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Synthesis and reactivity of *N,N′*-bis [*o*-(diphenylphosphino)benzylidene-2,2′-diimino-1,1′-binaphthylene (Binap-P_2N_2). Crystal structure of [Ag(Binap-P_2N_2)][BF_4]

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Abstract

The condensation of a racemic mixture of 2,2′-diamino-1,1′-binaphthylene with two equivalents of *o*-(diphenylphosphino)benzaldehyde gives a racemic mixture of *N,N′*-bis[*o*-(diphenylphosphino)benzylidene-2,2′-diimino-1,1′-binaphthylene (Binap-P_2N_2) (I) in good yield. The coordination behaviour of I towards Cu^I and Ag^I has been explored. The interaction of I with one equivalent of $Cu(Ph_3P)_2Br$ and $[Cu(CH_3CN)_4][PF_6]$ in CH_2Cl_2 gives Cu(Binap-P_2N_2)Br (II) and [Cu(Binap-P_2N_2)][PF_6] (III) in 60% and 74% yield, respectively. In II the Binap-P_2N_2 ligand acts as a tridentate chelating agent, with the two phosphino groups and one of the two imino groups coordinated to the Cu, whereas in III it acts in tetradentate chelating mode. A variable temperature $^{31}P\{^1H\}$ NMR study of II reveals that the coordinated and the uncoordinated imino groups of the tridentate Binap-P_2N_2 ligand undergo a facile intramolecular exchange even at −55°C. The interaction of I with one equivalent of $AgBF_4$ in CH_2Cl_2 gives [Ag(Binap-P_2N_2)][BF_4] (IV) in 79% yield. In IV, the Binap-P_2N_2 ligand acts as a tridentate chelating agent, with the two phosphino groups and one of the two imino groups coordinated to the Ag. The structure of IV has been established by an X-ray diffraction study. The distance between Ag and N(2) is 2.56(1) Å, and the non-bonding distance between Ag and N(1) is > 3.0 Å.

Key words: Silver; Copper; Imine; Multidentate ligands; Crystal structure

1. Introduction

The potential of polydentate ligands having both soft and hard centres that are good bridging ligands for the preparation of heterobimetallic complexes containing an oxophilic metal and a late transition metal has led to extensive studies of the synthesis and reactivity of polydentate ligands containing both phosphine and nitrogen base groups [1–3]. Recently, we examined the reactivity of *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]ethylenediamine (P_2N_2) towards transition metal complexes, and showed that the P_2N_2 ligand can act as bridging, bi-, tri-, or tetra-dentate ligand depending on the reaction conditions [4–6]. In this paper we report the results of a study of the reactions of the analogous diiminodiphosphino ligand, *N,N′*-bis[*o*-(diphenylphosphino)benzylidene]-2,2′-diimino-1,1′-binaphthyl (Binap-P_2N_2) (I) with Cu^I and Ag^I.

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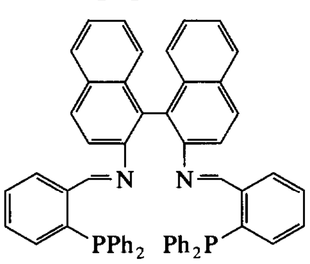
2. Results and discussion

2.1. Synthesis of Binap-P_2N_2 (I)

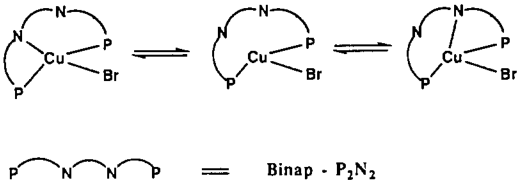
After a racemic mixture of 2,2′-diamino-1,1′-binaphthylene had been treated with two equivalents of *o*-(diphenylphosphino)benzaldehye in refluxing absolute ethanol for 12 h, work up gave orange solid, Binap-P_2N_2 in 55% yield. The IR spectrum of **I** exhibits a strong C=N stretch at 1612 cm^{-1}. In addition to signals from the phenyl protons, the ^1H NMR spectrum exhibits a doublet ($J_{(P-H)} = 5.6$ Hz) at δ 8.94 ppm for the imino protons. The $^{31}P\{^1H\}$ NMR spectrum of **I** exhibits a singlet at δ −16.5 ppm. On the basis of these spectroscopic data the following structure is proposed for Binap-P_2N_2:



Binap-P_2N_2 (I)

2.2. Synthesis of [Cu(Binap-P_2N_2)Br] (II)

A mixture of racemic Binap-P_2N_2 with one equivalent of $Cu(Ph_3P)_2Br$ in dichloromethane was refluxed for 12 h, after which work up gave orange crystals of stoichiometry [Cu(Binap-P_2N_2)Br]-CH_2Cl_2 (**II**) in moderate yield (60%) after recrystallization from a CH_2Cl_2/Et_2O mixture. The structure of **II** was established by an X-ray diffraction study, which revealed that the Binap-P_2N_2 ligand behaves as a tridentate ligand, with the two phosphino groups and one of the two imino groups coordinated to the Cu. The ambient temperature $^{31}P\{^1H\}$ NMR spectrum of **II** exhibits a broad singlet at δ −12.4 (width at half-height, 150 Hz) which broadens slightly on cooling to −55°C (width at half-height, 160 Hz). This suggests that the coordinated imino group and the uncoordinated imino group of **II** undergo a facile intramolecular exchange as shown in Scheme 1. Similar dynamic behaviour was reported for $[Cu(P_2N_2)(^tBuNC)][ClO_4]$ [7].



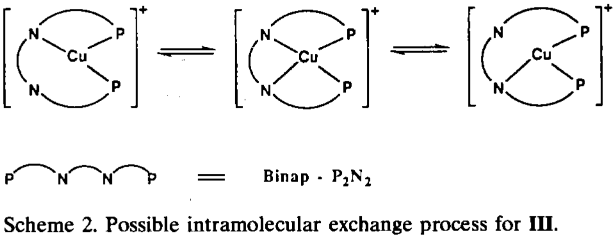
Scheme 1. Proposed mechanism for the dynamic behaviour of **II**.

2.3. Synthesis of [Cu(Binap-P_2N_2)][PF_6] (III)

After a racemic mixture of Binap-P_2N_2 had been treated with one equivalent of $[Cu(CH_3CN)_4][PF_6]$ in refluxing dichloromethane for 12 h, work up gave orange crystals of stoichiometry [Cu(Binap-P_2N_2)][PF_6] (**III**) in good yield (74%) after recrystallization from a CH_2Cl_2/Et_2O mixture. The ambient temperature $^{31}P\{^1H\}$ NMR spectrum of **III** exhibits a broad singlet, δ 11.6 (width at half-height 75 Hz) and a heptet at δ −145.1 (J(P–F)=712.3 Hz) from the phosphorus of the Binap-P_2N_2 ligand and the PF_6 anion, respectively; both signals are unchanged by cooling to −55°C. The ^{31}P spectroscopic data suggest that **III** is a tetrahedral complex, with the Binap-P_2N_2 ligand acting as a tetradentate ligand. However, the structure of the analogous silver complex, [Ag(Binap-P_2N_2)][BF_4], shows that the silver complex is three-coordinate, with the two phosphino groups and one of the two imino groups of the Binap-P_2N_2 ligand coordinated to the silver (*vide infra*). Thus, the spectroscopic data cannot rule out the possibility that **III** is a three-coordinated complex in which the coordinated and the uncoordinated imino groups of the tridentate Binap-P_2N_2 ligand undergo a facile intramolecular exchange, as shown in Scheme 2. Preliminary X-ray diffraction data confirm that **III** is a tetrahedral complex with the phosphino and imino groups coordinated to the Cu [8].

2.4. Synthesis of [Ag(Binap-P_2N_2)][BF_4] (IV)

A mixture of racemic Binap-P_2N_2 and one equivalent of $AgBF_4$ was refluxed in a dichloromethane/acetonitrile mixture for 12 h. Work-up gave yellow crystals of stoichiometry [Ag(Binap-P_2N_2)][BF_4]·0.5CH_2Cl_2 (**IV**) in good yield (79%) after recrystallization from a CH_2Cl_2/Et_2O mixture. The IR spectrum of the complex in KBr exhibited strong bands due to the imino groups (ν(C–N) 1622 and 1600 cm^{-1}) and the BF_4 group (ν(B–F) 1088 cm^{-1}). The $^{31}P\{^1H\}$ spectrum of **IV** exhibits two doublets (J(P–P) = 37.0 Hz) of equal intensity at δ 17.2 and 32.3 ppm, indicating that both phosphorus atoms of the Binap-P_2N_2 ligand are coordinated and non-equivalent. In addition to signals



Scheme 2. Possible intramolecular exchange process for **III**.

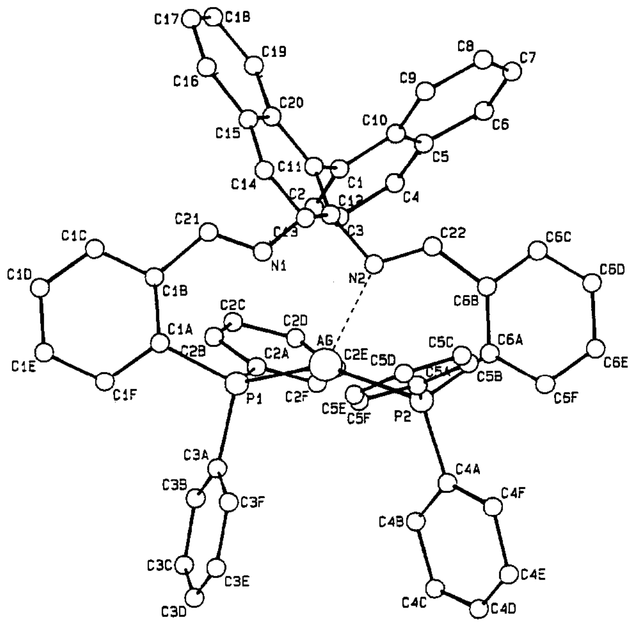


Fig. 1. A perspective view of the molecular structure of $[Ag(C_{58}H_{42}N_2P_2)][BF_4]$. Selected bond lengths (Å) and bond angles (°): Ag–P(1), 2.379(3); Ag–P(2), 2.415(4); Ag–N(2), 2.56(1); N(1)–C(2), 1.45(1); N(1)–C(21), 1.26(1); N(2)–C(12), 1.44(2); N(2)–C(22), 1.27(1); P(1)–Ag–P(2), 151.0(1); P(1)–Ag–N(2), 134.1(3); P(2)–Ag–N(2), 74.6(3); N(1)–C(21)–C(1B), 122(1); N(2)–C(22)–C(6B); 127(1).

from the phenyl protons, the ^1H NMR spectrum of **IV** exhibited a singlet at δ 8.33 and a broad multiplet at δ 8.07, of relative intensity of 1:1, for the methyne protons of the two imino groups of the Binap-P_2N_2 ligand. The signal from the methyne protons of the two imino groups of the free Binap-P_2N_2 ligand is δ 8.94. Thus, the resonance at δ 8.33 that is closer to that of the free Binap-P_2N_2 ligand can be assigned to the methyne proton of the uncoordinated imino group, and the signal at δ 8.07 to the methyne proton of the coordinated imino group (*vide infra*). The structure of **IV** was established by an X-ray diffraction study. A perspective drawing is shown in Fig. 1, and selected bond lengths and bond angles are given in the caption. A stereoscopic drawing of **IV** is shown in Fig. 2.

The solid state structure of **IV** is consistent with the spectroscopic data and shows the complex to be a distorted three-coordinated species. The silver atom is bonded to two P and one N atom of the Binap-P_2N_2 ligand; it deviates 0.07 Å from the plane defined by these three atoms. The two Ag–P bond distances are significantly different [0.036(7) Å]. The exceptionally long Ag–N(2) distance [2.56(1) Å] indicates a very weak interaction. However, this bonding interaction in the solid state is significant, and is believed to persist in solution, since the ^1H and ^{31}P NMR data suggested non-equivalent environments for the imino protons and phosphorus, respectively. The P(1)–Ag–P(2) angle [151.0(1)°] is similar to those in $[Ag(Ph_2PC_{20}H_{14}\text{-}PPh_2)X]$, X = Cl, $SnCl_3$, NO_3, ClO_4 [9]. The non-bonding distance between Ag and N(1) is 3.10(2) Å. The dihedral angle between the two least-squares planes of the naphthene units in the binaphthene moiety is 74.8°. Such an irregular coordination environment for Ag^I has been observed in $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$ [10] (pz = pyrazolyl) which contains a distorted trigonal planar Ag^I with a normal [2.194(4) Å] and a long [2.411(4) Å] Ag–N bond; the angle P–Ag–N is 160°. The Ag–N(2) distance [2.56(1) Å] of **IV** is comparable to the long Ag–N distance [2.411(4) Å] in $[Ag\{P(C_6H_4Me\text{-}p)_3\}\{BPh_2(pz)_2\}]$, and thus can be considered as weak interaction. The observed structural feature of **IV** can be viewed in terms of two tightly bound ligands interacting with the two sp-hybrid or-

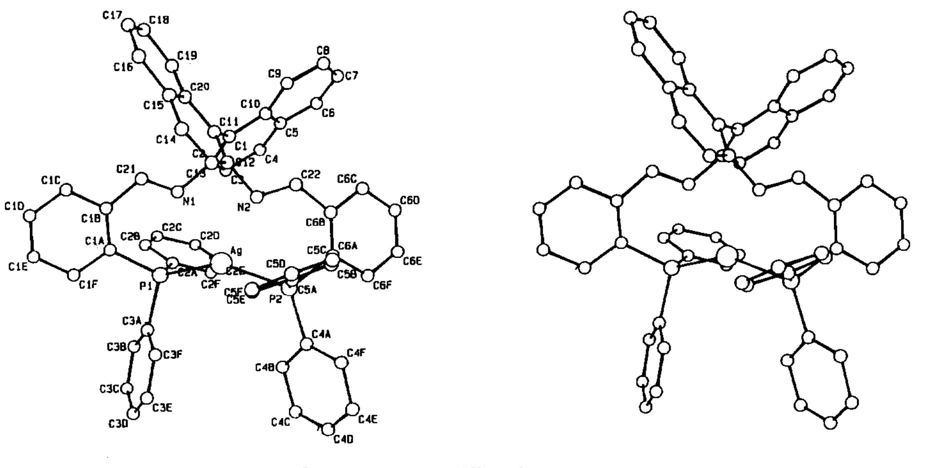


Fig. 2. Stereoscopic drawing of $[Ag(C_{58}H_{42}N_2P_2)][BF_4]$.

bitals of the metal, with the third ligand interacting weakly with one of the metal p-orbitals.

In contrast to the P_2N_2 ligand, which is tetrahedrally coordinated to both Cu^{I} and Ag^{I} [7], the Binap-P_2N_2 ligand, while tetrahedrally coordinated to the Cu^{I}, is three-coordinated to the Ag^{I}. This may due to the fact that the Binap-P_2N_2 ligand is more rigid than the P_2N_2 ligand, so that the size of the pocket formed by the ligand in a tetrahedrally coordinated environment is less flexible for the Binap-P_2N_2 than for the P_2N_2 ligand. As a result, the less rigid P_2N_2 ligand can accommodate larger ions better than the more rigid Binap-P_2N_2 ligand in the tetrahedrally coordinated environment.

3. Experimental details

Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. IR spectra (KBr pellets) were recorded on a Hitachi 270-30 IR spectrometer, data are given in cm^{-1}. NMR spectra were recorded on a JEOL FX90Q spectrometer or on a JEOL EX270 spectrometer. Chemical shifts of ^{1}H NMR spectra were referenced to internal deuterated solvents and then re-calculated to TMS = δ 0.0 ppm. ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. ^{1}H and ^{31}P{^{1}H} NMR data are given in Table 1.

All operations were carried out under nitrogen or *in vacuo*. All chemicals used were of reagent grade. Solvents were dried by standard procedures, distilled and deaerated prior to use. Melting points were taken in sealed capillaries and are uncorrected.

o-(Diphenylphosphino)benzaldehyde [7], 2,2'-diamino-1,1'-binaphthylene [11], $Cu(Ph_3P)_2Br$ [12] and $[Cu(CH_3CN)_4][PF_6]$ [13] were prepared by published methods. $AgBF_4$ was purchased from Aldrich and used as received.

3.1. Synthesis of Binap-P_2N_2 (I)

A solution of racemic mixture of 2,2'-diamino-1,1'-binaphthylene (1.35 g, 4.75 mmol) and *o*-(diphenylphosphino)benzaldehyde (2.76 g, 9.50 mmol) in absolute ethanol (60 cm^3) was refluxed for 12 h. A clear pale orange solution was obtained. The solution was concentrated to *ca.* 20 cm^3 and cooled to -20°C to give yellow solid which was filtered off and washed with n-hexane (2×10 cm^3). The yellow solid was then recrystallized from CH_2Cl_2/n-hexane which was filtered off and dried *in vacuo* to give an analytical pure sample of **I**. Yield: 2.12 g, 55%; m.p. 118–121°C. IR (in KBr): 3048m, 1612vs, 1584s, 1498m, 1462s, 1192m, 812m, 742vs, 692m, 510m, 480m cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): δ -16.5(s) ppm. ^{1}H NMR ($CDCl_3$): imino protons, δ 8.94 (2H, d; J(P–H) = 5.6 Hz) ppm; phenyl protons, δ 6.67–7.92 (40H, m) ppm.

3.2. Synthesis of Cu(Binap-P_2N_2)Br (II)

A solution of Binap-P_2N_2 (0.21 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) was slowly added to a stirred solution of $Cu(Ph_3P)_2Br$ (0.17 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred under reflux for 12 h, to give a bright red solution. The solvent was removed *in vacuo*, and the red residue was re-dissolved in a minimum amount of CH_2Cl_2 and chromatographed on silica gel with a 1:1 mixture of CH_2Cl_2/acetone as eluent. The orange band obtained was concentrated to *ca.* 5 cm^3, 5 cm^3 of Et_2O were added, and the mixture was cooled to -20°C to give orange-red crystals, which were filtered off and dried *in vacuo*. Yield: 0.16 g, 60%; m.p. 278–281°C (dec). Anal. Found: C, 66.5; H, 4.3; N, 2.1. $C_{58}H_{42}N_2BrP_2Cu \cdot CH_2Cl_2$ calc.: C, 66.9;

TABLE 1. ^{1}H and ^{31}P{H} NMR data

Compound	^{1}H [a]	Assignment	^{31}P [b]	Assignment
I	8.94 d (2)	N=C*H*–, J(P–H) = 5.6 Hz	-16.5 s	*P*$_2$N$_2$
	6.67–7.92 m (40)	Phenyl		
II	8.12 s (2)	N=C*H*–	-12.4 br, s	*P*$_2$N
	6.80–7.75 m (40)	Phenyl		
III	8.28 s (2)	N=C*H*–	-11.6 br, s	*P*$_2$N
	6.50–7.80 m (40)	Phenyl	-145.1 hept; J(P–F) = 712.3 Hz	*P*F$_6^-$
IV [c]	8.33 s (1)	N=C*H*–	32.2 d; J(P–P) = 37.0 Hz	*P*N$_2$P
	8.07 m (1)	N=C*H*–	17.2 d; J(P–P) = 37.0 Hz	PN$_2$*P*
	7.00–7.95 m (40)	Phenyl		

[a] In $CDCl_3$ at 30°C, referenced to Me_4Si (δ0.00). [b] In $CDCl_3$ at 30°C, referenced to external 85% H_3PO_4 (δ0.00), negative for upfield shift. [c] In d_6-acetone at 30°C. Abbreviations: s, singlet; d, doublet; hept, heptet; m, multiplet; br, broad.

H, 4.2; N, 2.6%. IR (in KBr): 3060m, 1612s, 1586w, 1470s, 1430vs, 1184w, 1092m, 814w, 738s, 690s, 498w cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −12.4 (br, s) ppm. ^{1}H NMR ($CDCl_3$): imino protons, δ 8.12 (2H, s) ppm; phenyl protons, δ 6.80–7.75 (40H, m) ppm; CH_2Cl_2 protons, δ 5.30 (2H, s) ppm.

3.3. Synthesis of [Cu(Binap-P_2N_2)][PF_6] (III)

The procedure was similar to that for **II**. [Cu(CH_3CN)$_4$][PF_6] (0.08 g, 0.25 mmol) and Binap-P_2N_2 (0.21 g, 0.25 mmol) were used. Orange crystals were obtained from a CH_2Cl_2/Et_2O mixture. Yield: 0.19 g, 74%, m.p. 206–209°C (dec). Anal. Found: C, 67.6; H, 4.1; N, 2.5. $C_{58}H_{42}N_2F_6P_3Cu$ calc.: C, 67.2; H, 4.1; N, 2.7%. IR (in KBr): 3050w, 1608s, 1586s, 1424w, 1030vs, 816w, 684w cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 11.6 (br, s); δ −145.1 (heptet, J(P–F) = 712.3 Hz) ppm. ^{1}H NMR ($CDCl_3$): imino protons, δ 8.28 (2H, s) ppm; phenyl protons, δ 6.50–7.80 (40H, m) ppm.

3.4. Synthesis of [Ag(Binap-P_2N_2)][BF_4] (IV)

A solution of Binap-P_2N_2 (0.21 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) was slowly added to a solution of $AgBF_4$ (0.05g, 0.25 mmol) in CH_3CN (10 cm^3). The solution was refluxed for 12 h to give a yellow solution. Removal of the solvent gave a yellow residue, which was washed with n-hexane (2 × 10 cm^3). The residue was re-dissolved in 10 cm^3 of CH_2Cl_2 and the solution was filtered and then concentrated to *ca.* 5 cm^3, and 5 cm^3 of Et_2O was added. The CH_2Cl_2/Et_2O solution was then cooled to −20°C to give yellow crystals, which were filtered off and dried *in vacuo*. Yield: 0.22 g, 79%; m.p. 193–196°C (dec). Anal. Found: C, 65.4; H, 4.2; N, 2.2. $C_{58}H_{42}N_2P_2BF_4Ag \cdot 0.5CH_2Cl_2$ calc.: C, 65.9; H, 4.0; N, 2.6%. IR (in KBr): 3052m, 1622s, 1600s, 1508m, 1490m, 1442s, 1302m, 1200m, 1088vs, 828m, 760s, 700s, 500w cm^{-1}. ^{31}P{^{1}H} NMR (acetone-d_6): δ 17.2 (d, J(P–P) = 37.0 Hz), δ 32.2 (d, J(P–P) = 37.0 Hz) ppm. ^{1}H NMR (acetone-d_6): imino protons, δ 8.33 (1H, s), δ 8.07 (1H, m) ppm; phenyl protons, δ 7.00–7.95 (40H, m) ppm; CH_2Cl_2 protons, δ 5.77 (1H, s) ppm.

3.5. X-Ray diffraction study

Crystals of **IV** suitable for X-ray diffraction study were grown from CH_2Cl_2/Et_2O as a solvate of stoichiometry **IV** · $0.5CH_2Cl_2$. A yellow crystal of dimensions 0.22 × 0.33 × 0.42 mm^3 was mounted on a glass

TABLE 2. Crystal data, data collection and processing parameters

Molecular formula	$[Ag(C_{58}H_{42}N_2P_2)]BF_4 \cdot 0.5CH_2Cl_2$
Molecular weight	1023.66 (1066.12)
Colour and habit	Yellow block
Unit cell parameters	
a (Å)	13.865 (3)
b (Å)	13.965 (7)
c (Å)	15.477 (9)
V (Å^3)	2599.6
α (°)	103.53 (6)
β (°)	109.41 (5)
γ (°)	102.69 (4)
Z	2
Density (calcd) (g cm^{-3})	1.362
Space group	$P\bar{1}$ (No. 2)
Radiation	Graphite-monochromatized Mo Kα λ = 0.71073 Å
Temperature (K)	293
Absorption coefficient (cm^{-1})	5.2
Crystal size (mm^3)	0.22 × 0.33 × 0.42
Scan type and rate (° min^{-1})	ω–2θ; 1.27 − 8.24
Scan range	0.64 + 0.34 tan θ
Collection range	$h, \pm k, \pm l$; $2\theta_{max} = 45°$
Unique data measured	6740
Observed data with $I \geq 3\sigma(I)$, *n*	5262
Number of variables, *p*	400
$R = \Sigma \| F_o \| - \| F_c \|\| / \Sigma \| F_o \|$	0.090
Weighting scheme	$w = 1/\{1 + [(F_o - 31.0)/145.4]^2\}$
$R_w = [\Sigma(\|F_o\| - \|F_c\|)^2 / \Sigma_w \|F_o\|^2]^{1/2}$	0.112
Residual extrema in final difference map (e Å^{-3})	1.13 to −1.06

fibre with epoxy resin. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). A total of 6740 unique reflections ($2\theta \leq 45°$) were measured; 5262 of these had $I \geq 3\sigma(I)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors but no absorption correction was applied. Crystal data, data collection parameters, and results of the analysis are given in Table 2. The structure was solved by a combination of Patterson and direct methods (DIRDIF) [14] and refined by full matrix least-squares technique. The hydrogen atoms were generated in their idealized positions (C–H bond fixed at 0.96 Å) and included in structure factor calculations but not in the refinement. Refinement was by full-matrix least-squares. All calculations were carried out on a Micro VAX-II computer using the Enraf-Nonius SDP program [15]. Final atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallography Data Centre.

Acknowledgment

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