

Crystal structure and spectroscopic properties of aquadichlorido{1,1'-[(pyridine-2,6-diyl- κ N)bis(methylene)]bis(4-butyl-4,5-dihydro-1H-1,2,4-triazole-5-thione- κ N²)}cobalt(II)

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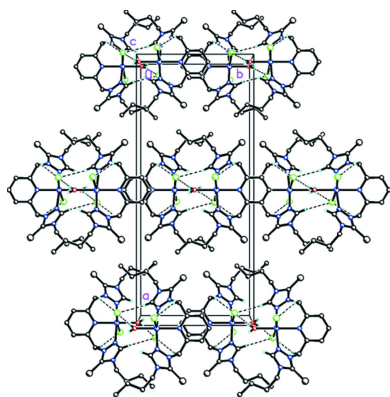
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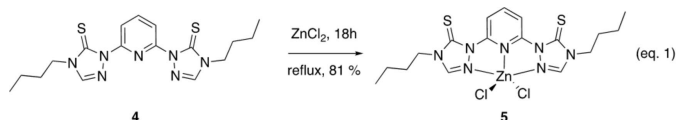
The structure of the title compound, [CoCl₂(C₁₉H₂₇N₇S₂)(H₂O)], at 173 K has monoclinic (*C*2/*c*) symmetry. We report here the synthesis, single-crystal structure, electrospray mass spectrum and NMR spectroscopy of a new six-coordinate cobalt(II) pincer complex. The pincer ligand, in this complex, which is novel, coordinates *via* three nitrogen atoms (two triazole and one pyridine). The ligand is ambidentate and can coordinate *via* three nitrogen atoms or two sulfur and one nitrogen atoms. The cobalt(II) metal center has pseudo-octahedral geometry and based on the single-crystal structure, the pincer ligand coordinates in a meridional fashion with the metal and adjacent six-membered ring ligands all in a similar plane and forming two slightly distorted boat configurations. The other two coordinated monodentate ligands are one water molecule and two chloride ions with four cobalt(II) complexes in the unit cell. The asymmetric unit of the complex is comprised of half the pyridine ring and water molecule with the Co^{II} atom at the center of the pincer situated about a twofold axis. The Co–N, Co–O, and Co–Cl bond lengths are consistent with single bonds. In the crystal, the complex forms a three-centre bifurcated weak hydrogen-bonding interaction with a chlorine ion, forming one intermolecular interaction with the pincer group and a water molecule and a second intramolecular interaction with a C–H group within the pincer group. Crystal packing is also highlighted with *C*₂(6)*a*<*a* infinite chains forming along [001] supported by *R*₂²(8)*a*>*a* ring motifs, forming a three-dimensional supramolecular network structure. While some stacking of the pyridine rings in the unit cell is observed, there are no relevant π – π interactions in the crystal packing. The ¹H and ¹³C{¹H} NMR spectra of the complex are consistent with a plane of symmetry being present. The electrospray mass spectrum, which was collected in positive ion mode, showed the loss of one water molecule and one chloride ligand from the complex. In the future, we plan to screen this cobalt(II) complex for electrocatalysis reactivity.



1. Chemical context

Pincer ligands are tridentate ligands that coordinate to metal centers either in a meridional or facial manner (Peris & Crabtree, 2018; Gunanathan & Milstein, 2014). The resulting pincer complexes are robust and have been utilized as catalysts in a variety of reactions (Szabó & Wendt, 2014). Pincer complexes can be prepared using a wide range of metal centers. The donor atoms of the pincer ligand to the metal can be carbon, oxygen, nitrogen, phosphorous, or sulfur (Peris &

Crabtree, 2018). Pincer ligand precursors can be tuned electronically by including electron-withdrawing or electron-donating groups, and sterically by including bulky substituents (van Koten & Milstein, 2013; van Koten & Gossage, 2015). Previously, Miecznikowski and co-workers prepared tridentate pincer ligand precursors with sulfur, nitrogen and sulfur donor atoms (Miecznikowski *et al.*, 2011, 2012) (Fig. 1). The pincer ligand precursors were metallated with zinc(II)chloride in order to prepare zinc(II) model complexes of liver alcohol dehydrogenase (Miecznikowski *et al.*, 2011, 2012) (see reaction scheme below). In 2012, Miecznikowski and co-workers reported the preparation of a pincer ligand precursor based on a bis-triazole starting material that could coordinate *via* sulfur, nitrogen, and sulfur donor atoms or *via* three nitrogen donor atoms (Miecznikowski *et al.*, 2012). It was reported that the novel ambidentate tridentate pincer ligand precursor was metallated with $ZnCl_2$ to give a new tridentate NNN-bound pincer zinc(II) pincer complex: dichloro(η^3 -*N,N,N*-[2,6-bis(3-[*N*-butyl]triazol-5-thione-1-yl)]pyridine)zinc(II), [(NNN)ZnCl₂] (Fig. 1).



In this study, our aim was to prepare a cobalt(II) pincer complex that contained a pincer ligand precursor with methylene moieties connecting each triazole substituent to the pyridine in the pincer ligand precursor (Fig. 2). We wondered if the cobalt(II) metal center would coordinate to the pincer ligand *via* three nitrogen atoms as observed for the zinc(II) complex or *via* sulfur, nitrogen, and sulfur donor atoms. In this communication, we report the preparation, spectroscopic characterization, electrospray mass spectrometry, and single crystal structure of a cobalt(II) pincer complex that contains an ambidentate ligand (Fig. 2).

2. Structural commentary

We report here the synthesis, single crystal structure, electrospray mass spectrum and NMR spectroscopy of a new six-coordinate cobalt(II) pincer complex, $C_{19}H_{29}Cl_2CoN_7OS_2$, at 173 K whose structure has monoclinic ($C2/c$) symmetry (Fig. 3). The pincer ligand, in this complex, which is novel, coordinates *via* three nitrogen atoms (two triazole and one

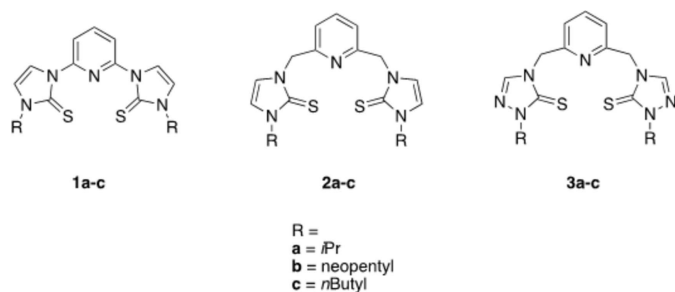


Figure 1
SNS ligand precursors prepared by Miecznikowski *et al.* (2011, 2012).

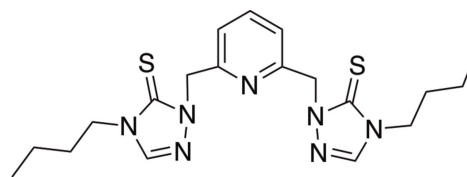


Figure 2
Structure of the ambidentate pincer ligand precursor.

pyridine). The ligand is ambidentate and can coordinate *via* three nitrogen atoms or two sulfur and one nitrogen atom. The cobalt(II) metal center has a pseudo-octahedral geometry and based on the single crystal structure, the pincer ligand coordinates in a meridional fashion with the metal and adjacent six-membered ring ligands all in a similar plane and forming two slightly distorted boat configurations [Co1/N2/N2/C3/C4/N4: $Q1 = 0.743(6) \text{ \AA}$, $\theta = 89.9^\circ$, $\varphi = 345.8(5)^\circ$; Co1/N4/C4A/C3A/N2A/N1A (atoms with the suffix A are generated by the symmetry operation $1 - x, y, -z + \frac{1}{2}$): $Q2 = 0.743(6) \text{ \AA}$, $\theta = 90.1(5)^\circ$, $\varphi = 185.3(5)^\circ$] (Cremer & Pople, 1975). The other two coordinated monodentate ligands are one water molecule and two chloride ions with four cobalt(II) complexes in the unit cell. The asymmetric unit of the complex is comprised of half the pyridine ring and water molecule with the Co^{II} atom at the center of the pincer situated about a twofold axis. The Co–N, Co–O, and Co–Cl bond lengths are consistent with single bonds. The cobalt–nitrogen (triazole) and cobalt–nitrogen (pyridine) bond lengths are comparable to those previously reported [triazole Co–N = 2.127(2) and 2.093(2) \AA ; pyridine Co–N = 2.187(3) \AA (Fang *et al.*, 2019)]. The Co–O(water)

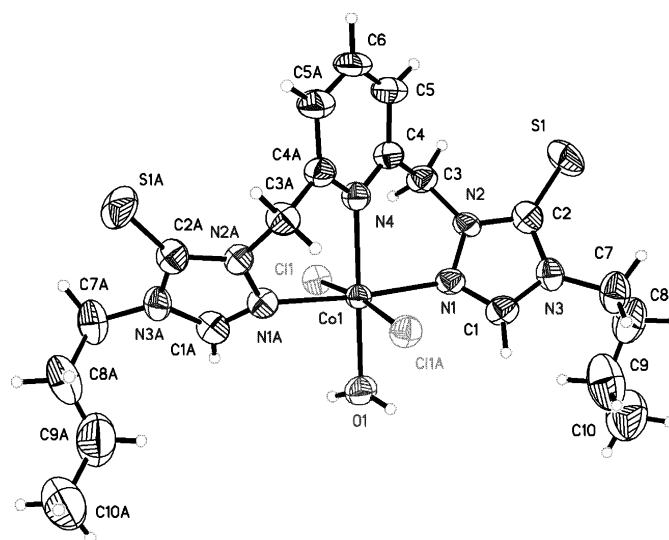


Figure 3
A view of the molecular structure of $C_{19}H_{29}Cl_2CoN_7OS_2$, **8**, showing the atom-labeling scheme and displacement ellipsoids drawn at the 30% probability level. The molecule crystallizes in the $C2/c$ space group with a twofold rotation axis perpendicular to a *c*-glide plane along the center of the pincer ligand through to the metal ion transforming the two asymmetric units into the complete complex and containing four cobalt(II) complexes per unit cell. Atoms with the suffix A are generated by the symmetry operation $1 - x, y, -z + \frac{1}{2}$.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots Cl ⁱ	0.84	2.24	3.075 (4)	171
C1—H1A \cdots O1 ⁱⁱ	0.95	2.69	3.429 (7)	135
C3—H3A \cdots Cl1	0.99	2.55	3.360 (8)	138

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 1, -y + 1, -z + 1$.

bond length is comparable to previously reported values [2.09 (3) Å; See *et al.*, 1998]. The cobalt–chloride bond lengths are longer than previously reported (2.31 Å; Di Vaira & Orioli, 1965). The C=S bond length of 1.655 (7) Å is more consistent with a carbon–sulfur double bond (1.61 Å; Trzhtsinskaya & Abramova, 1991).

3. Supramolecular features

In the crystal, the complex forms a three-centre bifurcated weak hydrogen-bonding interaction (Table 1) with a chlorine ion, forming one intermolecular interaction with the pincer group and a water molecule and a second intramolecular interaction with a C–H group within the pincer group. The crystal packing is also highly supported by $R_2^2(8)>a>a$ ring motifs, forming a three-dimensional supramolecular network structure (Fig. 4). While some stacking of the pyridine rings in the unit cell is observed, there are no relevant π – π interactions or classical hydrogen bonds in the crystal packing. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complex are consistent with a

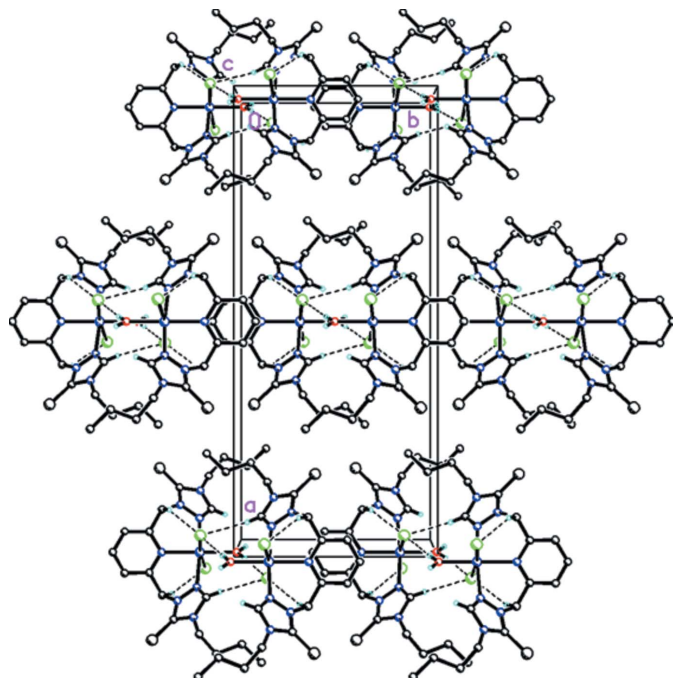


Figure 4
A view of the packing and the unit cell along the c axis for the title complex, **8**. Dashed lines indicate $C_2^2(6)>a<a$ infinite chains forming along (001) and $R_2^2(8)>a>a$ ring motifs forming a three-dimensional supramolecular network structure. Stacking of the pyridyl rings face-to-face along the c axis is observed.

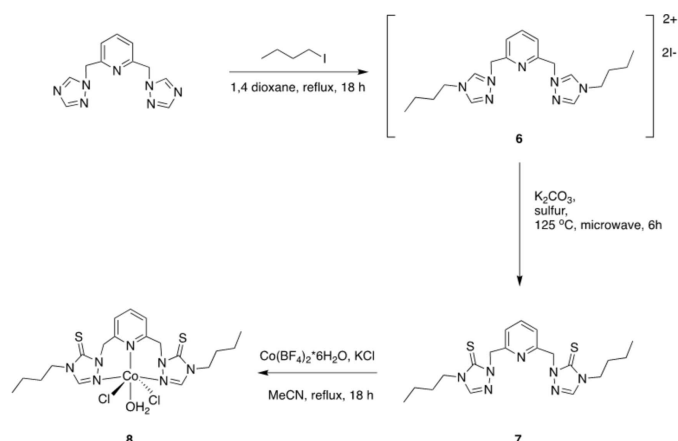
plane of symmetry being present. The electrospray mass spectrum, which was collected in positive ion mode, showed the loss of one water molecule and one chloride ligand from the complex (see Fig. S1 in the supporting information). In the future, we plan to screen this cobalt(II) complex for electrocatalysis reactivity.

4. Database survey

The NNN pincer ligand precursor used in this study is novel. A related NNN pincer ligand, **4**, has only been metallated with ZnCl_2 to afford a five-coordinate zinc(II) complex (Miecznikowski *et al.*, 2013). To the best of our knowledge (following a search using Sci-Finder Scholar) no other metal complexes that contain this ligand precursor have been reported in the literature.

5. Synthesis and crystallization

The preparation of the title complex, **8**, and the corresponding ligand precursors **6** and **7** were accomplished according to the scheme below. The precursor for complex **6** has been reported previously (Guino-o *et al.*, 2015).



2,6-Bis[(4-butyl-4H-1,2,4-triazol-1-yl)methyl]pyridine diiodide (Miecznikowski *et al.*, 2011): In a 100 ml round-bottom flask, 3.0501 g (0.0126 mol) of 2,6-bis[(1H-1,2,4-triazol-1-yl)methyl]pyridine was dissolved in 25 ml of 1,4 dioxane. To this solution 13.958 g (0.0759 mol) of iodobutane were added. This solution was heated at reflux for 18 h. After allowing the solution to cool, the mother liquor was decanted off. The precipitate was dissolved in minimal methanol and transferred to a round-bottom flask. The solvent was then removed under reduced pressure. Yield: 3.85 g (0.00748 mol) (59.4% yield).

The product was characterized using ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

^1H NMR (DMSO- d_6 , 400 Mhz): δ 10.32 (s, 2H, triazole, CH), 9.30 (s, 2H, triazole, CH), 7.97 (m, 1H, pyridine CH), 7.52 (m, 2H, pyridine CH), 5.75 (s, 4H, CH_2 linker), 4.32 (m, 4H, n -butyl CH_2), 1.85 (m, 4H, n -butyl CH_2), 1.32 (m, 4H, n -butyl CH_2), 0.92 (m, 6H, n -butyl CH_3). **$^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 100 Mhz):** δ 152.59 (pyridine C), 144.91 (triazole CH), 143.51 (triazole CH), 138.95 (pyridine CH), 122.85 (pyridine CH),

Table 2
Experimental details.

Crystal data	
Chemical formula	[CoCl ₂ (C ₁₉ H ₂₇ N ₇ S ₂)(H ₂ O)]
<i>M_r</i>	565.44
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	26.3412 (8), 11.4270 (3), 8.6226 (3)
β (°)	90.465 (3)
<i>V</i> (Å ³)	2595.31 (13)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	8.80
Crystal size (mm)	0.32 × 0.24 × 0.1
Data collection	
Diffractometer	Rigaku Oxford Diffraction Gemini Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.050, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7187, 2483, 1935
<i>R_{int}</i>	0.077
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.614
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.082, 0.235, 1.07
No. of reflections	2483
No. of parameters	149
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	1.40, -0.65

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015b), *SHELXL* (Sheldrick, 2015a) and *OLEX2* (Dolomanov *et al.*, 2009).

55.74 (CH₂ linker), 47.42 (*n*-butyl CH₂), 30.82 (*n*-butyl CH₂), 18.79 (*n*-butyl CH₂), 13.34 (*n*-butyl CH₃).

2,2'-[Pyridine-2,6-diylbis(methylene)]bis(4-butyl-1,2,4-triazole-3-thione) (Miecznikowski, 2012): In a 35 mL microwave reactor vessel, 0.2694 g (5.228 × 10⁻⁴ mol) of **6** were dissolved in 15 mL of MeCN. To this solution, 0.800 g (0.0249 mol) of sulfur and 0.2162 g (0.001564 mol) of potassium carbonate were added. This mixture was heated at 398 K for 6 h in the microwave reactor. After the reaction was complete, the undissolved solids were removed by vacuum filtration and the remaining solvent was removed under reduced pressure. The product was purified by dissolving the product in CH₂Cl₂ and filtering it through an alumina column to removed undissolved sulfur. Mass product = 0.0934 g (2.24 × 10⁻⁴ mol) (42.8% yield).

The product was characterized using ¹H and ¹³C{¹H} NMR spectroscopy. The key feature of the NMR is that one of the acidic protons of the triazole, δ 10.32 in **6** was absent in the product and was presumably replaced with the thione moiety. There was also considerable shifting, to lower ppm values, of the aromatic, methylene and *n*-butyl CH₂ proton resonances in **7** compared to the starting material **6**.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 8.65 (*s*, 2H, triazole, CH), 7.75 (*m*, 1H, pyridine CH), 7.02 (*s*, 2H, pyridine CH), 5.41 (*s*, 4H, CH₂ linker), 3.98 (*m*, 4H, *n*-butyl CH₂), 1.72 (*m*, 4H, *n*-butyl CH₂), 1.29 (*m*, 4H, *n*-butyl CH₂), 0.92 (*m*, 6H, *n*-butyl CH₃). **¹³C {¹H} NMR (DMSO-*d*₆, 100 MHz),** δ 166.03 (C=S), 155.02 (pyridine C), 141.41 (triazole CH), 137.92 (pyridine CH), 120.23 (pyridine CH), 53.03 (CH₂ linker), 45.14 (*n*-butyl

CH₂), 29.91 (*n*-butyl CH₂), 19.04 (*n*-butyl CH₂), 13.47 (*n*-butyl CH₃).

Aquadichloro-(*n*3-*N,N,N*)-[2,6-diylbis(methylene)]bis(4-[*N*-butyl]triazol-5-thione-1-yl)]pyridinecobalt(II) [C₁₉H₂₉Cl₂N₇OS₂Co]: In a 100mL round-bottom flask, 0.0934 g (2.24 × 10⁻⁴ mol) of (C₁₉H₂₇N₇S₂) were combined with 0.076 g (2.2 × 10⁻⁴ mol) of cobalt(II)tetrafluoroborate [Co(BF₄)₂·6H₂O] and combined with 0.0333 g (4.43 × 10⁻⁴ moles) of potassium chloride (KCl) and dissolved in 10 mL of acetonitrile. The solution was refluxed for 20 h. The following day, the solution was filtered to remove undissolved material and the solvent was removed under reduced pressure. Yield: 0.162 grams (quantitative). Purple needle-shaped crystals suitable for X-ray diffraction were grown by a slow vapor diffusion of diethyl ether in to an acetonitrile solution containing the cobalt complex.

Analysis calculated for [C₁₉H₂₉Cl₂CoN₇S₂]·H₂O: (583.46): C, 39.11; H, 5.36; N, 16.80. Found: C, 39.33; H, 5.07; N, 17.11.

¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.61 (*s*, 2H, triazole, CH), 7.71 (*t*, 1H, pyridine CH), 6.91 (*d*, 2H pyridine CH), 5.37 (*s*, 4H, CH₂ linker), 3.95 (*m*, 4H, *n*-butyl CH₂), 1.70 (*m*, 4H, *n*-butyl CH₂), 1.26 (*m*, 4H, *n*-butyl CH₂), 0.88 (*t*, 6H, *n*-butyl CH₃). **¹³C {¹H} NMR (DMSO-*d*₆, 100 MHz),** δ 164.95 (C=S), 153.93 (pyridine C), 140.47 (triazole CH), 136.91 (pyridine CH), 119.19 (pyridine CH), 51.98 (CH₂ linker), 44.13 (*n*-butyl CH₂), 28.87 (*n*-butyl CH₂), 18.01 (*n*-butyl CH₂), 12.47 (*n*-butyl CH₃).

The ¹H NMR and ¹³C{¹H} spectrum of the complex was acquired in DMSO-*d*₆. The NMR spectrum was consistent with the title complex. There was not considerable shifting of the proton resonances compared to the starting bis-thione precursor. In the ¹³C{¹H} NMR spectrum, the C=S resonance shifted about δ 1 ppm to a lower chemical shift value.

The cyclic voltammograms of **7** and **8** are given in Figs. S1 and S2, respectively, in the supporting information. In both **7** and **8** the supporting electrolyte is 0.2 *M* tetrabutylammonium tetrafluoroborate. The reference electrode is Ag wire, the working electrode is glassy carbon and the counter electrode is a platinum wire. The scan rate is 100 mV s⁻¹.

Electronic absorption spectrum of 8 in acetonitrile (1.89 mM) (see Fig. S4 in the supporting information): UV–Visible data: λ (nm), ϵ (M⁻¹cm⁻¹) (1.89 mM in MeCN) 234.00 (2480); 244.00 (2480); 368.00 (158); 574.00 nm (sh) (386); 589.00 (428); 682.00 (648).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were positioned geometrically (O–H = 0.84, C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O, C\text{-methyl})$.

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supporting information

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Crystal structure and spectroscopic properties of aquadichlorido{1,1'-[(pyridine-2,6-diyl- κ N)bis(methylene)]bis(4-butyl-4,5-dihydro-1H-1,2,4-triazole-5-thione- κ N²)}cobalt(II)

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: ShelXT (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015a); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Aquadichlorido{1,1'-[(pyridine-2,6-diyl- κ N)bis(methylene)]bis(4-butyl-4,5-dihydro-1H-1,2,4-triazole-5-thione- κ N²)}cobalt(II)

Crystal data

[CoCl₂(C₁₉H₂₇N₇S₂)(H₂O)]

$M_r = 565.44$

Monoclinic, *C2/c*

$a = 26.3412$ (8) Å

$b = 11.4270$ (3) Å

$c = 8.6226$ (3) Å

$\beta = 90.465$ (3)°

$V = 2595.31$ (13) Å³

$Z = 4$

$F(000) = 1172$

$D_x = 1.447$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 3680 reflections

$\theta = 5.1\text{--}71.4^\circ$

$\mu = 8.80$ mm⁻¹

$T = 173$ K

Plate, violet

0.32 × 0.24 × 0.1 mm

Data collection

Rigaku Oxford Diffraction Gemini Eos diffractometer

Detector resolution: 16.0416 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.050$, $T_{\max} = 1.000$

7187 measured reflections

2483 independent reflections

1935 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.077$

$\theta_{\max} = 71.3^\circ$, $\theta_{\min} = 3.4^\circ$

$h = -31 \rightarrow 32$

$k = -14 \rightarrow 13$

$l = -10 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.082$

$wR(F^2) = 0.235$

$S = 1.07$

2483 reflections

149 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0964P)^2 + 26.3272P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.40 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.65 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2018/1
 (Sheldrick 2015b),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0012 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.500000	0.67881 (12)	0.250000	0.0337 (5)
Cl1	0.54526 (6)	0.66425 (15)	0.00348 (19)	0.0453 (5)
S1	0.67541 (8)	0.8989 (2)	0.5267 (3)	0.0709 (7)
O1	0.500000	0.4946 (6)	0.250000	0.0528 (18)
H1	0.490570	0.453156	0.174640	0.079*
N1	0.5694 (2)	0.6878 (5)	0.3822 (6)	0.0404 (13)
N2	0.5993 (2)	0.7856 (5)	0.3730 (7)	0.0400 (13)
N3	0.6244 (2)	0.6944 (6)	0.5757 (7)	0.0439 (14)
N4	0.500000	0.8712 (7)	0.250000	0.0396 (17)
C1	0.5856 (3)	0.6350 (7)	0.5066 (8)	0.0451 (16)
H1A	0.571981	0.563686	0.544692	0.054*
C2	0.6333 (3)	0.7948 (7)	0.4898 (9)	0.0472 (17)
C3	0.5931 (3)	0.8675 (6)	0.2452 (9)	0.0454 (16)
H3A	0.594825	0.824119	0.145975	0.054*
H3B	0.621543	0.924266	0.247439	0.054*
C4	0.5441 (3)	0.9327 (6)	0.2516 (8)	0.0456 (16)
C5	0.5448 (4)	1.0553 (7)	0.2553 (11)	0.065 (2)
H5	0.576185	1.096191	0.261514	0.078*
C6	0.500000	1.1154 (10)	0.250000	0.076 (4)
H6	0.500000	1.198536	0.250002	0.092*
C7	0.6532 (3)	0.6589 (9)	0.7150 (10)	0.065 (2)
H7A	0.629478	0.621798	0.788644	0.078*
H7B	0.666974	0.730085	0.765450	0.078*
C8	0.6957 (4)	0.5769 (11)	0.6865 (13)	0.083 (3)
H8A	0.717687	0.573444	0.780111	0.100*
H8B	0.716444	0.606952	0.599897	0.100*
C9	0.6777 (5)	0.4566 (15)	0.6479 (17)	0.116 (5)
H9A	0.661282	0.459438	0.544311	0.139*
H9B	0.651149	0.435140	0.723408	0.139*
C10	0.7162 (6)	0.3608 (15)	0.6464 (19)	0.125 (5)
H10A	0.743434	0.381083	0.574431	0.188*
H10B	0.700015	0.287769	0.612867	0.188*
H10C	0.730446	0.350724	0.750896	0.188*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0320 (7)	0.0305 (8)	0.0387 (8)	0.000	-0.0011 (6)	0.000
Cl1	0.0447 (9)	0.0495 (10)	0.0417 (9)	0.0014 (7)	0.0047 (7)	-0.0035 (7)
S1	0.0442 (10)	0.0749 (15)	0.0934 (17)	-0.0210 (10)	-0.0088 (10)	-0.0141 (12)
O1	0.079 (5)	0.038 (4)	0.041 (4)	0.000	-0.007 (3)	0.000
N1	0.035 (3)	0.041 (3)	0.045 (3)	-0.008 (2)	0.003 (2)	0.005 (2)
N2	0.032 (3)	0.037 (3)	0.052 (3)	-0.013 (2)	-0.002 (2)	0.004 (2)
N3	0.028 (3)	0.058 (4)	0.046 (3)	-0.002 (2)	-0.001 (2)	-0.001 (3)
N4	0.041 (4)	0.037 (4)	0.041 (4)	0.000	-0.001 (3)	0.000
C1	0.037 (3)	0.047 (4)	0.052 (4)	0.000 (3)	0.009 (3)	0.010 (3)
C2	0.031 (3)	0.053 (4)	0.058 (4)	-0.002 (3)	0.003 (3)	-0.002 (3)
C3	0.041 (4)	0.043 (4)	0.052 (4)	-0.010 (3)	0.005 (3)	0.008 (3)
C4	0.052 (4)	0.040 (4)	0.045 (4)	-0.003 (3)	-0.002 (3)	0.001 (3)
C5	0.072 (5)	0.038 (4)	0.086 (6)	-0.008 (4)	-0.014 (5)	0.006 (4)
C6	0.080 (9)	0.030 (6)	0.119 (12)	0.000	-0.035 (8)	0.000
C7	0.043 (4)	0.096 (7)	0.055 (5)	-0.001 (4)	-0.004 (4)	0.006 (5)
C8	0.057 (5)	0.117 (10)	0.075 (6)	0.012 (6)	-0.011 (5)	0.012 (6)
C9	0.089 (8)	0.154 (14)	0.104 (10)	0.022 (9)	-0.028 (7)	-0.035 (9)
C10	0.106 (10)	0.141 (13)	0.129 (12)	0.026 (10)	-0.028 (9)	0.008 (10)

Geometric parameters (\AA , $^\circ$)

Co1—Cl1	2.4512 (16)	C3—H3A	0.9900
Co1—Cl1 ⁱ	2.4512 (16)	C3—H3B	0.9900
Co1—O1	2.104 (7)	C3—C4	1.493 (10)
Co1—N1	2.149 (6)	C4—C5	1.401 (11)
Co1—N1 ⁱ	2.148 (6)	C5—H5	0.9500
Co1—N4	2.198 (8)	C5—C6	1.367 (11)
S1—C2	1.655 (7)	C6—H6	0.9500
O1—H1	0.8403	C7—H7A	0.9900
O1—H1 ⁱ	0.8403	C7—H7B	0.9900
N1—N2	1.370 (7)	C7—C8	1.482 (14)
N1—C1	1.300 (9)	C8—H8A	0.9900
N2—C2	1.346 (9)	C8—H8B	0.9900
N2—C3	1.454 (9)	C8—C9	1.491 (18)
N3—C1	1.360 (9)	C9—H9A	0.9900
N3—C2	1.387 (10)	C9—H9B	0.9900
N3—C7	1.472 (10)	C9—C10	1.493 (19)
N4—C4 ⁱ	1.357 (8)	C10—H10A	0.9800
N4—C4	1.357 (8)	C10—H10B	0.9800
C1—H1A	0.9500	C10—H10C	0.9800
Cl1 ⁱ —Co1—Cl1	172.22 (10)	N2—C3—C4	112.6 (6)
O1—Co1—Cl1 ⁱ	86.11 (5)	H3A—C3—H3B	107.8
O1—Co1—Cl1	86.11 (5)	C4—C3—H3A	109.1
O1—Co1—N1 ⁱ	92.74 (16)	C4—C3—H3B	109.1

O1—Co1—N1	92.74 (16)	N4—C4—C3	118.8 (6)
O1—Co1—N4	180.0	N4—C4—C5	122.0 (8)
N1 ⁱ —Co1—Cl1 ⁱ	92.61 (15)	C5—C4—C3	119.2 (7)
N1—Co1—Cl1	92.61 (15)	C4—C5—H5	120.3
N1—Co1—Cl1 ⁱ	87.76 (15)	C6—C5—C4	119.3 (9)
N1 ⁱ —Co1—Cl1	87.76 (15)	C6—C5—H5	120.3
N1 ⁱ —Co1—N1	174.5 (3)	C5—C6—C5 ⁱ	119.7 (11)
N1 ⁱ —Co1—N4	87.26 (16)	C5—C6—H6	120.2
N1—Co1—N4	87.26 (16)	C5 ⁱ —C6—H6	120.2
N4—Co1—Cl1	93.89 (5)	N3—C7—H7A	108.5
N4—Co1—Cl1 ⁱ	93.89 (5)	N3—C7—H7B	108.5
Co1—O1—H1	124.3	N3—C7—C8	115.1 (8)
Co1—O1—H1 ⁱ	124.346 (2)	H7A—C7—H7B	107.5
H1—O1—H1 ⁱ	111.3	C8—C7—H7A	108.5
N2—N1—Co1	119.7 (4)	C8—C7—H7B	108.5
C1—N1—Co1	133.5 (5)	C7—C8—H8A	109.1
C1—N1—N2	103.9 (6)	C7—C8—H8B	109.1
N1—N2—C3	120.5 (5)	C7—C8—C9	112.3 (9)
C2—N2—N1	113.6 (6)	H8A—C8—H8B	107.9
C2—N2—C3	125.9 (6)	C9—C8—H8A	109.1
C1—N3—C2	108.0 (6)	C9—C8—H8B	109.1
C1—N3—C7	126.9 (7)	C8—C9—H9A	107.9
C2—N3—C7	125.1 (6)	C8—C9—H9B	107.9
C4 ⁱ —N4—Co1	121.2 (4)	C8—C9—C10	117.6 (11)
C4—N4—Co1	121.2 (4)	H9A—C9—H9B	107.2
C4 ⁱ —N4—C4	117.6 (8)	C10—C9—H9A	107.9
N1—C1—N3	111.8 (6)	C10—C9—H9B	107.9
N1—C1—H1A	124.1	C9—C10—H10A	109.5
N3—C1—H1A	124.1	C9—C10—H10B	109.5
N2—C2—S1	129.8 (6)	C9—C10—H10C	109.5
N2—C2—N3	102.7 (6)	H10A—C10—H10B	109.5
N3—C2—S1	127.5 (6)	H10A—C10—H10C	109.5
N2—C3—H3A	109.1	H10B—C10—H10C	109.5
N2—C3—H3B	109.1		
Co1—N1—N2—C2	162.7 (5)	C1—N3—C2—N2	-1.2 (8)
Co1—N1—N2—C3	-17.8 (8)	C1—N3—C7—C8	83.9 (10)
Co1—N1—C1—N3	-160.2 (5)	C2—N2—C3—C4	-111.9 (8)
Co1—N4—C4—C3	3.1 (7)	C2—N3—C1—N1	1.0 (8)
Co1—N4—C4—C5	-178.5 (6)	C2—N3—C7—C8	-94.5 (11)
N1—N2—C2—S1	-178.3 (6)	C3—N2—C2—S1	2.3 (11)
N1—N2—C2—N3	1.1 (8)	C3—N2—C2—N3	-178.4 (6)
N1—N2—C3—C4	68.7 (8)	C3—C4—C5—C6	175.3 (6)
N2—N1—C1—N3	-0.3 (8)	C4 ⁱ —N4—C4—C3	-176.9 (7)
N2—C3—C4—N4	-58.7 (8)	C4 ⁱ —N4—C4—C5	1.5 (6)
N2—C3—C4—C5	122.8 (8)	C4—C5—C6—C5 ⁱ	1.5 (6)
N3—C7—C8—C9	-72.6 (12)	C7—N3—C1—N1	-177.6 (7)
N4—C4—C5—C6	-3.1 (12)	C7—N3—C2—S1	-3.1 (11)

C1—N1—N2—C2	-0.5 (8)	C7—N3—C2—N2	177.5 (7)
C1—N1—N2—C3	179.0 (6)	C7—C8—C9—C10	-168.6 (12)
C1—N3—C2—S1	178.2 (6)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...C11 ⁱⁱ	0.84	2.24	3.075 (4)	171
C1—H1A...O1 ⁱⁱⁱ	0.95	2.69	3.429 (7)	135
C3—H3A...C11	0.99	2.55	3.360 (8)	138

Symmetry codes: (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$.