

# Synthesis, Characterisation and Crystal Structure of a Copper(II) Dichromate Complex with the N,N'-Bis(2-pyridylmethylene)butane-1,4-diamine Schiff Base Ligand

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The new complex  $\text{Cu}[\text{L}^1]\text{Cr}_2\text{O}_7$  has been synthesised with the N,N'-bis(2-pyridylmethylene)butane-1,4-diamine Schiff base  $\text{L}^1$ ,  $[\text{NC}_5\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_4\text{N}=\text{CHC}_5\text{H}_4\text{N}]$ , and characterised with elemental analyses and different spectroscopic and electrochemical studies. The structure of the new complex has been established by single crystal X-ray diffraction. The complex crystallises in the monoclinic system with space group  $P2_1/c$  having cell parameters  $a = 14.7(5)$ ,  $b = 9.22(2)$ ,  $c = 16.2(5)$  Å,  $\beta = 116.9(1)^\circ$ , and  $Z = 4$ . The  $\text{Cr}_2\text{O}_7^{2-}$  unit is bonded through one terminal oxygen donor end to the central Cu(II) chelated by the Schiff base ligand.

**Key words:** Copper(II), Dichromate, Schiff Base, Synthesis, X-Ray Structure

## Introduction

Inherently acentric molecules can provide building blocks for the synthesis of new framework materials with promising ferroelectric and second-order non-linear optical (NLO) behaviour. For example, potassium dihydrogenphosphate is a well-known ferroelectric material with discrete  $\text{PO}_4^{3-}$  tetrahedra [1]. The dichromate anion  $[\text{Cr}_2\text{O}_7]^{2-}$ , is another attractive candidate in this series for study. The advantage of the use of dichromate over molybdate and tungstate as bridging ligand lies in the simplicity of the solution equilibria: molybdate and tungstate tend to undergo complicated hydrolysis to give a variety of species, whereas only chromate and dichromate are involved in a dynamic equilibrium [2].  $\text{HCrO}_4^-$  and  $[\text{Cr}_2\text{O}_7]^{2-}$  remain in equilibrium between physiologically accessible pH values of 5–6. Nowadays, metal complexes containing  $\text{CrO}_4^{2-}$  or  $\text{Cr}_2\text{O}_7^{2-}$  as a ligand are gaining more and more attention owing to their spectroscopic [3, 4], structural [5, 6], magnetic, thermal [7, 8] and catalytic [7] properties.

Chromate and dichromate complexes have long been recognised for their genotoxic and mutagenic effects in living cells, leading to the development of cancer in humans [9]. Considering the redox pathways of the carcinogenic Cr(VI) anion and the interac-

tion of its metabolites Cr(V), Cr(IV) and Cr(III) with DNA [10–12], the lowering of its mutagenic activity has been explained by the mode of the chromate ion binding to the metal-organic ligand core. Metal chromate(VI) complexes with 1,10-phenanthroline or 2,2'-bipyridyl, tested by the standard Ames test, exhibited significantly lower activity than the reference compounds potassium dichromate and potassium chromate [13]. As the observed carcinogenicity of Cr(VI) depends on the ability of its oxoanions to cross the cell membrane by the anion-transport system, the symmetry of the Cr(VI) species may influence the effectiveness of this membrane crossing and here lies the importance of the coordination chemistry of complexes with chromium(VI) anions (chromates, dichromates, polychromates *etc.*) [6]. Previously we have reported one dichromato-bridged Ni(II) polymeric complex [14]. In continuation of our investigations we report here the synthesis, spectroscopic and electrochemical studies and X-ray crystal structure of a new copper(II) complex bearing a dichromate anion in coordination.

## Results and Discussion

### Infrared spectrum

The solid state Fourier Transform infrared spectrum of the complex is fully consistent with its crys-

tal structure. The metal bonded  $\nu_{\text{str}}(\text{CH}=\text{N})$  imine stretching frequencies were observed as intense bands at 1597 and 1625  $\text{cm}^{-1}$ . The peaks at 895, 916, 936 and 951  $\text{cm}^{-1}$  are due to various  $\nu_{\text{str}}(\text{Cr}-\text{O})$  stretching modes [15a]. The peaks at 215 and 544  $\text{cm}^{-1}$  are due to the Cr–O–Cr symmetric bending and stretching vibrations. The infrared bands for the dichromate moiety are in good agreement with those reported for  $\text{K}_2\text{Cr}_2\text{O}_7$  [15b]. Ligand coordination to the Cu(II) metal center is substantiated by two bands at 475 and 504  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{str}}(\text{Cu}-\text{N})$  and  $\nu_{\text{str}}(\text{Cu}-\text{O})$ , respectively [16a]. The bands at 1595, 1474, 1458 and 1441  $\text{cm}^{-1}$  are assigned to the pyridine skeleton [16b]. All the above frequencies found for the complex match well with similar structures reported in the literature.

#### UV/vis spectrum

Although the electronic spectra of the copper complexes with multidentate Schiff base ligands are not in general good indicators of geometry, they do help to support it. The solution electronic spectrum of the title complex in acetonitrile solution shows a  $d-d$  transition band at 645 nm (broad) and two ligand-to-metal charge transfer (LMCT) bands at 370 nm ( $\epsilon = 3900 \text{ M}^{-1} \text{ cm}^{-1}$ ) and at 270 nm ( $\epsilon = 3200 \text{ M}^{-1} \text{ cm}^{-1}$ ).

The bands in the region 464–337 nm may be assigned to the  $n-\pi^*$  transitions of the azomethine group. In the spectra of this type of complexes, the bands due to the azomethine chromophore are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion [17].

#### Cyclic voltammetry

The electrochemical activity of the compound was studied using tetraethylammonium perchlorate as the supporting electrolyte at a scan rate of 50  $\text{mV s}^{-1}$ . A one electron reductive response is observed, which may be due to the following electrode reaction:  $[\text{Cu}^{\text{II}}(\text{L}^1)]^{2+} + e^- \rightarrow [\text{Cu}^{\text{I}}(\text{L}^1)]^+$ , where  $\text{L}^1$  is the Schiff base ligand. The measurement shows reproducibility in the range 0.08 to  $-0.08 \text{ V}$  without any decomposition. The one electron stoichiometry of the couples have been confirmed by comparing [18] the current height with that for the standard Cu(II)/Cu(I) couple.

#### Room temperature magnetic susceptibility study

The complex as a solid exhibits r. t. magnetic susceptibility as expected for isolated  $d^9$  transition metal

centres. The effective magnetic moment ( $\mu_{\text{eff}}$ ) value is found to be 1.74 B.M. at 300 K. The value is consistent with the expected spin-only magnetic moment of a  $S = 1/2$ , Cu (II)  $d^9$  electronic system.

#### X-Ray crystal structure of the complex

The title complex crystallises in the monoclinic space group  $P2_1/c$ . A perspective view of **1** with the atom numbering scheme is presented in Fig. 1 as an ORTEP plot, and the packing diagram is shown in Fig. 2 (displacement ellipsoids are drawn at the 50 % probability level for non-hydrogen atoms). Selected interatomic distances and angles are provided in Table 1. The complex is heteronuclear, containing one  $[\text{Cr}_2\text{O}_7]^{2-}$  anion and a cationic unit  $[\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_4)]^{2+}$  bridged through a Cu-coordinated dichromate oxygen atom.

In the cationic part, the neutral Schiff base ligand,  $\text{L}^1$ , is tetradentate, coordinating *via* two imino and two pyridine nitrogen atoms to the central Cu(II) ion. The coordination polyhedron around the Cu(II) center can be best described as highly distorted trigonal bipyramidal (tbp). The distortion from ideal geometry may arise from the asymmetric non-planar nature of the Schiff base. The butylidene part of the Schiff base  $\text{N}(2)-\text{C}(7)-\text{C}(8)-\text{C}(9)-\text{C}(10)-\text{N}(3)$  is puckered due to  $sp^3$  hybridisation of the carbon atoms in the saturated fragment of the chelating ligand. The central metal coordination sphere includes the tetradentate Schiff base, chelating through two pyridine nitrogens [N(1), N(4)] and two imine nitrogens [N(2), N(3)], and one termi-

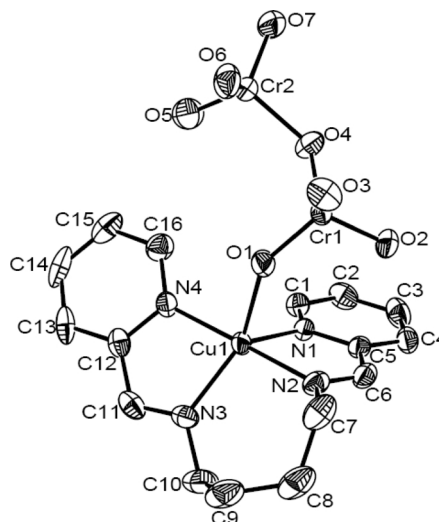
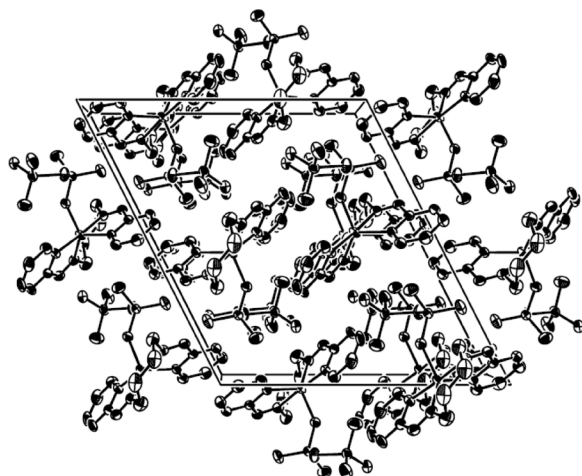


Fig. 1. ORTEP view of **1** with atom labeling scheme.

Fig. 2. Packing diagram of the complex **1**.

nal dichromate oxygen O(1). This coordination is common for Cu(II) with either square pyramidal (spy) or trigonal bipyramidal (tbp) geometry. Recently, some complexes have been reported in which the Cu(II) ion adopts a geometry that is intermediate between spy and tbp [18, 19]. Addison *et al.* [20] have introduced an angular structural parameter  $\tau$  (index of trigonality) for distinguishing between a trigonal bipyramidal and a square pyramidal geometry in five-coordinate metal complexes,  $\tau = (\beta - \alpha)/60$ , where  $\alpha$  and  $\beta$  are the two largest coordination angles.

Generally,  $\tau = 0$  indicates an ideal square pyramidal, and  $\tau = 1$  an ideal trigonal bipyramidal geometry [20]. In our case, the value of  $\tau$  is 0.597 for **1**, which indicates that the geometry around the central copper atom may be more precisely described as a compromise between tbp and spy structures. In other words, the complex ion exhibits a CuN<sub>4</sub>O chromophore coordination mode with highly distorted (3+2) (NNO + NN) trigonal bipyramidal geometry around the metal centre.

The mean basal triangular plane is occupied by the one pyridine nitrogen atom N(1), one imine nitrogen atom N(3) of the tetradentate Schiff base and one dichromate oxygen atom O(1). The two axial sites are occupied by the pyridine nitrogen atom N(4) and an imine nitrogen atom N(2) from the Schiff base. The Cu(1)–N(1), Cu(1)–N(2), Cu(1)–N(3), Cu(1)–N(4) and Cu(1)–O(1) distances are 2.157(2), 1.967(2), 2.008(2), 1.972(2) and 2.046(2) Å, respectively, or, in simpler terms, axial bond lengths are slightly shorter than equatorial bond lengths. The equatorial N(3)–Cu(1)–N(1), N(3)–Cu(1)–O(1), N(1)–Cu(1)–O(1) and axial N(4)–Cu(1)–N(2) bond

Table 1. Selected bond lengths (Å) and angles (deg) for **1**.

| Bond lengths |          | Bond angles     |          |
|--------------|----------|-----------------|----------|
| Cu(1)–N(1)   | 2.157(2) | O(1)–Cu(1)–N(1) | 96.0(1)  |
| Cu(1)–N(2)   | 1.967(2) | O(1)–Cu(1)–N(2) | 88.6(1)  |
| Cu(1)–N(3)   | 2.008(2) | O(1)–Cu(1)–N(3) | 139.5(1) |
| Cu(1)–N(4)   | 1.972(2) | O(1)–Cu(1)–N(4) | 89.5(1)  |
| Cu(1)–O(1)   | 2.046(2) | N(1)–Cu(1)–N(2) | 80.3(1)  |
| Cr(1)–O(1)   | 1.644(2) | N(1)–Cu(1)–N(3) | 124.5(1) |
| Cr(1)–O(2)   | 1.613(2) | N(1)–Cu(1)–N(4) | 104.1(1) |
| Cr(1)–O(3)   | 1.608(2) | N(2)–Cu(1)–N(3) | 96.8(1)  |
| Cr(1)–O(4)   | 1.777(2) | N(2)–Cu(1)–N(4) | 175.4(1) |
| Cr(2)–O(4)   | 1.815(2) | N(3)–Cu(1)–N(4) | 82.0(1)  |
| Cr(2)–O(5)   | 1.617(2) | O(1)–Cr(1)–O(2) | 110.2(1) |
| Cr(2)–O(6)   | 1.614(2) | O(1)–Cr(1)–O(3) | 109.4(1) |
| Cr(2)–O(7)   | 1.616(2) | O(1)–Cr(1)–O(4) | 110.2(1) |

angles are 124.5(1), 139.5(1), 96.0(1) and 175.4(1)° respectively. The Cu(II) centre deviates from the mean basal plane formed by N(1), N(3) and O(1) by 0.010(2) Å towards N(4).

The deviation from the trigonal pyramidal geometry is indicated by the axial-equatorial bond angles which vary from 80.3(1)–104.1(1)° from the normal value of 90°. The L<sup>1</sup> ligand is somewhat twisted at the copper centre. There is apparent strain in the butyl chain shown by torsion angles differing markedly from normal *gauche* and *trans* angles. The bond angles and bond lengths of **1** are close to the values in related pentacoordinated complexes reported elsewhere in the literature [18, 19, 21, 22].

The Cr<sub>2</sub>O<sub>7</sub><sup>2–</sup> anion is in an almost staggered conformation, in contrast to the situation found in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. In potassium dichromate, two CrO<sub>4</sub><sup>2–</sup> tetrahedra are in a nearly eclipsed conformation [23], when viewed along the line joining the Cr atoms. The O–Cr–O bond angles in **1** are between 106.9(1) and 111.1(1)°, close to the tetrahedral value of 109.5°. The Cr–O–Cr bridging angle is 125.2(1)°. The O(1)–Cr(1)–O(4)–Cr(2) torsion angle is 65.9(1)°. The Cr–O terminal bond lengths are in the range 1.608(2)–1.617(2) Å and agree well with those reported previously for the uncoordinated unit of CrO<sub>4</sub><sup>2–</sup> [24–27]. The bridging Cr–O bonds are longer and in the range 1.777(2)–1.815(2) Å.

## Conclusion

The combination and crystallisation of the molecular ions [Cr<sub>2</sub>O<sub>7</sub>]<sup>2–</sup> and [Cu(C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>)]<sup>2+</sup>, has resulted in the complex **1**. Here the bridging character of the dichromate anion is absent unlike in other dichromate complexes [28]. The weaker tendency of

the dichromate ion for coordination in comparison to the chromate ion is due to the higher negative charge of the terminal oxo atoms of the  $\text{CrO}_4^{2-}$  in comparison to  $\text{Cr}_2\text{O}_7^{2-}$  as well as to steric factors. This observation is in line with the fact that dichromates are generally more soluble than chromates in polar media. From physicochemical and biological studies it is known that among the various forms of chromium(VI), tetrahedral  $\text{CrO}_4^{2-}$  ions dominate at physiological pH and are easily transported through the cellular membrane. Once they enter the cell, they oxidise its constituents and undergo a metabolic reduction,  $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$ . The removal of this genotoxic effect can be achieved by inhibiting the redox process of the chromium(VI) through its complexation or extra-cellular reduction. To achieve this goal, the informations about the role of the “environment” around the chromium ion, the reactants concentration, the medium, the temperature is surely to be gathered.

## Experimental Section

### Materials

All chemicals and solvents used for the syntheses were of analytical grade. Pyridine-2-carboxaldehyde, 1,4-diaminobutane, and potassium dichromate were all purchased from Aldrich Chemical Co. and used without further purification. Copper perchlorate hexahydrate  $[\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}]$  was prepared by treatment of copper carbonate  $[\text{Cu}(\text{CO}_3)_2 \cdot \text{Cu}(\text{OH})_2]$  (E. Merck, India) with 60 % aqueous perchloric acid (E. Merck, India) followed by slow evaporation on a steam bath. It was then filtered through a fine glass frit and preserved in a  $\text{CaCl}_2$  desiccator.

**Caution:** Although no problems were encountered in this work, perchlorate salts in presence of organic ligands are potentially explosive in nature. Compounds should be prepared in small quantities and handled with utmost care.

### Preparation of the ligand and the complexes

**Schiff base ligand:**  $[\text{NC}_5\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_4\text{N}=\text{CHC}_5\text{H}_4\text{N}]$  ( $\text{L}^1$ )

The tetradentate Schiff base ligand was prepared by the condensation of a dry methanolic solution of the pyridine-2-carboxaldehyde with 1,4-diaminobutane (2 : 1 mmol ratio) and refluxing for half an hour at 40 °C following the literature procedure [29].

$\text{Cu}[\text{NC}_5\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_4\text{N}=\text{CHC}_5\text{H}_4\text{N}]\text{Cr}_2\text{O}_7$  (**I**)

20 mL of a methanolic solution of the ligand  $\text{L}^1$  (4 mmol) was added dropwise to a vigorously stirred warm solution of

$\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$  (0.354 g, 1 mmol) in 10 mL of methanol. A greenish precipitate appeared. It was just dissolved on adding methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) drop by drop avoiding excess. After filtration the solution was cooled to 0 °C in an ice bath followed by slow addition of an aqueous solution of potassium dichromate (0.294 g, 1 mmol). Dark green crystals suitable for X-ray analysis appeared after one night standing. Yield: 65 % with respect to the copper salt.

**Physical and spectroscopic data:** M. p. 145 °C. – UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon_{\text{max}}$ ) = 370 nm (4.85). – IR (KBr disc):  $\nu$  = 1625 (CH=N, strong), 1597, 916 (Cr–O, medium), 895, 544 (Cr–O–Cr, medium), 504 (Cu–O, weak), 475 (Cu–N, weak), 215 (Cr–O–Cr, medium). – F. w. 545.8703 (calcd. 545.8763 for  $\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_4)\text{Cr}_2\text{O}_7$ ). Calcd. C 35.20, H 3.32, N 10.26, Cu 11.64; found C 35.81, H 3.29, N 10.25, Cu 11.52.

### Physical techniques

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHN Elemental Analyser. Copper was estimated following the standard iodometric procedure. The Fourier Transform infrared spectrum was recorded on a Perkin-Elmer RXI FT-IR spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$  as a KBr disc and the UV/vis spectrum on a Perkin-Elmer Lambda-40 spectrometer using HPLC grade acetonitrile as solvent at 300 K in 1 cm quartz cuvettes. The cyclic voltammetric measurement was performed using an EG & G PARC electrochemical analysis system (model 250-5-0) under a dry  $\text{N}_2$  atmosphere using the conventional, three electrode configuration in acetonitrile (HPLC grade) with tetraethylammonium perchlorate as the supporting electrolyte. A planar EG & G PARC G0229 glassy carbon milli electrode was used as the working electrode at a scan rate of  $\nu = 50 \text{ mV s}^{-1}$ . Formal potential  $E_0 = 0.5(E_{\text{pa}} + E_{\text{pc}})$ ,  $E_{\text{pa}}$  and  $E_{\text{pc}}$  being anodic and cathodic peak potentials, respectively;  $\Delta E_{\text{p}}$  is the peak-to-peak separation. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for junction contributions.

### X-Ray crystallographic data collection and structure refinement

A good diffraction quality, air stable single crystal of **1** ( $0.08 \times 0.30 \times 0.43 \text{ mm}^3$ ) was selected and mounted on a Nonius KappaCCD diffractometer equipped with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystal data were collected using COLLECT [30a] at a temperature of 123(2) K. The unit cell parameters were determined from the least-squares refinement of 25 centered reflections in the range of 3.11 to 28.18° using  $\phi$  and  $\omega$  scans. Cell refinements were carried out using HKL SCALEPACK [30b]. No significant intensity variation was observed. A total of 26102 reflections (4723 independent reflections,  $R_{\text{int}} = 0.034$ ) were

Table 2. Crystal and structure refinement data.

|                                                 |                                                                                      |
|-------------------------------------------------|--------------------------------------------------------------------------------------|
| Empirical formula                               | Cu(C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> )Cr <sub>2</sub> O <sub>7</sub>    |
| Formula weight                                  | 545.8703                                                                             |
| Crystal system                                  | monoclinic                                                                           |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                   |
| <i>a</i> , Å                                    | 14.6901(5)                                                                           |
| <i>b</i> , Å                                    | 9.1798(2)                                                                            |
| <i>c</i> , Å                                    | 16.1782(5)                                                                           |
| $\beta$ , deg                                   | 116.904(1)                                                                           |
| <i>V</i> , Å <sup>3</sup>                       | 1945.5(1)                                                                            |
| <i>Z</i>                                        | 4                                                                                    |
| Calcd. density, mg m <sup>-3</sup>              | 1.864                                                                                |
| $\mu$ , mm <sup>-1</sup>                        | 2.229                                                                                |
| <i>F</i> (000), e                               | 1100                                                                                 |
| $\theta$ range of data coll., deg               | 3.11 to 28.18                                                                        |
| Limiting indices                                | $-19 \leq h \leq 19$ , $-12 \leq k \leq 12$ ,<br>$-21 \leq l \leq 21$                |
| Total data/unique data/ <i>R</i> <sub>int</sub> | 26102 / 4723 / 0.034                                                                 |
| Observed data [ $I \geq 2\sigma(I)$ ]           | 3933                                                                                 |
| Refined parameters                              | 271                                                                                  |
| Weighting scheme ( <i>w</i> )                   | $[\sigma^2(F_o^2) + (0.0267P)^2 + 3.1942P]^{-1}$ ,<br>$P = ([F_o]^2 + 2[F_c]^2)/3$ . |
| Goodness-of-fit on <i>F</i> <sup>2</sup>        | 1.045                                                                                |
| <i>R</i> <sub>1</sub> [ $I \geq 2\sigma(I)$ ]   | 0.046                                                                                |
| <i>wR</i> <sub>2</sub> (all data)               | 0.069                                                                                |

collected applying the boundary condition  $I \geq 2\sigma(I)$ . An empirical absorption correction was applied to intensity values ( $T_{\max} = 1.0$ ,  $T_{\min} = 0.763$ ) using SADABS [30c]. Data reduction was carried out using HKL DENZO and SCALEPACK.

The final structure was solved by Direct Methods using the program SHELXS-97 [30d] and refined with full-matrix least-squares techniques on *F*<sup>2</sup> using SHELXL-97 [30d]. The molecular graphics and crystallographic illustrations were prepared using the XSEED [30e] program. For all non-hydrogen atoms the anisotropic displacement parameters have been refined. Hydrogen atoms of the aromatic rings and the imino groups were placed geometrically and refined as riding model taken from a difference Fourier map and refined with isotropic thermal parameters. Maximum and minimum peaks (e Å<sup>-3</sup>) in the final difference Fourier synthesis were 0.462 and -0.454. Selected crystallographic data and structure refinement parameters are summarised in Table 2.

#### Supplementary material

CCDC 618650 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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