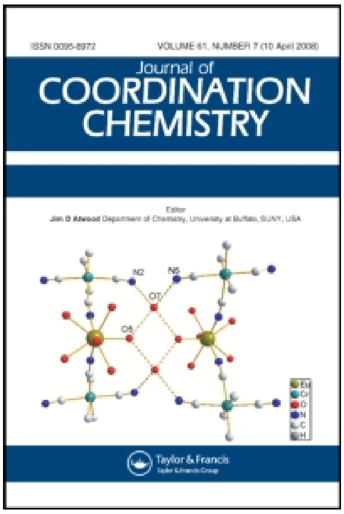

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Synthesis, crystal structure, and photoluminescence of a new Zn(II) molecular box compound derived from a two-armed bis-terdendate ligand

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Synthesis, crystal structure, and photoluminescence of a new Zn(II) molecular box compound derived from a two-armed bis-terdendate ligand

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The dinuclear compound $Zn_2(HL^2)_2(ClO_4)_2(C_2H_5OH)_{0.5}(H_2O)_2$ (**1**) based on di(2-acetylpyridyl)-6,6′-dicarboxylic acid hydrazone-2,2′-bipyridine (H_2L^2) has been obtained *via* self-assembly. X-ray crystallography indicated the formation of a molecular box rather than a helicate. The photoluminescence properties of **1** in the solid state have an emission at *ca* 500 nm with excitation at 400 nm at room temperature.

Keywords: Molecular box; Self-assembly; Photoluminescence

1. Introduction

Self-assembly may produce well-defined architectures in a spontaneous and directed manner in metallosupramolecular chemistry [1]. This requires tailored ligands to match the intrinsic stereochemical properties of a particular metal ion. In turn, metal ions allow diverse and robust edifices to be assembled because metal-donor bonds are highly directional [2]. By tailoring features of the ligand such as donor shape, type, and coordination number with the variation of the spacer groups separating coordination sites, diverse structural motifs with different topologies can be generated [3–5]. One hot pursuit is to design helicate or molecular box complexes *via* spontaneous processes [6]. From the viewpoint of ligand design, to obtain a helical complex, the ligands should contain multiple coordinating sites to match the geometrical requirement of metal centers. Furthermore, it must offer sufficient flexibility to wrap around two (or more) metal centers as a connecting strand to form a helical mode. In general, the helicate involves ligands being twisted around metal centers [7]. Alternatively, if the metal units are at the vertices of a square and bridged by rigid bifunctional ligands at the same side, a molecular box forms [8]. The outcome of self-assembly, i.e., helicate *versus* molecular box, will depend on the balance between rigidity and flexibility in the ligand.

We recently reported that a series of terdendate ligands containing pyridyl substituents (scheme 1), such as H_2L^{1-2}, may act as the bridges in the synthesis of

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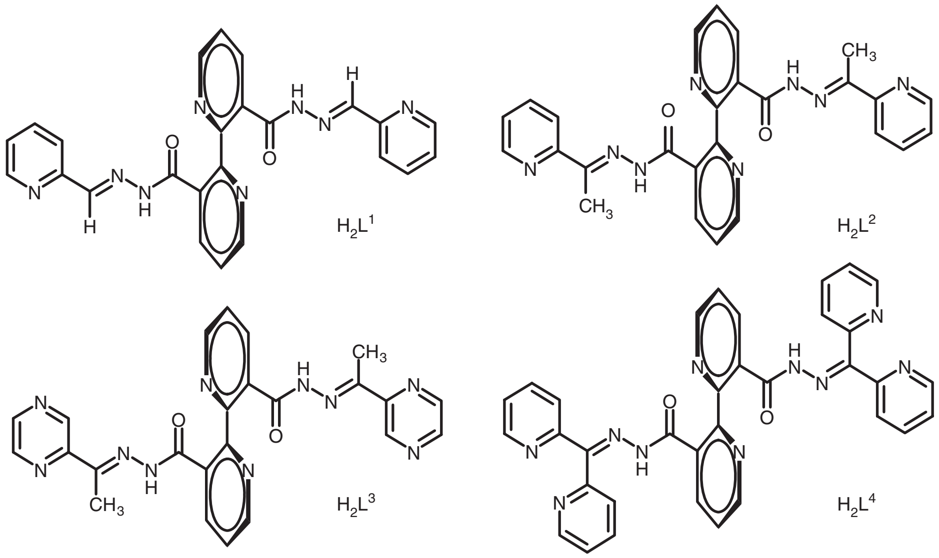

Scheme 1. The chemical structure of H_2L^{1-4} used for the formation of helicate or molecular box.

metallohelicate complexes through reaction with first row transition metals, i.e., Co^{2+} and Ni^{2+} [9, 10]. For ligands of the type H_2L^1–H_2L^4 (scheme 1), it has been proposed that match between the stereochemical preferences of metal ion and binding possibility of the donor can give rise to helicate formation in the resultant solid-state structures [11]. However, recent work in our laboratories has cast some doubt upon this supposition. We believe that intramolecular interactions, such as weak *intramolecular* (interstrand) face-to-face $\pi \cdots \pi$ and edge-to-face C–H $\cdots \pi$ interactions between the spacer aromatic rings, may be a contributing factor in "fine-tuning" the self-assembly structure [12]. Herein, we present further evidence for this assertion and report the structural characterization of a dinuclear molecular box incorporating Zn(II), $[Zn_2(HL^2)_2]^{2+}$. X-ray diffraction analysis indicated the formation of a molecular box rather than a helicate. In the solid state, **1** shows photoluminescence with an emission at *ca* 500 nm from excitation at 400 nm at room temperature.

2. Experimental

2.1. *Materials and methods*

2.1.1. General. All chemicals were of reagent grade quality obtained from commercial sources and used without purification. Elemental analyses (C, H, and N) were carried out with a Perkin Elmer 2400 analyzer. Infrared (IR) spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets from 4000 to 400 cm^{-1}. ^1H-NMR spectra were performed on a DRX500 Bruker spectrometer at 298 K with tetramethylsilane (TMS) as an internal reference. Electrospray mass spectra were carried out on a LCQ system (Finnigan MAT, USA) with methanol as mobile phase.

Solid photoluminescent spectra were performed on an AB Series-2 fluorescence spectrometer. Thermogravimetric analyses were carried out with a TA2000/2960 unit at a heating rate of 10°C min^{-1} under nitrogen.

2.1.1.1. *Di(2-acetylpyridyl)-6,6′-dicarboxylic acid hydrazone-2,2′-bipyridine* (H_2L^2). H_2L^2 is prepared according to the literature method [9, 10] by refluxing a mixture of dicarboxylic acid hydrazide-2,2′-bipyridine (2 mmol, 0.54 g) and 2-acetylpyridine (4 mmol, 0.48 g) in methanol (40 mL) in the presence of several drops of acetic acid. The resulting yellow solution was heated to boiling with stirring for 4 h. Then volume was reduced at reduced pressure to *ca* 5 mL and a pale yellow precipitate formed, which was collected by filtration, washed with methanol:ether (v : v, 1 : 3), and dried over P_2O_5 *in vacuo*. Yield: 0.69 g, 72%. Spectroscopic data for H_2L^2: ^{1}H-NMR (DMSO-d$_6$), δ 11.31 (1H, s, NH), 9.16 (1H, d, $J=8.6$ Hz), 8.64 (1H, d, $J=8.3$ Hz), 8.52 (1H, d, $J=7.1$ Hz), 8.31 (1H, d, $J=7.1$ Hz), 8.10 (1H, t, $J=11.1$ Hz), 7.88 (1H, t, $J=16.3$ Hz), 7.56 (1H, d, $J=7.1$ Hz), and 2.32 (3H, s, $-CH_3$). IR (solid KBr pellet, cm^{-1}): 3448.58(m), 1663.77(s), 1580.94(m), 1433.13(m), 1364.08(m), 1147.26(m), 783.46(m), and 675.19(m). ESI–MS: *m*/*z* 479.3 for $[H_2L^2+H]^+$, Calcd for $C_{26}H_{23}N_8O_2$, 479.52.

2.1.1.2. *Synthesis of* $(C_{52}H_{42}N_{16}O_4Zn_2)(ClO_4)_2(C_2H_5OH)_{0.5}(H_2O)_2$ (**1**). $Zn(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 0.038 g) dissolved in 15 mL methanol was added to a suspension of H_2L^2 (0.1 mmol, 0.048 g) in 10 mL methanol. The solution was stirred at reflux for 20 min to obtain a pale yellow solution and left as such at room temperature. After several days, pale yellow block crystals were obtained (0.044 g, 65.0%). Anal. Calcd for $(C_{52}H_{42}N_{16}O_4Zn_2)(ClO_4)_2(C_2H_5OH)_{0.5}(H_2O)_2$: H, 3.69; C, 47.49; and N, 16.73. Found: H, 3.72; C, 47.65; and N, 16.95%. ESI–MS: *m*/*z* 541.24 (Calcd for $[Zn_2(HL^2)_2]^{2+}$, 541.11). IR (solid KBr pellet, cm^{-1}): 2446.54(m), 1651.14(m), 1572.06(m), 1508.23(m), 1152.55(s), 1120.73(s), 1091.02(s), 759.02(w), and 628.12(w).

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with care.

2.2. *X-ray crystallography*

Intensities were collected on a Siemens Smart-CCD diffractometer with graphite monochromated Mo-Kα ($\lambda=0.71073$ Å) using SMART and SAINT programs [13]. A total of 45 frames of data were collected at 298 K with an oscillation range of 1° per frame and an exposure time of 10 s per frame. Indexing and unit cell refinement were based on all the observed reflections from the 45 frames. The structure was solved by direct methods and refined on F^2 by full-matrix least squares with SHELXTL, version 5.1 [14]. All the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogens were located geometrically, or those of solvent were found on Fourier difference maps; all hydrogens were refined in a riding model. Major disorder was observed in the perchlorate. Three oxygens of ClO_4^- were distributed over two positions, i.e., O12 (O12′), O13 (O13′), and O14 (O14′), and they were refined with site occupation factors (SOF) of 50%. A certain number of restraints were set during the refinement: DFIX 1.430 0.01 Cl1 O11 Cl1 O12 Cl1 O13 Cl1 O14; DFIX 1.430 0.01 Cl1 O11 Cl1 O12′ Cl1 O13′ Cl1 O14′; DFIX 2.320 0.02 O11 O12 O11 O13 O11 O14 O12 O13 O12 O14 O13 O14; DFIX 2.320 0.02 O11 O12′ O11 O13′ O11 O14′ O12′ O13′ O12′

O14′ O13′ O14′ and ISOR 0.02 O12′ > O12. Crystallographic data for the title compound are given in table 1.

3. Results and discussion

Interaction of $Zn(ClO_4)_2 \cdot 6H_2O$ with H_2L^2 at reflux gave a light yellow solid whose elemental analyses data are in good agreement with the general molecular formula $[Zn(HL^2)]_n$ as expected for a complex consisting of two ligands with two-armed tridentate donor sites and two six-coordination metal ions. Electrospray ionization–mass spectrometry (ESI–MS) in acetonitrile/methanol shows the strongest peak at m/z 541.24 which corresponds to the most abundant ion $[Zn_2(HL^2)_2]^{2+}$ with isotopic peaks separated by 0.5, which confirmed the 2+ charge borne by the cation. The presence of one strong $[Zn_2(HL^2)_2]^{2+}$ peak confirmed M_2L_2 species with high stability even under the electron spray conditions.

By slowly evaporating ethanol solution of **1**, single crystals suitable for X-ray diffraction were obtained in moderate yield. X-ray diffraction analysis revealed that **1** crystallized in monoclinic space group $P2_1/n$. As shown in figure 1, the asymmetric unit contains one zinc ion, one ligand, and some solvent molecules. The octahedral zinc is coordinated by two N_2O tridentate chelating units from different ligands to form a C_2-sysmmetrical side-by-side cation $[(M,P)\text{-}Zn_2(HL)_2]$ [15]. Complex **1** displays a centrosymmetric bimetallic molecular box as shown in figure 2, in which Zn(1) and Zn(1A) are bridged by two ligands to form a 2 : 2 metal : ligand dinuclear cationic species with Zn $\cdots$ Zn separation of 6.680 Å. Two chelating units coordinate to a Zn in a *mer* configuration with both pairs of carbonyl oxygens and pyridyl nitrogens in a *cis* relationship, whereas the imino nitrogens are *trans* to each other. The distances of bonds are 2.165(4) and 2.227(4) Å for Zn1–O1 and Zn1–O2, respectively. The Zn–N distances range from 2.0375 to 2.1295 (Å). Bond angles around Zn range from 72.91(15) to 158.14(18), suggesting the Zn(II) is located in a heavily distorted octahedral environment. The C–O bond distances of 1.234 and 1.289 Å for C(21)–O(2) and C(8)–O(1), respectively, together with 1.339 for C(21)–N(7) and 1.305 Å for C(8)–N(3) suggest that the proton on N(3) is lost and H_2L^2 is a monoanionic ligand during coordination to zinc, which is common for this type of ligand [9]. Bipyridine units are twisted with respect to each other (dihedral angle −104.1°) and a cavity between two pairs of pyridyl units results.

H_2L^2 has two tridentate coordination sites, i.e., N_2O like a pocket, the free rotation around the bond C8–C9 and/or C21A–C22A (symmetry code: $-x$, $-y+3$, $-z$) makes two tridentate pockets toward the same direction to correspondingly yield the molecular box. However, the rotation is not anticipated; indeed we have previously observed that H_2L^2 can assemble with Ni^{2+} and Co^{2+} to double-helical structure rather than molecular box due to the free rotation of ligand framework [9, 10] (table 2). In that case, coordination to the metal ions also induces configuration changes within H_2L^2 and rotation results in aromatic rings defining the desired aryl-lined cavity toward the opposite direction. Weak intramolecular $\pi \cdots \pi$ stacking interaction, which links pyridyl ring I (C14–C18, N5) and ring IIA (C22A–N8A, C26A) (symmetry code A: $-x$, $-y+3$, $-z$) in the antiparallel mode, is characterized by the shortest inter-planar atom $\cdots$ atom separation (C17 $\cdots$ C24A) of 3.513 Å and dihedral angle of −165.4°.

Table 1. Crystallographic data and refinement parameters for **1**.

Empirical formula	$C_{53}H_{52}Cl_2N_{16}O_{14.5}Zn_2$
Formula weight	1346.75
Crystal color, habit	Pale yellow, block
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	12.931(3)
b	10.383(2)
c	24.602(5)
β	94.822(4)
Volume (Å^3), Z	3291.4(11), 4
Calculated density (g cm^{-3})	1.359
Absorption coefficient (mm^{-1})	0.881
F(000)	1384
Crystal size (mm^3)	0.3 × 0.2 × 0.2
Reflections/restraints/parameters	5771/56/430
Goodness-of-fit (S)	1.002
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0883$, $wR_2 = 0.2332$

$R_1 = \Sigma|F_o|-|F_c|/|\Sigma|F_o|$. $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

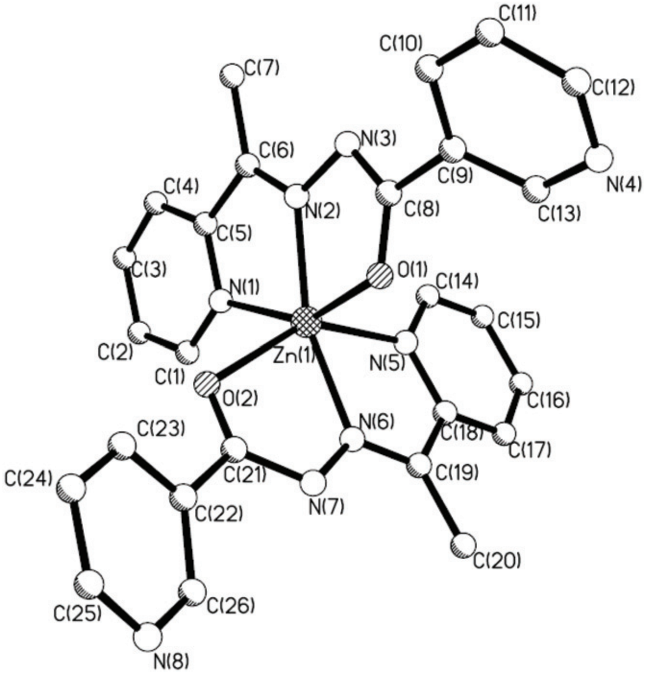

Figure 1. Atomic numbering scheme for the asymmetric unit of the cation of **1**. Ellipsoids are represented with 50% probability.

Non-covalent interactions may be a main driving force in the formation of molecular box instead of helicate, potential influences need to be further studied. Alternatively, the additional methyl substituent on H_2L^2 in comparison to H_2L^1 may add to the steric effect not allowing the methyl to position on the same side if the helicate structure

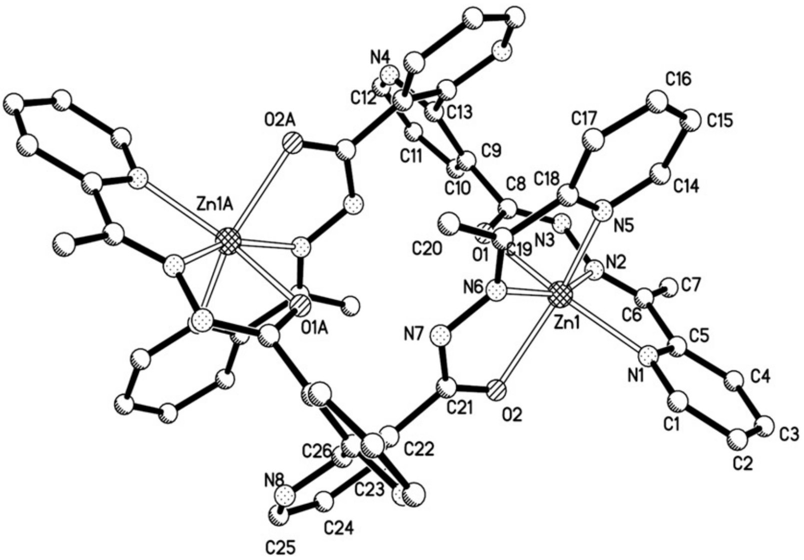

Figure 2. Cationic $[Zn_2(HL^2)_2]^{2+}$ structure with selected atom labels. Hydrogens, counterions, and solvent molecules are omitted for clarity. Ellipsoids are represented with 50% probability.

Table 2. Selected bond distances (Å) and bond angles (°) for **1**.

Zn1–N2	2.037(5)	N2–Zn1–N6	158.14(18)
Zn1–N6	2.064(4)	N2–Zn1–N1	76.64(19)
Zn1–N1	2.122(5)	N6–Zn1–N1	125.07(18)
Zn1–N5	2.129(5)	N5–Zn1–O1	97.15(17)
Zn1–O1	2.165(4)	N2–Zn1–O2	112.70(17)
Zn1–O2	2.227(4)	N6–Zn1–O2	72.91(15)
O1–C8	1.277(6)	N1–Zn1–O2	90.99(17)
O2–C21	1.228(6)	N5–Zn1–O2	145.13(16)
N2–C6	1.273(7)	O1–Zn1–O2	92.40(15)
N2–N3	1.408(7)	N1–Zn1–O1	149.44(16)
N6–C19	1.272(7)	N2–Zn1–O1	74.04(16)
N6–N7	1.369(6)	N2–Zn1–N5	102.17(19)
N7–C21	1.351(7)	N1–Zn1–N5	97.26(19)
N3–C8	1.315(7)	N6–Zn1–N5	74.67(17)
		N6–Zn1–O1	84.80(15)
		C6–N2–N3	120.4(5)
		C19–N6–N7	121.8(4)
		C21–N7–N6	114.0(4)

forms. However, in the box structure reported herein, the methyl substituents locate at different sides of the ligand, which effectively precludes the steric effect. As shown in figure 3, the molecular boxes stack parallel along the crystallographic *a*-axis to form a channel in which the free solvent and perchlorate resided.

Although supramolecular multidimensional architectures with helicate structure are frequently reported [16, 17], the discrete molecular box is rare. It is unexpected that a helix did not form in **1**. The reason a box structure forms is not that the geometry of metal ion is incompatible with helix formation, as observed in the solid state about octahedral Co(II) and Ni(II) with similar ligands H_2L^{1-4}. This point is different from

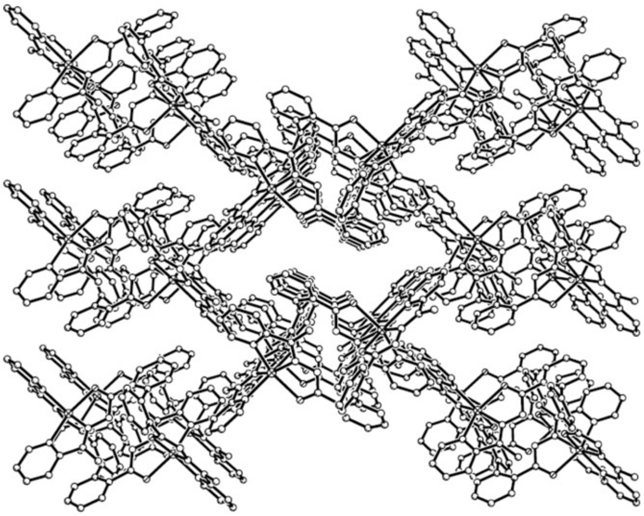

Figure 3. The crystal packing of **1** along the crystallographic *a*-axis. Hydrogens, counterions, and solvent molecules in the channel are omitted for clarity.

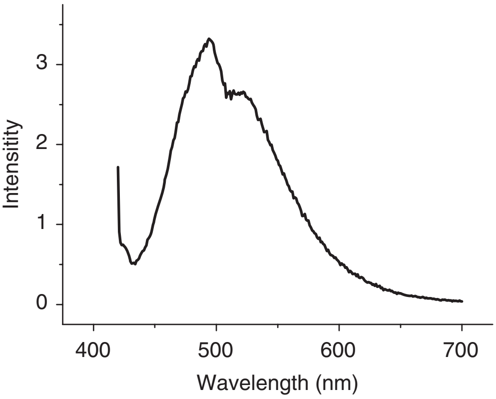

Figure 4. Solid-state photoluminescence spectra of **1** at room temperature. $\lambda_{ex} = 400$ nm.

Nieuwenhuyzen and co-workers' result [18], in which they pointed out that metal ions with a preference for tetrahedral geometry favor "box" formation over helix formation. If a helicate did form, the ligand should have enough flexibility and give a very distorted structure in the solid state as found previously. Dreos *et al.* [19] synthesized a dinuclear box by the reaction of methylaquacobaloxime and 1,4-phenylenebisboronic acid as a rigid linker. Zhu and co-workers [20] reported a Pt(II) molecular box introducing phenylene rings into the ligand to import rigidity to the macrocycle.

Luminescent compounds are of interest due to their various applications in chemical sensors, photochemistry, and electroluminescent displays. The photoluminescence spectra of **1** and free neutral ligand H_2L^2 were measured at room temperature. The free ligand was not luminescent, but **1** showed the fluorescence (figure 4). This may be caused by charge-transfer transition between ligands and metal centers [21, 22] and ligand coordinating to zinc which effectively increases the rigidity and reduces loss of energy by radiation-less decay [23–26]. Emissions of **1** may be attributed to a joint contribution of the intraligand transitions or charge-transfer transitions between the coordinated ligands and the metal center.

4. Conclusion

Previous study indicated some helicates have been obtained even if bipyridine-bridged bis-multidentate H_2L^2 and different metal ions are used. The success in isolating a molecular box rather than helicate starting from the same ligand is another example of unpredictable self-assembly. The current result indicates that self-assembly is influenced by steric effects of ligand and intramolecular non-covalent interactions in addition to metal ions with different coordination geometry.

Supplementary material

Supplementary data CCDC 691108 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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