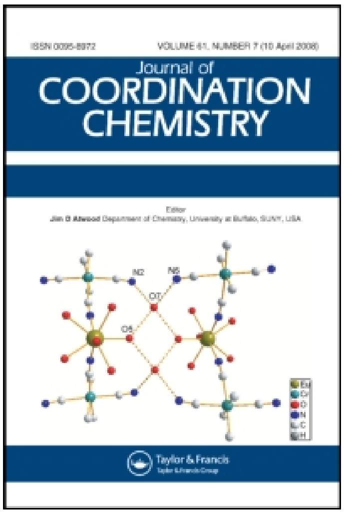

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Synthesis, structure, magnetism, and electrochemical properties of a linear pentanuclear Ni$_5$ compound derived from an oligo--pyridylamino ligand: Ni$_5$(-dmpdda)$_4$(NCS)$_2$

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Synthesis, structure, magnetism, and electrochemical properties of a linear pentanuclear Ni_5 compound derived from an oligo-α-pyridylamino ligand: $Ni_5(\mu\text{-dmpdda})_4(NCS)_2$

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The synthesis, crystal structures, electrochemical, and magnetic properties of a linear pentanuclear Ni_5 compound derived from an oligo-α-pyridylamino ligand, $[Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$ [dmpdda-H_2 = *N*,*N′*-di(4-methylpyridin-2-yl)pyridine-2,6-diamine], are reported. $Ni_5(\mu\text{-dmpdda})_4(NCS)_2$ involve a Ni_5 linear chain unit with all of the Ni–Ni–Ni angles being nearly 180°, terminated by two axial ligands. The pentanuclear linear metal chain is helically wrapped by four *syn–syn–syn–syn* type dmpdda^{2-} ligands. There are two types of Ni–Ni distances in this complex. Terminal Ni–Ni distances bonded with the axial ligand are longer (2.377 Å); the inner Ni–Ni distances are short at 2.2968 Å. Terminal Ni(II) ions bonded with the axial ligands are square-pyramidal (NiN_4NCS) with long Ni–N bonds (2.092 Å), consistent with a high-spin Ni(II) configuration. The inner three Ni(II) ions have short Ni–N (1.901–1.925 Å) bond distances, consistent with a square planar (NiN_4), diamagnetic arrangement of a low-spin Ni(II) configuration. This compound exhibits magnetic behavior similar to $[Ni_5(\mu\text{-tpda})_4(NCS)_2]$, indicating an antiferromagnetic interaction of two terminal high-spin Ni(II) ions.

Keywords: $Ni_5(\mu\text{-dmpdda})_4(NCS)_2$; Magnetism; Electrochemical; Structure

1. Introduction

Extended metal atom chain (EMAC) complexes are very important to a fundamental understanding of metal–metal interactions and in potential applications such as molecular metal wires and switches [1]. Two major lines of experimental development have been: (1) an extension to other metals, i.e., Cr, Co, Cu, Ru, and Rh, and (2) lengthening of the metal chains by use of longer polypyridylamide ligands. A series of tri- [2], tetra- [3], penta- [4], hexa- [5], hepta- [6], and nona-nuclear [7] metal string

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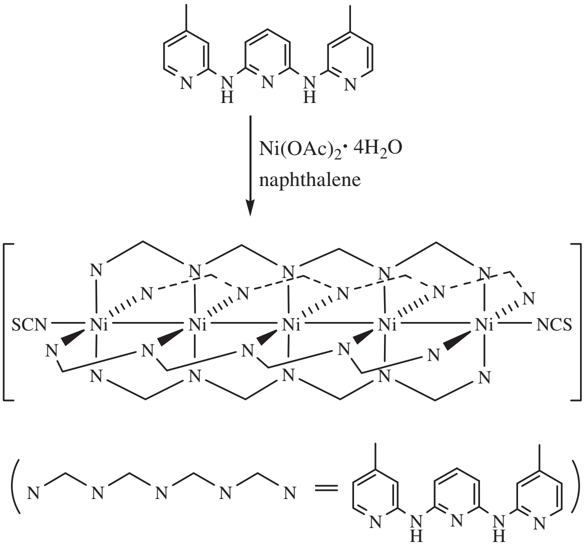
complexes have been synthesized. Development of Ni metal string is favored because Ni is more stable and active than Cr, Ru, etc. In 1968, $Ni_3(dpa)_4Cl_2$ was reported as trinuclear nickel EMAC [8]. Extensive work developed [9, 10] and the correct structure for this compound was recognized [11]. This development began to reveal the breadth of the field.

$[Ni_5(\mu_5\text{-tpda})_4C1_2]$ was reported as pentanickel EMAC [12]. Then $[Ni_5(\mu_5\text{-tpda})_4X_2]$ ($X = Cl^-, CN^-, N_3{}^-$, NCS^-) series was reported in 1998 [13]. In 1999, heptanuclear nickel metal string $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ was obtained [14]; then a nonanuclear nickel metal string $[Ni_9(\mu_9\text{-peptea})_4Cl_2]$ was synthesized [7]. In 2003, pyridine-modulated $[Ni_5(etpda)_4Cl_2]$ was obtained and studied for electrochemical and magnetic properties [15]. In this article, we use CH_3^- as an electron-releasing group to form a pentanuclear nickel complex, characterized by X-ray structure, and investigate its magnetic and electrochemical properties. The introduction of methyl to the ligand significantly improves the reactivity, resulting in very pure target compounds, and increases the compound activity. All these provide a base for various pyridine-modulated oligo-α-pyridylamino ligands.

2. Experimental

2.1. *General*

The ligand was synthesized by palladium catalyzed cross-coupling of aromatic amine and halide, in the presence of $Pd_2(dba)_3$, BINAP, Bu^tONa in refluxing benzene under argon (scheme 1), and characterized by MS(FAB) and IR. The $[Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$ compound was synthesized by reacting $Ni(OAc)_2 \cdot 4H_2O$ with dmpdda-H_2 in an argon atmosphere using naphthalene as solvent.



Scheme 1. The preparation of $Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$ complex.

The yield was high. The compound showed considerable solubility in common organic solvents such as CH_2Cl_2, chloroform, benzene, methanol, and acetone. IR spectra were performed with a Perkin Elmer FT-IR Spectrometer PARAGON 1000 from 400 to $4000\,cm^{-1}$. FAB-MS mass spectra were obtained with a JEOL JMS-700 HF double focusing spectrometer operating in the positive ion detection mode. Molar magnetic susceptibility was recorded on a SQUID system with 2000 Gauss external magnetic field. Electrochemistry was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in CH_2Cl_2 deoxygenated by purging with prepurified nitrogen. Cyclic voltammetry was conducted with the use of a homemade three-electrode cell equipped with a BAS glassy carbon ($0.07\,cm^2$) platinum ($0.02\,cm^2$) disk as the working electrode, a platinum wire as the auxiliary electrode, and a homemade Ag/AgCl (saturated) reference electrode. The reference electrode is separated from the bulk solution by a double junction filled with electrolyte solution. Potentials are reported *versus* Ag/AgCl (saturated) and referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple which occurs at $E_{1/2} = +0.54\,V$ *versus* Ag/AgCl (saturated). The working electrode was polished with 0.03 µm aluminium on Buehler felt pads and put under ultrasonic radiation for 1 min prior to each experiment. The reproducibility of individual potential values was within ±5 mV. The spectroelectrochemical experiments were accomplished with the use of a 1 mm cuvette, a 100 mesh platinum gauze as working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (saturated) reference electrode.

2.2. *Synthesis of H_2dmpdda*

A mixture of (4-methyl-2-pyridyl) amine (10.9 g, 0.1 mol), dibromopyridine (10 g, 0.42 mol), $Pd_2(dba)_3$ (0.77 g, 2 mol%), BINAP (1.05 g, 4 mol%) and Bu^tONa (13.7g, 0.143 mol) in dry benzene (300 mL) was refluxed under argon with stirring for 3.5 days. Then the solvent was removed, the crude product washed with water and benzene, dried in air, and purified by column chromatography over silica gel (dichloromethane : acetone, 5 : 1) giving white crystals. Yield = 65%. MS (FAB): m/z (%) 292 (100) $[M]^+$. IR (KBr) $\nu\,cm^{-1} = 3257$ w, 3185 w, 3031 w, 1607 m, 1559 m, 1533 m, 1517 m, 1452 m, 1418 vs, 1382 s, 1345 m, 1301 s, 1256 m, 1236 w, 1180 s, 1160 m, 1046 w, 986 m, 859 m, 816 m, 765 w, 728 w, 611 w, 579 w, 524 w, and 441 w.

2.3. *Synthesis of $[Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$*

$Ni(OAc)_2 \cdot 4H_2O$ (710 mg, 2.60 mmol), H_2dmpdda (500 mg, 1.71 mmol), and naphthalene (35 g) were placed in an Ehrlenmeyer flask. The mixture was heated under argon and then NaNCS (1730 mg, 21 mmol) was added. The reaction continued for another 2 h. The product was transferred to hexane for washing out naphthalene after being cooled, and then 100 mL CH_2Cl_2 was used to extract the complex. A blue purple complex was obtained after evaporation. Single crystals suitable for X-ray diffraction were obtained from diffusion of ether to a chloroform solution. Yield = 60%. IR (KBr) $\nu\,cm^{-1} = 2073$, 1564, 1612, 1442, 1406, 1340, 1162, 1007, and 771; MS(FAB): m/z (%) 1567 (70) $[M]^+$, 1508 (80) $[M{-}NCS]^+$ (scheme 1).

2.4. *X-ray crystallography*

Chosen crystals were mounted on a glass fiber. Data collection was carried out on a NONIUS Kappa CCD diffractometer at 150(1) K using Mo-Kα radiation ($k = 0.71073$ Å) and a liquid nitrogen low-temperature controller. Cell parameters were retrieved and refined using the DENZO-SMN software on all reflections. Data reduction was performed on the DENZO-SMN software. Semi-empirical absorption was based on symmetry equivalent reflections and absorption corrections were applied with the SORTAV program. All the structures were solved using SHELXS-97 [16] and refined with SHELXL-97 [17] by full-matrix least-squares on F^2. The R factors are higher than usual case because (a) the molecules are quite large and contain solvent molecules and (b) some atoms were found in disordered positions in every molecule. We carefully examined structures and concluded that the *P2(1)/c* option is best.

3. Results and discussion

3.1. *Description of crystal structures*

The crystal data are listed in table 1 and the structure is shown in figure 1. Selected interatomic distances and angles are listed in table 2. There are two chemically equivalent units in the complex. As in other oligo-α-pyridylamino metal string complexes, the five Ni(II) ions are co-linear with the Ni–Ni–Ni angles in the range 179.52°–180; the pentanickel chain is helically wrapped by four deprotonated ligands, all-*syn* coordinated. The length of the Ni_5 chain is 9.347 Å. The molecular structure is disordered because it contains both left-turn and right-turn helical forms of ligands. The molecule resides on a crystallographic site of 2-fold symmetry with the central

Table 1. Crystallographic data and structural refinement.

Formula	$C_{70}H_{60}N_{22}Ni_5S_2$, 0.5($C_2H_4Cl_4$), 3($CH_2Cl_2$)
Formula weight	1906.77
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions (Å, °)	
a	21.3548(5)
b	18.4822(4)
c	20.7320(5)
β(°)	91.7790(12)
V(Å^3)	8178.6(3)
Z	4
D_{Calcd} (g cm^{-3})	1.548
μ(Mo-Kα) (mm^{-1})	1.500
T(K)	150(2)
F(000)	3896
Reflections collected	38572
Independent reflections/R_{int}	14123/0.0702
Independent reflections with [$I > 2\sigma(I)$]	9011
Goodness-of-fit on F^2	1.178
R_1 [$I > 2\sigma(I)$]	0.1196
wR_2 [$I > 2\sigma(I)$]	0.3046
Largest difference in peak/hole (e Å^{-3})	1.471/−1.206

nickel on a 2-fold axis perpendicular to the molecular chain. The central nickel is at the symmetric center and the NCS^- are not disordered, whereas bridging ligands are disordered. Two types of Ni–Ni bond lengths are found in the $[Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$ unit. The outer ones, connected to the axial ligands, are 2.377(2) Å and inner ones are 2.2968(16) Å. Both are slightly shorter than those which are found in the pentanickel complexes, $[Ni_5(\mu_5\text{-etpda})_4Cl_2]$ and $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$ (the Ni–Ni bond lengths are 2.385(2), 2.389(2), and 2.304(2), 2.306(1) Å, respectively), and comparable to those in $[Ni_5(\mu_5\text{-tpda})_4(NCS)_2]$ (the Ni–Ni bond lengths are 2.367(2) Å and 2.298(2) Å, respectively) [13]. The Ni–N distances are in the order, central $Ni\text{–}N_{py}$ [Ni(3)–N] $<$ $Ni\text{–}N_{amino}$ [Ni(2)–N] $<$ terminal $Ni\text{–}N_{py}$ [Ni(1)–N] from the charge distribution on $dmpdda^{2-}$. The same trend has also been observed in other $[M_5(\mu_5\text{-tpda})_4X_2]$ complexes ($M = Cr, Co,$ and Ni) [12] and for $[Ni_5(etpda)_4Cl_2]$ [15]. If the Ni–Ni bonds are ignored, the three inner Ni ions are four-coordinate and square planar.

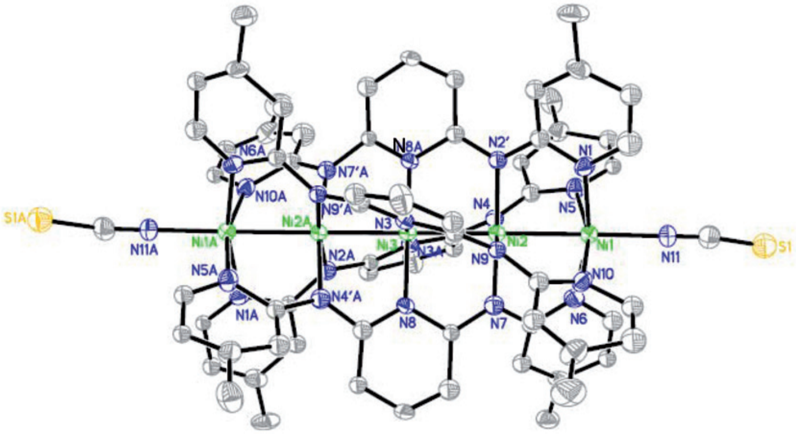


Figure 1. The molecular structure of $Ni_5(\mu\text{-dmpdda})_4(NCS)_2]$. Label A represents symmetrically related positions. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°).

Ni(1)–Ni(2)	2.377(2)	Ni(2)–Ni(3)	2.2968(16)
$Ni(1)\text{–}N_{outer}$	2.092(11)	$Ni(2)\text{–}N_{amino}$	1.92(6)
$Ni(3)\text{–}N_{py}$	1.90(11)	$Ni\text{–}N_{NCS}$	2.018(13)
Ni(3)–Ni(2)–Ni(1)	179.52(10)	Ni(2)–Ni(3)–Ni(2)#1	180.0
N(11)–Ni(1)–Ni(2)	178.1(4)	N(1)–Ni(1)–Ni(2)	84.1(3)
N(6)–Ni(1)–Ni(2)	81.9(3)	N(10)–Ni(1)–Ni(2)	82.2(3)
N(5)–Ni(1)–Ni(2)	82.9(3)		
N(11)–Ni(1)–N(6)	96.5(5)	N(1)–Ni(1)–N(6)	165.9(5)
N(11)–Ni(1)–N(10)	98.8(5)	N(1)–Ni(1)–N(10)	89.5(5)
N(6)–Ni(1)–N(10)	88.7(5)	N(11)–Ni(1)–N(5)	96.1(5)
N(1)–Ni(1)–N(5)	88.2(5)	N(6)–Ni(1)–N(5)	90.0(5)
N(10)–Ni(1)–N(5)	165.1(4)	N(11)–Ni(1)–N(1)	97.5(5)
N(8)–Ni(3)–N(8)#1	180.0(3)	N(8)–Ni(3)–N(3)#1	89.9(4)
N(8)#1–Ni(3)–N(3)#1	90.1(4)	N(8)–Ni(3)–N(3)	90.1(4)
N(8)#1–Ni(3)–N(3)	89.9(4)	N(3)#1–Ni(3)–N(3)	180.000(2)

Symmetry transformation for #1: $-x+1$, $-y$, $-z+1$.

The mean Ni–N distances of 1.90–1.92 Å are short, consistent with Ni–N distance, *ca* 1.90 Å, usually found in low-spin ($S = 0$) square planar Ni(II) configurations [18]. The terminal Ni(II) ions are square pyramidal, NiN_4X. The basal plane consists of four independent $dmpdda^{2-}$ ligands at 2.09 Å, consistent with a high-spin Ni(II) configuration for these terminal Ni(II) ions [19]. N–Ni1–Ni2 angles are in the range 81.9(3)°–84.1(3)°. From table 2 we also can see N–Ni1–N angles exist in two ranges of 88.2(5)°–98.8(5)° and 165°.

3.2. *Electrochemistry*

The redox properties of EMACs are pivotal for their function as molecular devices. The loss and gain of electrons provide bistable states, which are the basis of molecular switches, and the electron transfer (electron flow) through the molecules endues them with electron conductivity as molecular wires. Therefore, it is essential to study the electrochemical properties of these metal strings. The cyclic voltammograms show that this complex exhibits one reversible one-electron redox couple ($E_{1/2} = 0.59$ V, figure 2). $Ni_5(tpda)_4(NCS)_2$ in CH_2Cl_2 solution, using similar conditions has an oxidation wave at $E_{1/2}$ of 0.68 V [20]. This indicates that the methyl-substituted complex is more readily oxidizable, similar to the ethyl-substituted complex.

To determine the oxidation states, spectroelectrochemical techniques were employed. Figure 3 shows the spectral changes at various applied potentials, i.e., from 0.56 to 0.68 V. The peaks at 293 and 590 nm decrease and those at 367 and 724 nm increase as the applied potential increases. The absorption spectrum was restored when the applied potential of 0.56 V was set back to 0.00 V. This indicates that the electrochemical process is reversible and the wave at $E_{1/2} = 0.59$ V corresponds to the oxidation of $[Ni_5(dmpdda)_4(NCS)_2]$ to form $[Ni_5(dmpdda)_4(NCS)]^+$. The band at 1030 nm in the near IR region can be ascribed to the intervalence charge transfer of oxidation product

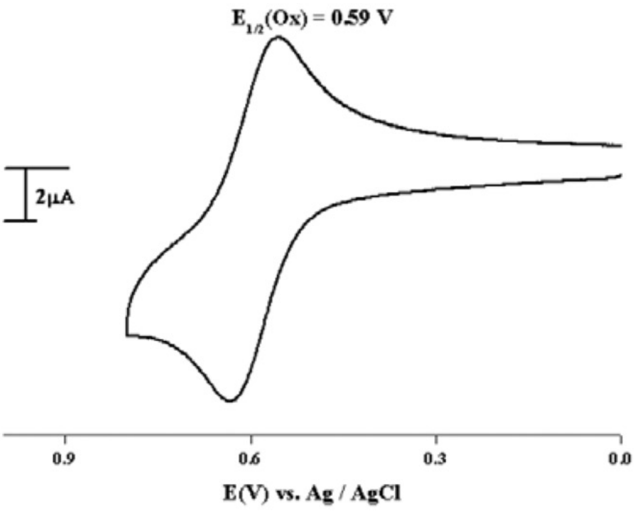


Figure 2. Cyclic voltammograms of pentanickel(II) EMAC in CH_2Cl_2 containing 0.1 M TBAP.

Ni^{11+}. The clear isosbestic points at 370, 642, and 1125 nm indicate that no intermediates were produced during the oxidation process.

3.3. *Magnetic susceptibility of pentanickel metal string complex*

The experimental curves of the molar magnetic susceptibility χ_M (●) and effective magnetic moment (μ_{eff}) (□) with respect to temperature (T), as well the fitting of $\chi_M T$ are displayed in figure 4. The observed magnetic moment μ_{eff} of the complex at room-temperature is 3.94, and fitting parameters are $ja = -30.8$ and $g = 2.08$.

Both the structural and magnetic properties of $Ni_5(dmpdda)_4(NCS)_2$ resembles the unsubstituted homolog $Ni_5(tpda)_4(NCS)_2$. In both cases, the inner $Ni \cdots Ni$

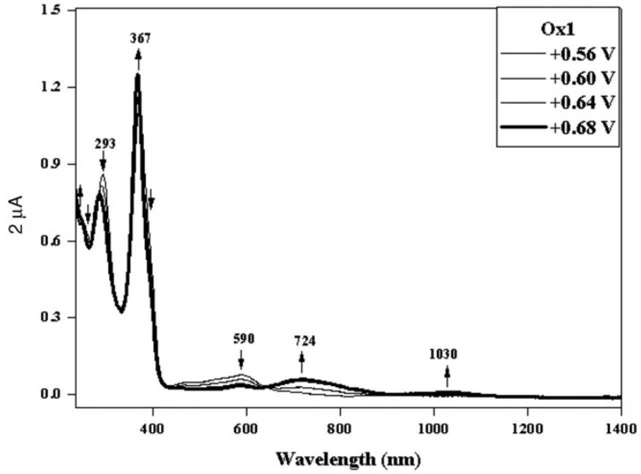


Figure 3. Spectral changes for oxidation of the complex in CH_2Cl_2 with 0.1 M TBAP at various applied potentials from 0.56 to −0.68 V.

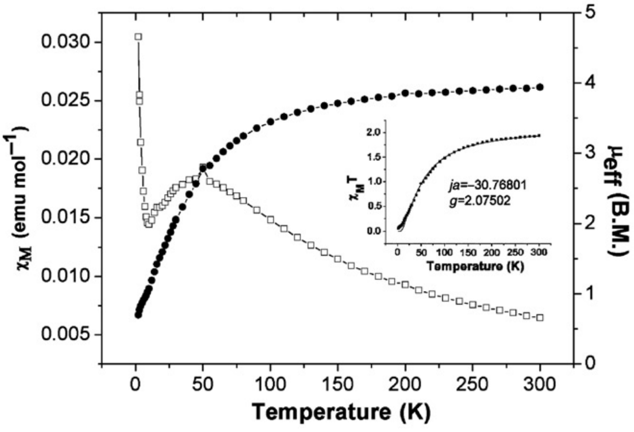


Figure 4. Temperature-dependent μ_{eff} (●, right axis) and molar magnetic susceptibility (□, left axis) for the complex. Inset: The fitting of $\chi_M T$ the reciprocal dependence of the magnetic susceptibility on temperature. The solid lines result from least-square fits of the Curie–Weiss law.

distances are shorter than the outer ones by about 0.08 Å. The Ni–N distances for three inner Ni–N atoms are similar and much shorter than those for the outer ones by 0.1 Å. These observations indicate the three inner nickels are essentially low-spin square coordination, while the outer ones are high-spin square pyramidal; there are no Ni–Ni bonds.

4. Conclusion

This work introduced the preparation of a pyridine modulated oligo-α-pyridylamino ligand, and its pentanuclear nickel(II), methyl-substituted nickel metal string complex. The pentanickel metal string complex is co-linear. Electrochemical studies showed one reversible oxidation, $E_{1/2} = 0.59$ V, which is lower than that of $Ni_5(tpda)_4(NCS)_2$ ($E_{1/2} = 0.68$ V). The magnetic behavior is similar to $[Ni_5(\mu_5\text{-tpda})_4(NCS)_2]$ and obeys the Curie–Weiss law with $ja = -30.8$ and $g = 2.08$.

Supplementary material

CCDC-699928 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from "The Cambridge Crystallographic Data Centre" *via* www.ccdc.cam.ac.uk./data/request/cif.

Acknowledgements

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