

Is copper(I) really soft? Probing the hardness of Cu(I) with pyridinecarboxaldehyde ligands

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Abstract. Cu(I) complexes of formula $\text{Cu}(\text{PPh}_3)_2\text{LClO}_4$ [L = 2 or 3 pyridine carboxaldehyde] are synthesised and characterised to explore the coordination of an aldehyde, a hard and neutral oxygen donor to a soft Cu(I) centre. The structural and spectroscopic results illustrate that only in 2-pyridinecarboxaldehyde, the 'C=O' group coordinates to soft Cu(I) centres due to a favourable chelate effect, while in 3-pyridinecarboxaldehyde, it remains uncoordinated. Upon chelation via N and O donors, 2-pyridinecarboxaldehyde resembles bipyridine or phenanthroline in terms of its bite angle and spectroscopic features. Such chelation can be easily challenged with coordinating anions like bromide, or more basic pyridines. A drastic change in the MLCT absorption signals the decomplexation of the 'C=O' group. The observed results point out that the Cu(I) centre can readily exchange the hard 'O' donor for softer ligands.

Keywords. Cu(I) complexes; pyridinecarboxaldehyde; HSAB; competition reactions; chelate effect.

1. Introduction

The preference of copper(I) for soft donor ligands such as phosphines, thiols, alkenes or alkynes is well established¹. Accordingly, HSAB theory classifies Cu(I) as a soft acid². The reduction of Cu(II) ions in the presence of soft donors, and the ready oxidation of Cu(I) in the presence of hard donors like N or O further confirm the view that copper(I) is soft³. Given this scenario, it is not surprising that the synthesis and characterization of Cu(I) complexes containing only hard donors is a challenging task. There are several instances where Cu(I) is found to accommodate both soft and hard donors in its coordination sphere. Thus, carbon monoxide stabilises Cu(I) with primary amines (hard σ donating nitrogen ligands) in its coordination sphere⁴. Similarly in $\text{Cu}_2(\text{dppe})_3(\text{NCS})_2$ [dppe = *bis*(diphenylphosphino)ethane], the Cu(I) centre is stabilised with phosphine and the ambidentate thiocyanate anion coordinates through the harder N end rather than S, the softer end⁵.

Although neutral oxygen donors are rare, oxoanions, possessing an electrostatic advantage are commonly found in the coordination sphere of Cu(I)⁶. Recently phosphine oxide has been shown to bind with Cu(I), in the presence of phosphines⁷. Related studies on Cu(I) complexes of *bis*-phosphine monoxide (BPMO), ligands that can offer both phosphine and phosphine oxide coordination has been studied by us⁵. The coordination of a phosphine oxide (P=O) to the metal center has been shown via ³¹P NMR and X-ray

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diffraction studies. A favourable chelation mode and a balanced coordination sphere with two soft and two hard donors are driving forces for the stabilisation of P=O coordinated Cu(I) complexes. These studies show that an appropriate coordination environment can force the Cu(I) centre to accept hard donors.

In the present work, the possibility of obtaining oxygen coordination from a 'C=O' group (aldehyde) has been probed. Using 2-pyridinecarboxaldehyde, a chelating ligand and 3-pyridinecarboxaldehyde as an appropriate control ligand, the coordination of neutral 'O' to Cu(I) was probed in a variety of situations.

2. Experimental

2.1 General

Pyridine and 4-methylpyridine were obtained from Ranbaxy, India and Fluka, USA respectively. All other substituted pyridines used are from Aldrich, USA and used as received. Triphenyl phosphine was obtained from Loba-Chemie, India. The solvents were distilled using standard procedures⁸. Reactions were done under an atmosphere of pure dry nitrogen.

2.2 Physical methods

¹H NMR spectra were recorded on a Bruker 200 MHz instrument. The UV-Vis absorption and IR spectroscopic studies were performed on Bruker instruments. IR spectra were recorded in the solid state dispersed in KBr pellets.

2.3 Synthesis

2.3a $[Cu(PPh_3)_2(C_5H_4N-2-CHO)]ClO_4$ (1): About 0.07 g of $Cu(CH_3CN)_4ClO_4$ was dissolved in 10 ml of dichloromethane. To this solution 0.11 g of PPh_3 was added. After 5 min of stirring, 0.04 ml of 2-pyridinecarboxaldehyde was added. The resulting bright yellow orange solution was further stirred for 15 min. The solvent was evaporated under vacuum and the resulting oil was triturated with 30 ml of petroleum ether. The product was obtained as a free flowing yellow orange solid. Yield 0.15 g. ¹H NMR: (Acetone-*d*₆, 293 K): **d** 10.14 (s, 1H), **d** 9.0 (d, 1H), **d** 8.42–8.38 (m, 2H), **d** 7.54–7.50 (d, 1H) [C_6H_5NO], **d** 7.47–7.25 (m, 30H) [PPh_3].

2.3b $[Cu(PPh_3)_2(C_5H_4N-3-CHO)]ClO_4$ (2): A similar procedure was also used to synthesise a complex with 3-pyridinecarboxaldehyde and Cu(I). Yield 0.13 g. ¹H NMR: (Acetone-*d*₆, 293 K): **d** 10.03 (s, 1H), **d** 9.04 (m, 2H), **d** 8.42–8.36 (d, 1H) [C_6H_5NO], **d** 7.74–7.35 (m, 30 PPh_3 +1 C_6H_5NO).

2.4 Crystallography

Single crystals of **1** and **2** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the respective complex. A yellow orange thin needle of complex **1** was selected for indexing and data collected on a Bruker AXS single crystal diffractometer equipped with Smart Apex CCD detector and a sealed Mo source working at 2.2 KW and 50/35 (KV/mA). Intensity data were collected at room temperature. A pale yellow rectangular crystal of complex **2** was selected for indexing and data were

collected at 25°C on an Enraf-Nonius CAD4 single crystal diffractometer equipped with graphite-monochromatized Mo K α radiation.

All computations were performed using the WINGX package⁹. The Data were corrected for Lorentz, polarization and absorption effects using DIFABS¹⁰. The positions of the heavy atoms were determined by SHELX-86¹¹. The remaining atoms were located from difference Fourier analysis using SHELXL-97¹¹. Hydrogen atoms were included in the final stage of the refinement on calculated positions bonded on their carrier atoms.

2.4a *Crystal data for 1:* C₄₂H₃₅NO₅P₂ClCu, triclinic, space group *P* $\bar{1}$, $a=9.9917(11)\text{\AA}$, $b=28.497(3)\text{\AA}$, $c=28.502(3)\text{\AA}$, $\alpha=118.708(2)^\circ$, $\beta=96.659(3)^\circ$, $\gamma=96.730(3)^\circ$, $V=6929.1(13)\text{\AA}^3$, $\rho=0.83$ to 20.00° , $Z=6$, $D_c=1.125\text{ Mg m}^{-3}$, $R_1=0.1040$, $wR_2=0.2762$, $\text{Goof}=1.046$.

2.4b *Crystal data for 2:* C₄₂H₃₅NO₅P₂ClCu, monoclinic, space group *P21/c*, $a=9.908\text{ \AA}$, $b=38.525\text{ \AA}$, $c=10.775\text{ \AA}$, $\beta=110.47^\circ$, $V=3853.2\text{ \AA}^3$, $\rho=1.06$ to 19.50° , $Z=4$, $D_c=1.378\text{ Mg m}^{-3}$, $R_1=0.1280$, $wR_2=0.3403$, $\text{Goof}=1.178$.

3. Results and discussion

The 'C=O' group is not a common donor for Cu(I) due to its hard nature. Kitagawa *et al* reported several polymeric copper complexes with extended lattices possessing 'C=O' coordination¹². In such systems, the coordination of acetone to Cu(I) centres are necessary and function as scaffolds in the formation of supramolecular frameworks. In few other cases, where the Cu(I) centre exhibits low coordination, complexation with 'C=O' is observed¹³. Highly polarised carbonyls such as those in cyclopropenones, phenalenone or tropones have been used to form complexes with copper(I)phosphines. In the known copper complexes of substituted pyridine, 2-benzoyl pyridine was shown to be a chelating ligand interacting through the *keto* group and the pyridine N¹⁴. The present study explores the coordination behaviour of the 'C=O' group in mononuclear, four coordinated copper complexes without additional interactions. A ligand that contains 'C=O', as an additional functional group, is expected to coordinate through the chelate effect in a very similar way to the BPMO ligands. Complexes of formula Cu(PPh₃)₂LCIO₄ have been synthesised and characterised where L is 2-pyridine-carboxaldehyde or 3-carboxaldehyde to study the coordination behavior of the 'C=O' donor. Use of the weakly coordinating anion ClO₄⁻, and a labile acetonitrile permit synthesis of the complexes in good yield. The related structural and physical properties are discussed.

3.1 Electronic absorption

Reaction of [Cu(CH₃CN)₄]ClO₄ with triphenylphosphine and 2-pyridine carboxaldehyde results in an intense yellow orange coloured complex **1**, with a I_{max} at 409 nm due to MLCT transitions (figure 1). A similar reaction with 3-pyridinecarboxaldehyde produces only a faintly yellow coloured complex **2**. While intense MLCT transitions (with I_{max} between 350–400 nm) are common for bipyridine or phenanthroline coordinated Cu(I) complexes with the CuP₂N₂ chromophores¹⁵, pyridine complexes are transparent in the visible region¹⁵. Although it is difficult to find a similar chromophore, 2-benzoylpyridine complexes are closest in structure and spectroscopic features. Hence origin of an intense

colour in 2-pyridinecarboxaldehyde system, is attributed to the formation of a 'bipyridine like' chromophore upon coordination of the C=O group as found in the 2-benzoylpyridine complexes (figure 2)¹⁴. However, coordination of the CHO group to the same Cu(I) centre cannot be realised from the 3 position of pyridine, unlike complex **1**. Hence it is not surprising that complex **2** does not produce an intense colour confirming the non-coordinating behaviour of the CHO group.

3.2 Infrared spectra

IR spectroscopy is a useful tool to monitor the coordination of the CHO group present in pyridines. IR studies are summarised in figure 3. Prior to complexation, the $\nu_{\text{C=O}}$ vibration of the CHO groups present in free ligands, occur very close to one another and do not depend on their position in the pyridine ring. (1710 cm^{-1} for 2-pyridinecarboxaldehyde and 1708 cm^{-1} for 3-pyridinecarboxaldehyde.) In complex **1**, however, the $\nu_{\text{C=O}}$ occurs at 1654 cm^{-1} , much lower than is observed in the free ligand. This can be attributed to the weakening of the C=O bond upon complexation with the metal centre. Whereas in complex **2**, $\nu_{\text{C=O}}$ occurs at 1715 cm^{-1} , close to the value observed in the free ligand and consistent with that expected for an uncomplexed CHO group.

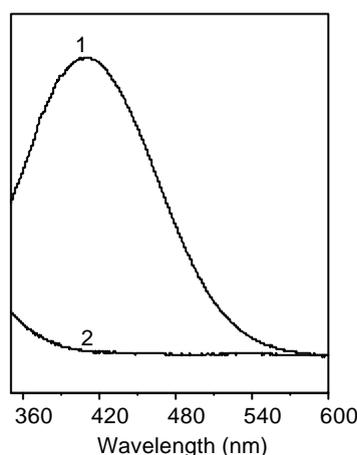


Figure 1. UV-Vis spectrum of (1) complex **1** [I_{max} 409 nm, ϵ 1983 $\text{M}^{-1} \text{cm}^{-1}$] and (2) complex **2**.

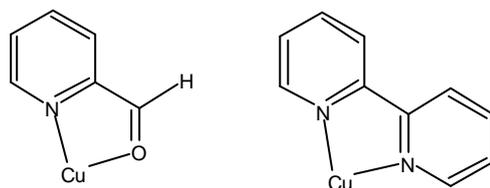


Figure 2. Coordination of 2-pyridinecarboxaldehyde resembles bipyridine.

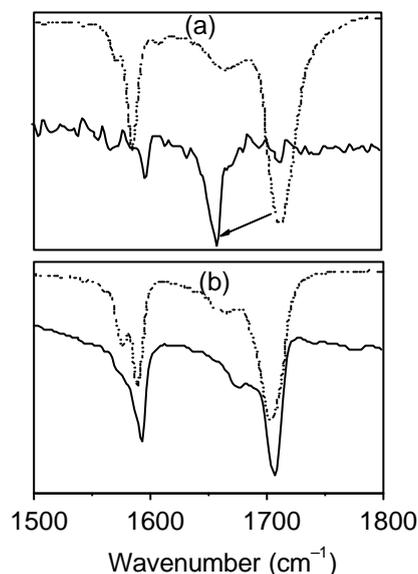


Figure 3. IR showing $\nu_{\text{C=O}}$ vibrations of (a) complex **1** and (b) complex **2**. (The broken trace indicates spectrum of the corresponding free ligand.)

3.3 Molecular structure

Single crystals of the complexes prepared in this study were very thin and weakly diffracting. As a result the diffraction data obtained are not of high quality. However, the molecular structure could be ascertained unambiguously from the available data. This confirms the expected coordination proposed on the basis of spectroscopic methods.

The molecular structure of the complex **1** (figure 4a and table 1) reveals three molecules in the asymmetric unit with slight differences in bond lengths and angles. In each molecule two triphenyl phosphines and a nitrogen from the pyridine ring are coordinated to the metal centre. Similarly in each molecule, the metal centre nearly lies in the plane formed by the nitrogen and phosphorous atoms (deviating only 0.38 Å from the plane). The oxygen present in the CHO group is facing the metal atom in a chelating mode. The Cu(I)-O distances are in the usual range between 2.20 to 2.21 Å and reveals coordination of oxygen to the copper atom. The observed bite angle of 2-pyridine-carboxaldehyde is very similar to the reported values of bipyridine or phenanthroline ligands. The perchlorate counter anions were not coordinated and were located far from the cation. Hence it is clear that in complex **1**, the metal centre adopts a distorted pyramidal geometry with oxygen coordination in the fourth position.

Interestingly, in the structure of complex **2** (figure 4b, table 2) the 'C=O' group remains non-coordinating as expected from the spectroscopic results and the position of the 'C=O' is occupied by an oxygen atom of the perchlorate anion! However, the Cu(I)-O distance is longer than the usual bond length involving oxoanion coordination, and indicates a weak interaction. The metal centre adopts a severely distorted tetrahedral geometry. Noticeably, the angles, N(1)-Cu(1)-O(1) and P(2)-Cu-P(1) are acute. Although reasons for the deviation from the tetrahedral geometry are not apparent, the observed arrangement of phenyl rings and the weak interactions of the anion with it may be

responsible. The weak interactions might be necessary to hold the anion, which is coordinated to the metal centre.

3.4 Competition reaction

3.4a Influence of the counter anion: Coordination of an oxygen atom to the Cu(I) centre can be turned 'off' in various situations. Our earlier study on phosphine oxide-bonded Cu(I) complexes with BPMO ligands, indicated that the P=O coordination is stable only with the non interacting ClO_4^- . The bromide ion for example can expel it from the coordination sphere. As complex **1** is a 'C=O' analogue of the P=O bonded Cu(I) complex, similar challenge experiments were performed by adding tetrabutylammonium bromide. The bromide ion is moderately soft and possesses the advantage of electrostatic

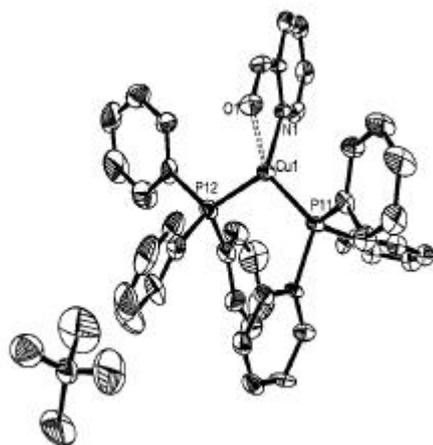


Figure 4a. Molecular structure of complex **1** at the 30% probability level (Hydrogen atoms are omitted).

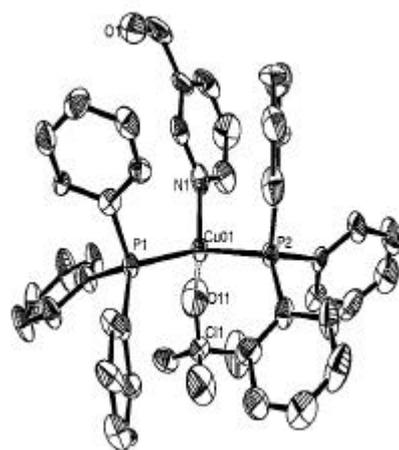


Figure 4b. Molecular structure of complex **2** at the 30% probability level (Hydrogen atoms are omitted).

Table 1. Selected bond angles and distances for complex **1**.

Molecule	Bond distances (Å)		Bond angles (deg)	
I	Cu(1)–N(1)	2.055(8)	N(1)–Cu(1)–O(1)	76.9(3)
	Cu(1)–O(1)	2.215(7)	N(1)–Cu(1)–P(12)	113.5(3)
	Cu(1)–P(12)	2.243(4)	O(1)–Cu(1)–P(12)	110.9(2)
	Cu(1)–P(11)	2.245(3)	N(1)–Cu(1)–P(11)	120.2(2)
			O(1)–Cu(1)–P(11)	110.9(2)
			P(12)–Cu(1)–P(11)	117.09(12)
II	Cu(2)–N(2)	2.043(8)	N(2)–Cu(2)–O(2)	77.1(4)
	Cu(2)–O(2)	2.204(8)	N(2)–Cu(2)–P(22)	120.0(2)
	Cu(2)–P(22)	2.244(3)	O(2)–Cu(2)–P(22)	111.1(2)
	Cu(2)–P(21)	2.247(4)	N(2)–Cu(2)–P(21)	113.6(3)
			O(2)–Cu(2)–P(21)	110.8(3)
			P(22)–Cu(2)–P(21)	117.05(12)
III	Cu(3)–N(3)	2.043(8)	N(3)–Cu(3)–O(3)	77.0(3)
	Cu(3)–O(3)	2.205(8)	N(3)–Cu(3)–P(31)	113.3(3)
	Cu(3)–P(31)	2.243(4)	O(3)–Cu(3)–P(31)	110.9(3)
	Cu(3)–P(32)	2.247(3)	N(3)–Cu(3)–P(32)	120.4(3)
			O(3)–Cu(3)–P(32)	110.7(2)
			P(31)–Cu(3)–P(32)	117.12(12)

Table 2. Selected bond angles and distances for complex **2**.

Bond distances (Å)		Bond angles (deg)	
Cu(01)–N(1)	2.04(2)	N(1)–Cu(01)–O(11)	87.3(9)
Cu(01)–O(11)	2.26(2)	N(1)–Cu(01)–P(2)	105.9(5)
Cu(01)–P(2)	2.260(6)	O(11)–Cu(01)–P(2)	112.7(6)
Cu(01)–P(1)	2.268(5)	N(1)–Cu(01)–P(1)	111.6(6)
		O(11)–Cu(01)–P(1)	101.8(6)
		P(2)–Cu(01)–P(1)	129.5(2)

attraction. Any competition caused by the bromide ion to the Cu–O bond could be identified by a dramatic change in the colour of the complex. As depicted in figure 5, the MLCT transition in the complex **1** completely disappears on adding bromide. Presumably the bromide ion enters the coordination sphere, and the chelated structure is lost. The removal of the C=O group from the coordination sphere is in contrast to the bipyridine or phenanthroline containing copper phosphine complexes. While in phenanthroline or bipyridine complexes, it is not possible to dislodge the second coordinating atom, in the present system, the weakly coordinating 'C=O' group can be removed from the coordination sphere of Cu(I) quite readily. The drastic colour change accompanying removal of the 'C=O' group from Cu(I) coordination makes it a sensor for the presence of anions like bromide (*vide supra*) and stronger bases like methyl pyridine (*vide infra*).

3.4b Competition reactions with better bases: Coordination of O from 2-pyridinecarboxaldehyde is shown to be weak in the presence of an interacting counter anion. In a similar experiment, the stability of O coordination, to the Cu(I) system {[Cu(PPh₃)₂]⁺cation} in presence of a non-chelating pyridine ligand is examined. It had

been observed in phenanthroline systems that more basic the ligand, stronger the complexation to Cu(I)¹⁶. Hence non chelating pyridines with better donating properties (larger the pK_a , stronger the donation) than that of 2-pyridinecarboxaldehyde are expected to compete with the chelated structure. A four-fold excess of a non chelating pyridine was used to probe the strength of the chelating ligand in complex **1**. The binding of pyridine and their pK_a values show a clear relationship (figure 6 and table 3). As expected, the more basic pyridines compete efficiently with 2-pyridinecarboxaldehyde. In comparison with pyridines possessing similar pK_a values (scheme 1) 2-pyridinecarboxaldehyde coordinates more efficiently. Although the chelation can offer only a hard donating O atom, such a chelation tilts the balance in favor of complex **1** even in the presence of an excess of non-chelating pyridine. However, the chelation of a hard

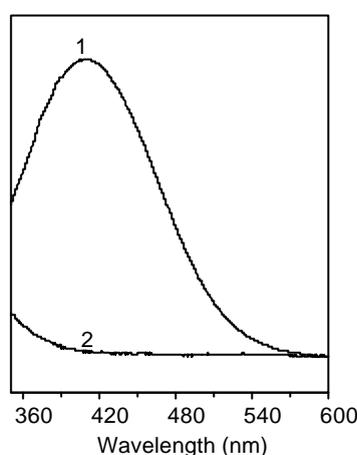


Figure 5. Effect of anion in MLCT transitions; (1) complex **1** with ClO_4^- counter anion; (2) after adding tetrabutyl ammonium bromide(1:1).

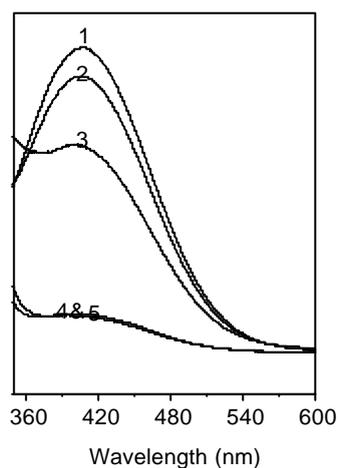
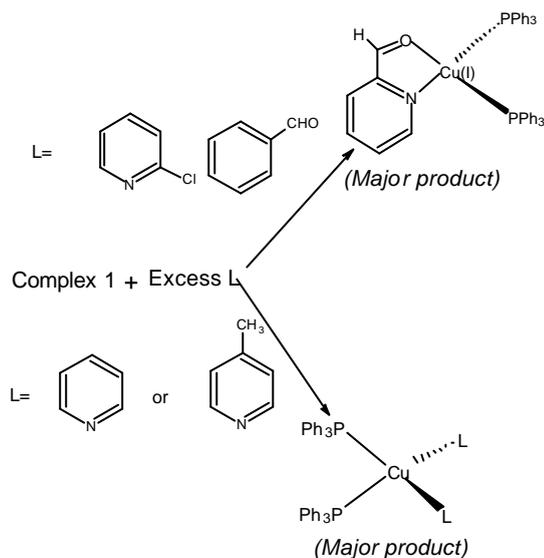


Figure 6. Competition experiments with substituted pyridines arranged in increasing order of basicity. Details are given in table 3.

Table 3. Results of competition reaction.

Competing pyridine	<i>pKa</i> of competing pyridine ¹⁷	% of 1
2-Pyridinecarboxaldehyde	3.80	100 (control)
2-Chloropyridine	0.72	90
3-Pyridinecarboxaldehyde	3.80	70
Pyridine	5.20	15
4-Methylpyridine	6.03	15

**Scheme 1.**

donor in **1** is not sufficient to offset the stronger Cu–N bond formed by better bases. These results highlight the flexibility of the Cu(I) ion in accommodating hard donors in the coordination sphere.

4. Summary

2-Pyridinecarboxaldehyde offers a chelate advantage for the coordination of the hard ‘C=O’ donor group to the $[\text{Cu}(\text{PPh}_3)_2]^+$ moiety in the presence of soft ligands. Such a coordination unit resembles the bipyridine system with a strong MLCT absorption. X-ray structural studies illustrate the importance of chelation for the coordination of ‘C=O’ group to the copper atom. Although the ‘C=O’ group binds to the soft Cu(I), such an interaction is favored only when there is no competition from the anion or from the ligand. The moderately soft bromide ion, possessing electrostatic attraction competes effectively with the ‘C=O’ coordination. The event is signaled by the disappearance of the MLCT absorption. Thus complex **1** can function as a visible anion sensor. Similarly, in the presence of a better N donor, the chelation in **1** gives way. However a N donor with comparable basicity to the 2-pyridinecarboxaldehyde, does not compete even when it is present in excess. All these results point out a delicate balance in the coordination preferences of Cu(I).

Acknowledgements

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