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Di(2-pyridyl) Ketone Complexes of Cu^I- and Cu^{II}-Containing Iodide and Thiocyanate Ligands: An Unusual Case of a Mixed-Aldol Condensation

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Complexes containing di(2-pyridyl) ketone (*dpk*) as a bi- (*N*,*N*) and tridentate (*N*,*N*,O) ligand have been synthesised[1,2] and characterized by spectral and structural studies. Products **1** and **2** are polymorphs of the polymeric copper(I) complex $[Cu(dpk)(NCS)]_n$ containing *dpk* with thiocyanate anions which bridge to form a one-dimensional continuous polymer chain. The novel dinuclear copper(II) complex $[Cu_2(dpk\cdot acetone)_2(NCS)_2]$ (**3**) was formed when **1** and **2** were allowed to stand in the supernatant. In this instance it appears that a transition-metal-promoted aldol condensation has occurred between the solvent acetone and the ketone carbonyl of *dpk* to produce the novel ligand, *dpk·acetone*. Product **3** contains two five-coordinate copper(II) ions, both with trigonal bipyramidal coordination, bridged through deprotonated hydroxy groups on each *dpk·acetone*. A chemical rationalisation for the formation of **3** is proposed. The dinuclear copper(I) complex $[Cu_2(dpk)_2I_2]$ (**4**) is also reported, which contains two four-coordinate copper(I) ions that are bridged together through iodide ions.

Introduction

Copper(I) complexes containing *N*-heterocyclic ligands are of interest due to the possibility of harnessing their light-absorbing and redox properties for potential applications[3,4] such as solar energy capture,[5] organic light-emitting diodes,[6] and oxygen sensors.[7] Polydentate heterocyclic ligands such as di(2-pyridyl) ketone (*dpk*) are important building blocks for the preparation of coordination compounds, and metallo-supramolecular assemblies.[8] The *dpk* ligand is extremely versatile since it has the ability to chelate through multiple donor sites. It is capable of behaving as a bidentate or tridentate ligand chelating through *N*,*N*, *N*,*O*, or *N*,*N*,*O* donor atoms respectively,[1,2] and when coordinated to a metal centre the ketone C=O group is susceptible to nucleophilic addition. Subsequently, *dpk* can transform to a chemically modified ligand through in situ processes, which are not readily achieved through conventional organic methods.[8]

For example, in the presence of water the ketone carbonyl can undergo hydration forming a *gem-diol* ($dpk\cdot H_2O$), or in the presence of alcohols (e.g. methanol) an "alcoholated" ($dpk\cdot ROH$) hemi-ketal derivative can form, as indicated in Figure 1.[9] The resulting species can coordinate in either protonated or deprotonated form, and thus the possibilities for *dpk* coordination are extensive.[8] The negatively charged oxygen atom from the deprotonated hydroxy group, can increase the likelihood of bridging between metal centres, however the precise mechanism of whether the oxygen atom coordinates to the metal before or after hydration is unknown. If it occurs before hydration then there is a direct activation of the carbonyl towards nucleophilic attack, whereas if it occurs after hydration it is due to the polarisation effect of the metal on the hydroxy group.[10]

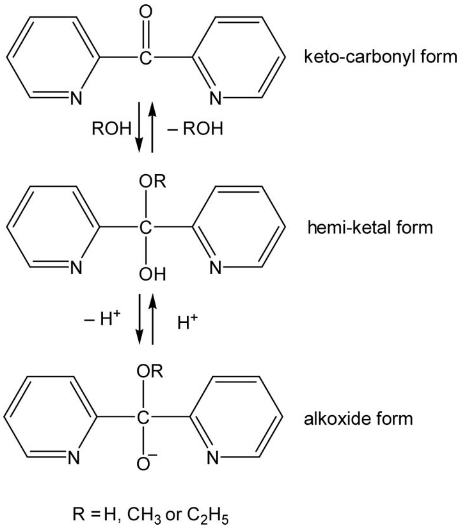

Figure 1. The hydrated/alcoholated *dpk* derivative.[2,9]

The hydrated and alcoholated derivatives of *dpk* are quite common; recently however more interest has developed for other nucleophiles to attack the ketone carbonyl.[8] In situ

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cyanomethylation of the carbonyl group on *dpk* was observed on reaction of a divalent metal salt with *dpk* in the presence of a catalytic base,[11] and Abrahams et al.[12] have observed nucleophilic attack with bisulfite, and pyrazole.

In situ metal-promoted aldol condensation reactions have been observed in the presence of basic solutions containing acetone and an additional carbonyl group, either ketone or aldehyde. This condensation reaction has been reported recently by Hussain et al.[13] who found that a new aldol ligand was generated when *o*-vanillin reacted in the presence of Dy(III), potassium hydroxide and acetone.

The Perlepes group[8] have also explored the reactions of the *dpk* ligand extensively and have published a review summarising this work. Recently, similar to Hussain, where acetone was able to form a nucleophilic enolate,[13] Perlepes observed a $\mathrm{Ni^{II}}$-promoted mixed-aldol condensation with *dpk* in the presence of a strong base, potassium hydroxide, to form the novel ligand observed here in compound **3**. However, there has not been a detailed study reported of this work.

Other transition-metal-promoted reactions have also been observed with *dpk*. In particular, an in situ cyanomethlyation of the ketone carbonyl in the presence of a $\mathrm{Ni^{II}}$ salt, where an α-alkylation of acetonitrile formed the ligand *dpk*·MeCN.[11] Also, in the presence of $\mathrm{Co^{II}}$ or $\mathrm{Ni^{II}}$ acetate, Wu et al.[14] reported an in situ nucleophilic addition of L-proline as a secondary amine to the ketone carbonyl.

As part of our studies on Cu-*dpk* systems, we have isolated four new complexes, two of which are polymorphs of one another, one is an iodo-bridged dimer and the other is a dimer resulting from a facile mixed-aldol reaction between *dpk* in a copper complex and acetone solvent in the presence of NaSCN.

Both thiocyanate and iodide ions are known to form dimer or polymer bridging complexes, making it possible to form neutral networks.[15,16] Although several N-heterocyclic ligands, including 2,2′-bipyridine (*bipy*), 1,10-phenanthroline (*phen*) and 2,9-dimethyl-1,10-phenanthroline (*dmp*) have been incorporated into neutral copper(I) thiocyanate polymeric networks,[3,4,15,17] *dpk* analogues have not been explored in any detail. The closest study to the work reported here is that of Goher et al.[18] who investigated complexes containing copper(I) with iodide and thiocyanate and uncoordinated N-protonated *dpk*.

Results and Discussion

Products **1** and **2** were prepared by reacting copper(I) thiocyanate and excess sodium thiocyanate with *dpk* in acetone and water, to form black needle-like, and black block-like crystals of $[\mathrm{Cu}(dpk)(\mathrm{NCS})]_n$ in good yields (70%). The colour of these materials suggested the copper ion was present in the +1 state. When products **1** and **2** were left in the supernatant overnight they re-dissolved completely. This was accompanied by a change in colour of the supernatant from purple-red to dark green. The dark green supernatant was left to stand, and within two days product **3** was isolated as large green block-like crystals. The colour of this material suggested that the copper had been oxidized and was now present in the +2 state. FT-IR spectra of **1** and **2** were identical; the presence of coordinated NCS being indicated by strong bands at ca. 2090 $\mathrm{cm^{-1}}$. The presence of C=O was also inferred from strong bands at 1685 $\mathrm{cm^{-1}}$. The FT-IR spectrum of **3** was similar to **1** and **2**, with bands at 2076 $\mathrm{cm^{-1}}$ (s, NCS), and 1711 $\mathrm{cm^{-1}}$ (w, C=O). The compositions of **1**, **2**, and **3** were confirmed by single-crystal X-ray diffraction, which provided unambiguous structural characterisation of each complex.

The chemical formulae of **1** and **2** are the same, however the spatial distribution of the *dpk* ligands are different, and give rise to different crystal packing. Hence (**1**) and (**2**) are polymorphs. Both complexes contain a continuous chain of four-coordinate copper(I) species, which are bridged together through thiocyanate groups (both N– and S– donor) forming a one-dimensional polymeric chain. The copper(I) cation is coordinated to three nitrogen atoms (two from the *dpk* ligand, and one from the bridging thiocyanate), and one sulfur atom from the other bridging thiocyanate, forming a distorted tetrahedral structure. The cationic +1 charge on the copper is counter-balanced by the coordinated thiocyanate anion. The molecular unit of **1** and **2** has the composition $[\mathrm{Cu}(dpk)(\mathrm{NCS})]_n$ (Figure 2); this is comparable to the *bipy, phen, and dmp* $\mathrm{Cu^{I}}$-thiocyanate analogues previously reported.[3,4,15,19] The monomeric unit of **1** contains mirror symmetry, with the copper, the thiocyanate ion and the carbonyl on the *dpk* ligand lying on the crystallographic plane. This type of mirror symmetry has been observed previously with $[\mathrm{Cu}(dafone)(\mathrm{NCS})]_n$ (where *dafone* = 4,5-diaza-

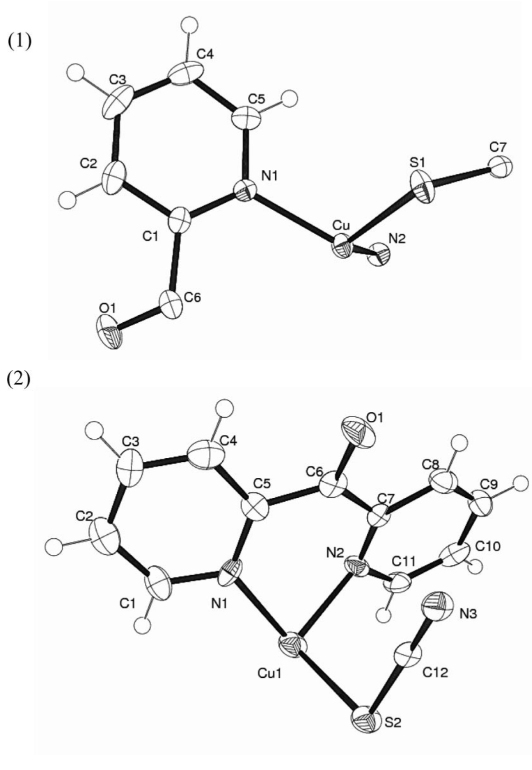

Figure 2. Asymmetric unit of **1** and **2**.

fluoren-9-one).[3] The orthorhombic complex exists as a one-dimensional copper(I) polymeric chain, bridged through thiocyanate and further associated through edge-to-face (EF) π-π interactions and electrostatic dipole-dipole interactions.

The EF interactions occur through the aromatic protons of the bound *dpk* ligand and the aromatic ring of identical neighbours at a distance of 2.940 Å (H-to-ring centre distance), which is indicative of a weak interaction (ca. 2.5–2.7 Å strong interaction) in accordance with Jennings et al.[20] and an angle of 65.11°(edge-tilted, T-shaped EF interactions).[20] A dipole-dipole electrostatic interaction is observed between neighbouring ketone C=O groups, at a distance of 3.181 Å. The slight negative charge on the oxygen atom causes charge repulsion between the ketone C=O groups on the *dpk*, with the carbonyl group being deviated from the aromatic groups. The alternating spatial positions of the *dpk* ligands along the Cu-chain are reminiscent of the *syndiotactic* form of polypropylene.[21] (Figure 3).

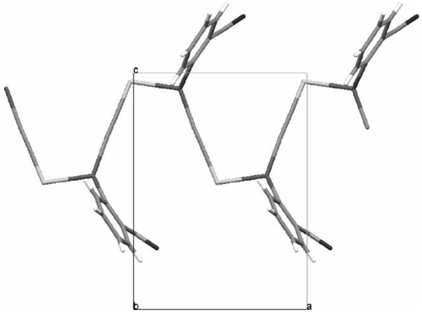

Figure 3. Packing of **1** along the *b* axis "syndiotactic" form.

The mirror symmetry observed in **1** is not evident in polymorph **2**. However, similar to **1**, **2** exists as a one-dimensional copper(I) polymeric chain bridged through thiocyanate anions in which the spatial distribution about the Cu-centre is akin to the *isotactic* form of polypropylene,[21] whereby the *dpk* ligands are located on the same side of the Cu-chain backbone, i.e. they have the same stereo configuration. **2** is a monoclinic complex associated through EF π-π interactions and H-bonding. The EF interactions occur between an N1 aromatic ring and the N1 aromatic protons on an identical neighbouring complex with a distance of 2.913 Å and an angle of 65.91°. Interactions between the N2 ring and N2 aromatic protons are also observed at a distance of 2.914 Å. Weak H-bonding is observed between the ketone carbonyl and the aromatic protons at a distance of 3.163 Å (Figures 4, 5, 6 and Table 1).

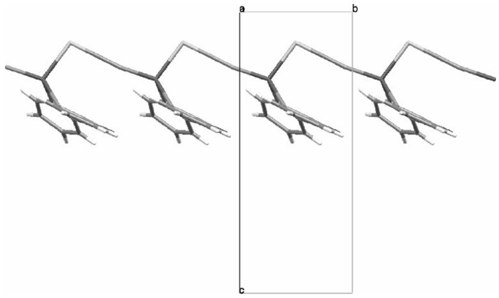

Figure 4. Packing of **2** along *a* axis "isotactic" form.

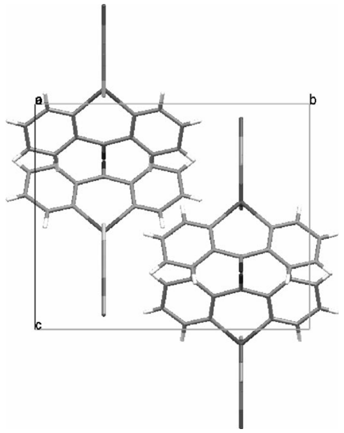

Figure 5. Packing of **1** along the *a* axis.

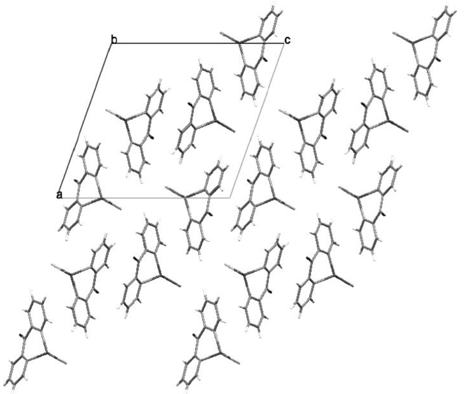

Figure 6. Packing of **2** along the *b* axis.

Complex **3** is a novel structure which exists as a dinuclear copper(II) complex of formula [Cu_2(*dpk·acetone*)$_2$(NCS)$_2$] (Figure 7 and Table 2). The molecular unit contains two five-coordinate copper(II) ions, with trigonal-bipyramidal coordination, which are bridged through a deprotonated hydroxy group on each bridging *dpk·acetone* ligand, and also through the two nitrogen atoms on each ligand, resulting in each *dpk·acetone* exhibiting bridging chelation to copper using the *N*,*N'*,O tridentate mode. A similar transformation has recently been observed in the preparation of a Ni^{II} complex.[8] The anionic charge on the deprotonated hydroxy groups, along with two coordinating thiocyanate groups, counter-balance the cationic charge on the two copper(II) cations. Each copper(II) ion is coordinated by two N atoms from different *dpk·acetone* ligands (Cu–N 1.978–2.211 Å), one N atom from a thiocyanate (Cu–N 1.959–1.965 Å) and two O atoms from the deprotonated hydroxy groups from different *dpk·acetone* ligands (Cu–O 1.955–1.974 Å), with a Cu–Cu non-bonding distance of 2.874–2.893 Å. The asymmetric unit comprises two dinuclear complexes with different symmetries. The monoclinic complexes exist as ribbons of the alternating dinuclear copper complexes, which are associated by a network of H-bonding

Table 1. Significant bond lengths and angles for compounds **1** and **2**.

1		**2**	
Bond lengths [Å]			
Cu1–N1	2.051(1)	Cu1–N1	2.035(6)
		Cu1–N2	2.063(9)
Cu1–N2	1.911(2)	Cu1–N3	1.919(8)
Cu1–S1	2.347(7)	Cu1–S1	2.335(3)
N2–C7	1.153(3)	N3–C12	1.15(1)
S1–C7	1.658(2)	S1–C12	1.66(1)
C6–O1	1.220(3)	C6–O1	1.22(1)
Bond angles [°]			
Cu1–N1–C1	117.2(1)	Cu1–N1–C1	120.0(6)
		Cu1–N2–C11	116.5(6)
Cu1–N2–C7	176.4(2)	Cu1–N3–C12	171.5(8)
Cu1–S1–C7	104.42(8)	Cu1–S1–C12	99.7(3)
N2–Cu1–S1	118.01(7)	N3–Cu1–S1	107.6(3)
C5–C6–C5	125.6(2)	C5–C6–C7	123.9(8)
N1–Cu1–N1	94.13(6)	N1–Cu1–N2	90.0(3)

Table 2. Significant bond lengths and angles for compound **3**.

Bond lengths [Å]		Bond angles [°]	
Cu1–N7	1.979(2)	Cu1–O5–Cu3 (bite)	95.10(8)
Cu1–N10	2.186(2)	Cu3–O6–Cu1 (bite)	95.01(8)
Cu1–N12	1.965(3)	N10–Cu1–N12	103.0(1)
Cu1–O5	1.956(2)	N11–Cu3–N9	97.3(1)
Cu1–O6	1.963(2)	N12–Cu1–O5	100.06(9)
Cu3–N8	2.212(2)	N7–Cu1–N10	103.2(1)
Cu3–N9	1.982(2)	N8–Cu3–O6	77.39(8)
Cu3–N11	1.959(3)	N8–Cu3–N11	96.5(1)
Cu3–O5	1.965(2)	N9–Cu3–O5	81.39(9)
Cu3–O6	1.961(2)	Cu2–O2–Cu4 (bite)	93.61(8)
Cu2–N1	1.994(2)	Cu4–O1–Cu2 (bite)	93.92(8)
Cu2–N3	2.208(2)	N1–Cu2–O1	80.91(9)
Cu2–N6	1.970(3)	N3–Cu2–N6	99.5(1)
Cu2–O1	1.972(2)	N4–Cu4–N5	98.0(1)
Cu2–O2	1.966(2)	N5–Cu4–N2	104.9(1)
Cu4–N2	2.171(2)	N6–Cu2–N1	97.9(1)
Cu4–N4	1.981(2)	O1–Cu4–N2	78.29(9)
Cu4–N5	1.959(3)	O2–Cu2–N3	77.51(8)
Cu4–O1	1.958(2)	O2–Cu4–N4	81.90(9)
Cu4–O2	1.974(2)		

through the deprotonated oxygen and the acetone-carbonyl to neighbouring aromatic protons and methylene acetone protons. The angle between the central carbon bridging the two pyridine rings has decreased (C–C–C ca. 108°) when compared to *dpk* complexes which contain a ketone C=O group (C–C–C ca. 125°). This angle change has been observed in other complexes where *dpk* has undergone hydration,[1] and is consistent with a change from a trigonal keto group to a tetrahedral *gem-diol* (Figure 1).

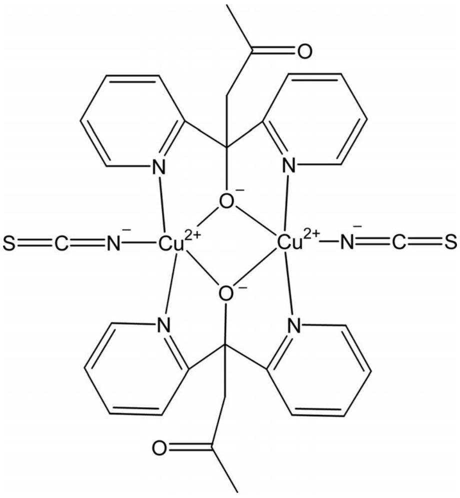

Figure 7. Complex **3**.

Complex **4** was prepared in a similar manner to **1** and **2**, but with the iodo forms of the copper and sodium salt being used instead of the thiocyanate analogues. Iodo ligands were selected in this instance as they are known to be excellent bridging candidates.[16,22–24] **4** is a new structure and exists as a dinuclear copper(I) complex of formula [$Cu_2(dpk)_2I_2$]. The molecular unit contains two four coordinate copper(I) cations, with tetrahedral coordination and their charge balanced by bridging iodide anions.

Cu^I polynuclear compounds often contain short Cu–Cu distances between 2.38–3.2 Å.[25] The contact distance of 2.546 Å in **4** is comparable to that seen in other Cu^+/Cu^+ dimers, for example, [$Cu_2I_2(phen)_2$] where it is 2.663 Å.[24] Each copper(I) ion is coordinated by two N atoms from *dpk* (Cu–N 2.032–2.036 Å), and two I atoms (Cu–I 2.596–2.622 Å). This type of Cu_2I_2 halide-bridged square dimer has been seen previously with other N-heterocyclic ligands.[16,22–24] Analogous Cu_2X_2 (where X = F, Cl or Br) species which contain a halide-bridged square dimer include Cu_2Br_2 having a Cu–Cu non-bonding distance of 2.850 Å.[26]

Complex **4** is monoclinic and exists as layers. The complexes are associated with their identical neighbour through a combination of weak π–π interactions and hydrogen bonding. In addition, an intermolecular OFF π–π interaction with an interplanar distance of 3.473 Å, runs along the *b* axis (see Figure 8 and Table 3), and occurs between the

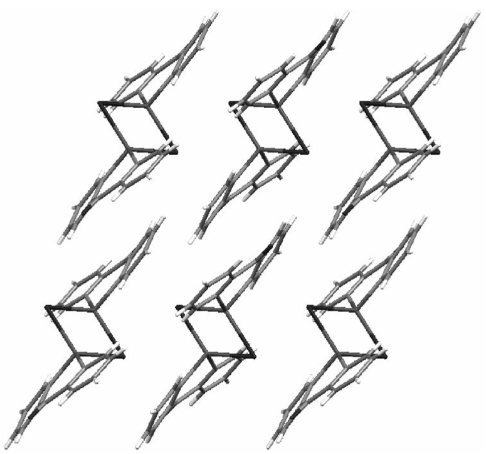

Figure 8. Packing of **4** along *b* axis.

N1-coordinated *dpk* rings. H-bonding is observed between protons on the aromatic rings and the ketone carbonyl and iodide ions (O···H 2.437 Å, I···H 3.162 Å).

Table 3. Significant bond lengths and angles for compound **4**.

Bond lengths [Å]		Bond angles [°]	
Cu1–N1	2.033(9)	N2–Cu1–N1	94.24(4)
Cu1–N2	2.037(9)	C7–C6–C1	126(1)
Cu1–I1	2.622(2)	Cu1–I1–Cu1	58.40(5)
Cu1–I1	2.597(1)		
C6–O1	1.24(2)		

Magnetic Measurements

The short non-bonding distance (2.874–2.893 Å) between the Cu^{II} centres in **3**, suggest that magnetic interactions may be present. Thus, the magnetic moment and magnetic susceptibility were measured for complex **3** and the results are presented in Figure 9. Although the more usual magnetic behaviour in Cu^{II} d^9 dimeric species is a spin-pairing *anti*-ferromagnetic interaction (J – ve) as we have reported in previous studies,[27] a ferromagnetic interaction (J + ve) is not unique,[28–30] and complex **3** represents a further example.

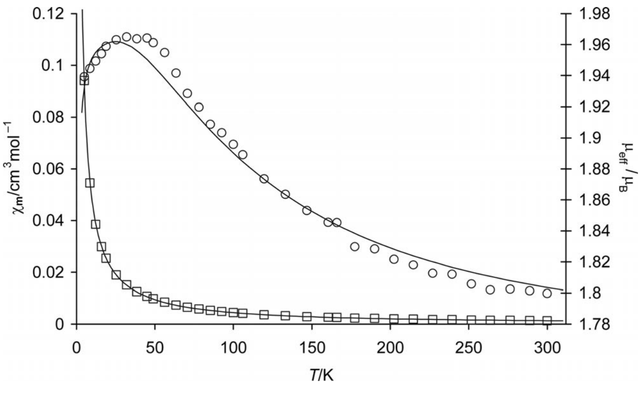

Figure 9. Plot of χ_m (□)and μ_{eff} (○) (per Cu) vs. temperature [K] for **3**.

The data were fitted to the modified Bleaney–Bowers relationship[31] given in Equation (1) for a Cu^{II} dimer, the spin Hamiltonian $H = -2J\ S_1S_2$ where J is the exchange coupling parameter and $S_1 = S_2 = 1/2$ (interacting local spins).

$$\chi_{cu} = \frac{Ng^2\beta^2}{KT}\left[3 + \exp\left|\frac{-2J}{KT}\right|\right]^{-1}\left|1 - P\right| + \frac{Ng^2\beta^2 P}{4KT} + N\alpha \qquad (1)$$

At ambient temperature, **3** was found to be paramagnetic with an isotropic g factor (g = 1.97), which is similar when compared to other copper complexes with *dpk* derivatives, where isotropic factors varied from g = 2.00–2.06.[32,33] An effective magnetic moment of 1.81 μ_B per Cu^{II} ion, as expected for non-interacting Cu^{II} d^9 ions.[25] The magnetic moment increased to 1.96 μ_B at 40 K. The μ_{eff} vs. T (K) plot shows an increase in μ_{eff} as the temperature is lowered, followed by a steep drop at low temperatures (40 K) which is characteristic of ferromagnetic coupling[34] and is confirmed by the positive J value of +45.2 cm^{-1}. The data for **3** is comparable to the magnetic data observed in other ferromagnetic alkoxo-bridged[29,30] and azido-bridged[28] complexes, with similar M–O–M angles and magnetic susceptibility plots, see Table 4.

Mechanistic Considerations

Many polymeric complexes of copper(I) have been synthesised previously, and in most cases their usefulness has been frustrated by insolubility. This was also the case with polymorphs **1** and **2**, which were insoluble in a wide range of polar and non-polar solvents. However, when the insoluble copper(I) complexes were left in their mother liquor over several days, dissolution occurred, even under ambient laboratory conditions. The red, aqueous acetone solution that contained black crystals of **1** and **2** transformed into an emerald green solution in air, and deposited the copper(II) complex **3** as green crystals.

In ketones, the hydrated *gem-diol* form and the carbonyl ketone are in equilibrium in an aqueous medium (Figure 1), with the equilibrium often favouring the keto form. However, strong electron-withdrawing substituents on the carbonyl group increase the electrophilic nature of the carbonyl carbon,[10] thus increasing its susceptibility to attack by weak nucleophiles such as water, and favouring the hydration reaction. It is also well-documented that, in the presence of divalent metal ions, *dpk* is able to undergo hydration across the ketone C=O group to form a *gem-diol*.[1,2,8] Hemiketals have also been known to form in alcoholic medium (Figure 1), where chelation to the metal

Table 4. Various Cu–O–Cu angles and J values.

Ferromagnetic	Cu^{2+}–O–Cu^{2+} [°]	J [cm^{-1}]
3	93.6–95.1	45.2
Azido-bridged $[Cu_4L^{dur}(\mu_2N_3)_4](PF_6)_4·4H_2O·6CH_3\text{-}CN]$[a][28]	96.6–98.1	94
$[Cu_2L(OAc)]·6H_2O$[29]	91.8–102.5	49.2
Antiferromagnetic		
Hydroxo-bridged $[Cu_4L^{dur}(\mu_2\text{-}OH)_4](ClO_4)_4]$[a][28]	95.7–97.9	–27

[a] L^{dur} = 1,2,4,5-tetrakis(1,4,7-triazacyclonon-1-ylmethyl)benzene), H_3L = 2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine.

centre occurs through *N*,*N*,O coordination, and the resultant –C–OH groups deprotonate to yield a mono-anionic ligand.[9]

It can be seen that complex **3** has *N*,*N*′,O-coordination, and a *gem-diol* has not formed, but rather the acetone in solution has been deprotonated to provide a carbanion nucleophile which can attack the metal activated *dpk* carbonyl group and form an alkoxide, which is then coordinated to the copper as illustrated in Figure 10. The reaction is analogous to an aldol condensation which occurs when a carbonyl group with an α-hydrogen atom undergoes a nucleophilic attack by base to form an enolate ion. The enolate ion can then undergo an addition reaction to a second carbonyl group. This step is often followed by a relatively facile dehydration to generate an alkene, however in the present case the reactivity of the hydroxy group is masked when it becomes bound to the Cu^{2+} ion, thus blocking the dehydration process.[21] The formation of **3** in significant yields is quite surprising under the mild conditions of our experiment, and it would appear that unreacted starting material contained in the mother liquor is responsible for initiation of the reaction. A large excess of sodium thiocyanate was added to the reaction mixture to ensure that the copper(I) thiocyanate would dissolve. Hence, we suggest it is the unreacted thiocyanate behaving as a weak base that is the most likely candidate to initiate the formation of the enolate. Hussain[13] and Perlepes[8] have used strong base to initiate the formation of enolates, but in the present work, we have observed similar results with much weaker bases.

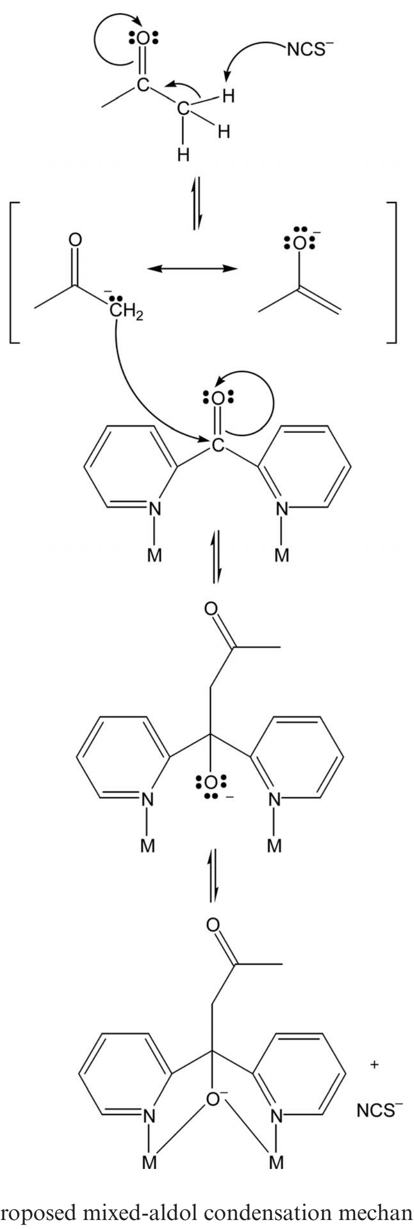

Figure 10. Proposed mixed-aldol condensation mechanism for conversion of **1/2** into **3**.

Conclusions

During studies into the reaction of *dpk* with Cu_2X_2 (where X = NCS^- or I^-) three novel complexes were isolated. These included two neutral Cu^I polymeric complexes **2** and **1**, which are polymorphs, a dinuclear Cu^{II} complex **3** and a dinuclear Cu^I complex **4**. The formation of **3** is suggested to arise from a transition-metal-promoted mixed-aldol condensation, which occurs between the acetone solvent and the ketone carbonyl of *dpk* to produce the novel ligand *dpk·acetone*. The ferromagnetic behaviour observed in **3** is in agreement with coupling between Cu^{II} centres which has been observed in several other Cu^{II} compounds of similar structure.

Experimental Section

General: Di(2-pyridyl) ketone (99%, $C_{11}H_8N_2O$), and Cu^I thiocyanate (99% CuSCN) were obtained from Aldrich. Sodium thiocyanate (99%, NaSCN), Potassium iodide (KI, 99%), and copper(I) iodide (99%, CuI) were purchased from Ajax Chemicals. All chemicals were used as supplied without further purification.

Characterisation Techniques: All products were analysed by FTIR and, characterised structurally by single crystal XRD. FTIR spectra were obtained on a Perkin–Elmer Spectrum 100 spectrometer using KBr discs. The discs were prepared by grinding the sample (1–2 mg) and IR-grade KBr (100 mg), into a homogeneous powder using a mortar and pestle. The powder was then placed in a die press (Specac 13 mm), and compacted under vacuum for approximately 5 min using 8 tons of pressure. The spectra were collected using the following conditions: scan range 4000–400 cm^{-1}; number of scans 8; single beam; resolution: 4 cm^{-1}.

Synthesis of Complexes

Cu^I Complexes $[Cu(dpk)(NCS)]_n$ (1) and (2) and Cu^{II} Complex $[Cu_2($*dpk·acetone*$)_2(NCS)_2]$ (3): Complexes **1** and **2** were synthesised according to the procedure described by La Monica,[35] with some modification. CuSCN (0.12 g, 1 mmol) and NaSCN (0.81 g, 10 mmol) were dissolved in a 1:3 aqueous-acetone (20 mL) solution. The resulting pink solution was filtered and to this *dpk* (0.37 g, 2 mmol) in acetone (5 mL) was added. The mixture was stirred and heated mildly (approx. 40 °C) for 10 min. A combination of black block-like and black needle-like crystals, **1** and **2** respectively, were isolated from a purple-red supernatant in 70% yield within 2 h. When **1** and **2** were left to stand in the supernatant at ambient temperature for three days, large green block crystals of

Table 5. Summary of single crystal structure determination data for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{12}H_8CuN_3OS$	$C_{12}H_8CuN_3OS$	$C_{67.5}H_{67}Cu_4N_{12}O_{10.5}S_4$	$C_{11}H_8Cu IN_2O$
Molecular weight	305.81	305.81	1596.73	374.63
Crystal class	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pmna*	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	8.1396(2)	14.3219(9)	21.932(7)	9.9663(7)
b [Å]	13.4112(3)	5.7110(3)	15.142(5)	9.4446(9)
c [Å]	11.0248(2)	15.0857(9)	23.223(7)	12.4390(10)
α [°]	90	90	90	90
β [°]	90	109.377(7)	113.514(5)	104.602(8)
γ [°]	90	90	90	90
V [Å^3]	1203.49(5)	1164(12)	7072(4)	1133.01(16)
Z	4	4	4	4
Crystal shape, colour	prism, black	prism, black	block, green	prism, black
Crystal size [mm]	0.17 × 0.11 × 0.07	0.04 × 0.03 × 0.02	0.40 × 0.50 × 0.50	0.04 × 0.03 × 0.02
Temperature [K]	130(2)	130(2)	130(2)	130(2)
Radiation wavelength [Å]	1.54184	1.54184	0.71073	1.54184
Radiation	Cu-K_α	Cu-K_α	Mo-K_α	Cu-K_α
θ min./max [°]	3.29/72.40	3.69/67.45	1.65/27.68	4.58/73.14
Index ranges	$-9 \leq h \geq 9$	$-16 \leq h \geq 17$	$-28 \leq h \geq 28$	$-12 \leq h \geq 9$
	$-16 \leq k \geq 16$	$-6 \leq k \geq 6$	$-19 \leq k \geq 19$	$-11 \leq k \geq 9$
	$-13 \leq l \geq 9$	$-13 \leq l \geq 18$	$-29 \leq l \geq 30$	$-15 \leq l \geq 12$
Reflections	1235	2000	15959	2150
R_1 [$F^2 > 2\sigma(F^2)$]	0.0252	0.0732	0.046	0.0446
wR [F^2]	0.0666	0.1374	0.1051	0.0995
S	0.955	0.779	0.846	0.695

3 formed in 15% yield, and the supernatant changed to a dark green colour.

1 and 2: IR (KBr): $\tilde{\nu}$ = 3426 (m), 2091 (s), 1685 (s), 1581 (s), 1304 (s), 1278 (s), 935 (s) 750(s), 663 (s) cm^{-1}.

3: IR (KBr): $\tilde{\nu}$ = 3420 (m), 2075 (s), 1711 (w), 1594 (s), 1465 (s), 1432 (s), 1101 (s), 1090 (s), 760 (m), 557 (s)) cm^{-1}.

4: IR (KBr): $\tilde{\nu}$ = 3414 (m), 1662 (s), 1579 (s), 1304 (s), 1276 (s), 1009 (s), 934 (s) 746 (s) 662(s) cm^{-1}.

Cu^I Complex [Cu$_2$(dpk)$_2$I$_2$] (4): Preparation according the same procedure as for **1**, except CuI and KI were used in place of CuSCN and NaSCN. Black block crystals were isolated in 60% yield.

Crystal Structure Determination: Single crystal data for compounds **1** to **4** were collected and integrated using a Bruker Smart CCD area detector system at 130 K using Mo-K_α radiation. The structures were solved by direct methods, using SHELXS-97,[36] and refined using SHELXL-97.[36] A mixed strategy was used for the refinement of hydrogen atoms. Hydrogen atoms attached to carbon atoms were placed in calculated positions with a C–H distance of 0.93 Å, whilst hydrogen atoms attached to oxygen atoms were located from difference Fourier maps, and refined without constraint. Owing to the large amount of disordered solvent, a SQUEEZE[37] routine had to be applied to (**3**) in order to obtain a satisfactory refinement. Molecular graphics were performed using ZORTEP,[38] SHELXTL[39] and Mercury[40] programs. Selected crystal data for **1**–**4** are presented in Tables 1, 2, 3 and 5.

CCDC-779366 (for **1**), -779367 (for **3**), -779368 (for **2**), -779369 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: Variable-temperature magnetic susceptibilities were measured on ca. 20 mg samples of powders using a Quantum Design MPMS5 Squid magnetometer in a field of 1 T. Samples were contained in gel capsules which were held in the centre of a soda straw, in turn fixed to the end of the sample rod. The instrument was calibrated against the accurately known susceptibilities of a standard Pd pellet (Quantum Design) and that of CuSO$_4$·5H$_2$O.

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