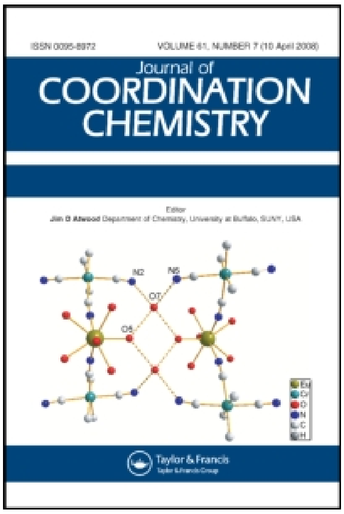

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THE CRYSTAL STRUCTURE OF 1,6-DIAMINO-1,1,6,6-TETRAMETHYL-2,4-HEXADIYNE AND STUDIES OF ITS COMPLEXES WITH COBALT(II), NICKEL(II) AND COPPER(II)

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THE CRYSTAL STRUCTURE OF 1,6-DIAMINO-1,1,6,6-TETRAMETHYL-2,4-HEXADIYNE AND STUDIES OF ITS COMPLEXES WITH COBALT(II), NICKEL(II) AND COPPER(II)

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The diacetylene 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne has been prepared from 1,1-dimethyl propargylamine and a complete structure determination has been carried out. Some new compounds of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne with cobalt, nickel and copper have been prepared. The compounds have been characterised by analysis, magnetic moments, vibrational and electronic spectra. The thiocyanate compound of cobalt and the chloro-compounds of nickel and copper were found to have octahedral-based structures. The chloro-compound of cobalt has a tetrahedral structure.

Keywords: Diacetylenes, amino group, X-ray structure, cobalt(II), nickel(II), copper(II)

INTRODUCTION

Scientific challenge and technological utility have combined to promote diacetylenes into a privileged position of research, and this is reflected in an abundance of publications in the chemical, physical and patent literature. Solid state polymerisation of diacetylenes produces polydiacetylenes.[1–5] These polymers are obtained by a 1,4-addition reaction of the diacetylene monomers.[6,7] For the 1,4-addition to be successful a distance of less than 4Å must be present between the C_1 atom of one diacetylene and the C_4 atom of an adjacent diacetylene. The optical and electrical properties of the polydiacetylenes have been the subject of a number of publications.[6–16]

In this paper we discuss the diacetylene 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne. We have determined the crystal structure of this compound in order to study the feasibility of it being able to undergo polymerisation. Earlier structures from these laboratories have already provided information on the molecular structure and crystal packing of monomeric diacetylenes.[17,18] We also report some complexes formed by 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne and the transition metals cobalt, nickel and copper. The compound 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne has four possible sites for coordination to a metal ion comprising the nitrogen atoms of the amine groups and the carbon–carbon triple bonds. Spectral and magnetic studies have been used to characterise each compound and to establish the stereochemistry of the metal ion.

EXPERIMENTAL

Preparation of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne (L).

1,1-dimethylpropargylamine (8.31g), water (10 cm^3), copper(I) chloride (9.9 g) and concentrated ammonia (20.5 cm^3) were placed in a flask connected to a source of oxygen gas and the gas bubbled through the mixture which was shaken for 12 hours. The reaction mixture was filtered and the filtrate extracted continuously into ether for 48 hours. The ether was then evaporated to yield crude 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne as brownish crystals. The product was recrystallised from petrol as colourless needles (6.6 g: 80.3%) with a melting point of 50–51°C.

Preparation and Characterisation of the Metal Complexes

(a) Chloride ligand complexes

Solutions containing 0.1 mol of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne and 0.1 mol of each of the transition metal salts in 60 cm^3 of ethanol were mixed together and heated on a water bath until the metal complex precipitated. The precipitated compound was filtered, washed with ethanol and dried in a desiccator over calcium chloride.

(b) Thiocyanate ligand complex

0.01 mol of nickel(II) nitrate dissolved in 60 cm^3 of warm ethanol was added to 0.01 mol of potassium thiocyanate in 60 cm^3 of warm ethanol. The resulting precipitate was removed by filtration and 0.05 mol of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne was added to the filtrate. After warming the mixture on a water bath the precipitated complex was filtered, washed with ethanol and dried in a desiccator over calcium chloride.

TABLE I
Analytical and magnetic data for the ligand and its complexes.

		Calc(%)				Found(%)				
Compound	Colour	C	H	N	M	C	H	N	M	μ(B.M.)
$C_{10}H_{16}N_2.0.5H_2O$	Colourless	69.32	9.89	16.17		69.31	9.88	16.18		
$Co(SCN)_2L$	Blue	42.80	4.72	16.52	17.40	42.50	4.73	16.55	17.46	5.01
$CoCl_2L$	Blue	40.82	5.44	9.52	20.06	40.85	5.44	9.54	20.10	4.42
$NiCl_2L\,H_2O$	Yellow	38.49	5.77	8.98	18.83	38.51	5.79	9.01	18.91	3.66
$CuCl_2L$	Green	40.20	5.36	9.38	21.27	40.24	5.40	9.39	21.31	2.11

These new complexes are listed in Table I. The metal ion content was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; The carbon, hydrogen and nitrogen analyses were carried out on a Carlo Erba Elemental Analyser. The electronic spectra (Table II) were obtained using a Beckmann ACTA MIV spectrophotometer. The magnetic moments (Table I) were obtained by the Gouy Method using the calibrant $Hg[Co(SCN)_4]_2$. Each magnetic moment has been corrected for

TABLE II
Electronic spectral data (cm^{-1}) for the complexes.

Compound	Peak position	Dq	B	β
$CoCl_2L$	6666 15873	362	779	0.80
$Co(SCN)_2L$	8330 15748 21978	740	848	0.85
$NiCl_2L\,H_2O$	8666 14814 24920	866	915	0.88
$CuCl_2L$	14084			

diamagnetism using Pascals constants.[19] The infrared absorption spectra, (Table III) were measured in KBr (4000–600 cm^{-1}) and polytheylene discs (600–200 cm^{-1}) using a Perkin-Elmer 598 spectrophotometer.

TABLE III
Main i.r. bands in the ligand and its complexes (cm^{-1}).

Compound	$\nu_{O-H}(H_2O)$	$\nu_{AS}(NH_2)$	$\nu_S(NH_2)$	ν_{CNS}	$\nu_{C\equiv C}$	ν_{M-X}
L	3700–3000(br,m)	3320(m)	3260(m)			
$Co(SCN)_2L$		3270(m)	3100(m)	2100(s)	2160(vw)	
$CoCl_2L$		3258(m)	3150(m)		2174(vw)	325(w)
$NiCl_2L\,H_2O$	3700–3000(br,s)				2136(vw)	228(w)
$NiCl_2L$*		3234(m)	3150(m)			
$CuCl_2L$		3280(m)	3140(m)		2134(vw)	260(w), 300(w)

* $NiCl_2L$ obtained by heating $NiCl_2L\ H_2O$ on a thermobalance at a fixed temperature until constant weight was obtained. Abbreviations are as follows: br = broad; s = strong; m = medium; vw = very weak; w = weak.

Crystal and Molecular Structure of 1,6-Diamino-1,1,6,6-tetramethyl-2,4-hexadiyne

Single crystals of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne were grown from petrol. The crystal was aligned along a non-unique axis and the initial cell parameters were estimated from oscillation and Weissenberg photographs. The space group *P2/c* was determined from systematic absences and the subsequent successful refinement. Intensity data were collected on an ENRAF-Nonius CAD4 diffractometer with ULT1 attachment at 185 ± 1 K. The positions of 25 automatically centred reflections were used to calculate a least-squares orientation matrix from which accurate cell parameters were determined. Intensity data for 1991 unique reflections were obtained using graphite monochromated Mo*K*α radiation (ω/2θ scans, ω scan rate 1.0–6.6° min^{-1}, ω scan width $0.8 + 0.34\tan\theta$, θ range 1.5–25°).

Crystal Data

$C_{10}H_{17}N_2O_{0.5}$, Formula Weight = 173.26. Monoclinic, $P2/c$, $F(000) = 378$, a = 9.487(4), b = 6.163(2), c = 19.653(3)Å, β = 102.211(2)°, V = 1123.03Å^3, D_c = 1.0216 g cm^{-3}, Mo$K\alpha$ radiation, $\lambda = 0.71069$Å, $\mu = 0.36\,\mathrm{cm}^{-1}$.

Non-hydrogen atoms were located using automatic direct methods (SHELX 86[20]). H atoms whose positions were revealed in a ΔF synthesis were positionally refined but with an overall isotropic thermal parameter [0.00637(15)Å^2 at convergence]. Non-hydrogen atoms were refined anisotropically. A weighting scheme $W^{-1} = [\sigma^2(F_o) + 0.003525(F_o)^2]$ was employed. Refinement converged at $R = 0.0427$, $Rw = 0.0521$, for 1666 data, $F \geqq 2.00\sigma(F)$. The final ΔF map showed no peaks or troughs greater than ± 0.2eÅ^{-3}. Final atomic positions are listed in Table IV. Tables of anisotropic thermal parameters and of structure factors are available from the Editor on request.

TABLE IV
Fractional coordinates of atoms and equivalent isotropic thermal parameters (Å^2) of non-H-atoms in 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne.

	x	*y*	*z*	*Ueq*
C(3A)	−0.32348(14)	0.62987(23)	0.61271(7)	0.0272(7)
C(2A)	−0.40364(15)	0.78846(23)	0.56277(7)	0.0286(7)
C(1A)	−0.46483(15)	0.92259(25)	0.52308(7)	0.0299(7)
N(A)	−0.22281(14)	0.74298(22)	0.66938(7)	0.0323(7)
C(4A)	−0.23610(20)	0.4797(3)	0.57561(9)	0.0400(9)
C(5A)	−0.42883(20)	0.4991(3)	0.64535(10)	0.0446(10)
C(3B)	−0.17952(14)	0.99114(22)	0.36202(7)	0.0269(8)
C(2B)	−0.32115(15)	0.96114(22)	0.31404(7)	0.0284(7)
C(1B)	−0.43470(15)	0.95155(23)	0.27328(7)	0.0288(7)
N(B)	−0.06068(13)	0.97332(24)	0.32505(7)	0.0357(7)
C(4B)	−0.15781(22)	0.8227(3)	0.41971(9)	0.0473(10)
C(5B)	−0.17579(21)	1.2208(3)	0.39170(10)	0.0468(11)
O	0.00000	0.4545(3)	0.75000	0.0433(10)
H(NA1)	−0.169(3)	0.828(4)	0.6504(11)	
H(NA2)	−0.2777(25)	0.833(4)	0.6898(11)	
H(A1)	−0.1630(23)	0.558(4)	0.5549(11)	
H(A2)	−0.3030(23)	0.404(4)	0.5397(11)	
H(A3)	−0.1830(23)	0.363(4)	0.6085(11)	
H(A4)	−0.4952(24)	0.589(4)	0.6704(11)	
H(A5)	−0.4923(25)	0.422(4)	0.6110(11)	
H(A6)	−0.3717(22)	0.388(4)	0.6811(11)	
H(NB1)	−0.0839(24)	1.083(4)	0.2869(11)	
H(NB2)	−0.0678(23)	0.833(4)	0.3032(11)	
H(B1)	−0.1620(23)	0.684(4)	0.3996(11)	
H(B2)	−0.2353(23)	0.838(4)	0.4514(11)	
H(B3)	−0.0601(25)	0.837(4)	0.4504(11)	
H(B4)	−0.2590(24)	1.247(3)	0.4131(11)	
H(B5)	−0.1914(23)	0.332(4)	0.3491(11)	
H(B6)	−0.0795(25)	1.234(3)	0.4225(11)	
H(O)	0.0721(24)	0.545(4)	0.7715(11)	

RESULTS AND DISCUSSION

The ligand 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne (L) crystallises with two independent molecules (A and B, Figures 1 and 2 respectively) in the asymmetric unit. Each has crystallographically imposed molecular symmetry, C_i and C_2, respectively. However, A and B are barely different. The torsion angle N–C(1)- - - - C(1′)–N′ in A is required to be 180°. In B it is 179.81°. This similarity between A and B effectively results in C_{2h} symmetry for both molecules.

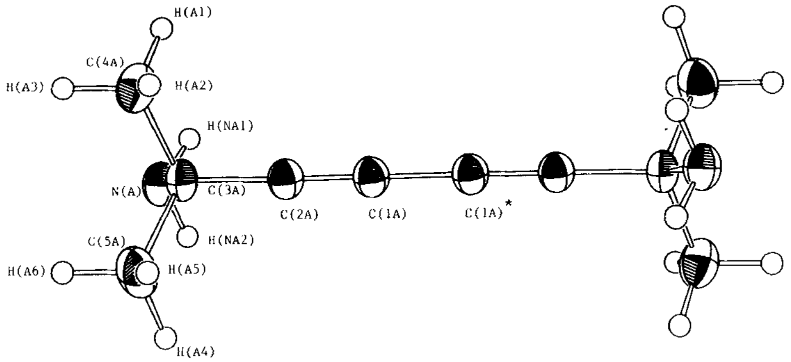

FIGURE 1 Perspective drawing of molecule A of L.

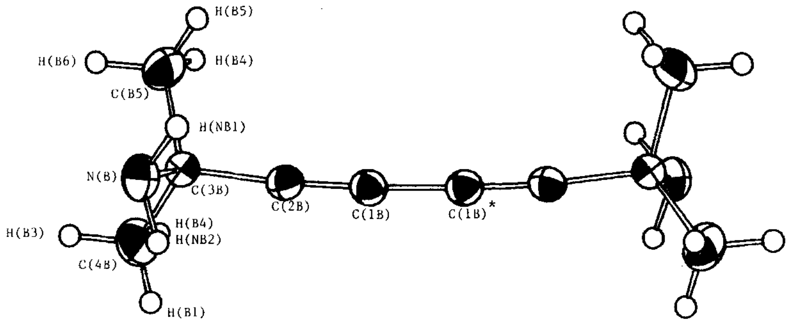

FIGURE 2 Perspective drawing of molecule B of L.

Tables V and VI list, respectively, internuclear distances and interbond angles. Comparison of esd's of nominally single bond C–C distances in L with those in related species[17,18] shows the current structure to be among the most accurate yet determined. Mean C(1)–C(1′), C(1)–C(2) and C(2)–C(3) distances in L agree very well with those in comparable molecules, and imply conjugation of the two acetylenic moieties to some degree. The six atom spines of the two independent molecules are essentially linear (although that of B is slightly less so). Of fundamental importance in crystallographic analyses of hexa-2,4-diyne species is the correlation of close intermolecular contacts with polymerisation, a C_1- - - - -C_4^* contact <4Å appearing to be critical.

TABLE V
Interatomic distances (Å) in 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne.

C(3A)–C(2A)	1.4769(20)	C(3B)–C(2B)	1.4805(19)
C(3A)–N(A)	1.4793(19)	C(3B)–N(B)	1.4688(19)
C(3A)–C(4A)	1.5268(22)	C(3B)–C(B)	1.5186(24)
C(3A)–C(5A)	1.5267(23)	C(3B)–C(B)	1.5282(24)
C(2A)–C(1A)	1.1988(20)	C(2B)–C(1B)	1.2003(20)
C(1A)–C(1A′)	1.3866(20)	C(1B)–C(1B′)	1.3758(20)
N(A)–H(NA1)	0.869(23)	N(B)–H(NB1)	0.998(23)
N(A)–H(NA2)	0.909(23)	N(B)–H(NB2)	0.964(23)
C(4A)–H(A1)	1.001(22)	C(4B)–H(B1)	1.064(22)
C(4A)–H(A3)	1.026(22)	C(5B)–H(B3)	0.997(22)
C(5A)–H(A4)	1.037(23)	C(5B)–H(B4)	0.983(23)
C(5A)–H(A5)	0.935(23)	C(5B)–H(B5)	1.068(22)
C(5A)–H(A6)	1.047(22)	C(5B)–H(B6)	0.987(22)
		O–HO	0.913(22)

TABLE VI
Bond angles (°) in 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne.

C(2A)–C(3A)–N(A)	110.37(12)	C(2B)–C(3B)–N(B)	111.33(12)
C(2A)–C(3A)–C(4A)	109.82(12)	C(2B)–C(3B)–C(4B)	110.64(13)
C(2A)–C(3A)–C(5A)	109.74(12)	C(2B)–C(3B)–C(5B)	107.59(12)
N(A)–C(3A)–C(4A)	108.42(12)	N(B)–C(3B)–C(4B)	108.73(12)
N(A)–C(3A)–C(5A)	107.95(12)	N(B)–C(3B)–C(5B)	107.45(12)
C(4A)–C(3A)–C(5A)	110.51(13)	C(4B)–C(3B)–C(5B)	111.06(13)
C(3A)–C(2A)–C(1A)	177.62(15)	C(3B)–C(2B)–C(1B)	175.39(15)
C(2A)–C(1A)–C(1A′)	179.70(16)	C(2B)–C(1B)–C(1B′)	177.08(15)
C(3A)–N(A)–H(NA1)	107.8(15)	C(3B)–N(B)–H(NB1)	104.5(13)
C(3A)–N(A)–H(NA2)	106.2(15)	C(3B)–N(B)–H(NB2)	107.4(14)
H(NA1)–N(A)–H(NA2)	105.3(21)	H(NB1)–N(B)–H(NB2)	106.9(19)
C(3A)–C(4A)–H(A1)	113.2(13)	C(3B)–C(4B)–H(B1)	108.8(14)
C(3A)–C(4A)–H(A2)	107.6(14)	C(3B)–C(4B)–H(B2)	111.9(12)
C(3A)–C(4A)–H(A3)	111.6(12)	C(3B)–C(4B)–H(B3)	110.6(13)
H(A1)–C(4A)–H(A2)	110.0(19)	H(B1)–C(4B)–H(B2)	110.9(18)
H(A1)–C(4A)–H(A3)	107.8(18)	H(B1)–C(4B)–H(B3)	106.7(19)
H(A2)–C(4A)–H(A3)	106.4(18)	H(B2)–C(4B)–H(B3)	107.8(18)
C(3A)–C(5A)–H(A4)	115.8(13)	C(3B)–C(5B)–H(B4)	111.1(13)
C(3A)–C(5A)–H(A5)	110.2(14)	C(3B)–C(5B)–H(B5)	107.4(18)
C(3A)–C(5A)–H(A6)	109.6(12)	C(3B)–C(5B)–H(B6)	104.9(13)
H(A4)–C(5A)–H(A5)	104.6(19)	H(B4)–C(5B)–H(B6)	116.5(18)
H(A5)–C(5A)–H(A6)	108.3(19)	H(B5)–C(5B)–H(B6)	112.4(19)
H(O)–O–H(O′)	105.0(20)		

In the crystal of L there are no C_1- - - -C_4^* contacts <4Å, consistent with the failure of L to polymerise readily under standard conditions.[21] An unexpected result of the crystallographic analysis was the location of half a molecule of water of crystallisation per molecule of diyne (0 on C_2 axis). However, calculations reveal no evidence of H-bonding, either of the type N–H- - - -O or O–H- - - -N. The formulation of crystals of L as $C_{10}H_{16}N_2.0.5H_2O$ (omitted from the original patent, U.S. Patent 2867662. Jan. 6th, 1959) was confirmed by accurate microanalysis (Table I) and infrared spectroscopy (broad absorption at 3700–3000 cm^{-1}).

In Table I the analytical results for the complexes are shown to be in good agreement with the given formulae. The nickel compound is hydrated while the cobalt and copper compounds are anhydrous. The main infrared absorption bands together with their description and assignments are given in Table III. The infrared spectrum of the compound $NiCl_2LH_2O$ shows broad absorption bands in the region 3700–3000 cm^{-1} indicating the presence of water of crystallisation.[22] The bands in the 2130–2180 cm^{-1} region have been assigned to C≡C vibrations. Bands due to NH_2 vibrations move to lower frequency in the complexes, suggesting that the amine groups bond to the metal ions.[23] The strong peaks at 2100 cm^{-1} in the thiocyanate complex is indicative of a bridging thiocyanate group.[24] The assignment of the metal–chloride bands for nickel and copper compounds are similar to those previously reported in the literature for chloro-bridged complexes[25] while the cobalt compound has metal–chloride bands which are indicative of terminally bound halide ligands.[26] The d–d bands for the electronic spectra are shown in Table II. The position of the bands indicates that the cobalt ion in the chloro-complex is in a tetrahedral environment.[26] The Dq value in Table II for this compound is consistent with this stereochemistry.[27] The copper compound has a broad absorption band at 14084 cm^{-1}. This suggests an octahedral environment since square-planar copper(II) compounds show bands of near equal intensity at about 15000–18000 cm^{-1} [28-30] and regular tetrahedral compounds have bands below 10000 cm^{-1}.[31] The electronic spectra of the nickel complex and the thiocyanate complex of cobalt suggest that the metals lie in octahedral environments.[22,32]

The magnetic moment for the chloro-compound of cobalt is consistent with the cobalt ion in a tetrahedral environment[26] while the magnetic moments of the nickel complex and the thiocyanate complex of cobalt, Table 1, are indicative of an octahedral environment for these metal ions.[22] The magnetic moment for the copper compound is higher than the spin-only value of 1.73 B.M. suggesting some orbital contribution. The β values (Table 2) suggest some ionic character in the metal–ligand bonds in these complexes.

The poor solubility of the complexes in both polar and non-polar solvents implies that they have polymeric structures. No single crystals of the complexes were obtained during their formation from ethanolic solution. Thus without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. The bands observed in the chloro compounds of copper and nickel between 260–228 cm^{-1} and in the cobalt thiocyanate compound at 2100 cm^{-1} would suggest the presence of bridging chloride and thiocyanate groups, respectively.[24,25] One possibility is that these structures consist of a polymeric chain of atoms with the 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne molecule as bridging units between adjacent chains, affording an infinite sheet. The chloro-compound of cobalt has a tetrahedral structure in which the cobalt ions are bonded to two chloride atoms and to the nitrogens of 1,6-diamino-1,1,6,6-tetramethyl-2,4-hexadiyne ligand. Its insolubility, together with the inability of L to function as a simple bidentate (non-bridging) ligand, is consistent with an oligomeric structure.

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