Synthesis, Structure and Fluorescence Properties of a Trinuclear Zn(II) Complex with *N,N,O*-donor Schiff Base Ligands and Bridging Acetates

Shyamapada Shit[a], Joy Chakraborty[a], Brajagopal Samanta[a], Georgina M. Rosair[b], and Samiran Mitra[a]

[a] Department of Chemistry, Jadavpur University, Kolkata - 700032, West Bengal, India
[b] Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U. K.

Reprint requests to Prof. Samiran Mitra. Fax: 91-033-2414 6414 / 6210.
E-mail: smitra_2002@yahoo.com

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A new centrosymmetric trinuclear Zn(II) complex $[Zn_3L_2(CH_3COO)_4]$ (**1**) has been synthesized by the reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with a tridentate *N,N,O*-donor Schiff base ligand HL $[C_5H_4NC(CH_3)=NC_6H_4(OH)]$ and systematically characterized by elemental analysis, FT-IR, UV/Vis and thermal methods. Single crystal X-ray structure analysis reveals that three Zn(II) centers are in two different coordination environments. Two terminal Zn(II) centers adopt a distorted square-pyramidal geometry leaving the central Zn(II) in a distorted octahedral environment. Two adjacent metal centers are connected through single μ_2-phenolato as well as double μ-acetato-O,O′ *syn-syn* bridges. Fluorescence properties of the complex as compared to the ligand indicate that the former can serve as a potential photoactive material.

Key words: Trinuclear Schiff Base Complex, Five- and Six-coordinated Zinc(II), Crystal Structure, μ_2-Phenolato and Double μ-Acetato-*O,O*′ *syn-syn* Bridges, Fluorescence

Introduction

Multidentate Schiff base ligands have played an important role in the development of coordination chemistry as they readily form reasonably stable complexes with most transition metal ions [1 – 3]. Schiff base transition metal complexes have been of great interest for many years [4] due to their important role in homogeneous or heterogeneous catalysis [5 – 9] and magnetism [10], and offer wide applications as antibacterial, antiviral and antifungal agents [11]. Schiff bases are also considered as potential anticancer drugs [12], and when administered as their metal complexes, the anticancer activity is enhanced in comparison to the free ligand [13, 14]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [15, 16] because of their ability to possess unusual configurations, structural lability, and sensitivity to molecular environments [17]. Moreover, the design and synthesis of novel coordination compounds based on transition or non-transition metals and multifunctional bridging ligands is of great research interest, due to the interesting topologies and potential applications of the complexes as functional materials. Schiff base ligands have been proven to be very effective in constructing supramolecular architectures such as coordination polymers, including double and triple helicates [18, 19], due to their capacity to function as chelator as well as connector. In this connection, various bridging ligands have been used, such as carboxylates which are very effective due to their versatile bridging modes. Thus transition metal complexes with Schiff base ligands and bridging carboxylates have been of great interest for a long time.

Zinc(II) cations, due to their d^{10} electronic configuration, form complexes with a flexible coordination environment, and the geometries of these complexes can vary from tetrahedral to octahedral, and severe distortions of the ideal polyhedra occur easily. Due to the general lability of d^{10} metal ion complexes, the formation of coordination bonds is reversible which enables metal ions and ligands to rearrange during the process of self-organization to give highly ordered network structures. The terminal or blocking co-ligands, which are usually used along with the bridging ligand to complete the metal coordination sphere, can alter the supramolecular assembly and consequently the type of structure formed taking advantage of the flexibility of the coordination sphere. Zinc(II) chemistry plays an

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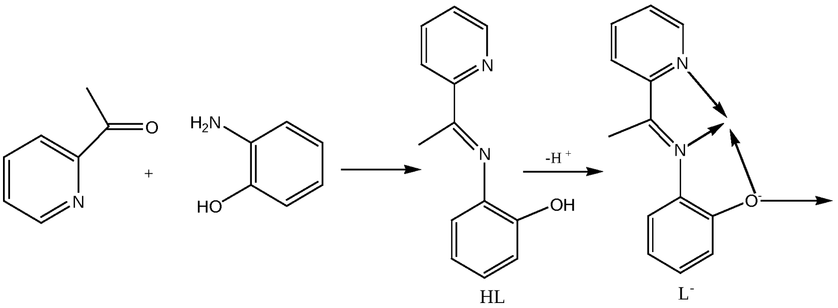

Scheme 1. Synthetic scheme of the Schiff base (HL) and coordination modes of L^-.

important role in biological systems. Zinc-containing carboxylato-bridged complexes form a variety of structural motifs in hydrolytic metalloenzymes, such as phosphatases and aminopeptidases [20, 21]. The catalytic role of zinc comprises Lewis acid activation of the substrate, generation of a reactive nucleophile (Zn–OH) and stabilization of leaving groups. Zinc(II) Schiff base complexes have often been found to be photochemically active.

Working on Schiff base zinc(II) complexes [22, 23] with bridging carboxylates, we report herein a new centrosymmetric trinuclear zinc(II) Schiff base complex $[Zn_3L_2(CH_3COO)_4]$ (**1**), obtained by the reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with a tridentate *N*,*N*,*O*-donor Schiff base ligand HL $[C_5H_4NC(CH_3){=}NC_6H_4(OH)]$ (Scheme 1). Systematic characterization of the complex was done by microanalytical, FT-IR, UV/Vis and thermal methods. Single crystal X-ray structural analysis has revealed that two terminal and one central zinc(II) ions in **1** adopt distorted square pyramidal and distorted octahedral geometry, respectively. The trinuclear units are held together through μ_2-phenolato and double μ-acetato-*O*,*O′* *syn-syn* bridging modes. Fluorescent properties of **1** indicate its potential to act as a promising photoactive material.

Results and Discussion

Fourier transform infrared spectra

The solid-state Fourier transform infrared spectra of HL and **1** were recorded on an FT-IR spectrophotometer in the range 4000–200 cm^{-1}. The samples were studied as powder dispersed in KBr pellets. For HL, a sharp strong peak for the imine (CH=N) group and a broad band for the phenolic OH group were observed at 1645 and 3398 cm^{-1}, respectively. HL shows strong sharp bands at 1586, 1473 and 1430 cm^{-1} corresponding to the pyridine skeleton [24a].

However, the azomethine stretching frequency is lowered by 25 cm^{-1} in **1** and observed at 1620 cm^{-1}, indicating the coordination of the imine (CH=N) nitrogen atom, as further supported by bands in the range 459 cm^{-1} corresponding to a ν(Zn–N) vibration. The absence of a peak around 3398 cm^{-1} in **1** indicates the absence of ν(OH) due to deprotonation followed by complexation [24b]. The bidentate bridging coordination mode of the acetate ion is revealed by the characteristic asymmetric and symmetric stretching vibrations at 1596 and 1446 cm^{-1}, respectively. The difference, $\Delta\nu$ $[\nu_{\text{asym}}(COO) - \nu_{\text{sym}}(COO)]$ of 150 cm^{-1} is quite low as compared to 164 cm^{-1} observed in the ionic acetate [24c]. An additional medium band assigned to ν(Zn–O) at 365 cm^{-1} is observed for **1** [23]. Complex **1** also exhibits strong sharp bands in the regions 1605–1597, 1485–1460, 1445–1420, 1055–1040 and 1015–1005 cm^{-1}, corresponding to the coordinated pyridine ring [24a].

X-Ray crystal structure of $[Zn_3L_2(CH_3COO)_4]$ (1)

The crystal structure of **1** as revealed from the X-ray diffraction study consists of a trinuclear molecule with a central Zn(II) ion lying on a center of inversion. Fig. 1 shows an ORTEP view of **1** with the atom labeling scheme adopted.

The trinuclear complex is built up of two mononuclear ZnL moieties linked through bridging acetate and μ_2-phenolato groups to the central Zn atom. This structure is analogous to a previously reported manganese complex [25a]. The coordination geometry around the terminal Zn centers (Zn1 and Zn1#1) may be regarded as distorted square pyramidal, described by the Addison distortion parameter (τ = 0.32) [25b] [the *cisoid* angles vary in the range of 76.11(5)–118.98(5)° and the *transoid* angles vary in the range of 133.61(5)–152.61(5)°, respectively]. The equatorial plane of a terminal Zn atom (Zn1) is formed by the pyridine nitro-

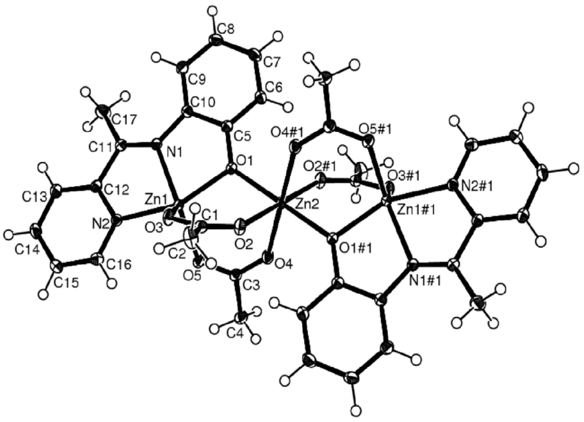

Fig. 1. ORTEP view of **1** with crystallographic labeling scheme adopted. Displacement ellipsoids are shown at the 50 % probability level. (Symmetry code to equivalent positions: #1 $2-x$, $-y$, $2-z$).

Table 1. Selected bond lengths (Å) and angles (deg) for **1**, with estimated standard deviations in parentheses.

Zn(1)–O(3)	1.9826(13)	Zn(1)–O(5)	1.9866(13)
Zn(1)–O(1)	2.0214(12)	Zn(1)–N(2)	2.1191(14)
Zn(1)–N(1)	2.1486(14)	Zn(2)–O(1)	2.0706(12)
Zn(2)–O(4)	2.0852(12)	Zn(2)–O(2)	2.1295(13)
O(1)–Zn(1)–N(1)	78.23(5)	O(1)–Zn(2)–O(1)$^{\#1}$	180.0
O(1)$^{\#1}$–Zn(2) –O(4)	90.65(5)	O(1)$^{\#1}$–Zn(2)–O(2)	89.82(5)
O(4)–Zn(2)–O(2)$^{\#1}$	86.13(5)	O(3)–Zn(1)–O(1)	104.83(5)
O(3)–Zn(1)–N(2)	95.90(5)	O(1)–Zn(1)–N(2)	152.61(5)
O(5)–Zn(1)–N(1)	133.61(5)	O(3)–Zn(1)–O(5)	106.38(5)
N(2)–Zn(1)–N(1)	76.11(5)	O(5)–Zn(1)–O(1)	100.12(5)
O(1)–Zn(2)–O(4)	89.35(5)	O(5)–Zn(1)–N(2)	90.79(5)
O(1)–Zn(2)–O(2)	90.18(5)	O(3)–Zn(1)–N(1)	118.98(5)
O(4)–Zn(2)–O(2)	93.87(5)		

Equivalent atoms generated by symmetry code: $^{\#1}$ $2-x$, $-y$, $2-z$.

Table 2. Hydrogen bonding parameters (Å, deg) for **1**.

D–H···A	D–H	H···A	D···A	∠D–H···A
C(6)–H(6)···O(2)$^{\#2}$	0.95	2.47	3.163(2)	130
C(9)–H(9)···O(3)$^{\#3}$	0.95	2.46	3.329(2)	152
C(15)–H(15)···O(2)$^{\#4}$	0.95	2.54	3.299(2)	138
C(15)–H(15)···O(1)$^{\#5}$	0.95	2.46	3.311(2)	150

Equivalent atoms generated by symmetry codes: $^{\#2}$ $1-x$, $1-y$, $1-z$; $^{\#3}$ $-x$, $1-y$, $1-z$; $^{\#4}$ $1/2-x$, $-1/2+y$, $1/2-z$; $^{\#5}$ $-1/2+x$, $1/2-y$, $-1/2+z$.

gen atom N2, and the phenolic oxygen atom O1 of the Schiff base, the imine nitrogen atom N1 and the oxygen atom O5 of one bridging acetate while another oxygen atom (O3) of the other bridging acetate group occupies the axial position. The bond lengths Zn1–N1 2.1486(14), Zn1–N2 2.1191(14), Zn1–O1 2.0214(12), Zn1–O5 1.9866(13) and Zn1–O3 1.9826(13) Å are in the range observed for similar systems [25c].

However, the coordination geometry of the central zinc ion (Zn2) may be best described as distorted octahedral, formed by six oxygen atoms from the same Schiff base ligands and acetate ions which coordinate the terminal zinc ions. Thus two Schiff base ligands and four acetate ions act as bridges between the two terminal zinc ions (Zn1 and Zn1#1) and the central zinc ion (Zn2). The four equatorial positions are occupied by the phenolato oxygen atoms O1/O1#1 in *trans* position [Zn2–O1 2.0706(12) Å], and two oxygen atoms O4/O4#1 of two acetate groups [Zn2–O4 2.0852(12) Å]. The two axial positions are occupied by O2/O2#1 [Zn2–O2 2.1295(13) Å] from the other two bridging acetate ligands. *Cisoid* angles vary in the range of 86.13(5) – 93.87(5)° while the *transoid* angles are 180° as required by symmetry. The four acetate ions connect the three zinc ions in a doubly μ-acetato-O,O′ *syn-syn* bridging mode, whereas in the related Mn system, the *syn-anti* mode has been observed [25a]. The three zinc ions are in a perfectly linear arrangement required by symmetry. The distances between the central zinc ion (Zn2) and the two terminal zinc ions are 3.3420(3) Å. A few crystal structures of trinuclear Zn(II) complexes are reported in the literature with either a linear or a bent structure [23, 26 – 28]. The planes between the bridging acetate groups in **1** are 78.66(2)°. There is no classical hydrogen bonding present, but there are several CH···O hydrogen bonds, the closest C···O distance being 2.46 Å. Selected bond lengths and angles are presented in Table 1, and the relevant hydrogen bonding parameters are summarized in Table 2, respectively.

Thermogravimetric analysis

The TGA curve of complex **1** indicates that the compound is stable up to 190 °C, above which it undergoes decomposition in two steps. A total mass loss of 27.6 % per formula unit corresponds to the release of four acetate groups in the temperature range 191 – 289 °C, followed by the loss of two molecules of Schiff base ligand between 290 – 350 °C, corresponding to a total mass loss of 68.19 %.

Absorption and fluorescence spectra of HL and 1

The electronic absorption and emission spectra of HL and **1** recorded in dilute methanolic solutions are shown in the Fig. 2.

The absorption spectrum of HL shows absorptions at 342 and 405 nm while **1** exhibits two absorption peaks at 382 and 445 nm. The absorption profile of **1**

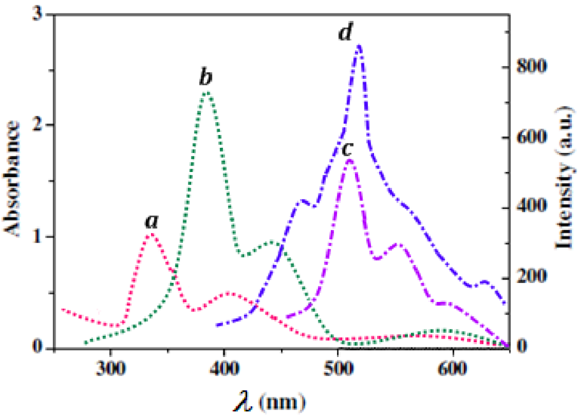

Fig. 2. (a) UV/Vis absorption spectrum of HL and (b) the spectrum of **1**, both recorded in methanolic solutions ($c = 3 \times 10^{-5}$ mol L^{-1}); (c) emission spectrum of HL and (d) the spectrum of **1**, both recorded in methanolic solutions ($c = 2 \times 10^{-6}$ mol L^{-1}).

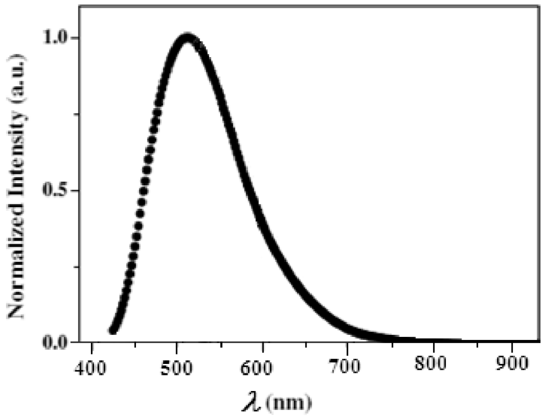

Fig. 3. Normalized luminescence spectrum of **1** in methanolic solution ($c = 2 \times 10^{-6}$ mol L^{-1}).

is similar to that of the free ligand, but the peaks of **1** are bathochromically shifted which gives a supporting evidence of the complexation to Zn(II) [29]. As shown in the Fig. 2, the emission spectra of **1** also closely resemble that of HL. Blue-green emission for both HL and **1** was observed with maxima at 510 and 511 nm, respectively. An additional shoulder peak for both HL and **1** was also detected. The enhanced fluorescence efficiency of the complex may be attributed to the coordination of the ligands to the zinc(II) ions which effectively increases the rigidity of the ligands and reduces the loss of energy *via* radiationless thermal vibrations [30].

To have a better understanding of the effect of the ligand conformations on the photoluminescent properties of the complex, the normalized photoluminescence spectrum of **1** in methanolic solution was also recorded (Fig. 3). The emission maximum wavelength was found at 511 nm when **1** was exposed to light of 390 nm wavelength.

Conclusion

In this paper we have reported the synthesis and the spectral and structural characterization of a new trinuclear centrosymmetric zinc(II) Schiff base complex. The Zn(II) centers are in two different coordination environments. The two terminal Zn(II) centers are five-coordinate with distorted square-pyramidal geometry whilst the central Zn(II) is six-coordinate and adopts a distorted octahedral geometry. Terminal Zn(II) ions are attached to the central Zn(II) ion through double μ_2-phenolato as well as through double μ-acetato-*O*,*O′* *syn-syn* bridges. Fluorescence properties of the complex indicate that it can serve as potential photoactive material.

Experimental Section

Materials

All chemicals and solvents used for the syntheses were of analytical grade. $Zn(CH_3COO)_2 \cdot 2H_2O$ (Fluka), 2-aminophenol (E. Merck), and 2-acetylpyridine (Aldrich Chemical Co. Inc.) were used as received.

Physical techniques

The Fourier transform infrared spectra of HL and **1** were recorded on a Perkin Elmer Spectrum RX I FT-IR spectrophotometer with a KBr disc in the range 4000 – 200 cm^{-1}. Elemental analyses (C, H, and N) were carried out using a Perkin Elmer 2400 II elemental analyzer. Thermogravimetric analyses were carried out at a heating rate of 10 °C/min with a Mettler-Toledo star TGA/SDTA-851^{e} thermal analyzer system in a dynamic atmosphere of N_2 (flow rate 80 mL/min) in an alumina crucible for the range 25 – 400 °C. The electronic absorption and fluorescence spectra were recorded on a Perkin Elmer Lambda-40 UV/Vis spectrometer and a Spex fluorolog II spectrofluorimeter, respectively.

Preparation of the ligand and the complex

Schiff base ligand: $[C_5H_4NC(CH_3)=N\,C_6H_4(OH)]$ *(HL)*

The Schiff base ligand HL was prepared by the reflux condensation of 2-acetylpyridine (0.606 g, 5 mmol) and 2-aminophenol (0.545 g, 5 mmol) in 50 mL of methanol for 3 h. The resulting deep-red solution was subjected to TLC which revealed the presence of some unreacted starting materials

Table 3. Crystal data and structure refinement for **1**.

Chemical formula	$C_{34}H_{34}N_4O_{10}Zn_3$
M_r	854.82
Crystal system	monoclinic
Space group	$P2_1/n$ (no.14)
a, Å	10.9512(5)
b, Å	14.6704(6)
c, Å	10.9756(4)
β, deg	104.628(2)
V, Å^3	1706.17(12)
Z	2
T(K)	100(2)
λ(MoK_α), Å	0.71073
D_{calcd}, g cm^{-3}	1.664
μ(MoK_α), cm^{-1}	21.56
F(000), e	872
θ range for data collection, deg	2.73 – 32.35
hkl range	$-16 \le h \le 16$, $-22 \le k \le 22$, $-16 \le l \le 16$
Total/unique data/R_{int}	29921/6089/0.0560
Observed data [$I \ge 2\sigma(I)$]	4611
Data/restraints/parameters	6089/0/235
Final $R1/wR2$ indices [$I \ge 2\sigma$ (I)]	0.0322/0.0683
Final $R1/wR2$ indices[a] (all data)	0.0530/0.0752
GoF[b] (F^2)	1.017
$\Delta\rho$(max/min), e Å^{-3}	0.474/−0.483

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0333P)^2 + 0.1721P]^{-1}$, where $P = (\text{Max}(F_o{}^2,0) + 2F_c{}^2)/3$; [b] GoF$= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

along with the Schiff base product. The Schiff base product was isolated by column chromatography over silica gel (SRL) 60 – 120 mesh size, using a mixture of light petroleum and ethyl acetate (v/v, 1 : 1). The subsequent evaporation of this eluent yielded the pure ligand in liquid form. The solution of the purified ligand was then evaporated under reduced pressure to yield a gummy mass, which was dried and stored *in vacuo* over $CaCl_2$for subsequent use. Yield: 0.954 g (90 %).

[$Zn_3L_2(CH_3COO)_4$] (*1*)

The solid Schiff base ligand HL (0.424 g, 2 mmol) was dissolved in methanol (20 mL). A gently warmed solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.658 g, 3 mmol) in methanol (10 mL) was added, and the mixture was stirred vigorously for 2 h at 50 °C. The resulting deep-red solution was then filtered, and the filtrate was left undisturbed. After 15 d brownish-red spindle-shaped X-ray diffraction-quality single crystals of **1** separated upon slow evaporation of the filtrate. They were filtered and dried *in vacuo* over $CaCl_2$. Yield: 0.650 g (76 %) with respect to the metal substrate.

Physical and spectroscopic data: For HL: UV/Vis (CH_3OH): λ_{max} = 342 (ε = 3800 M^{-1} cm^{-1}) and 405 nm (ε = 1480 M^{-1} cm^{-1}). – IR (KBr disc): ν_{str} = 1645 (CH=N, strong), 3398 (phenolic-OH, medium) cm^{-1}. – Analysis for HL (212.254): calcd. C 73.56, H 5.70, N 13.20; found C 73.59, H 5.68, N 13.24. For **1**: M. p. 155 °C. – UV/Vis (CH_3OH): λ_{max} = 382 (ε = 5700 M^{-1} cm^{-1}) and 445 nm (ε = 3560 M^{-1} cm^{-1}). – IR (KBr disc): ν_{str} = 1620 (CH=N, strong), 459 (Zn–N, weak), 365 (Zn–O, weak) cm^{-1}. – Analysis for **1**: (852.825 for $C_{34}H_{34}N_4O_{10}Zn_3$): calcd. C 47.77, H 4.01, N 6.55; found C 47.75, H 3.98, N 6.54.

X-Ray crystallographic data collection and structure refinement

A good diffraction-quality, air-stable single crystal of **1** ($0.18 \times 0.20 \times 0.24$ mm^3) was mounted on a Bruker SMART CCD area diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). Crystal data were collected using Bruker SMART [31a] software at a temperature of 100(2) K. Cell refinements were carried out using Bruker SAINT [31b]. No significant intensity variation was observed. Multiscan absorption correction was applied to the intensity values (T_{max} = 0.6975, T_{min} = 0.6256) empirically using SADABS [31c]. Data reduction was performed using Bruker SAINT [31b]. The structure of **1** was solved by Direct Methods using the program SHELXS-97 and refined with full-matrix least-squares based on F^2 using SHELXL-97 [31d]. For all non-hydrogen atoms, the anisotropic displacement parameters have been refined successfully. Hydrogen atoms of the aromatic rings and the imino groups were placed geometrically and refined as a riding model taken from a Fourier difference map and refined with isotropic thermal parameters. The molecular graphics and crystallographic illustrations of the complex were prepared using ORTEP [31e] and Bruker SHELXTL [31f] programs. All the relevant crystallographic data and structure refinement parameters are summarized in Table 3.

Supplementary data

CCDC 645543 contains 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.

Acknowledgements

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