

Eight-fold Interpenetrating Diamond-like Metal-Organic Frameworks Constructed with an N- and O-Donor Ligand for Cadmium(II) and Manganese(II)

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Hydrothermal reactions of (*E*)-4-(2-(1*H*-imidazol-4-yl)vinyl)benzoic acid (HL) with Cd(II) and Mn(II) salts yield the complexes [Cd(L)₂] (**1**) and [Mn(L)₂] (**2**), which have been characterized by single-crystal and powder X-ray diffraction, IR spectroscopy, and elemental and thermogravimetric analyses. Complexes **1** and **2** are isomorphous and isostructural, displaying an uninodal 4-connected 8-fold interpenetrating 3D **dia** framework architecture with (6⁶) topology. These frameworks exhibit high thermal stability up to 400 °C. The luminescence and non-linear optical (NLO) properties were investigated.

Key words: Cd(II) and Mn(II) Complexes, Structural Characterization, Fluorescence, NLO Properties, Metal-Organic Frameworks

Introduction

Recently, the design and assembly of metal-organic frameworks (MOFs) have attracted increasing attention in the field of supramolecular coordination chemistry and crystal engineering due to their intriguing architectures and potential applications as functional materials [1–5]. Current efforts have been focused on the exploration of such hybrid materials with interesting topologies and multifunctional properties, such as catalytic, absorbent, magnetic and electric, and fluorescence and nonlinear optical (NLO) effects [6–10]. It is well-known that functional properties of complexes are largely dependent on the nature of the metal centers and bridging ligands, and their architectures. For example, Mn(II), Co(II), Ni(II), and Cu(II) *etc.* could be bridged by ligands to form polynuclear subunits which may mediate magnetic interactions [11]; complexes containing metal centers with *d*¹⁰ electron configuration, such as Zn(II) and Cd(II), may exhibit excellent luminescence properties [12]; moreover, when complexes crystallize in an acentric space group, as it may be induced by an asymmetric ligand such as 4-(pyridin-4-yl)benzonitrile, then

the non-centrosymmetric structure may show second-order non-linear optical (NLO) effects [13]. Consequently, the construction of MOFs has become one of the main aims of crystal engineering in coordination chemistry [14–16]. Undoubtedly, the selection of suitable ligands and metal salts plays a crucial role in the formation of complexes.

In the present work, the ligand (*E*)-4-(2-(1*H*-imidazol-4-yl)vinyl)benzoic acid (HL) was employed as an organic building block for new frameworks. The HL ligand has several remarkable features: (1) its rigid skeleton can reduce the coordination uncertainty and may favor the assembly of polymers with high stability; (2) its asymmetry may induce non-centrosymmetric structures of complexes which show NLO properties; (3) the 1*H*-imidazol-4-yl group can be deprotonated to give imidazolate ligands which are adaptive building units, as demonstrated by zeolitic imidazolate framework (ZIF) materials [17]; (4) its extended molecular structure tends to form entangled architectures. We report herein the synthesis and characterization of two new coordination polymers, [Cd(L)₂] (**1**) and [Mn(L)₂] (**2**). Their luminescence and non-linear optical (NLO) properties were also investigated.

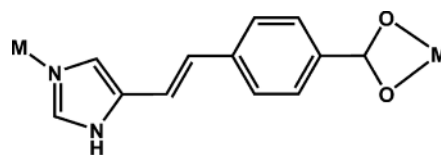
Results and Discussion

Preparation

The hydrothermal reactions of Cd(II) and Mn(II) salts with HL at 180 °C in the presence of KOH yield two new complexes: [Cd(L)₂] (**1**) and [Mn(L)₂] (**2**), which are stable in air.

Crystal and molecular structure of [Cd(L)₂] (**1**)

Determination of the structures of **1** and **2** by X-ray crystallography has revealed similar crystal and molecular dimensions. Both complexes crystallize in the orthorhombic space group *Aba2* with *Z* = 4 (Table 1).



Scheme 1. The coordination modes of the L[−] ligand in **1** and **2**.

Apart from the same crystal system and space group, complexes **1** and **2** exhibit very similar cell parameters (Table 1) and atom coordinates, which indicate that **1** and **2** are isomorphous and isostructural except slight difference in bond lengths and bond angles (Table 2). Therefore, only the structure of **1** is discussed in detail here.

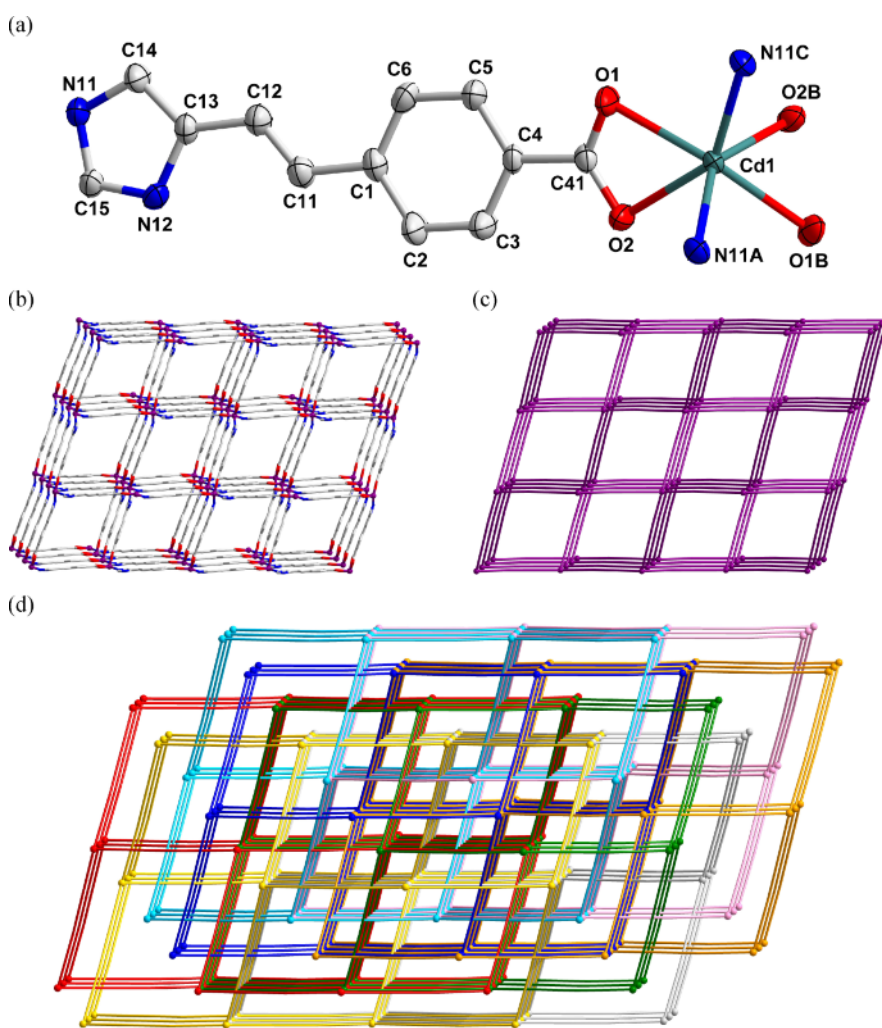


Fig. 1 (color online). (a) The coordination environment of the Cd(II) center in **1** (displacement ellipsoids at the 30% probability level; hydrogen atoms omitted for clarity); (b) view of the 3D framework architecture in **1**; (c) schematic representation of the uninodal 4-connected 3D framework in **1**; (d) schematic representation of the eight-fold interpenetrating 3D frameworks of **1**.

	1	2
Formula	C ₂₄ H ₁₈ CdN ₄ O ₄	C ₂₄ H ₁₈ MnN ₄ O ₄
<i>M_r</i>	538.82	481.36
Crystal size, mm ³	0.20 × 0.10 × 0.10	0.20 × 0.10 × 0.10
Crystal system	orthorhombic	orthorhombic
Space group	<i>Aba2</i>	<i>Aba2</i>
<i>a</i> , Å	12.951(3)	12.849(3)
<i>b</i> , Å	21.656(4)	21.151(5)
<i>c</i> , Å	8.2868(16)	8.3701(19)
<i>V</i> , Å ³	2324.2(8)	2274.7(9)
<i>Z</i>	4	4
<i>D</i> _{calcd} , g cm ⁻³	1.54	1.41
$\mu(\text{MoK}\alpha)$, cm ⁻¹	1.0	0.6
<i>F</i> (000), e	1080	988
<i>hkl</i> range	−16 → +13, −28 → +26, ±10	−16 → +14, −27 → +25, ±10
θ range, deg	1.88–28.00	2.49–28.16
Refl. measured / unique / <i>R</i> _{int}	7019 / 2733 / 0.0785	6930 / 2679 / 0.0641
Param. refined	150	150
<i>R</i> (<i>F</i>) ^a / <i>wR</i> (<i>F</i> ²) ^b (all refl.)	0.0647 / 0.1441	0.0612 / 0.0699
χ (Flack)	−0.06(7)	−0.02(3)
GoF (<i>F</i> ²) ^c	0.968	0.880
$\Delta\rho_{\text{fin}}$ (max / min), e Å ⁻³	1.49 / −1.36	0.28 / −0.22

Table 1. Crystal structure data and numbers pertinent to data collection and structure refinement of **1** and **2**.

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

[Cd(L) ₂] (1)			
Cd(1)–O(1)	2.377(4)	Cd(1)–O(2)	2.350(5)
Cd(1)–O(1)#1	2.377(4)	Cd(1)–O(2)#1	2.350(5)
Cd(1)–N(11)#2	2.238(5)	Cd(1)–N(11)#3	2.238(5)
O(1)–Cd(1)–O(2)	54.74(15)	O(1)–Cd(1)–O(1)#1	134.1(3)
O(1)–Cd(1)–O(2)#1	93.97(19)	O(1)–Cd(1)–N(11)#2	90.88(15)
O(1)–Cd(1)–N(11)#3	117.96(16)	O(1)#1–Cd(1)–O(2)	93.97(19)
O(2)–Cd(1)–O(2)#1	98.6(3)	O(2)–Cd(1)–N(11)#2	144.95(16)
O(2)–Cd(1)–N(11)#3	89.50(19)	O(1)#1–Cd(1)–O(2)#1	54.74(15)
O(1)#1–Cd(1)–N(11)#2	117.96(16)	O(1)#1–Cd(1)–N(11)#3	90.88(15)
O(2)#1–Cd(1)–N(11)#2	89.50(19)	O(2)#1–Cd(1)–N(11)#3	144.95(16)
N(11)#2–Cd(1)–N(11)#3	103.2(3)		
[Mn(L) ₂] (2)			
Mn(1)–N(11)	2.156(3)	Mn(1)–N(11)#1	2.156(3)
Mn(1)–O(1)#2	2.240(2)	Mn(1)–O(2)#2	2.252(2)
Mn(1)–O(1)#3	2.240(2)	Mn(1)–O(2)#3	2.252(2)
N(11)–Mn(1)–N(11)#1	100.05(14)	O(1)#2–Mn(1)–N(11)	147.60(8)
O(2)#2–Mn(1)–N(11)	90.31(9)	O(1)#3–Mn(1)–N(11)	90.66(8)
O(2)#3–Mn(1)–N(11)	116.13(8)	O(1)#2–Mn(1)–N(11)#1	90.66(8)
O(2)#2–Mn(1)–N(11)#1	116.13(8)	O(1)#3–Mn(1)–N(11)#1	147.60(8)
O(2)#3–Mn(1)–N(11)#1	90.31(9)	O(1)#2–Mn(1)–O(2)#2	57.74(7)
O(1)#2–Mn(1)–O(1)#3	96.48(12)	O(1)#2–Mn(1)–O(2)#3	94.10(8)
O(1)#3–Mn(1)–O(2)#2	94.10(8)	O(2)#2–Mn(1)–O(2)#3	139.39(13)
O(1)#3–Mn(1)–O(2)#3	57.74(7)		

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**^a.

^a Symmetry transformations used to generate equivalent atoms: for **1**: #1 $-x, 1-y, z$; #2 $1/2-x, -1/2+y, 1+z$; #3 $-1/2+x, 3/2-y, 1+z$; for **2**: #1 $-x, 1-y, z$; #2 $1/2-x, 1/2+y, 1+z$; #3 $-1/2+x, 1/2-y, -1+z$.

Complex **1** shows a 3D entangled architecture containing eight interpenetrating 3D frameworks. The carboxylic group of the HL ligand is deprotonated to leave the L[−] anion, as confirmed by the absence of vibration

bands at 1690–1730 cm^{−1} in the IR spectrum (see Experimental Section). The asymmetric unit consists of one Cd atom with occupancy of 0.5 and one L[−] ligand. Its coordination environment is shown in Fig. 1a

together with the atom numbering scheme. Cd1 is six-coordinated with distorted octahedral geometry by four carboxylate O atoms from two different L^- ligands with an average Cd–O bond length of 2.364 Å and two imidazolyl N atoms from two different L^- ligands with a Cd–N bond length of 2.238(5) Å. The bond angles around Cd(II) vary from 54.74(15) to 144.95(16)° (Table 2). The carboxylate group in the L^- ligand exhibits a $\mu_1-\eta^1:\eta^1$ -chelating coordination mode, with almost identical C–O bond lengths [1.244(7) Å and 1.252(7) Å] consistent with electron delocalization. Each 1*H*-imidazol-4-yl group is coordinated to a single metal center and is not deprotonated. The existing hydrogen bond N(12)–H(9)···O(2)#1 [#1: $-x, 3/2 - y, -1/2 + z$; N(12)···O(2)#1 = 2.813(7) Å; \angle N(12)–H(9)···O(2)#1 = 176°] plays an important role in constructing and stabilizing the solid-state structure. Each L^- ligand acts as a μ_2 -linear bridge to link two different metal centers, and each metal center is coordinated by four different L^- ligands. The interconnection of metals and ligands extends infinitely to form a 3D neutral framework (Fig. 1b). Using topology to analyze the structure, each Cd(II) could be regarded as a 4-connector node, and each L^- ligand as 2-connector node simplified as a linear bridge, and thus, the 3D framework in **1** could be simplified as an uninodal 4-connected 3D **dia** network with (6⁶) topology (Fig. 1c) [18]. The extended point symbol is [6(2).6(2).6(2).6(2).6(2).6(2)]. Interestingly, there are eight interpenetrating frameworks in the structure of **1** (Fig. 1d).

Crystal and molecular structure of [Mn(L)₂] (**2**)

Complex **2** also crystallizes in the orthorhombic system with space group *Aba2* (Table 1). Each Mn(II) center in **2** is six-coordinated by two N atoms and four O atoms and exists in the high-spin configuration ($g = 2$, $S = 5/2$) as deduced from the magnetic moment ($\mu_{\text{eff}} = 5.98 \mu_B$) which has been determined with a Gouy magnetic balance at room temperature. The coordinative bond lengths around Mn(II) are in the range of 2.156(3)–2.252(2) Å (Table 2), which is comparable to reported values for high-spin Mn(II) [19–22].

PXRD and thermal stability of complexes **1** and **2**

The phase purity of **1** and **2** could be proven by powder X-ray diffraction (PXRD) measurements.

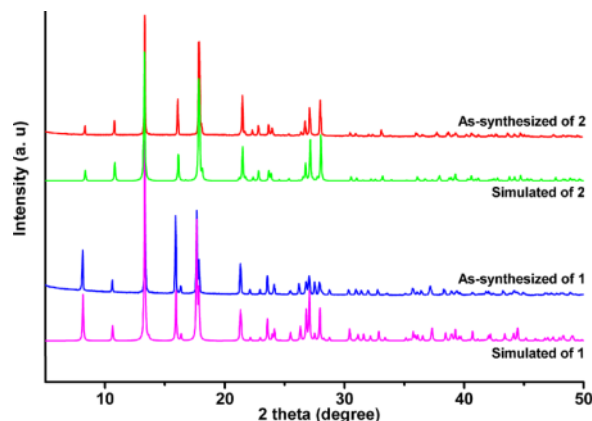


Fig. 2 (color online). The PXRD patterns of complexes **1** and **2**.

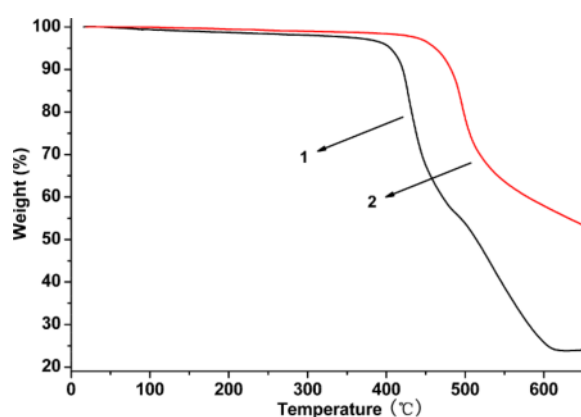


Fig. 3 (color online). TGA curves of complexes **1** and **2**.

As shown in Fig. 2, each PXRD pattern of the as-synthesized sample is consistent with the simulated one.

Thermogravimetric analyses (TGA) were carried out for complexes **1–2**, and the results are shown in Fig. 3. No obvious weight loss can be observed before the decomposition of the frameworks at 400 °C for **1** and 432 °C for **2**, proving high thermal stability and confirming the absence of solvent in their structure.

Non-linear optical properties

It is known that non-centrosymmetric structures may exhibit second-order non-linear optical (NLO) effects [23, 24]. Therefore, the optical properties of **1** and **2** were investigated to evaluate their potential application as second-order NLO materials. Approximate es-

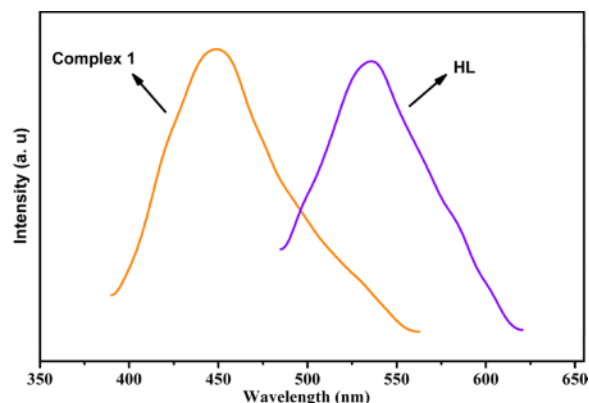


Fig. 4 (color online). Emission spectra of **1** and HL in the solid state at room temperature.

timations were carried out with a pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm. The result obtained from a powdered sample (80–150 μm diameters) in the form of a pellet (Kurtz powder test) was compared with that obtained for urea. The preliminary experimental results revealed that complexes **1** and **2** exhibit strong powder SHG intensity compared to that for urea, the response being 1.4 and 1.2 times, respectively.

Luminescence properties

Previous studies have shown that coordination compounds containing d^{10} metal centers such as Cd(II) may exhibit excellent luminescence properties and have potential applications as photoactive materials [25, 26]. Therefore, the luminescence of complex **1** and the HL ligand has been investigated in the solid state at room temperature. As shown in Fig. 4, intensive fluorescence can be observed with emission bands at 449 nm ($\lambda_{\text{ex}} = 378$ nm) for **1** and at 535 nm ($\lambda_{\text{ex}} = 411$ nm) for HL. This fluorescence may be tentatively assigned to intra-ligand transitions of the coordinated L^- ligands, since a similar emission is observed for the free HL [25, 26]. The observed blue shift of the emission maximum for **1** vs. that of HL may be considered to originate from the deprotonation and the metal coordination of the ligand L^- [27, 28].

Conclusion

(*E*)-4-(2-(1*H*-Imidazol-4-yl)vinyl)benzoic acid (HL) reacts with cadmium and manganese salts under

hydrothermal conditions to provide the two complexes $[\text{Cd}(\text{L})_2]$ (**1**) and $[\text{Mn}(\text{L})_2]$ (**2**). Complexes **1** and **2** are isomorphous and isostructural, displaying an uninodal 4-connected 8-fold interpenetrating 3D *dia* framework architecture with (6^6) topology. The frameworks of **1** and **2** exhibit high thermal stability up to 400 $^\circ\text{C}$ and exhibit strong non-linear optical (NLO) properties; complex **1** also shows intense fluorescence.

Experimental Section

All commercially available chemicals were of reagent grade and were used as received without further purification. A slightly revised experimental procedure was used to synthesize the HL ligand [29]. Elemental analyses of C, H, and N were taken on a Perkin-Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10 $^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418$ Å) radiation at room temperature. The second-order non-linear optical (NLO) intensity was estimated by measuring a powder sample of 80–150 μm diameter in the form of a pellet relative to urea. A pulsed Q-switched Nd:YAG laser with a wavelength of 1064 nm was used to generate a second-harmonic-generation (SHG) signal from powder samples. The backscattered SHG light was collected by a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5 nm, and all measurements were carried out under the same experimental conditions.

Preparation of $[\text{Cd}(\text{L})_2]$ (**1**)

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.8 mg, 0.1 mmol), HL (21.4 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless-steel container and heated at 180 $^\circ\text{C}$ for 3 d. After cooling to room temperature, colorless needle-shaped crystals of **1** were collected by filtration and washed with water and ethanol several times; yield 41 % based on HL. – $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4\text{Cd}$ (538.82): calcd. C 53.50, H 3.37, N 10.40; found C 53.22, H 3.16, N 10.66. – IR (KBr pellet, cm^{-1}): $\nu = 1589$ (m), 1533 (s), 1392 (s), 1301 (w), 1180 (w), 1110 (s), 976 (m), 948 (m), 864 (m), 835 (m), 807 (m), 765 (m), 695 (m), 638 (m).

Preparation of [Mn(L)₂] (2)

Complex **2** was obtained by the same hydrothermal procedure as that used for the preparation of **1** except using MnBr₂ (21.5 mg, 0.1 mmol) instead of Cd(NO₃)₂·4H₂O. After cooling to room temperature, colorless needle-shaped crystals of **2** were collected by filtration and washed with water and ethanol several times; yield 36 % based on HL. – C₂₄H₁₈N₄O₄Mn (481.36): calcd. C 59.88, H 3.77, N 11.64; found C 59.72, H 3.96, N 11.60. – IR (KBr pellet, cm^{−1}): ν = 1598 (m), 1562 (m), 1535 (s), 1415 (s), 1295 (w), 1182 (w), 1098 (s), 978 (w), 950 (w), 866 (m), 809 (m), 774 (m), 647 (m).

X-Ray structure determinations

The crystallographic data collections for complexes **1** and **2** were carried out on a Bruker Smart Apex CCD area-detector diffractometer using graphite-monochromatized MoK α radiation (λ = 0.71073 Å) at 293(2) K. The diffraction data were integrated by using the program SAINT [30], which was also used for the corrections of decay and of

Lorentz and polarization effects. Semi-empirical absorption corrections were applied using the program SADABS [31]. The structures of **1** and **2** were solved by Direct Methods, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXS/L-97 crystallographic software package [32, 33]. All hydrogen atoms at C atoms were generated geometrically, while the hydrogen atoms at N12 in **1** and **2** could be located at reasonable positions in difference Fourier maps. The crystal data and details of data collection and structure refinement for both complexes are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

CCDC 894698 and 894699 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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