Magnetic and optical characterization of one-dimensional isostructural σ-bonded tetracyanoquinodimethanido complexes of nickel(II) and copper(II)†

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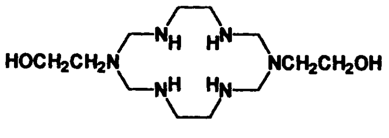
The complex $[CuL(tcnq)_2]$ [L = 3,10-bis(2-hydroxyethyl-1,3,5,8,10,12-hexaazacyclotetradecane); tcnq = 7,7,8,8-tetracyanoquinodimethane] has been prepared and crystallographically characterized. Its structure consists of linear chains of alternating copper–macrocycle and tetracyanoquinodimethanide dimers σ bonded to the copper atoms through a nitrile group. The compound is an insulator. The magnetic properties of both the copper and corresponding nickel compounds are the sums of the contributions arising from the transition-metal ion in octahedral symmetry and of $(tcnq)_2{}^{2-}$ dimers. The magnetic data were fitted by a model which accounts for contributions from independent Curie spins for the cation and a thermally activated triplet state for the dimerized anions. No magnetic interactions between the metal ion and tcnq's have been observed, even at low temperatures.

In charge-transfer compounds of transition-metal complexes of 7,7,8,8-tetracyanoquinodimethane, tcnq, this strong electron-acceptor molecule is present either as a radical ion $tcnq^{\bullet -}$ or as weakly π-bonded dimers $(tcnq)_2{}^{2-}$. Many of these compounds show interesting physical properties. For example, a series of metallocene–tcnq complexes show interesting magnetic properties:[1] the one-dimensional phase of $[Fe(\eta\text{-}C_5Me_5)_2][tcnq]$ was found to be metamagnetic,[2a] while $[Cr(\eta\text{-}C_5Me_5)_2][tcnq]$[2b] and $[Mn(\eta\text{-}C_5Me_5)_2][tcnq]$[2c] show spontaneous magnetization below 10 K. Other tcnq salts are good electrical conductors.[3] We have recently prepared a new radical-ion salt where the transition-metal ion is bound to the nitrogen of the nitrile group of the tcnq molecule through a σ-bond. The complex $[NiL(tcnq)_2]$, where L = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane, contains paramagnetic transition-metal fragments and dimeric $(tcnq)_2{}^{2-}$ radical anions which act as bridges between two adjacent $[Ni(macrocycle)]^{2+}$ units.[4] This compound is one of the few new examples of σ-bonded tcnq derivatives reported in which a linear-chain structure is observed.[5] These chains are interacting *via* hydrogen bonds formed by the hydroxo group and one nitrile group of a neighbouring tcnq. The one-dimensional nature of the crystal structure of $[NiL(tcnq)_2]$ prompted us to study the magnetic properties to find out whether co-operative magnetic effects were present in these solids. This paper describes the synthesis, the crystal structure of the analogous $[CuL(tcnq)_2]$, and a magnetic study of both compounds.

Experimental

All the reactions were carried out in an inert atmosphere using a standard Schlenk technique.[6] Solvents were reagent grade and degassed prior to use.



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Syntheses

Dichloro-[3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane]metal(II), $[MCl_2L]$ (M = Cu or N). These complexes were prepared by a previously reported method.[7] The purity of the compounds was checked by elemental analysis.

[3,10-Bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane]bis(7,7,8,8-tetracyanoquinodimethanido)copper(II), $[CuL(tcnq)_2]$. An ethanolic solution of Li(tcnq)[8] was added dropwise to a solution of $[CuCl_2L]$ in EtOH–water (25:1) in a 1:2 molar ratio. The resulting solution was stirred for about 12 h and the deep blue solid formed was filtered off, washed with degassed water and diethyl ether and finally dried under vacuum over P_4O_{10}. Yield: 86%. Good-quality crystals for X-ray studies were obtained by slow diffusion of a Li(tcnq) ethanolic solution into the EtOH–water solution of the dichloro copper complex (Found: C, 56.5; H, 4.8; N, 25.7. $C_{36}H_{38}CuN_{14}O_2$ requires C, 56.7; H, 5.0; N, 25.7%).

$[NiL(tncq)_2]$. The synthesis of this compound was described previously.[4] Its purity was checked by elemental analysis and infrared spectroscopy (see below).

Physical measurements

Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense of Madrid. Diffuse-reflectance spectra for pure and MgO-diluted samples were measured on a Cary 5 spectrophotometer equipped with a

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† *Non-SI units employed:* G = 10^{-4} T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, emu = $10^6/4\pi \times$ SI.

diffuse-reflectance accessory. Infrared spectra were recorded on a Perkin-Elmer 16PC Fourier-transform spectrometer as KBr pellets. Temperature-dependent magnetic susceptibilities of powdered samples were measured by a Quantum Design model MPSM SQUID magnetometer, in the range 5–300 K and at applied fields up to 5 T. Isothermal magnetization experiments, as a function of field, were performed at two different temperatures. Data were corrected for the magnetization of the sample holder and for atomic diamagnetism as calculated from Pascal's constants. Two-probe powder electrical conductivity measurements at room temperature were made by using an apparatus described elsewhere.[9]

X-Ray crystallography

The fundamental crystal data are summarized in Table 1. A deep blue crystal of prismatic shape was coated with epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections within a range 2θ 13–24°. The intensities were corrected for Lorentz-polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from ref. 10. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinements.[11]

Since no trend in ΔF *vs.* F_o or $(\sin\theta)/\lambda$ was observed, a final refinement was undertaken with unit weights and isotropic thermal motion for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. The final difference synthesis showed no significant electron density.

An alternative refinement was carried out using no absorption correction and the weighting scheme $w = K/(a + b|F_o| + c|F_o|^2)^2$, where $K = 0.546$, $a = 2.344$, $b = -0.581$, and $c = 0.102$ for $|F_o| < 7$ and $a = 0.210$. $b = 0.094$, $c = -0.001$ for $7 < |F_o| < 33$. This afforded similar agreement factors. The structural model obtained from both refinements was the same within error. Most of the calculations were carried out with the X-Ray 80 system.[12]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference numbers 186/93 and 186/94.

Results and Discussion

The complex [CuL(tcnq)$_2$] was synthesized and characterized by following the same procedures used for the corresponding nickel(II) compound. It is dark blue, slightly soluble in acetonitrile and Me$_2$SO and slowly decomposes in the air. Single crystals for X-ray studies were obtained by slow diffusion of an ethanolic Li(tcnq) solution in a solution containing the copper(II) complex [CuCl$_2$L] under an inert atmosphere.

Crystal structure of [CuL(tcnq)$_2$]

The compound crystallizes in the triclinic space group $P\bar{1}$. An ORTEP view and the atomic labelling of the molecular unit is shown in Fig. 1 Selected bond lengths and angles are listed in Table 2.

The copper atom in the molecular unit is six-co-ordinated to four nitrogen atoms of the macrocyclic ligand and to two nitrogen atoms from two different tcnq$^{\bullet -}$ groups. It occupies an inversion centre and both tcnq groups are axially bonded. The copper environment is a tetragonally elongated octahedron with copper–nitrogen bond distances of 2.009(4) and 2.002(4) Å for the macrocycle and 2.521(4) Å for the axial nitrogen atoms. The tetragonal elongation is more pronounced than that observed in other pseudo-octahedral CuN$_6$ environments.[5b,14] The macrocycle adopts a chair conformation.

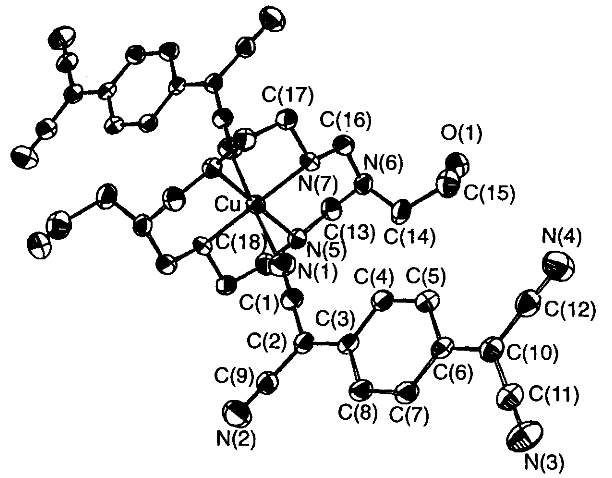

Fig. 1 An ORTEP plot of [CuL(tcnq)$_2$] with atomic labelling

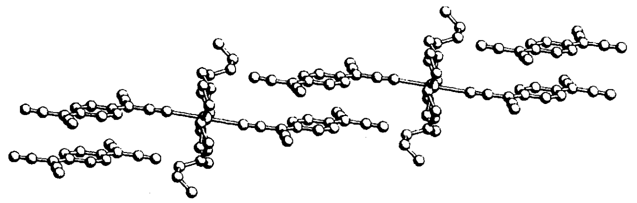

Fig. 2 Eclipsed dimer stacking mode of the (tcnq)$_2$$^{2-}$ and CuL units, showing the one-dimensional motif of the structure

The intramolecular distances of the tncq groups are typical of ionized molecules.[15] Neighbouring tcnq groups belonging to different molecular units overlap in a ring-over-ring mode, along the cell diagonal. The separation between the planes defined by the quinonoid rings is 3.249(6) Å. This interplanar distance is similar to that of the corresponding nickel(II) analogue, 3.252(7) Å, and to that observed in [M(C$_6$Me$_6$)$_2$][tcnq]$_2$ (M = Fe or Ru).[16] A shorter distance has been found in [Fe(η-C$_5$Me$_5$)$_2$][tcnq]$_2$, 3.10 Å,[17] and a longer distance in the α phase of [Cr(C$_6$H$_3$Me$_3$-1,3,5)$_2$][tcnq]$_2$, 3.47 Å.[18] A one-dimensional chain formed by the metal ions and dimeric radical units is then observed along the [111] direction of the unit cell. A view of the arrangement of the molecular units along the chains is shown in Fig. 2. In contrast with the nickel compound, where adjacent chains are held together by hydrogen bonds between the hydroxo groups and tcnq nitrogen atoms of a neighbouring unit, the copper derivative does not show these hydrogen bonds. The shortest distance is between O(1) and N(4′) 3.245(7) Å, with a hydrogen to nitrogen distance of 2.657(5) Å, too long to be considered as a real bond. This fact might be due to the Jahn–Teller distortion on the copper which pushes the tcnq units away from the hydroxo groups.

Optical spectra

The solid-state electronic spectrum of [CuL(tcnq)$_2$] shows at room temperature a lowest-energy absorption in the near-infrared region at 10 500 cm^{-1} which is very broad and intense. Other absorptions are in the visible region. The first is broad and two maxima at 15 200 and 16 500 cm^{-1} could be identified. Another appears at 26 500 cm^{-1} with a shoulder at 31 000 cm^{-1}. On the basis of the single-crystal structure, the optical spectrum is the overlap of absorptions arising from the (tcnq)$_2$$^{2-}$ dimeric species and that of the CuN$_6$ chromophore. The copper(II) d orbitals undergo a low-symmetry splitting, by a pronounced tetragonal distortion due to the Jahn–Teller effect. Tetragonal elongation results in a d$_{x^2-y^2}$ ground state and in this site

Table 1 Crystal and refinement data for [CuL(tcnq)$_2$]

Formula	$C_{36}H_{38}CuN_{14}O_2$
M	762.3
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	8.081(3)
b/Å	8.7910(9)
c/Å	13.098(3)
α/°	104.73(1)
β/°	96.83(2)
γ/°	93.47(2)
Z	1
U/Å^3	889.5(4)
D_c/g cm^{-3}	1.42
F(000)	397
T/K	295
Diffractometer	Enraf-Nonius
Radiation	Graphite-monochromated Mo-Kα (λ = 0.710 69 Å)
μ(Mo-Kα)/cm^{-1}	6.67
Crystal dimensions/mm	0.2 × 0.3 × 0.3
2θ Range/°	1–56
Scan technique	ω–2θ
Data collected	(−10, −11, 0) to (10, 11, 17)
Unique data	4286
Observed reflections [$I > 3\sigma(I)$]	3224
R_{int}	0.0160
Standard reflections	3 every 61
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.067
$R' = (\Sigma w\Delta^2 F/\Sigma w\lvert F_o\rvert^2)^{\frac{1}{2}}$	0.076
Goodness of fit	
$[\Sigma w(F_o - F_c)^2/(N - N_v)]^{\frac{1}{2}}$	1.50
$[\Sigma w(I_o - I_c)^2/(N - N_v)]^{\frac{1}{2}}$	2081
Maximum shift/error	0.2
Absorption correction range	0.70–1.33

Table 2 Bond lengths (Å) and angles (°) for [CuL(tcnq)$_2$]

Cu–N(1)	2.521(4)	N(7)–C(17)	1.487(6)
Cu–N(5)	2.009(4)	C(1)–C(2)	1.418(6)
Cu–N(7)	2.002(4)	C(2)–C(3)	1.404(7)
O(1)–C(15)	1.393(8)	C(2)–C(9)	1.421(8)
N(1)–C(1)	1.150(6)	C(3)–C(4)	1.413(7)
N(2)–C(9)	1.141(9)	C(3)–C(8)	1.427(6)
N(3)–C(11)	1.148(7)	C(4)–C(5)	1.354(7)
N(4)–C(12)	1.147(9)	C(5)–C(6)	1.434(6)
N(5)–C(13)	1.481(7)	C(6)–C(7)	1.412(8)
N(5)–C(18)	1.467(7)	C(6)–C(10)	1.397(7)
N(6)–C(13)	1.430(7)	C(7)–C(8)	1.357(7)
N(6)–C(14)	1.448(6)	C(10)–C(11)	1.418(6)
N(6)–C(16)	1.440(6)	C(10)–C(12)	1.413(8)
N(7)–C(16)	1.487(7)	C(14)–C(15)	1.51(1)
N(5)–Cu–N(7)	94.0(2)	C(4)–C(3)–C(8)	117.2(4)
N(1)–Cu–N(7)	87.0(2)	C(3)–C(4)–C(5)	121.8(5)
N(1)–Cu–N(5)	88.7(2)	C(4)–C(5)–C(6)	121.1(5)
N(1)–C(1)–C(2)	179.4(6)	C(5)–C(6)–C(10)	121.0(4)
N(2)–C(9)–C(2)	178.4(6)	C(5)–C(6)–C(7)	116.8(4)
N(3)–C(11)–C(10)	179.0(6)	C(7)–C(6)–C(10)	122.2(5)
N(4)–C(12)–C(10)	179.1(6)	C(6)–C(7)–C(8)	122.0(5)
C(1)–C(2)–C(9)	114.8(4)	C(3)–C(8)–C(7)	121.1(5)
C(2)–C(3)–C(8)	120.8(4)	C(6)–C(10)–C(12)	122.3(5)
C(1)–C(2)–C(3)	121.0(4)	C(6)–C(10)–C(11)	122.7(5)
C(3)–C(2)–C(9)	124.1(4)	C(11)–C(10)–C(12)	114.9(5)
C(2)–C(3)–C(4)	122.0(4)		

symmetry three electronic transitions are expected. The first ($d_{z^2} \longrightarrow d_{x^2-y^2}$) appears in the near infrared, the other two ($d_{xy} \longrightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$) in the visible.[19] On the other hand, for (tcnq)$_2$$^{2-}$ dimers three types of electronic transitions are expected in the same optical region. The first, resulting from charge transfer between tcnq$^{\bullet -}$ ions, has been observed between 9000 and 12 000 cm^{-1}.[20] The band at 10 500 cm^{-1} can be assigned as due to the intermolecular charge transfer. The second band, *i.e.* due to the lowest locally excited state of the tcnq$^-$, is between 16 000 and 18 000 cm^{-1}, and the third of the same type ranges between 25 000 and 30 000 cm^{-1}. From the reflectance spectrum it is quite difficult to identify and assign the d–d bands of the copper(II) chromophore, due to the presence of the intense and broad bands of the tcnq ions.

There is a direct correlation between the observed molecular structure and the infrared spectra for these compounds. Sharp ν(C≡N) absorptions are observed for [CuL(tcnq)$_2$] at 2168m, 2184s and 2196s cm^{-1}. The same pattern is observed for the nickel(II) analogue at 2180, 2196 and 2209 cm^{-1} respectively, although shifted to higher energies. These bands are characteristic of (tcnq)$_2$$^{2-}$ units, *cf.* 2157, 2176 and 2184 cm^{-1} for [Fe(η-C$_5$Me$_5$)$_2$]$_2$[tcnq]$_2$, where the (tcnq)$_2$$^{2-}$ dimer has an interplanar separation of 3.10 Å and the tcnq molecules are not σ bonded.[17] The difference in the energy shift of these modes can be therefore ascribed to the M–N bonding and to the strength of this bond, *i.e.* for the nickel complex the observed shift to higher energies is related to the shorter apical Ni–N bond length (2.175 Å) when compared to that of the copper analogue. Information on the degree of ionization of the tcnq molecule is obtained by looking at the b_{1u} ν_{20} mode of tcnq. This is quite sensitive to the degree of ionization and appears at 1545 cm^{-1} for the neutral molecule and at 1508 cm^{-1} for singly ionized tcnq.[21] For the present compounds the values of 1509 and 1510 cm^{-1} are comparable with that for tcnq$^{\bullet -}$.

Magnetic properties

The magnetic properties of [ML(tcnq)$_2$] (M = Ni or Cu) have been studied by bulk susceptibility.

[NiL(tcnq)$_2$]. The powder magnetic susceptibility as a function of temperature was measured over the range 5–300 K (Fig. 3). Below 30 K, the molar susceptibility can be described by the Curie–Weiss law $\chi = C/(T - \theta)$, where C and θ are 1.35 emu K and −3.7 K, respectively. The value of C is consistent with the presence of Ni^{II}, S = 1, in octahedral symmetry. Above 50 K the thermal behaviour of the susceptibility is not linear. The effective magnetic moment μ_{eff} decreases from 4.4 μ_B at room temperature to 3.23 μ_B at 50 K, indicating antiferromagnetic coupling between the nearest-neighbour tcnq anions. At room temperature the magnetic moment is higher than expected for two $S = \frac{1}{2}$ uncorrelated spins and one S = 1 spin for the octahedral nickel(II) ion, suggesting a contribution from temperature-independent paramagnetism. The magnetism of [NiL(tcnq)$_2$] therefore arises from a three-spin system: two spins $S = \frac{1}{2}$ localized on the tcnq radical ions and a third one on the complex, *i.e.* Ni^{II} (d^8, S = 1). The crystal structure of this complex has been reported previously.[4] The nickel(II) ion is six-co-ordinated, surrounded by four nitrogen atoms of the macrocyclic ligand and two axial ones from monodentate tcnq ions. Each acceptor ion holds one unpaired electron. The tcnq radical ions belonging to two adjacent molecules form dimeric moieties at the intradimer distance of 3.25 Å. The susceptibility therefore reflects the antiferromagnetic coupling of the spins located on the anions with a singlet ground state and an energetically accessible triplet state. At low temperatures the magnetism arises only from isolated nickel(II) S = 1 ions in octahedral symmetry, while the (tcnq)$_2$$^{2-}$ ions are in a diamagnetic ground state. The experimental data were fitted by assuming the presence of nickel(II) in octahedral symmetry and dimeric (tcnq)$_2$$^{2-}$ radical species[22] in the unit cell. The molar magnetic susceptibility was then the sum of three contributions [equation (1)] where N is Avogadro's

$$\chi_{tot} = \frac{2Ng_{Ni}^2\mu_B^2}{3k_BT} + \frac{Ng^2\mu_B^2}{k_BT}\left(\frac{2}{3 + \exp(-2J/k_BT)}\right) + N_\alpha \quad (1)$$

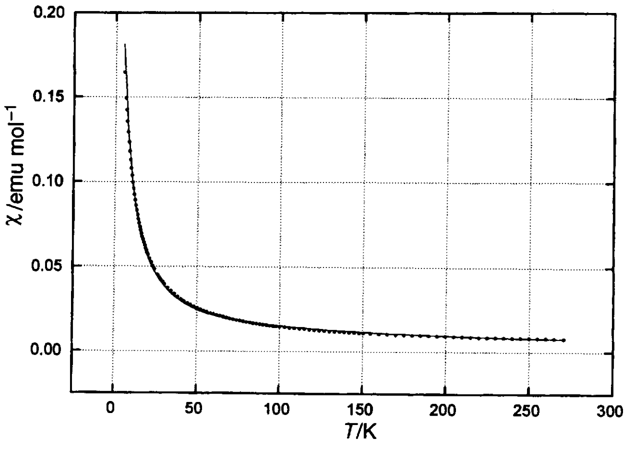

Fig. 3 Temperature dependence of the molar magnetic susceptibility for [NiL(tcnq)$_2$] in the range 5–300 K at 500 G. (●) Experimental points; (—) calculated values

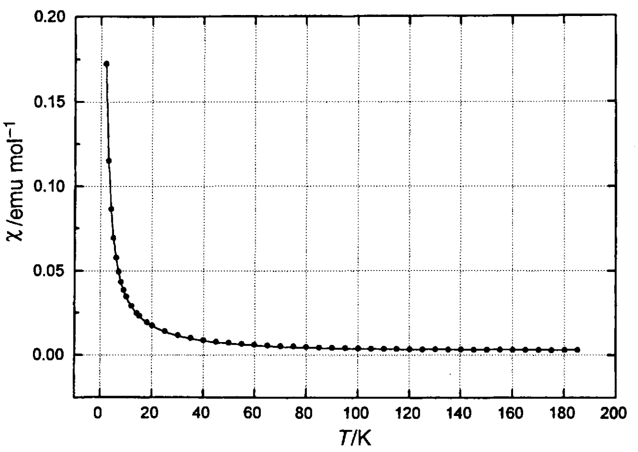

Fig. 4 Temperature dependence of the molar magnetic susceptibility for [CuL(tcnq)$_2$] in the range 2–190 K at 2000 G. Key as in Fig. 3

number, k_B is Boltzmann's constant, μ_B is the Bohr magneton, g are the Landé g factors, $2J/k_B$ is the singlet–triplet gap in Kelvin and N_α is the temperature-independent paramagnetism. The magnetic data above 20 K were fitted by this equation, giving $2J/k_B = -240$ K and $N_\alpha = 1.4 \times 10^{-3}$ emu. The Curie constant was fixed at $C = 1.1644$ emu K, which corresponds to $g_{Ni} = 2.16$. The R value of the fitting was 0.0007. As stated above, at low temperatures a small deviation from the Curie law is observed. This could be an indication of the presence of zero-field splitting, which is one of the most important sources of paramagnetic anisotropy in nickel(II) octahedral ions.[23] The parameter D measures the zero-field splitting of the ground state. Equation (2) for the average magnetic susceptibility takes

$$\langle\chi\rangle = (2Ng_{Ni}^2\mu_B^2/3k_BT)\{[2 - 2\exp(-x)]/x + \exp(-x)\}/[1 + 2\exp(-x)] \quad (2)$$

into account this single-ion anisotropy where $x = D/k_BT$. If relation (2) is used as the first term of equation (1) for χ_{tot}, the fitting gives the parameters $2J/k_B = -189$ K, $D/k_B = 13$ K and $N_\alpha = 6.91 \times 10^{-4}$ emu; g_{Ni} was fixed at 2.16. The results of the two fittings do not differ greatly.

[CuL(tcnq)$_2$]. The temperature dependence of the magnetic susceptibility in the range 2–300 K is shown in Fig. 4. At low temperatures, *i.e.* 2–30 K, $1/\chi$ *vs.* T is linear. The effective magnetic moment obtained from the Curie constant C, using the relation $\mu_{eff} = 2.828C^{\frac{1}{2}}$ is 1.68 μ_B which corresponds to one unpaired electron, arising from the copper in oxidation state II; this value is lower when compared to that expected for Cu^{II} in D_{4h} symmetry, *i.e.* 2.1 μ_B. Magnetization experiments as a function of the field have also been performed on the same sample at temperatures 5 and 10 K. The corresponding plots are both linear and the slopes consistent with the presence of one unpaired electron at low temperatures. There is no evidence of magnetic interactions between copper(II) and radical-ion spins. The magnetic moment increases from 1.66 μ_B at 2 K to 2.15 μ_B at 190 K, suggesting that the contribution to the magnetic susceptibility from the radical-ion species becomes important at high temperatures. An attempt to fit the magnetic susceptibility *vs.* temperature data in the range 2–190 K has been made by using equation (3).[21] The first term represents the contribution

$$\chi_{tot} = \frac{Ng_{Cu}^2\mu_B^2}{4k_BT} + \frac{Ng^2\mu_B^2}{k_BT}\left(\frac{2}{3 + \exp(-2J/k_BT)}\right) \quad (3)$$

arising from the isolated copper(II) ions and the second that from the (tcnq)$_2{}^{2-}$ species; g was fixed at 2.0023. The best fit to the data gave $2J/k_B = -382$ K and $g_{cu} = 1.92$.

Conclusion

We have synthesised and characterized a new σ-bonded tcnq–Cu^{II} compound, in which the radical ion tcnq$^{\bullet-}$ is co-ordinated to the metal. The solid-state structure features [Cu(N$_4$)]–(tcnq)$_2{}^{2-}$–[Cu(N$_4$)]. . . linear chains, with two nitrogen atoms, belonging to two different tcnq units, co-ordinated in axial positions. The crystal structure is similar to that observed for the nickel analogue. In these compounds the cations are magnetically isolated, while the anions couple antiferromagnetically. The magnetic behaviour can be interpreted by a singlet–triplet model for dimerized (tcnq)$_2{}^{2-}$ units ($2J/k_B = -189$ and -382 K for Ni and Cu, respectively) and a Curie model for the transition-metal ion in octahedral symmetry. No interactions between neighbouring metal–ion and anion sites have been observed, even at low temperatures.

Acknowledgements

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