(12)	N1-Co-N4 (α)	121.95(11)	N1-Ni-N4	92.90(12)	N1-Zn-N4	111.69(11)
N2-Cu-N5	162.57(12)	N2-Co-N5 (β)	130.10(12)	N2-Ni-N5	169.37(12)	N2-Zn-N5	129.15(12)

Table 2. Crystallography parameters for complexes **1-NO$_2$**, **2**, **3**, and **4**.

Complex	**1-NO$_2$**	**2**	**3**	**4**
Chemical formula	$C_{30}H_{20}N_6O_8S_2Cu$	$C_{30}H_{20}N_6O_8S_2Co$	$C_{31}H_{26}Cl_2N_6O_{10}S_2Ni$	$C_{31}H_{22}Cl_2N_6O_8S_2Zn$
Formula weight	720.18	715.58	836.30	806.93
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P-1	Pbca	$P2_12_12_1$	$P2_1/n$
a (Å)	10.886(7)	15.5950(10)	10.2413(13)	16.996(2)
b (Å)	10.900(7)	17.3877(11)	14.7107(18)	8.7489(10)
c (Å)	13.177(8)	22.1119(14)	22.500(3)	22.838(3)
α (°)	97.685(7)	90	90	90
β (°)	97.766(9)	90	90	105.239(2)
γ (°)	98.998(7)	90	90	90
V (Å^3)	1510.9(16)	5995.9(7)	3389.8(7)	3276.5(7)

Color and habit	Clear dark green block	Red plate	Clear pale green needle	Clear pale yellow block
Size	0.420x0.112x0.070	0.114x0.069x0.029	0.511x0.046x0.035	0.420x0.173x0.074
Z	2	8	4	4
T (K)	100(2)	100(2)	100(2)	296(2)
Radiation type	MoKα	MoKα	MoKα	MoKα
D_{calc} g cm^{-3}	1.583	1.585	1.639	1.636
μ (mm^{-1})	0.924	0.775	0.921	1.102
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0526$ $wR_2 = 0.1010$	$R_1 = 0.0393$ $wR_2 = 0.0742$	$R_1 = 0.0398$ $wR_2 = 0.0660$	$R_1 = 0.0410$ $wR_2 = 0.1094$
R indices (all data)	$R_1 = 0.1060$ $wR_2 = 0.1208$	$R_1 = 0.0833$ $wR_2 = 0.0906$	$R_1 = 0.0624$ $wR_2 = 0.0723$	$R_1 = 0.0495$ $wR_2 = 0.1148$
Goodness-of-fit (GOF)	0.973	1.005	1.038	1.073

Table 3. τ_4 values for copper, cobalt and zinc complexes containing 4-nitro-*N*-(quinolin-8-yl)benzenesulfonamide ligands.

Complex	α	β	τ
1-NO$_2$	138.47°	162.66°	0.418
2	121.954°	130.08°	0.766
4	113.039°	128.310°	0.841

Table 4. μ_{eff} values obtained at 295 K.

Complex	μ_{eff} (BM)
1-NO$_2$	2.37
1-Me	1.87
1-H	2.01
2	3.04

Table 5. μ_{eff} Values obtained at 300 K using the Evans NMR method for copper derivatives **1-NO$_2$**, **1-Me**, and **1H**.

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1-H	1.81