Supramolecular Architecture in Nickel(II) Polyamine Tetracyanoquinodimethanido Systems

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Three different supramolecular architectures corresponding to $[Ni(dien)_2](TCNQ)_2$ (dien = 1,4,7-triazaheptane; TCNQ = 7,7,8,8-tetracyanoquinodimethane), $[Ni(trien)(TCNQ)_2]$ (trien = 1,4,7,10-tetraazadecane), and $[Ni(cyclam)(TCNQ)_2]$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) have been prepared and crystallographically characterized: $[Ni(dien)_2](TCNQ)_2$, triclinic, $P\bar{1}$, $a = 8.319(2)$ Å, $b = 9.074(2)$ Å, $c = 11.145(3)$ Å, $\alpha = 80.91(2)°$, $\beta = 74.10(2)°$, $\gamma = 82.12(2)°$, $Z = 1$; $[Ni(trien)(TCNQ)_2]$, orthorombic, *Pccn*, $a = 22.677(7)$ Å, $b = 7.888(5)$ Å, $c = 15.801(3)$ Å, $Z = 4$; $[Ni(cyclam)(TCNQ)_2]$, triclinic, $P\bar{1}$, $a = 8.699(2)$ Å, $b = 9.752(3)$ Å, $c = 10.138(2)$ Å, $\alpha = 87.29(2)°$, $\beta = 77.14(2)°$, $\gamma = 75.00(2)°$, $Z = 1$. All of them are built by dimeric units $(TCNQ)_2{}^{2-}$ which are out of the coordination sphere in $[Ni(dien)_2](TCNQ)_2$ and σ-coordinated to the metal in *cis* and *trans* positions in $[Ni(trien)(TCNQ)_2]$ and $[Ni(cyclam)(TCNQ)_2]$, respectively. In the two latter compounds the bonded dimeric units $(TCNQ)_2{}^{2-}$, formed by intermolecular interactions, give rise to infinite chains consisting of alternating $[Ni(N_4)]^{2+}$ and $(TCNQ)_2{}^{2-}$ moieties in the crystal. The existence of hydrogen bonds between the TCNQ nitriles and amine groups belonging to the metal fragments stabilizes the supramolecular architecture, increasing the dimensionality of the interactions. The spectroscopic and magnetic properties are discussed according to the structural models.

Introduction

In the field of molecular networks containing organic radicals, macroscopic properties like magnetic order or electric conductivity can be produced when the appropriate supramolecular arrangement is attained.[1] On this basis, when paramagnetic metallic centers are coassembled with organic radicals as building blocks in the moelcular networks, "hybrid" materials combining the properties of the organic and inorganic components can be formed.[2]

Special attention have been received the assemblage of organonitrile radicals with copper complexes because of the wide possibilities of interaction that can be found. The first approach was directed to study donor−acceptor interactions between planar copper complexes with π electron density, such as Schiff bases and TCNQ (7,7,8,8-tetracyanoquinodimethane), with formation of integrated systems.[3] When complexes with the metal fully coordinated such as $[Cu(phen)_3]^{2+}$ are used, new compounds, $[Cu(phen)_3](TCNQ)_2$, without direct interaction between the metal and the TCNQ are formed.[4]

The ability of reduced $TCNQ^-$ units to coordinate to metallic fragments acting as σ-donor ligands can be used to built extended molecular assemblies, since the transition metals offer the possibility of orientate the coordinated radicals in the solid.[5] Since the report of the interesting copper compounds with DCNQI (*N,N′*-dicyanoquinonediimine), a metallic polymer,[6] and with TCNQ, electrically bistable material,[7] great efforts have been devoted to the study of molecular materials with σ interaction between the metal and the polynitrile. Cornelissen[8] reported the compound $[Cu(abpt)_2(TCNQ)_2]$ (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) with the copper atom octahedrally coordinated to six nitrogen atoms, four in the equatorial plane from the abpt ligands and two apical ones belonging to the σ-monodentate $TCNQ^-$ anion radicals. These

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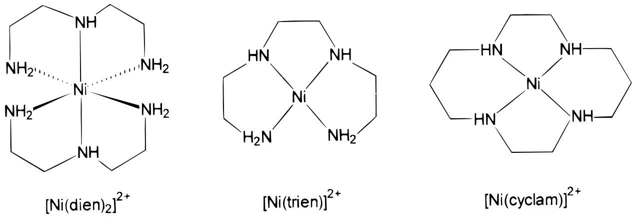
Table 1. Crystal and Refinement Data for the Obtained Compounds

compd	$[Ni(dien)_2](TCNQ)_2$	$[Ni(trien)(TCNQ)_2]$	$[Ni(cyclam)(TCNQ)_2]$
formula	$C_{32}H_{34}N_{14}Ni$	$C_{30}H_{26}N_{12}Ni$	$C_{34}H_{32}N_{12}Ni$
mol wt	673.4	613.3	667.4
cryst system	triclinic	orthorombic	triclinic
space group	$P\bar{1}$ (No. 2)	*Pccn* (No. 56)	$P\bar{1}$ (No. 2)
a, Å	8.319(2)	22.677(7)	8.699(2)
b, Å	9.074(2)	7.888(5)	9.752(3)
c, Å	11.145(3)	15.801(3)	10.138(2)
α, deg	80.91(2)	90	87.29(2)
β, deg	74.10(2)	90	77.14(2)
γ, deg	82.12(2)	90	75.00(2)
Z	1	4	1
V, $Å^3$	795(4)	2826(2)	809.8(4)
ρ_{calcd}, g cm^{-3}	1.41	1.44	1.37
temp, K	295	295	295
radiation	graphite monochromated Mo Kα ($\lambda = 0.710\,69$ Å)		
μ(Mo Kα), cm^{-1}	6.57	7.3	6.43
R^a	0.063	0.065	0.056
$R_w{}^a$	0.074	0.073	0.059

[a] $R = \sum|\Delta F|/\sum|F_o|$; $R_w = (\sum w\Delta^2F/\sum w|F_o|^2)^{1/2}$.

Chart 1



coordinated TCNQ's are dimerized forming diamagnetic dianions $(TCNQ)_2{}^{2-}$ with each organic anion coordinated to a different copper atom, thus forming infinite linear chains.

As a part of our project directed to the study of the supramolecular organization in solids containing organic radicals and paramagnetic complexes, we have chosen metallic fragments containing nitrogen-donor ligands because of the variety of posibilities in the coordination environments and the electronic behavior. In this paper we report the synthesis, structural characterization and the properties of three different molecular architectures containing $[NiL_N]^{2+}$ and $(TCNQ)_2{}^{2-}$ units.

The metallic fragments used are shown in Chart 1. Their behavior toward $TCNQ^-$ is also compared with those previously reported in the literature.

Experimental Section

All the reactions have been carried out under oxygen-free nitrogen. The starting materials, LiTCNQ,[9] $[Ni(dien)_2](ClO_4)_2$,[10] $[Ni(trien)](ClO_4)_2$,[11] and $[Ni(cyclam)](ClO_4)_2$,[12] have been obtained by the published methods and their purity checked by elemental analyses.

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

Bis(1,4,7-triazaheptane)nickel(II) 7,7,8,8-Tetracyanoquinodimethanide, $[Ni(dien)_2](TCNQ)_2$. A solution of LiTCNQ, 0.22 g (1 mmol) in 15 mL of methanol, was added to a stirred solution of $[Ni(dien)_2](ClO_4)_2$ in 20 mL of methanol in a 1:2 molar ratio of metal complex to TCNQ. The resulting solution was stirred for 3 h, and the deep blue solid that formed was filtered off, washed with methanol and diethyl ether and dried under vacuum. Yield: 70%. Found: C, 56.8; H, 5.0; N, 28.8. Calcd for $C_{32}H_{34}N_{14}Ni$: C, 57.0; H, 5.1; N, 29.1. IR (cm^{-1}): 3289 s, 2178 vs, 2156 m, 1578 m, 1500 m, 1347 m, 1177 m, 831 w, 723 w.

Bis(7,7,8,8-tetracyanoquinodimethanido)(1,4,7,10-tetraazadecane)nickel(II), $[Ni(trien)(TCNQ)_2]$. A solution of LiTCNQ, 0.22 g (1 mmol) in 15 mL of methanol, was added dropwise to a solution of the $[Ni(trien)](ClO_4)_2$ in 15 mL of MeOH−water (1:2) in a 2:1 molar ratio. The resulting solution was stirred for about 5 h, and the deep blue solid that precipitates was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Yield: 68%. Found: C, 58.5; H, 4.2; N, 26.9. Calcd for $C_{30}H_{26}N_{12}Ni$: C, 58.7; H, 4.2; N, 27.4. IR (cm^{-1}): 3271 m, 2202 w, 2190 s, 2176 vs, 2163 s, 2157 s, 1578 m, 1500 m, 1339 m, 1179 m, 829 w, 722 w.

Bis(7,7,8,8-tetracyanoquinodimethanido)(1,4,8,11-tetraazacyclotetradecane)nickel(II), $[Ni(cyclam)(TCNQ)_2]$. A solution of LiTCNQ, 0.22 g (1 mmol) in 15 mL of methanol, was added dropwise to a solution of $[Ni(cyclam)](ClO_4)_2$ in 15 mL of MeOH−water (1:2) in a 2:1 molar ratio. The resulting solution was stirred for about 3 h, and the deep blue solid was filtered off, washed with three portions of 20 mL of water and then with methanol and diethyl ether, and dried under vacuum. Yield: 60%. Found: C, 60.3; H, 4.7; N, 24.8. Calcd for $C_{34}H_{32}N_{12}Ni$: C, 61.2; H, 4.8; N, 25.2. IR (cm^{-1}): 3225 m, 2186 s, 2182 vs, 2161 m, 1584 m, 1504 m, 1348 m, 1177 m, 825 w, 722 w.

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 solution and 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 MPMS-5S SQUID magnetometer manufactured by Quantum Design. The temperature dependence of the magnetization in the range between 5 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-ray Structure Determinations. Good quality single crystals of the three compounds were obtained by slow difussion of a LiTCNQ methanolic solution into a MeOH−water solution of the corresponding perchlorate complex. A summary of the fundamental crystal data is reported in Table 1. In the three cases a deep-blue crystal of prismatic shape was resin epoxy coated and mounted in a *κ* diffractometer. The cell dimensions were refined by least-squares fitting the *θ* values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni were taken from ref 13. The structures were solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of isotropic refinements.[14]

Since no trend in ΔF vs F_o or $(\sin\theta)/\lambda$ was observed in any of the three solving processes, a final refinement was undertaken with unit

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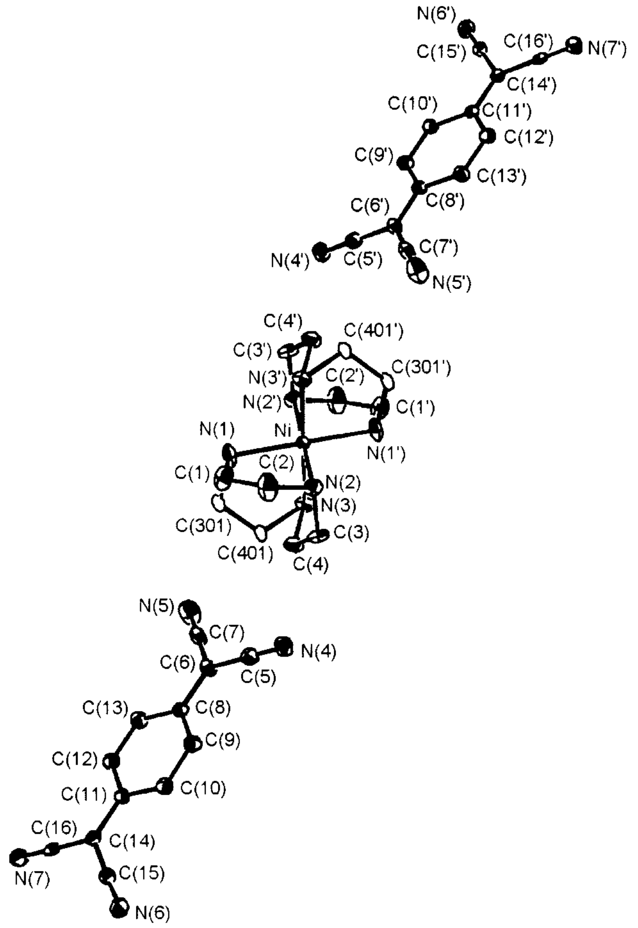


Figure 1. ORTEP view and atom labeling of the molecular unit of [Ni(dien)$_2$](TCNQ)$_2$.

weights and 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. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system.[15]

In the solving process of the structure of [Ni(dien)$_2$](TCNQ)$_2$ positional disorder was found for the dien ligand. In this case the final anisotropic refinement was carried out for all the non-hydrogen atoms, including those involved in the disorder whose population factors were also refined giving values of $^2/_3$ and $^1/_3$ for the alternative positions.

Results and Discussion

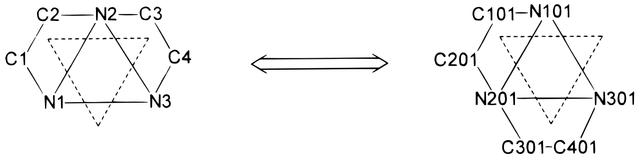
The synthesized TCNQ compounds have been obtained by metathesis reactions from the parent perchlorate derivatives. They are dark blue in color and slightly soluble only in good donor solvents such as acetonitrile or DMSO, and their solutions rapidly decompose in the air.

The formation of *cis*-[Ni(trien)(TCNQ)$_2$] from the planar [Ni(trien)]$^{2+}$ probably occurs with the influence of the solvent. As a first step the addition of two MeOH molecules gives the hexacoordinated *trans*-[Ni(trien)(MeOH)$_2$] which undergoes a rapid interconversion to the *cis* isomer without nickel−nitrogen cleavage, as has been proved in aqueous solution.[16] The interconversion is followed by the substitution of MeOH by TCNQ$^-$. If the first step were the addition of TCNQ$^-$ in the *trans* positions, the low solubility of the resulting complex would prevent the isomerization to the isolated compound.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ni(dien)$_2$](TCNQ)$_2$

Ni−N1	2.129(9)	C8−C9	1.42(1)
Ni−N2	2.107(8)	C8−C13	1.42(1)
Ni−N3	2.118(8)	C9−C10	1.36(2)
N4−C5	1.15(1)	C10−C11	1.41(1)
N5−C7	1.14(2)	C11−C12	1.43(1)
N6−C15	1.14(1)	C11−C14	1.39(1)
N7−C16	1.14(1)	C12−C13	1.37(2)
C5−C6	1.41(1)	C14−C15	1.44(1)
C6−C7	1.42(2)	C14−C16	1.42(1)
C6−C8	1.40(2)		
N2−Ni−N3	86.2(3)	Ni−N2−C2	108.8(7)
N1−Ni−N3	88.8(3)	Ni−N3−C4	110.4(6)
N1−Ni−N2	81.1(3)	Ni−N1−C301	102(1)
Ni−N1−C1	110.4(6)	Ni−N3−C401	105(1)
Ni−N2−C3	107.7(7)		

Scheme 1



Crystal Structure of [Ni(dien)$_2$](TCNQ)$_2$. An ORTEP view of the molecular unit is shown in Figure 1. Bond lengths and angles are listed in Table 2.

The crystal structure can be described as formed by cationic [Ni(dien)$_2$]$^{2+}$ and dimeric anionic (TCNQ)$_2$$^{2-}$ units.

In the cation the nickel atom, which lies on an inversion center, is six-coordinated to the nitrogen atoms of two dien ligands, related by symmetry. The nickel−nitrogen distances range from 2.107(8) to 2.129(9) Å as is usual in octahedral nickel(II) complexes.[17] The three nitrogen atoms of the dien ligand are coordinated in *fac* positions to the metal atom. This coordination minimizes the strains in the aliphatic chain, as it can be observed in the angles around the nickel atom, very close to the ideal 90°, ranging from 88.8(3)° for N1−Ni−N3 to 81.1(3)° for N1−Ni−N2.

The dien ligands show positional disorder in the crystal. The disorder can be interpreted either as the result of a 120° rotation around a pseudo-3-fold axis perpendicular to the octahedron face, where the amine is coordinated, or as a 180° rotation around a hypothetical 2-fold axis passing throught N3 and the center of the C1−C2 bond (see Scheme 1).

The disorder gives rise to a change in the amine atom distribution, as can be seen in the scheme, although five of the seven atoms remain in the same positions; that is N1 and N201 are coincident, as are N2 and N101, N3 and N301, C1 and C201, and C2 and C101. The net effect of the disorder is to change C3 and C4 to the new positions C301 and C401. From the obtained population factors approximately $^2/_3$ of the molecules have the dien atoms as in the left figure of the scheme and $^1/_3$ as in the right figure.

The two TCNQ groups in the unit cell are symmetry related and are uncoordinated to the metal. The interatomic distances are characteristic of the radical anion TCNQ$^-$.[18]

The TCNQ molecule is not planar, since the two exocyclic −C(CN)$_2$ planes are tilted 3.5(4) and 6.3(4)°, respectively, relative to the central quinoid ring plane. Both ends are tilted in the same direction, conferring a slight boat conformation on the TCNQ.

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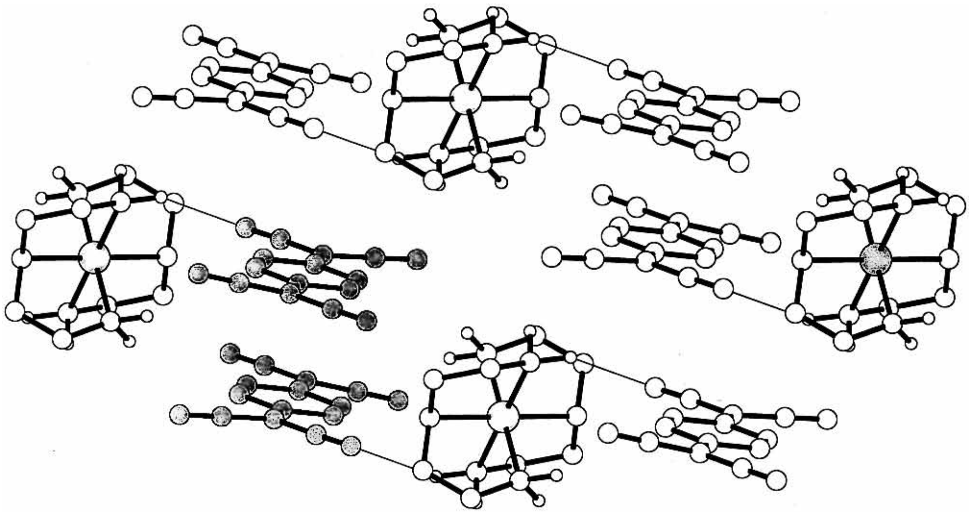


Figure 2. View of the crystal packing in $[Ni(dien)_2](TCNQ)_2$ showing the hydrogen bonds as single lines. One of the dimeric anions $(TCNQ)_2^{2-}$ is represented as darkened spheres.

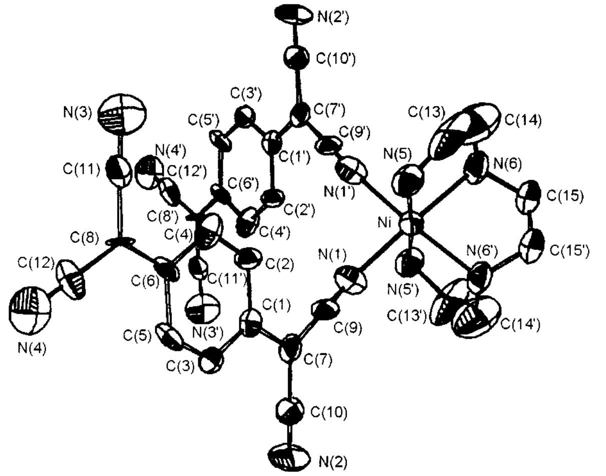


Figure 3. ORTEP view and atom labeling of the molecular unit of $[Ni(trien)(TCNQ)_2]$.

The two symmetric TCNQ groups overlap in the ring over ring mode,[4] forming dimeric dianions $(TCNQ)_2^{2-}$. In the TCNQ dimers the centers (quinoid rings) are closer than the ends (nitrile groups). The interplanar distance between the quinoid rings, 3.23(1) Å, lies in the usual range for uncoordinated TCNQ dimers.[8,19]

One of the nitrile groups of each TCNQ is hydrogen bridged to one of the amine dien groups. The parameters of this hydrogen bond are N3−H4 = 1.021(7) Å, N4···H4 = 2.246(8) Å, and an angle of 152°. In this sense each $[Ni(dien)_2]^{2+}$ is hydrogen-bonded to two different dimers and each $(TCNQ)_2^{2-}$ is linked to two different cations (Figure 2).

The dimeric anions are stacked in the crystal, forming 1-D chains, approximately perpendicular to the direction of the hydrogen bonds. The shortest distance between dimers in the stack is 3.70(2) Å, excluding intradimeric interactions.

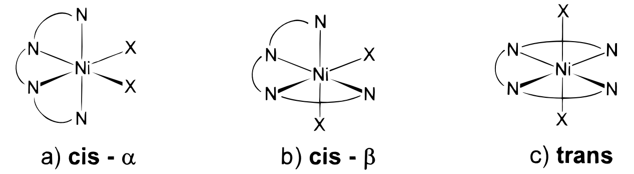
The $[Ni(dien)_2]^{2+}$ cations are located between the stacks, completely isolated from other groups except for the hydrogen bonds, previously mentioned.

Crystal Structure of [Ni(trien)(TCNQ)₂]. An ORTEP view of the molecular unit is shown in Figure 3. Selected bond lengths and angles are listed in Table 3.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Ni(trien)(TCNQ)_2]^a$

Ni−N1	2.12(1)	C1−C7	1.44(2)
Ni−N5	2.06(1)	C2−C4	1.38(2)
Ni−N6	2.12(1)	C3−C5	1.36(2)
N1−C9	1.12(2)	C4−C6	1.42(2)
N2−C10	1.10(3)	C5−C6	1.44(2)
N3−C11	1.15(3)	C6−C8	1.44(2)
N4−C12	1.13(2)	C7−C9	1.43(2)
N5−C13	1.46(3)	C7−C10	1.47(3)
N6−C14	1.51(3)	C8−C11	1.43(2)
N6−C15	1.46(2)	C8−C12	1.42(2)
C1−C2	1.42(2)	C13−C14	1.37(4)
C1−C3	1.41(2)	C15−C15′	1.50(2)
N5−Ni−N6	83.9(6)	N5−Ni−N6′	98.9(4)
N1−Ni−N6	167.1(5)	N1−Ni−N5′	92.2(5)
N1−Ni−N5	85.2(5)	N1−Ni−N6′	92.7(5)
N1−Ni−N1′	94.9(5)	N6−Ni−N6′	82.0(4)
N5−Ni−N5′	177.0(5)	Ni−N1−C9	163(1)
Ni−N5−C13	108(1)	Ni−N6−C14	107(1)
Ni−N6−C15	110(1)	C14−N6−C15	115(2)

[a] The atoms labeled by primes (′) are obtained by the following symmetry operation: $^1/_2 - x$, $^1/_2 - y$, z.



a) **cis - α**   b) **cis - β**   c) **trans**

Figure 4. Topological isomers of $[Ni(trien)X_2]$.

The molecule lies on a 2-fold axis with the nickel atom coordinated to six nitrogen atoms, four from the trien ligand and the other two coming from two coordinated TCNQ molecules.

The geometry around the nickel atom is distorted octahedral. The two TCNQ ligands are coordinated in cis positions while the trien adopts the cis-α configuration (Figure 4a) since it is the configuration for which the coordinated nitrogen atoms come closest to a strain-free tetrahedral arrangement.[20] The other two configurations, cis-*β*[21] (Figure 4b) and trans[16] (Figure 4c), force increasing strains in the secondary nitrogens, which must adopt an intermediate planar-tetrahedral configuration. A similar distorted octahedral environment is found in the isothiocyanato

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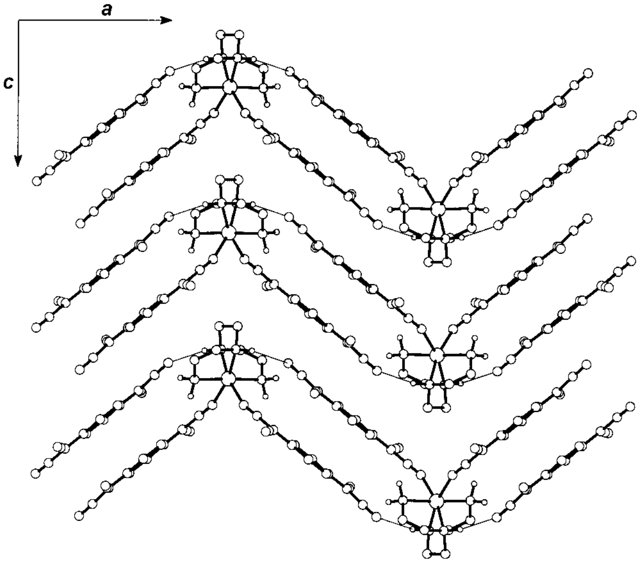

Figure 5. View of the parallel chains for [Ni(trien)(TCNQ)$_2$] in the *ac* plane, showing the hydrogen bonds as single lines.

complex [Ni(trien)(NCS)$_2$],[22] whereas the perchlorate starting complex [Ni(trien)](ClO$_4$)$_2$[16] shows a planar configuration around the nickel atom.

The nickel−nitrogen distances for the trien ligand are 2.06(1) and 2.12(1) Å, the shortest distance corresponding to the primary nitrogen atoms. These distances lie in the usual range expected for octahedral nickel(II) complexes.[17] The N−C and C−C distances in the trien are also typical for this ligand, although all the observed distances are 0.02−0.06 Å shorter in this complex than in the related isothiocyanato one, indicating that the trien ligand is more constrained around the nickel atom. On the contrary the Ni−N$_{TCNQ}$ distance, 2.12(1) Å is 0.4 Å, longer than the Ni−N$_{NCS}$ distance, indicating a weaker coordination of the TCNQ ligand.

The octahedral environment around the nickel has a best equatorial plane formed by the atoms N1, N5, N6, and N5′, with N1′ and N6′ lying above and below this plane and forming an angle of 167(4)°. The equatorial plane is highly distorted with the metal atom in the plane but N5 and N1 lying above the plane 0.05(1) and 0.13(1) Å, respectively, and N5′ and N6 lying below the plane 0.03(1) and 0.11(1) Å, respectively.

Both TCNQ groups bonded to the same nickel atom are symmetry related by the 2-fold axis that passes through the nickel atom and the center of the C15−C15′ bond; the quinoid ring planes of both TCNQ's are rotated to each other, forming an angle of 106(1)°. The TCNQ molecule is almost planar and the distances found within the molecule are typical for the σ-coordinated radical-anion TCNQ$^-$.[6,23,24]

The packing of the molecule in the crystal gives rise to the overlapping of two TCNQ groups of adjacent molecules by a $\pi-\pi$ interaction of the respective rings (Figure 5). The TCNQ overlapping corresponds to the ring over ring mode but with one TCNQ shifted relative to the other 0.92(3) Å through the molecular transverse axis. This overlapping shows an interplanar distance of 3.18(1) Å, typical of the formation of dimeric (TCNQ)$_2^{2-}$ units.[6,24]

As a consequence of the dimerization, the [Ni(trien)(TCNQ)$_2$] units arrange in the crystal forming chains with alternating [Ni(trien)] and (TCNQ)$_2$ units bound together. The angle formed by the two TCNQ units bonded to the same nickel atom is responsible of the almost perpendicular orientation of consecutive dimers along the chains. These chains are oriented parallel along the crystal *a* axis (Figure 5).

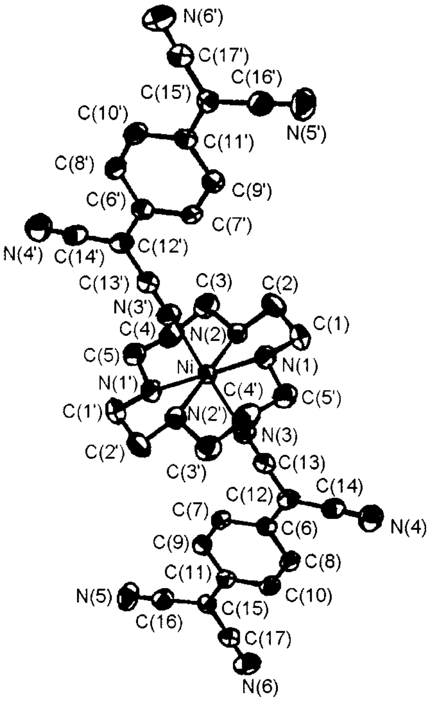

Figure 6. ORTEP view and atom labeling of the molecular unit of [Ni(cyclam)(TCNQ)$_2$].

Intra- and interchain hydrogen bonds between the uncoordinated TCNQ nitrile groups and the amine nitrogens of the trien ligand. The first bond is observed between N4 (the nitrile opposite to that coordinated to the nickel atom) and the secondary amine group, N6, of the adjacent [Ni(trien)] unit, with bond distances of N6−H601 = 1.01(1) Å and N4···H601 = 2.18(1) Å and an angle of 162.4(7)°. The existence of this hydrogen bond results in a double interaction between the [Ni(trien)] and the (TCNQ)$_2$ units since each TCNQ is σ-bonded to one nickel atom and hydrogen bonded to the trien ligand that surrounds the opposite nickel atom.

The second hydrogen bond is found between N2 (the nitrile closer to that coordinated to the metal) and the primary amine, N5, belonging to a parallel chain along the *b* axis. The bond parameters are N5−H502 = 1.00(1) Å and N2···H502 = 2.30(2) Å and bond angle of 162.9(7)°.

The crystal array can be seen as formed by parallel chains −Ni(trien)−(TCNQ)$_2$−Ni(trien)−(TCNQ)$_2$− extended along the *a* axis with hydrogen bond interactions with the adjacent chains in the *b* direction but without any observable interaction with the adjacent chains along the *c* direction.

Crystal Structure of [Ni(cyclam)(TCNQ)$_2$]. An ORTEP view of the molecular unit is shown in Figure 6. Bond lengths and angles are listed in Table 4.

The nickel atom in the molecular unit lies on an inversion center and is six-coordinated. In the equatorial plane the metal atom is bonded to the four macrocyclic nitrogen atoms at 2.063(6) and 2.049(6) Å, distances between 0.005 and 0.015 Å shorter than the equivalent isothiocyanate derivative.[25] The macrocycle ligand adopts a chair conformation. The two apical positions that complete the coordination are occupied by nitrile groups of two TCNQ molecules with a nickel−nitrogen distance of

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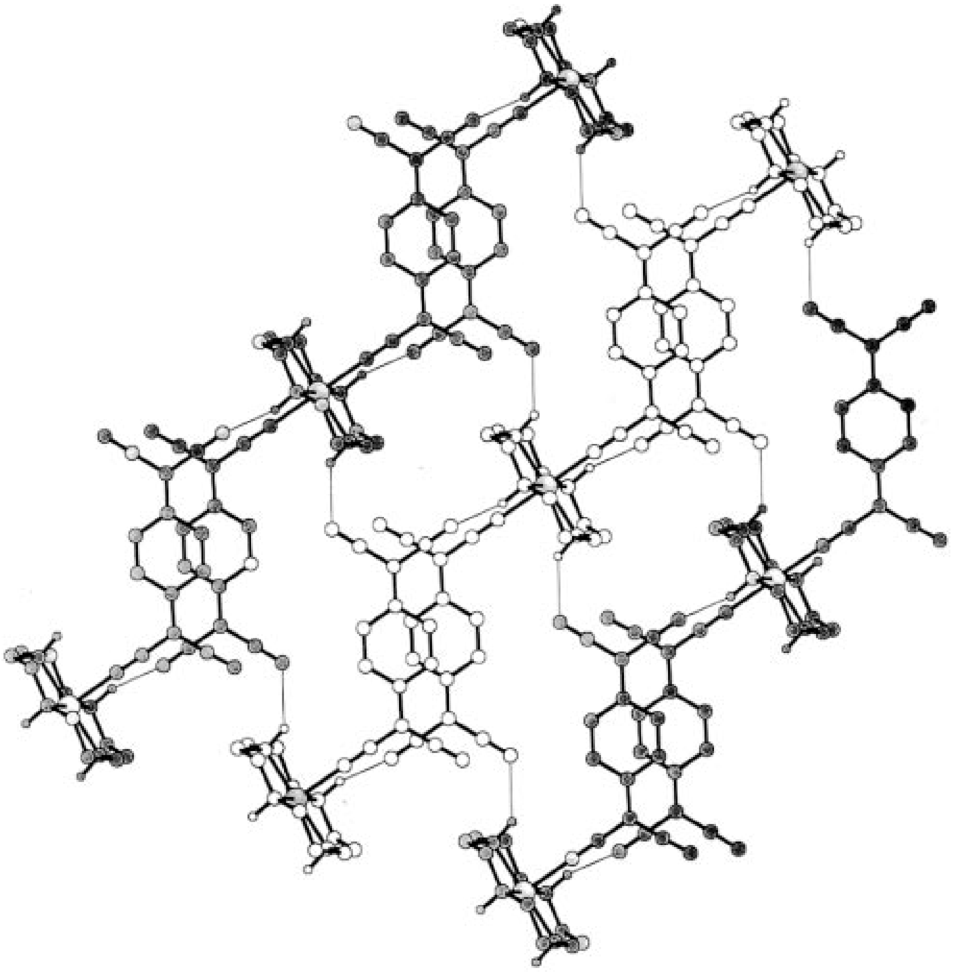

Figure 7. Crystal packing of [Ni(cyclam)(TCNQ)$_2$] showing the hydrogen bond intra- and interchains as single lines. The alternating chains are represented as white and dark colors, respectively.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Ni(cyclam)(TCNQ)$_2$]

Ni−N1	2.063(6)	C7−C9	1.345(9)
Ni−N2	2.050(5)	C8−C10	1.353(9)
Ni−N3	2.165(2)	C9−C11	1.422(6)
N3−C13	1.144(6)	C10−C11	1.418(9)
N4−C14	1.147(9)	C11−C15	1.414(8)
N5−C16	1.139(9)	C12−C13	1.409(7)
N6−C17	1.141(7)	C12−C14	1.410(9)
C6−C7	1.420(8)	C15−C16	1.415(9)
C6−C8	1.418(6)	C15−C17	1.416(7)
C6−C12	1.416(8)		
N2−Ni−N3	89.2(2)	Ni−N2−C3	116.8(4)
N1−Ni−N3	90.3(2)	Ni−N2−C2	107.1(4)
N1−Ni−N2	85.0(2)	Ni−N3−C13	178.7(5)
Ni−N1−C1	105.9(4)		

2.165(2) Å; as expected, this distance is longer than the apical Ni−NCS distances in the previously mentioned derivative. The coordination environment around the nickel atom is similar to that found in [Ni(N$_4$OH)(TCNQ)$_2$].[6a]

The equatorial plane around the nickel atom and the quinoid TCNQ plane are quasi perpendicular with an angle of 87.7(2)°; this value is similar to that found in other derivatives having two TCNQ's coordinated in *trans* positions.[6] The axial bond Ni−N−C is almost linear with an angle of 178.7(5)°.

The intramolecular distances of the TCNQ groups are typical of σ-monodentate ionized molecules.[6,23,24] Neighboring TCNQ groups belonging to different molecular units overlap in a ring-over-ring mode but with one TCNQ shifted relative to the other 0.815(3) Å along the molecular transverse axis (Figure 7). This overlapping shows an interplanar distance of 3.18(1) Å, characteristic of dimeric (TCNQ)$_2$$^{2-}$ units.[6,24] Every TCNQ of the dimeric unit coordinates a different nickel atom, and the dimer acts as a bridge between metallomacrocyclic units, originating infinite chains −[Ni(N$_4$)]−(TCNQ)$_2$−[Ni(N$_4$)]−(TCNQ)$_2$−, typical of the derivatives having only anionic σ-coordinated TCNQ$^-$.[6,24]

These chains are arranged parallel in the crystal and interact with the adjacent ones through hydrogen bonds. Two different hydrogen bonds are found in the crystal; the first one is an intrachain bond similar to that commented for [Ni(trien)-(TCNQ)$_2$] that originates a double interaction between the metallomacrocycle and the dimeric anion. The bond distances and angle found are N2−H021 = 1.006(7) Å, H021···N6 = 2.052(8) Å, and 156.3(3)°. The second hydrogen bond is an interchain one between the N5 uncoordinated nitrile group of the TCNQ and the N1 amine of the macrocycle; the values for these parameters are N1−H011 = 1.008(8) Å, H011···N5 = 2.349(6) Å, and 135.2(8)°. With these bonds the four amine groups of the macrocycle are hydrogen bonded to the nitrile groups of four different TCNQ units, two of them belonging to the same chain and the other two belonging to chains located at both sides of the chain being considered (Figure 7). The chains connected by these hydrogen bonds define a plane, and the chains situated above and below this plane do not interact via hydrogen bonds, although a certain overlapping between (TCNQ)$_2$$^{2-}$ dimers is possible since the exocyclic nitrile groups of different chains are separated only by 3.25(1) Å. This overlap does not originate, however, any electronic delocalization in the structure.

Spectroscopic Studies. The IR spectrum of the TCNQ derivatives is frequently diagnostic about the formal oxidation state and the coordinative status of these organic acceptor molecules.[26] The infrared spectra of the three compounds, measured in KBr pellets, show the characteristic absorptions of electronically isolated dimeric units $(TCNQ)_2^{2-}$.[27] In the δ-(C−H) region, 860−820 cm^{-1}, only one band is observed, clearly indicating that only the radical anion is present.[6,7] Sharp ν(CN) bands are observed for the three compounds, at 2178 and 2156 cm^{-1} for $[Ni(dien)_2](TCNQ)_2$, 2202, 2190, 2176, 2163 and 2157 cm^{-1} for $[Ni(trien)(TCNQ)_2]$, and 2186, 2182, and 2161cm^{-1} for $[Ni(cyclam)(TCNQ)_2]$. The higher number of absorptions and the shift to higher energies in the spectra of $[Ni(trien)(TCNQ)_2]$ and $[Ni(cyclam)(TCNQ)_2]$ with respect to $[Ni(dien)_2](TCNQ)_2$ is indicative of the presence of σ-bonded Ni−TCNQ in those compounds. The different pattern of bands in $[Ni(trien)(TCNQ)_2]$ is probably indicative of the different coordination mode (*cis* positions) found in this compound.

The solid-state electronic spectra of the three compounds are almost identical. They show absorptions at 8900, 13 600, 17 800, 25 900, 34 000, and 39 500 cm^{-1}. These bands are broad and intense corresponding to $(TCNQ)_2^{2-}$ dimers and dominate the spectra. The corresponding nickel(II) d → d transitions are less intense and obscured by the former bands. The first band is broad and results from the intradimer charge-transfer transition (CT_1) between radical anions ($TCNQ^-TCNQ^- \rightarrow TCNQ^0TCNQ^{2-}$), usually observed in the 11 000−7500 cm^{-1} range.[28] The maxima at 13 600, 17 800, and 25 900 cm^{-1} can be attributed to locally excited levels of the anion radical, corresponding to the intramolecular transitions $^2B_{2g} \rightarrow {}^2B_{1u}$, $^2B_{2g} \rightarrow {}^2A_u$, and $^2B_{2g} \rightarrow {}^2B_{3u}$, respectively.[29] Finally, the bands at 34 000 and 39 500 cm^{-1} can be assigned to charge-transfer bands involving the polyamine unit.[30]

The electronic spectra of very diluted, ca. 10^{-6} M, acetonitrile solutions of all derivatives show the transitions of uncoordinated $TCNQ^-$.[31] These spectra show two transitions, the two locally excited levels LE_1 and LE_2 that appear at 11 900 cm^{-1} and 25 400 cm^{-1}, respectively, in the free anion radical. The intensity ratio between $\epsilon(25\,400)/\epsilon(11\,900)$ is 0.5, a clear indication that only $TCNQ^-$ is present in solution.[32]

Magnetic Measurements. The bulk static magnetic susceptibility has been measured over the temperature range 5−300 K. The three compounds present a magnetic behavior variation typical of non interacting octahedral nickel(II) ions. The susceptibility vs temperature plots follow the Curie−Weiss law ($\chi = C/[T - \Theta]$).

For $[Ni(dien)_2](TCNQ)_2$ the Curie constant has a value of $C = 1.16$ emu K mol^{-1}, corresponding to an effective magnetic moment of 3.04 μ_B ($\mu_{eff} = 2.828C^{1/2}$) and a Weiss temperature of $\Theta = -0.30$ K. The values found for $[Ni(trien)(TCNQ)_2]$ are $C = 1.12$ emu K mol^{-1}, i.e. $\mu_{eff} = 2.99\ \mu_B$, and $\Theta = -0.43$ K, and for $[Ni(cyclam)(TCNQ)_2]$ the values are $C = 0.92$ emu K mol^{-1}, i.e. $\mu_{eff} = 2.71\ \mu_B$, and $\Theta = -1.76$ K. The low Θ values, obtained in the fittings, are due to the zero-field splitting effect for nickel(II). The $TCNQ^-$ units do not contribute to the total magnetic susceptibility even at room temperature, thus indicating a strong antiferromagnetic coupling in the dimeric $(TCNQ)_2^{2-}$ by π overlapping, leading to a singlet ground state.

Concluding Remarks

The interaction mode between TCNQ and metallic fragments depends on the metal environment in the transition metal center, as is shown by the different structural types reported in this work. In the case of $[Ni(dien)_2]^{2+}$, where the metal is coordinatively saturated, the TCNQ is unable to coordinate and no direct interaction is observed. When the metal has vacant positions that can be occupied by the TCNQ, σ coordination occurs. The *cis* or *trans* coordination of the two anion radicals is determined by the steric requirements of the amine ligand that completes the coordination. Thus, the compound with a macrocyclic tetraamine directs the entering TCNQ's to opposite positions, while an open chain tetraamine, such as trien, allows a *cis* coordination that minimizes strains around the metal atom, and that is, to our knowledge, the first example of this type of coordination in TCNQ derivatives.

Independently of the coordination mode, the obtained compounds contain TCNQ groups as radical anions, $TCNQ^-$, which are always dimerized as $S = 0$ dianions $(TCNQ)_2^{2-}$. The charge localization induced by this dimerization is responsible for the optical and magnetic properties shown by these species.

The dimerization of the radical anions shows some differences that depend on the TCNQ coordinative status. With uncoordinated radical anions, $[Ni(dien)_2](TCNQ)_2$, the ring over ring overlapping affords a completely eclipsed dimer, while, for coordinated TCNQ's, $[Ni(trien)(TCNQ)_2]$ and $[Ni(cyclam)(TCNQ)_2]$, there is only a partial overlap with both radicals parallel along the longitudinal axis but displaced along the transverse one.

The formation of the dimers allows the description of the three structures as formed by $[NiN_x]^{2+}$ ($x = 4, 6$) and $(TCNQ)_2^{2-}$ units. The different metallic fragments are one of the determinant factors responsible for the different supramolecular arrangements found. The other factor is the formation of hydrogen bonds between the uncoordinated nitrile groups of the TCNQ and the amine nitrogens of the other ligands. These interactions connect the different building blocks in the structure and give rigidity to the infinite chains formed with the tetraamine derivatives through the intrachain hydrogen bonds that, along with the σ-bond, doubly link the TCNQ to the metallic fragments. On the other side, the interchains bonds extend the dimensionality of the interactions forming layers of parallel chains connected through these hydrogen bonds.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (30 pages). Ordering information is given on any current masthead page.

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