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STABILIZATION OF TCNQ ANION RADICAL WITH DI- AND TRIAMINE COMPLEXES OF NICKEL AND COPPER

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Abstract—The reactivity of the organic acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) in its neutral or anionic radical forms with saturated di- and triamino derivatives of nickel and copper such as the cationic complexes with ethylenediamine, $[M(en)_3]^{2+}$, trimethylenediamine, $[M(tn)_2(H_2O)_2]^{2+}$, and diethylenetriamine, $[M(dien)_2]^{2+}$, is discussed on the basis of the metal environment stability. The products obtained show either substitution of some labile ligands from the metal coordination sphere and σ-coordination of the anionic TCNQ or alternatively displacement of the counter-ion by anionic TCNQ with maintenance of the coordination around the metal. The complexes studied show the TCNQ groups forming dimeric, or trimeric, anionic associations with strong antiferromagnetic intradimer coupling between the radical units. The complex $[Ni(dien)_2](TCNQ)_2$ shows a weaker TCNQ–TCNQ coupling with a singlet–triplet equilibrium observable at temperatures above 60 K from its contribution to the total magnetic susceptibility of the complex.

The field of the donor–acceptor compounds involving metallic fragments and organic acceptor molecules challenges synthetic work to design interesting supramolecular systems.[1] Depending on the electronic properties of both building blocks and on their relative arrangement, the macromolecular structure presents different physical properties.

The organic molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) is a highly versatile acceptor molecule due to its ability to form stable radical species (TCNQ⁻, $TCNQ^{2-}$) and the ability of the reduced radical TCNQ⁻ to coordinate to a metal centre as a σ-donor via one or more of its nitrile groups; other characteristics of these species are their high tendency to dimerize via π–π interactions[2] and the ability to stabilize uncommon environments such as in $[Ru(TCNQ)(PPh_3)_2]_2$.[3]

In order to study the influence of the metallic units in this type of compound we have chosen nickel and copper fragments containing polydentate nitrogen donor ligands because of the possibility of stabilizing different metal environments. In this field we have recently reported the σ-bonded species $[NiL(TCNQ)_2]$ (L = tetraazamacrocycles) that show an octahedral environment for the metal atom with the monodentate TCNQ⁻ ligands in apical positions. The TCNQ groups of adjacent molecules strongly interact to form diamagnetic dimeric units $(TCNQ)_2^{2-}$ and the solid can be seen as parallel chains of $[NiL]^{2+}$ held together by dimeric $(TCNQ)_2^{2-}$.[4]

In contrast, in other fully characterized nickel–TCNQ compounds, such as the porphyrinate $[Ni(TMP)(TCNQ)]$[5] and the annulene $[Ni(h-Medbtaa)(TCNQ)]$,[6] the solid is formed by integrated stacks of TCNQ and the metallomacrocyclic units. Other nickel tetraazamacrocycles have been studied and, from spectroscopic data, segregated stacks of TCNQ⁻ and metallic cations have been

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proposed.[7] With bidentate N–N donor ligands there are several examples of nickel derivatives: [Ni (bpy)₃](TCNQ)₂,[2] [Ni(abpt)₂(TCNQ)₂],[8] [Ni(en)₂ (TCNQ)ₓ], $x = 2, 3$,[7] but no structural data have been reported.

Copper complexes having both bidentate nitrogen donor ligands and TCNQ units have been extensively studied due to the possibility of modulation of the copper(II)/copper(I) redox potential and subsequent stabilization of electronic densities over the copper ion. Only a few examples have been structurally characterized with examples of coordinated[8] and uncoordinated[9] TCNQ.

As part of a project to obtain stacks of TCNQ units induced by metallic complexes we report the study of the reactivity of cationic hexa-coordinated nickel and copper complexes with bi- or tridentate amine ligands towards anionic TCNQ salts. The copper complexes that exhibit a higher tendency towards reduction and a very different stability in their environments with chelate ligands are expected to show a different behaviour relative to their nickel analogues.[10]

EXPERIMENTAL

Preparation of compounds

All reactions have been carried out under oxygen-free nitrogen using dried and degassified solvents when necessary. The starting complexes [M(en)₃]X₂, [M(tn)₂(H₂O)₂]X₂ and [M(dien)₂]X₂ (M = Ni, Cu; X = ClO₄⁻, NO₃⁻; en = H₂N— CH₂CH₂NH₂, tn = H₂NCH₂CH₂CH₂NH₂, dien = H₂NCH₂CH₂NHCH₂CH₂NH₂) have been prepared by the reaction of the metal salt MX₂ and excess of the amine ligand using methanol as solvent.[11] Analytical data for the new complexes are given in Table 1.

Bis(tetracyanoquinodimethanido) complexes

The complexes having two TCNQ in their formulae, with the exception of [Cu(dien)(TCNQ)₂], were prepared by addition of a methanol solution of LiTCNQ to a stirred methanol solution of the corresponding metallic complex in a molar ratio, metal complex to TCNQ, of 1:2. After 1 h of stirring the dark-blue solid that formed was filtered off, washed with methanol and dried *in vacuo* over P₄O₁₀. Typical yields are over 75%.

When the reaction mixture of the dien derivative was left for several days, the complex [Ni(CN)₂ (dien)] appeared as a violet solid, that was filtered off and dried *in vacuo*.

Table 1. Analytical data for the new complexes

Compound	Found (Calc.) (%)		
	C	H	N
1, [Ni(en)₃](TCNQ)₂	55.4 (55.6)	5.4 (5.6)	29.9 (30.2)
2, [Ni(tn)₂(TCNQ)₂]	58.2 (58.6)	4.5 (4.6)	27.5 (27.3)
3, [Ni(tn)₂(TCNQ)₃]	61.1 (61.5)	3.9 (3.9)	26.0 (27.3)
4, [Cu(tn)(TCNQ)₂]	59.1 (59.4)	3.5 (3.3)	25.5 (25.6)
5, [Ni(dien)₂](TCNQ)₂	56.8 (57.0)	5.0 (5.0)	28.8 (29.1)
6, [Ni(dien)₂](TCNQ)₃	59.8 (60.2)	4.1 (4.3)	28.3 (28.7)
7, [Cu(dien)(TCNQ)₂]	58.6 (58.4)	3.8 (3.7)	26.6 (26.8)

Tris(tetracyanoquinodimethanido) complexes

These complexes were prepared by successive additions of solution of LiTCNQ in methanol and TCNQ in acetonitrile over a stirred methanol solution of the metal salt in a molar ratio 2:1:1 and worked up as above. When [Cu(dien)₂](NO₃)₂ was used the complex with two TCNQ groups, [Cu (dien)(TCNQ)₂], was formed. Yields: 68–76%.

Reaction of [Ni(TCNQ)₂]·2H₂O with amines

The complexes [Ni(tn)₂(TCNQ)₂] and [Ni (dien)₂](TCNQ)₂ have also been prepared by overnight stirring of a methanol suspension of [Ni(TCNQ)₂]·2H₂O with excess of the amine, followed by filtration of the solid formed. Yield: 45–50%.
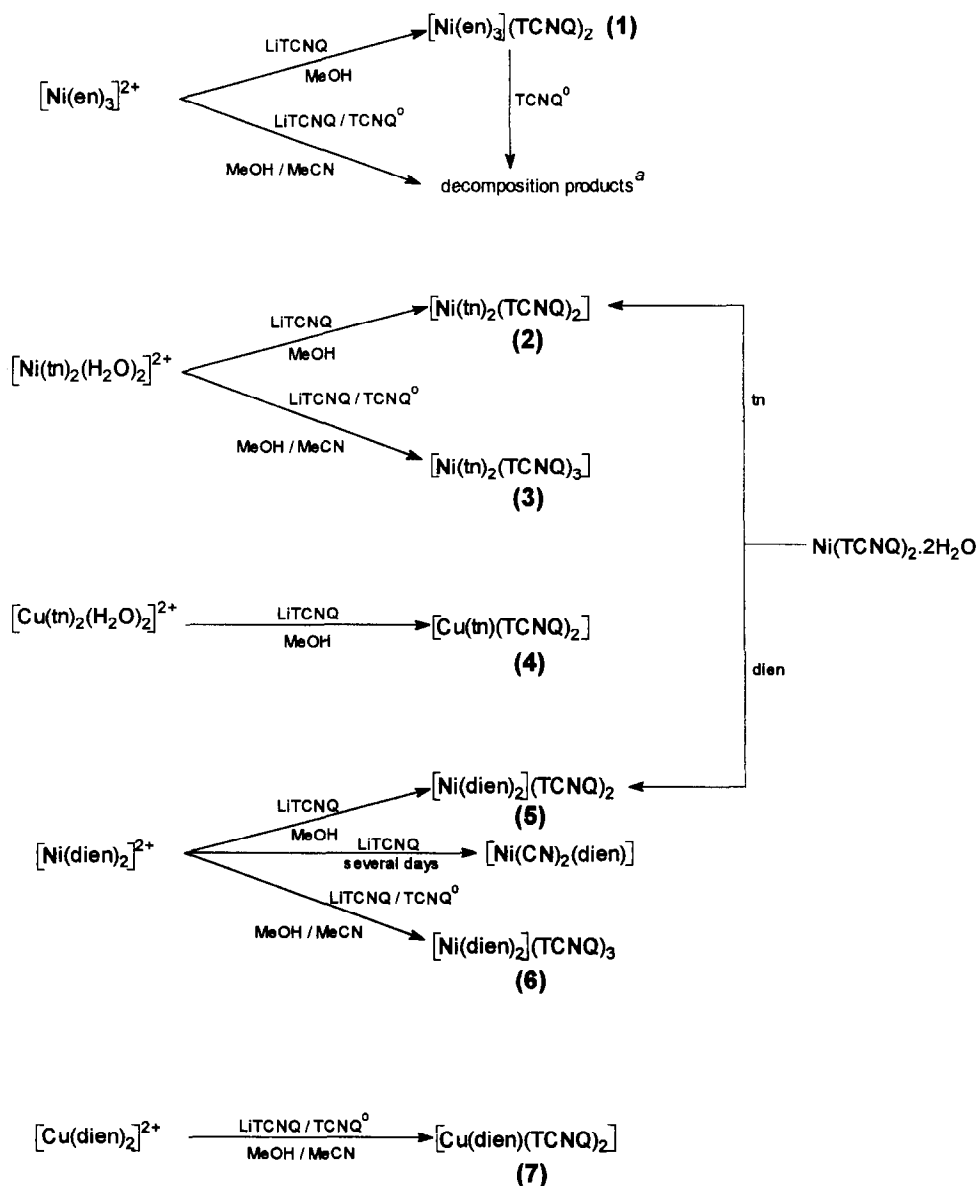
Physical measurements

The apparatus and general techniques used to determine the physical measurements have been described elsewhere.[4]

RESULTS AND DISCUSSION

The reactions studied, with an indication of the complexes obtained, are shown in Scheme 1.

Bidentate amines

The reaction of [Ni(en)₃]X₂, X = ClO₄⁻, with LiTCNQ led to the displacement of the counterions and the formation of [Ni(en)₃](TCNQ)₂ (**1**).

Scheme 1 content:

$[Ni(en)_3]^{2+}$ →(LiTCNQ, MeOH)→ $[Ni(en)_3](TCNQ)_2$ **(1)**

$[Ni(en)_3]^{2+}$ →(LiTCNQ/TCNQ^0, MeOH/MeCN)→ decomposition products^a

(1) →(TCNQ^0)→ decomposition products^a

$[Ni(tn)_2(H_2O)_2]^{2+}$ →(LiTCNQ, MeOH)→ $[Ni(tn)_2(TCNQ)_2]$ **(2)**

$[Ni(tn)_2(H_2O)_2]^{2+}$ →(LiTCNQ/TCNQ^0, MeOH/MeCN)→ $[Ni(tn)_2(TCNQ)_3]$ **(3)**

$[Cu(tn)_2(H_2O)_2]^{2+}$ →(LiTCNQ, MeOH)→ $[Cu(tn)(TCNQ)_2]$ **(4)**

Ni(TCNQ)$_2$.2H$_2$O — tn → **(2)**; dien → **(5)**

$[Ni(dien)_2]^{2+}$ →(LiTCNQ, MeOH)→ $[Ni(dien)_2](TCNQ)_2$ **(5)**

$[Ni(dien)_2]^{2+}$ →(LiTCNQ, several days)→ $[Ni(CN)_2(dien)]$

$[Ni(dien)_2]^{2+}$ →(LiTCNQ/TCNQ^0, MeOH/MeCN)→ $[Ni(dien)_2](TCNQ)_3$ **(6)**

$[Cu(dien)_2]^{2+}$ →(LiTCNQ/TCNQ^0, MeOH/MeCN)→ $[Cu(dien)(TCNQ)_2]$ **(7)**

^{a} Mixtures of di and tricyanoaminoderivatives of TCNQ

Scheme 1.

The same reaction but using neutral TCNQ or a mixture of LiTCNQ and TCNQ$^\circ$ gave rise to a mixture of green solids. Similar products were obtained by reaction of 1 and neutral TCNQ, indicating that the presence of this molecule plays an important role in the observed process.

This behaviour can be interpreted in terms of the previously described reactions[12] between neutral TCNQ and primary or secondary amines:

The characteristic IR absorption bands for the cyano groups of the tricyano derivative can be observed in the IR spectra of those green products, suggesting that the TCNQ has reacted with the previously coordinated ethylenediamine. However, the great variety of species that can be formed by this process precluded every attempt to isolate pure compounds from the mixture.

When trimethylenediamine (tn) was used the less
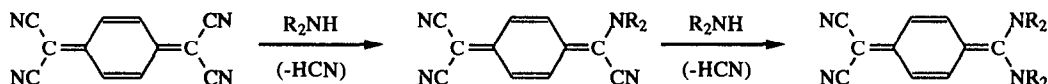
stable six-membered chelate rings facilitated the formation of bischelate derivatives, the axial positions usually being occupied by labile ligands, such as water molecules as in $[Ni(tn)_2(H_2O)_2](NO_3)_2$. This complex can react further with TCNQ by displacement of the labile water molecules, and the reaction with LiTCNQ occurs in this way with the formation of $[Ni(tn)_2(TCNQ)_2]$ (2). The same compound can be prepared by reaction of the previously known $[Ni(TCNQ)_2]\cdot 2H_2O$ with amine ligand, but the purity of the samples obtained by this route is very dependent on the reaction conditions.

The reaction of $[Ni(tn)_2(H_2O)_2]^{2+}$ with a mixture of LiTCNQ and neutral TCNQ only afforded the dark blue $[Ni(tn)_2(TCNQ)_3]$ (3), and no indication of the green tricyano derivatives was found, in contrast to the observed behaviour of the ethylenediamine complex.

A completely different reaction was observed with the copper complex $[Cu(tn)_2(H_2O)_2]^{2+}$, whose reaction with LiTCNQ occurred with displacement of one diamine ligand and reduction of the metal formal oxidation state to copper(I) and the formation of $[Cu(tn)(TCNQ)_2]$ (4).

Tridentate amines

The bis(diethylenetriamine) complex $[Ni(dien)_2]$ $(NO_3)_2$ reacted with LiTCNQ or the mixture LiTCNQ/TCNQ° with the displacement of the counter-ion and the formation of $[Ni(dien)_2]$ $(TCNQ)_2$ (5) and $[Ni(dien)_2](TCNQ)_3$ (6), respectively.

If the reaction mixture was left standing for prolonged periods of time, violet crystals of $[Ni(CN)_2(dien)]$ were obtained, probably due to the reaction of the triamine with the TCNQ and the formation of the above-mentioned amino-cyanoquinodimethane species and the liberation of cyano groups in a similar way to the observed behaviour of the ethylenediamine complexes. No doubt the higher stability of the dien complexes towards TCNQ has to be attributed to the formation of two chelate rings for the triamine ligand, stabilizing its bonding to the metal atom.

In a behaviour similar to that found for 2, 5 can also be obtained from $[Ni(TCNQ)_2]\cdot 2H_2O$ by reaction with excess dien.

The behaviour of the copper derivative [Cu (dien)$_2$](NO$_3$)$_2$ is radically different from that of the nickel analogue since no pure product has been isolated in the reaction with LiTCNQ, while the reaction with LiTCNQ/TCNQ° occurred with the displacement of one triamine ligand and the formation of $[Cu(dien)(TCNQ)_2]$ (7). This behaviour is probably due to the lower stability of the starting

bischelate complex due to Jahn–Teller distortion, as has been observed in the flattening of the copper octahedral environment in the parent compound, for which the secondary amine nitrogens show distances of 2.02 Å to the copper, whereas the primary amine nitrogen atoms are bonded at distances of 2.17–2.29 Å.[13]

Due to the distortion in the octahedral environment of the metal atom, the reaction with the mixture LiTCNQ/TCNQ° probably occurs with the attack of the neutral TCNQ to one primary dien nitrogen and the formation of one of the tricyanoquinodimethane derivatives mentioned above. The formation of this species can help to displace one dien ligand from the coordination sphere of the copper atom in a process followed by the binding of two anionic TCNQ⁻. As mentioned above, a penta-coordinated geometry would be expected for the derivative thus formed.

The formation of a penta-coordinate species in the reaction with TCNQ can be explained in terms of a higher stability of the final product in a geometry observed for analogous species such as $[Cu(dien)(O_2CH)]^+$, for which a square pyramidal environment with similar distances, 2.01–2.03 Å, for the three dien nitrogen atoms has been found.[14] The two oxygen atoms occupy the fourth basal corner and the apical position of an adjacent cationic group. This arrangement can be extrapolated to our derivative 7 with the oxygen positions occupied by TCNQ nitrogens, since we have recently found a similar *cis* coordination of anionic TCNQ groups in a nickel derivative.[15]

As for the propylenediamine derivatives, the lower stability of the dipropylenetriamine complexes gave rise to modifications in the metal coordination sphere along with the formation of aminocyanoquinodimethane derivatives, but no pure species could be isolated either for nickel or for copper complexes.

Spectroscopic studies

The number and frequencies of the IR bands of TCNQ are highly indicative of its oxidation state and coordinative status. Thus, the $v(C{\equiv}N)$ bands are indicative of the presence or absence of coordinated TCNQ groups.[16] In a similar way the $\delta(C{-}H)$ bands in the 800–880 cm^{-1} region indicate the presence of TCNQ molecules in different oxidation states.[17]

The main absorption bands for the complexes studied here are indicated in Table 2.

From this basis 1, 2, 5 and 7 show one single band at 820–827 cm^{-1}, indicating that only TCNQ⁻ is present. The $v(C{\equiv}N)$ bands for 1 and 5 are

Table 2. IR, magnetic and electrochemical data for the new complexes

Compound	IR (cm^{-1})			μ (B.M.)	$E_{1/2}$ (V)
	$v(C\equiv N)$	$v(C\equiv C)$	$\delta(C{-}H)$	(T, K)	
1, [Ni(en)$_3$](TCNQ)$_2$	2190s	1575s	820m	2.89	−0.382
	2180s	1500s			0.184
	2160s				0.85^a
2, [Ni(tn)$_2$(TCNQ)$_2$]	2204s	1573s	820m	3.19	−0.385
	2186s	1496s			0.179
	2163s				0.652^a
3, [Ni(tn)$_2$(TCNQ)$_3$]	2190s	1570s	820m	2.87	−0.378
	2170s	1495s	830m		0.173
	2150s				0.645^a
4, [Cu(tn)(TCNQ)$_2$]	2205w	1570s	835m	Diamag.	−0.047
	2165s	1495s			0.424
	2145s				0.609
	2110sh				
5, [Ni(dien)$_2$](TCNQ)$_2$	2170s	1570s	827m	3.57	−0.385
	2150s	1495s		(40)	0.169
					0.704^a
6, [Ni(dien)$_2$](TCNQ)$_3$	2210sh	1575s	830m	3.26	−0.383
	2180s	1500s	840m		0.173
	2150s				0.70^a
7, [Cu(dien)(TCNQ)$_2$]	2195s	1565s	825s	1.96	
	2150s	1505s			

^{a} Anodic process.

attributable to the a_g and b_u vibration modes for the uncoordinated anion radical and appear at lower frequencies relative to 2 and 7, for which σ-coordinated TCNQ$^-$ is expected.

Complexes 3 and 6 exhibit bands for both neutral and radical TCNQ groups in the two regions mentioned above, suggesting that both species are present in these compounds. In the region of the TCNQ $\delta(C{-}H)$, two bands are clearly distinguishable, indicating that the TCNQ groups show different charge distributions.

Finally, the diamagnetic complex 4 is expected to have one neutral and one anionic TCNQ groups bonded to the metal, in a similar way to the related [Cu(en)(TCNQ)$_2$].[18] However, the presence of a single band at 835 cm^{-1} may indicate complete delocalization of the charge between two identical TCNQ groups in the dimeric (TCNQ)$_2^-$, with each supporting 0.5 electron charge.

The electronic spectra can only be obtained from very dilute solutions in solvents such as DMSO or acetonitrile, due to the insolubility of the TCNQ derivatives. These spectra show the two transitions expected for the TCNQ groups,[19] the two locally excited levels LE$_1$ at 842 nm and LE$_2$ at 394 nm in the free anion radical TCNQ$^-$. The intensity ratio

for these two bands is a clear indicator of the oxidation state of the TCNQ groups present in solution, since neutral TCNQ only shows the band at 394 nm. As a reference, solutions of LiTCNQ, with only TCNQ$^-$ present, show a ratio $\varepsilon(394)/\varepsilon(842)$ of 0.5. This value is higher when both neutral and anionic TCNQ are present: 1.25 for one neutral and two anionic TCNQ and 2.0 for one neutral and one anionic TCNQ groups formed in concentrated solutions of the trimeric (TCNQ)$_3^{2-}$ and the dimeric (TCNQ)$_2^-$, exhibiting formal charges of $-2/3$ and $-1/2$ per TCNQ, respectively.[20]

The ratio found for the complexes studied suggests that only TCNQ$^-$ or its dimer (TCNQ)$_2^{2-}$ is present in the solutions of 1, 2, 5 and 7. Complexes 3 and 6 are expected to be formed by the trimers (TCNQ)$_3^{2-}$, while the dimeric (TCNQ)$_2^-$ should be the species present in solutions of 4, since the diamagnetic behaviour of this complex indicates a tetrahedral copper(I) complex.

The diffuse reflectance spectra of these complexes, interpreted together with the $v(CN)$ IR bands, are indicative of the coordinative status of the TCNQ$^-$ unit. Thus, when this anionic group is σ-coordinated to the metal, a well-defined set of bands is observed. As an example, the spectrum of

NiL^R(TCNQ)$_2$ [L^R = 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane] with two coordinated TCNQ[4] shows three bands centred at 850, 640 and 360 nm [Fig. 1(a)]. The first and third bands can be attributed to the two locally excited states found in solution, while the second is characteristic of the formation of the dimeric unit (TCNQ)$_2^{2-}$ that usually appears in the solid state and in concentrated solutions. This behaviour is found in 2 [Fig. 1(c)], suggesting a hexa-coordinated environment for the nickel atom with two bidentate amine ligands and two monodentate TCNQ groups, probably in axial positions [Fig. 2(a)], as found in the above-mentioned macrocyclic complex.

In contrast the spectra of complexes with unco-ordinated TCNQ show, along with the band at 360 nm, a broad absorption between 550 and 900 nm with a minimum of transmittance at 830–860 nm [Fig. 1(b)]. This type of spectrum is found in the rest of the nickel complexes suggesting that, with the exception of 3, the initial metal environment is retained on reaction with TCNQ$^-$ and these groups only act as counter-ions of the cationic coordination compounds. Complex 3 should have a similar coordination sphere to that proposed for 2, but the third TCNQ molecule would bridge adjacent coordinative units by the formation of trimeric (TCNQ)$_3^{2-}$, as shown in Fig. 2(b). The absence of labile monodentate ligands in the nickel complexes with en or dien seems to be due to the avoidance of the coordination of the anionic TCNQ and retention of the metal environment [Fig. 2(c)].

Copper complexes showed similar behaviour and, as expected for the presence of coordinated TCNQ, their solid-state diffuse reflectance electronic spectra were very similar to that reported for
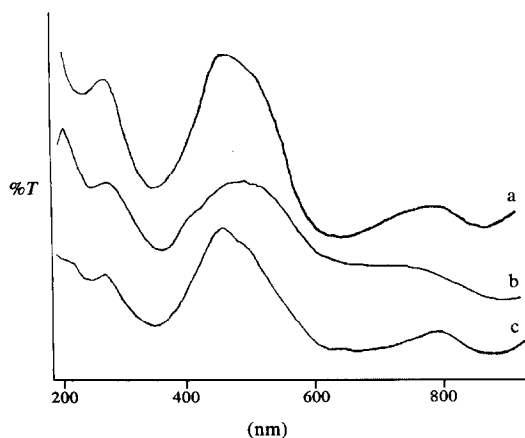
2. As we have previously commented, the presence of coordinated TCNQ in the copper complexes is compatible with the metal environment proposed: tetrahedral for copper(I) in 4 and penta-coordinated with the dien ligand in the basal positions for 7 [Fig. 2(d)].

Electrical conductivity and voltammetric studies

The electrical conductivity in the solid state of these complexes was determined in compressed powdered samples by a two points method at room temperature. All the complexes behaved as insulators ($\sigma < 10^{-7}$ S cm^{-1}), except 4, for which a higher conductivity was found ($\sigma = 10^{-5}$ S cm^{-1}).

The cyclic voltammograms of these complexes showed the two characteristic quasi-reversible waves corresponding to the TCNQ$^\circ$/TCNQ$^-$ and TCNQ$^-$/TCNQ^{2-} couples. The values of these waves at +0.17 and −0.38 V in DMFA solution corresponded to the free TCNQ molecule. These results indicate that the TCNQ is always unco-ordinated in solution, a fact previously suggested by the electronic spectra. The breakage of the σ-bond proposed for 2 and 3 indicates that this interaction must be weaker than the intradimer or trimer interactions between TCNQ groups, since the latter species are much more easily observed in solution. Along with the waves for the TCNQ redox processes, all the nickel complexes exhibited an oxidation peak at potentials of 0.65–0.85 V. This peak can be attributed to the nickel(II) oxidation for an [Ni(N)$_4$(solvent)$_2$] or an [Ni(N)$_6$] environment, as is suggested by the small shifts observed relative to the values for the starting complexes.[4]

The voltammogram of 4 showed two reversible waves for TCNQ shifted to higher potentials relative to free TCNQ, as expected for σ-coordinated TCNQ groups.[16] There is also a third reversible process at 0.61 V attributable to the Cu^I/Cu^{II} couple in this complex.

Magnetic measurements

The measurements of the magnetic susceptibility of these complexes at different temperatures show that, with the exception of 5, all follow the Curie law with an almost constant moment attributable only to the unpaired electrons on the metal complex: two for nickel(II) and one for copper(II) (Fig. 3). The contribution of the TCNQ groups must then be negligible for these complexes, indicating that an antiferromagnetic coupling between the TCNQ groups of the anionic dimer exists and is strong enough to yield diamagnetic species, even at room temperature.
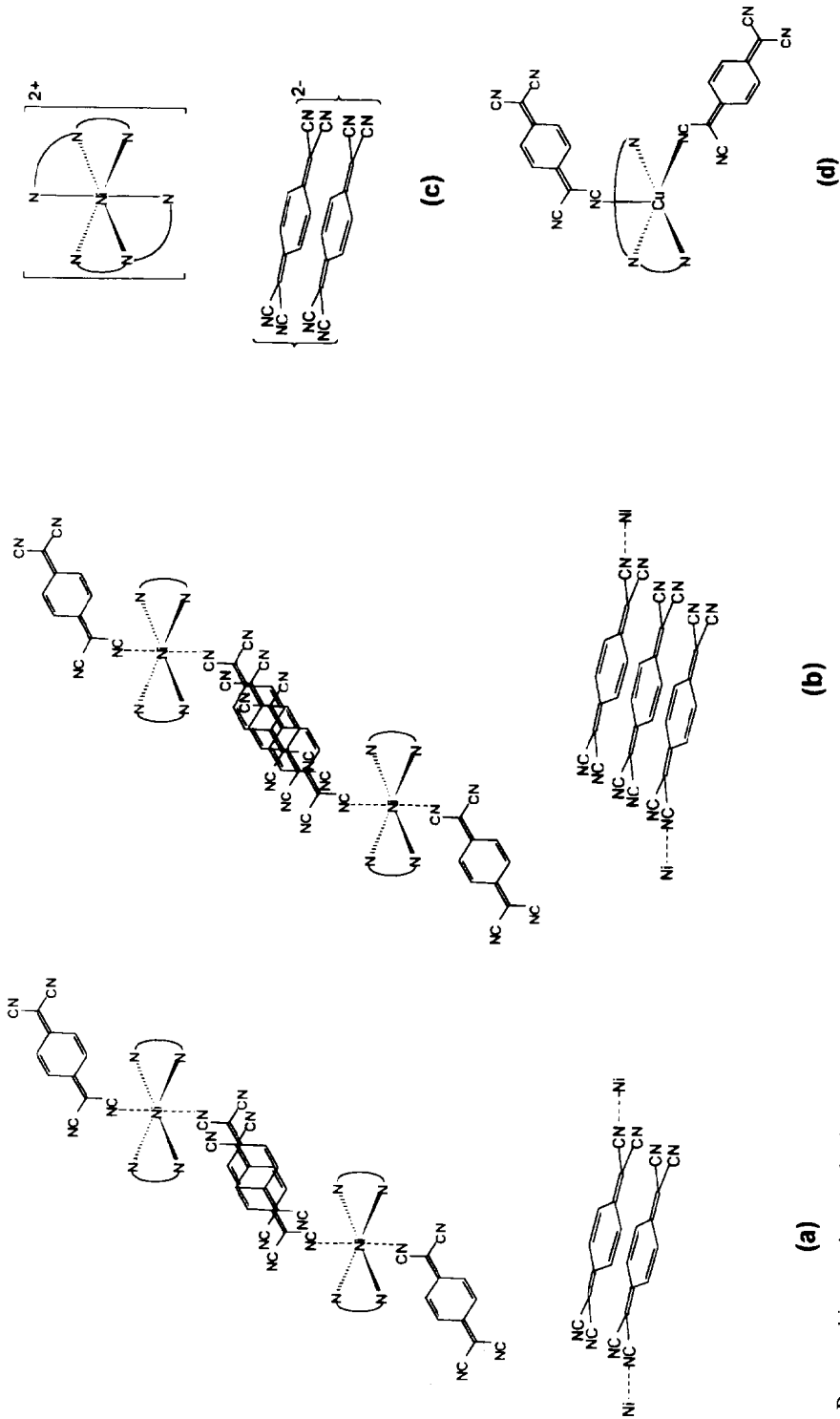

Fig. 1. Diffuse relectance electronic spectra for: (a) [NiL^R(TCNQ)$_2$],[4] (b) [Ni(tn)$_2$(TCNQ)$_3$] and (c) [Ni(tn)$_2$(TCNQ)$_2$].

Fig. 2. Proposed interaction modes between TCNQ and the metallic centres in : (a) [Ni(tn)$_2$(TCNQ)$_2$], (b) [Ni(tn)$_2$(TCNQ)$_3$], (c) [Ni(dien)$_2$](TCNQ)$_2$, no direct interaction expected, and (d) [Cu(dien)(TCNQ)$_2$].

Complex 5 exhibited a magnetic moment that varied with temperature above 60 K (Fig. 3), suggesting that there is an important contribution due to the equilibrium between singlet and triplet states for dimeric $(TCNQ)_2^{2-}$. The magnetic moment increased with temperature as expected for a higher population in the excited triplet state. The antiferromagnetic coupling is therefore lower for this complex since a paramagnetic contribution to the total susceptibility value is found above 60 K.

The magnetic susceptibility data for this complex were fitted to the sum of the Curie and Bleaney–Bowers[21] equations:

$$\chi_M = \frac{2Ng_{Ni}^2\beta^2}{3kT} + \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3+\exp(-2J/kT)}\right] + N_\alpha,$$

where the first term corresponds to the magnetic susceptibility due to the metallic centre according to the Curie law and the third is the temperature-independent paramagnetism taken as 200×10^{-6} emu per nickel atom, while the central term shows the magnetic contribution of the organic radical dimers. The best fit to the experimental data was obtained using the points above 60 K, for which the following values were obtained: $g_{Ni} = 2.528$; $g = 2.012$; $J = -153$ cm^{-1} (Fig. 3). The J value is high enough to yield diamagnetic units at low temperatures and is in the range found in other derivatives with similar behaviour.[22]

CONCLUSION

The reactions of di- and tridentate amino derivatives of nickel and copper with anionic TCNQ reveal the lower stability of the copper complexes, since all the copper derivatives exhibit displacement
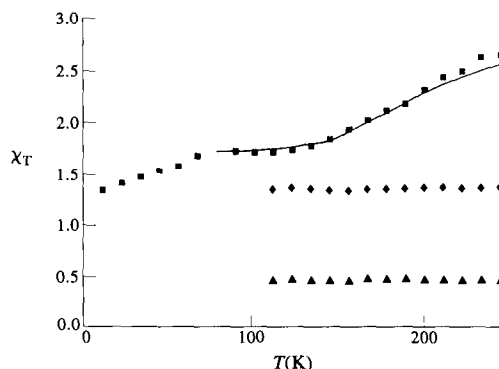
of coordinated amine or decomposition after reaction with TCNQ⁻.

The much more stable nickel derivatives show a strong TCNQ–TCNQ intradimer interaction and, only when the parent complex had labile ligands, weak σ-nitrile metal–TCNQ bonds. The latter interaction is broken in solution, where independent TCNQ⁻, $(TCNQ)_2^{2-}$ or $(TCNQ)_3^{2-}$ and the cationic metallic amine complex are found. The solid species can thus be seen as chains of alternate nickel complex and $(TCNQ)_x^{2-}$ that held the nickel atoms together.

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Fig. 3. Temperature dependence of $\chi_m T$ (emu mol^{-1} K) for [Ni(dien)$_2$](TCNQ)$_2$ (■), [Ni(dien)$_2$](TCNQ)$_3$ (♦) and [Cu(dien)(TCNQ)$_2$] (▲). The solid line results from a least-squares fit using the parameters and equation described in the text.

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