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FULL PAPER

Complexation of 3,4-bis(cyanamido)cyclobutane-1,2-dione dianion with copper. Crystal structures and spectroscopic data of copper-(I) and -(II) complexes

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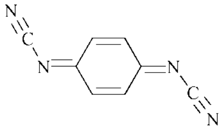
Three complexes $[Cu_2(PPh_3)_4(MeCN)_2(\mathit{cis}\text{-}(NCN)_2sq)]\cdot MeCN$ **1**, $\{[Cu_2(dien)_2(\mathit{cis}\text{-}(NCN)_2sq)_2]\cdot 5H_2O\}_n$ **2** and $[Cu(tren)(\mathit{cis}\text{-}(NCN)_2sq)]$ **3** where $[\mathit{cis}\text{-}(NCN)_2sq]^{2-}$ = 3,4-bis(cyanamido)cyclobutane-1,2-dione dianion, have been synthesized and characterized by electronic absorption and IR spectroscopies. The structures of the three complexes have been determined by X-ray crystallography. Complex **1** is present as a dinuclear copper(I) compound. Complex **2** is made of infinite chains with copper(II) atoms bridged by the bis monodentate $[\mathit{cis}\text{-}(NCN)_2sq]^{2-}$ ion. In the mononuclear complex **3** the co-ordination of the cyanamido group unusually occurs *via* the amido nitrogen and not by the nitrile group; this is accompanied by an important distortion of the co-ordinated cyanamido group. The co-ordination mode of the cyanamido moiety is discussed in regard to IR data and crystallographic results.

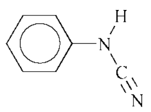
The squarate ion (3,4-dihydroxybut-3-ene-1,2-dionate), $C_4O_4^{2-}$, is an intriguing ligand due to its high symmetry and its electronic delocalization. The study by Habenschuss and Gerstein[1] of the crystal structure and magnetic properties of $Ni(C_4O_4)(H_2O)_2$ has revealed an unexpected polymeric solid-state structure and a ferromagnetic behaviour at very low temperatures. Owing to its formal similarity with the well known oxalate ligand and in view of studies on magnetic interactions between metal ions, many copper(II) squarate complexes have been investigated.[2–6] However, reported magnetic measurements on the structurally characterized squarato-bridged complexes show that no or only weak antiferromagnetic interactions occur between paramagnetic centres.

Several species, derived from the squarate entity, have been synthesized, in which one or more of the oxygen atoms have been substituted by other atoms or groups (sulfur, selenium, nitrogen, dicyanomethylene or cyanamide); they are called pseudo-oxocarbons[7] and considered as cyclobutenediylium dyes.[8] These compounds are characterized by extensive π electron delocalization, interesting redox behaviour and, for some of them, strong colours and intrinsic electrical conductivity.[9] Several complexes of these pseudo-oxocarbons have been prepared in order to obtain new materials with these properties. Among these pseudo-oxocarbons, our interest is now focused on derivatives in which one or more of the oxygen atoms are replaced by cyanamide groups NCN.[10]

Our interest in cyanamide ligands arises from the discovery by Hünig and co-workers[11] of a radical anion copper salt of *N*,*N′*-dicyano-*p*-benzo-2,5-dimethylquinone diimine (derivative of DCNQI shown) with an increasing conductivity as the temperature is reduced (high value 5×10^5 S cm^{-1} at 3.5 K).

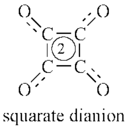
Since the discovery of this π-electron/metal system, further research has shown that both the nature of the cation and that of the substituents grafted on the ligand have very important effects on the electronic properties of these new conductors.[12] Crutchley *et al.*[13] have largely investigated the co-ordination chemistry of phenylcyanamide ligands (which may be viewed as reduced forms of DCNQIs), in both neutral and anionic forms with copper as metal.





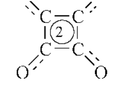
Bearing in mind the analogy of the squarate ring with the phenyl one (the $C_nO_n^{2-}$ family is considered as aromatic)[6,14] and the interesting redox properties of the pseudo-oxocarbons, cyanamide squarates may be good challenges in order to obtain new materials. These compounds can react with transition metals to lead to new complexes: molecular materials characterized by electron transport chains, compounds exhibiting magnetic exchange between metal ions, or electrochromic materials.

As a first step, we report here on the syntheses, physical properties and crystallographic investigations of complexes of Cu^I and Cu^{II} with a dianionic cyanamide squarate ligand: 3,4-bis(cyanamido)cyclobutane-1,2-dione dianion $[\mathit{cis}\text{-}(NCN)_2sq]^{2-}$.[15] The crystallographic results lead us to discuss the co-ordination properties of the cyanamido moiety.



squarate dianion

$[C_4O_4]^{2-}$ or sq^{2-}



$[\mathit{cis}\text{-}(NCN)_2sq]^{2-}$

Experimental

Syntheses

All solvents and chemicals were reagent grade or better and

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used as received unless otherwise noted. Squaric acid, cyanamide, dien and tren were purchased from Acros. Bis(triphenylphosphine)copper(I) nitrate was prepared by the method of Cotton and Goodgame,[16] dibutyl squarate according to Lunelli *et al.*[17] Owing to the problems arising from the interpretation of IR spectra (*vide infra*) we have also prepared the Ph_4P^+ salt of the ligand for comparison.

Disodium 3,4-bis(cyanamido)cyclobutane-1,2-dionate dihydrate $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$. This compound was obtained by reaction of cyanamide with the dibutyl ester of squaric acid according to a method adapted from Sprenger and Ziegenbein.[8] All the reactions were conducted under dinitrogen. Dibutyl squarate (9.2 g, 41 mmol) and cyanamide (3.4 g, 82 mmol) were dissolved in dry butanol (100 cm^3). This orange solution was heated under reflux for one hour. A cold filtered sodium butoxide solution (40 cm^3, 1.8 g of Na) was added dropwise. After addition of 150 cm^3 of butanol, the whole mixture was stirred under reflux for 2 hours. An orange product was obtained; it was washed several times with methanol and diethyl ether and dried under vacuum. Two successive recrystallizations from water gave analytically pure $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$ as yellow crystals (80%). IR data (KBr disc)/cm^{-1}: 3500–3260m, 2210m, 2163vs, 2120w (sh), 1790m, 1630s, 1557s, 1529s, 1450vs, 1215w, 1186w, 1022w, 1000w, 866w, 569m. These values agree with those found by Lunelli and Monari.[18]

$[Ph_4P]_2[cis\text{-}(NCN)_2sq]\cdot 4H_2O$. This salt was prepared by mixing in a 2 : 1 ratio Ph_4PBr and $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$ in water. An orange solid precipitated immediately. It was filtered off, washed with water and dried under vacuum (98%). IR data (KBr disc)/cm^{-1}: 3434w (br), 3057w, 2167m (sh), 2120vs, 1768m, 1634s, 1585m, 1512vs, 1434vs, 1186w, 1162w, 1108vs, 994m, 852w, 761m, 723vs, 688s, 526vs.

$[Cu_2(PPh_3)_4(MeCN)_2(cis\text{-}(NCN)_2sq)]\cdot MeCN$ 1. A methanol solution (80 cm^3) of $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$ (121 mg, 0.5 mmol) was added dropwise to an acetonitrile solution (120 cm^3) of $[Cu(NO_3)(PPh_3)_2]$ (650 mg, 1 mmol). The solution changed from yellow to orange. After slow evaporation, a yellow powder was obtained. By recrystallization in hot acetonitrile, yellow crystals of **1** were obtained (48%) (Found: C, 68.57; H, 4.76; N, 6.16. Calc. for $C_{84}H_{69}Cu_2N_7O_2P_4$: C, 69.13; H, 4.77; N, 6.72%). IR data (KBr disc)/cm^{-1}: 3053m, 2315w, 2149vs, 1778m, 1697m, 1627m, 1543vs, 1479s, 1400vs (br), 1180w, 1158w, 1094s, 1069w, 1026w, 997m, 849w, 745s, 693vs, 517s, 505s.

$\{[Cu_2(dien)_2(cis\text{-}(NCN)_2sq)_2]\cdot 5H_2O\}_n$ 2. dien (206 mg, 2 mmol) in water (20 cm^3) was added to copper(II) nitrate (465 mg, 2 mmol) in water (20 cm^3). The blue colour of the solution rapidly intensified and turned to strong blue. $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$ (484 mg, 2 mmol) in water (40 cm^3) was added. At the end of this addition the solution was dark green and a green powder precipitated. The mixture was stirred for 30 min to ensure complete reaction and then filtered. The precipitate was washed with ethanol, diethyl ether, and vacuum dried. The product was then recrystallized from a water solution as green crystals. Other crystals with identical analysis may be also obtained from slow evaporation of the solution (30%) (Found: C, 32.45; H, 4.72; N, 26.16. Calc. for $C_{20}H_{36}Cu_2N_{14}O_9$: C, 32.30; H, 4.88; N, 26.37%). IR data (KBr disc)/cm^{-1}: 3430–3220m (br), 2950w, 2885w, 2230w (sh), 2188s, 2165s, 2142vs, 1777m, 1644m, 1524s, 1431s, 1136w, 1088w, 1027m, 900w, 853w, 670w, 554w. Powder conductivity measurements indicate that **2** is an insulator.

$[Cu(tren)(cis\text{-}(NCN)_2sq)]$ 3. To a water solution (15 cm^3) of copper(II) nitrate (465 mg, 2 mmol), a water solution (15 cm^3) of tren (292 mg, 2 mmol) was added. To this dark blue solution, $Na_2[cis\text{-}(NCN)_2sq]\cdot 2H_2O$ (484 mg, 2 mmol) in water (30 cm^3) was added. After concentration to 25 cm^3 under vacuum at 40 °C the product crystallized as yellow crystals (45%) (Found: C, 38.83; H, 4.92; N, 29.77. Calc. for $C_{12}H_{18}CuN_8O_2$: C, 38.96; H, 4.91; N, 30.30%). IR data (KBr disc)/cm^{-1}: 3326m, 3281m, 3261m, 3232m, 3138m, 2201m, 2167vs, 1822w, 1771m, 1661s, 1578m, 1530vs, 1465m, 1418vs (br), 1357m, 1313m, 1270w, 1234w, 1179w, 1115w, 1057m, 1015m, 992m, 970m, 902m, 858w, 748m, 650m, 559m, 538m.

Physical measurements

The complexes are isolated as air-stable crystals. All three are soluble in dmf and, as shown by conductivity measurements, are not dissociated in this solvent even if fragmentation of the polymer **3** may occur. UV-visible spectra have been recorded in dmf solution on a Cary 1E spectrophotometer, IR spectra in the solid state in KBr pellets using a Brucker Vector 22 spectrometer. Measurements in dmso or dmf solutions were carried out on a 1760-X Perkin-Elmer Infrared Fourier Transform spectrometer. In the 2–300 K temperature range, magnetic susceptibility measurements were made for powdered samples using a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. $HgCo(NCS)_4$ was used as a calibrant (susceptibility at 20 °C, 16.44×10^{-6} cm^3 mol^{-1}). The molar susceptibilities were corrected for diamagnetism using Pascal's constants.[19] Corrections were estimated as -161.92×10^{-6} and -161.64×10^{-6} cm^3 mol^{-1} for all the atoms of **2** and **3** respectively.

X-Ray data collection and structure determination for 1, 2 and 3

The data were collected[20] on a Stoe Imaging Plate Diffractometer System (IPDS), equipped with an Oxford Cryosystems cooler device, at 160 K using Mo-Kα radiation with a graphite monochromator The structures were solved using direct methods[21] and refined[22] by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculations with a riding model (except those of the methyl of the disordered acetonitrile molecule in **1**), with U_{iso} equal to 1.1 times that of the atom of attached. Refinements on F_o^2 were made for all reflections. Conventional R factors were based on F_o ($F_o > 4\sigma(F_o)$), with F_o set to zero for negative F_o^2. The atomic scattering factors and anomalous dispersion terms were taken from the standard compilation.[23] Crystallographic data are summarized in Table 1.

CCDC reference numbers 153403–153405.

See http://www.rsc.org/suppdata/dt/b0/b009239h/ for crystallographic data in CIF or other electronic format.

Results

Selected bond lengths and angles from the structural determinations of $[Cu_2(PPh_3)_4(MeCN)_2(cis\text{-}(NCN)_2sq)]\cdot MeCN$ **1**, $\{[Cu_2(dien)_2(cis\text{-}(NCN)_2sq)_2]\cdot 5H_2O\}_n$ **2** and $[Cu(tren)(cis\text{-}(NCN)_2sq)]$ **3** are given in Tables 2, 3 and 4 respectively. The crystal structure of $Tl_2[cis\text{-}(NCN)_2sq]$ has been described by Lunelli and Monari.[18] and that of the dianion will be compared to those obtained for the copper complexes.

Crystal structure of $[Cu_2(PPh_3)_4(MeCN)_2(cis\text{-}(NCN)_2sq)]\cdot MeCN$ 1

A view of the molecule, along with the numbering scheme, is shown in Fig. 1. The compound consists of discrete binuclear $[Cu_2(PPh_3)_4(MeCN)_2(cis\text{-}(NCN)_2sq)]$ molecules and one disordered acetonitrile in the lattice. There are two copper(I) ions, separated by 12.1158(5) Å and bridged by the bis monodentate $[cis\text{-}(NCN)_2sq]^{2-}$ ion. It appears that there is little energy difference between four-co-ordinated tetrahedral and three-co-ordinated planar copper(I) complexes. In the presence of soft donor atoms the stereochemistry of copper(I) is very flexible:

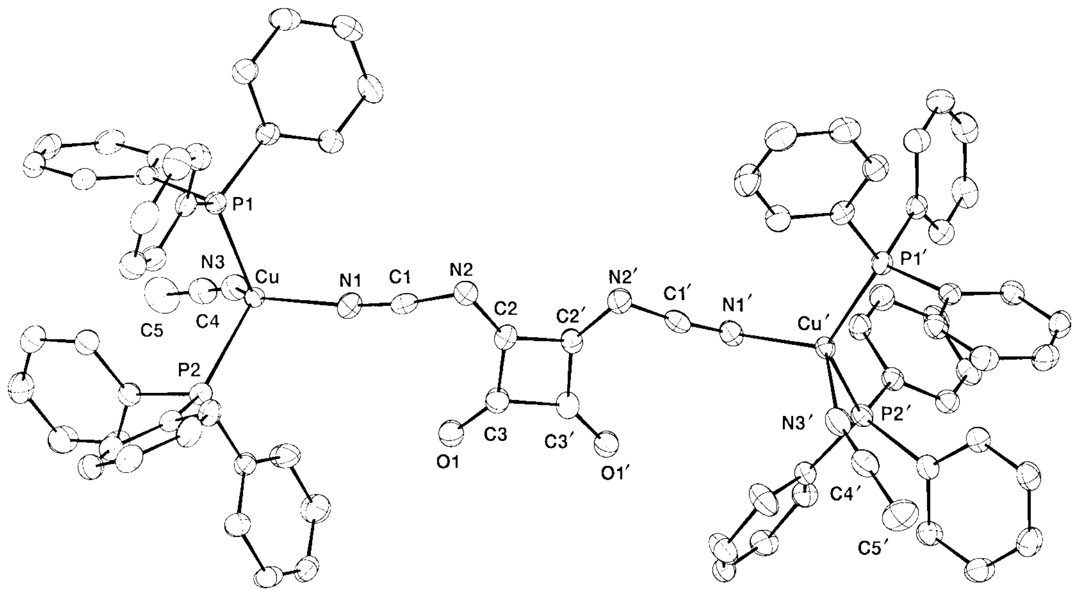


Fig. 1 An ORTEP[24] drawing of $[Cu_2(PPh_3)_4(MeCN)_2(\textit{cis}\text{-}(NCN)_2sq)]\cdot MeCN$ **1**.

Table 1 Crystallographic data for $[Cu_2(PPh_3)_4(MeCN)_2(\textit{cis}\text{-}(NCN)_2sq)]\cdot MeCN$ **1**, $\{[Cu_2(dien)_2(\textit{cis}\text{-}(NCN)_2sq)_2]\cdot 5H_2O\}_n$ **2** and $[Cu(tren)(\textit{cis}\text{-}(NCN)_2sq)]$ **3**

	1	**2**	**3**
Formula	$C_{84}H_{69}Cu_2N_7O_2P_4$	$C_{20}H_{36}Cu_2N_{14}O_9$	$C_{12}H_{18}CuN_8O_2$
Formular weight	1459.42	743.71	369.88
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1$	$Pna2_1$
a/Å	12.744(3)	6.982(2)	15.085(3)
b/Å	22.012(4)	14.712(3)	12.966(2)
c/Å	25.191(5)	14.746(3)	7.637(2)
β/°	91.40(3)	90.35(2)	
U/Å^3	7064(3)	1514.7(5)	1496.6(4)
Z	4	2	4
λ/Å	0.71073	0.71073	0.71073
μ(Mo-Kα)/cm^{-1}	7.48	14.76	14.87
T/K	160 ± 2	160 ± 2	160 ± 2
Measured reflections	12889	11671	11033
Independent reflections	5443	5417	2877
R_{int}	0.0460	0.0352	0.0499
R obs., all	0.0406, 0.0485	0.0281, 0.0288	0.0334, 0.0394
wR obs., all	0.1066, 0.1126	0.0551, 0.0552	0.0622, 0.0643

with the same metal/ligand stoichiometry, some complexes can be found with different stereochemistries; on the other hand, complexes with different stoichiometries may occur with the same ligand. In **1** each copper(I) ion is four-co-ordinated by two phosphorus atoms of two PPh_3 molecules, one nitrogen of a CH_3CN molecule and a nitrogen atom from one cyanamido group of the ligand $[\textit{cis}\text{-}(NCN)_2sq]^{2-}$. The geometry around copper is not tetrahedral as expected but is better described as 3 + 1 trigonal pyramidal with a quasi planar CuP1P2N1 entity (angles from 113.79(6) to 123.69(3)°), the Cu atom deviation being 0.3550(3) Å from the P1P2N1 plane. The nitrogen atom N3 of the bonded acetonitrile molecule occupies an axial co-ordination site (angles from 91.97(7) to 103.4(1)° with the three in-plane atoms). The poor co-ordination of the acetonitrile molecule is also confirmed by the Cu–N3 distance (2.157(3) Å) while the Cu–N1 distance is 2.013(3) Å. The Cu–N distance is 1.99 Å in $[Cu(MeCN)_4]^+$.[25]

Free anionic cyanamide squarate is expected to be planar due to the strong coupling of the cyanamido group with the squarate π system and its crystal structure confirms this assertion.[18] In the complex the ligand is almost planar with a crystallographic symmetry axis in the middle of the squarate ring. The dihedral angle between the NCN group and the squarate ring is 8(2)°. The two NCN groups are oriented away from each other and the same conformation is observed in the free anion. The cyanamide ligand bonds in a linear mode (Cu–N1–C1 173.1(2)°), the most classical mode for a NCN group. The different co-ordination modes of cyanamide ligands will be discussed in the following part of this work. The ligand is affected by complexation, giving an elongation of the sq–N bond (1.32(4) Å in the dianion and 1.345(4) Å in the complex) and a shortening of the terminal C–N bond (1.21(4) Å in the dianion and 1.160(4) Å in the complex); this corresponds to an increase of the nitrile bond character. This is consistent with the value of the Cu–N–C angle close to 180° (*vide infra*). The C–C distances in the ring are in the range 1.427(6) to 1.494(6) Å and are indicative of a delocalized π system as observed in the squarate ion.[26] The C3–O1 distance of 1.223(4) Å is normal for a carbonyl group. The angle Cu–N–C(acetonitrile) is normal as expected.

Crystal structure of $\{[Cu_2(dien)_2(\textit{cis}\text{-}(NCN)_2sq)_2]\cdot 5H_2O\}_n$ 2

A view of the structure, along with the numbering scheme, is shown in Fig. 2. The structure of **2** is made of infinite chains of $[Cu_2(dien)_2(\textit{cis}\text{-}(NCN)_2sq)_2]$ units. Within these units the two different copper(II) ions (labelled as Cu1 and Cu2) are bridged by the bis monodentate $[\textit{cis}\text{-}(NCN)_2sq]^{2-}$ ion. Each copper

Table 2 Selected bond lengths (Å) and angles (deg) for $[\mathrm{Cu_2(PPh_3)_4(MeCN)_2}(\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq})]\cdot\mathrm{MeCN}$ **1** with e.s.d.s in parentheses

Cu–P1	2.2959(8)	Cu–N1	2.013(3)
Cu–P2	2.3018(8)	Cu–N3	2.157(3)
P1–C6	1.819(3)	P2–C24	1.833(3)
P1–C12	1.831(3)	P2–C30	1.822(3)
P1–C18	1.826(3)	P2–C36	1.816(3)
N1–C1	1.160(4)	C1–N2	1.309(4)
N2–C2	1.345(4)	C2–C2′	1.427(6)
C3–C3′	1.494(6)	C2–C3	1.459(4)
C3–O1	1.223(4)	N3–C4	1.140(4)
C4–C5	1.437(5)		
P1–Cu–P2	123.69(3)	P1–Cu–N1	113.79(6)
P1–Cu–N3	102.83(7)	N1–Cu–N3	103.4(1)
P2–Cu–N1	114.84(7)	P2–Cu-N3	91.97(7)
Cu–N1–C1	173.1(2)	N1–C1–N2	171.8(3)
Cu–N3–C4	153.8(2)	N3–C4–C5	178.7(3)
C1–N2–C2	118.1(2)	N2–C2–C3	134.6(3)
N2–C2–C2′	134.1(2)	C2–C3–C3′	88.7(2)
C2′–C2–C3	91.3(2)	C2–C3–O1	133.6(3)
C3′–C3–O1	137.7(2)		

Symmetry operation: $'\ -x, y, \frac{1}{2} - z$.

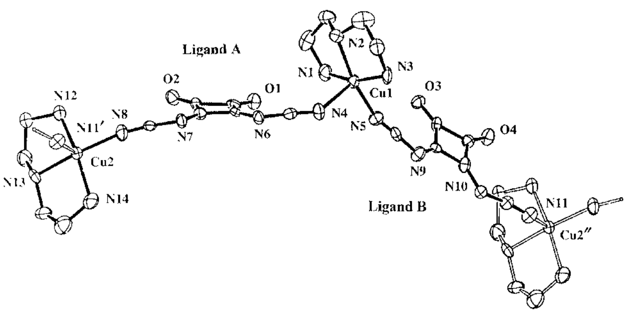


Fig. 2 ORTEP drawing of $\{[\mathrm{Cu_2(dien)_2}(\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq})_2]\cdot 5\mathrm{H_2O}\}_n$ **2**.

Table 3 Selected bond lengths (Å) and angles (deg) for $\{[\mathrm{Cu_2(dien)_2}(\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq})_2]\cdot 5\mathrm{H_2O}\}_n$ **2** with e.s.d.s in parentheses

Cu1–N1	2.024(2)	Cu2–N12	2.024(2)
Cu1–N2	2.017(2)	Cu2–N13	2.020(2)
Cu1–N3	2.031(2)	Cu2–N14	2.020(2)
Cu1–N4	2.262(2)	Cu2–N8	1.968(2)
Cu1–N5	1.957(2)	Cu2–N11′	2.239(2)
N4–C5	1.172(3)	C5–N6	1.324(3)
N6–C6	1.319(3)	C6–C7	1.470(3)
C7–C8	1.505(3)	C7–O1	1.234(3)
C8–O2	1.238(3)	C8–C9	1.452(3)
C9–C6	1.429(3)	C9–N7	1.344(3)
N7–C10	1.285(3)	C10–N8	1.157(3)
N5–C11	1.178(3)	C11–N9	1.281(3)
N9–C12	1.340(3)	C12–C13	1.466(3)
C13–C14	1.499(3)	C13–O3	1.233(3)
C14–C15	1.473(3)	C14–O4	1.214(3)
C15–C12	1.410(3)	C15–N10	1.323(3)
N10–C16	1.310(3)	C16–N11	1.156(3)
N1–Cu1–N2	84.8(1)	N12–Cu2–N13	83.88(9)
N1–Cu1–N3	162(2)	N12–Cu2–N14	163.2(2)
N1–Cu1–N4	102.22(9)	N12–Cu2–N8	90.76(9)
N1–Cu1–N5	90.9(1)	N12–Cu2–N11′	101.27(9)
N2–Cu1–N3	84.2(1)	N13–Cu2–N14	84.9(1)
N2–Cu1–N4	95.21(9)	N13–Cu2–N8	162.61(9)
N2–Cu1–N5	166.10(9)	N13–Cu2–N11′	98.24(8)
N3–Cu1–N4	92.96(9)	N14–Cu2–N8	96.2(1)
N3–Cu1–N5	96.4(1)	N14–Cu2–N11′	92.76(9)
N4–Cu1–N5	98.62(9)	N8–Cu2–N11′	99.03(9)
Cu1–N4–C5	138.7(2)	Cu1–N5–C11	162.0(2)
Cu2–N8–C10	165.8(2)	Cu2″-N11–C16	140.0(2)
N4–C5–N6	173.6(2)	N5–C11–N9	168.7(2)
C5–N6–C6	116.1(2)	C11–N9–C12	122.3(2)
N6–C6–C7	139.8(2)	N9–C12–C13	140.0(2)
N6–C6–C9	129.5(2)	N9–C12–C15	127.9(2)
C7–C6–C9	90.6(2)	C13–C12–C15	92.0(2)
C6–C7–C8	88.5(2)	C12–C13–C14	88.2(2)
C7–C8–C9	88.3(2)	C13–C14–C15	88.2(2)
C8–C9–C6	92.3(2)	C14–C15–C12	91.4(2)
C8–C9–N7	139.6(2)	C14–C15–N10	137.0(2)
C6–C9–N7	128.1(2)	C12–C15–N10	131.6(2)
C9–N7–C10	121.4(2)	C15–N10–C16	117.6(2)
N7–C10–N8	169.4(2)	N10–C16–N11	173.1(3)

Symmetry operations: $'\ x, 1 + y, -1 + z;\ ''\ x, -1 + y, 1 + z$.

atom (Cu1 or Cu2) is surrounded by five copper atoms belonging to other chains at distances of about 7–8 Å. Each copper is five-co-ordinated in a distorted square pyramidal mode. Three nitrogen atoms of the dien molecule and one nitrogen atom of a $[\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq}]^{2-}$ ion are in an almost square planar configuration. The co-ordination sphere is completed by another nitrogen atom of a different $[\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq}]^{2-}$ ion in the apical position. Such a structure, classical for dien complexes, has been observed in $[\mathrm{Cu(dien)(SCN)_2}]$.[27] Examination of the bond angles and lengths reveals that each anionic cyanamide ligand does not coordinate equivalently to the copper atoms. At Cu1, the structure is best described as 4 + 1 co-ordination, with four in plane bonds of normal lengths (1.957(2) to 2.031(2) Å) and the fifth one Cu1–N4 being longer (2.262(2) Å). So, the two different $[\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq}]^{2-}$ ions are not equivalent at Cu1. Cu2 is also five-co-ordinated, with four in plane bonds of normal lengths (1.968(2) to 2.024(2) Å) and the fifth one Cu2–N11′ which is longer (2.239(2) Å). Cu1 and Cu2 are lifted out of the plane of the four nitrogen atoms by distances of 0.2543(3) and 0.2718(3) Å respectively. A correlation between the longest Cu–L distance and the distance ρ between the copper atom and the other four in-plane atoms has been proposed by Hathaway.[28] This correlation is confirmed for both Cu1 and Cu2.

In the elementary unit, two different $[\textit{cis}\text{-}(\mathrm{NCN})_2\mathrm{sq}]^{2-}$ are present, one of them defined by C6C7C8C9 (labelled as ligand A), which is poorly co-ordinated to Cu1 (Cu–N4 2.262(2) Å) and strongly to Cu2 (Cu2–N8 1.968(2) Å) and the other one, defined by C12C13C14C15 (labelled as ligand B), strongly co-ordinated to Cu1 (Cu1–N5 1.957(2) Å) and poorly to Cu2″ (Cu2″–N11 2.239(2) Å). The four NCN groups of the two cyanamide ligands complex the metal with end-on nitrile-metal interactions. However, the modes of co-ordination of these groups are very different and they do not coordinate equivalently to copper atoms. For ligand A, one of the cyanamido group adopts an almost linear mode of co-ordination (Cu2–N8–C10 165.8(2)°) with an angle C9–N7–C10 of 121.4(2)° whilst the other one is more bent (Cu1–N4–C5 138.7(2)°) with an angle N4–C5–N6 of 173.6(2)°. For ligand B the Cu1–N5–C11 angle is 162.0(2)° with a N5–C11–N9 angle of 168.7(2)° and the value of Cu2″–N11–C16 is 140.0(2)° with N11–C16–N10 being 173.1(3)°. The terminal CN bond distances are also affected by complexation and are related to the mode of co-ordination. We will discuss the variations of the bond distances and angles of the NCN group in the later part of this paper.

The coplanarity of the cyanamido group with the phenyl ring is a common feature of the phenylcyanamide complexes resulting in a π-delocalized system including both the π electrons of the ring and those of the cyanamido moiety. Concerning ligands A and B, the two NCN groups deviate significantly from the ring plane. For A the NCN groups deviate on the same side of the squarate ring: the N4C5N6 group, which is the less co-ordinated, is little affected with a dihedral angle of 7(2)°; the more strongly co-ordinated N8C10N7 deviates with a dihedral angle of 15(2)°. For B, the two NCN groups deviate above and below the squarate mean plane: the more strongly co-ordinated N9C11N5 group has a dihedral angle of 19(1)°, while the other forms an angle of −10(2)°. In A and B the two cyanamido groups are also oriented away from each other as is observed in the free anion.

The C–C distances in the two squarate rings are in the range 1.410(3) to 1.505(3) Å and are indicative of a delocalized π

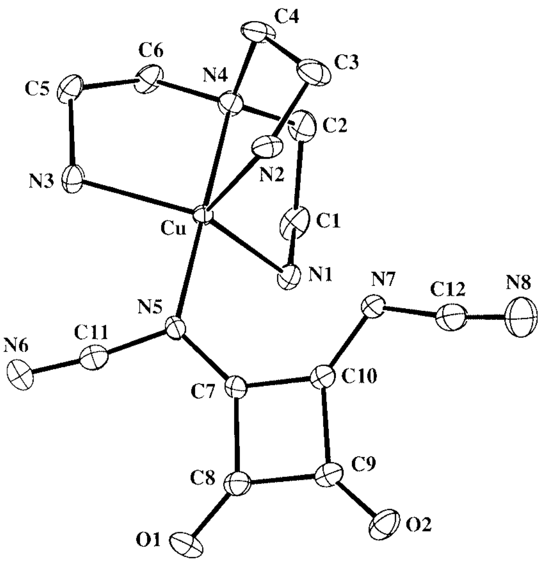


Fig. 3 ORTEP drawing of [Cu(tren)(*cis*-(NCN)$_2$sq)] **3**.

Table 4 Selected bond lengths (Å) and angles (deg) for [Cu(tren)(*cis*-(NCN)$_2$sq)] **3** with e.s.d.s in parentheses

Cu–N1	2.035(3)	Cu–N2	2.121(2)
Cu–N3	2.070(2)	Cu–N4	2.050(3)
Cu–N5	2.027(3)		
N5–C7	1.357(4)	N5–C11	1.327(4)
N7–C10	1.322(4)	N7–C12	1.323(4)
C7–C8	1.458(4)	C9–C10	1.481(4)
C8–C9	1.498(4)	C10–C7	1.422(4)
C11–N6	1.156(4)	C12–N8	1.158(5)
C8–O1	1.232(4)	C9–O2	1.224(4)
N1–Cu–N2	112.5(2)	N2–Cu–N4	84.5(1)
N1–Cu–N3	129.7(1)	N2–Cu–N5	98.8(1)
N1–Cu–N4	84.9(2)	N3–Cu–N4	84.57(9)
N1–Cu–N5	92.5(1)	N3–Cu–N5	95.3(1)
N2–Cu–N3	115.2(1)	N4–Cu–N5	176.5(2)
Cu–N5–C11	116.0(2)	Cu–N5–C7	125.3(2)
N6–C11–N5	173.4(3)	N8–C12–N7	172.8(4)
C11–N5–C7	116.6(3)	C12–N7–C10	118.3(3)
N5–C7–C8	135.1(3)	N7–C10–C9	137.0(3)
N5–C7–C10	132.8(3)	N7–C10–C7	132.2(3)
C7–C8–C9	88.8(2)	C10–C9–C8	88.2(2)
C7–C8–O1	136.2(3)	C10–C9–O2	136.1(3)
C7–C10–C9	90.9(2)	C10–C7–C8	92.1(2)
C8–C9–O2	135.7(3)	C9–C8–O1	135.0(3)

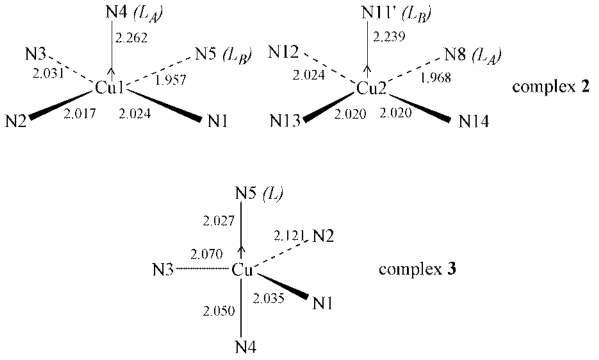


Fig. 4 The copper atom surroundings in compounds **2** and **3**.

system as observed in the squarate ion.[26] However, here, as in the free ligand, the double bond character is mainly localized on the C–C bond situated between the two NCN groups. The C–O distances are normal for a carbonyl group. As is typical for (dien)Cu^{II} complexes, the conformation of the dien ligand is such that the primary amine nitrogen atoms occupy *trans* positions in the co-ordination sphere.[27–29] The angles of dien are normal for a copper(II) complex.[30,31]

A large hydrogen bond network involves the nitrogen atoms of the dien molecules and the five unco-ordinated water molecules.

Crystal structure of [Cu(tren)(*cis*-(NCN)$_2$sq)] 3

A view of the molecule, along with the numbering scheme, is shown in Fig. 3. The crystal structure consists of neutral mononuclear molecules containing a copper(II) ion with an approximate trigonal bipyramidal co-ordination geometry. Copper is displaced by 0.1929(4) Å from the equatorial plane. This slightly distorted geometry is classical for copper(II) trigonal bipyramidal stereochemistry.[28] The tren terminal nitrogen atoms are in the equatorial positions (Cu–N distances ranging from 2.035(3) to 2.121(2) Å) and the tren central nitrogen and the amido nitrogen of the cyanamide are in the axial positions (Cu–N4 2.050(3) Å and Cu–N5 2.027(3) Å respectively). The N–Cu–N angles in the equatorial plane are close to the ideal trigonal value of 120°, ranging from 112.5(2) to 129.7(1)°. In the complex [Cu(tren)(NH$_3$)][ClO$_4$]$_2$, which presents a trigonal bipyramidal stereochemistry,[32] the two axial Cu–L distances are *ca.* 0.1 Å shorter than the three equatorial Cu–L distances, this is less obvious for **3**. The value of the axial N–Cu–N angle is very close to 180° (176.5(2)°). The Cu–N bond distances are in agreement with those of previously reported tren-containing copper(II) complexes.[4,32,33]

Concerning the ligand [*cis*-(NCN)$_2$sq]$^{2-}$, only one of the NCN groups is co-ordinated to copper. The squarate ring including oxygen atoms is almost planar and the unco-ordinated cyanamido group lies approximately in this plane (the dihedral angle between the squarate ring and N7C12N8 being 4(3)°). Concerning the co-ordinated NCN group, two points may be underlined: first the co-ordination unusually occurs *via* the amido nitrogen with angles at this atom close to 120° (116.0(2) to 125.3(2)°); furthermore, associated with this co-ordination, a large distortion is observed for the cyanamido group. While the co-ordinated amido nitrogen N5 lies in the plane of the squarate ring, a large deviation from the ideal plane is observed for the N5C11N6 group with a dihedral angle of 24(2)°. However, this loss of planarity does not affect significantly the delocalized π system: the C_{ring}–N_{amido} bond distances are 1.357(4) and 1.322(4) Å for the co-ordinated and unco-ordinated NCN groups respectively. The C–C distances in the squarate ring are normal.

The hydrogen bond network involves the nitrogen atoms N1, N2 and N3 of the tren ligand, the unco-ordinated nitrogen atoms of the nitrile groups (N8 and N6) and the oxygen atoms of the squarate group.

The copper atom surroundings in compounds **2** and **3** are presented in Fig. 4.

Discussion

Magnetism

(DCNQI)$^{2-}$ ligands have been shown to be remarkably effective for antiferromagnetic superexchange metal–metal coupling as has been evidenced in dinuclear or mixed-valence ruthenium complexes,[34] with ruthenium ions separated by approximately 13 Å. Similarly, antiferromagnetic superexchange properties have been observed in copper(II) dimers,[14] but with considerable attenuation compared to their ruthenium analogues.

Compound **1** is diamagnetic as expected. For **2** and **3**, the variation of χ_m with temperature within the 2–300 K domain is consistent with a Curie–Weiss law giving $C = 0.5119$ cm^3 K mol^{-1} and $\theta = -3.6075$ K for **2** and $C = 0.5138$ cm^3 K mol^{-1} and $\theta = -4.4033$ K for **3**. This indicates that no coupling occurs between the copper atoms in **2**.

Table 5 IR data [ν(N=C=N)] for X_2[*cis*-$(NCN)_2$sq] salts (X = Na, PPh_4 or Tl) and for complexes **1**, **2**, **3**[a]

Compound	KBr	DMSO	DMF
Na_2[*cis*-$(NCN)_2$sq]	**2163**, 2120sh[b]	2163sh, **2122**[b] 2165sh, **2125**[c]	2168sh, **2125**[b]
$[PPh_4]_2$[*cis*-$(NCN)_2$sq]	2167sh, **2120**[b]	2155sh, **2121**[b]	2158sh, **2121**[b]
Tl_2[*cis*-$(NCN)_2$sq]	**2120**[d]	2165sh, **2125**[c]	
1	**2149**[b]		2164sh, **2149**[b]
2	**2188**, **2165**, **2142**[b]		2180sh, **2149**, **2135**[b]
3	2201m, **2167**[b]		2187sh, **2147**, **2135**[b]

[a] In cm^{-1}. In bold characters: the strongest bands. Abbreviations: m, medium; sh, shoulder. [b] This work. [c] Ref. 36. [d] Ref. 18.

Electronic spectroscopy

The spectrum of Na_2[*cis*-$(NCN)_2$sq] in methanol, recorded by Kohler *et al.*, is characterized by a band at 316 nm.[35] However Lunelli *et al.*[36] report for the UV-vis absorption band in dmf values of 385 nm for the disodium salt and 323 nm for the dithallium salt. According to these authors, these two different values are characteristic of the presence in the solution of two conformers with different orientations of one of the two NCN groups, the ratio of the two conformers being dependent on the nature of the counter ion.

Our disodium salt spectrum also recorded in dmf is characterized by a π–π^* absorption at 324 nm (log $\varepsilon = 4.52$), little affected in the complexes, since it is observed at 321 (log $\varepsilon = 4.54$) and 318 nm (4.40) for **2** and **3** respectively. For **1**, the π–π^* absorptions consist of a large band between 270 and 330 nm with an ill defined maximum arising from the phenyl groups and the ligand itself. Aside from this band, the spectra of **2** and **3** show two major transitions. The low energy band at 606 nm (log $\varepsilon = 2.35$) for **2** and 682 nm (log $\varepsilon = 2.20$) for **3** is suggested to arise from a ligand field transition (d–d) by analogy with the spectra of $[Cu(bpy)_2(PhNCN)]$ complexes[13] or $[\{Cu(dien)\}_2(\mu\text{-}Cl_2dicyd)][CF_3SO_3]_2$ (Cl_2dicyd = 1,4-dicyanamido-2,5-dichlorobenzene dianion).[14] High energy bands are assigned to a π–σ^* LMCT transitions of the cyanamide–Cu^{II} chromophore: they are observed at 402 (log $\varepsilon = 3.08$) and 469 nm (2.58) for **2**, 407 (log $\varepsilon = 2.79$) and 508 nm (2.48) for **3**.

Co-ordination modes and IR

When cyanamides are used as ligands in co-ordination chemistry the problem is not straightforward. First they can react in their neutral or deprotonated forms and a number of complexes have been described with neutral cyanamides acting as ligands.[37,38] However, the most characteristic feature of cyanamide is a π-bond system extended over the three atoms (or more when the cyanamido group is linked to an unsaturated group). It results in very stable anionic forms, which may be considered as diimides. As a result the N–C–N unit is linear and the amide nitrogen surrounding is planar because there is a contribution from the amide π lone-pair electrons to the CN (nitrile) unit.

The IR spectra of cyanamides and related diimides have been discussed. Khorama first reported that disubstituted diimides have infrared absorption bands close to 2150 cm^{-1}.[39] It is now assumed that a characteristic peak in the range 2150–2100 cm^{-1} is assigned to N=C=N stretching.[40] For the dianion of phenylcyanamide, ν(N=C=N) is observed at 2102 cm^{-1}.[41] The ν(N=C=N) is also observed in this domain for the NCN derivatives of the squarate ion.

However, comparing our own results with those obtained by Lunelli and Monari,[18] the solid state spectra of [*cis*-$(NCN)_2$sq]$^{2-}$ seem largely to depend on the nature of the counter ion as evidenced by Table 5. The most reasonable explanation, postulated by these authors, is that the different spectra are due to different conformers (A, B and C), though geometry C appears unlikely. In the solid state one of the conformers (A or B) will be prevalent, the higher frequency being attributed to the higher-energy form, *i.e.* B. Owing to the small size of Na^+, the form B is predominant for this salt, but not so with the bulkier Tl^+ and $PPh_4{}^+$ salts. Lunelli *et al.*[36] have shown that these two conformers also coexist in solution with the predominant form A. Its corresponding band is observed between 2120 and 2125 cm^{-1}. Thus, we have chosen the 2120 cm^{-1} value as reference for ν(N=C=N) of free [*cis*-$(NCN)_2$sq]$^{2-}$, and compared this value with the solid state IR data of the complexes. This choice is supported by the crystal data of the three complexes in which the ligand is in A configuration.

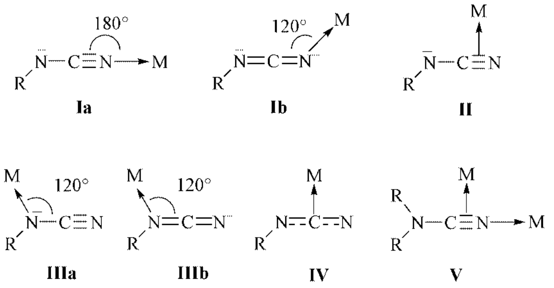
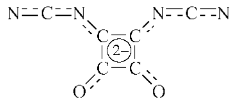
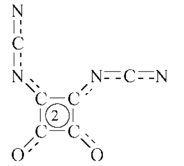


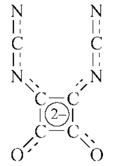
Fig. 5 Different co-ordination modes of cyanamide ligands (with the ideal angles).



A, C_{2v}



B, C_s



C, C_{2v}

Organonitriles have two potential co-ordination sites, namely the nitrile–nitrogen lone pair (end-on) and the carbon–nitrogen triple bond (side-on). The majority of the nitrile complexes involves end-on co-ordination. In most of them the M–N–C angle is close to 180°, and a small but significant shortening of the CN bond length is expected upon complexation. This is due to the σ donation from the nitrogen lone pair of the nitrile, which has some antibonding character. The C–N bond strength increase upon co-ordination is associated with the ν(CN) shift to higher frequency. However, some examples of end-on co-ordinated nitrile complexes with ν(CN) bands at lower frequencies were observed for benzonitrile and acrylonitrile complexes. In copper complexes involving dicyanomethylenesquarates as ligands we have recently observed the same phenomena.[42,43]

Co-ordination of cyanamide ligands to metal cations (Fig. 5) can occur *via* one of the two nitrogen atoms [nitrile (end-on co-ordination, forms Ia or Ib) or amido (form III)], more rarely π complexes (side-on, form II) may be obtained. As for nitriles, end-on co-ordination is characterized by a positive shift $\Delta\nu$(N=C=N) ranging from 20 to 47 cm^{-1}.[44] Some complexes with a metal atom co-ordinated to the carbon atom (form IV) have also been described.[45,46] In a molecular molybdenum dimer,[47,48] the same NCN group is bonded to two metal atoms, the ligand being side-on π-bonded to one metal and end-on to the other one (form V). Co-ordination to the amido nitrogen (form III) has been discussed by Crutchley and co-workers[49] and for such a complex a ν(N=C=N) value similar to that of free cyanamide $NCNH_2$ is expected.

The affinity of transition metal cations for co-ordination to the nitrile nitrogen atom (form Ia) may be explained by the donor properties of the nitrile group. The steric hindrance arising from bulky groups attached to the amido moiety may also prevent co-ordination to the amido nitrogen. In this case, the bond angle between the cyanamido group and the metal ion is largely determined by the two resonance structures α and β. If

$$\underset{\alpha}{R{-}N{-}C{\equiv}N} \qquad \underset{\beta}{R{-}N{=}C{=}N^-}$$

the metal is only co-ordinated to the terminal nitrogen atom *via* the nitrile lone pair (α), an ideal bond angle (M–N–C) of 180° may be expected. Co-ordination of the resonance structure β to a metal ion *via* the terminal nitrogen atom should result in an ideal bond angle of 120°. In fact, in the bonding description of the cyanamido group, the contribution from both resonance structures α and β occurs and expected co-ordination angle values lie between 120 and 180°. The linkage isomerism of the cyanamido group is best illustrated by the crystal structure of $[Cu(2,2'\text{-bipy})(2,3\text{-}Cl_2C_6H_3NCN)_2]$[13] where two non-equivalent configurations coexist and differ significantly.

Bearing in mind the large variety of cyanamide co-ordination modes, the correct ones can't be determined from IR data only.

To our knowledge, complex **1** is the first copper(I) complex of an anionic cyanamide ligand described to date. Mixed-valence copper complexes (oxidation state 1.3) have been obtained with the radical anions of DCNQI and a number of $Cu(DCNQI)_2$ have structurally been characterized (form **1a** for the ligand).[11] In **1** the ligand bonds to the metal atom in a linear mode (Cu–N1–C1 173.1(2)°). Consistent with this, a positive shift of 29 cm^{-1} is observed for ν(N=C=N) (2120 and 2149 cm^{-1} for the free ligand and the complex respectively). In the same region a band of weak intensity at 2315 cm^{-1} is attributed to ν(CN) of the co-ordinated acetonitrile molecule while the absorption band of free acetonitrile is observed at 2253 cm^{-1}.[50,52] Moreover, the bands observed around 1600 cm^{-1} exhibit also a positive shift while the carbonyl groups are not implied in the complexation.

In **2** the cyanamide ligands do not coordinate equivalently to the copper atoms. The IR spectra of this complex (in KBr pellets or in dmf solution) show multiple ν(N=C=N) bands. For all of them a positive shift is observed, illustrating the non-equivalence of the end-on bonded cyanamido groups.

In **3** the copper is uncommonly co-ordinated to the amido nitrogen atom *via* the σ lone pair and is slightly displaced from the equatorial plane towards the cyanamide ligand. A comparison between the donor properties of acetonitrile and cyanamides (end-on or amido co-ordinated) was published in 1968 by Henneike and Drago.[37] However, this study refers to non-deprotonated cyanamides where co-ordination of amido nitrogen occurs by a π lone pair with a subsequent modification of the π system, while in **3** co-ordination occurs by a σ lone pair. A number of complexes with an amido nitrogen implied in complexation are described,[53,54] but associated with an additional complexation by the nitrile group. In these circumstances the IR data (where available) cannot be compared to our results. The IR spectrum of **3** shows two ν(N=C=N) bands, at 2201 and 2167 cm^{-1} respectively. While one of the two N=C=N groups is not co-ordinated, these two bands exhibit a positive shift compared with those of the free ligand. We have attributed the most shifted band ($\Delta\nu$(N=C=N) = 81 cm^{-1}) to the amido-co-ordinated N=C=N group. For co-ordination occurring by the amido nitrogen atom the ν(N=C=N) value would be expected to be close to that of free $NCNH_2$ at 2260 cm^{-1}.[49]

Table 6 In **2**, comparison between copper–ligand bond lengths (Å) and Cu–N–C angles (°)

	Cu–N–C	Cu–N
Cu1–N5	162.0(2)	1.957(2)
Cu2–N8	165.8(2)	1.968(2)
Cu1–N4	138.7(2)	2.262(2)
Cu2–N11′	140.0(2)	2.239(2)

It has been suggested that the Cu–cyanamide bond length would be a function of the copper oxidation state.[13] However, we have observed a bond length of 2.013(3) Å in the copper(I) complex **1**, and in the range of 1.957(2) to 2.262(2) Å in **2**, implying that there is no correspondence between the oxidation state of the copper atom and the Cu–cyanamide bond length. In our opinion, independently of the metal oxidation state, a number of factors may modify the copper–ligand bond lengths. The study of some complexes which contain both three- and four-co-ordinated copper(I) has clearly revealed that, for the same oxidation state, the shortest bond lengths are observed around trigonal copper atoms, in agreement with the steric repulsion differences.[55,56] Considering complex **2**, the two different copper(II) atoms are both five-co-ordinated in a square pyramidal configuration and two different cyanamido groups are linked to each metal atom. The Cu–cyanamide bond lengths reported in Table 6 seem to be directly related to the co-ordination mode (form **1a** or **1b**) *i.e.* to the Cu–N–C angle value (form **I** being associated with the shortest bond lengths). This assertion may be supported by the tendency of orbitals with more σ character to form shorter σ bonds.[57]

Acknowledgements

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