The synthesis and crystal structures of pyridine-2,6-dicarboxamide oxime, $C_7H_9N_5O_2$, and its nickel(II) and copper(II) co-ordination compounds

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The crystals of pyridine-2,6-dicarboxamide oxime, $C_7H_9N_5O_2$, are monoclinic, space group $P2_1$ with $a = 7.569(1)$, $b = 4.695(1)$, $c = 12.534(2)$ Å, $\beta = 106.50(2)°$ and $Z = 2$. The reaction of the ligand with nickel(II) sulfate hexahydrate yielded purple crystals of formula $[Ni(C_7H_9N_5O_2)_2][SO_4]\cdot5H_2O$ which crystallized in the triclinic space group $P\bar{1}$ with $a = 7.502(1)$, $b = 11.493(2)$, $c = 15.526(1)$ Å, $\alpha = 104.60(1)°$, $\beta = 101.91(6)°$, $\gamma = 97.35(1)°$ and $Z = 2$. The reaction of the ligand with copper(II) sulfate pentahydrate resulted in a green crystalline complex of formula $[\{Cu(C_7H_9N_5O_2)(SO_4)\}\cdot2H_2O]_n$ which crystallized in the monoclinic space group $P2_1/n$ with $a = 10.427(3)$, $b = 8.876(2)$, $c = 13.777(4)$ Å, $\beta = 93.254(1)°$ and $Z = 4$. The nickel complex consists of discrete $[Ni(C_7H_9N_5O_2)_2]^{2+}$ cations and sulfate anions, the cation existing in a slightly distorted octahedral complex with bonding through the heterocyclic and oxime nitrogen atoms. The copper complex consists of a two-dimensional polymeric chain of $Cu(C_7H_9N_5O_2)$ units connected by bridging sulfate groups.

The literature contains reports of the structure of amide oximes (amidoximes) which can co-ordinate as bi-,[1–3] tri-,[4] tetra-[5] and hexa-dentate[6] ligands. The majority of these amidoximes are aliphatic compounds which form five-membered rings utilizing the diimine moiety, $-N=C-C=N-$, involving oxime and imine nitrogens as the co-ordination sites with transition-metal atoms. Pyridine-2,6-dicarboxamide oxime (pyridine-2,6-diamidoxime), $C_7H_9N_5O_2$ **I**, Fig. 1, possesses the structural requirements to react as a tridentate ligand with the heterocyclic and two oxime nitrogen atoms forming five-membered rings with transition-metal ions.

Compound **I** has been used in the spectrophotometric determination of iron(III) in strong alkaline solutions,[7] however the literature contains no references to the structure of **I** or to the synthesis and structure of its solid transition-metal co-ordination compounds. This research was carried out with the specific purpose of determining the structure of **I** as well as those of the complexes formed with nickel(II) sulfate and copper(II) sulfate.

The results of this investigation are compared with other potentially tridentate ligands having a pyridine ring substituted at the 2,6 positions, *i.e.* pyridine-2,6-dihydroxamic acid, pyridine-2,6-dicarboxylic acid and 2,2′ : 6′,2″-terpyridine.

Experimental

2,6-Dicyanopyridine was synthesized from pyridine-2,6-dicarboxylic acid (Aldrich Chemical Co.) according to the procedure of Banks and Brookes.[8] Density measurements were made by the flotation method using a mixture of diethyl ether and carbon tetrachloride for pyridine-2,6-diamidoxime and a mixture of benzene and 1,2-dichloroethane for the nickel and copper complexes. Microanalyses (C, H, N) were performed by Galbraith Laboratories, Inc., Knoxville, TN. Metal and anion analyses were performed using gravimetric procedures.

Preparation of pyridine-2,6-diamidoxime, $C_7H_9N_5O_2$ I

An aqueous solution (100 cm³) containing hydroxylamine hydrochloride (4.86 g, 70 mmol) neutralized with sodium hydroxide (2.8 g, 70 mmol) was added to ethanol (100 cm³) containing 2,6-dicyanopyridine (3.87 g, 30 mmol). The reaction mixture was heated at 70 °C with stirring for 0.5 h, and upon
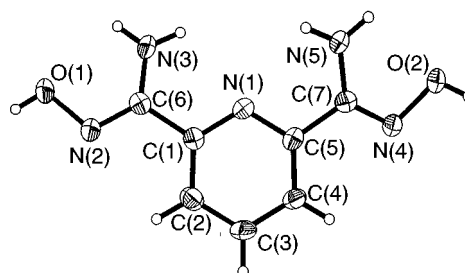

Fig. 1 Crystal structure of $C_7H_9N_5O_2$ **I** showing the atomic numbering scheme

cooling to 10 °C yielded **I** (5.21 g, 89%), m.p. 214 °C (decomp.) (Found: C, 42.98; H, 4.51; N, 35.78. $C_7H_9N_5O_2$ requires C, 43.07; H, 4.65; N, 35.88%). $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc): 3486 (asym) and 3421 (sym) (NH); 3421 and 3276 (sym) (OH); 1656 (sym) (C=N); 958 (sym) (NO). NMR [$(CD_3)_2SO$; standard $SiMe_4$]: δ_H(250 MHz) 9.86 (s, 2 H, NO–H), 7.85 (m, AB_2, 3 H, pyridine ring), 6.29 (s, 4 H, NH_2); δ_C(90 MHz) 202.0 (C^6 and C^7), 201.4 (C^1 and C^5), 189.1 (C^3), 171.6 (C^2 and C^4).

Preparation of bis(pyridine-2,6-diamidoxime)nickel(II) sulfate pentahydrate, $[Ni(C_7H_9N_5O_2)][SO_4]\cdot5H_2O$ 1

Solid **I** (3.90 g, 20 mmol) was added to a heated aqueous solution (100 cm³) containing nickel(II) sulfate hexahydrate (2.63 g, 10 mmol). The resulting purple solution was stirred at 80–90 °C for 1 h and allowed to stand overnight at room temperature. The resulting purple crystals of **1** were filtered off and washed with absolute ethanol and diethyl ether (5.30 g, 83.5%) {Found: C, 26.31; H, 4.31; N, 21.93; Ni, 9.11; SO_4, 14.86. $[Ni(C_7H_9N_5O_2)]-[SO_4]\cdot5H_2O$ requires C, 26.47; H, 4.44; N, 22.05; Ni, 9.24; SO_4, 15.12%}. $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc): 3546 (asym) and 3420 (sym) (NH); 3169 (sym) (OH); 1655 (sym) (C=N); 917 (sym) (NO).

Preparation of (pyridine-2,6-diamidoxime) copper(II) sulfate dihydrate, $[Cu(C_7H_9N_5O_2)(SO_4)]\cdot2H_2O$ 2

Solid **I** (3.90 g, 20 mmol) was added to a heated aqueous solution (100 cm³) containing copper(II) sulfate pentahydrate (2.50 g, 10 mmol). This resulted in an almost immediate precipitation of a green complex contaminated by excess ligand. The con-

Table 1 Summary of crystal data

Compound	$C_7H_9N_5O_2$	$[Ni(C_7H_9N_5O_2)_2][SO_4] \cdot 5H_2O$	$[Cu(C_7H_9N_5O_2)(SO_4)] \cdot 2H_2O$
M	195.18	635.21	390.82
T/K	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/n$
a/Å	7.569(1)	7.502(1)	10.427(3)
b/Å	4.695(1)	11.493(1)	8.876(2)
c/Å	12.534(2)	15.526(1)	13.777(4)
α/°	—	104.60(1)	—
β/°	106.50(2)	101.96(1)	93.254(1)
γ/°	—	97.35(1)	—
U/Å^3	427.12(1)	1244.29(3)	1273.02(1)
Z	2	2	4
D_c/g cm^{-3}	1.518	1.669	2.039
D_m/g cm^{-3}	1.510	1.656	2.024
Crystal size/mm	$0.40 \times 0.32 \times 0.07$	$0.40 \times 0.32 \times 0.26$	$0.050 \times 0.30 \times 0.30$
λ(Mo-Kα)/Å	0.710 73	0.710 73	0.710 73
Transmission factors (max, min)	0.8223, 0.7599	0.8549, 0.7585	0.8326, 0.6066
Data collection range (θ/°)	1.69–28.23	1.87–28.30	2.39–28.25
$F(000)$	204	640	796
Reflections measured	2599	7891	7815
Observed reflections	1618	5578	2976
R [$I > 2\sigma(I)$]	0.0713	0.1141	0.0737
R' *	1.1413	0.1441	0.0737
Largest difference peak, hole/e Å^{-3}	0.067, -0.361	0.105, -0.675	0.093, -0.661
Goodness of fit	1.101	1.052	1.128

Full-matrix least-squares refinement on F^2; semiempirical absorption correction based on ψ scans. * Weighting scheme $w = 1/[\sigma^2(F) + 0.0022F^2]$.

taminant was removed by filtering the reaction solution at the boiling point yielding **2** (3.02 g, 77.3%) {Found: C, 21.36; H, 3.25; Cu, 16.40; N, 17.77; SO$_4$, 24.37. [Cu(C$_7$H$_9$N$_5$O$_2$)(SO$_4$)]· 2H$_2$O requires C, 21.51; H, 3.35; Cu, 16.26; N, 17.92; SO$_4$, 24.58%}. $\tilde{\nu}_{max}$/cm^{-1} (KBr disc): 3481 (asym) and 3351 (sym) (NH); 3162 (sym) (OH); 1658 (sym) (C=N); 908 (sym) (NO).

X-Ray crystallography

Slow evaporation of dilute aqueous solutions of **I** and **1** at room temperature yielded crystals suitable for X-ray crystallographic analysis. Crystals of **2** were obtained from a saturated aqueous solution. All geometric and intensity data were taken using an automated four-circle Siemens SMART X-ray diffractometer. Pertinent crystallographic data are given in Table 1. Intensity data were reduced by routine procedures and calculations were carried out by the application of the direct methods program SOLV of SHELXTL.[9] The determination of the space group for the ligand involved a comparison of the values for N(total), N(int > 3σ), mean intensity and mean intensity/σ for the lattice exceptions. The values for these parameters for a P-type lattice are 0. From this, the crystal system M and the lattice type P were selected and a mean $[E^{E-1}]$ value of 0.717 was calculated. This value, when compared to the expected mean values of 0.968 for the centrosymmetric and 0.736 for the non-centrosymmetric systems, indicates a non-centrosymmetric system. Systematic absence exceptions indicate that a 2(1) screw axis is present. In addition, $P2(1)/m$ gives unreasonable structures for the centric configuration, therefore the chosen model was deemed appropriate. Hydrogen atom positions were calculated in idealized positions.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/565.

Results and Discussion

The literature does not appear to contain any references con-

cerning the structure of pyridine-2,6-diamidoxime **I** or solid complexes formed by it and transition-metal ions. This ligand was prepared by the reaction of an ethanolic solution of 2,6-dicyanopyridine with a neutralized aqueous solution of hydroxylamine hydrochloride giving **I** (Fig. 1) as the only solid product. The infrared spectrum of **I** shows four bands between 3500 and 3000 cm^{-1}. If the 3486 and 3421 cm^{-1} absorptions are assigned as the ν(asym) and ν(sym) NH stretching frequencies, respectively the two additional bands can be assigned to OH stretching frequencies. These two OH bands can arise from O–H$\cdots$O and O–H$\cdots$N hydrogen bonding, both of which are present in the uncomplexed solid ligand. Two such OH stretching frequencies are observed in solid oximes[10] and the probability of such hydrogen bonding is greater in amidoximes. Deuteration of **I** by recrystallization from 99.5% deuterium oxide results in the disappearance of the NH and OH stretching frequencies. Three bands which appear at 2612, 2566 and 2383 cm^{-1} are assigned to ν(asym) ND, ν(sym) ND and OD, respectively. The ^{1}H NMR shifts are listed in the Experimental section, however it should be noted that the NH and OH peaks are both concentration and temperature dependent. In addition both peaks disappear upon shaking the sample with 1 drop of D$_2$O, showing the lability of these hydrogens.

The crystal structure of **I** (Fig. 1) shows that the solid ligand crystallizes in the amide oxime (CNH$_2$=NOH), rather than the hydroxylamine imine (CNHOH=NH) structure which conforms with all other reported amidoximes.

Analysis of the packing diagram for **I** shows considerable hydrogen bonding between the ligand molecules. This hydrogen bonding involves amine hydrogens with oxime oxygens and amine hydrogens with amine nitrogens. In addition, oxime hydrogens of one molecule are hydrogen bonded to oxime oxygens of a second molecule. This considerable hydrogen bonding supports the infrared stretching assignments given for NH and OH.
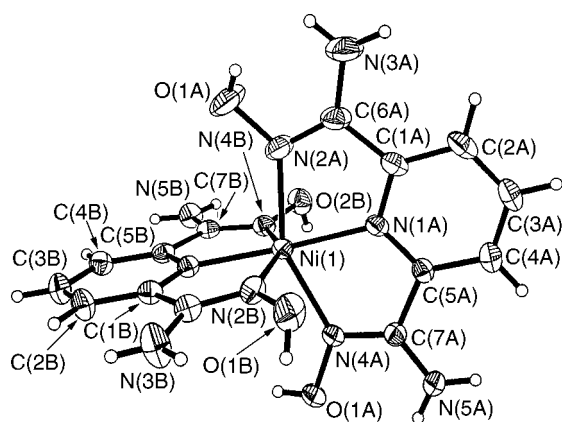
Selected bond lengths and angles for several amidoxime ligands are listed in Table 2. The C=N and NO bond lengths of the oxime group for the six listed compounds are quite comparable with those of pyridine-2,6-diamidoxime. The bond angles for C=N–O of the oxime group and N=C–N of the amidoxime group show little variation with the exception of those for 2-

Compound	C=N	N–O	C=N–O	N=C–N	Ref.
N-Benzoyl-*syn*-benzamidoxime	1.272	1.438	110.7	123.9	11
2,2′-Iminobis(acetamidoxime)	1.278	1.426	109.0	125.6	12
2-(3,4-Methylenedioxy phenyl)-2-hydroxy-2-acetamidoxime	1.284	1.435	110.0	125.1	13
Formamidoxime	1.288	1.415	109.7	126.7	14
2-Methyl-*N*,*N*-dimethylbenzamidoxime	1.287	1.424	112.1	117.7	15
Pyridine-2-amidoxime	1.291	1.419	109.1	123.4	1
Pyridine-2,6-diamidoxime	1.288	1.434	108.7	125.1	This work

Table 3 Selected bond lengths (Å) and angles (°) for [Ni($C_7H_9N_5O_2$)]-[SO_4]·$5H_2O$ **1**

Ni(1)–N(1A)	2.007(2)	C(1A)–C(2A)	1.400(4)
Ni(1)–N(2A)	2.132(2)	C(2A)–C(3A)	1.368(5)
Ni(1)–N(4A)	2.117(2)	C(3A)–C(4A)	1.387(5)
Ni(1)–N(1B)	2.002(2)	C(4A)–C(5A)	1.393(4)
Ni(1)–N(2B)	2.136(2)	C(5A)–N(1A)	1.333(4)
Ni(1)–N(4B)	2.124(2)	C(6A)–N(2A)	1.298(4)
N(1A)–C(1A)	1.339(4)	C(7A)–N(4A)	1.297(4)
N(1A)–C(1A)–C(2A)	121.2(3)	Ni(1)–N(1A)–C(5A)	119.6(2)
C(1A)–C(2A)–C(3A)	118.6(3)	Ni(1)–N(1A)–C(1A)	120.1(2)
C(2A)–C(3A)–C(4A)	120.2(3)	Ni(1)–N(2A)–C(6A)	116.3(2)
C(3A)–C(4A)–C(5A)	118.2(3)	Ni(1)–N(4A)–C(7A)	116.3(2)
C(4A)–C(5A)–N(1A)	121.6(3)	N(1A)–Ni(1)–N(4A)	76.2(1)
N(1A)–C(1A)–C(6A)	113.0(3)	N(1A)–Ni(1)–N(2A)	75.7(1)
C(1A)–C(6A)–N(2A)	114.8(3)	N(1A)–Ni(1)–N(1B)	174.6(1)

Fig. 3 Molecular structure of [Cu($C_7H_9N_5O_2$)(SO_4)]·$2H_2O$ **2** showing the atomic numbering scheme

Fig. 2 Crystal structure of [Ni($C_7H_9N_5O_2$)][SO_4]·$5H_2O$ **1** showing the atomic numbering scheme. The water molecules and counter anion have been omitted for clarity
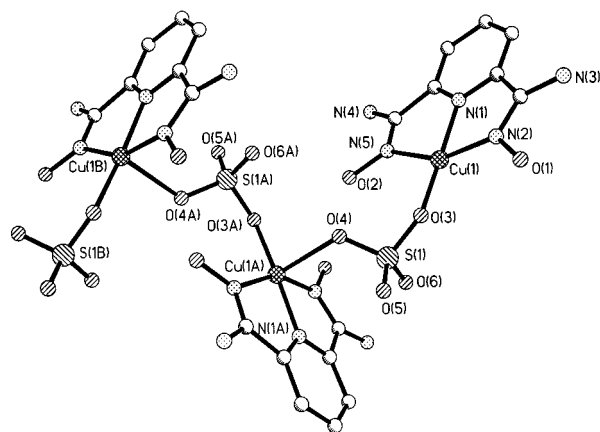
Fig. 4 Molecular configuration of the Cu($C_7H_9N_5O_2$) moiety in complex **2** showing co-ordination by the SO_4 groups

methyl-*N*,*N*-dimethylbenzamidoxime. This can be attributed to steric factors caused by the two methyl groups on the amine nitrogen which are not present in any of the other amidoximes.

The reaction of nickel(II) sulfate with **I** produces a purple 1:2 solid complex of formula **1**. Conductivity measurements in aqueous solution show **1** to be a 1:1 electrolyte consisting of [Ni($C_7H_9N_5O_2$)]$^{2+}$ cations and SO_4^{2-} anions. The crystal structure of **1** (Fig. 2) confirms the 1:2 Ni^{II}–ligand co-ordination where neither the anion nor the water molecules are involved in the co-ordination. The nickel(II) ion is six-co-ordinated through the oxime and heterocyclic nitrogens of the two ligand molecules. The resulting configuration is a slightly distorted octahedron. This distortion results from non-equivalent Ni–N bond lengths (Table 3). The two Ni–N (imine) bond lengths are essentially equivalent but shorter than the four Ni–N (oxime) which are not mutually equivalent. Although other geometrical isomers are possible, the compound investigated has the polar *trans* positions occupied by the heterocyclic nitrogens. The oxime nitrogens are in the equatorial plane.

The two co-ordinated ligands are at approximately 90° to each other. The crystal structure of **I** shows the oxime nitrogens

are not available for tridentate co-ordination in conjunction with the pyridine nitrogen. Upon addition of nickel(II), free rotation about the C(1)–C(6) and C(5)–C(7) bonds results in proper positioning of the oxime nitrogens as shown in Fig. 2. This same rotation upon complexation was observed for pyridine-2-amidoxime.[1] A comparison of the same bond lengths and angles for the free ligand and the nickel(II) complex shows little change in **I** and **1**.

The reaction of **I** with copper(II) sulfate did not give the expected monomeric product but rather a two-dimensional linear polymer (Fig. 5). The copper atom is co-ordinated to a single ligand molecule which is tridentate using the heterocyclic and oxime nitrogens. This copper–ligand unit is bonded to two sulfate groups by Cu–O bonds resulting in five-co-ordinated copper(II) atoms. The monomeric unit can be considered to have the formula, [Cu($C_7H_9N_5O_2$)(SO_4)]·$2H_2O$ (Fig. 3) where the water molecules are not involved in co-ordination. The Cu–O bonds formed between any two Cu($C_7H_9N_5O_2$) moieties with a single sulfate group are quite dissimilar in bond length. The Cu(1A)–O(3A) bond length is 1.901 Å, whereas the Cu(1A)–O(4) bond length is 2.379 Å (Fig. 4). The arrangement of monomeric units in the polymer can be seen in Fig. 4. Alternate ligands bonded to a copper atom are parallel to each other and any two adjacent copper-bonded ligands are at 93.8° to
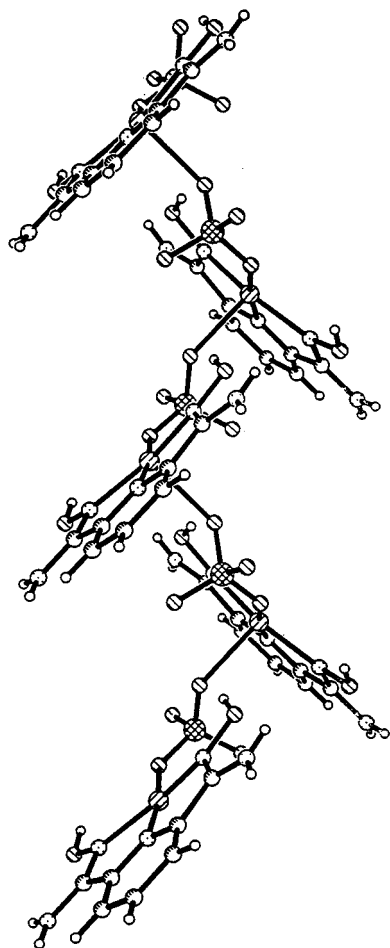
Fig. 5 Crystal packing diagram of [Cu(C₇H₉N₅O₂)(SO₄)] **2**. Waters of crystallization have been omitted for clarity

Table 4 Selected bond lengths (Å) and angles (°) for $C_7H_9N_5O_2$ **I**

N(1)–C(1)	1.339(6)	C(6)–N(2)	1.288(6)
C(1)–C(2)	1.394(6)	C(6)–N(3)	1.364(6)
C(2)–C(3)	1.384(7)	N(2)–O(1)	1.428(5)
C(3)–C(4)	1.380(7)	C(5)–C(7)	1.484(6)
C(4)–C(5)	1.389(6)	C(7)–N(4)	1.298(6)
C(5)–N(1)	1.348(5)	C(7)–N(5)	1.345(6)
C(1)–C(6)	1.488(6)	N(4)–O(2)	1.436(5)
N(1)–C(1)–C(2)	122.6(4)	C(1)–C(6)–N(3)	116.9(4)
C(1)–C(2)–C(3)	118.6(5)	C(6)–N(2)–O(1)	109.5(4)
C(2)–C(3)–C(4)	119.4(4)	N(1)–C(5)–C(7)	114.1(4)
C(3)–C(4)–C(5)	118.6(4)	C(5)–C(7)–N(4)	118.5(4)
C(4)–C(5)–N(1)	122.6(4)	C(5)–C(7)–N(5)	116.7(4)
C(5)–N(1)–C(1)	118.1(4)	C(7)–N(4)–O(2)	108.7(4)
N(1)–C(1)–C(6)	115.9(4)	N(2)–C(6)–N(3)	125.5(4)
C(1)–C(6)–N(2)	117.4(4)	N(4)–C(7)–N(5)	124.7(4)

Table 5 Selected bond lengths (Å) and angles (°) for [Cu(C₇H₉-N₅O₂)(SO₄)]·2H₂O **5**

Cu(1)–N(1)	1.930(2)	C(4)–C(5)	1.387(3)
Cu(1)–N(2)	2.025(2)	C(5)–N(1)	1.336(2)
Cu(1)–N(5)	2.022(2)	C(1)–C(6)	1.492(2)
Cu(1)–O(3)	1.901(2)	C(6)–N(2)	1.304(2)
N(1)–C(1)	1.334(2)	N(2)–O(1)	1.403(2)
C(1)–C(2)	1.386(3)	C(5)–C(7)	1.486(3)
C(2)–C(3)	1.396(3)	C(7)–N(5)	1.308(3)
C(3)–C(4)	1.391(3)	N(5)–O(2)	1.399(2)
N(1)–C(1)–O(3)	172.10(7)	Cu(1)–N(1)–C(1)	119.01(13)
Cu(1)–N(1)–C(5)	118.63(13)	N(1)–C(1)–C(6)	112.2(2)
N(1)–C(5)–C(7)	112.0(2)	C(1)–C(6)–N(2)	113.4(2)
C(5)–C(7)–N(5)	113.7(2)	C(6)–N(2)–Cu(1)	116.12(13)
C(7)–N(5)–Cu(1)	115.35(13)	N(2)–Cu(1)–N(1)	78.89(7)
N(5)–Cu(1)–N(1)	78.97(7)		

each other (Fig. 5). This arrangement of ligands results in a helical configuration with respect to the axis of the copper atoms, not unlike that reported for copper(II)–carboxylate[16] and –thiother–carboxylate complexes.[17] A major difference is that the copper complex reported herein forms the chain through sulfate bridging groups while the carboxylate– and (thioether)carboxylate–copper(II) complexes do not involve an anionic bridge. The helix of our compound is stabilized by hydrogen bonding between adjacent chains resulting in a *syn-anti* pyridine-2,6-diamidoxime helix-like chain bridged by sulfate groups. Another major difference in the complexation is that the copper(II)–pyridine-2,6-diamidoxime does not involve ionization of the ligand. Complexes with copper(II) and either of the two carboxylic acid ligands involve ionization of the carboxylate group to form the helical chain. A comparison of the bond lengths and angles for the free ligand (Table 4) and the copper complex (Table 5) shows little ligand distortion upon complexation. Attempts to synthesize a non-polymeric 1:1 or 2:1 ligand:copper(II) monomeric species using copper(II) sulfate were unsuccessful. Work is in progress using the potentially non-co-ordinating copper(II) tetrafluoroborate, to negate polymer formation in the chelate.

This research has ascertained that pyridine-2,6-diamidoxime crystallizes in the amidoxime configuration, C=NOH(NH₂), as do all other amidoximes for which the structure has been determined. When complexed with nickel(II) sulfate pentahydrate, this ligand forms a 2:1 ligand:nickel(II) cationic complex which uses the heterocyclic and oxime nitrogens. Complexation with copper(II) sulfate results in a two-dimensional polymer consisting of Cu(C₇H₉N₅O₂) units bridged by sulfate groups through Cu–O bonds. Polymerization is sustained by each complexed copper(II) atom reacting with the oxygen atoms of two sulfate groups.

When compared to non-amidoxime tridentate ligands, the following observations can be made. 2,2′:6′,2″-Terpyridine forms only monomeric species with transition-metal ions.[18] Pyridine-2,6-dihydroxamic acid is reported to form only polymeric species[19] using ionized hydroxamic acid hydrogens without anionic bridging groups. In the case of pyridine-2,6-dicarboxylic acid, it has been reported that the diacid can react both in a monomeric and a polymeric fashion,[20] therefore pyridine-2,6-diamidoxime comes closest to the corresponding diacid in its complexation behaviour.

Acknowledgements

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