



Synthesis through proton transfer reaction, structure and spectroscopic characterization of novel anionic nickel(II) complex with pyridine-2,6-dicarboxylic acid and 4-aminobenzenesulfonamide

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ABSTRACT

A novel nickel complex of the formula moiety, $(C_6 H_9 N_2 O_2 S)_2^{2+} [Ni (C_{14} H_6 N_2 O_8)]^{2-} (C_6 H_8 N_2 O_2 S).4(H_2O)$ was synthesized and its crystal structure determined by X-ray diffraction and characterized by IR and UV-VIS spectroscopy. The complex crystallizes in the monoclinic system and $P2_1/c$ space group. It has a distorted octahedral structure, consisting of six-coordinated Ni (II) unit with two pyridine-2,6-dicarboxylate ligands through O,N,O' -tridentate coordination mode. XRD structure shows that two dipic ligands are almost perpendicular to each other. Extensive hydrogen bonding, $C-H \cdots \pi$ and $\pi \cdots \pi$ interactions lead to the formation of 3D supramolecular framework.

Keywords: Nickel(II) complex; Structure; Supramolecular framework; FTIR, XRD.

INTRODUCTION

The preparation and characterization of a proton-transfer compounds have been considered by chemists in recent years [1]. A review on the literature showed that dicarboxylic containing fragments in the resulting proton transfer compounds can function as suitable ligands in the synthesis of metal-organo complexes [2-3]. In this regard, 2,6-Pyridinedicarboxylic acid is found to be suitable ligand for this project as it is well known versatile N,O chelator in co-ordination chemistry due to its diverse coordination modes [4-7], and also because of its relevance to the development of more effective anti-HIV agents [8-10], effects on insulin-mimetic [7,11], applications in Crystal engineering, bioinorganic, aqueous chemistry and biological functions and other potential applications [12-14]. As a part of my project on designing and

synthesizing new mixed ligand complexes of transition metal containing isomers of dipic ligands, I herein, report the synthesis, crystal structure and spectroscopic characterization of the title complex.

MATERIALS AND METHODS

Materials : Nickel chloride, Pyridine-2,6-dicarboxylic acid (H₂dipic) and 4-aminobenzenesulfonamide (ABS) were purchased from Sigma-Aldrich and methanol from Merck. Except methanol, other chemicals were used without further purification.

Synthesis : 2mmol of ABS (0.68g) was dissolved in 20ml of methanol and to it was added NiCl₂ (1mmol, 0.129g). It was diluted to 40ml by addition of methanol and refluxed for one hour. 2 mmol of H₂dipic (0.33g), dissolved in 20 ml of methanol, was added drop wise. Clear green colored solution was obtained which was concentrated to 30ml and kept for crystallization. After 10 days, light-green needles appeared. It was filtered and washed with cold methanol and dried in air. Yield: 34%. Anal. Cal. for C₃₂ H₄₀ N₈ Ni O₁₈ S₃ (%): C, 39.236; H, 4.116; N, 11.439; Ni, 5.992; O, 29.398; S, 9. Found(%): C, 39.912; H, 3.902; N, 11.247; S, 9.0406.

Physical Measurements : Elemental analyses for C, H, N and S were carried out on Flash 2000 Organic Elemental Analyzer. UV-Vis spectra was measured on a Shimadzu UV-2450 PC spectrophotometer at room temperature. Infrared (IR) spectra were recorded on a Nicolet iS10 instrument using KBr pellets. The single crystal X-ray structure was performed on an Oxford Diffraction Xcalibur Diffractometer equipped with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073\text{\AA}$) at 300°K.

X-Ray crystallography

A suitable single crystal of title compound (C₃₂ H₄₀ N₈ Ni O₁₈ S₃) was selected and mounted on a Xcalibur, Eos Diffractometer. Using Olex2 [15], the structure was solved with the ShelXS [16] structure solution program by Direct Methods. Refinements were performed using the ShelXL [17] refinement package using Least Squares minimization. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were placed in calculated positions with a C–H bond distance of 0.93Å. Table 1 lists crystallographic details. For further details on the crystal structure investigations and refinements, see the ‘‘Supplementary material’’.

Table-1: Crystal data and structure refinement

Identification code	TS-Ni-11	Z	4
Empirical formula	C ₃₂ H ₄₀ N ₈ Ni O ₁₈ S ₃	μ (mm ⁻¹)	0.716
Formula weight	979.62	ρ_{calc} (mg/mm ³)	1.595
Temperature	300 K	F(000)	2032.0
Crystal system	monoclinic	Crystal size/mm ³	0.6 × 0.1 × 0.08
Space group	P2 ₁ /c	θ range for data collection	5.44 to 50°
a	7.1237(6) Å	Index ranges	-8 ≤ h ≤ 8, -39 ≤ k ≤ 37, -18 ≤ l ≤ 20
b	33.223(5) Å	Reflections collected	17794
c	17.5142(17) Å	Independent reflections	7193[R(int) = 0.0564]
α	90.00°	Data/restraints/parameters	7193/4/622
β	100.284(8)°	Goodness-of-fit on F ²	0.924
γ	90.00°	Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0621, wR ₂ = 0.1486
Volume,	4078.5(8) Å ³	Final R indexes [all data]	R ₁ = 0.1151, wR ₂ = 0.1875

RESULTS AND DISCUSSION

Spectroscopic Characterization : IR spectra were recorded in the range 4000-400 cm^{-1} . The $\nu(\text{O-H})$ associated with free water molecules are observed as very strong and broad bands in 3566.9 – 3383 cm^{-1} region typically with a maxima at 3482.3 cm^{-1} . The peak at 3264 cm^{-1} may be assigned to $-\text{NH}_2$ (aromatic amine). Predominant vibrations of H_2dipic associated with O-H are 2800 cm^{-1} $\{\nu(\text{O-H})\}$, 1417 cm^{-1} $\{\delta(\text{O-H})\}$ and 927 cm^{-1} $\{\gamma(\text{O-H})\}$ [18-20]. However, none of these bands were observed, indicating the deprotonation of $-\text{COOH}$ group and coordination with the Ni(II). In the unidentate carboxylate complex, $\nu(\text{C=O})$ is higher than $\nu_{\text{as}}(\text{COO}^-)$ and $\nu(\text{C-O})$ is lower than $\nu_{\text{s}}(\text{COO}^-)$ [21]. As a result, the separation between $\nu(\text{C=O})$ and $\nu(\text{C-O})$ is much larger in unidentate complexes than in the free carboxylate ion. In this Ni(II) complex, the presence of $-\text{COO}^-$ group is revealed by IR spectrum which shows absorption bands at 1667 and 1385 cm^{-1} corresponding to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ vibrations respectively. Large difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, $\Delta\nu = 262 \text{ cm}^{-1}$, suggests a unidentate binding mode of the carboxylate group to the Ni(II) ion. The peak observed at 1289.1 and 1152 cm^{-1} can be assigned to $\nu_{\text{as}}(\text{SO}_2)$ and $\nu_{\text{s}}(\text{SO}_2)$ respectively. Normally, the S-N stretching vibration of free ABS exhibits a moderate band in the region ca. $905 \pm 30 \text{ cm}^{-1}$. In the present study also, the band was observed at 908 cm^{-1} unshifted. This brings to the light that the $-\text{NH}_2$ group of ABS is not involved in the coordination with the metal ion. The interpretations of IR spectra are well supported by XRD structure.

The UV visible spectra of the complex was recorded in a methanolic solution in the range of 200 to 800nm. The UV-VIS spectra shows peaks at 268nm and 210nm, which may be assigned to ligand-centered $n-\pi^*$ and $\pi-\pi^*$ respectively. Like in the case of a similar complex reported [22], d-d and charge transfer peaks were not observed.

Description of the crystal structure : The reaction of ABS, nickel chloride and H_2dipic in methanolic solution resulted in the formation of air stable title compound, $(\text{C}_6 \text{H}_9 \text{N}_2 \text{O}_2 \text{S})_2^{2+} [\text{Ni} (\text{C}_{14} \text{H}_6 \text{N}_2 \text{O}_8)]^{2-} (\text{C}_6 \text{H}_8 \text{N}_2 \text{O}_2 \text{S})_4(\text{H}_2\text{O})$ or $(\text{ABSH})_2 [\text{Ni}(\text{dipic})_2] (\text{ABS})_4\text{H}_2\text{O}$ (where dipic is pyridine-2,6-dicarboxylate and ABSH is 4-ammoniumbenzenesulfonamide). The two dipic ligands are coordinated to Ni^{2+} via their carboxylates and nitrogen donors resulting in the formation of anionic nickel complex; $[\text{Ni}(\text{dipic})_2]^{2-}$. The $[\text{Ni}(\text{dipic})_2]^{2-}$ divalent anion is charge-balanced by two ABSH monovalent cations. The longer C-N bond distances (due to charge repulsion) of ABSH (1.462Å) than that of ABS (1.355 Å) is indicative of ABS being protonated. This is further supported by the longer N-H bond lengths in ABSH than in ABS.

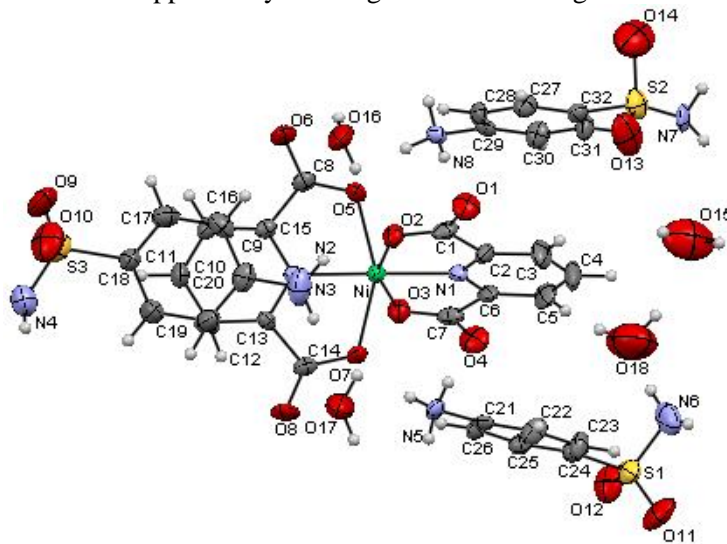


Figure-1: ORTEP structure of the title compound viewed along *a* direction with atom numbering scheme (50% displacement ellipsoids). Hydrogen atoms are not labeled for clarity.

XRD structure shows that the central nickel(II) ion is coordinated by two dipic ligands through O,N,O'-tridentate coordination mode (Fig-1 & 2). This also reveals that only one oxygen atom of each carboxylate group is involved in coordination, i.e., each carboxylate group in a ligand is acting as a monodentate donor, which is supported by infrared data as discussed earlier. The geometry of the resulting NiN₂O₄ coordination can be described as distorted octahedron. The Ni-N bond length varies from 1.970(4) to 1.985(4) Å and Ni-O distances vary from 2.134(3) to 2.149(3) Å which lie within the previously reported values of similar complex {[Ni(dipic)₂ Ni(H₂O)₅].2H₂O} [23]. The two dianionic (dipic)²⁻ units are almost perpendicular to each other as the bond angles of all O-Ni-O' are very close to 90°, i.e., 88° for {O(5)-Ni-O(2)}, 97° {O(5)-Ni-O(3)}, 96° {O(7)-Ni-O(2)}, and 88° {O(7)-Ni-O(3)} and also the bond angle of N(1)-Ni-N(2) is 178.67° which is very close to 180°. From the bond angles it can be inferred that the nitrogen atoms, N(1) and N(2), are placed in the axial positions, one above and the other below the horizontal plane and the four oxygen atoms, O(2), O(3), O(5) and O(7), are occupying the equatorial position in the distorted octahedral complex (Figure-2). Some important bond lengths and bond angles are listed in the Table-2 and Table-3 respectively.

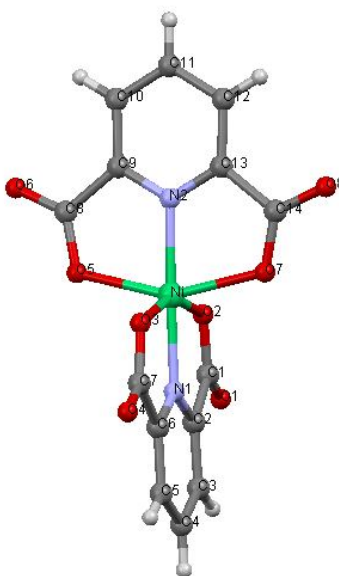


Figure-2: Structure of the title compound viewed along *c*-axis, showing the nitrogen and oxygen atoms occupying the axial and equatorial positions respectively. Other moieties are removed for clarity.

Table -2: Selected bond lengths

Atom	Atom	Length/Å
Ni	N1	1.970(4)
Ni	N2	1.985(4)
Ni	O2	2.145(3)
Ni	O3	2.149(3)
Ni	O5	2.134(3)
Ni	O7	2.138(3)
N3	C15	1.359(7)
N5	C21	1.461(6)
N8	C29	1.456(6)

Table -3: Selected Bond angles

Atom	Atom	Atom	Angle/°
O5	Ni	O7	154.55(14)
O5	Ni	O2	88.06(12)
O5	Ni	O3	97.82(13)
O7	Ni	O2	96.89(12)
O7	Ni	O3	88.50(12)
O2	Ni	O3	154.27(14)
N2	Ni	O5	77.44(14)
N2	Ni	O7	77.10(14)
N2	Ni	O2	101.82(13)

N3	H3B	0.852(4)	N2	Ni	O3	103.91(13)
N5	H5C	0.990(5)	N1	Ni	O5	103.59(14)
N8	H8C	0.937(6)	N1	Ni	O7	101.85(14)
			N1	Ni	O2	77.44(13)
			N1	Ni	N2	178.67(14)
			N1	Ni	O3	76.83(13)

The crystal packing is stabilized by an intermolecular O-H...O and N-H...O hydrogen bonding interactions. The ABSH cations are acting as H-donors to form strong intermolecular hydrogen bondings [N(8)-H(8C)...O(5) and N(5)-H(5B)...O(7)] with the two coordinated O atoms [O(5) and O(7)] and also with the two non-coordinated O atoms of the chelating dipic ligands [N(8)-H(8B)...O(6) and N(5)-H(5A)...O(8)]. Intermolecular H-bondings formed by water lattice molecules play an important role in bridging the two amide groups of ABSH and ABS [N(4)-H(4B)...O(15) and N(6)-H(6B)...O(18)]. Also, they connect the amino group of ABS and the dipic ligand [N(3)-H(3B)...O(17) and O(17)-H(17B)...O(8)], contributing to the formation of 2D supramolecular network (Fig-3). The distances of all N...O being 2.708 to 3.002 Å, are suitable for the normal N...O hydrogen bond distances (2.73-3.03 Å) [24-27]. Table-4 list the main hydrogen bond distances and angles.

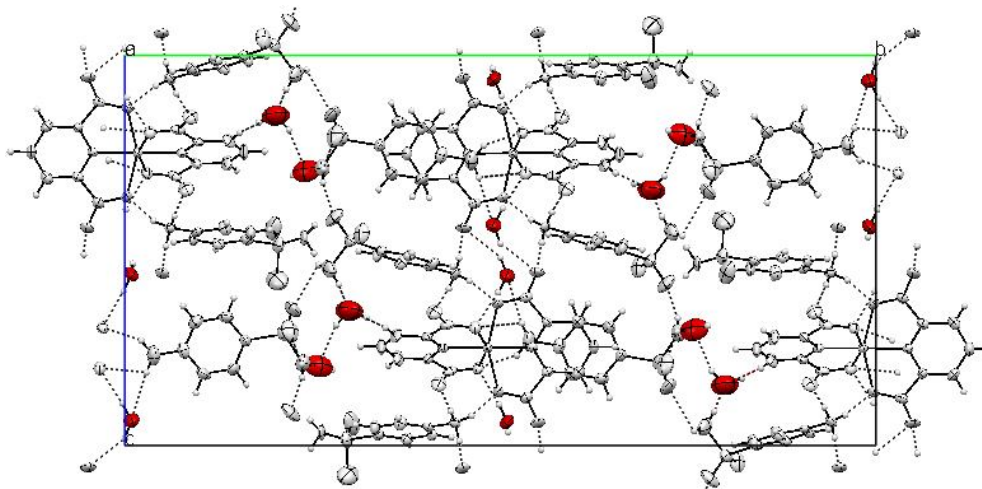


Figure-3: Crystal Packing diagram along *a* axis including 2D supramolecular network connected by hydrogen bonding interactions (dashed lines). Oxygen atoms of water molecules are colored.

Table-4: Selected geometrical parameters of hydrogen bonds (Å and °)

D—H...A	d(D—H)/ Å	d(H...A)/ Å	d(D...A)/ Å	d(D...A)/Å	∠ (DHA)/°
N3-H3A...O2	0.85(4)	2.33(5)	2.999(6)	136(4)	136.01
N3-H3B...O3	0.85(4)	2.59(7)	3.020(6)	113(5)	112.34
N3-H3B...O17	0.85(4)	2.36(5)	3.205(7)	171(8)	172.11
N4-H4A...O11	0.82(5)	2.44(5)	3.236(8)	164(5)	163.66
N4-H4B...O15	0.97(6)	2.07(6)	2.988(9)	156(6)	156.42
N5-H5A...O8	0.86(7)	1.92(6)	2.769(6)	167(6)	167.35
N5-H5B...O7	0.85(5)	1.89(5)	2.727(6)	169(5)	168.55

N5-H5C...O4	0.99(5)	1.69(5)	2.678(6)	175(3)	175.09
N6-H6B...O18	1.07(9)	1.94(10)	3.002(11)	169(6)	168.73
N8-H8A...O1	0.87(4)	1.82(4)	2.688(6)	173(3)	173.13
N8-H8B...O6	0.91(5)	1.95(4)	2.792(6)	153(4)	153.20
N8-H8C...O5	0.94(6)	1.80(6)	2.708(6)	164(5)	163.70
O17-H17B...O8	1.02(11)	2.27(10)	2.873(6)	117(6)	115.20
O18-H18A...O15	0.8500	2.0100	2.8264	161.00	159.99
C5-H5...O18	0.9300	2.5800	3.501(11)	172.00	171.81
C23-H23...N7	0.9300	2.5900	3.505(7)	169.00	168.83

In addition, there are other weak hydrogen bonding interactions of the types C-H...O and C-H...N and C-H... π and π ... π stacking interactions which altogether further extend from 2D network to 3D supramolecular framework (Fig-4). The C-H... π distances range from 2.860 to 2.948 Å while the distances of π ... π interactions (centroid-centroid) between the two neighboring aromatic rings range from 3.754 to 3.952 Å (Fig-5).

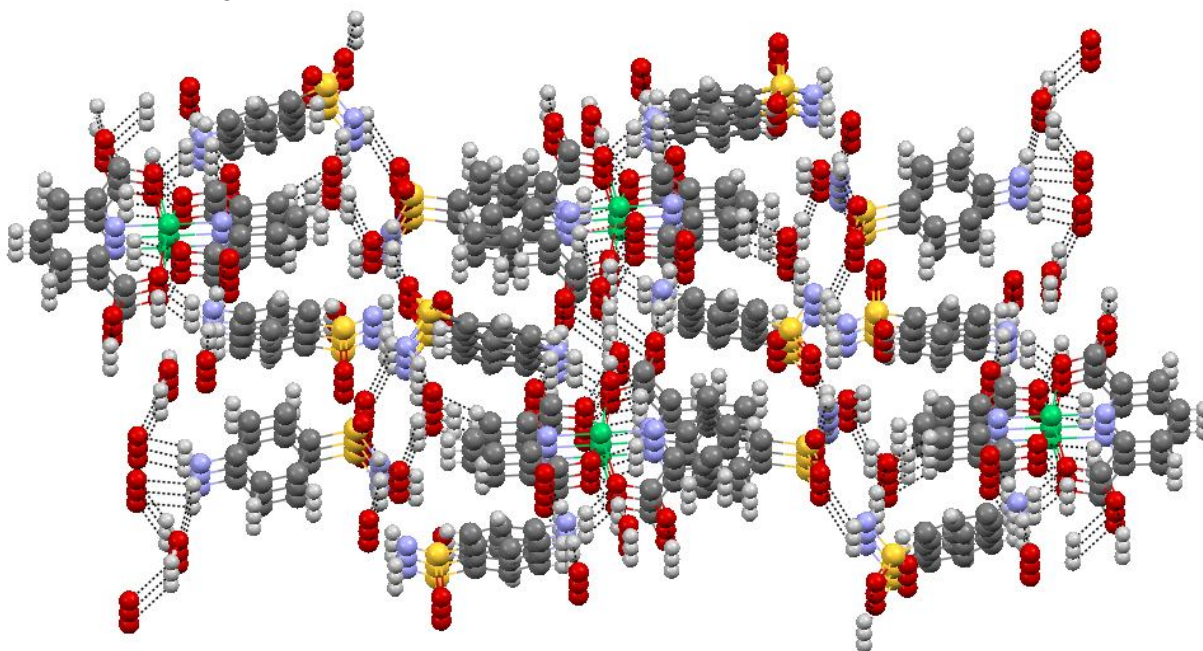


Figure-4: The 3D supramolecular framework of the title compound connected by extensive hydrogen bonding, C-H... π and π ... π stacking interactions.

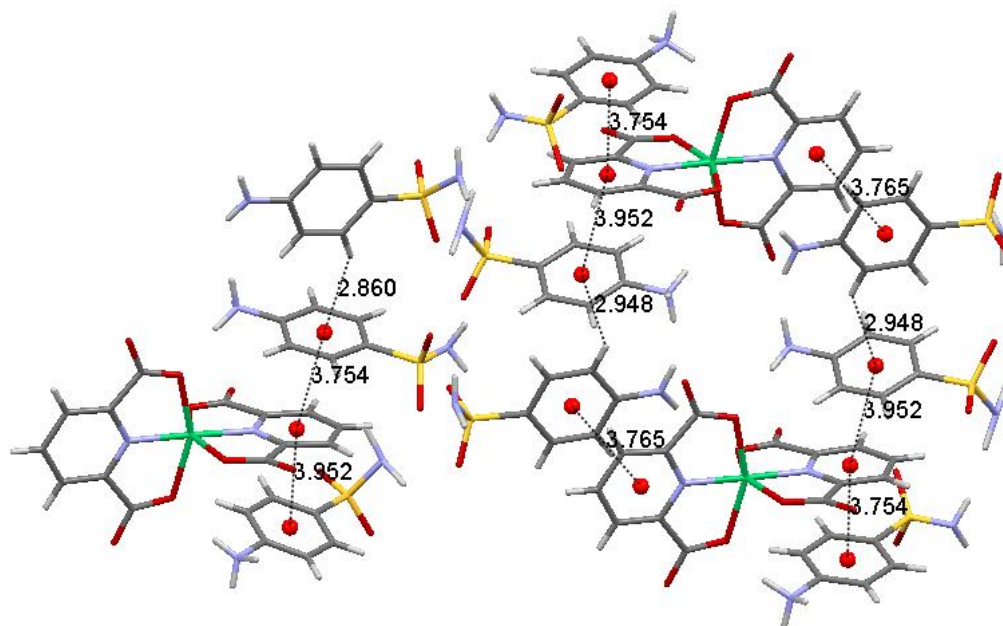


Figure-5: The C-H $\cdots\pi$ and $\pi\cdots\pi$ stacking interactions and their distances (Å). Water molecules are removed for clarity.

APPLICATIONS

This anionic Nickel(II) complex is expected to be a potential anti-microbial agent and homogeneous catalyst in organic conversions. These studies are underway.

CONCLUSIONS

A novel anionic complex of Ni(II) with Pyridine-2,6-dicarboxylic acid and 4-aminobenzenesulfonamide was successfully synthesized through proton transfer reaction. The carboxylate groups are deprotonated while the aniline groups of ABS gets protonated and thus the anionic nickel(II) complex is charge-balanced. The complex has distorted octahedral structure and the two dipic ligands are almost perpendicular to each other. The supramolecular framework is largely a consequence of a wide range of non-covalent interactions, consisting of hydrogen bonding, C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions.

Supplementary material : CCDC 861494 contains the supplementary crystallographic data of this complex and it can be obtained free of charge from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: 044-(0)1223-762-910, Fax: 044-(0)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk].

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