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Delocalized TCNQ Stacks in Nickel and Copper Tetraazamacrocyclic Systems

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New derivatives of formula [M(dieneN$_4$)](TCNQ)$_3$, M = Ni or Cu and dieneN$_4$ = cis- or *trans*-hexamethyltetraazacyclotetradecadiene, have been obtained. The TCNQ units show electronic delocalization and formation of 1D stacks, with no direct interactions with the metal cations. The stack is not uniform and can be seen as formed by trimeric dianions (TCNQ)$_3^{2-}$. The electronic delocalization favors the conductivity in these materials, which behave as good semiconductors. The crystal structures of the trans derivatives have been solved: [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$, triclinic, *P*-1, $a = 8.809(2)$ Å, $b = 10.896(2)$ Å, $c = 13.727(2)$ Å, $\alpha = 103.04(1)°$, $\beta = 101.23(2)°$, $\gamma = 109.37(2)°$, $Z = 1$; [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$: triclinic, P-1, $a = 7.872(1)$ Å, $b = 9.840(1)$ Å, $c = 14.819(1)$ Å, $\alpha = 92.32(1)°$, $\beta = 95.05(1)°$, $\gamma = 95.66(1)°$, $Z = 1$.

Introduction

The possibility of combining organic radicals derived from donor or acceptor molecules as TTF or TCNQ and transition-metal fragments has attracted the interest of many researchers in the field of molecular solids. At the present the correlation between the supramolecular organizations and the associated properties continues attracting attention.[1] For synthetic chemists it is a real challenge to find some keys to understanding the main factors that can determine the wide variety of supramolecular organizations.

One of the problems in establishing some keys is the practical absence of systematic studies focusing the influence of the different factors concerning the radicals and the transition-metal fragments. As the interesting revisions of H. Endres[2] and W. Kaim[3] have pointed out, one of the important factors to be considered in the TCNQ derivatives is the high σ-donor ability of the anion radical, which permits the design of concrete supramolecular architectures by application of the concepts and models of coordination chemistry.

We have been interested in a systematic study of the reactivity of TCNQ$^-$ radicals, or mixtures of TCNQ$^-$/TCNQ species, toward paramagnetic transition-metal fragments having different auxiliary N-donor ligands which contribute to the stabilization of different coordination numbers and stereochemistries. The reaction of neutral TCNQ with copper(II) or nickel(II) derivatives affords integrated stacks with very low electronic transfer between the donor and acceptor units.[4]

Different architectures are observed when the anion radical TCNQ$^-$ reacts with copper(II) or nickel(II) derivatives. Depending on the metal environment stability two different supramolecular architectures with dimerized (TCNQ)$_2^{2-}$ have been obtained. When the metal has a closed stable coordination environment, there is not direct metal−TCNQ interaction and the organic acceptors dimerize in isolated (TCNQ)$_2^{2-}$ units. The crystal packing of these compounds is driven by electrostatic interactions between the cationic metal fragments and the anionic TCNQ dimers that alternate in the crystal.[5] A different situation is found when the metal atom has either vacant coordinative positions or labile ligands which can be easily displaced by the anion radical TCNQ$^-$. In these compounds the TCNQ is σ coordinated to the metal by one nitrile group. The dimerization of the anion radicals is also observed, leading

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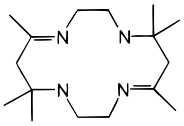
to the formation of infinite chains in which the $(TCNQ)_2^{2-}$ dimers bridge consecutive metallic units.[5e,6]

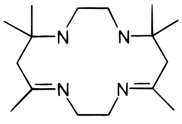
The common feature found in these compounds is the formation of the dimeric dianion from the anion radical, the only TCNQ species present in the solid.

A different situation occurs when a mixture of neutral and anionic TCNQ is used in the reaction with the metal fragments. Thus, we have obtained polymorphs of the compound [Cu(cyclam)$(TCNQ)_3$],[7] in which the chains $-$Cu$-$$(TCNQ)_2$$-Cu-$ previously mentioned are observed, but now there is an extra TCNQ molecule joining adjacent chains by π overlap. The TCNQs are clearly different, with those bonded to the metal having the characteristics of radical anions while those between chains are formally neutral. As a consequence there should be a practically unappreciable electronic delocalization between the TCNQ units.

We have not found previous studies of the type of interaction between a mixture of TCNQ in its neutral and anionic forms and the metal derivatives that have no tendency to coordinate the organic acceptor. From the comparison with the known structural types found in TCNQ compounds we could expect a higher electronic delocalization in a way similar to that found in $Cs_2(TCNQ)_3$.[8] In this way we present here the results of the reactivity between TCNQ in different oxidation states and $[Ni(N_4)]^{2+}$ and $[Cu(N_4)]^{2+}$ fragments in which we exclude the possibilities of direct interaction between the metal atom and the TCNQ radical by the use of unsaturated azamacrocycles that stabilize tetracoordinated metal environments.[5d,9] The macrocycles used are



trans-dieneN$_4$



cis-dieneN$_4$

Experimental Section

All the reactions have been carried out under oxygen-free nitrogen. [Ni(*cis*-dieneN$_4$)]$(ClO_4)_2$,[10] [M(*trans*-dieneN$_4$)]$(ClO_4)_2$ (M = Ni, Cu),[11] and $Et_3NH(TCNQ)_2$[12] were obtained by published methods, and their purities were checked by elemental analyses.

Hazard Warning. *Perchlorate salts are potentially explosive and should be used in small amounts and handled with care.*[13]

All the new compounds have been obtained by the same method: A solution containing 1 mmol of $Et_3NH(TCNQ)_2$ in 15 mL of acetonitrile was dropwise added over a solution of 0.5 mmol of the perchlorate metallomacrocycle in 15 mL of methanol. After complete mixing a dark blue solid appeared, which was filtered off, washed with methanol and diethyl ether, and dried under vacuum.

(5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)nickel(II) (7,7,8,8-Tetracyanoquinodimethanide), [Ni(*cis*-dieneN$_4$)](TCNQ)$_3$. Yield: 59%. Anal. Calcd for $C_{52}H_{44}N_{16}Ni$: C, 65.6; H, 4.6; N, 23.5. Found: C, 65.1; H, 4.8; N, 23.5. IR (cm^{-1}): 2155vs, 1566m, 1508m, 1331m, 1149m, 986m, 829w, 782w.

(5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) (7,7,8,8-Tetracyanoquinodimethanide), [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$. Yield: 66%. Anal. Calcd for $C_{52}H_{44}N_{16}Ni$: C, 65.6; H, 4.6; N, 23.5. Found: C, 66.2; H, 4.6; N, 23.9. IR (cm^{-1}): 2190s, 2177vs, 2155vs, 1562m, 1525m, 1500m, 1328m, 1119m, 831w, 789w.

(5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) (7,7,8,8-Tetracyanoquinodimethanide), [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$. Yield: 67%. Anal. Calcd for $C_{52}H_{44}N_{16}Cu$: C, 65.3; H, 4.6; N, 23.4. Found: C, 65.0; H, 4.7; N, 23.5. IR (cm^{-1}): 2197s, 2162vs, 1561m, 1530m, 1507m, 1330m, 1158m, 990m, 825w.

Physical Measurements. Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. Infrared spectra were recorded as KBr pellets on a Nicolet Magna-550 FT-IR spectrophotometer. Electronic diffuse-reflectance spectra were recorded on a Cary-5 spectrophotometer equipped with a praying mantis 3000$-$200 nm accessory. Magnetic experiments were made on polycrystalline samples using a SQUID magnetometer MPMS-XL-5 manufactured by Quantum Design. The temperature dependence of the magnetization in the range between 2 and 300 K was recorded using a constant magnetic field of 0.5 T. The experimental data have been corrected for the magnetization of the sample holder and for atomic diamagnetism as calculated from the known Pascal's constants. X-band powder EPR spectra have been obtained on a Bruker ESP 300 apparatus equipped with a Bruker ER035M gausometer and an Oxford JTC4 cryostat. Electrical conductivity measurements at variable temperature were performed either by the two (single crystals) or four (powder) point methods, using an APD cryogenics INC HC2 helium cryostat.[14]

X-ray Structure Determination. Good quality crystals have been obtained by slow diffusion of dilute reactant solutions. For the two compounds studied a deep blue prismatic crystal was coated with resin epoxy and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensity data were collected by the $\omega-2\theta$ technique and corrected for Lorentz and polarization effects. Atomic scattering factors were taken from ref 15.

The structure was solved by Patterson and Fourier methods and refined by applying full-matrix least-squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. The calculations were carried out with the SHELXL93 software package.[16] A summary of the fundamental crystal data is given in Table 1.

Results and Discussion

The reaction between $Et_3NH(TCNQ)_2$ and the perchlorate salts of the unsaturated metallomacrocycles described above gives rise to derivatives of general formula $[M(N_4)](TCNQ)_3$. In these derivatives, especially in the nickel ones, no charge transfer between the TCNQ and the metal is expected, and the anionic species $(TCNQ)_3^{2-}$ should be present in these com-

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Table 1. Crystal and Refinement Data for [M(*trans*-dieneN$_4$)](TCNQ)$_3$

compd	[Ni(*trans*-dieneN$_4$)](TCNQ)$_3$	[Cu(*trans*-dieneN$_4$)](TCNQ)$_3$
empirical formula	$C_{52}H_{44}N_{16}Ni$	$C_{52}H_{44}N_{16}Cu$
mol wt	951.6	956.4
cryst syst	triclinic	triclinic
space group	*P*-1 (no. 2)	*P*-1 (no. 2)
a, Å	8.809(2)	7.872(1)
b, Å	10.896(2)	9.840(1)
c, Å	13.727(2)	14.819(1)
α, deg	103.04(1)	92.32(1)
β, deg	101.23(2)	95.05(1)
γ, deg	109.37(2)	95.66(1)
Z	1	1
V, Å^3	1157.7(4)	1136.5(2)
D_{calcd}, Mg m^{-3}	1.37	1.40
temp, K	293	293
λ(Mo *K*α), Å	0.71073	0.71073
μ, cm^{-1}	4.76	5.34
R1,[a] $I > 2\sigma(I)$	0.052	0.085
wR2,[b] $I > 2\sigma(I)$	0.065	0.184

[a] $R1 = \sum(|F_o| - |F_c|)^2/\sum F_o^2$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

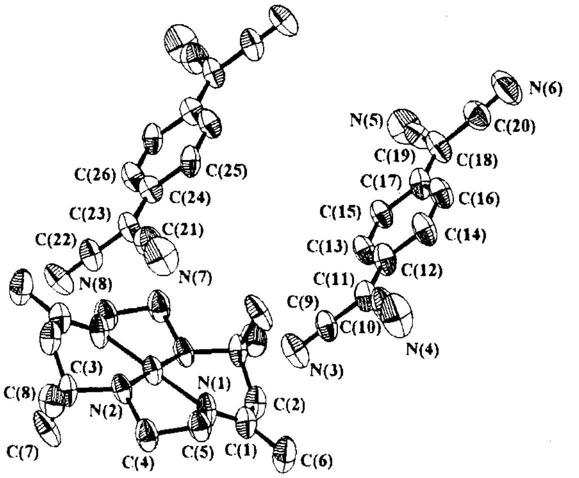

Figure 1. ORTEP view (30% thermal ellipsoids) and atom labeling of [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$. The atom labeling of the copper compound is identical.

pounds. The TCNQ either can be equally charged as in Cs$_2$(TCNQ)$_3$[8] or have the two extra electrons located on two radical anions, the third TCNQ remaining in the neutral state, as in [Cu(cyclam)(TCNQ)$_3$].[7] Since the starting material is composed of one neutral and one anionic TCNQ per formula unit, we expect an excess of neutral TCNQ in these reactions. This fact is confirmed by the appearance from the reaction mixture of TCNQ crystals after prolonged crystallization periods.

Crystal Structure of [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$. An ORTEP view of the molecular unit is shown in Figure 1. The most significant bond lengths are listed in Table 2.

The nickel atom, located on an inversion center, is tetracoordinated in a square-planar environment. The two nickel−nitrogen distances are 1.905(5) and 1.934(6) Å, the shorter distance corresponding to the sp^2 nitrogen. The bond distances and angles of the macrocycle are similar to those found in the starting [Ni(*trans*-dieneN$_4$)](ClO$_4$)$_2$,[17] or in the isomeric [Ni(*cis*-dieneN$_4$)]$^{2+}$.[5d,18]

There are two crystallographically different TCNQ molecules, types A and B. In the unit cell we found two TCNQ type A molecules, symmetry related by an inversion center located between them, and one TCNQ type B molecule whose middle point coincides with another inversion center. All the TCNQs are parallel with an angle between planes of 0.12(2)°. The TCNQ π clouds overlap with distances of 3.13(1) Å (A−B) and 3.45(1) Å (A−A). The longitudinal axis of all the TCNQs are quasi parallel along the stack, the TCNQ B being rotated only 4.6(8)° relative to the TCNQ A, giving rise to a monodimensional stack. These different distances enable the stack to be seen as formed by TCNQ trimers ABA (Figure 2). The overlap inside the trimer is of the type ring over external bond (Figure 3a).

Table 2. Selected Bond Lengths (Å) for [M(*trans*-dieneN$_4$)](TCNQ)$_3$

[Ni(*trans*-dieneN$_4$)](TCNQ)$_3$		[Cu(*trans*-dieneN$_4$)](TCNQ)$_3$	
Ni−N1	1.905(5)	Cu−N1	1.96(1)
Ni−N2	1.934(6)	Cu−N2	2.03(1)
N3−C9	1.134(8)	N3−C9	1.11(2)
N4−C10	1.143(11)	N4−C10	1.11(2)
N5−C19	1.144(12)	N5−C19	1.14(2)
N6−C20	1.121(9)	N6−C20	1.13(2)
N7−C21	1.141(12)	N7−C21	1.14(1)
N8−C22	1.140(8)	N8−C22	1.11(2)
C9−C11	1.440(8)	C9−C11	1.47(2)
C10−C11	1.429(11)	C10−C11	1.40(2)
C11−C12	1.391(11)	C11−C12	1.36(2)
C12−C13	1.422(10)	C12−C13	1.43(2)
C12−C14	1.434(8)	C12−C14	1.44(2)
C13−C15	1.348(11)	C13−C15	1.32(2)
C14−C16	1.340(11)	C14−C16	1.32(1)
C15−C17	1.425(7)	C15−C17	1.44(2)
C16−C17	1.420(10)	C16−C17	1.41(2)
C17−C18	1.401(11)	C17−C18	1.37(2)
C18−C19	1.423(12)	C18−C19	1.45(2)
C18−C20	1.426(8)	C18−C20	1.42(2)
C21−C23	1.416(12)	C21−C23	1.47(2)
C22−C23	1.432(8)	C22−C23	1.42(2)
C23−C24	1.406(11)	C23−C24	1.38(2)
C24−C25	1.425(7)	C24−C25	1.42(2)
C24−C26	1.436(10)	C24−C26	1.40(2)
C25−C26′	1.349(11)	C25−C26′	1.34(2)

There is a great deal of work relating the carbon−carbon bond distances in every TCNQ to the degree of charge held on it.[19] By using the Kistenmacher relation, we can deduce that the two extra electrons are almost equally distributed over all the

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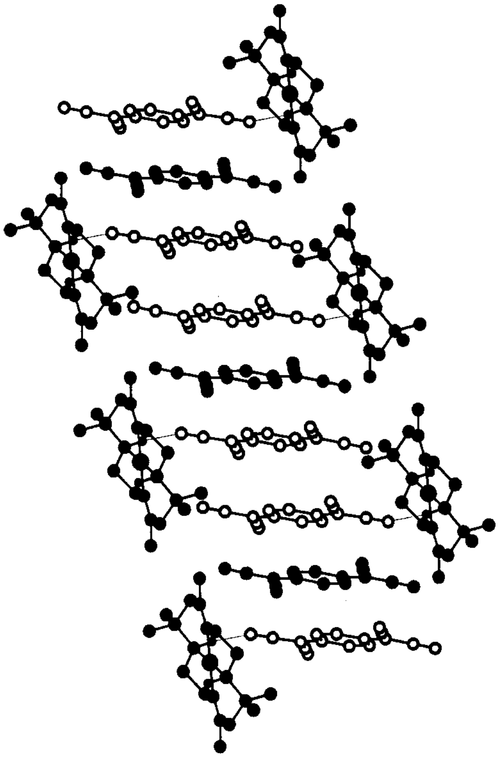

Figure 2. View of the stack in [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$: TCNQ A, white circles, TCNQ B, black circles.

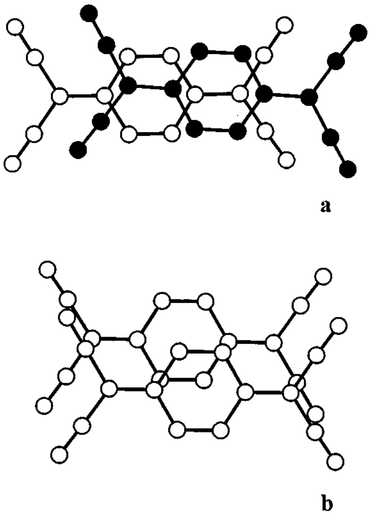

Figure 3. View of the TCNQ overlap in [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$: (a) A−B overlap (intratrimer), (b) A−A′ overlap (intertrimers).

TCNQs since each type A unit has a charge of approximately −0.6 and the type B unit of −0.7. In this way we can see the trimers as dianions (TCNQ)$_3^{2-}$, with the two electrons delocalized among the three molecules. The overlap takes place between the double bonds of the quinoid rings since the TCNQ type A molecules have their longitudinal axis parallel but shifted 1.72(1) Å along the perpendicular direction (Figure 3b). The longer intertrimer distance (3.45(1) Å) indicates that the electrons are delocalized inside the trimers, but this delocalization almost disappears along the chain, a fact that must be reflected in the conductivity value.

Although the TCNQ is not directly coordinated to the metal, the organic stack is not completely isolated from the metallomacrocycles, which are located at both sides of the TCNQ stack, forming an angle of 116.2(2)° with the TCNQs. The macrocycles are linked by hydrogen bonds with the TCNQ A in the only interaction between the anionic and the cationic parts of the compound. The data of this hydrogen bond are N2−H2 = 1.009(5) Å, H2···N6 = 1.973(8) Å, and angle N2−H2−N6 = 169(1)°. Due to the crystal symmetry each macrocycle is hydrogen bonded to two TCNQ units belonging to different stacks.

Crystal Structure of [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$. This structure is similar to that described for the nickel compound. Its labeling scheme is identical to that shown in Figure 1 for the nickel derivative. Selected bond lengths are listed in Table 2. With the limitations imposed by the poorer quality of the crystal, we can conclude that the bond distances and angles are similar to those for the nickel derivative.

This compound also presents two crystallographically different TCNQ molecules, TCNQ A, located on a general position, and TCNQ B, located on an inversion center. These TCNQs overlap in the ring over external bond mode (Figure 3a), forming a monodimensional stack integrated by trimeric species (TCNQ)$_3^{2-}$ with intratrimer distances of 3.19(2) Å and intertrimer distances of 3.25(2) Å. The more similar distances agree with a greater delocalization along the chain confirmed by the conductivity values.

The TCNQ stacks are also separated by rows of cationic metallomacrocycles, hydrogen bonded to the organic acceptors, N2−H2 = 0.91(2) Å, H2···N8 = 2.27(3) Å, and angle N2−H2−N8 = 142(1)°. In contrast with the nickel derivative this H-bond is formed by the TCNQ B, which due to its centrosymmetric nature bridges two metallomacrocycles, while in the nickel compound the TCNQ A formed only one bond per molecule.

A second difference between the nickel and the copper compounds is the intertrimer overlapping. Thus, while in the nickel derivative it is lateral along the transverse axis, in the copper derivative a frontal ring over external bond of the same type as that found inside the trimers is observed. Since the TCNQs belonging to different trimers are slipped in the direction opposite that found inside the trimer, the stack is formed by a sort of zigzag chain (Figure 4). A similar stack of dianionic trimers has been found in a molybdenum dithiocarbamate derivative,[20] although in this case the trimers are much more isolated with greater intrastack distances, a fact that must give rise to poorer conductive properties.

Electrical Conductivity. The three compounds are semiconductors with room temperature conductivity values measured in pressed powdered samples of 8.3×10^{-3}, 3.1×10^{-3}, and 3.3×10^{-3} S cm^{-1} for [Ni(*cis*-dieneN$_4$)](TCNQ)$_3$, [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$, and [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$, respectively.

The single-crystal conductivity for the two *trans*-dieneN$_4$ derivatives has also been measured by the two-probe method in the temperature range 300−170 K. Both compounds show the expected semiconducting behavior with room temperature conductivity values of 0.155 S cm^{-1} for the nickel and 0.145 S cm^{-1} for the copper compound. Assuming an inverse exponential dependence of the single-crystal conductivity with temperature, activation energies of 0.35 eV for the nickel and 0.12 eV for the copper compound are obtained. The lower activation energy of the latter could be correlated with the shorter intramolecular distances found in the TCNQ stack of the copper compound.

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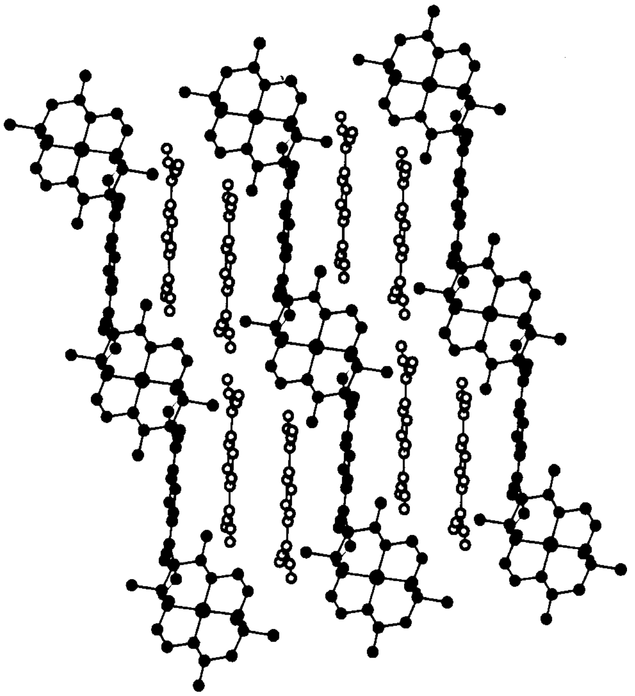

Figure 4. TCNQ stack in [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$: TCNQ A, white circles; TCNQ B, black circles.

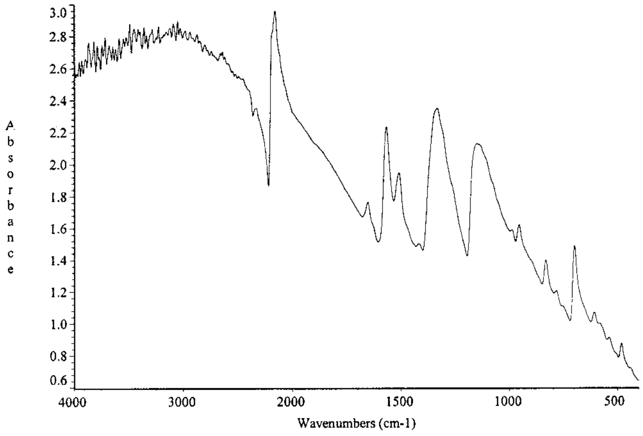

Figure 5. IR spectrum in a KBr pellet of [Ni(*cis*-dieneN$_4$)](TCNQ)$_3$.

Optical Spectra. In consonance with the delocalization suggested by the conductivity values, the IR spectra of both compounds present a very broad electronic absorption centered around 3200 cm^{-1} with the TCNQ vibronic modes superimposed on it, a characteristic feature of derivatives showing electronic delocalization (Figure 5).[21]

The IR spectrum of the TCNQ derivatives is very illustrative about the formal oxidation state and the coordinative status of these organic acceptor molecules.[22] Thus, the neutral TCNQ shows the characteristic vibration frequencies ν(CN) = 2228 cm^{-1}, ν_{20}(b$_{1u}$) = 1530 cm^{-1}, ν_{34}(b$_{2u}$) = 1524 cm^{-1}, ν_4(a$_g$) = 1424 cm^{-1}, ν_{50}(b$_{3u}$) = 860 cm^{-1}, and ν_7(a$_g$) = 705 cm^{-1}, while for the radical anion the vibration modes can be observed at 2194/2177, 1577, 1507, 1386, 824, and 722 cm^{-1}. Especially significant about the charge degree are the *ungerade* bands ν_{20} (which appears at 1507 cm^{-1} in our compounds) and ν_{50} (at 824 cm^{-1}), both shifted to lower frequencies when the charge on the TCNQ is increased.[23]

The broadening of the bands in our derivatives makes it difficult to obtain definite conclusions from the IR frequency values; however, the splitting of the band in the 1500−1550 cm^{-1} range can suggest the presence of TCNQ in intermediate oxidation states as deduced from the structural data of [Ni(*trans*-dieneN$_4$)](TCNQ)$_3$.

The solid-state electronic spectra of the three compounds are very similar, with absorption bands at 26200, 17300, 11600, 7100, and 4200 cm^{-1}. The first two bands are characteristic of TCNQ derivatives and correspond to the two first locally excited levels of the anion radical, while the band at 11600 cm^{-1} has been assigned to a charge-transfer involving radical anions.[24] The two lower frequency bands are very broad and characteristic of mixed valence TCNQ compounds.[25] The most interesting band is that centered at 4200 cm^{-1} resulting from a charge transfer between radical anionic and neutral species (CT$_2$), which appears around 6000 cm^{-1} and shifts to lower frequencies when the charge delocalization increases.

Magnetic Properties. The bulk static magnetic susceptibility has been measured over the temperature range 2−300 K for the three compounds.

The nickel derivatives are weakly paramagnetic. This magnetism should come from the anion radicals, as the nickel is in a square-planar environment. The observed behavior can be fitted to a Curie law (C/T) plus a temperature-independent paramagnetic contribution (TIP). The C and TIP values are C = 0.005 emu·K·mol^{-1} and TIP = 800 × 10^{-6} emu·mol^{-1} for the *cis* derivative and C = 0.025 emu·K·mol^{-1} and TIP = 730 × 10^{-6} emu·mol^{-1} for the *trans* derivative. The low C values (approximately 0.01 and 0.06 electron per formula) indicate the presence of small amounts of paramagnetic impurities that may come from isolated TCNQ$^-$ radicals in the structure (1 every 225 or 45 TCNQ molecules, respectively). On the other side, the observed TIP values may have, besides the TIP contribution from the Ni(II) ions (on the order of (100−150) × 10^{-6} emu·mol^{-1}), a Pauli parmagnetic contribution coming from the delocalized electrons of the anion radicals. These values are in the range of the Pauli paramagnetism observed in other conducting radical salts.[26] It is interesting to note that in both Ni compounds the TIP contribution is higher than that of the Cu one. Nevertheless, this fact may be an experimental artifact coming from the very low signals measured in the Ni compounds and only reflects the experimental difficulty in making the diamagnetic corrections (from the sample and the sample holder). In fact, at high temperatures the diamagnetic signal coming from the sample holder is on the same order (and even higher) as the paramagnetic signal of the Ni samples, and thus, these diamagnetic corrections become crucial. That means that the TIP values of both Ni compounds must be considered as approximate rather than exact values, removing the necessity of attributing the extra TIP to the Pauli-like paramagnetism.

The copper compound follows a Curie law with C = 0.3879 emu·K·mol^{-1} with a TIP of 288 × 10^{-6} emu·mol^{-1} (Figure

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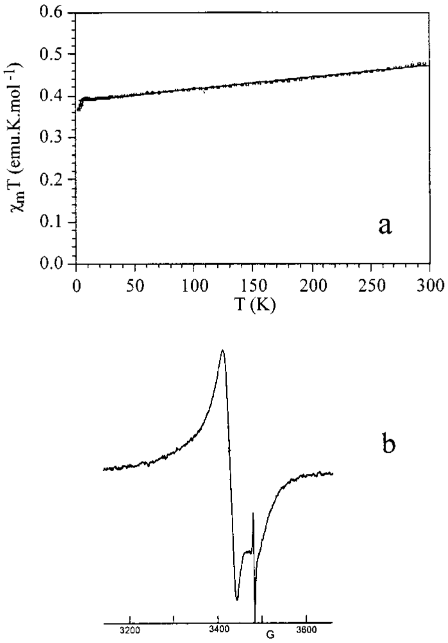

Figure 6. (a) χ_mT product as a function of temperature for [Cu(*trans*-dieneN$_4$)](TCNQ)$_3$. The solid line represents the best fit to a Curie law with a TIP contribution. (b) Room temperature EPR spectrum of a powdered sample of the same compound.

6a). As for the nickel derivatives, this TIP is larger than that coming from Cu(II) (60×10^{-6} emu·mol^{-1}) and probably arises from an incomplete diamagnetic correction. The C value corresponds to that expected for a Cu(II) ion ($S = 1/2$) with a g value of 2.034, very close to that observed by EPR (Figure 6b). In fact, the room temperature EPR spectrum of a powdered sample shows a large isotropic signal ($\Delta H = 32$ G) centered at $g = 2.038$, corresponding to the square-planar Cu(II) ions, which coexists with a narrow line ($\Delta H = 4$ G) centered at $g = 2.003$, corresponding to a very small amount of isolated TCNQ$^-$ impurities. This small amount of paramagnetic impurities is almost impossible to detect from the static susceptibility measurements as they are masked by the signal of the cations (which is 2 orders of magnitude bigger, as deduced from the ratio between the areas of the EPR signals). In the low-temperature EPR spectrum the copper signal shows the typical axial pattern since it is split into a parallel component ($g_{\|} = 2.10$) and a perpendicular one ($g_{\perp} = 2.03$). There is no significant variation however in the medium g value, 2.05.

These results indicate on one hand that the Cu(II) ions are magnetically well isolated, as expected from the good isolation imposed by the tetraaza ligand and the weak hydrogen bonds between these rings and the TCNQ units and, on the other hand, that the electrons located in the organic stacks do not contribute to the magnetic susceptibility since the trimeric units (TCNQ)$_3^{2-}$ hold two spins and their ground state must be diamagnetic. The thermally accessible triplet state should be scarcely populated even at room temperature, and therefore the contribution to the magnetic susceptibility of the TCNQ radicals is negligible.

Conclusion

The presence of TCNQ units not fully reduced favors the formation of stacks with electronic delocalization. This delocalization is also favored by the uncoordination of the TCNQ to the metal atom as is immediately evidenced by comparison with the compound [Cu(cyclam)](TCNQ)$_3$,[7] also with three TCNQ units and two negative charges per metal atom. In this case the charges are completely localized, and we have two radical anions coordinated to the metal atom and forming dimeric dianions and one neutral TCNQ that overlaps with them: AA··B··AA··B··AA. In contrast, the compounds here described form trimers with all the TCNQs in the same formal oxidation state, and the stack mode is ABA···ABA···ABA. It seems obvious that the coordination of the TCNQ molecule is responsible for their higher or lower electronic delocalization degree.

Conductivity measurements show that these compounds are semiconductors with high room-temperature conductivities and high activation energies in agreement with the trimeric structure of the TCNQ stacks. From the magnetic point of view, the weak bond between the TCNQ radicals and the metallic centers prevents any exchange coupling between the metal centers.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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