

## The Crystal Structure of 1,4-Bis(4-pyridyl)butadiyne and a Study of its Complexes with Cobalt(II), Nickel(II) and Copper(II)

J. R. ALLAN, M. J. BARROW, P. C. BEAUMONT, L. A. MACINDOE, G. H. W. MILBURN\* and A. R. WERNINCK

Department of Applied Chemical Sciences, Napier College, Edinburgh, U.K.

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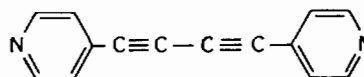
### Abstract

The diacetylene 1,4-bis(4-pyridyl)butadiyne has been prepared from 1-ethynyl pyridine. The purity of the 1,4-bis(4-pyridyl)butadiyne was confirmed by the melting point determination,  $^1\text{H}$  NMR spectroscopy and by elemental analysis. A complete X-ray structure has been carried out on this compound. The preparation and some properties of complexes of 1,4-bis(4-pyridyl)butadiyne with cobalt, nickel and copper are described. Solubility studies, together with spectral and magnetic properties indicate that these compounds have polymeric octahedral structures.

### Introduction

The combination of scientific challenge and technological usefulness has brought the study of diacetylenes to a most prominent position as is amply reflected in the abundance of recent research publications in the chemical, physical and patent literature. Optical and electrical properties of the polydiacetylenes have also been the subject of a number of publications [1–11]. These polymers may be obtained by solid state polymerisation of diacetylene monomers [12–14] by a 1,4-addition reaction [1, 2]. For the 1,4 addition to be successful, the distance between the  $\text{C}_1$  atom of one acetylene molecule and the  $\text{C}_4$  atom of an adjacent acetylene molecule in the crystalline monomer must not exceed 4 Å [15].

In this paper, we discuss the diacetylene 1,4-bis(4-pyridyl)butadiyne. We have examined the crystal structure of this compound in order to investigate the possibility of polymerisation. Earlier studies in these laboratories have provided information on the molecular structure and crystal packing of monomeric diacetylenes [16]. We also report the metallo-organic compounds formed by 1,4-bis(4-pyridyl)butadiyne and the transition metals cobalt, nickel and copper. The compound 1,4-bis(4-pyridyl)butadiyne has four possible sites for coordination to a metal ion; the nitrogen atoms in each of the rings and the triple bonds between the carbon atoms.



1,4-bis(4-pyridyl)butadiyne

Spectral and magnetic studies have been used to characterise each compound and to establish the type of coordination.

### Experimental

(A) 1,4-bis(4-pyridyl)butadiyne was prepared by the method of Ciana and Haim [17] (melting point (m.p.) 203–204 °C,  $^1\text{H}$  NMR (deuteriochloroform):  $\delta$  7.25 (2H $\beta$ ), 8.45 (2H $\alpha$ )).

(B) A solution containing 0.1 mol of 1,4-bis(4-pyridyl)butadiyne and 0.1 mol of each of the transition metal salts in 60 cm<sup>3</sup> of ethanol was refluxed for 48 h. The solution was cooled and the resulting precipitate was filtered. The precipitate, which was a powder, was washed with warm ethanol and dried in a desiccator over calcium chloride.

(C) 0.01 mol of nickel(II) nitrate dissolved in 60 cm<sup>3</sup> of warm ethanol was added to 0.01 mol of potassium thiocyanate in 60 cm<sup>3</sup> of warm ethanol. The resulting precipitate was removed by filtration and 0.01 mol of 1,4-bis(4-pyridyl)butadiyne was added to the filtrate. After refluxing for 48 h the precipitated complex was filtered, washed with ethanol and dried in a desiccator over calcium chloride.

The complexes prepared by these methods are listed in Table I and are all new compounds. The analysis of the metal ion content was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; the carbon, hydrogen and nitrogen analysis was carried out on a Carlo Erba Elemental Analyser. The electronic spectra (Table II) were obtained using a Beckman ACTA MIV spectrophotometer. The magnetic moments (Table I) were obtained by the Gouy Method using the calibrant  $\text{Hg}[\text{Co}(\text{SCN})_4]$ . Each magnetic moment has been corrected for diamagnetism using Pascals constants [18]. The infrared absorption spectra (Table III) were obtained by using KBr (4000–600 cm<sup>-1</sup>) and polyethylene

\*Author to whom correspondence should be addressed.

TABLE I. Analyses and Magnetic Moments of the Compounds

Compound <sup>a</sup>	Method of preparation	Theory (%)				Experimental (%)				$\mu$ (BM)
		C	H	N	M	C	H	N	M	
Co(CNS) <sub>2</sub> (BPB)	B	50.92	14.85	2.12	15.54	50.32	14.86	2.02	15.46	4.62
CoCl <sub>2</sub> (BPB)	B	50.31	8.38	2.39	17.64	49.49	8.14	2.37	17.66	5.19
Ni(CNS) <sub>2</sub> (BPB)	C	50.69	14.77	2.11	15.50	49.01	12.85	1.77	15.46	3.02
NiCl <sub>2</sub> (BPB)	B	50.34	8.39	2.39	17.59	50.62	8.20	2.10	17.56	3.46
CuCl <sub>2</sub> (BPB)·2H <sub>2</sub> O	B	44.85	7.47	3.20	18.76	44.97	7.14	2.58	18.81	1.88

<sup>a</sup>BPB = 1,4-bis(4-pyridyl)butadiyne.

TABLE II. Electronic Spectra of the Compounds (cm<sup>-1</sup>)

Compound <sup>a</sup>	Peak position	<i>Dq</i>	<i>B</i>	$\beta$
Co(CNS) <sub>2</sub> (BPB)	$\bar{\nu}_1 = 9708$ $\bar{\nu}_3 = 21000$	1094	835	0.86
CoCl <sub>2</sub> (BPB)	$\bar{\nu}_1 = 8333$ $\bar{\nu}_2 = 16528$ $\bar{\nu}_3 = 21222$	819	850	0.86
Ni(CNS) <sub>2</sub> (BPB)	$\bar{\nu}_1 = 6494$ $\bar{\nu}_2 = 10204$ $\bar{\nu}_3 = 22727$	649	897	0.86
NiCl <sub>2</sub> (BPB)	$\bar{\nu}_1 = 8196$ $\bar{\nu}_2 = 13514$ $\bar{\nu}_3 = 24096$	819	868	0.83
CuCl <sub>2</sub> (BPB)·2H <sub>2</sub> O	$\bar{\nu}_1 = 12500$			

<sup>a</sup>BPB = 1,4-bis(4-pyridyl)butadiyne.

TABLE III. Infrared Spectra<sup>a</sup> (4000–200 cm<sup>-1</sup>) for the Compounds

Compound <sup>b</sup>	$\bar{\nu}(\text{O-H})$ (H <sub>2</sub> O)	$\bar{\nu}(\text{C}\equiv\text{C})$	$\bar{\nu}(\text{C}=\text{N})$	Ring vibrations	$\bar{\nu}(\text{C-S})$	$\bar{\nu}(\text{M-N})$	$\bar{\nu}(\text{M-Cl})$
BPB		2210(w)		1596(m) 1405(m)			
Co(CNS) <sub>2</sub> (BPB)			2092(m)	1608(m) 1590(m)	770(w)	290(w)	
CoCl <sub>2</sub> (BPB)		2160(w)		1600(m) 1415(m)		250(w)	234(w)
Ni(CNS) <sub>2</sub> (BPB)			2096(m)	1612(m) 1420(m)	776(w)	290(w)	
NiCl <sub>2</sub> (BPB)		2216(w)		1612(m) 1420(m)		260(w)	255(w), 207(w)
CuCl <sub>2</sub> (BPB)·2H <sub>2</sub> O	3620–3100br (s)	2210(w)		1610(m) 1420(m)		240(w)	220(w)

<sup>a</sup>br, broad; s, strong; m, medium; w, weak. <sup>b</sup>BPB = 1,4-bis(4-pyridyl)butadiyne.

discs (600–200 cm<sup>-1</sup>) on a Perkin-Elmer 598 spectrophotometer. Single crystals of 1,4-bis(4-pyridyl)butadiyne were grown from acetone. The X-ray data were obtained on a ENRAF-NONIUS CAD4 diffractometer with an ULT1 low temperature nitrogen gas stream attachment. The crystal used for diffractometry had dimensions 0.5 × 0.1 × 0.05 mm. Unit cell parameters were determined by least-squares from the setting angles of 25 automatically centred reflections. Intensity data were measured by  $\omega/2\theta$  scans for  $1.5 < \theta < 20$  with scan speeds of 1.0–6.6

min<sup>-1</sup> and scan widths of  $(0.8 + 0.34 \tan\theta)^\circ$ . Two standard reflections measured every two hours showed no decay. 1053 reflections were measured, 913 unique.

#### Crystal Data

$T = 185 \pm 1$  K. C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>. Formula weight = 204.39. Monoclinic,  $a = 3.810(6)$ ,  $b = 23.075(5)$ ,  $c = 5.851(2)$  Å,  $\beta = 90.39(8)^\circ$ ,  $V = 514.4$  Å<sup>3</sup>.  $D_e = 1.318$  Mg m<sup>-3</sup> for  $Z = 2$ .

TABLE IV. Atomic Parameters<sup>a</sup>

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>eq</sub>/U<sub>iso</sub></i>
C1	0.0522(11)	0.52087(19)	0.5749(7)	0.0345(20)
C2	0.1439(11)	0.55778(19)	0.7070(7)	0.0362(22)
C3	0.2552(11)	0.60153(19)	0.8645(7)	0.0335(20)
C4	0.2146(13)	0.66046(21)	0.8163(8)	0.0409(25)
C5	0.3178(15)	0.70011(23)	0.9769(9)	0.0494(28)
C6	0.4981(12)	0.63023(23)	1.2204(8)	0.0410(25)
C7	0.4065(11)	0.58715(21)	1.0734(7)	0.0358(23)
N1	0.4615(10)	0.68697(18)	1.1786(7)	0.0460(22)
H4	0.082(13)	0.6706(21)	0.672(9)	0.053(14)
H5	0.270(13)	0.7406(23)	0.941(8)	0.054(15)
H6	0.629(13)	0.6236(21)	1.369(9)	0.053(14)
H7	0.441(10)	0.5463(18)	1.115(6)	0.026(10)

<sup>a</sup>e.s.d.s given in parentheses.TABLE V. Bond Lengths (Å)<sup>a</sup>

C1	C1'	1.360(4)	C2	C3	1.429(6)
C1	C2	1.201(6)	C3	C7	1.388(6)
C3	C4	1.397(7)	C4	H4	1.01(5)
C4	C5	1.368(7)	C7	H7	0.98(4)
C7	C6	1.358(7)	C5	H5	0.97(5)
C5	N1	1.332(6)	C6	H6	1.01(5)
C6	N1	1.339(7)			

<sup>a</sup>e.s.d.s given in parentheses.

Space group  $P2_1/n$  ( $C_{2h}^5$ , No. 14) by systematic absences. Graphite monochromated Mo K $\alpha$  radiation.  $\bar{\lambda} = 0.71069$  Å,  $\mu = 0.56$  cm<sup>-1</sup>,  $F(000) = 212$ .

Data were corrected for Lorentz and polarisation effects but not for absorption. Structure solution was by direct methods using SHELX-86 [19a]. All non-hydrogen atoms were located in the best *E* map and all the H atoms located from subsequent difference Fourier synthesis. Weighted least-squares anisotropic refinement using SHELX-76 [19b] of all non-H atoms with isotropic refinement of all H atoms, gave a final  $R = 0.069$  over 589 reflections with  $F > 4\sigma(F_o)$ . Six further observed

reflections (120, 130, -101, -111, -211 and -221) had been removed from the data set on the basis of consistently poor agreement between  $F_o$  and  $F_c$ . The final weighting scheme was  $w^{-1} = [1 + 0.00567(F_o - 7)^2]$ . A final difference Fourier synthesis showed no residual electron density outside the range of  $\pm 0.3$  e Å<sup>-3</sup>. Atomic scattering factors were from International Tables for X-ray Crystallography (1974). Computations were performed on an Acorn ACW 443 workstation. Final atomic parameters are given in Table IV, and details of the intramolecular geometry in Tables V and VI.

## Results and Discussion

The compound 1,4-bis(4-pyridyl)butadiyne crystallises as monoclinic crystals. Figure 1 shows a single molecule to indicate the atomic labelling scheme, and Figs. 2 and 3 illustrate the packing of molecules in the crystal. For a monomeric species in space group  $P2_1/n$  with two molecules per cell, each molecule must lie across a crystallographic centre of symmetry. Since the deviations from planarity of the atoms within an asymmetric unit (one half molecule) are negligible, it follows that the molecule has  $D_{2h}$  sym-

TABLE VI. Bond Angles (°)

C3	C2	C1	179.6(5)	C4	C3	C2	121.7(4)
C7	C3	C2	121.2(4)	C7	C3	C4	117.1(4)
C5	C4	C3	118.8(4)	H4	C4	C3	116.7(27)
C6	C7	C3	119.1(4)	H7	C7	C3	120.2(23)
H4	C4	C5	124.1(27)	N1	C5	C4	124.8(5)
H5	C5	C4	116.3(29)	H7	C7	C6	120.7(23)
N1	C6	C7	125.0(4)	H6	C6	C7	123.9(28)
H5	C5	N1	118.8(29)	C6	N1	C5	115.2(4)
H6	C6	N1	110.7(28)	C1'	C1	C2	179.9(4)

<sup>a</sup>e.s.d.s given in parentheses.

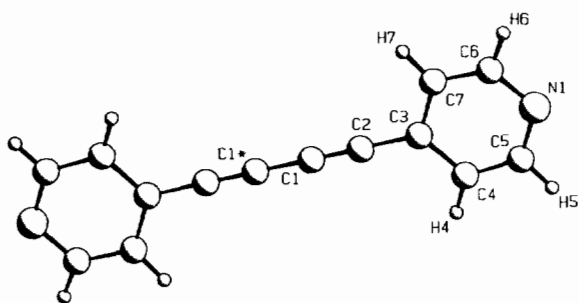


Fig. 1. Atom labelling.

metry in which the coplanarity of the molecule of the pyridine rings is rigorous and crystallographically imposed.

There is no experimental evidence to support the idea that this crystalline form of 1,4-bis(4-pyridyl)-butadiyne might undergo solid state polymerisation. Neighbouring molecules are closest packed in the  $x$  direction ( $a = 3.180$ ) but inspection of Fig. 3 shows that the orientation of adjacent molecules is not ap-

propriate for intermolecular 1,4 solid state polymerisation of the diacetylene units. The relevant distance, between C2 of one molecule and C2' of a neighbour related by inversion and a unit translation along  $x$ , is 4.52 Å and this distance is well outside the limit of about 4 Å proposed by Schmidt [15]. In the present structure the C2–C2' distance is actually at its closest at 4.48 Å for molecules separated by unit translations along the  $z$  axis. Here the relative molecular orientations are also favourable for crystal phase polymerisation excepting that the C2–C2' separation is still too great and any closer approach (within this crystal geometry) is inhibited by intermolecular van der Waals interactions to H6 and H7. It may also be argued that the very limited degree of conformational mobility in the molecule (only a rotation about the C2–C3 bond is possible) makes 1,4-bis(4-pyridyl)-butadiyne an unlikely candidate for solid state polymerisation.

In Table I the analytical results for the complexes are shown. They agree with the given formulae and the stoichiometry of the compounds showing that only one molecule of 1,4-bis(4-pyridyl)butadiyne is

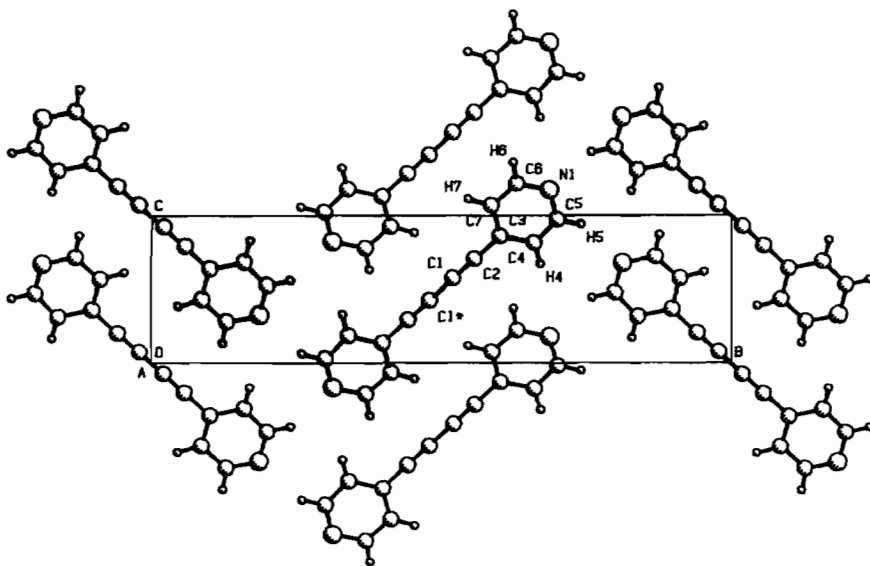


Fig. 2. Crystal packing: a view down the  $x$  axis of the unit cell.

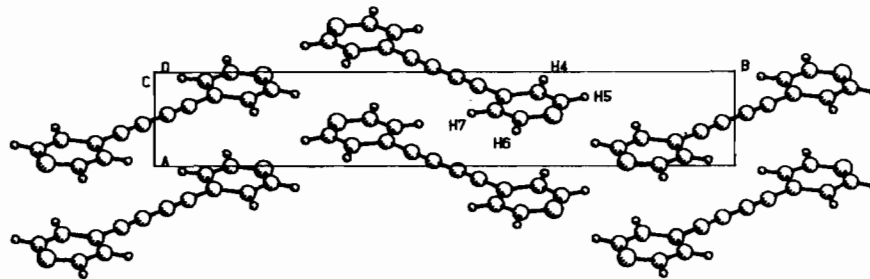


Fig. 3. Crystal packing: a view down the  $z$  axis of the unit cell.

present in each of the compounds. All of the compounds are anhydrous, with the exception of the chloro compound of copper which has two molecules of water present.

The wavenumbers of the infrared absorption bands together with their descriptions and assignments are given in Table III. The infrared spectrum of the compound  $\text{CuCl}_2(\text{BPB})2\text{H}_2\text{O}$  showed a broad absorption band in the region  $3600\text{--}2160\text{ cm}^{-1}$  indicating the presence of water of crystallisation [18]. The bands in the  $2216\text{--}2160\text{ cm}^{-1}$  region for cobalt, nickel and copper compounds have been assigned to the  $\nu(\text{C}\equiv\text{C})$  vibration. The  $\nu(\text{C}\equiv\text{C})$  vibration is little altered from the value of the free ligand showing that no bonding is taking place with the metal ions. In the  $2000\text{--}600\text{ cm}^{-1}$  region the spectra of the complexes are very similar to that of 1,4-bis(4-pyridyl)butadiyne except for the bands due to ring vibrations of the aromatic ring, which move to higher frequency in the complexes. This would suggest that the nitrogen atoms in the aromatic ring are coordinated to the metal ions in all cases [20]. The bands around  $2095\text{ cm}^{-1}$  in the thiocyanate complexes are indicative of bridging thiocyanate groups [21, 22]. The assignments for the metal chloride bands (Table III) are similar to those previously reported in the literature for bridging chloride complexes [20]. Metal nitrogen bands which are observed for all of the complexes are shown in Table III.

The d-d bands from the electronic spectra of the complexes are shown in Table II. The positions of the bands indicate the metal ion in each of the compounds is in an octahedral environment [20]. The  $Dq$  values in Table II for the cobalt and nickel compounds are consistent with the stereochemistry [23]. The copper compound has a broad absorption band at  $12\,500\text{ cm}^{-1}$ . This suggests an octahedral environment for the copper atom [20] since square planar copper(II) compounds show bands of near equal intensity at about  $15\,000\text{--}18\,000\text{ cm}^{-1}$  [24-26] and regular tetrahedral compounds have bands below  $10\,000\text{ cm}^{-1}$  [27].

The magnetic moments for the cobalt and nickel compounds, Table I show that the metal ions are in an octahedral environment [18]. The magnetic moment of the copper compound is higher than the spin only value of 1.73 BM suggesting some orbital contribution to the magnetic moment in this compound. The poor solubility of the compounds in both polar and non-polar solvents implies that the compounds have polymeric structures [20].

No single crystals of the complexes were obtained during their formation from ethanolic solutions. It was therefore not possible to carry out single crystal X-ray analysis on the metal complexes. It is possible however to draw inferences regarding these structures from spectroscopic and magnetic data that were obtained for these metal complexes.

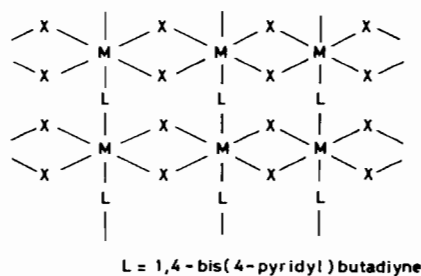


Fig. 4. Proposed polymeric structure.

In the infrared spectra the bands at  $220\text{--}260\text{ cm}^{-1}$  in the chloro compounds [18] and at around  $2095\text{ cm}^{-1}$  in the thiocyanate compounds [19, 20] would suggest the presence of bridging halogen and thiocyanate groups. It is therefore proposed that the structure consists of a polymeric chain of atoms with the 1,4-bis(4-pyridyl)butadiyne molecules as bridging units between adjacent chains, Fig. 4. The 1,4-bis(4-pyridyl)butadiyne molecules are coordinated to the metal ions through the nitrogen atoms of the aromatic rings. In the copper compound the water molecules are attached by hydrogen bonding. The  $\beta$  values observed in Table II would suggest some ionic character in the metal-ligand bonds in these complexes.

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