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Synthesis, Crystal Structures and Properties of $[Cu(L1)_2(py)_2(H_2O)](H_2O)$ [HL1 = N-(5-ethyl-[1,3,4]−thiadiazole-2-yl)-toluenesulfonamidate] and $[Cu(L2)_2(py)_2(H_2O)]$ [HL2 = N-(5-ethyl-[1,3,4]−thiadiazole-2-yl)-benzenesulfonamidate]

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Dedicated to Professor Alfonso Castineiras on the Occasion of his 65th Birthday

Abstract. A series of new *N*-sulfonamidate ligands and their cooper(II) complexes, $[Cu(N\text{-}(5\text{-ethyl-}[1,3,4]\text{-thiadiazole-2-yl})\text{-toluenesulfonamidate})_2(py)_2(H_2O)](H_2O)$ (**1**) and $[Cu(N\text{-}(5\text{-ethyl-}[1,3,4]\text{-thiadiazole-2-yl})\text{-benzenesulfonamidate})_2(py)_2(H_2O)]$ (**2**) have been synthesized and characterized. The X-ray crystal structures of the complexes **1** and **2** have been determined. In the both two complexes, the Cu^{2+} ion is five-coordinated, forming a CuN_4O chromophore. The ligands act as monodentate, coordinating the metal ion through a single $N_{\text{thiadiazole}}$ atom. The molecules from the reaction medium (pyridine and water) also participate to the coordination of Cu^{2+} ion as monodentate ligands. Both two complexes have a slightly distorted square pyramidal geometry. The chemical properties of the complexes have been studied by FT-IR, electronic and EPR spectroscopic methods.

Keywords: Copper; Sulfonamides; Crystal structures

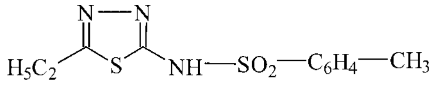
Introduction

The study of *N*-substituted heterocyclic sulfonamide ligands was shown their ability to coordinate biologically important metallic ions. The sulfonamides structures are varied and complex, and offer multiple possibilities to coordinate metallic ions depending on the type of donors atoms in the molecule (O, S, N), the stereochemistry of the compounds, the nature of the metallic ion that can form complexes, the nature of the anion of the salt that offers the central ion, the conditions for the synthesis of the complexes [1−4].

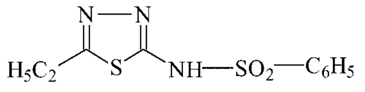
The pharmacological activity and the chelating properties of sulfonamides allow the synthesis of metallic complexes with various therapeutic activities, which serve as models for metalloenzymes [5−11].

Metallic ions, including Cu^{2+}, and their coordinative compounds, can produce in the presence of reducing agents, reactive free radical species which can cleavage the DNA molecule. This property has spurred studies concerning their use in complexes with Fe^{2+}, Mn^{2+}, Cu^{2+} etc. ions as potential "artificial chemical nucleases" [3, 4, 10, 11].

In the present paper we report the synthesis and the physicochemical characterization of two news N-substituted heterocyclic sulfonamides: HL1 = N-(5-ethyl-[1,3,4]−thiadiazole−2-yl)-toluenesulfonamide and HL2 = N-(5-ethyl-[1,3,4]−thiadiazole−2-yl)-benzenesulfonamide (scheme 1). Two complexes of these sulfonamido ligands with Cu^{2+} were prepared and their structures determined by X-ray diffraction. Their IR, ESR, electronic spectra and its magnetic susceptibility were investigated and discussed, along with the structural and spectral comparisons with those of the analogous complexes.



N-(5-ethyl-[1,3,4]–thiadiazole–2-yl)-toluenesulfonamide **(HL1)**



N-(5-ethyl-[1,3,4]–thiadiazole–2-yl)-benzenesulfonamide **(HL2)**

Scheme 1

Results and Discussion

Crystal structures of $[Cu(L1)_2(py)_2(H_2O)](H_2O)$ (1) and $[Cu(L2)_2(py)_2(H_2O)]$ (2)

Relevant bond distances and angles for the complexes **1** and **2** are collected in Table 1.

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Table 1 Selected bond distances /Å and angles /° for compounds **1** and **2**

1		**2**	
Bond distances		*Bond distances*	
Cu(1)−N(2a)	1.986(4)	Cu(1)−N(2b)	1.987(3)
Cu(1)−N(2b)	2.004(4)	Cu(1)−N(2a)	1.987(3)
Cu(1)−N(2)	2.055(4)	Cu(1)−N(1)	2.059(3)
Cu(1)−N(1)	2.062(5)	Cu(1)−N(2)	2.059(3)
Cu(1)−O(1W)	2.216(4)	Cu(1)−O(1W)	2.232(4)
Bond angles		*Bond angles*	
N(2a)−Cu(1)−N(2b)	165.7(2)	N(2b)−Cu(1)−N(2a)	174.7(2)
N(2a)−Cu(1)−N(2)	89.4(2)	N(2b)−Cu(1)−N(1)	88.44(12)
N(2b)−Cu(1)−N(2)	90.7(2)	N(2a)−Cu(1)−N(1)	90.97(12)
N(2a)−Cu(1)−N(1)	90.3(2)	N(2b)−Cu(1)−N(2)	90.97(12)
N(2b)−Cu(1)−N(1)	87.3(2)	N(2a)−Cu(1)−N(2)	88.44(12)
N(2)−Cu(1)−N(1)	170.5(2)	N(1)−Cu(1)−N(2)	167.10(2)
N(2a)−Cu(1)−O(1W)	97.9(2)	N(2b)−Cu(1)−O(1W)	92.65(9)
N(2b)−Cu(1)−O(1W)	96.3(2)	N(2a)−Cu(1)−O(1W)	92.65(9)
N(2)−Cu(1)−O(1W)	96.2(2)	N(1)−Cu(1)−O(1W)	96.44(10)
N(1)−Cu(1)−O(1W)	93.3(2)	N(2)−Cu(1)−O(1W)	96.44(10)

Figures 1 and 2 show molecular structures with the atom numbering scheme of the complexes **1** and **2**, respectively.

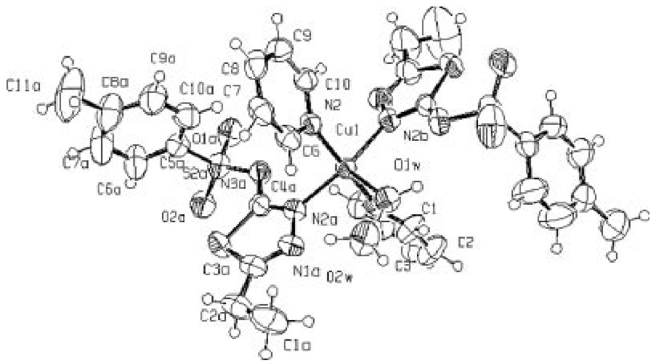

Fig. 1 ORTEP drawing of the $[Cu(L1)_2(py)_2(H_2O)](H_2O)$ (**1**) complex

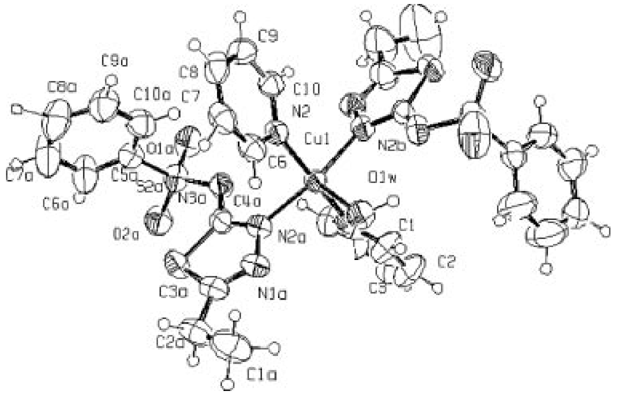

Fig. 2 ORTEP drawing of the $[Cu(L2)_2(py)_2(H_2O)]$ (**2**) complex

The crystal structures of **1** and **2** contain a CuN_4O entity in a slightly distorted square pyramidal geometry. In the basal plane Cu^{2+} is coordinated by two nitrogen atoms of the two thiadiazole rings $N_{thiadiazole}$ from the sulfonamidate ligands and two nitrogen atoms from each pyridine molecules $N_{pyridine}$. The $Cu-N_{thiadiazole}$ lengths (1.986 (4)−2.004 (4) Å) are smaller than those corresponding to the other complexes with ligands containing a thiadiazole ring [12, 13]. $Cu-N_{pyridine}$ lengths (2.055 (4)−2.062 (5) Å) are consonant with those measured for similar compounds. One water O atom [O(1W) in **1** and **2**] occupies the axial position with a bond length of 2.216(4) Å (**1**) and 2.232(4) Å (**2**). The angles between the atoms in the equatorial plane are of about 90° [87.3(2)−90.7(2)° (**1**) and 88.44(12)−90.97(12)° (**2**)] and those between the atoms on the axial plane and the equatorial plane are similar [93.3(2)−97.9(2)° (**1**) and 92.65 (9)−96.44 (10)° (**2**)]. The distances almost equal between Cu and N atoms in the ecuatorial plane, the distance significantly bigger between Cu and O atom in the axial plane and the angles forming the coordination polyhedron confirm the slightly distorted square pyramidal structure for the complexes **1** and **2**. The bond-length change are described by the tetragonality (T^5). The tetragonality values, 0.91 (compound **1**) and 0.91 (compound **2**), fit into the range expected for square pyramidal complexes [14]. The in-plane angular distortions described by the ratio τ represents a percentage of trigonal distortion of a square-pyramidal geometry [15]. The τ value of 0.08 for compound **1** and 0.12 for compound **2** indicates a very slight distortion. It is noteworthy that the coordination of Cu^{2+} takes place through the $N_{thiadiazole}$ atom instead though the deprotonated $N_{sulfonamido}$ atom. This is a consequence of the charge delocalization between the sulfonamido and the thiadiazole ring. In the complexes **1** and **2**, the both sulfonamidate ligands (HL1) and (HL2) acting as monodentate as they coordinate through a nitrogen atom of the thiazole heterocycle. The sulfonamide molecules of this type can behave as bidentate ligands as well through the N atom from the thiadiazole moiety and through one of the O atoms and even through the $N_{sulfonamido}$ atom from the sulfonamido moiety [16]. As it is expected the pyridine and the water molecules participate in the coordination as monodentate ligands. For the complex **1**, the crystalline packing of the symmetrical unit also includes a water molecule from the reaction medium, that does not coordinate the Cu^{2+} ion.

Spectroscopic and magnetic properties

The IR spectra of both complexes present a similar pattern. The most remarkable difference occurs in the band corresponding to the stretching vibration of the thiadiazole ring, which is shifted from 1530 cm^{-1} (HL1) and 1565 cm^{-1} (HL2) in the free ligands to 1444 cm^{-1} (**1**) and 1510 cm^{-1} (**2**) in the complexes. The characteristic band corresponding to the $\nu(S-N)$ appears at 932 cm^{-1} (**1**) and 935 cm^{-1} (**2**) shifted ca. 20 cm^{-1} to higher frequencies with respect to those of the uncoordinated ligands. These modifications in the thiadiazole heterocycle and in the sulfonamide group are attributed to the involvement to the $N_{thiadiazole}$ atom in coodination of Cu^{2+} and to the deprotonation of the sulfonamido moiety [17−19].

Bands due to the antisymmetric and symmetric vibration modes of the $S{=}O_2$ bonds are recorded close to 1319 and 1142 cm^{-1}, ca. 20 cm^{-1} lower than those corresponding to the free ligands [20, 21]; such a decrease can be related to the electron transfer from the deprotonated, negatively charged N atom to the sulfonyl oxygen atoms, which results in partial single-bond character for the S−O bonds [22]. Such electron transfer increases the bond order of the S−N moiety, thus accounting for the 25 cm^{-1} shift towards higher wavenumbers of the band due to the stretching mode of this bond. The lack of bands close to 3200 cm^{-1}, which were originally present in the spectra of the free ligands confirm deprotonation of the N−H bonds. This deprotonation of $N_{\text{sulfonamido}}$ atom determines a weak conjugation effect among the three N, S, O atoms of the moiety. Literature indicates that the bands corresponding to the coordinated pyridine molecules participating in the coordination appear at 3057 cm^{-1}, 1450 cm^{-1}, 1080 cm^{-1}, 1035 cm^{-1}, 1008-995 cm^{-1}, 660 cm^{-1}, 440 cm^{-1} [23−25]. In the IR spectrum of the both complexes a band appears at ca. 1085 cm^{-1}, interpreted as corresponding to pyridine (as it does not appear in the free ligands spectrum). The other bands be attributed to pyridine, as they sometimes overlap the frequencies corresponding to moieties of the ligand. In general, the patterns of the IR spectra are similar to those observed for other cooper *N*-sulfonamide derivatives [4, 21].

The solid electronic spectra of the both complexes display a band near 400 nm (396 nm for complex **1** and 401 nm for complex **2**) assigned to a LMCT transition. The complex **1** exhibits a d-d band at 591 nm and the complex **2** show a d-d band at 583 nm. This pattern, characteristic for distorted square-pyramidal cooper(II) complexes, agrees well with the crystallographic data [26].

The polycrystalline X-band EPR spectra of both complexes are axial. The EPR parameters, obtained by simulation [27] are $g_{\parallel} = 2.22$, $g_{\perp} = 2.069$ and $A_{\parallel} = 150 \times 10^{-4}$ cm^{-1} for complex **1** (figure 3) and $g_{\parallel} = 2.23$, $g_{\perp} = 2.05$ for complex **2**. According to the Bertini classification, the value of $A_{\parallel}$ for complex **1** can be correlated with the structure of the complex [28]. Thus, values between 130 and 160 cm^{-1} correspond to a square pyramidal or distorted trigonal bipyramidal arrangement. As $g_{\parallel} > g_{\perp}$ in the complexes, the unpaired electron must be in the $d_{x^2-y^2}$ (or d_{xy}) orbital [23]. The EPR parameters of complex **1** and **2** reflect the square pyramidal coordination of Cu^{2+} ion.

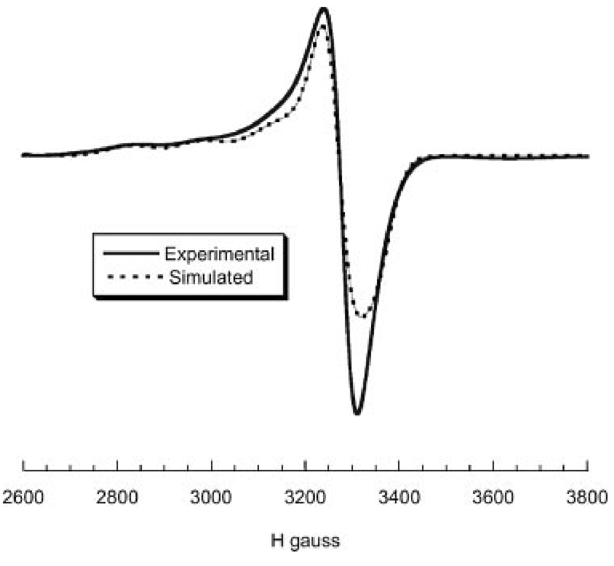

Fig. 3 X Band EPR of the compound **1**

The room temperature magnetic moments of complexes **1** ($\mu_{\text{eff}} = 1.73$ MB) and **2** ($\mu_{\text{eff}} = 1.83$ MB) are consistent with the presence of a single unpaired electron.

Experimental Section

Materials and physical measurements

Copper sulfate pentahydrate, benzenesulfonylchloride, toluenesulfonylchloride, 2-amino-5-ethyl-[1,3,4]−thiadiazole and pyridine were purchased from commercial sources and used as received.
Elemental analysis(C, N, H, S) were performed on a Perkin-Elmer device, using the combustion technique. IR spectra were recorded with a Perkin-Elmer FT-IR 1730 spectrophotometer using powder samples in KBr disks, in the 4000-400 cm^{-1} range. Fast ion bombardment (FAB) mass spectra were obtained on a VG Autospec spectrometer in m-nitrobenzene as a solvent. Diffuse reflectance spectra (nujol mulls) were carried out on a Shimadzu UV-2101 PC spectrophotometer. Magnetic susceptibilities were measured at room temperature with the Faraday MSB-MKI balance. $Hg[Co(NCS)_4]$ was used as susceptibility standard. Electronic paramagnetic resonance (EPR) spectra were performed at room temperature with a Bruker ELEXSYS spectrometer operating at the X-band frequency.

Syntheses of the ligands

N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-toluenesulfonamide (HL1)

A solution containing 1 mmol of 2-amino-5-ethyl-[1,3,4]-thiadiazole and 0.9 mmoles of toluenesulfonylchloride in 6 ml of pyridine was heated at reflux for 1 h, at 60 °C. The mixture was added to 10 ml of cold water and stirred for several minutes. The resulting solid was recrystallized from ethanol. Data for **HL1**(yield 87 %). $C_{11}H_{13}N_3S_2O_2$ (283): C 46.64 (calc.46.70); H 4.59 (4.63); N 14.84 (14.80); S 22.61 (22.65) %.

IR (KBr) (ν_{max} (cm^{-1})): 1530 (thiadiazole); 1319, 1142 $\nu(SO_2)$; 916 ν(S−N). **Solid UV/Vis** (λ_{max}) (nm): 318 ($\pi \rightarrow \pi^*$). **FAB**: m/z 284 $[M-H^+]$.

N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-benzenesulfonamide (HL2)

This ligand was obtained following the procedure described above. In this case, 1 mmol of 2-amino-5-ethyl-[1,3,4]-thiadiazole and 0.9 mmoles of benzenesulfonylchloride were mixed. Data for **HL2** (yield 72 %). $C_{10}H_{11}N_3S_2O_2$ (269): C 44.65 (calc. 44.60); H 4.06 (4.08); N 15.54 (15.61); S 23.80 (23.79) %.

IR (KBr) (ν_{max} /cm^{-1})): 1565 (thiadiazole); 1315, 1154 $\nu(SO_2)$; 918 ν(S−N). **Solid UV/Vis** (λ_{max}) (nm): 312 ($\pi \rightarrow \pi^*$). **FAB**: m/z 270 $[M-H^+]$.

Synthesis of the complexes **[Cu(N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-toluenesulfonamidate)$_2$(py)$_2$(H$_2$O)](H$_2$O) (1)** *and* **[Cu(N-(5-ethyl-[1,3,4]-thiadiazole-2-yl)-benzenesulfonamidate)$_2$(py)$_2$(H$_2$O)] (2)**

A solution of $CuSO_4 \cdot 5H_2O$ (4 mmol) in 20 ml of pyridine : H_2O [v : v = 1 : 1] was added dropwise, under continuous stirring to a solution of HL1 respectively HL2 ligand (1 mmol) dissolved in 25 ml pyridine : H_2O [v : v = 2 : 3]. The resulting solution was stirred at room temperature for one hour and left to stand at room temperature. After one respectively three months by the slow evaporation of the solvent, blue crystals (compound **1**) and green-blue crystals (compound **2**) suitable for X-ray diffraction were obtained.

Data for compound **1:** (yield 65 %). $C_{32}H_{38}CuN_8S_4O_6$ (822.4): C 46.68 (calc. 46.71); H 4.64 (4.62); N 13.64 (13.62); S 15.68 (15.57) %.

IR (KBr) (ν_{max} /cm^{-1})): 1444 (thiadiazole); 1300, 1142 $\nu(SO_2)$; 932 $\nu(S-N)$. **Solid UV/Vis** (λ_{max}) (nm): 300 ($\pi \rightarrow \pi^*$), 396 (LMCT), 591 (d-d).

Data for compound **2:** (yield: 58 %). $C_{30}H_{32}CuN_8S_4O_5$ (776.42): C 46.39 (calc. 46.43); H 4.12 (4.10); N 14.43 (14.38); S 16.49 (16.49) %.

IR (KBr) (ν_{max} (cm^{-1})): 1510 (thiadiazole); 1298, 1136 $\nu(SO_2)$; 935 $\nu(S-N)$. **Solid UV/Vis** (λ_{max}) (nm): 314 ($\pi \rightarrow \pi^*$), 401(LMCT), 583 (d-d).

X-ray structure determination

Data collection of **[Cu (L1)$_2$(py)$_2$(H$_2$O)](H$_2$O) (1).** A blue crystal, size 0.15 × 0.19 × 0.25 mm, monoclinic, space group $P2_1/c$ (determined from the systematic absences) was used. Data collection was performed at 293° K on a Nonius Kappa-CCD single crystal diffractometer, using Mo K_α radiation ($\lambda = 0.7173$ Å). Crystal-detector distance was fixed at 35 mm, and a total of 90 images were collected using the oscillation method, with scan angle per frame 2° oscillation and 12s. exposure time per image. Data collection strategy was calculated with the program Collect [29]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [30]. Unit cell dimensions were determined from 8270 reflections between $\theta = 0.998°$ and 27.485°. Crystal structure was solved by direct methods, using the program SIR-97 [31]. Anisotropic least-squares refinement was carried out with SHELXL-97 [32]. All non hydrogen atoms were anisotropically refined. Hydrogen atoms were located in a difference Fourier map and located geometrically. Geometrical calculations were made with PARST [33, 34]. The crystallographic plots were made with ORTEP [35]. A summary of the crystal data, experimental details and refinement results is listed in Table 2.

Data collection of **[Cu (L2)$_2$(py)$_2$(H$_2$O)] (2).** A blue crystal, size 0.12 × 0.14 × 0.16 mm, monoclinic, space group P2/n (determined from the systematic absences) was used. Data collection was performed at 293° K on a Nonius Kappa-CCD single crystal diffractometer, using Mo K_α radiation ($\lambda = 0.7173$ Å). Crystal-detector distance was fixed at 40 mm, and a total of 162 images were collected using the oscillation method, with scan angle per frame 2° oscillation and 10s exposure time per image. Data collection strategy was calculated with the program Collect [29]. Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack [30]. Crystal structure was solved by direct methods, using the program SIR-97 [31]. Anisotropic Least-squares refinement was carried out with SHELXL-97 [32]. All non hydrogen atoms were anisotropically refined. Hydrogen atoms were located in a difference Fourier map and located geometrically. Geometrical calculations were made with PARST [33, 34]. The crystallographic plots were made with ORTEP [35]. A summary of the crystal data, experimental details and refinement results is listed in Table 2.

Crystallographic data without structure factors fot the two strctures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 645240 and CCDC 645241. Copies of the data can be obtained free of change from the CDCC, 12 Union Road, Cambridge CB2 1EZ, UK: e-mail for deposition:deposit@ccdc.cam.ac.uk, fax: +44-1223-336033.

Table 2 Crystal data and refinement for [Cu(L1)$_2$(py)$_2$(H$_2$O)](H$_2$O) **(1)** *and* [Cu(L2)$_2$(py)$_2$(H$_2$O)] **(2)**

Complexes	**1**	**2**
Empirical formula	$C_{32}\ H_{38}\ Cu\ N_8\ O_6\ S_4$	$C_{30}\ H_{32}\ Cu\ N_8\ O_5\ S_4$
Formula weight	822.4	776.42
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, P/n2
Unit cell dimensions	a = 15.9070(4) Å	a = 13.9020(4) Å
	b = 15.6950(4) Å β = 118.3131(10)°	b = 9.1690(2) Å β = 107.6010(12)°
	c = 17.4540(5) Å	c = 14.4230(4) Å
Volume	3836.27(18) A^3	1752.40(8) A^3
Z	4	4
Calculated density	1.424 Mg/m^3	1.471 Mg/m^3
Absorption coefficient	0.840 mm^{-1}	0.912 mm^{-1}
F(000)	1708	802
Crystal size	0.15 × 0.19 × 0.25 mm	0.16 × 0.14 × 0.12 mm
θ range for data collection	1.93 to 27.48°	1.78 to 27.49°
Limiting indices	$-20 \le h \le 20$, $-18 \le k \le 20$, $-22 \le l \le 22$	$-17 \le h \le 17$, $-10 \le k \le 11$, $-18 \le l \le 18$
Reflections collected/unique	15037 / 8768 [R(int) = 0.0553]	6948 / 3998 [R(int) = 0.0575]
Completeness to θ = 27.48	99.7 %	99.6 %
Data/restraints/parameters	8768 / 0 / 456	3998 / 0 / 224
Goodness-of-fit on F^2	1.041	1.016
Final R indices [I>2σ(I)]	R1 = 0.0630, wR2 = 0.1681	R1 = 0.0533, wR2 = 0.1324
R indices (all data)	R1 = 0.1538, wR2 = 0.2461	R1 = 0.1140, wR2 = 0.1753
Largest diff. Peak and hole	0.697 and −1.148 e$^-$ Å^{-3}	0.183 and −0.191 e$^-$ Å^{-3}

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