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ORIGINAL PAPER

Synthesis, X-ray Structure Analysis and Spectroscopic Characterization of *trans*-Aquabis(*μ*-benzoato-κ^2*O*:*O*′) bis[*μ*-*N*,*N*′-bis(4-methoxyphenyl) formamidinato-κ^2*N*:*N*′] dimolybdenum(II)

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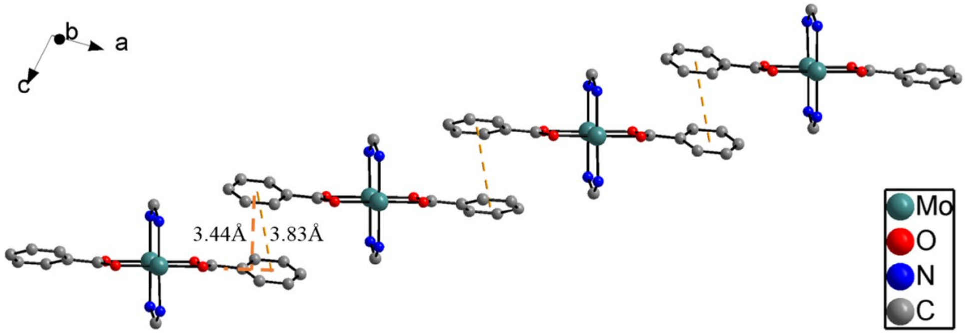
Abstract The title compound, *trans*-$Mo_2(DAniF)_2(OOCC_6H_5)_2(H_2O)$ (**I**) has a quadruply bonded Mo_2^{4+} unit equatorially coordinated by two *N*,*N*′-bis(4-methoxyphenyl) formamidinate (referred as DAniF) ligands and two benzoate ($OOCC_6H_5$) groups in transverse, and axially coordinated by one aqua oxygen atom. The compound crystallizes in the space group *C*2/*c* with one molecule in the asymmetric unit and features a Mo–Mo bond length of 2.0983(4) Å, which is typical for dimolybdenum quadruple bonds. In the crystal, the offset π–π stacking between pairs of phenyl rings creating a one-dimensional linear chain perpendicular to the Mo–Mo directions, with a distance between phenyl rings of 3.44 Å and the center-to-center distance of 3.83 Å. The coordinated water oxygen atoms act as donors and uncoordinated methoxyl group oxygen atoms act as acceptors in intermolecular O–H···O hydrogen bonds. π–π stacking between phenyl rings assemble the molecules into a three-dimensional framework.

Graphical Abstract The offset π–π stacking between phenyl rings of quadruply bonded Mo_2^{4+} paddle-wheel molecules create a one-dimensional linear chain.



Keywords Crystal structure · Dimolybdenum · Quadruple bonds · Intermolecular interactions

Introduction

Intermolecular weak interactions generally include hydrogen bonds, π–π stacking, cation-π interactions, and others,

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with hydrogen bonds playing a prominent role in supramolecular and template chemistry [1–3]. The intermolecular interaction of benzene has been studied extensively, especially in the last three decades, both by experimental and theoretical methods as a prototype for the π–π stacking [4–7] as phenyl–phenyl π–π stacking plays an important role in determining the conformation of organic molecules [8], the structure and stability of proteins and polynucleotides, [9] and in directing the stereoselectivity of organic transformations [10].

We became interested in making dimetal compounds having phenyl rings suitable for forming novel supramolecular arrays using phenyl–phenyl π–π stacking. The key to success in creating dimetal units is a design that selectively blocks some coordination sites, for example by using one to three nonlabile three-atom bridging ligands. For this purpose, a new quadruply bonded dimolybdenum compound with two transoid C_6H_5 pendants was prepared. Compound **I** is a mixed–ligand complex, *trans*-$Mo_2(DAniF)_2(OOCC_6H_5)_2{\cdot}(H_2O)$, on which auxiliary ligands DAniF [11] [*N,N′*-bis(4-methoxyphenyl) formamidinate] are used to block the unnecessary coordination sites. Given the transoid geometry of the building block, intermolecular phenyl–phenyl π–π stacking was expected to generate infinite extension of the supramolecular motifs.

Experimental

Materials and Methods

All manipulation and procedures were performed in a nitrogen atmosphere, using either a nitrogen drybox or standard Schlenk line techniques. Solvents were freshly distilled in a nitrogen atmosphere by employing standard procedures or dried and degassed using a Glass Contour solvent purification system. The starting materials DAniF [11], $Mo_2(OOCCH_3)_4$ [12, 13] and *trans*-$Mo_2(DAniF)_2(OOCCH_3)_2$ [14] were prepared according to published methods. Elemental analyses for C, H and N were performed with a Vario EL III elemental analyzer. ^1H NMR spectra were recorded with a Mercury-300 NMR spectrometer with chemical shifts (δ in ppm) referenced to $CDCl_3$. Electronic spectra in CH_2Cl_2 were measured in a range of 300 to 800 nm on a Agilent 8453 UV–Vis spectrophotometer. Raman spectra were collected on a Nicolet Almega XR laser Raman spectrometer.

Synthesis of the *trans*-$Mo_2(DAniF)_2(OOCC_6H_5)_2(H_2O)$ (I)

To the solution of *trans*-$Mo_2(DAniF)_2(OOCCH_3)_2$ (0.41 g, 0.50 mmol) in 15 mL of THF, was added 2.0 mL $NaOCH_3$ solution (0.5 M in methanol). After stirring for about 2 h, a colorless microcrystalline material was removed by filtration. An excess of benzoic acid (0.16 g, 1.3 mmol) was added to the filtrate. After stirring at room temperature for an additional 1 h, the solvent was removed under vacuum, and the residue was washed with ethanol (2 × 15 mL), then dried under vacuum. The yellow solid was dissolved in THF (15 mL) and the solution was layered with hexanes. Yellow block-shaped crystals formed after several days. Yield: 0.26 g (55%). Anal. Calcd for $C_{44}H_{42}Mo_2N_4O_9$: C, 54.89; H, 4.40; N, 5.82; found: C, 54.94; H, 4.38; N, 5.87 (Scheme 1).

X-ray Crystal Structure Determinations

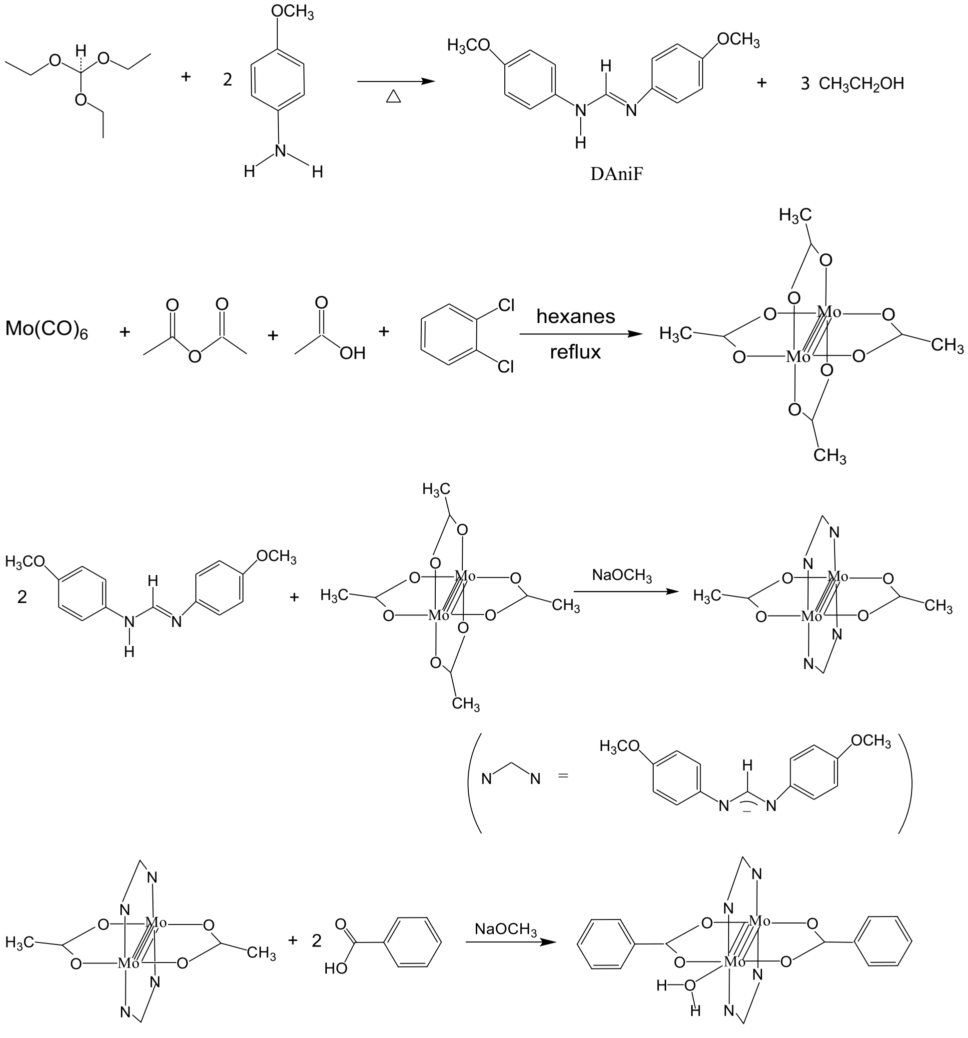
Determination of unit cell and data collection of the compound **I** were performed on a Bruker CCD diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293 K. The data integration and reduction were carried out with SAINT-plus software [15]. An empirical absorption correction was applied to the collected reflections with SADABS [16], and the space group was determined using XPREP [17]. The structure was solved by the direct methods with SHELXS-2014 and refined by full matrix least-squares with SHELXL-2014 [18] on F^2. All nonhydrogen atoms were refined with anisotropic thermal parameters. The water H atoms were located from the difference Fourier map and included as riding atoms, with O–H = 0.85 Å (lattice water). The C-bound H atoms were positioned geometrically and refined as riding atoms, with C–H = 0.93 Å (aromatic) or 0.96 Å (methyl) and Uiso(H) = kUeq(C), where k = 1.5 for the methyl group and 1.2 for all H atoms bonded to the aromatic C atoms. All structures were examined using the Addsym subroutine of PLATON [19] to ensure that no additional symmetry could be applied to the models. The molecular graphics were done using XP in SHELXTL [20] and DIAMOND [21]. Crystal data and structural refinement parameters are summarized in Table 1 and selected bond lengths and bond angles are listed in Table 2.

Results and Discussion

Crystal Structure

Crystals *trans*-$Mo_2(DAniF)_2(OOCC_6H_5)_2{\cdot}(H_2O)$ (**I**) were obtained by crystallization from THF/C_6H_{14} solution. The single crystal structure of (**I**) is shown in Fig. 1. The title compound crystallized in the space group *C*2/*c* with one molecule in the asymmetric unit. The molecule has a quadruply bonded Mo_2^{4+} unit, equatorially coordinated by two DAniF ligands and two benzoate ($OOCC_6H_5$) groups in transverse forming a paddle-wheel-type structure,

Scheme 1 Reaction scheme for the synthesis of the title compound



trans-$Mo_2(DAniF)_2(OOCC_6H_5)_2(H_2O)$

and axially coordinated by one aqua oxygen atom with a Mo2–O1w distance of 2.475(2) Å. The Mo1–Mo2 bond length of 2.0983(4) Å is typical for dimolybdenum quadruple bonds [22]. The Mo–O lengths in the equatorial positions range from 2.1002 (16) Å for Mo1–O4 to 2.1329 (16) Å for Mo2–O3, and the Mo–N lengths are 2.132 (2) Å for Mo1–N2 and 2.149 (2) Å for Mo2–N1, respectively (Table 2). The dihedral angle between the phenyl ring and the adjacent five-membered ring (Mo_2O_2C) is 18.706(8)°. In comparison, in compound *trans*-$Mo_2(DAniF)_2(OOCC_6F_5)_2\cdot(THF)_2$ **(II)** [23], the dihedral angle between the pentafluoro-phenyl ring and adjacent five-membered ring (Mo_2O_2C) is 26.902(9)°, and the larger dihedral angle can be attributed to the strong O···F repulsion. The presence of Mo–Mo quadruple bonds, which act as an electron withdrawing group, increase the electron density on the oxygen atoms, and thus enhance O···F repulsion.

In compound **I**, the offset π–π stacking between pairs of phenyl rings creates a one-dimensional ladder chain as illustrated in Fig. 2. The perpendicular distance between phenyl rings is 3.44 Å and the center-to-center distance is 3.83 Å.

In compound **II**, perfluorophenyl–perfluorophenyl interaction occurs in an offset face to face stacking fashion with an interplanar distance of 3.30 Å and a center to center distance of 3.53 Å. The above results suggest that the π–π stacking interactions between perfluorophenyl rings are stronger than those between phenyl rings. While, in compound $Mo_2(DAniF)_3(OOCC_6H_5)$ (**III**) having only one phenyl ring in the equatorial position of the paddle–wheel structure [24], the π–π stacking between pairs of phenyl rings was not observed owing to the steric effect of DAniF ligand in transverse of the phenyl ring. The phenyl ring and the (Mo_2O_2C) fragment are nearly co-planar, making a dihedral angle of 3.24 (13)°. So we infer that the dihedral angle of 18.706(8) ° is induced by π–π stacking between phenyl rings in compound **I** (Fig. 3).

Table 1 Crystal data and structure refinement for Compound **I**

Empirical formula	$C_{44}H_{42}Mo_2N_4O_9$
Formula weight	962.70
Crystal color	Yellow
Crystal size (mm)	0.23 × 0.20 × 0.20
Crystal system	Monoclinic
space group	*C2/c*
a (Å)	16.2976 (13)
b (Å)	22.6595 (17)
c (Å)	11.6105 (9)
α (deg)	90.00
β (deg)	101.2570 (10)
γ (deg)	90.00
Volume (Å^3)	4205.2 (6)
Z	4
d_{calcd} (g/cm^3)	1.521
μ (mm^{-1})	0.657
F (000)	1960
λ (Å)	0.71073
Temperature	293(2) K
θrange (deg)	2.18 to 25.00
h,k,l range	$-19 \le h \le 19$ $-26 \le k \le 21$ $-13 \le l \le 13$
Reflections collected/unique	10,803/3709 [R(int) = 0.0226]
Completeness to θ	99.9% (θ = 25.00)
Max. and min. transmission	0.877 and 0.860
Data/restraints/parameters	3701/0/270
Goodness-of-fit on F^2	1.030
Final R indices [I > 2σ(I)]^a	$R_1 = 0.0257$ $wR_2 = 0.0641$
R indices (all data)	$R_1 = 0.0348$ $wR_2 = 0.0693$
Largest diff. Peak and hole(e·Å^{-3})	0.455 and −0.327

[a] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$

Table 2 Selected bond lengths (Å) for **I**

Mo1–Mo2	2.0983 (4)
Mo1–O4	2.1002 (16)
Mo1–N2	2.132 (2)
Mo2–O3	2.1329 (16)
Mo2–N1	2.149 (2)
Mo2–O1W	2.475 (2)

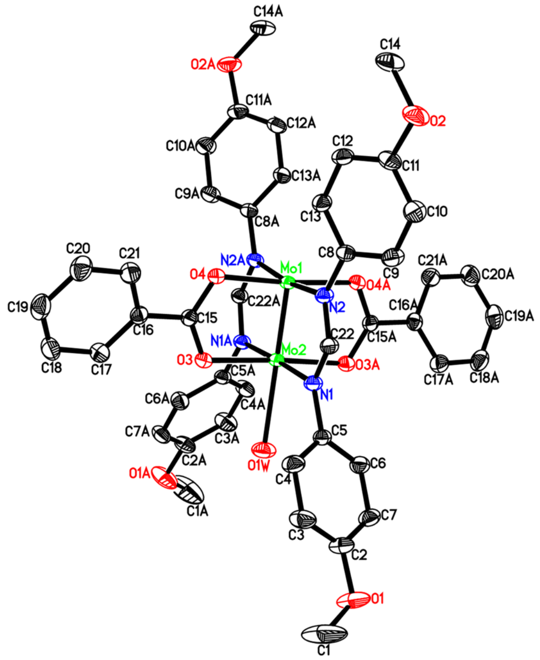


Fig. 1 Molecular structure of the title compound drawn with displacement ellipsoids at the 30% probability level

Intermolecular O–H···O hydrogen bonds link the Mo dimers into two-dimensional sheet (Fig. 4), where coordinated water oxygen atoms serve as H-bond donors and uncoordinated methoxyl group oxygen atoms serve as H-bond acceptors [O1w···O1i = 2.797(3) Å]. In summary, the dimers are assembled by O–H···O hydrogen bonds and π–π stacking between phenyl rings into a three-dimensional framework, as shown in Fig. 5.

^{1}H NMR Spectra

The ^{1}H NMR of compound **I** is depicted in Fig. 6. ^{1}H NMR ($CDCl_3$): 8.35 (s, 2H, –NCHN–), 8.31 (d, 2H, aromatic), 7.48 (s, 1H, aromatic), 7.46 (d, 2H, aromatic), 6.84 (d, 8H, aromatic), 6.79 (d, 8H, aromatic), 3.75 (s, 12H, $-OCH_3$). There are two doublets and one singlet in the range from 8.31 to 7.46 ppm, which correspond to the aromatic protons from the phenyl ligands. Two sets of doublets at 6.84 to 6.76 ppm stem from hydrogen atoms of the anisyl groups. The signals for the methoxy groups of the anisyl groups appear as singlets at 3.74 ppm. The ^{1}H NMR spectra are consistent with the above described crystal structure.

Absorption and Raman Spectra

Figure 7a shows the absorption spectra in visible region of compound **I**. The intense absorption at lower energy, λ_{max} 541 nm (ε, 2.2 × 10^4 L mol^{-1} cm^{-1}), can be assigned as a MLCT (metal ligand charge transfer) δ–π* transition. Moreover, Fig. 7b shows the Raman spectrum of compound **I**, In which the band at 402 cm^{-1} is attributed to *ν* (Mo–Mo), and

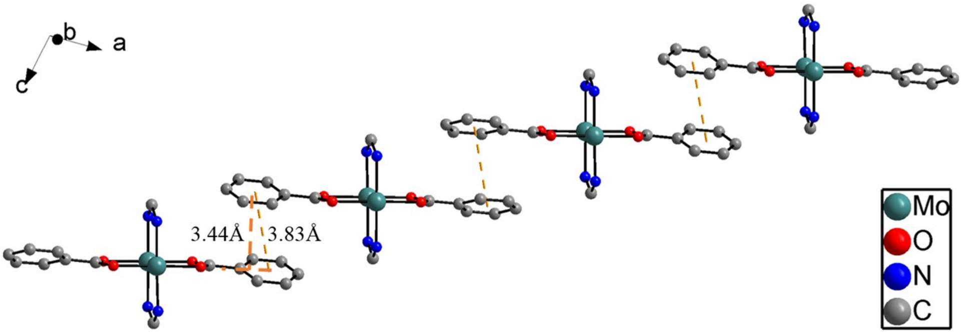


Fig. 2 Part of a one-dimensional linear chain formed by the π–π stacking in compound **I**

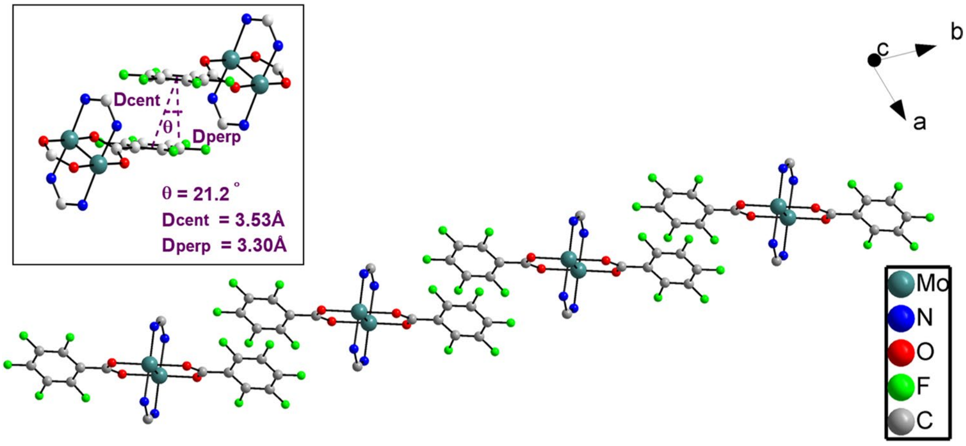


Fig. 3 Part of a one-dimensional linear chain formed by π–π stacking in compound **II** [23]

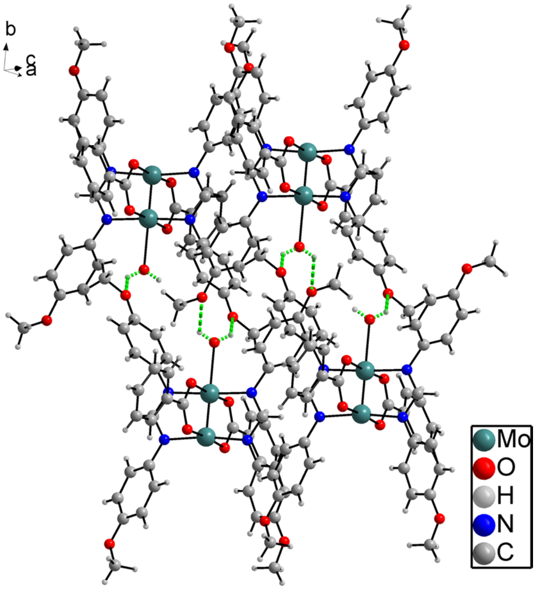


Fig. 4 A view of O–H···O hydrogen bonds in compound **I**

the vibrations observed at 1395, 1490 and 1594 cm^{-1} correspond to ν (C–C) and ν (CO_2–C) [25]. The Raman spectrum is in agreement with the structure determined by X-ray diffraction.

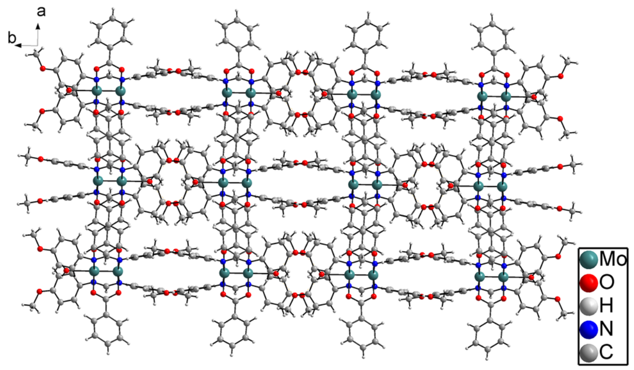


Fig. 5 Crystal packing of compound **I**

Conclusion

In summary, a novel dimolybdenum paddle–wheel structure has been synthesized and characterized in which O–H···O hydrogen bonds and π–π stacking between phenyl rings assemble the compound **I** into a three-dimensional framework. Moreover, the dihedral angle of 18.706(8)° in **I** is induced by the π–π stacking between phenyl rings, but the π–π stacking interactions between phenyl rings are weaker than those between perfluorophenyl rings.

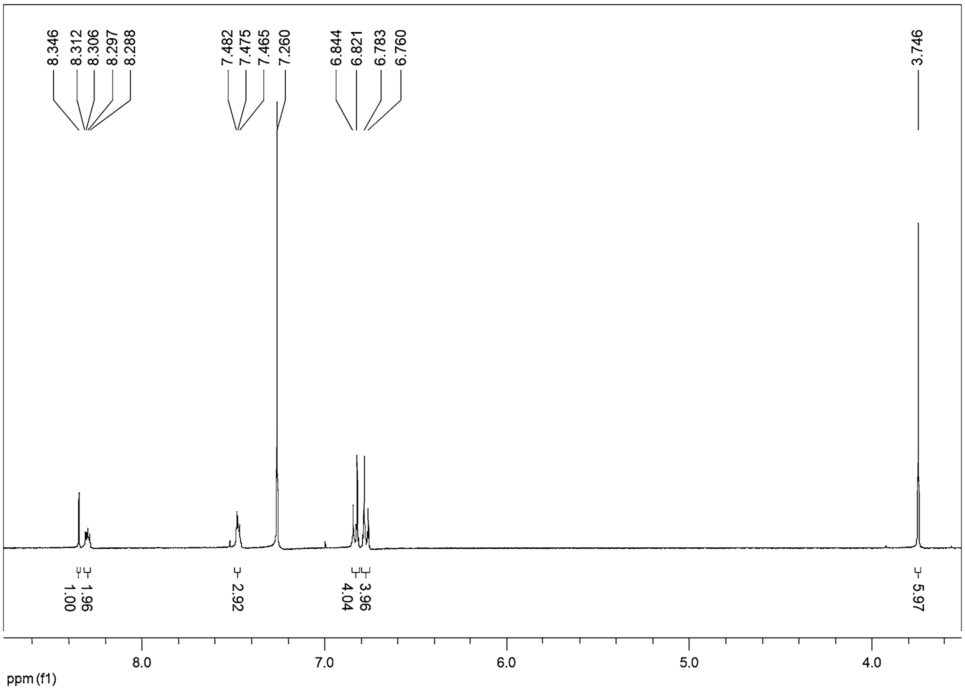


Fig. 6 ^{1}H NMR spectrum of the title compound

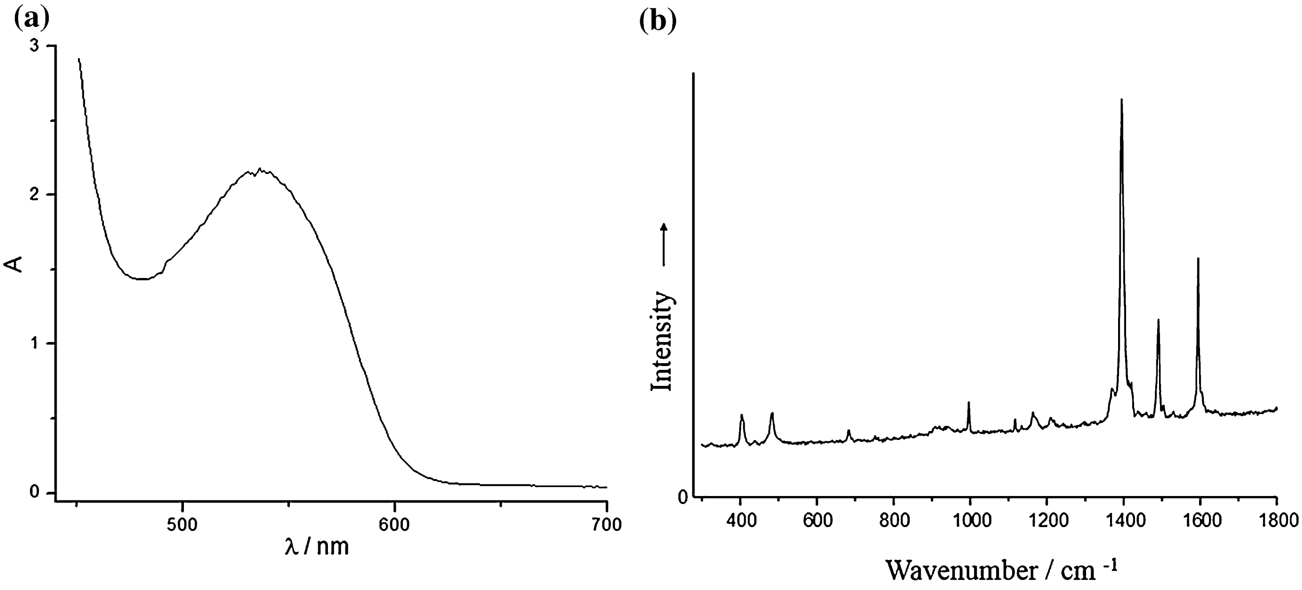


Fig. 7 **a** Electronic spectrum of the title compound; **b** Raman spectrum of the title compound with laser excitation at 514.5 nm

Supplementary Materials

CCDC-1021162 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

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