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# Organocyanide coordination chemistry: Syntheses, structural characterisations and magnetic properties of copper (II) complexes with a di-imine/pyridine ligand

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#### Abstract

The reactions between the copper (II) salts  $[CuXL]PF_6$  (L: 2,6-[1-(2,6-diisopropylphenylimino)ethyl]pyridine) (X = Cl 1, X = Br 2) and LiTCNQ, in a DMF/water mixture, or Et<sub>3</sub>NH(TCNQ)<sub>2</sub>, in acetone, produced the new complexes [CuXL(TCNQ)] (X = Cl 3, X = Br 4). For both compounds, crystallographic studies have clearly evidenced the existence of dimeric complexes  $[{CuClL}(TCNQ)]_2$  owing to  $\pi$ - $\pi$  overlap between two adjacent TCNQ<sup>-</sup> radical anions. Compound 1 reacted with Et<sub>4</sub>N(C<sub>10</sub>N<sub>7</sub>) to afford the monouclear derivative  $[CuClL(C_{10}N_7)]$  (5), while its reaction with  $K_2C_{10}N_6$  produced the dinuclear complexe  $[(CuClL)_2(C_{10}N_6)]$  (6). The crystal structures of complexes 5 and 6 have been determined by X-ray crystallography. Magnetic studies have revealed that compound 6 displays weak antiferromagnetic interactions between the two metal centres, conversely compounds 3 and 5 exhibit purely paramagnetic behaviours.

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Keywords: Polynitrile ligands; Copper (II); Di-imine pyridine ligand; Crystal structures

## 1. Introduction

Organic polynitrile derivatives are fascinating units since, when associated with inorganic entities, they may lead to a wide variety of molecular arrangements that mostly display physical properties of significant interest in the field of magnetism and electrical conduction [1-3].

Among these compounds, the tetracyanoquinodimethane (TCNQ) derivatives (Scheme 1) have long been studied owing to their specific properties. Actually, a high electron affinity, associated with particular geometrical and electronic features (planarity of TCNQ, near planarity of TCNQ<sup>--</sup>, and presence of delocalised  $\pi$  systems), allows  $\pi$ - $\pi$  molecular interactions resulting in numerous combinations with transition metal complexes: charge transfer salts, simple and complex TCNQ salts involving bonded or non-bonded  $[(\text{TCNQ})_n]^{m--}$  units with  $n \ge m$  [4].

Another interest deals with the highly conjugated cyanocarbanions or azacyanocarbanions, synthesised from the tetracyanoethylene TCNE (Scheme 1) [5]. By reaction with inorganic fragments, these species are able

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to generate discrete or extended polymeric structures owing to a great number of nearby cyano groups unable to be related to the same metal centre; nevertheless so far only few studies have been reported [6–8].

In the course of a recent study on the reactivity of di-imine/pyridine ligand L towards copper derivatives, we reported that  $[CuXL]^+$  units can be bridged with anions such as the copper (I) anion  $Cu_2Br_4^{2-}$  to afford polynuclear structures [9]. We became thus interested in studying the ability of organic polynitrile anions to bridge such inorganic ion. In this paper, we discuss the crystalline structures and the magnetic properties of three new copper (II) derivatives, including the 2,6-[1-(2,6-diisopropylphenylimino)ethyl]pyridine ligand L (Scheme 2).

# 2. Experimental

All reactions were performed in Schlenk tubes under a dry dioxygen-free dinitrogen atmosphere. Solvents were distilled using standard techniques and were thoroughly deoxygenated before use. The starting materials, compound 1 [9], LiTCNQ and  $Et_3NH(TCNQ)_2$  [10],  $Et_4N(C_{10}N_7)$  and  $K_2(C_{10}N_6)$  [5], were prepared as described in the literature. Elemental analyses were performed by the "Service Central d'Analyses du CNRS", Vernaison, France. IR spectra were obtained with a Nicolet Nexus spectrometer (KBr pellets).

# 2.1. $[(CuClL)_2(TCNQ)_2]$ (3)

Method 1: Compound 1 [CuClL]PF<sub>6</sub> (330 mg, 0.43 mmol) was dissolved in dimethylformamide (30 mL) to afford a brown solution. An aqueous solution of LiTCNQ (91 mg, 0.43 mmol in 30 mL of water) was then added and the mixture was stirred for 30 mn. A green precipitate was formed, which was then filtered off and washed with pentane (2 × 30 mL). Recrystallisation from acetone at -20 °C gave a green crystalline product. Yield: 337 mg (30%).

*Method 2:* A mixture of complex 1 [CuClL]PF<sub>6</sub> (530 mg, 0.73 mmol) and (Et<sub>3</sub>NH)<sub>2</sub>TCNQ (370 mg, 0.73 mmol) was stirred in acetone (50 mL) at room temperature for 12 h. The dark solution was filtered, concentrated under reduced pressure and kept at  $-20 \,^{\circ}$ C for 7 days. After filtration, green crystals were isolated. Yield: 526 mg (80%). *Anal.* Calc. for C<sub>45</sub>H<sub>47</sub>ClCu-N<sub>7</sub>·2(CH<sub>3</sub>)<sub>2</sub>CO: C, 68.0; H, 6.6; N, 10.9. Found: C, 67.6; H, 6.4; N, 10.9%. IR (KBr, cm<sup>-1</sup>): 2963m, 2927m and 2868m ( $\nu_{CH}$ ); 2187s and 2153m ( $\nu_{CN}$ ); 1618w and 1581m ( $\nu_{CN}$  imine); 827m ( $\delta_{CH}$ ).

# 2.2. $[(CuBrL)_2(TCNQ)_2]$ (4)

Compound **4** was prepared in a similar manner according to method 2, but all samples were slightly contamined by co-crystallisation with TCNQ. Yield: 488 mg (75%). *Anal.* Calc. for C<sub>45</sub>H<sub>47</sub>BrCuN<sub>7</sub>·0. 3(TCNQ): C, 65.5; H, 5.5; N, 12.9. Found: C, 64.7 H, 5.9; N, 13.6%. IR (KBr, cm<sup>-1</sup>): 2963m, 2928m and 2868m ( $v_{CH}$ ); 2187s and 2152m ( $v_{CN}$ ); 1617w and 1581m ( $v_{CN}$  imine); 827m ( $\delta_{CH}$ ).



# 2.3. $[CuClL(C_{10}N_7)]$ (5)

A stoichiometric mixture of compound **1** [CuClL]PF<sub>6</sub> (200 mg, 0.28 mmol) and (Et<sub>4</sub>N)(C<sub>10</sub>N<sub>7</sub>) (96 mg, 0.28 mmol) was refluxed in acetone (60 mL) for 24 h. After cooling to r.t., the orange solution was filtered off, reduced to dryness under low pressure, extracted with methylisobutylketone (20 mL) and then left at low temperature ( $-30 \,^{\circ}$ C) for 4 days. Light orange crystals were collected. Yield: 189 mg (75%). *Anal.* Calc. for C<sub>43</sub>H<sub>43</sub>ClCuN<sub>10</sub>·C<sub>6</sub>H<sub>12</sub>O: C, 64.5; H, 6.2; N, 15.6. Found: C, 64.5; H, 6.2; N, 15.2%. IR (KBr, cm<sup>-1</sup>): 2966m, 2928m and 2869m ( $v_{CH}$ ); 2217m ( $v_{CN}$ ); 1588m ( $v_{C=N}$ ).

# 2.4. $[{CuClL}_2(C_{10}N_6)]$ (6)

A mixture of compound 1 [CuClL]PF<sub>6</sub> (242 mg, 0.33 mmol) and K<sub>2</sub>(C<sub>10</sub>N<sub>6</sub>) (94 mg, 0.33 mmol) in acetone (60 mL) was kept under stirring at room temperature for 36 h. The mixture was then filtered and the resulting solution was reduced to dryness under low pressure, extracted with acetone or methylisobutylketone (20 mL) and then left at low temperature (-30 °C) for 4 days. Yellow crystals were collected. Yield: 330 mg (60%). *Anal.* Calc. for C<sub>76</sub>H<sub>86</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>12</sub>·3C<sub>3</sub>H<sub>6</sub>O: C, 66.3; H, 6.8; N, 10.9. Found: C, 65.9; H, 7.1; N, 10.1%. IR (KBr, cm<sup>-1</sup>): 2963m, 2928m and 2869m ( $v_{CH}$ ); 2185vs, 2176m and 2128w ( $v_{CN}$ ); 1707 ( $v_{C=O}$ ); 1619 and 1590m ( $v_{C=N}$ ).

| Table 1 |      |     |           |            |       |       |         |       |   |
|---------|------|-----|-----------|------------|-------|-------|---------|-------|---|
| Crystal | data | and | structure | refinement | for c | compo | unds 3, | 5 and | 6 |

# 2.5. X-ray structures

Single crystals of 3, 5 and 6 suitable for X-ray studies were mounted on a Nonius-Kappa CCD diffractometer. The crystal of 5 was of rather lower quality. The unit cell determinations and data collections were carried out with Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) at low temperature. The measured intensities were reduced with DENZO program [11]. The structures were solved via direct methods with sHELXs97 and further refined with full-matrix least-squares methods (SHELXL97) based on  $|F^2|$  [12]. Solvent molecules were found in all three structures: 1.2 of acetone per copper in 3, 1 of methylisobutylketone per copper atom in 5 and 3 of this last solvent per two copper atoms in 6. All non-hydrogen atoms, except those of a disordered over the symmetry centre acetone molecule of occupancy 0.2 in 3, were refined with anisotropic thermal parameters. The hydrogen atoms bound to anisotropically refined atoms were included in calculated positions and refined with a riding model, while those of highly disordered solvent molecule were neglected. Crystallographic and refinement data are gathered in Table 1.

# 2.6. Magnetic measurements

ESR spectra were run on a Bruker Elexys spectrometer (X-band). The solid state magnetic susceptibility measurements were carried out on powder samples using either a Gouy balance Johnson Matthey at room

|   | 3                              | 5                              | 6   |
|---|--------------------------------|--------------------------------|---|
| Empirical formula                           | C48.60H54.20ClCuN7O1.20        | C49H55ClCuN10O                 | C <sub>94</sub> H <sub>122</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>12</sub> O <sub>3</sub> |
| M   | 854.58                         | 899.02                         | 1666.02   |
| Temperature (K)                             | 200(2)                         | 110                            | 120   |
| Crystal system, space group                 | triclinic, $P\overline{1}$     | triclinic, $P\overline{1}$     | monoclinic, $P2_1/n$  |
| a (Å)                                       | 9.1906(2)                      | 10.0001(4)                     | 16.7911(4)  |
| b (Å)                                       | 13.7655(4)                     | 11.2441(5)                     | 32.0245(8)  |
| c (Å)                                       | 19.1629(7)                     | 21.6821(11)                    | 17.0989(4)  |
| α (°)                                       | 95.8700(10)                    | 85.951(2)                      |   |
| β (°)                                       | 92.2760(10)                    | 82.782(2)                      | 92.178(2)   |
| γ (°)                                       | 103.589(2)                     | 88.999(3)                      |   |
| $V(\text{\AA}^3)$                           | 2339.04(12)                    | 2412.53(19)                    | 9187.9(4)   |
| Z   | 2                              | 2                              | 4   |
| $D_{\text{calc}}$ (Mg m <sup>-3</sup> )     | 1.213                          | 1.238                          | 1.204   |
| Absorption coefficient $(mm^{-1})$          | 0.567                          | 0.554                          | 0.575   |
| F(000)                                      | 901                            | 946                            | 3544  |
| Crystal size (mm <sup>-3</sup> )            | $0.25 \times 0.20 \times 0.03$ | $0.25 \times 0.20 \times 0.10$ | $0.25 \times 0.20 \times 0.05$  |
| $\theta$ range (°) for collection           | 2.43-30.46                     | 2.72-30.66                     | 1.018-30.508  |
| hkl/ranges                                  | $-13 + 12, \pm 19, -23 + 26$   | $-14 + 13, \pm 15, -30 + 28$   | $\pm 19, -34 + 29, \pm 19$  |
| Reflections collected/unique $(R_{int})$    | 17841/11894 (0.1020)           | 16867/11571/7344 (0.404)       | 19215/11974/7929 (0.0452)   |
| Data/restraints/parameters                  | 11894/0/529                    | 11 571/0/560                   | 11974/0/1018  |
| Final <i>R</i> indices $[I > 2\sigma(I)]$   | $R_1 = 0.0740, wR_2 = 0.1327$  | 0.0599, 0.1787                 | 0.0592, 0.1078  |
| R indices (all data)                        | $R_1 = 0.1620, wR_2 = 0.1669$  | 0.1106, 0.2359                 | 0.1341, 0.1583  |
| Goodness-of-fit on $F^2$                    | 1.023                          | 0.795                          | 1.038   |
| Largest difference peak, hole (e $Å^{-3}$ ) | 0.766, -0.465                  | 0.546, -0.792                  | 1.096, -0.591   |

temperature or commercial SQUID magnetometers from Quantum Design from 2 to 300 K. Magnetic studies for compound **6** were carried out on powder samples at 0.1 T after field cooling, in the temperature range 2– 300 K, with a MPMS-XL SQUID magnetometer from Quantum Design. The susceptibility was corrected for the sample holder and the diamagnetic contributions of all atoms Isothermal magnetisation measurements were performed at K with magnetic fields of up to 5 T.

The susceptibilities were corrected for the intrinsic diamagnetism of the sample container.

#### 3. Results and discussion

#### 3.1. Syntheses and general characterisation

The reactions of the salts [CuXL]PF<sub>6</sub> (X = Cl 1, X = Br 2) with LiTCNQ in DMF/water mixtures at room temperature afforded after recrystallisation in acetone the new 1:1 derivatives [CuXL(TCNQ)] (X = Cl 3, X = Br 4) in low yields. Surprisingly, similar reactions completed with a slight excess of the TCNQ mixedvalence salt Et<sub>3</sub>NH(TCNQ)<sub>2</sub> in acetone at room temperature provided compounds 3 and 4 in better yields and not, as expected, the 1:2 TCNQ mixed-valence salts [CuXL](TCNQ)<sub>2</sub> (Scheme 2).

Examination of the reactions of the azacyanocarbanions (Scheme 1) towards compound 1 evidenced their reactivity, but several difficulties were encountered for separation and purification precluding the full-characterisation of new derivatives, except in the case of the  $C_{10}N_7^{-}$  and  $C_{10}N_6^{2-}$  anions (Scheme 2).

Hence, reaction of **1** with  $Et_4N(C_{10}N_7)$  allowed the formation of the well-defined derivative **5** for which the elemental analysis is in good agreement with the formula [CuClL( $C_{10}N_7$ )]. On the contrary, the reaction of  $K_2C_{10}N_6$  with compound **1** led to the new compound **6** for which the elemental analyses support a 2:1 copper:organic anion ratio, and consequently the  $Cu_2Cl_2L_2(C_{10}N_6)$  formula.

The IR spectra of compounds **3–6** clearly exhibit the usual absorption bands of the corresponding polynitrile ligand and the coordinated di-imine/pyridine ligand. For the latter, and as previously noticed for parent compounds, the  $vCN_{imine}$  position attests that the di-imine/ pyridine ligand acts according to its classical terdentate coordination mode and not with its unusual bidentate mode [13].

Concerning the TCNQ unit of **3** and **4**, previous studies show that IR spectroscopy can be used as a diagnostic tool to estimate the charge of this unit. Significant decreases of the wave numbers are observed for the vCN and  $\delta$ CH vibrations when passing from TCNQ (2225 and 850 cm<sup>-1</sup>, respectively) to TCNQ<sup>-</sup> (2180, 2150 and 825 cm<sup>-1</sup>, respectively) [4]. The corresponding

wave numbers found for 3 and 4 (see Section 2) clearly attest the presence of TCNQ<sup>-</sup> anions in these compounds.

The IR spectra of complexes **5** and **6** also exhibit absorption bands in the range 2220–2120 cm<sup>-1</sup> assigned to vCN vibrations (see Section 2). The positions of these bands are slightly shifted with respect to those of the corresponding anion (2218 and 2202 cm<sup>-1</sup> in (Et<sub>4</sub>N)C<sub>10</sub>N<sub>7</sub>; [7] 2191, 2174 and 2121 cm<sup>-1</sup> in K<sub>2</sub>C<sub>10</sub>N<sub>6</sub> [8]), suggesting the coordination of the polynitrile anions or at least the existence of some bonding interactions between these anions and the inorganic fragment.

# 3.2. Crystal structures

Compounds **3** and **5** crystallise in the triclinic group  $P\overline{1}$ ; each unit cell contains two asymmetric units consistent with one copper (II) cation  $[CuClL]^+$ , one nitrile entity (TCNQ in **3**,  $C_{10}N_7^-$  in **5**) and molecules of solvent of crystallisation (1.2 molecule of acetone in **3**, 1 molecule of methylisobutylketone in **5**). Compound **6** crystallises in the monoclinic space group  $P2_1/n$ ; the asymmetric unit contains one dinuclear unit [{CuClL}<sub>2</sub>(C<sub>10</sub>N<sub>6</sub>)] and three molecules of solvent (methylisobutylketone).

#### 3.2.1. Copper coordination and di-imine/pyridine ligand

For the three compounds, within the [CuClL] unit, the copper atom is surrounded by one chlorine atom and three nitrogen atoms from the di-imine/pyridine terdentate ligand defining an essentially square planar geometry (Figs. 1-3). However, some distortions of the co-ordination polyhedron, with respect to the square, are observed (Table 2): (i) the bond angle values around the metal atom deviate from the ideal values (N-Cu-N from 77.86(18)° to 78.96(10)°, N–Cu–X from  $98.23(13)^{\circ}$  to  $102.01(12)^{\circ}$ ), due to the usual bite of the terdentate ligand, and (ii) the N<sub>3</sub>Cl tetra-atomic systems are not exactly planar but exhibit slight butterfly-like deformations. The Cu-N metal-ligand bond lengths are usual with Cu-N<sub>imine</sub> bond lengths (from 2.066(3) to 2.097(4) Å) somewhat longer than the Cu– $N_{pv}$  bond lengths (from 1.930(4) to 1.943(3) Å) and in good agreement with those previously reported. The Cu-Cl bond lengths distances also agree with previous literature values [9,14].

In fact, in the three compounds, a short contact between the copper centre and one nitrogen atom of a polynitrile unit allows the square-planar copper (II) to extend its co-ordination number up to five. The nitrogen atom occupies the apical position at 2.463(3) Å from the copper atom in **3** and at 2.335(3) Å in **5**. These bond lengths traduce moderate interactions with respect to those previously observed in quite a similar compound [Cu<sub>2</sub>L<sub>1</sub>(TCNQ)<sub>2</sub>] (2.378(8) Å) [15] or in the pseu-



Fig. 1. ORTEP representation of the asymmetric unit and atoms labelling in compound 3.

do-octahedral derivative  $[Cu(L_2)_2(TCNQ)_2]$  (Cu–N 2.442(5) Å); [16] these interactions are also clearly evidenced by the elevation of the copper atom above the N<sub>3</sub>Cl mean plane toward the apex (0.158(2) Å in **3** and 0.145(2) Å in **5**).

In **6**, it is worthy of note that the apical Cu–N bond lengths are much shorter (Cu···N 2.197(5) and 2.180(5) Å), indicating that in this molecular complex the  $C_{10}N_6^{2-}$  anion acts as a strongly bonded bridging li-



Fig. 2. ORTEP representation of the asymmetric unit and atoms labelling in compound **5**.

gand between two metallic fragments. The intradimer copper-copper distance is quite long (10.898 Å).

At last, concerning the di-imine pyridine ligands, a careful examination of the bond lengths, including those of the  $C_{py}$ - $C_{imine}$  and even the  $C_{imine}$ -CH<sub>3</sub> bonds (Table 2), clearly indicates a high  $\pi$  electronic delocalisation within these ligands.

# 3.2.2. Polynitrile unit structures

In compound 3, the TCNQ species exhibits its usual features: the overall shape and size parameters are close to those reported for RbTCNQ (Table 3) [17,18]. The estimated charge  $\rho = -0.96$ , calculated from the Kistenmacher's relation, corroborates in this compound the existence of anionic TCNQ units [19].

Furthermore, the TCNQ entities form isolated centrosymmetric dimeric anions  $[(TCNQ)_2]^{2-}$  according to a usual ring-ring (R–R) stack characterised by a transversal slipping of ca. 1.2 Å and an interplanar distance of 3.26 Å (Fig. 1). This latter distance is slightly longer than the distance observed for  $[{Fe(Cp)_2}_2](TCNQ)_2$ (3.147 Å) [20] or for  $[Cu_2L_1(TCNQ)_2]$  (3.15 Å) [15] but in the same range as distances observed in the compounds  $[M(L_3)_2](TCNQ)_2$  (M=Ni, Cu) (3.258 Å) [21] and { $[MoO(L_4)_3](TCNQ)_2$  (3.28 Å) [22]. The structure of **3** can therefore be described as an arrangement of  $[{CuClL}(TCNQ)_2$  dimers separated, in the crystal, by solvent molecules (acetone).

In addition, the powder X-ray diffraction patterns of **3** and **4** are similar, indicating that both compounds are isostructural.

In compound 5, the polynitrile ligand is built on a central nitrogen atom N(4), for which NC bond lengths (1.338(5) and 1.341(4) Å) and CNC angle value



Fig. 3. ORTEP representation of the asymmetric unit and atoms labelling in compound 6.

Table 2 Bond distances (Å) and angles (°) in the (CuClL) units for compounds  $3,\,5$  and 6

|       | 3   |   | 5                        |           | 6          |           |            |           |
|-------|---|---|--------------------------|-----------|------------|-----------|------------|-----------|
| Си с  | o-ordination  |   |                          |           |            |           |            |           |
| а     | 1.939(2)  |   | 1.943(3)                 |           | 1.935(4)   |           | 1.930(4)   |           |
| b     | 2.066(3)  | 2.072(2)  | 2.081(3)                 | 2.079(3)  | 2.097(4)   | 2.087(4)  | 2.093(4)   | 2.089(4)  |
| с     | 2.1705(9)   |   | 2.1953(9)                |           | 2.1927(13) |           | 2.1956(14) |           |
| α     | 78.96(10)   | 78.65(10)   | 78.48(11)                | 78.43(11) | 78.47(16)  | 78.23(16) | 78.77(19)  | 77.86(18) |
| β     | 101.24(8)   | 99.88(7)  | 101.02(8)                | 100.70(8) | 100.06(12) | 99.74(12) | 102.01(12) | 98.23(13) |
| L lig | and   |   |                          |           |            |           |            |           |
| d     | 1.340(4)  | 1.325(4)  | 1.337(4)                 | 1.332(4)  | 1.336(6)   | 1.336(6)  | 1.333(7)   | 1.343(7)  |
| е     | 1.485(4)  | 1.498(4)  | 1.495(6)                 | 1.485(5)  | 1.489(7)   | 1.477(7)  | 1.490(8)   | 1.476(8)  |
| f     | 1.294(4)  | 1.290(4)  | 1.295(4)                 | 1.285(4)  | 1.293(6)   | 1.293(6)  | 1.303(7)   | 1.284(6)  |
| g     | 1.487(4)  | 1.484(5)  | 1.496(4)                 | 1.493(4)  | 1.492(7)   | 1.483(7)  | 1.485(8)   | 1.489(7)  |
| ĥ     | 1.436(4)  | 1.452(4)  | 1.441(4)                 | 1.454(4)  | 1.453(6)   | 1.452(6)  | 1.442(7)   | 1.454(7)  |
| χ     | 118.1(2)  | 118.48(19)  | 119.3(2)                 | 118.4(2)  | 119.0(3)   | 118.4(3)  | 118.9(4)   | 119.5(4)  |
| δ     | 112.1(3)  | 112.4(3)  | 114.7(2)                 | 114.3(2)  | 114.7(3)   | 113.9(3)  | 113.5(4)   | 115.3(4)  |
|       | c $g$ $e$ $f$ $e$ $f$ $e$ $f$ $e$ $f$ $e$ $f$ $f$ $e$ $f$ | $\begin{array}{c} C \\ \delta \\ \chi \\ a \\ c \\ C$ | C<br>N <sub>3</sub><br>C |           |            |           |            |           |

(123.4(3)°) deeply argue in favour of a sp<sup>2</sup> hybridisation, and two essentially planar (CN)<sub>2</sub>C=C(CN) sub-units (Fig. 2, Table 4) [23]. However, the C<sub>10</sub>N<sub>7</sub> unit, which usually is essentially planar, deviates significantly from the planarity since a torsion angle of ca. 33° is observed between the two wings. It is likely that this torsion significantly reduces the repulsion between the two nitrile groups of the central (NC)CNC(CN) unit and allows a lowering of the central CNC angle (123.4° versus 128.3° and 129.2° for (Et<sub>4</sub>N)(C<sub>10</sub>N<sub>7</sub>) and Ag(C<sub>10</sub>N<sub>7</sub>), respectively) [7]. This deviation from the planarity does not preclude an important  $\pi$ -electronic delocalisation as shown by the carbon–carbon bond lengths, which are all in the range 1.386(5)–1.464(6) Å (Table 3).

Conversely in compound **5**, the monodentate  $C_{10}N_7^-$  ligands do not form any stack and in fact each complex must be considered as an isolated entity. Actually, the distance between two mean-plane anions is about 4 Å long, the shortest distance between the central nitrogen atoms (N4) is 6.803 Å long for anions belonging to two adjacent cells, 8.320 Å long for anions within a unit cell; these observations preclude any short contacts.

Table 3 Comparison of some bond lengths (Å) and estimation of the charge in the TCNQ moiety

| Compound | Reference | а        | b        | с        | d        | е        | b-c   | c–d    | c/(b+d) | (a+c)/(b+d) | $\rho^{\mathbf{a}}$ |
|----------|-----------|----------|----------|----------|----------|----------|-------|--------|---------|-------------|---------------------|
| 3        | this work | 1.370(5) | 1.420(5) | 1.417(5) | 1.418(5) | 1.151(5) | 0.003 | -0.001 | 0.499   | 0.982       | -0.96               |
| RbTCNQ   | [28]      | 1.373(1) | 1.423(3) | 1.420(1) | 1.416(8) | 1.153(7) | 0.003 | 0.004  | 0.500   | 0.984       | -1                  |
| TCNQ     | [17]      | 1.346(3) | 1.448(4) | 1.374(3) | 1.441(4) | 1.140(1) | 0.074 | -0.067 | 0.476   | 0.942       | 0                   |
| b c d d  |           |          |          |          |          |          |       |        |         |             |                     |

<sup>a</sup> Estimation of the charge  $\rho$  of the TCNQ unit using Kistenmacher relation [19]  $\rho = A[cl(b+d)] + B$  with A = -41.667 and B = 19.833.

Table 4 Selected bond distances (Å) and bond angles (°) of the  $C_{10}N_7^{-}$  units in compound 5,  $(Et_4N)(C_{10}N_7)$  and  $Ag(C_{10}N_7)$ 

|                | Compound 5         | $(Et_4N)(C_{10}N_7)$ [7]  | $Ag(C_{10}N_7)$ [7] |
|----------------|--------------------|---|---------------------|
| a              | 1.338(5), 1.341(4) | 1.317(4), 1.334(4)  | 1.33(1), 1.34(1)    |
| b              | 1.386(5), 1.389(5) | 1.361(4), 1.382(5)  | 1.36(1), 1.37(1)    |
| c <sup>a</sup> | 1.416(5)-1.464(6)  | 1.419(6)-1.460(5)   | 1.43(2)-1.47(2)     |
| da             | 1.141(5)-1.154(5)  | 1.134(4)-1.137(4)   | 1.13(1) - 1.14(1)   |
| α              | 123.4(3)           | 128.3(3)  | 129.2(9)            |
| β              | 123.6(3)           | 124.8(4)  | 124(1)              |
| γ              | 114.2(3)           | 116.2(4)  | 118(1)              |
| δ              | 122.1(3)           | 119.0(3)  | 118(1)              |
|                | NC b<br>c<br>d     | $ \begin{array}{c} CN \\ \alpha \\ a \\ a \\ \delta \\ CN \end{array} \begin{array}{c} \gamma \\ CN \\ CN \end{array} $ |                     |

<sup>a</sup> Lower to upper values.

In compound 6, as clearly described above, the  $C_{10}N_6^{2-}$  ligand, despite its six nitrile groups potentially bridging, shows only a µ2-bridging coordination mode (Fig. 3). The central fragment (C34–C37) is essentially planar within a maximum deviation of 0.02 Å from the corresponding mean plane and, associated with other structural features (for each of these four C atoms, sum of the three bond angles reaches 360°), is in agreement with an sp<sup>2</sup> hybridisation of the four central carbon atoms. However, the  $C_{10}N_6^{2-}$  ligand is not planar but has a propeller-shaped geometry of approximate  $D_3$  symmetry, since the axis passing through the central carbon atom (C35) appears as a pseudo threefold axis. The tilt angles between the mean central plane and the different  $C(CN)_2$  wing planes have an average value of 28.9°. This propeller-shaped geometry, previously reported for the  $C_{10}N_6^{2-}$  unit, decreases the CN···NC steric interactions between the nitrile groups of adjacent  $C(CN)_2$  wings (ca. 50 kJ mol<sup>-1</sup>) without a strong reduction (less than 9%) of the  $\pi$ -overlap [24]; it does not preclude an intense electronic delocalisation all over the ligand, as indicated by all CC bond lengths in the range 1.408(7)-1.435(8) Å (Table 5).

Finally, for the three compounds, the cyanide  $C_{sp}$ -N bond lengths, falling in the range 1.140–1.162 Å, correspond to typical values for  $C_{sp}$ -N<sub>sp</sub> bonds in such polynitrile compounds [20].

#### 3.3. Magnetic measurements

For all the compounds, EPR spectra, recorded on powdered and on solution samples at low and room temperatures, display the usual features for copper (II) cations in an axial environment (Table 6). Actually, the solution spectra show the axial pattern characteristic of square pyramidal copper (II). The parallel signals appear as quartets owing to the hyperfine coupling with the copper (I = 3/2) nucleus, the coupling constant values ( $A_{\parallel}$ ) being in the same order than those usually observed for copper (II) in similar environment. Table 5 Selected bond lengths (Å) and bond angles (°) of the  $C_{10}N_6^{2-}$  units in compound **6**,  $Ca(C_{10}N_6)(H_2O)_6$  and  $Cu(C_{10}N_6)(H_2O)_2$ 

|                      | Compound 6                      | Ca(C <sub>10</sub> N <sub>6</sub> )(H <sub>2</sub> O) <sub>6</sub> [24] | Cu(C <sub>10</sub> N <sub>6</sub> )(H <sub>2</sub> O) <sub>2</sub> [8] |
|----------------------|---------------------------------|---|--|
| a <sup>c</sup>       | 1.416(6)-1.429(7)               | 1.424   | 1.410(11)-1.425(6)   |
| b <sup>c</sup>       | 1.408(7)-1.435(8)               | 1.416, 1.426  | 1.391(7)-1.409(8)  |
| c <sup>c</sup>       | 1.140(6)-1.162(6)               | 1.15, 1.17  | 1.139(7)-1.141(7)  |
| $M{\cdots}N$         | <sup>a</sup> 2.180(5), 2.197(5) |   | <sup>b</sup> 1.977(5), 2.052(6)  |
| α <sup>c</sup>       | 119.1(4)-120.7(4)               | 120   | 119.9(3), 120.3(7)   |
| $\beta^{c}$          | 121.4(4)-123.1(5)               | 121.9, 122.6  | 122.3(5)-124.1(5)  |
| γ°                   | 114.2(4)-117.0(4)               | 115.5   | 113.5(5), 114.2(7)   |
| Tilt angle (average) | 28.9                            | 24  | 26.9   |
|                      |                                 |   |  |

<sup>a</sup> (4 + 1) coordination.

<sup>b</sup> (4+2) coordination.

<sup>c</sup> Lower to upper values.

Furthermore, for **3** and **4**, a supplementary signal at g = 2.004 is undoubtedly ascribable to the organic radical TCNQ<sup>--</sup>, traducing the dissociation of both complexes in solution. Conversely, on their powdered sample spectra, only one anisotropic signal, characteristic of an axial copper (II) atom, is observed. It is worthy to note that the narrow signal attributable to the organic radical TCNQ<sup>--</sup> is no more detected as it is often observed in the case of similar dimerised [(TCNQ)<sub>2</sub>]<sup>2-</sup> salts [25]. This fully agrees with the magnetic measurements.

At last, considering compound 6, the room and low temperature solution spectra exhibit similar patterns, suggesting for this derivative a discrete dimeric molecular structure even in solution.

The solid state magnetic susceptibility measurements were performed on compounds **3**, **5** and **6** within the 2-300 K temperature range.

The magnetic susceptibilities for compounds 3 and 5 obey a Curie law whose characteristics are given in Table 5. For 3, the magnetic moment  $(2.53 \mu_B)$  is in good agreement with two independent paramagnetic

copper (II) cations bridged with a diamagnetic  $[(\text{TCNQ})_2]^{2-}$  dimer (S = 0) according to the structural features, while for compound **5** the magnetic moment (1.81  $\mu_B$ ) corresponds to one isolated copper (II) ion.

Compound **6** shows at room temperature a  $\chi_m T$  product of 0.76 emu K mol<sup>-1</sup> that remains constant when decreasing temperature down to ca. 50 K. Below this temperature, the  $\chi_m T$  product slowly decreases to reach a value of 0.70 emu K mol<sup>-1</sup> at 2 K (Fig. 4). The room temperature  $\chi_m T$  value corresponds to the expected value for two copper (II) ions: 0.75 emu K mol<sup>-1</sup> for g = 2, and the smooth decrease at low temperatures indicates the presence of very weak antiferromagnetic interactions between the two Cu(II) centres.

From the structural data that show a dimeric structure in this compound, we have fitted the magnetic behaviour to the classical dimer model:

$$\chi_{\rm m}T = (3 * g^2/8) * (1/(3 + \exp(-2 * J/k_{\rm B} * T))),$$

| Table 6  |     |     |      |     |           |    |   |     |   |
|----------|-----|-----|------|-----|-----------|----|---|-----|---|
| Magnetic | and | ESR | data | for | complexes | 3, | 5 | and | 6 |

| Compound | $C (\text{emu}^3 \text{ K mol}^{-1})$ | <i>J</i> (K) | $\mu$ ( $\mu_{\rm B}$ ) | $g^{\mathrm{a}}$ | $g_{\parallel}{}^{\mathrm{b}} A_{\parallel}{}^{\mathrm{c}}$ | $g_{\perp}{}^{\mathrm{b}}$ |
|----------|---------------------------------------|--------------|-------------------------|------------------|---|----------------------------|
| 3        | 0.80                                  | 0            | 2.53                    | 2.057            | 2.153 (129)   | 2.057                      |
| 5        | 0.41                                  | 0            | 1.81                    | 2.058            | 2.235 (130)   | 2.061                      |
| 6        | 0.76                                  | -0.267       | 2.74                    | 2.093            | 2.239 (127)   | 2.081                      |

<sup>a</sup> Powder ESR spectra at 290 K.

<sup>b</sup> Frozen solution samples (acetone, 140 K).

<sup>c</sup> In 10<sup>-4</sup> T.



Fig. 4. Thermal variation of the  $\chi_m T$  product of 6. Solid line shows the best fit to a dimer model (see text).

where J is the intradimer exchange coupling. A very good fit over the whole temperature range (2–300 K) is obtained with g = 2.0054(3) and  $J/k_{\rm B} = -0.267(3)$  K (-0.185(2) cm<sup>-1</sup>) (solid line in Fig. 4). Note that this g value is slightly smaller than the one obtained from the EPR spectra, suggesting the presence of a very small amount of diamagnetic impurity in the sample that reduces the molar susceptibility but does not affect the EPR spectra. As expected, the intradimer magnetic coupling through the C<sub>10</sub>N<sub>6</sub> bridge is antiferromagnetic and very weak with a coupling constant similar to those obtained on other similar dimers connected through this ligand [26].

A confirmation of the spin ground state and of the presence of a weak intradimer antiferromagnetic interaction comes from the isothermal magnetisation at low temperature (Fig. 5) that can be very well reproduced with the sum of two Brillouin functions for a S = 1/2spin ground state with a very weak antiferromagnetic interaction (solid line in Fig. 5).



Fig. 5. Isothermal magnetisation of 6 at 2 K. Solid line shows the best fit to the sum of two S = 1/2 Brillouin functions with a weak antiferromagnetic interaction (see text).

# 4. Concluding remarks

These results clearly emphasise that new examples, where the polynitrile anions act as good ligands bring about magnetic interactions between metallic centres. Actually, despite a quite long Cu–Cu distance, the dinuclear complex [(CuClL)<sub>2</sub>(C<sub>10</sub>N<sub>6</sub>)] exhibits weak antiferromagnetic interactions. This is not surprising since strong magnetic couplings have recently been predicted between paramagnetic metal cations through very long bridging ligands such as dicyanoamidobenzene or analogues at distances as long as 25 Å [27]. In the aim to synthesise compounds exhibiting stronger magnetic interactions, further works are in progress with other di-imine/pyridine transition metal complexes.

#### 5. Supplementary material

CCDC Nos. 256226 (for 3), 256227 (for 5) and 256228 (for 6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdcca.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

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