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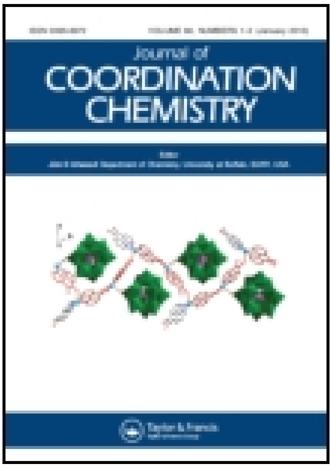

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N′-(3-Bromo-2-hydroxybenzylidene)isonicotinohydrazide and its oxovanadium(V) complex: synthesis, structures, and catalytic properties

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N′-(3-Bromo-2-hydroxybenzylidene)isonicotinohydrazide and its oxovanadium(V) complex: synthesis, structures, and catalytic properties

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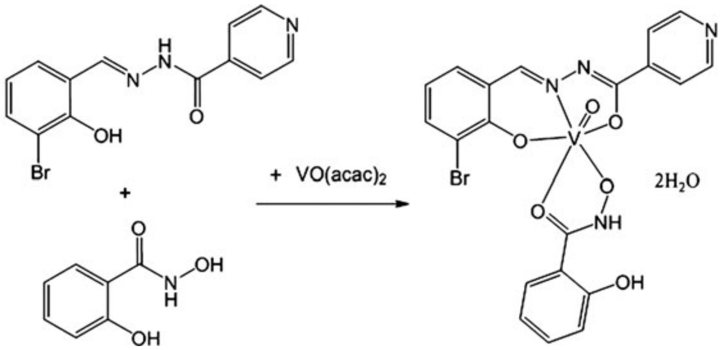

A new hydrazone *N′*-(3-bromo-2-hydroxybenzylidene)isonicotinohydrazide (H_2L) and its oxovanadium(V) complex, [VOLL′]·$2H_2O$ (L′ = 2-hydroxybenzohydroxamate), were prepared and structurally characterized by physico-chemical, spectroscopic methods, and single-crystal X-ray determination. The hydrazone coordinates to V through the phenolate oxygen, imino nitrogen, and enolate oxygen. The hydroxamate coordinates to V through the carbonyl oxygen and deprotonated hydroxyl oxygen. Vanadium in the complex is octahedral. The oxidation of olefins with the complex as catalyst was evaluated, which indicated that the complex showed catalytic efficiency in oxidation of several aliphatic and aromatic substrates under mild conditions, using *tert*-butyl hydrogen peroxide as oxidant.

Keywords: Schiff base; Oxovanadium complex; X-ray diffraction; Catalytic property; Coordination

1. Introduction

The catalytic epoxidation of olefins has been a subject of growing interest in the production of chemicals and fine chemicals since epoxides are key starting materials for a wide variety of products [1–3]. Great work has been carried out to explore new and efficient catalysts for these reactions. H_2O_2 has been used as the oxidant in these reactions because of its environment-friendly characteristic. Vanadium enzymes, such as vanadium-nitrogenases and

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vanadate-dependent haloperoxidases, have been found in nature [4–6]. Vanadium complexes with various organic ligands have shown interesting catalytic properties in many organic reactions [7–10]. Hydrazones are a polydentate ligand in coordination chemistry. The synthesis, characterization, and reactivity studies of oxovanadium complexes with hydrazone ligands have been reported [11–14]. Some of the complexes show interesting catalytic properties [15–17]. As an extension of work on such fields, and to explore more efficient oxidization catalysts, in the present article, a new hydrazone, *N'*-(3-bromo-2-hydroxybenzylidene)isonicotinohydrazide (H_2L), and its oxovanadium(V) complex, [VOLL′]·$2H_2O$ (L′ = 2-hydroxybenzohydroxamate), were prepared and characterized (scheme 1).

2. Experimental

2.1. *Materials and physical measurements*

All chemical reagents were of analytical reagent grade, purchased from Xiya Chemical Reagent Company. Microanalyses (C, H, and N) were performed using a Perkin Elmer 2400 elemental analyzer. Infrared spectra were carried out using a JASCO FT-IR model 420 spectrophotometer with KBr disks from 4000 to 200 cm^{-1}. UV–vis spectra were measured with a Perkin Elmer Lambda 18 spectrophotometer. GC analyses were carried out using a Shimadzu GC-2014C gas chromatograph. ^1H NMR spectra were recorded on a Bruker instrument at 400 MHz.

2.2. *Synthesis of H_2L*

A hot methanol solution (30 mL) of 3-bromosalicylaldehyde (10 mM, 2.01 g) was added to a hot methanol solution (30 mL) of isonicotinohydrazide (10 mM, 1.37 g). The mixture was stirred for 30 min at reflux, and the solvent was evaporated to dryness. Recrystallization from methanol gave single crystals of the compound. Yield: 93%. M.p. 163.0–165.0. Anal. Calcd for $C_{13}H_{10}BrN_3O_2$ (H_2L): C, 48.8; H, 3.1; N, 13.1. Found: C, 48.7; H, 3.2; N, 13.3%. ^1H NMR (DMSO-d_6): δ: 12.61 (s, 1H), 12.39 (s, 1H), 8.82 (s, 2H), 8.61 (s, 1H), 7.86 (d, 2H), 7.66 (dd, J = 7.9, 1.3 Hz, 1H), 7.57 (dd, J = 7.7, 1.4 Hz, 1H), 6.93 (t, 1H).

2.3. *Synthesis of [VOLL′]·$2H_2O$*

A hot methanol solution (15 mL) of $VO(acac)_2$ (1 mM, 0.26 g) was added to a hot methanol solution (15 mL) of H_2L (1 mM, 0.32 g). Then, 2-hydroxybenzohydroxamic acid (1 mM, 0.15 g) dissolved in 10 mL of water was added to the solution. The mixture was stirred for 30 min at reflux, and then cooled to room temperature, to give a brown solution. Single crystals of the complex, suitable for X-ray diffraction, were formed by slow evaporation of the methanol solution containing the complex in air for few days. Yield: 55%. Anal. Calcd for $C_{20}H_{18}BrN_4O_8$ V: C, 41.9; H, 3.2; N, 9.8. Found: C, 41.7; H, 3.1; N, 9.9%.

2.4. *X-ray diffraction*

X-ray diffraction was performed using a Bruker APEX2 CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to the established procedures where Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a wide range of 2θ angles. The positions of non-hydrogen atoms were located with direct methods. Subsequent Fourier syntheses were used to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. The amino H in H_2L and the water H in the complex were located from difference Fourier maps and refined isotropically. The remaining hydrogens were placed in calculated positions and constrained to ride on their parent atoms. The analysis was performed with the aid of SHELXS-97 and SHELXL-97 suite of codes [18, 19]. Crystallographic data for the complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

2.5. *Catalytic oxidation*

Catalytic experiments were carried out in a 50 mL glass round-bottom flask fitted with a reflux condenser and placed in an oil bath at prearranged temperature under continuous stirring. The oxidation was carried out as follows: the complex (0.032 mM) was dissolved in 10 mL of 1,2-dichloroethane. Then, 10 mM alkene was added to the reaction mixture and 30 mM TBHP was added. The reaction mixture was refluxed for 1 h. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

Table 1. Crystal data for H_2L and the complex.

	1	**2**
Chemical Formula	$C_{13}H_{10}BrN_3O_2$	$C_{20}H_{18}BrN_4O_8$ V
Fw	320.2	573.2
Crystal shape/color	Block/colorless	Block/brown
Crystal size (mm)	0.20 × 0.20 × 0.17	0.17 × 0.16 × 0.13
T (K)	298(2)	298(2)
λ (MoKα) (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$I2/a$
a (Å)	10.773(1)	19.8749(3)
b (Å)	16.131(2)	11.5570(2)
c (Å)	15.020(2)	19.4798(4)
β (°)	109.318(4)	93.179(2)
V (Å^3)	2463.2(4)	4467.5(1)
Z	8	8
μ (MoKα) (cm^{-1})	3.339	2.288
F (0 0 0)	1280	2304
T (min)	0.5548	0.6970
T (max)	0.6007	0.7552
D_{Calcd} (g cm^{-3})	1.727	1.705
Collected reflections	24,700	28,579
Unique reflections	4586	5554
Observed reflections [$I \geq 2\sigma(I)$]	3877	4322
Parameters	351	335
Restraints	2	9
Goodness of fit on F^2	1.040	1.062
R_1 [$I \geq 2\sigma(I)$]	0.0276	0.0389
wR_2 [$I \geq 2\sigma(I)$]	0.0646	0.0946
R_1 (all data)	0.0370	0.0587
wR_2 (all data)	0.0683	0.1036

Table 2. Selected bond lengths (Å) and angles (°) for H_2L and the complex.

H_2L			
Bond lengths			
C7–N1	1.275(3)	N1–N2	1.379(2)
N2–C8	1.353(3)	C8–O2	1.212(3)
C20–N4	1.274(3)	N4–N5	1.380(2)
N5–C21	1.355(3)	C21–O4	1.209(3)
The complex			
Bond lengths			
V1–O1	1.8754(13)	V1–O2	1.9679(13)
V1–O3	1.8719(13)	V1–O4	2.1849(13)
V1–O6	1.5868(14)	V1–N1	2.0884(17)
C7–N1	1.287(3)	N1–N2	1.399(2)
N2–C8	1.299(3)	C8–O2	1.301(2)
Bond angles			
O6–V1–O3	93.37(7)	O6–V1–O1	97.94(7)
O3–V1–O1	109.66(6)	O6–V1–O2	102.94(6)
O3–V1–O2	89.18(6)	O1–V1–O2	150.95(6)
O6–V1–N1	94.55(7)	O3–V1–N1	163.18(6)
O1–V1–N1	83.90(6)	O2–V1–N1	74.59(6)
O6–V1–O4	168.03(6)	O3–V1–O4	76.07(5)
O1–V1–O4	80.70(5)	O2–V1–O4	82.83(5)
N1–V1–O4	97.12(6)		

3. Results and discussion

The hydrazone ligand H_2L was readily prepared by condensation of equimolar quantities of 3-bromosalicylaldehyde with isonicotinohydrazide in methanol. The complex was synthesized by reaction of $VO(acac)_2$ with H_2L and 2-hydroxybenzohydroxamic acid in methanol in a 1 : 1 : 1 M proportion at reflux. Chemical formulas of the compounds have been confirmed by elemental analyses, IR spectra, and X-ray single-crystal structure determination.

3.1. *Structure description of H_2L and the complex*

Molecular structures of H_2L and the complex are presented in figures 1 and 2, respectively. There are two independent molecules in the asymmetric unit of H_2L. In both molecules of H_2L, the intramolecular O–H···N hydrogen bonds (table 3) make S(6) ring motifs [20]. The dihedral angles between the benzene and the pyridine rings of both molecules are 15.2(3)° and 22.5(3)°. The hydrazone coordinates to V through the phenolate oxygen, imino nitrogen, and enolate oxygen. The 2-hydroxybenzohydroxamate ligand coordinates through the carbonyl oxygen and hydroxy oxygen. The coordination geometry around V can be described as distorted octahedral, with the three donors of the hydrazone and the hydroxy oxygen of 2-hydroxybenzohydroxamate ligand defining the equatorial plane, and with the carbonyl oxygen of 2-hydroxybenzohydroxamate occupying one axial position. The other axial position of the octahedral coordination is furnished with an oxo. The hydrazone ligand coordinates to V in a meridional fashion forming five- and six-membered chelate rings with bite angles of 74.59(6)° and 83.90(6)°, which are similar to those observed in similar vanadium complexes [21, 22]. The displacement of V from the equatorial mean plane towards the axial oxo is 0.233(2) Å. The hydrazone is coordinated in its dianionic enolate form, which is evident from the bond lengths of C8–O2 [1.301(2) Å] and C8–N2 [1.299(3) Å] in

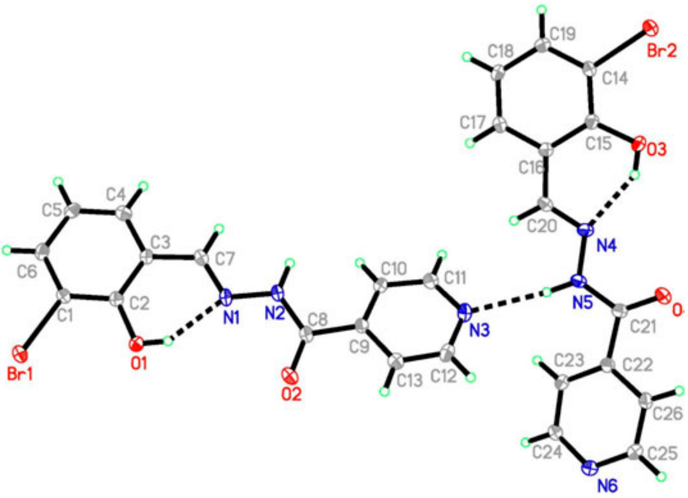


Figure 1. Molecular structure of H_2L with 30% probability thermal ellipsoids.

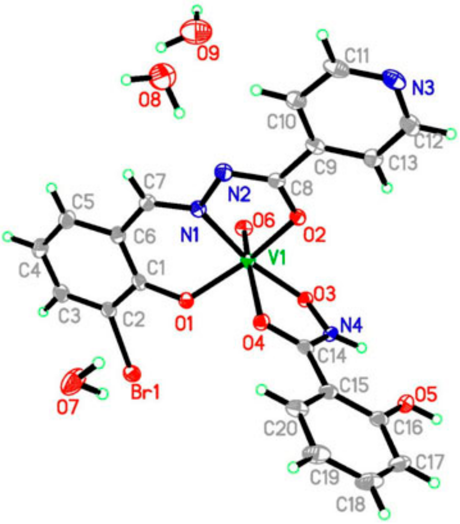


Figure 2. Molecular structure of the complex with 30% probability thermal ellipsoids.

the complex. The C8–O2 bond is much longer than the corresponding bonds (1.21 Å) in H_2L. The C8–N2 bond in the complex is much shorter than the corresponding bonds (1.35 Å) in H_2L. In addition, the C7–N1 [1.287(3) Å] in the complex is much longer than the corresponding value (1.27 Å) in H_2L. This indicates coordination through the imino nitrogen. The dihedral angle between the benzene and the pyridine rings of the hydrazone ligand of the complex is 13.8(3)°. The V–O, V–N, and V=O bonds in the complex are within normal ranges and similar to those observed in oxovanadium complexes with octahedral coordination [21–23].

Table 3. Distances (Å) and angles (°) involving hydrogen bonding of H_2L and the complex.

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	Angle (*D*–H···*A*)
H_2L				
O1–H1···N1	0.82	1.92	2.641(2)	146
O3–H3···N4	0.82	1.95	2.665(2)	146
N5–H5···N3	0.90(1)	2.26(1)	3.152(3)	174(3)
N2–H2···N6^{i}	0.90(1)	2.28(1)	3.160(3)	169(3)
The complex				
O9–H9B···N2^{ii}	0.96	2.128(2)	3.000(2)	151
O8–H8B···N2	0.96	1.845(7)	2.755(2)	158
O8–H8A···O4^{iii}	0.96	2.21(1)	3.032(2)	143
O7–H7B···N3^{iv}	0.96	1.878(2)	2.828(2)	171
O7–H7A···O9^{v}	0.96	2.022(2)	2.871(2)	147
O7–H7A···O9^{iii}	0.96	1.998(2)	2.832(2)	144
O5–H5···O7^{vi}	0.84	1.75	2.591(2)	173
N4–H4···O2^{vii}	0.88	2.44	3.099(2)	132
N4–H4···O5	0.88	1.92	2.587(2)	131

Note: Symmetry codes: (i) $-1 + x, y, z$; (ii) $3/2 + x, 1/2 + y, 3/2 + z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, 1/2 + y, 3/2 - z$; (v) $-1/2 + x, 1 - y, z$; (vi) $x, -1 + y, z$; (vii) $1 - x, -y, 1 - z$.

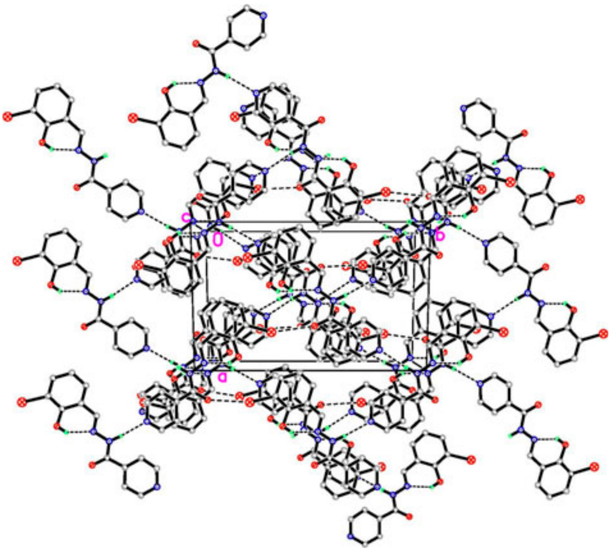


Figure 3. Molecular packing of H_2L. Hydrogen bonds are drawn as thin dashed lines.

In the crystal structures of both H_2L and the complex, molecules are linked through intermolecular hydrogen bonds (table 3), to form 3-D networks (figure 3 for H_2L, figure 4 for the complex).

3.2. *IR and UV–vis spectra*

The hydrazone shows stretching bands attributed to C=O, C=N, C–OH, and NH at 1685, 1617, 1146, and 3203 cm^{-1}, respectively. For the complex, the weak and sharp band

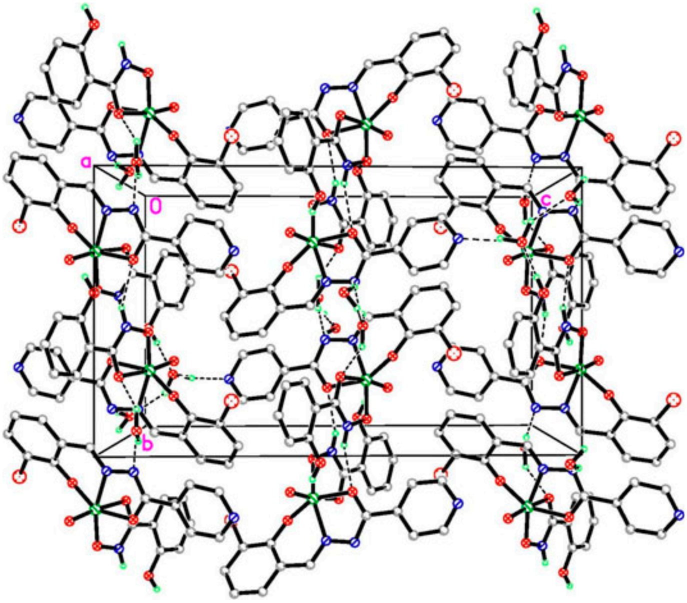
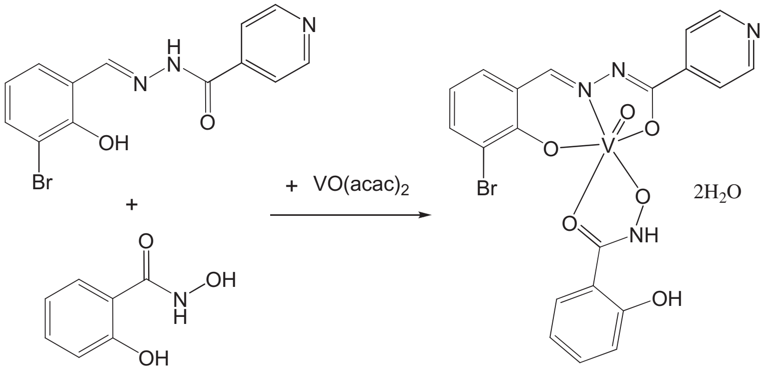


Figure 4. Molecular packing of the complex. Hydrogen bonds are drawn as thin dashed lines.

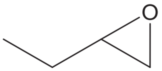
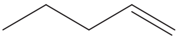
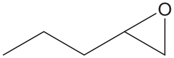
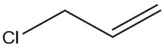
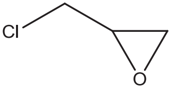
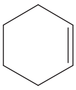
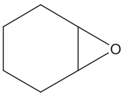
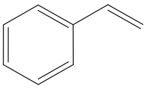
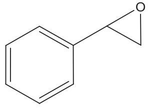
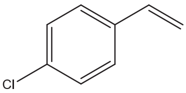
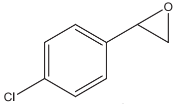
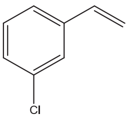
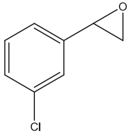
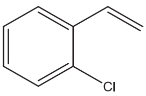
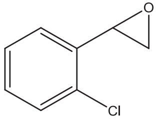


Scheme 1. The preparation of the complex.

indicative of the NH vibration is at 3277 cm^{-1}, and the weak and broad band indicative of the OH vibrations of water is centered at 3445 cm^{-1}. The strong band indicative of the C=N group of the complex is located at 1605 cm^{-1}. The V=O stretch occurs as a single sharp band at 985 cm^{-1} [24]. The weak peaks observed at low wave numbers (400–600 cm^{-1}) may be attributed to the V–O and V–N vibrations.

In the UV–vis region, H_2L shows bands at 215, 295, and 335 nm, and the complex shows bands at 221, 260, 350, and 450 nm. Weak bands at 400–500 nm were attributed to ligand-to-metal charge transfer from the p_π orbital on the phenolate oxygen to the empty d orbitals of the vanadium ion [25]. The bands in the region 310–350 nm for H_2L and the complex were assigned to n–π^* transitions [26]. The intense bands at 210–300 nm were assigned to intra-ligand π–π^* transitions [26].

Table 4. Catalytic oxidation of olefins catalyzed by the complex.[a]

Substrate	Product	Conversion (%)[b]
		74
		67
		80
		77
		87
		90
		96
		91

[a] The molar ratio of catalyst : substrate : TBHP is 1 : 300 : 1000. The reactions were performed in the mixture of CH_3OH/CH_2Cl_2 (V : V = 6 : 4; 1.5 mL).

[b] The GC conversion (%) was measured relative to the starting substrate after 1 h.

3.3. *Catalytic oxidation results*

The catalytic results are listed in table 4. Effective epoxide yields and 100% selectivity were observed for all aliphatic and aromatic substrates. In general, oxidation of aromatic substrates gave the corresponding epoxides in over 85% yields, while in the oxidation of aliphatic substrates, the conversion is lower than 80%. Based on this, isolated double bonds are less reactive than conjugated ones. For the aliphatic substrates, the conversion for the chloro-substituted methyloxirane is higher than the methyl or ethyl substituted species. For the aromatic substrates, the same phenomenon was observed. Thus, the complex has good catalytic properties on the chloro-substituted substrates.

4. Conclusion

A new hydrazone *N′*-(3-bromo-2-hydroxybenzylidene)isonicotinohydrazide was prepared and characterized. Based on this compound, a new oxovanadium(V) complex with 2-hydroxybenzohydroxamate as the co-ligand was prepared and characterized. Coordination of the ligand to V was discussed. The hydrazone ligand coordinates through the phenolate oxygen, imino nitrogen, and enolate oxygen. The complex is an effective catalyst for the oxidation of various aliphatic and aromatic olefins, especially for the chloro-substituted substrates.

Supplementary material

CCDC 1006767 for H_2L and 1006768 for the complex contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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