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Chiral Heterocyclic Ligands.
Part IV. Synthesis and Metal Complexes of 2,6-Bis(pyrazol-1-ylmethyl)pyridine and Chiral Derivatives

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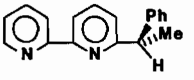
Abstract

Syntheses of the new tridentate ligand, 2,6-bis(pyrazol-1-ylmethyl)pyridine (**6**) and its chiral derivatives (**11–15**) are described. The preparations of complexes of these ligands with several divalent transition metal ions (Fe^{2+}, Ni^{2+}, Cu^{2+}, Ru^{2+}, Pd^{2+}) are reported. X-ray crystal structures have been determined for the $[Ni(\mathbf{6})_2](ClO_4)_2 \equiv$ **16** and $[Cu(\mathbf{13})(NCS)_2] \equiv$ **17** complexes. The salt **16** crystallises in the orthorhombic space group $P2_12_12$ with $a = 10.125(1)$, $b = 17.657(4)$, $c = 8.579(2)$ Å and $Z = 2$. The structure was refined to a conventional R factor of 3.9% and shows the nickel atom to lie on a crystallographic two-fold rotation axis in a 'symmetrical' octahedral environment. The complex **17** crystallises in the orthorhombic space group $P2_12_12_1$ with $a = 15.795(3)$, $b = 20.433(3)$, $c = 9.618(1)$ Å and $Z = 4$. The structure was refined to $R = 4.7\%$ and shows the bonding geometry at the five-coordinate copper atom to be intermediate between square pyramidal and trigonal bipyramidal. In both structures the six-membered chelate rings exist in boat conformations.

Introduction

Chiral bidentate phosphines have been extensively used as ligands in homogeneous asymmetric catalysis [1, 2]. However, in spite of the well established use of polydentate heteroaromatic ligands such as 2,2′-bipyridine in coordination chemistry, only recently have chiral heterocycles of this type been prepared for use in asymmetric synthesis [3–6]. The promising potential of such ligands is exemplified by the recently reported use of rhodium complexes derived from chiral bipyridines, such as **1**, and chiral pyrrole and pyridine imines, such as **2**, for enantioselective transfer hydrogenation [6, 7] and asymmetric hydrosilylation [3, 8, 9] of prochiral ketones.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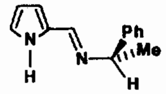
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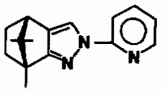
We are currently engaged in the synthesis and study of a variety of polydentate ligands comprising nitrogen heterocycles fused to a bornane framework, for example **3** [10] and **4** [11]. Such ligands are expected to offer two important advantages: firstly the spatial proximity of a chiral centre to the site of coordination should enhance the induced chirality experienced by a coordinated metal centre and, secondly, the conformationally rigid nature of the bornane group should reduce problems resulting from loss of asymmetric induction due to free rotation of the chiral centre as is possible with ligands such as **1** and **2**. These expectations are supported by a recent report that a titanocene complex derived from the carbocyclic diene **5** catalyses the enantioselective hydrogenation of 1-ethylstyrene with the highest optical yields yet reported [12]. Furthermore, it is now recognised [8] that C_2 symmetry, such as is present in ligand **4**, is a desirable feature for increased optical yields in asymmetric catalysis.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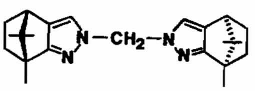
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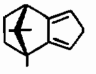
In this context we now report the syntheses of a number of chiral derivatives of the previously unreported tridentate ligand 2,6-bis(pyrazol-1-ylmethyl)pyridine (**6**). The preparation and properties of several transition metal complexes of these ligands and X-ray crystal structure determinations of pentacoordinate copper(II) and hexacoordinate nickel(II) complexes are also reported.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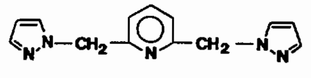
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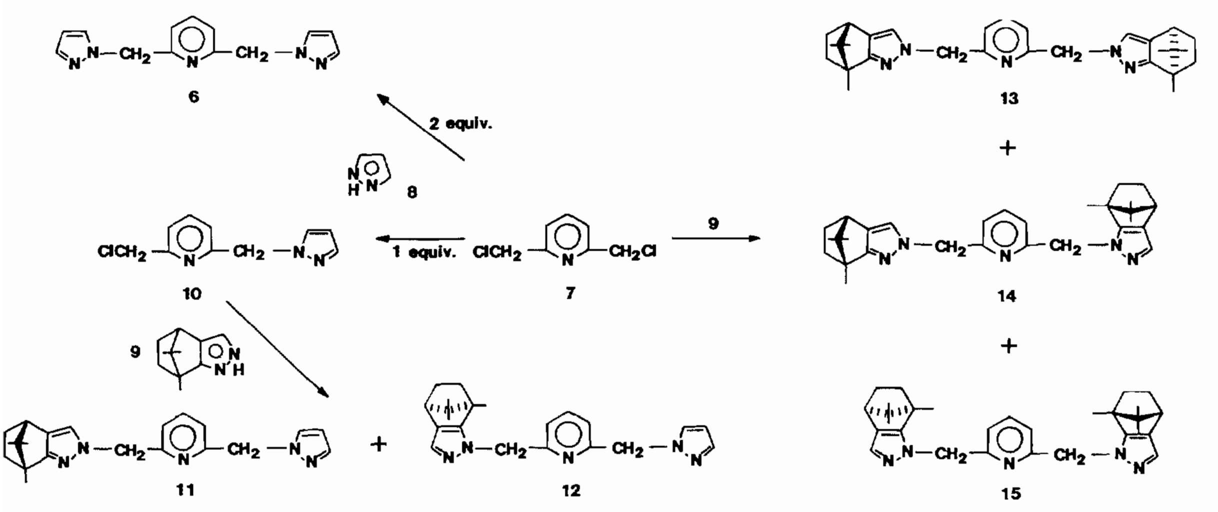
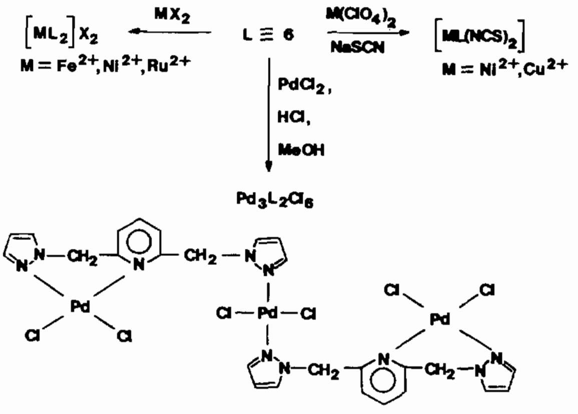


Scheme 1.

Results and Discussion

Preparation of Ligands

The tridentate ligands were prepared (Scheme 1) by phase-transfer catalysed [13, 14] reactions of 2,6-bis(chloromethyl)pyridine (**7**) with pyrazole (**8**) or its chiral derivative (**9**), in a manner analogous to that used to prepare related bidentate pyrazolylmethylpyridines [11]. Thus reaction of **7** with two molar equivalents of **8** produced 2,6-bis(pyrazol-1-ylmethyl)pyridine **6** in 90% yield. Similarly reaction between equimolar amounts of **7** and **8** allowed isolation of the mono-pyrazolyl chloride (**10**), which in turn was reacted with the chiral fused pyrazole (**9**) to produce a 4:1 mixture of the two chiral ligands **11** and **12**. The major product **11** was purified by radial chromatography and readily identified as that resulting from alkylation of the less hindred (N2) nitrogen by comparison with ^{1}H and ^{13}C NMR spectra of related literature compounds [11, 14–19]. In a similar way reaction of **7** with two equivalents of **9** produced a 12:3:1 mixture of three isomers **13**–**15** from which the isomers **13** and **14** were isolated by radial chromatography and the major isomer **13** identified as that resulting from preferential reaction of N2. It is noteworthy that the chiral ligand (**13**) possesses C_2 symmetry, which is thought to be an important property of chiral ligands in asymmetric catalysis [8].



Scheme 2.

Metal Complexes

The complexing properties of the new, achiral tridentate ligand (**6**) were first investigated (Scheme 2). Reaction of two equivalents of **6** with iron(II), nickel(II) and ruthenium(II) solutions produces octahedral complexes of the metal ion bound to two tridentate ligands. A single-crystal X-ray structure determination of the nickel perchlorate salt is described below. Reaction of nickel(II) and copper(II) perchlorate with one equivalent of **6** and sodium thiocyanate produces neutral five-coordinate complexes of the metal bound to the three nitrogens of the ligand and two thiocyanate anions.

Reaction of a methanolic solution of **6** with a solution of palladium chloride in 2 M HCl produced a complex to which we assign the structure shown in Scheme 2 and which possesses two molecules of the ligand coordinated to two *cis*-dichloro square planar palladium(II) atoms and one *trans*-dichloro square planar palladium. The *trans*-dichloro geometry is that expected for the coordination of $PdCl_2$ to a monodentate nitrogen ligand [20].

Having established that **6** is capable of tridentate coordination to a number of transition metal ions we then studied the complexing properties of the chiral derivatives **11**, **13** and **14**. Each of these ligands readily formed neutral $CuL(NCS)_2$ complexes by reaction with copper(II) perchlorate and sodium thiocyanate. The measured chiroptical parameters for these Cu(II) complexes are reported in 'Experimental' and a single crystal X-ray structure analysis of the Cu(II) complex formed from **13** is described below.

X-ray Structure Determinations

In order to confirm the structure and mode of coordination of the ligands as well as to determine the chelate ring conformations of the coordinated ligands, single crystal X-ray structure determinations of $[Ni(\mathbf{6})_2](ClO_4)_2$, *viz.* **16**, and $[Cu(\mathbf{13})(NCS)_2]$, *viz.* **17**, were carried out.

Figure 1 shows a perspective view of the cation of **16** and the atom labelling. The asymmetric unit of **16** contains one perchlorate anion and half the octahedral cation with the remainder of the structure related by a crystallographic two-fold rotation axis. The structure of the ligand and its tridentate chelation to the metal are thus confirmed. Tables I and II list bond lengths and angles respectively, with estimated standard deviations in parentheses. The bonding geometry about the central nickel atom is close to symmetrical octahedral. This is in contrast to the geometry in the nickel(II) terpyridine cation [21] and other terpyridine complexes [22–24] which have chelation angles*, α, substantially

TABLE I. Bond Lengths (A) for **16**

NI–N(1)	2.157(3)	Ni–N(22)	2.077(4)
Ni–N(62)	2.075(4)	N(1)–C(2)	1.347(5)
N(1)–C(6)	1.350(5)	C(2)–C(3)	1.386(6)
C(2)–C(2A)	1.511(6)	C(3)–C(4)	1.377(7)
C(4)–C(5)	1.373(7)	C(5)–C(6)	1.399(6)
C(6)–C(6A)	1.513(6)	C(2A)–N(21)	1.464(6)
N(21)–N(22)	1.357(5)	N(21)–C(25)	1.329(6)
N(22)–C(23)	1.323(6)	C(23)–C(24)	1.388(7)
C(24)–C(25)	1.367(8)	C(6A)–N(61)	1.472(6)
N(61)–N(62)	1.366(5)	N(61)–C(65)	1.321(6)
N(62)–C(63)	1.346(6)	C(63)–C(64)	1.405(7)
C(64)–C(65)	1.368(7)	Cl–O(1)	1.440(3)
Cl–O(2)	1.428(3)	Cl–O(3)	1.436(4)
Cl–O(4)	1.422(4)		

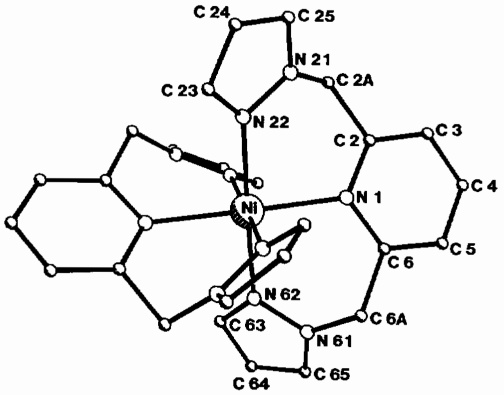


Fig. 1. Perspective view and atom labelling of the cation of **16**. Hydrogen atoms omitted for clarity.

TABLE II. Bond Angles (°) for **16**[a]

N(1)–Ni–N(22)	89.1(1)	N(1)–Ni–N(62)	88.8(1)
N(1)–Ni–N(22)'	90.1(1)	N(1)–Ni–N(62)	91.9(1)
N(1)–Ni–N(1)'	178.9(2)	N(22)–Ni–N(62)	177.1(1)
N(62)–Ni–N(62)'	95.6(2)	Ni–N(1)–C(2)	121.3(3)
Ni–N(1)–C(6)	120.3(3)	C(2)–N(1)–C(6)	117.7(3)
N(1)–C(2)–C(3)	122.3(4)	N(1)–C(2)–C(2A)	119.7(3)
C(3)–C(2)–C(2A)	177.8(4)	C(2)–C(3)–C(4)	119.3(4)
C(3)–C(4)–C(5)	119.5(4)	C(4)–C(5)–C(6)	118.3(4)
N(1)–C(6)–C(5)	122.7(4)	N(1)–C(6)–C(6A)	118.6(3)
C(5)–C(6)–C(6A)	118.7(4)	C(2)–C(2A)–N(21)	114.4(4)
C(2A)–N(21)–N(22)	120.0(4)	C(2A)–N(21)–C(25)	127.8(4)
N(22)–N(21)–C(25)	111.4(4)	Ni–N(22)–N(21)	121.2(3)
Ni–N(22)–C(23)	131.6(3)	N(21)–N(22)–C(23)	105.0(4)
N(22)–C(23)–C(24)	111.0(4)	C(23)–C(24)–C(25)	105.0(5)
N(21)–C(25)–C(24)	107.5(5)	C(6)–C(6A)–N(61)	110.7(3)
C(6A)–N(61)–N(62)	118.7(3)	C(6A)–N(61)–C(65)	129.2(4)
N(62)–N(61)–C(65)	112.0(4)	Ni–N(62)–N(61)	122.1(3)
Ni–N(62)–C(63)	130.9(3)	N(61)–N(62)–C(63)	104.6(3)
N(62)–C(63)–C(64)	110.2(4)	C(63)–C(64)–C(65)	105.1(4)
N(61)–C(65)–C(64)	108.1(4)	O(1)–C1–O(2)	107.6(2)
O(1)–C1–O(3)	109.3(2)	O(2)–C1–O(3)	110.2(2)
O(1)–C1–O(4)	110.0(2)	O(2)–C1–O(4)	109.5(2)
O(3)–C1–O(4)	110.2(2)		

[a] N(X)' related to N(X) by the transformation $-x$, $1 - y$, z.

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*α defined as the $N_{central}$–M–N_{distal} angle [22].

less than 90°. Similarly the normalised bite of the ligand **6**, defined as 2 sin(⟨α⟩/2), is 1.40 and considerably greater than that of terpyridine (typically 1.27 [22]). These differences can be ascribed to the greater flexibility of the six-membered chelate rings present in **16** relative to the five-membered chelate rings in terpyridine complexes. Furthermore, whereas the $M-N_{central}$ bond length in terpyridine complexes is greater than the $M-N_{distal}$ bond lengths, the opposite is true in the present case. However, the observed M–N bond lengths in **16** are comparable to those reported for the NiL_4Cl_2 complexes for L = pyridine [25] and L = pyrazole [26, 27]. The differences therefore reflect the different donor/acceptor properties of the π-excessive pyrazole relative to the π-deficient pyridine [28].

The pyridine and pyrazole rings are each planar to within 0.02 Å with the pyrazole meanplanes inclined to the pyridine meanplane at angles of 42.7° and 63.2°. This and other torsional angle differences destroy the non-crystallographic two-fold rotational symmetry present in the free ligand. The pyridine ring meanplane is inclined to the chelation plane, defined by Ni, N(1), N(22) and N(62), at an angle of 37.2°. As is the case for related structures [11, 29–31] the six-membered chelate rings exist in boat conformations. The perchlorate anion has ordered tetrahedral geometry and makes no close contacts with the cation.

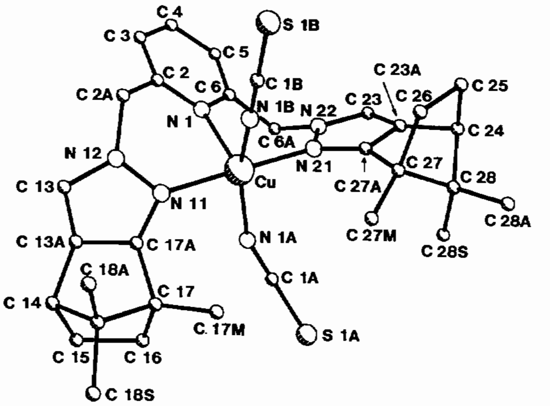

Fig. 2. Perspective view and atom labelling of **17**. Hydrogen atoms omitted for clarity.

Figure 2 shows a perspective view and atom labelling of the pentacoordinate copper complex (**17**). Tables III and IV list bond lengths and angles respectively. The coordination about the central copper atom is intermediate between trigonal bipyramidal, with axial pyrazole nitrogens, and square pyramidal, with axial pyridine nitrogen [24, 32–34]. Such geometry exists in other pentacoordinate complexes containing a tridentate ligand with two six-membered chelate rings [32]. It is noteworthy that in this case the $Cu-N_{pyridine}$ bond is substantially longer than the $Cu-N_{pyrazole}$ bond lengths, The heterocyclic rings are each planar to within 0.01 Å with the pyrazole meanplanes inclined to the pyridine ring at angles of 41.2° and 49.0°. The six-membered chelate rings both exist in boat conformations. However, whereas the palladium complex (**18**) of a related bidentate ligand exists [11] in the solid state in the boat conformation (**18b**) (Fig. 3), the chelate rings in **17** each exist in the conformation corresponding to **18a**. In solution these conformers are likely to be undergoing rapid interconversion. The bonding geometry of the bornane skeleton is similar to that observed in related structures [10, 11, 19]. The geometries of the two linear thiocyanate ligands are similar but they differ significantly in the angles (145.8° and 170.8°) they make to the metal, thereby destroying the approximate two-fold rotational symmetry of the complex.

TABLE III Bond Lengths (Å) for **17**

Cu–N(1A)	1.970(5)	Cu–N(1B)	1.972(6)
Cu–N(1)	2.246(6)		
Cu–N(11)	2.001(5)	Cu–N(21)	1.994(5)
N(1A)–C(1A)	1.151(8)	N(1B)–C(1B)	1.152(9)
C(1A)–S(1A)	1.627(6)	C(1B)–S(1B)	1.638(7)
N(1)–C(2)	1.330(8)	N(1)–C(6)	1.343(7)
C(2)–C(3)	1.388(9)	C(3)–C(4)	1.379(9)
C(4)–C(5)	1.381(9)	C(5)–C(6)	1.380(9)
C(2)–C(2A)	1.513(8)	C(6)–C(6A)	1.497(9)
C(2A)–N(12)	1.471(8)	C(6A)–N(22)	1.463(8)
N(11)–N(12)	1.376(7)	N(21)–N(22)	1.388(6)
N(11)–C(17A)	1.325(7)	N(21)–C(27A)	1.334(8)
N(12)–C(13)	1.367(8)	N(22)–C(23)	1.336(8)
C(13)–C(13A)	1.359(9)	C(23)–C(23A)	1.364(9)
C(13A)–C(14)	1.506(9)	C(23A)–C(24)	1.509(9)
C(13A)–C(17A)	1.389(9)	C(23A)–C(27A)	1.386(9)
C(14)–C(15)	1.558(9)	C(24)–C(25)	1.545(10)
C(14)–C(18)	1.566(9)	C(24)–C(28)	1.549(10)
C(15)–C(16)	1.552(9)	C(25)–C(26)	1.549(10)
C(16)–C(17)	1.558(9)	C(26)–C(27)	1.543(10)
C(17)–C(17A)	1.504(8)	C(27)–C(27A)	1.493(9)
C(17)–C(17M)	1.510(10)	C(27)–C(27M)	1.497(9)
C(17)–C(18)	1.587(8)	C(27)–C(28)	1.582(9)
C(18)–C(18S)	1.526(9)	C(28)–C(28S)	1.528(10)
C(18)–C(18A)	1.531(9)	C(28)–C(28A)	1.526(10)

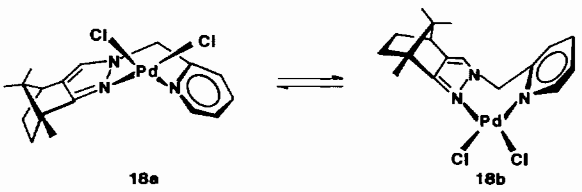

Fig. 3. Boat conformations for the chelate ring of **18**.

TABLE IV. Bond Angles (°) for 17

N(1A)–Cu–N(1B)	152.3(2)	N(11)–Cu–N(21)	179.1(2)
N(1A)–Cu–N(1)	106.9(2)	N(1B)–Cu–N(1)	100.8(2)
N(1A)–Cu–N(11)	91.3(2)	N(1B)–Cu–N(11)	90.4(2)
N(1A)–Cu–N(21)	87.9(2)	N(1B)–Cu–N(21)	90.5(2)
N(1)–Cu–N(11)	89.7(2)	N(1)–Cu–N(21)	90.2(2)
Cu–N(1A)–C(1A)	145.8(5)	Cu–N(1B)–C(1B)	170.8(5)
N(1A)–C(1A)–S(1A)	178.6(6)	N(1B)–C(1B))–S(1B)	179.8(4)
Cu–N(1)–C(2)	120.3(4)	Cu–N(1)–C(6)	120.0(4)
C(2)–N(1)–C(6)	118.0(5)	N(1)–C(2)–C(3)	124.0(5)
N(1)–C(2)–C(2A)	117.7(5)	C(3)–C(2)–C(2A)	118.3(6)
C(2)–C(3)–C(4)	117.0(6)	C(3)–C(4)–C(5)	120.0(6)
C(4)–C(5)–C(6)	118.8(6)	N(1)–C(6)–C(5)	122.2(5)
N(1)–C(6)–C(6A)	115.6(5)	C(5)–C(6)–C(6A)	122.1(5)
C(2)–C(2A)–N(12)	114.1(5)	C(6)–C(6A)–N(22)	113.2(5)
Cu–N(11)–N(12)	119.4(3)	Cu–N(21)–N(22)	121.9(4)
Cu–N(11)–C(17A)	134.8(4)	Cu–N(21)–C(27A)	134.2(4)
N(12)–N(11)–C(17A)	103.6(5)	N(22)–N(21)–C(27A)	103.8(5)
C(2A)–N(12)–N(11)	119.9(5)	C(6A)–N(22)–N(21)	119.4(4)
C(2A)–N(12)–C(13)	125.3(5)	C(6A)–N(22)–C(23)	128.6(5)
N(11)–N(12)–C(13)	111.5(5)	N(21)–N(22)–C(23)	111.2(5)
N(12)–C(13)–C(13A)	106.7(6)	N(22)–C(23)–C(23A)	107.6(5)
C(13)–C(13A)–C(14)	148.0(6)	C(23)–C(23A)–C(24)	149.7(6)
C(13)–C13A)–C(17A)	105.5(5)	C(23)–C(23A)–C(27A)	105.6(6)
C(14)–C(13A)–C(17A)	106.4(5)	C(24)–C(23A)–C(27A)	104.7(5)
C(13A)–C(14)–C(15)	105.0(5)	C(23A)–C(24)–C(25)	106.4(5)
C(13A)–C(14)–C(18)	99.2(5)	C(23A)–C(24)–C(28)	99.2(5)
C(15)–C(14)–C(18)	100.7(5)	C(25)–C(24)–C(28)	101.7(5)
C(14)–C(15)–C(16)	104.1(5)	C(24)–C(25)–C(26)	103.3(5)
C(15)–C(16)–C(17)	104.5(5)	C(25)–C(26)–C(27)	105.0(5)
C(16)–C(17)–C(17A)	103.6(5)	C(26)–C(27)–C(27A)	103.6(5)
C(16)–C(17)–C(17M)	117.2(5)	C(26)–C(27)–C(27M)	117.1(6)
C(16)–C(17)–C(18)	100.3(5)	C(26)–C(27)–C(28)	100.2(5)
C(17A)–C(17)–C(17M)	118.4(5)	C(27A)–C(27)–C(17M)	118.7(6)
C(17A)–C(17)–C(18)	97.4(5)	C(27A)–C(27)–C(28)	96.8(5)
C(17M)–C(17)–C(18)	116.8(5)	C(27M)–C(27)–C(28)	117.0(6)
N(11)–C(17A)–C(13A)	112.8(5)	N(21)–C(27A)–C(23A)	111.8(5)
N(11)–C(17A)–C(17)	137.4(5)	N(21)–C(27A)–C(27)	137.2(6)
C(13A)–C(17A)–C(17)	109.8(5)	C(23A)–C(27A)–C(27)	111.0(6)
C(14)–C(18)–C(17)	95.0(5)	C(24)–C(28)–C(27)	94.7(5)
C(14)–C(18)–C(18S)	113.3(5)	C(24)–C(28)–C(28S)	112.7(6)
C(14)–C(18)–C(18A)	112.8(5)	C(24)–C(28)–C(28A)	113.7(6)
C(17)–C(18)–C(18S)	113.8(5)	C(27)–C(28)–C(28S)	113.9(6)
C(17)–C(18)–C(18A)	114.4(5)	C(27)–C(28)–C(28A)	114.3(6)
C(18S)–C(18)–C(18A)	107.5(5)	C(28S)–C(28)–C(28A)	107.3(6)

Experimental

General Procedures

Infrared and ultraviolet spectra were recorded on Shimadzu IR27G and Varian DMS 100 spectrophotometers respectively. ^1H and ^{13}C NMR spectra were recorded on Varian T60 and CFT20 spectrometers respectively, for $CDCl_3$ solutions with Me_4Si as internal standard. Mass spectra were recorded on an A.E.I. MS902 spectrometer. Optical rotations were recorded with a JASCO ORD/CD-5 spectropolarimeter. Radial chromatography was performed on a Chromatotron (Harrison and Harrison) using Merck type 60 P.F.$_{254}$ silica gel.

2,6-Bis(chloromethyl)pyridine (**7**) and (4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-1H(2H)-indazole (**9**) were prepared according to the literature procedures [35–37].

Preparation of Ligands

Preparation of 6

A mixture of 2,6-bis(chloromethyl)pyridine hydrochloride (0.5 g, 2.35 mmol), pyrazole (0.32 g, 4.7 mmol), benzene (70 ml), 40% aqueous sodium hydroxide (12 ml) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed with stirring for 8 h and then stirred at room temperature overnight. The organic layer was then separated, dried (Na_2SO_4) and evaporated under reduced pressure to yield 2,6-bis(pyrazol-1-ylmethyl)pyridine (**6**) as an oil. Yield = 90%. ν_{max} (smear) 1600 cm^{-1}, 1470, 1400, 1300, 1090, 1050, 750. ^{1}H NMR δ_H 5.47, s, 4H, CH_2; 6.32, t, 2H, H4′; 6.83, d, 2H, H3, H5; 7.57, m, 5H, H3′, H4, H5′. ^{13}C NMR δ_C 57.4, CH_2; 106.3, C4′; 120.6, C3 and C5; 130.1, C5′; 138.1, C4; 140.0, C3′; 156.6, C2 and C6. Calc. for $C_{13}H_{13}N_5$: M^+, 239.1171. Found: M^+, 239.1169.

Preparation of 10

An equimolar mixture of **7** and pyrazole **8** was reacted as above to give an oil which was absorbed onto a radial chromatographic plate (silica, 2 mm). Elution with 1:1 ether–petroleum ether gave a forerun of **6**. Further elution gave 2-chloromethyl-6-(pyrazol-1-ylmethyl)pyridine (**10**) as an oil. Yield = 30%. ν_{max} (smear) 1600 cm^{-1}, 1470, 1400, 1300, 1100, 750. ^{1}H NMR. δ_H 4.63, s, 2H, CH_2Cl; 5.47, s, 2H, NCH_2; 6.30, t, 1H, H4′; 6.83, brd, 1H, H5; 7.33 brd, 1H, H3; 7.63, m, 3H, H4, H3′, H5′. ^{13}C NMR δ_C 46.5; CH_2Cl; 57.2; NCH_2; 106.3, C4′; 120.8, C5; 121.7, C3; 130.0, C5′;138.1, C4; 140.0, C3′; 156.3, C2; 156.6, C6. Calc. for $C_{10}H_{10}N_3Cl$: M^+, 207.0563. Found: M^+, 207.0568.

Preparation of 11 and 12

A mixture of **9** (0.23 g, 1.3 mmol), **10** (0.27 g, 1.3 mmol), benzene (70 ml), 40% aqueous sodium hydroxide (10 ml), and 40% aqueous tetrabutylammonium hydroxide (6 drops) was stirred and refluxed for 10 h. The organic layer was then separated, dried (Na_2SO_4) and evaporated under reduced pressure to yield an oil shown by ^{1}H NMR to be a 1:4 mixture of 2 isomers. The oil was absorbed onto a 2 mm silica radial chromatographic plate and elution with 1:3 ether–petroleum ether afforded the major isomer 2-(pyrazol-1-ylmethyl)-6-[((4*S*-7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(2H)-indazol-2-yl)methyl]pyridine (**11**) as colourless crystals. Yield = 60%. Melting point (m.p.) = 85–86.5 °C. ν_{max} (KBr) 2950 cm^{-1}, 1600, 1470, 1395, 1300, 750. ^{1}H NMR δ_H* 0.70, s, 3H, *syn*-C8″-CH_3; 0.93, s, 3H, *anti*-C8″-CH_3; 1.30, s, 3H, C7″-CH_3; 2.77, d, 1H, H4″; 5.37, s, 2H, C6-CH_2; 5.43, s, 2H, C2-CH_2; 6.30, t, 1H, H4′; 6.67, d, 1H, H5; 6.80, d, 1H, H3; 7.0, s, 1H, H3″; 7.40-7.67, m, 3H, H4, H3′, H5′. ^{13}C NMR δ_C 10.8, C7″-CH_3; 19.2, *syn*-C8″-CH_3; 20.6, *anti*-C8″-CH_3; 27.9, C5″; 33.9, C6″; 47.3. C4″; 50.3, C8″; 56.7, C6-CH_2; 57.4, C2-CH_2; 60.6, C7″; 106.2, C4′; 119.9, C5; 120.1, C3; 122.3, C3″;; 127.7, C3A″; 130.0, C5′; 138.0, C4; 139.9, C3′; 156.1, C2; 158.2, C6; 166.9, C7A″. Calc. for $C_{21}H_{25}N_5$: C, 72.6; H, 7.3; N 20.2. Found: C, 72.6 H, 7.4; N, 19.8%.

The minor isomer, 2-(pyrazol-1-ylmethyl)-6-[((4*S*, 7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(1H)-indazol-1-yl)methyl] pyridine (**12**) was not obtained pure but it characterised by the following data: ^{1}H NMR δ_H 0.73, s, 3H, *syn*-C8″-CH_3; 0.87, s, 3H, *anti*-C8″-CH_3; 1.18, s, 3H, C7″-CH_3; 2.75, d, 1H, H4″; 5.40, s, 2H, C6-CH_2; 5.45, s, 2H, C2-CH_2; 6.30, t, 1H, H4′; 6.9-6.7, H3, H5; 7.18, s, 1H, H3″; 7.7-7.4, m, 3H, H4, H3′, H5′. ^{13}C NMR δ_C 11.1, C7″-CH_3; 19.6, *syn*-C8″-CH_3. 20.4, *anti*-C8″-CH_3; 27.8, C5″; 33.5, C6″; 47.6, C4″; 52.4, C8″; 55.5, C6-CH_2; 57.4, C2-CH_2; 62.9, C7″; 106.2, C4′; 120.2, C5; 120.5, C3; 130.0, C5; 131.8, C3″; 138.0, C4; 140.0, C3′. Calc. for $C_{21}H_{25}N_5$: M^+, 347.2110. Found: M^+, 347.2075.

Preparation of 13–15

A mixture of **7** (0.3 g, 1.41 mmol) **9** (0.5 g, 2.84 mmol) benzene (80 ml), 40% aqueous sodium hydroxide (10 ml) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed with stirring for 7 h and then stirred at room temperature overnight. Workup as above gave an oil which was shown by ^{1}H NMR to be a *ca.* 12:3:1 mixture of three isomers. This mixture was absorbed onto a radial chromatographic plate (silica, 2 mm). Elution with 9:1 ether–petroleum ether afforded 2,6-bis[((4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(2H)-indazol-2-yl)methyl] pyridine (**13**) as an oil. Yield = 48%. ν_{max} (smear) 3000 cm^{-1}, 2900, 1590, 1470, 1400, 1300, 980, 780. ^{1}H NMR δ_H 0.70, s, 6H, *syn*-C8′-CH_3; 0.97, s, 6H, *anti*-C8′-CH_3; 1.32, s, 6H, C7′-CH_3; 2.77, d, 2H, H4′; 5.37, s, 4H, CH_2; 6.62, d, 2H, H3, H5; 7.00 s, 2H, H3′; 7.52, t, 1H, H4. ^{13}C NMR δ_C 10.8, C7′-CH_3; 19.2, *syn*-C8′-CH_3; 20.6, *anti*-C8′-CH_3; 27.9, C5′; 33.9, C6′; 47.4, C4′; 50.3, C8′; 56.8, CH_2; 60.6, C7′; 119.44, C3 and C5; 122.2, C3′; 127.6, C3A′; 137.8, C4; 157.8, C2 and C6; 166.8, C7A′. Calc. for $C_{29}H_{37}N_5$: M^+, 455.3049. Found: M^+, 455.3048.

Further elution afforded 2-[((4S 7R)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(1H)-indazol-yl)methyl]-6-[((4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(2H)-indazol-2-yl)methyl] pyridine (**14**) as an oil. Yield = 20%. ν_{max} (smear) 3000 cm^{-1}, 2900, 1590, 1470, 1450, 1430, 1400, 780. ^{1}H NMR δ_H 0.70, s, 3H, *syn*-C8″-CH_3; 0.73, s, 3H, *syn*-C8′-CH_3; 0.87, s, 3H, *anti*-C8′-CH_3; 0.97, s, 3H, *anti*-C8″-CH_3; 1.20, s, 3H, C7′-CH_3; 1.33, s, 3H, C7″-CH_3; 2.73, d, 2H, H4′, H4″, 5.37, s, 2H, C6-CH_2; 5.40, s, 2H, C2-CH_2; 6.60, d, 1H, H5; 6.67, d, 1H, H3; 7.00, s, 1H, H3″; 7.18, s, 1H, H3′; 7.5, t, 1H, H4. ^{13}C NMR δ_C 10.8, C7″-CH_3; 11.1, C7′-CH_3; 19.2, *syn*-C8″-CH_3; 19,6, *syn*-C8′-CH_3; 20.4, *anti*-C8′-CH_3; 20.6, *anti*-C8″-CH_3; 27.8, C5′ and C5″; 33.4; C6′; 33.9, C6″; 47.4, C4″; 47.7, C4′; 50.3, C8″;

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*X′ and X″ refer to numbering of substituents at C2 and C6 of pyridine respectively.

52.4, C8′; 55.5, C2-CH_2; 56.7, C6-CH_2; 60.6, C7″; 63.0, C7′; 119.5, C3 and C5; 122.3, C3″; 127.7, C3A″; 129.3, C3A′; 131.7, C3′; 137.8, C4; 154.0, C7A′; 157.4, C2; 158.0, C6; 166.9, C7A″. Calc. for $C_{29}H_{37}N_5$: M^+, 455.3049. Found: M^+, 455.3061.

Further elution afforded the minor isomer 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methano-(1H)-indazol-1-yl)methyl] pyridine (**15**) as an oil. Yield = 5%. ν_{max} (smear) 3000 cm^{-1}, 2900, 1590, 1470, 1450, 1430, 1400, 780. ^1H NMR δ_H 0.73, s, 6H, *syn*-C8′-CH_3; 0.87, s, 6H, *anti*-C8′-CH_3; 1.17, s, 6H, C7′-CH_3; 2.78, d, 2H, H4′; 5.42, s, 4H, CH_2; 6.67, d, 2H, H3, H5; 7.20, s, 2H, H3′; 7.53, t, 1H, H4. ^{13}C NMR δ_C 11.1, C7′-CH_3, 19.6, *syn*-C8′-CH_3, 20.4, *anti*-C8′-CH_3; 27.8, C5′; 33.4, C6′; 47.7, C4′; 55.6, CH_2; 63.0, C7′; 119.6, C3 and C5; 131.72, C3′; 137.8, C4.

Preparation of Complexes

Preparation of $[Fe(6)_2](ClO_4)_2$

To an aqueous solution of iron(II) perchlorate hexahydrate (0.14 g, 0.38 mmol) was added a methanolic solution of **6** (0.19 g, 0.79 mmol). Immediate precipitation of light green material occurred (0.24 g, yield 83%). Recrystallised from MeOH/H_2O. ν_{max} (KBr) 1600 cm^{-1}, 1430, 1400, 1260, 1080br, 970, 760, 620. $\lambda_{max}(CH_3CN)$ 373 sh nm (ϵ = 744 M^{-1} cm^{-1}), 416 (ϵ = 952). Calc. for $C_{26}H_{26}N_{10}O_8Cl_2Fe{\cdot}H_2O$: C, 41.6; H, 3.8; N, 18.6. Found: C, 41.8; H, 3.8; N, 18.7%.

Preparation of $[Ni(6)_2](ClO_4)_2 \equiv 16$

To an aqueous solution of nickel perchlorate hexahydrate (0.12 g, 0.33 mmol) was added an ethanolic solution of **6** (0.16 g, 0.67 mmol). Violet crystals were deposited (0.18 g, 75% yield). Crystals suitable for X-ray crystal study were obtained by recrystallisation from hot water. ν_{max} (KBr) 1620 cm^{-1}, 1440, 1420, 1290, 1100br, 770, 620. λ_{max} (CH_3CN) 538 nm (ϵ = 8.4 M^{-1} cm^{-1}). Calc. for $C_{26}H_{26}N_{10}O_8Cl_2Ni$: C, 42.4; H, 3.6; N, 19.0. Found: C, 42.5; H, 3.6; N, 18.9%.

Preparation of $[Ru(6)_2](PF_6)_2$

Ruthenium trichloride trihydrate (0.10 g, 0.38 mmol) and **6** (0.18 g, 0.75 mmol) were dissolved in water (10 ml) containing a drop of concentrated HCl. The solution was then refluxed for 1 h. The ruthenium was then reduced by sodium hypophosphite (1.8 ml of a solution prepared by neutralising 50% H_3PO_2 (0.8 ml) with 2 M NaOH (3.4 ml)). The solution was then further refluxed for 2 h and then filtered. The complex was precipitated as an olive green solid by dropwise addition of ammonium hexafluorophosphate. The product was recrystallised from H_2O/ethanol. ν_{max} (KBr) 1440 cm^{-1}, 1420, 1290, 1100, 830, 760, 550. λ_{max} (EtOH) 255 nm, 390. Calc. for $C_{26}H_{26}N_{10}F_{12}P_2Ru{\cdot}H_2O$: C, 35.2; H, 3.2; N, 15.8. Found: C, 35.3; H, 3.6; N, 15.3%.

Preparation of $[Ni(6)(NCS)_2]$

To an aqueous solution of nickel perchlorate hexahydrate (0.11 g, 0.3 mmol) was added a methanolic solution of **6** (0.07 g, 0.3 mmol). A pale blue solution resulted. To this solution was added an excess of sodium thiocyanate. Dark blue crystalline material deposited overnight (0.09 g, 72% yield). ν_{max} (KBr) 2100 cm^{-1} (NCS), 1610, 1410, 1290, 1070, 760. λ_{max} (DMF) 368 nm (ϵ = 26 M^{-1} cm^{-1}), 595 (ϵ = 12.5). Calc. for $C_{15}H_{13}N_7S_2Ni$: C, 43.5; H, 3.2; H, 23.7. Found: C, 43.7; H, 3.0; N, 23.7%.

Preparation of $[Cu(6)(NCS)_2]$

To a solution of copper perchlorate hexahydrate (0.2 g, 0.54 mmol) in water (5 ml) was added **6** (0.13 g, 0.54 mmol) in ethanol (5 ml). A deep blue solution resulted to which was added sodium thiocyanate (0.1 g, 1.2 mmol) in water (5 ml). Immediate precipitation of a green solid occurred. This was filtered and washed with ethanol (0.19 g, yield 84%). Dark green crystals were obtained via diffusion of ethanol into a solution of the complex dissolved in dimethylformamide. ν_{max} (KBr) 2100 cm^{-1} (NSC), 1480, 1300, 1080, 750, 630. λ_{max} (DMF) 398 nm (ϵ = 1090 M^{-1} cm^{-1}), 674 (ϵ = 120). Calc. for $C_{15}H_{13}N_7S_2Cu$: C, 43.0; H, 3.1; N, 23.4. Found: C, 42.3 H, 3.2; N, 22.8%.

Preparation of $[Pd_3(6)_2Cl_6]$

To a solution of palladium(II) chloride (0.13 g, 0.7 mmol) dissolved in hot 2 M HCl (8 ml) was added a methanolic solution of **6** (0.17 g, 0.7 mmol). Immediate precipitation of an orange solid occurred. The precipitate was collected and washed with ethanol and air dried. (It is not soluble in common solvents.) ν_{max} (smear) 1620 cm^{-1}, 1420, 1280, 1090, 770, 320. Calc. for $C_{26}H_{26}N_{10}Cl_6Pd_3{\cdot}H_2O$: C, 30.4 H, 2.7; N, 13.6; Cl, 21.1. Found: C, 30.4; H, 2.7; N, 13.8; Cl, 21.1%.

Preparation of $[Cu(11)(NCS)_2]$

To an aqueous solution of copper perchlorate hexahydrate (0.04 g, 0.1 mmol) was added a methanolic solution of **11** (0.04, 0.1 mmol) followed by excess sodium thiocyanate. The resulting green precipitate was collected. ν_{max} 2950 cm^{-1}, 2040, 1590, 1410, 1290, 1090, 760. λ_{max} (D.M.F.) 411 nm (ϵ = 910 M^{-1} cm^{-1}), 714 (ϵ = 130). $CD_\lambda(\Delta\epsilon)$ 640 nm (+0.31 M^{-1} cm^{-1}), 563(0), 445(−0.11), 410(0), 386(+0.05), 369(0). $ORD_\lambda([M])$ 700 nm (870° M^{-1} m^{-1}) 640(0), 596(−600), 426(−170), 318(−1100). Calc. for $C_{23}H_{25}N_7S_2Cu{\cdot}CH_3OH$: C, 51.5; H, 5.2; N, 17.5. Found: C, 51.7; H, 4.8; N, 17.0%.

Preparation of [Cu(13)(NCS)$_2$] ≡ 17

Copper perchlorate hexahydrate (0.03 g, 0.09 mmol) dissolved in H_2O (2 ml) had added a methanolic solution of **13** (0.04 g, 0.09 mol) followed by excess sodium thiocyanate. The resulting green precipitate was collected.

Crystals suitable for X-ray crystal study were obtained from the mother liquor after filtration of the precipitate. ν_{max} (KBr) 2950 cm^{-1}, 2075 (NCS), 1610, 1420, 1280, 1020, 780. λ_{max} (DMF) 408 nm ($\epsilon = 1520$ M^{-1} cm^{-1}) 733 ($\epsilon = 87$). CD$_\lambda$($\Delta\epsilon$) 574 nm (−0.35 M^{-1} cm^{-1}), 443(0), 398(+0.76), 313(+1.04). ORD$_\lambda$ ([M]) 690 nm (+160° M^{-1} m^{-1}), 666(0), 612(−560), 567(0), 532(+310), 480(+120), 432(+750), 412(0).

Preparation of [Cu(14)(NCS)$_2$]

To a methanolic solution of **14** (0.1 g, 0.2 mmol) was added an aqueous solution of copper perchlorate hexahydrate (0.08 g, 0.2 mmol). A deep green solution resulted. Sodium thiocyanate (0.04 g, 0.5 mmol) was then added resulting in precipitation of a green solid which was recrystallised from ethanol/H_2O. ν_{max} (KBr) 2950 cm^{-1}, 2075(NCS), 1610, 1460, 1285, 780. λ_{max}(DMF) 404 nm ($\epsilon = 1000$ M^{-1} cm^{-1}), 675($\epsilon = 250$). CD$_\lambda$($\Delta\epsilon$) 636 nm (+0.34 M^{-1} cm^{-1}), 530(0), 420(−0.12), 370(0), 356(+0.07), 348(0), 298(−0.80). ORD$_\lambda$([M] 648 nm (0° M^{-1} m^{-1}), 602(−800), 388(−430), 330(−1800). Calc. for $C_{31}H_{37}N_7S_2Cu$: C, 58.6; H, 5.9; N, 15.4. Found: C, 58.6; H, 6.0; N, 15.0%.

Crystallography

Table V lists crystal data and X-ray experimental details for **16** and **17**. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo Kα radiation. The measured densities were determined by flotation in acidic zinc bromide solutions. Cell parameters were determined by least squares refinement, the setting angles of 25 accurately centered reflections [$2\theta > 30°$) being used. Throughout data collection the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz, polarization and absorption effects.

The structures were solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. The absolute configuration employed for **17** was that consistent with the known [38] absolute configuration of (+)–camphor from which the ligand was synthesised. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic equivalent of their carrier atoms. The function minimized was

TABLE V. Crystal Data and X-ray Experimental Details

Compound	**16**	17
Formula	$C_{26}H_{26}N_{10}Cl_2O_8Ni$	$C_{31}H_{37}N_7S_2Cu$
M_r	736.2	635.4
a (Å)	10.125(1)	15.795(3)
b (Å)	17.657(4)	20.433(3)
c (Å)	8.579(2)	9.618(1)
V (Å^3)	1532.1(6)	3104.2(8)
Space group	$P2_12_12$	$P2_12_12_1$
Z	2	4
D_c (g cm^{-3})	1.59	1.36
D_m (g cm^{-3})	1.59	1.36
λ (Å)	0.71069	0.71069
F(000)	766	1332
μ (cm^{-1})	8.73	8.65
Radiation	Mo Kα	Mo Kα
Temperature (°C)	−130	−130
Crystal size (mm)	0.48 × 0.16 × 0.14	0.29 × 0.25 × 0.08
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$ (°)	55	55
Unique reflections	2062	2357
Observed reflections	1690	2357
Discrimination	$I > 3\sigma(I)$	$I > 3\sigma(I)$
g	0.00043	0.00025
R	0.039	0.047
R_W	0.048	0.044

TABLE VI. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **16**

Atom	x	y	z	U_{eq}[a]
Ni	0	5000	5173(1)	20(1)
N(1)	613(3)	3830(2)	5149(4)	22(1)
C(2)	1040(4)	3496(2)	3829(5)	24(1)
C(3)	1215(5)	2720(3)	3714(6)	32(1)
C(4)	904(5)	2267(2)	4968(6)	36(1)
C(5)	505(5)	2594(2)	6342(6)	32(1)
C(6)	392(4)	3383(2)	6399(5)	25(1)
C(2A)	1219(5)	3964(2)	2370(5)	30(1)
N(21)	1944(4)	4672(2)	2603(5)	28(1)
N(22)	1413(4)	5233(2)	3485(4)	27(1)
C(23)	2204(4)	5821(3)	3282(6)	29(1)
C(24)	3236(5)	5643(3)	2282(7)	43(2)
C(25)	3026(5)	4905(3)	1870(6)	40(2)
C(6A)	0(5)	3752(2)	7923(4)	27(1)
N(61)	−1302(4)	4116(2)	7784(4)	24(1)
N(62)	−1437(4)	4719(2)	6798(4)	25(1)
C(63)	−2729(4)	4896(3)	6864(5)	29(1)
C(64)	−3393(5)	4400(3)	7877(6)	32(1)
C(65)	−2438(4)	3921(3)	8424(6)	32(1)
C1	3583(1)	2943(1)	−926(1)	28(1)
O(1)	2247(3)	2838(2)	−396(4)	46(1)
O(2)	4161(4)	2210(2)	−1107(4)	41(1)
O(3)	3570(4)	3335(2)	−2392(5)	58(1)
O(4)	4314(4)	3364(2)	194(5)	64(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE VII. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for **17**

Atom	x	y	z	U_{eq}[a]
Cu	5389(1)	1719(1)	4559(1)	21(1)
N(1A)	5495(3)	839(2)	3739(5)	28(2)
C(1A)	5470(4)	284(3)	3943(7)	33(2)
S(1A)	5413(2)	−497(1)	4254(3)	61(1)
N(1B)	4948(3)	2332(3)	5967(6)	32(2)
C(1B)	4791(3)	2736(3)	6762(7)	27(2)
S(1B)	4563(1)	3309(1)	7893(2)	40(1)
N(1)	6227(3)	2387(2)	3315(5)	25(2)
C(2)	5922(4)	2942(3)	2798(7)	29(2)
C(3)	6422(4)	3443(3)	2274(7)	33(2)
C(4)	7288(4)	3359(3)	2348(6)	30(2)
C(5)	7619(4)	2784(3)	2869(7)	29(2)
C(6)	7071(4)	2310(3)	3351(6)	24(2)
C(2A)	4972(4)	3039(3)	2822(8)	34(2)
C(6A)	7377(4)	1664(3)	3886(6)	26(2)
N(11)	4420(3)	1933(2)	3299(5)	23(2)
N(21)	6360(3)	1494(2)	5794(5)	23(2)
N(12)	4486(3)	2457(2)	2406(5)	30(2)
N(22)	7194(3)	1564(2)	5363(5)	23(2)
C(13)	3863(4)	2446(3)	1420(7)	33(2)
C(23)	7734(4)	1430(3)	6394(7)	31(2)
C(13A)	3390(4)	1903(3)	1667(7)	27(2)
C(23A)	7267(4)	1263(3)	7534(7)	28(2)
C(14)	2672(4)	1466(3)	1222(7)	31(2)
C(24)	7226(4)	1040(3)	9028(7)	38(2)
C(15)	3105(4)	838(3)	640(7)	36(2)
C(25)	6845(4)	1615(4)	9862(7)	48(3)
C(16)	3523(4)	519(3)	1934(7)	34(2)
C(26)	5919(4)	1647(4)	9335(7)	43(3)
C(17)	3291(4)	985(3)	3160(7)	26(2)
C(27)	5847(4)	1092(3)	8253(7)	28(2)
C(17A)	3757(4)	1606(3)	2818(6)	23(2)
C(27A)	6429(4)	1304(3)	7116(7)	24(2)
C(17M)	3368(4)	712(3)	4614(7)	33(2)
C(27M)	4974(4)	867(4)	7881(8)	49(3)
C(18)	2378(4)	1217(3)	2685(7)	28(2)
C(28)	6461(4)	568(3)	8925(7)	36(2)
C(18S)	1729(4)	666(3)	2609(8)	39(2)
C(28S)	6637(5)	−22(3)	7992(9)	56(3)
C(18A)	1997(4)	1762(3)	3581(6)	33(2)
C(28A)	6165(5)	304(4)	10328(8)	59(3)

[a] See footnote to Table VI.

$\Sigma w(|F_c| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^{\,2}]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [39].

Final atom coordinates for **16** and **17** are listed in Tables VI and VII respectively, with estimated standard deviations in parentheses.

Supplementary Material

Tabulations of structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the author P.J.S.

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