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Coordination Chemistry Reviews
190–192 (1999) 447–470

COORDINATION CHEMISTRY REVIEWS

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Supramolecular architectures in low dimensional TCNQ compounds containing nickel and copper polyamine fragments

Loreto Ballester [a,*], Angel Gutiérrez [a], M. Felisa Perpiñán [a], M. Teresa Azcondo [b]

[a] *Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain*

[b] *Departamento de Química Inorgánica y Materiales, Facultad de Ciencias Experimentales y Técnicas, Universidad San Pablo-CEU, 28668-Boadilla del Monte, Madrid, Spain*

Accepted 13 March 1999

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[*] Corresponding author. Tel.: + 34-913944233; fax: + 34-91-3944352.
E-mail address: loretoba@eucmax.sim.ucm.es (L. Ballester)

PII: S0010-8545(99)00098-3

Abstract

The nickel(II) and copper(II) polyamine derivatives are adequate fragments to interact with the organic acceptor TCNQ, favoring the formation of σ bonds between the metal atom and the TCNQ nitrile groups. In its radical anion form, this molecule tends to form dimeric dianions $(TCNQ)_2^{2-}$ by overlapping of the π cloud with a neighboring radical. When the metal has a stable and coordinatively saturated environment these dianions remain uncoordinated, but if the metal has vacant positions or labile ligands formation of two M–TCNQ bonds is observed. In these cases the dianions are bridging two metal units forming infinite chains. In the dimers, the radicals are strongly antiferromagnetically coupled behaving as diamagnetic units. These compounds with localized electrons behave as insulators, or poor semiconductors. In its neutral form the TCNQ has a low coordinative ability, but its presence favors the overlap of the dianionic dimers to form infinite stacks. When both neutral and radical–anionic TCNQ are present in the reaction mixture the derivatives obtained usually have three TCNQ molecules per metal atom. Depending on the interactions between the TCNQ and the metal two situations are found: if all the TCNQ molecules are uncoordinated the electronic charge on the organic stack is delocalized, but if direct bonding to the metal is present, the bonded molecules show radical anion characteristics, while the uncoordinated TCNQ behave as neutral molecules. The presence of this neutral TCNQ weakens the coupling in the $(TCNQ)_2^{2-}$ dimers and a temperature dependent contribution from the TCNQ to the magnetic susceptibility is found. These compounds having mixed valence TCNQ units show a greater electronic delocalization and behave as good semiconductors with higher conductivity values and lower activation energies in the derivatives that do not show direct bonding between the metal and the TCNQ.

Keywords: TCNQ; Metallomacrocycles; Polyamine complexes; Charge transfer

Nomenclature

$[14]aneN_4$	1,4,8,11-tetraazacyclotetradecane
$[15]aneN_4$	1,4,8,12-tetraazacyclopentadecane
2,5-DM–DCNQI	2,5-dimethyl-N,N′-dicyanoquinonediimine
abpt	3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole
bpy	2,2′-bipyridine
dien	diethylenetriamine 1,4,7-triazaheptane
$dh[14]aneN_6$	3,10-dihydroxyethyl-1,3,5,8,10,12-hexaazacyclotetradecane
DMP	2,9-dimethyl-1,10-phenantroline
dpa	di-2-pyridylamine
dppm	bis(diphenylphosphino)methane
en	ethylenediamine

EtP	N-ethylphenazinium
hmedbtaa	hexamethyldibenzotetraaza-[14]-annulene
Me_6-[14]aneN_4	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
N_4*cis*diene	5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene
N_4*trans*diene	5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene
pdto	1,8-di-2-pyridyl-3,6-dithiaoctane
phen	1,10-phenanthroline
tatma	tetramethyltetraza[14]annulene
TCNQ	7,7,8,8-tetracyanoquinodimethane
TFA	trifluoroacetate
TMP	tetramethylporphyrinato(-2)
tn	1,3-diaminopropane
tpa	tris(2-pyridylmethyl)amine
tren	2,2′,2″-triaminotriethylamine
trien	triethylenetetraamine 1,4,7,10-tetraazadecane
TTF	tetrathiafulvalene
Tz	2,7,12,17-tetramethyl-1,6,11,16-tetraazaporphyrinogen

1. Introduction

The possibility of combining organic radicals derived from donor or acceptor molecules such as TTF or TCNQ, with transition metal fragments has attracted the interest of many researchers in the field of molecular solids, in particular the design of supramolecular organizations built by organonitrile radicals and paramagnetic metallic centers [1].

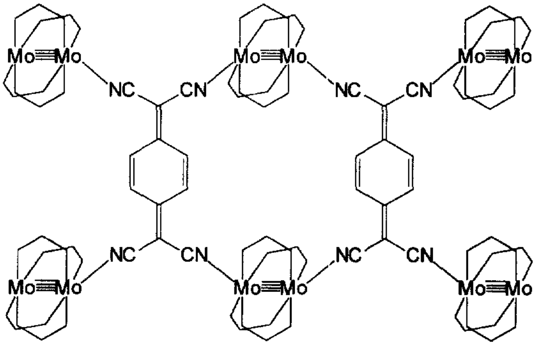
As the interesting reviews of Endres in 1983 [2] and Kaim in 1994 [3] pointed out, one of the important factors to be considered in the compounds of TCNQ, is the high σ-donor ability of the radical anions, $TCNQ^{-}$, which can help in the understanding of the supramolecular architectures formed by these species.

Beginning with the studies of Melby et al. [4] there have been numerous reports of solids having TCNQ radicals together with metallic fragments. However, until the last decade most of the TCNQ systems containing transition metals were studied by indirect structural methods with the number of structurally characterized examples remaining scarce. A higher number of X-ray crystallographic studies now available are of great help in understanding the diversity of supramolecular organizations.

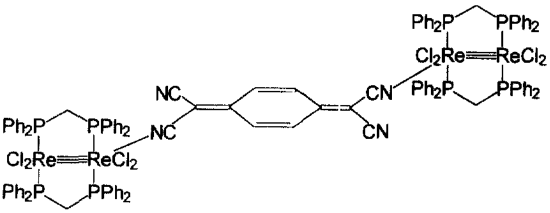
2. The TCNQ molecule as a ligand

The strong acceptor behavior of the TCNQ molecule is due to its low reduction potential to form the radical anion, which is well matched to the oxidation potentials of organic donors (TTF) or transition metal complexes (Cu^I/Cu^{II}, ferrocene/ferrocenium) [5]. The electron can be provided to the TCNQ by a charge transfer process from a donor molecule, if the difference in the respective reduction potentials is lower than 0.4 V [6]. By this reaction, typical donor–acceptor derivatives, such as TTF–TCNQ [7] or metallocene–TCNQ derivatives [8] have been obtained.

The charge transfer process between TCNQ and transition metal complexes depends on the donor character of the latter. In some species, the electronic transfer occurs with or without coordination of the organic acceptor, depending of the lability of the coordinated ligands. Dunbar and co-workers have obtained some examples of coordinated TCNQ that acts as a bridge between metal centers, e.g. $[Mo_2(TFA)_4(TCNQ)_{0.5}(m\text{-xylene})]$ (**1**) [9] and $[Re_2Cl_4(dppm)_2]_2(TCNQ)$ (**2**) [10].

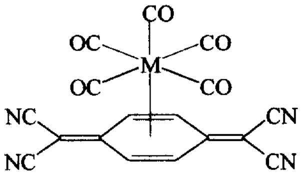


(**1**)



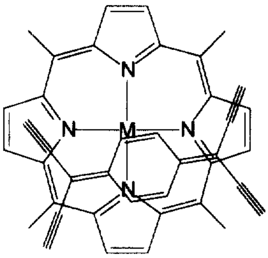
(**2**)

The π bond coordination of TCNQ is much less frequently observed. No fully characterized examples have been described, but a symmetrical interaction is proposed for $[M(CO)_5(TCNQ)]$ (**3**) M = Cr, W [11].



(3)

More common is the formation of donor–acceptor couples with π interactions when the metallic complex contains a planar delocalized π system that can interact with the TCNQ. In these cases weak interactions are observed, usually accompanied by a low degree of charge transfer between the metal donor and the organic acceptor. Representative examples with polyaza donor ligands are [Ni(TMP)](TCNQ) (4) [12], $[Ni(tatma)]_2(TCNQ)$ [13], [Ni(hmedbtaa)](TCNQ) [14], similar examples are described with Schiff base nickel and copper derivatives [15].



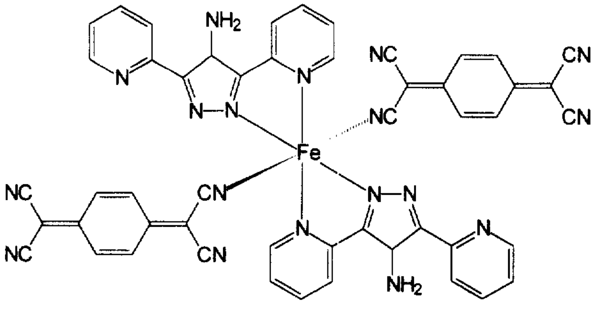
(4)

A different process occurs in the reaction between the previously formed radical anion $TCNQ^-$, with cationic metal counterions $[M^{II}L_x]^{n+}$:

$$[M^{II}L_x]^{n+}(X^-)_n + n\mathrm{LiTCNQ} \rightarrow [M^{II}L_x](TCNQ)_n + n\mathrm{LiX}$$

Compounds of first row transition metals contribute paramagnetic centers to the solid network, and the introduction of radical anions, $TCNQ^-$, should favor different interactions between spins, including cooperative phenomena. Different supramolecular architectures have been obtained. Their structures are mainly dominated by electrostatic interactions between both fragments and by the tendency of the radicals to be dimerized in different ways. Examples of this kind of interaction include metallocene fragments [8,16] and square–planar species of platinum group metals [17].

The radical anion shows a diminished π-accepting capability relative to neutral TCNQ, which imparts a greater σ-donor character to the anion. Examples of direct M–TCNQ interaction have been observed and characterized in iron(II) and manganese(II) compounds as $[Fe(abpt)_2(TCNQ)_2]$ (5) [18], $[Fe(MeOH)_4(TCNQ)_2]$-(TCNQ) [19], $[Mn(tpa)(TCNQ)(MeOH)](TCNQ)_2\cdot MeCN$ (6) [20] or [Mn(TCNQ)-$(TCNQ–TCNQ)_{0.5}(MeOH)_2]$ [21].



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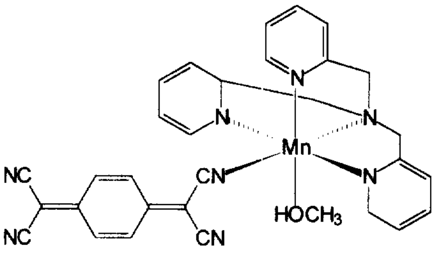

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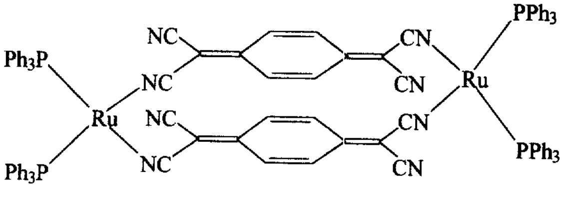


(7)

The coordination ability of the radical anion allows for the formation of polynuclear compounds with double bridges, $[Ru(PPh_3)_2(\mu^2\text{-TCNQ})]_2$ (7) [22], or with quadruply bridging TCNQ, e.g. the homoleptic $Ag(\mu^4\text{-TCNQ})$ [23]. Similar structures are expected for materials consisting of metal atoms and TCNQ. The most studied is Cu(TCNQ) which exhibits bistable switching phenomena [24], whose structure has been recently resolved showing the existence of two polymorphs with different physical properties [25].

3. Scope

The different behavior that is observed in these TCNQ compounds has induced us to systematize the derivatives formed with transition metals, focusing our interest on nickel(II) and copper(II) polyamine derivatives with the goal being to determine the different factors that can modify the architecture of the supramolecular network.

The main factors to be controlled in the metal–polyamine fragments are:

- The coordinative saturation or the unsaturation of the metal center.
- The variation in the donor character of the polyamine.
- The polyamine geometry, that can favor different coordination modes around the metal.
- The reaction conditions, with the use of radical anions in the reaction with the metal fragment, or the combined reactivity of neutral and anionic TCNQ.

These variables can allow the control of the following factors concerning the supramolecular architecture:

- The stacking modes of the TCNQ.
- The influence of the metal in these stacks.
- The electronic state of the metal and the organic fragments.
- The influence of weak interactions in the stabilization of the network.

Since the presence of TCNQ in different electronic states has proven to be the main factor in determining the supramolecular architecture, we will describe first the examples of derivatives obtained when only anionic TCNQ is used in the reaction and, afterwards, we will analyze the influence of additional neutral TCNQ. Finally, the properties derived from the different architectures will be briefly commented upon.

4. Nickel and copper derivatives having only anionic TCNQ

As previously mentioned, the formation of direct bonds between the metal atom and the radical anion $TCNQ^-$ can occur only when there is a vacant coordination site on the metal center or when there is a labile ligand occupying this position. If no vacancies are available, only electrostatic interactions between the metal cation and the organic anion are expected.

In the chemistry of nickel(II) and copper(II), the halide or solvent molecules usually behave as labile groups in the reaction with $TCNQ^-$ with isolation of $Ni(TCNQ)_2$ [26] and Cu(TCNQ) or $Cu(TCNQ)_2$ [4,23–25]. The structure of some of these simple compounds however, remains unknown, and this fact precludes a complete interpretation of their interesting properties.

The determination of the crystal structure is a severe limitation in the study of these compounds, due to the variety of interactions observed and to the relation between properties and supramolecular architecture. For this reason, we will mainly refer to the compounds whose crystal structure is known and can serve as a reference in the interpretation of the properties of the rest of derivatives.

4.1. Compounds without metal–TCNQ σ bonds

Several examples of reactions of anionic $TCNQ^-$ with nickel(II) or copper(II) polyamine complexes have been described. The coordination of three diamine ligands, $[M(N-N)_3]^{2+}$, or two triamine ligands, $[M(N_3)_2]^{2+}$ gives stable coordinative environments. The reaction of the respective salts with LiTCNQ takes places by a simple exchange of counterions, with formation of the derivatives of general formulae $[M(N-N)_3](TCNQ)_2$:$[Ni(en)_3](TCNQ)_2$ [27], $[Cu(phen)_3](TCNQ)_2$ [28], $[Ni(bpy)_3]$-$(TCNQ)_2$ [29]; or $[M(N_3)_2](TCNQ)_2$:$[Ni(dien)_2](TCNQ)_2$ [30], $[Cu(dien)_2](TCNQ)_2$ [27].

A common feature of these derivatives is their structure, formed by isolated metal cations, of approximate spherical shape, and dimeric dianions $(TCNQ)_2{}^{2-}$, formed by the π overlapping of two adjacent radicals.

The metal dications and the organic dianions are isolated in the network, linked only by electrostatic interactions. Usually there are weak hydrogen bonds between some of the nitrile groups of the anion and the amine groups of the metal cation, that connect the different building blocks which lend some stability to the network (Fig. 1).

A second class of derivatives without direct bonds M–TCNQ, is obtained when the metal atom has vacant axial positions that are not used due to the ligands stabilizing a square–planar environment by a higher electron donation. In this group we can classify the compounds $[M(N_4\textit{cis}diene)](TCNQ)_2$ [31], $[M(N_4\textit{trans}diene)](TCNQ)_2$ [32] (M = Ni, Cu) and $[Ni(Me_6\text{-}[14]aneN_4)](TCNQ)_2$ [33].

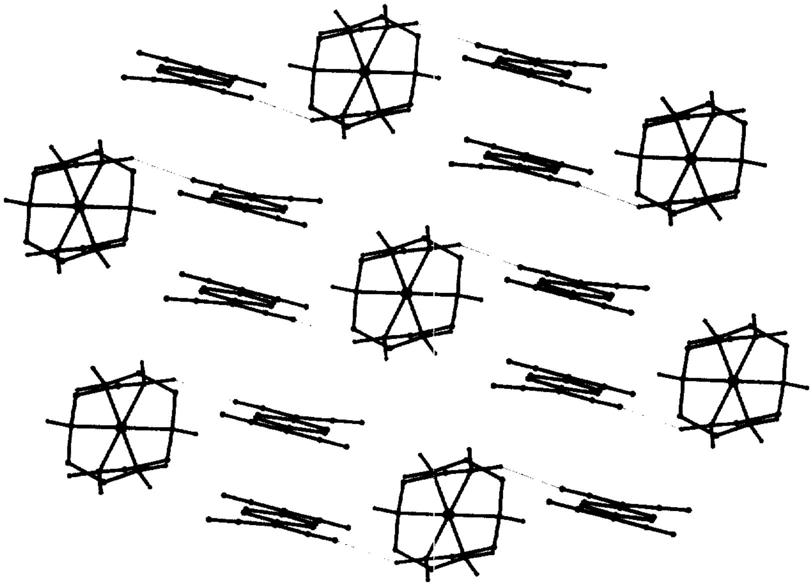


Fig. 1. Structure packing in $[Ni(dien)_2](TCNQ)_2$, Ref. [30].

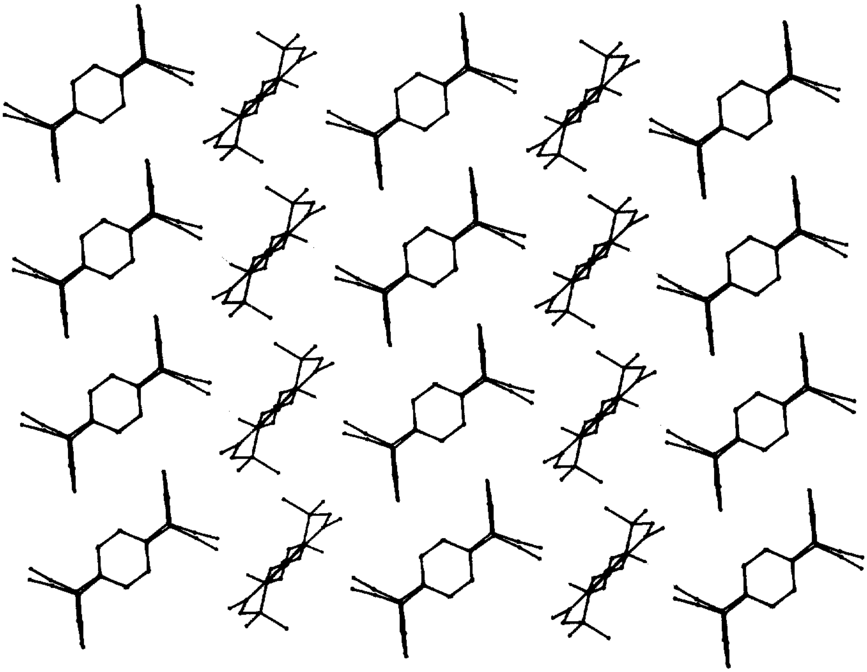


Fig. 2. Packing in the crystal structure of [Ni(N_4*cis*diene)](TCNQ)$_2$, Ref. [31].

Their structures are also formed by alternating metallomacrocyclic cations and organic dianions linked by electrostatic interactions. The metallomacrocycle plane and the TCNQ dimers are almost perpendicular and this orientation is favored by the formation of hydrogen bonds between the nitriles and the amino groups in the macrocycle (Fig. 2).

A different type of behavior is found in the derivatives [M(Tz)(MeOH)$_2$](TCNQ)$_2$ [34]. The copper compound shows a distorted octahedral environment with the macrocycle occupying the equatorial plane and methanols residing in the apical positions (Fig. 3). Due to its flexibility and big cavity size, adequate for second row transition metals [35], the macrocycle is shrunk around the copper atom and, probably due to the steric hindrance, the direct TCNQ coordination is precluded. As usual, the TCNQ$^-$ anions are π-dimerized and these dianions are linked to the coordinated methanols of different metallomacrocyclic cations through hydrogen bonds.

4.2. Compounds with metal–TCNQ σ bonds

When the electronic or steric factors are favorable, the presence of vacant coordination sites around the metal atom gives rise to the formation of direct metal–TCNQ σ bonds.

The first structurally characterized example was the derivative [Cu(abpt)$_2$(TCNQ)$_2$] [36]. The copper compound shows a six-coordinated environ-

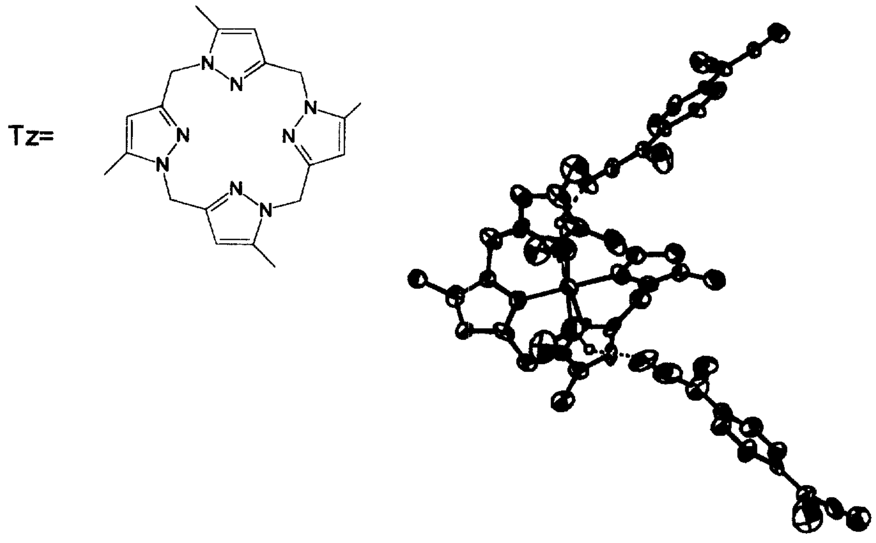


Fig. 3. The ligand Tz and molecular unit of $[Cu(Tz)(MeOH)_2](TCNQ)_2$.

ment with two abpt ligands bidentated in the equatorial plane and two radical anions coordinated in *trans* positions. The $TCNQ^{-}$ ligands are dimerized and, since they are coordinated in a monodentate fashion to a different metal atom, the structure is best described as 1-D chains:

$\ldots-[Cu(N_4)]-(TCNQ)_2-[Cu(N_4)]-(TCNQ)_2-\ldots$

The iron analogue is isomorphous and shows an interesting spin crossover transition at 280 K [18].

Similar structures have been found in the compounds with saturated tetraazamacrocycles of formula $[M(N_4)(TCNQ)_2]$, $N_4 = [14]aneN_4$ [30], $[15]aneN_4$ [37], $dh[14]aneN_6$ (M = Ni [38], M = Cu [39]). Their structures show infinite chains formed by metallomacrocycles and TCNQ dimers linked by σ bonds. The chains are also

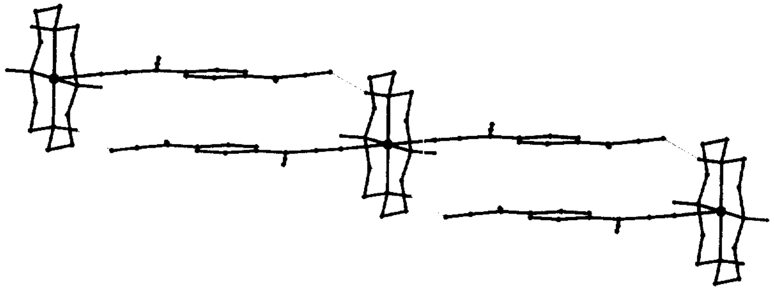
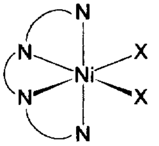


Fig. 4. Linear chains by TCNQ dimerization in $[Ni([14]aneN_4)(TCNQ)_2]$, Ref. [30].



cis - α

Fig. 5. The *cis*-α coordination mode of the trien ligand.

maintained by hydrogen bonds between one macrocyclic amine and an uncoordinated TCNQ (Fig. 4).

The derivatives [Ni(trien)(TCNQ)$_2$] [30] and [Ni(tren)(TCNQ)$_2$] [37] have been obtained with open tetraamines. The flexible structure of the trien ligand allows it to coordinate to the metal in the so-called *cis*-α mode (Fig. 5), leaving two *cis* positions for the TCNQ$^-$ radicals.

The TCNQ are also dimerized and the structure of the first derivative is formed by parallel chains:

…–[Ni(trien)]–(TCNQ)$_2$–[Ni(trien)]–(TCNQ)$_2$–…

In this case the *cis* coordination forces the consecutive TCNQ dimers to be quasi-perpendicular, giving a W shape to the chains in the crystal (Fig. 6).

The diamine derivatives [M(N–N)$_2$(H$_2$O)$_2$]X$_2$ or [M(N–N)$_2$X$_2$] have labile ligands that are easily displaced by anionic TCNQ$^-$ with formation of the compounds [Ni(en)$_2$(TCNQ)$_2$] [29], [M(tn)$_2$(TCNQ)$_2$] (M = Ni, Cu [27]) and [Cu(dpa)$_2$(TCNQ)$_2$] [40]. A six-coordinated molecular structure with two TCNQ bonded in *trans* positions, similar to those reported above is proposed for these derivatives.

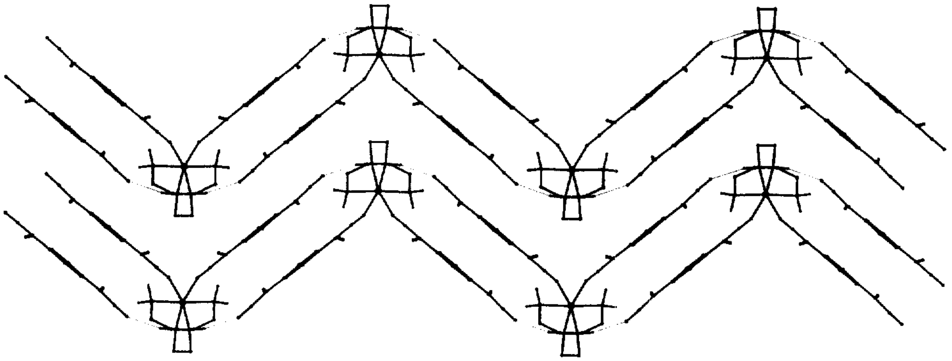
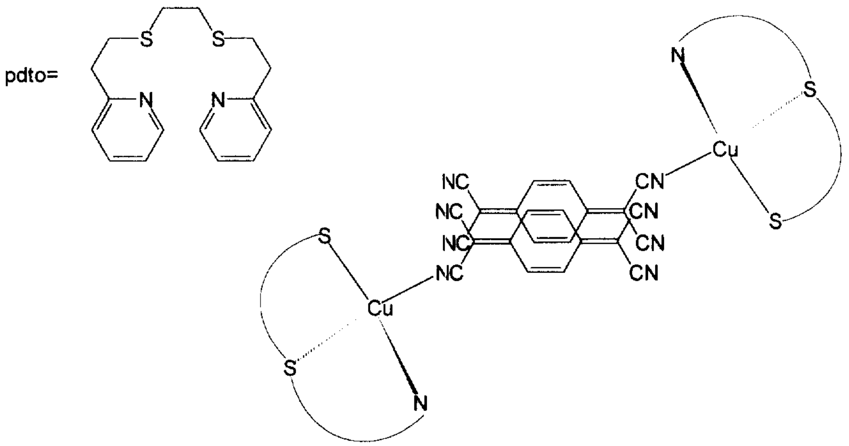


Fig. 6. Parallel chains in [Ni(trien)(TCNQ)$_2$], Ref. [30].



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5. Nickel and copper derivatives with anionic and neutral TCNQ

5.1. Di and triamine ligands

There have been several reported charge transfer processes between copper(II) and neutral TCNQ, with formation of copper(I) and anionic TCNQ$^-$. Some of these compounds are proposed to have σ bonds between the copper and the radical anion: [Cu(en)$_2$(TCNQ)$_2$] [41], [Cu(tn)(TCNQ)$_2$] [27], [Cu(dpa)(TCNQ)$_2$] [40]. Due to the charge transfer, these compounds are diamagnetic and better formulated as [Cu^I(N–N)(TCNQ$^-$)](TCNQ^0), with strong antiferromagnetic coupling between TCNQ$^-$ that are dimerized. In the en derivative the following charge transfer equilibrium is proposed:

$$\mathrm{Cu^{I}(en)(TCNQ^{-})(TCNQ^{0})} \rightleftharpoons \mathrm{Cu^{II}(en)(TCNQ^{-})_2}$$

from the magnetic susceptibility data, 7% of copper(II) is proposed to exist.

The coordination of anionic TCNQ is suggested by comparison with the structure of [Cu(pdto)(TCNQ)] (**8**) [42] where the copper(I) is tetrahedrally coordinated to

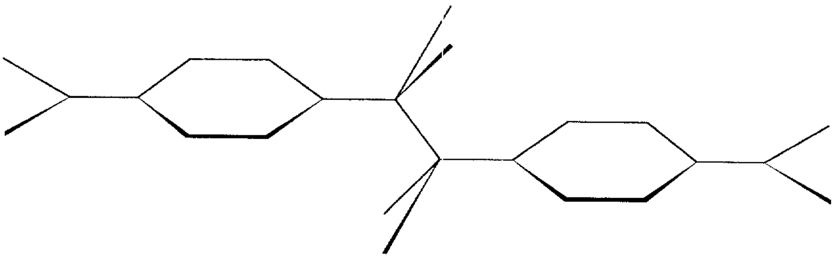


Fig. 7. Formation of σ bond in the (TCNQ)$_2$ dimers.

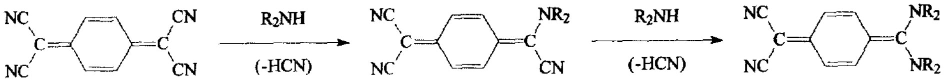


Fig. 8. Tri and dicyano derivatives formed by reaction of neutral TCNQ and primary amines.

two sulfur and one nitrogen atoms from the pdto ligand, and to one nitrile of a monodentate $TCNQ^-$. The compound is also diamagnetic by dimerization of the TCNQ radicals.

In the derivative $[Cu(DMP)_2]_2(TCNQ–TCNQ)$ the copper(I) is tetrahedrically coordinated by the phenanthroline ligands and the anionic unit is obtained by σ bond formation between the TCNQ groups (Fig. 7) without interactions with the metal fragment [43]. The formation of the σ bonded $(TCNQ–TCNQ)^{2-}$ outer sphere anion has been reported two other times, (EtP)(TCNQ–TCNQ) and $[Pt(bpy)_2]$-(TCNQ–TCNQ) [44]. In manganese chemistry Dunbar and co-workers have obtained examples of coordination of this dimeric ligand in [Mn(TCNQ–TCNQ)-$(MeOH)_4]$ and $[Mn(TCNQ)(TCNQ–TCNQ)_{0.5}(MeOH)_2]$ [21,45].

The nickel derivatives show only one stable oxidation state and the reaction with neutral TCNQ is different, since no charge transfer processes are available. If the nickel atom is in a stable coordination environment, as in $[Ni(en)_3]^{2+}$ or $[Ni(dien)_2]^{2+}$, the reaction with neutral TCNQ originates di or tricyanoderivatives of TCNQ [46], probably formed by the attack of the TCNQ molecule to the primary amine groups of the coordinated ligand (Fig. 8).

Rather different behavior is observed when the nickel atom has coordinative positions susceptible to be occupied by $TCNQ^-$, thus the reactions of $[Ni(en)_2]^{2+}$ or $[Ni(tn)_2(H_2O)_2]^{2+}$ with $TCNQ^-/TCNQ^0$ give, respectively, the derivatives $[Ni(en)_2(TCNQ)_2](TCNQ)$ [29] and $[Ni(tn)_2(TCNQ)_2](TCNQ)$ [27], whose proposed structures have anionic TCNQ dimerized and coordinated to the metal forming chains

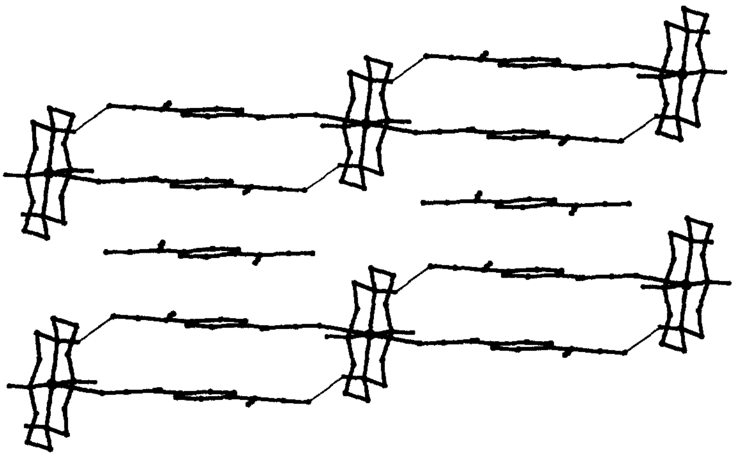


Fig. 9. TCNQ stacking in $[Cu([14]aneN_4)(TCNQ)_3]$, Ref. [47].

and with the neutral TCNQ molecules located between the chains as in the tetraazametallomacrocycle structures commented below.

5.2. Saturated tetraazamacrocycles

We have previously commented that the reaction with $TCNQ^-$ produces the derivatives $[M(N_4)(TCNQ)_2]$ with two TCNQ units coordinated in *trans* positions, and dimerized forming infinite linear chains. The reaction with a mixture of neutral and anionic TCNQ gives rise to derivatives of formula $[M(N_4)(TCNQ)_3]$ (N_4 = [14]aneN_4 [47], [15]aneN_4 [37]), better described as $[M(N_4)(TCNQ^-)_2](TCNQ^0)$.

The structure is based in the linear chains $[M(N_4)(TCNQ)_2]$. The coordinated TCNQ have structural parameters very close to those of the radical anion while the extra TCNQ is almost neutral and is located between the chains, connecting them by π overlapping (Fig. 9).

The derivative $[Cu([14]aneN_4)(TCNQ)_3]$ shows polymorphism and two different crystal structures have been described [47]. Both polymorphs show similar structural bases, the infinite chains $[Cu([14]aneN_4)(TCNQ)_2]$, and only differ in the overlapping mode of the neutral TCNQ. In one compound the neutral TCNQ is parallel to the anionic ones, forming infinite TCNQ stacks extended in a perpendicular direction relative to the metal–TCNQ chains (Fig. 10). In the second polymorph the neutral

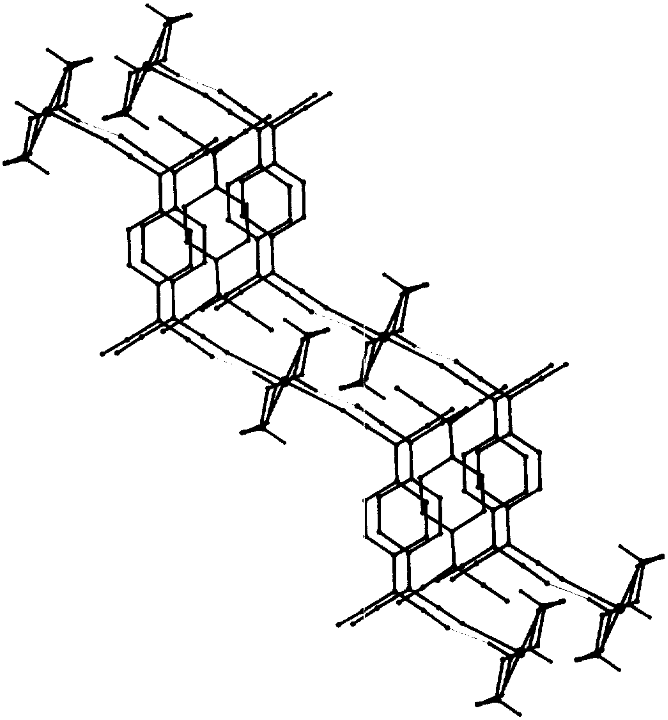


Fig. 10. Overlapping of neutral and anionic TCNQ in $[Cu([14]aneN_4)(TCNQ)_3]$, polymorph 1, Ref. [47].

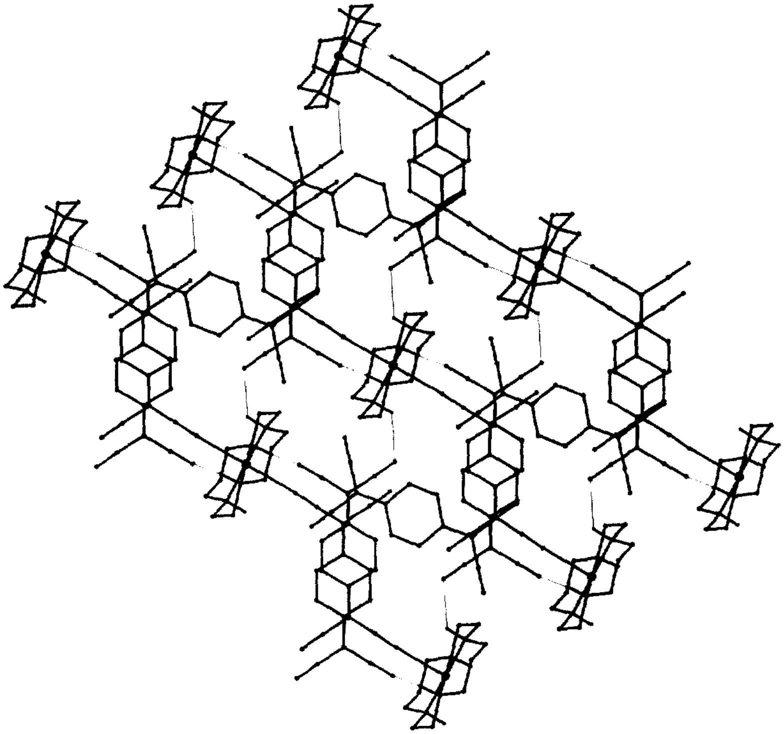


Fig. 11. Overlapping of neutral and anionic TCNQ in [Cu([14]aneN$_4$)(TCNQ)$_3$], polymorph 2, Ref. [47].

TCNQ is rotated 72° against the longitudinal axis of the radical anions and this orientation makes possible the overlap of every neutral TCNQ with radical anions belonging to four different metal–TCNQ chains, extending the dimensionality of the interaction in the three dimensions of the network (Fig. 11).

The TCNQ stacking of the first polymorph (Fig. 10) has also been observed in the copper compound with the related organic donor 2,5-DM-DCNQI, [Cu([14]aneN$_4$)](2,5-DM–DCNQI)$_{2.5}$ [48]. The structure of this compounds show stacks of formulae [Cu([14]aneN$_4$)](2,5-DM–DCNQI)$_2$ and [Cu([14]aneN$_4$)](2,5-DM–DCNQI)$_3$, both stacks have chains similar to those described here for the TCNQ derivatives of equal formula.

The TCNQ stacking mode of the second polymorph (Fig. 11) has no precedent in the literature. This compound was not formed by the usual method, the reaction between [M(N$_4$)]X$_2$ and a mixture of TCNQ$^-$/TCNQ^0, which is the synthetic procedure of the first polymorph. The second isomer has been obtained in the reaction between [Cu([14]aneN$_4$)(TCNQ)$_2$], with only the radical anion present, and elemental iodine. The equilibrium:

$$\mathrm{TCNQ}^- + 1/2\mathrm{I}_2 \rightleftharpoons \mathrm{TCNQ}^0 + \mathrm{I}^-$$

usually employed in the synthesis of the radical anion [4], is now displaced to the right, probably by crystallization of [Cu([14]aneN$_4$)(TCNQ)$_3$].

The macrocyclic derivatives with dh[14]aneN_6 do not form compounds of formula $[M(N_4)(TCNQ)_3]$. This fact can be attributed to the stabilization of [M(dh[14]aneN_6)-$(TCNQ)_2$] by formation of hydrogen bonds between the hydroxo macrocyclic groups and $TCNQ^-$ belonging to adjacent chains [38,39]. If the neutral TCNQ entered between the chains these hydrogen bonds would be broken, resulting in a destabilization of the structure.

5.3. Unsaturated tetraazamacrocycles

The cationic metallomacrocycles $[M(N_4diene)]^{2+}$, which have the metal in a square–planar environment and with no tendency of increasing its coordination number react with $TCNQ^-/TCNQ^0$ with formation of the species $[M(N_4diene)]$-$(TCNQ)_3$ [32,37].

In contrast with the behavior observed for the saturated macrocycle compounds the crystal structures of these new species show parallel TCNQ stacks separated by rows of isolated metallomacrocyclic cations (Fig. 12).

In the TCNQ stack all the molecules bear approximately the same negative charge; nevertheless two different interplanar distances are found in the stacks, indicating that the electronic delocalization is not complete and allowing the interpretation of the stack as being formed by trimeric dianions $(TCNQ)_3^{2-}$.

6. TCNQ structural parameters

The compounds we have previously described can be classified in four general types according to their TCNQ arrangements:

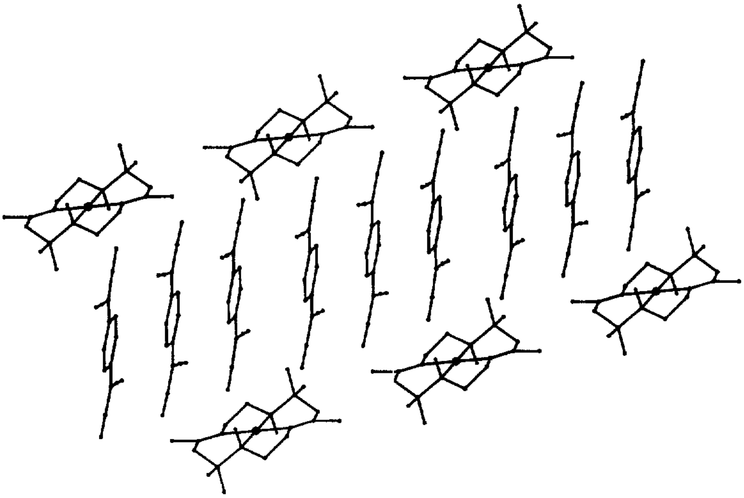
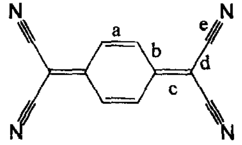


Fig. 12. Crystal packing in $[Ni(N_4\textit{trans}diene)](TCNQ)_3$, Ref. [37].

Table 1

Comparative bond distances in TCNQ molecules of different crystal arrangements[a]



	A	*b*	*c*	*d*	*e*	*b–c*	*c–d*	*c*/(*b*+*d*)	Ref.
TCNQ	1.345	1.448	1.374	1.441	1.140	0.074	−0.067	0.476	[51]
$TCNQ^-$	1.374	1.423	1.420	1.416	1.153	0.003	0.004	0.500	[52]
Type 1 $[Ni(N_4\textit{cis}diene)](TCNQ)_2$									
$TCNQ_a$	1.35	1.41	1.41	1.40	1.145	0.00	0.01	0.50	[31]
$TCNQ_b$	1.36	1.41	1.41	1.405	1.145	0.00	0.005	0.50	[31]
Type 2 $[Ni([14]aneN_4)](TCNQ)_2$									
TCNQ	1.349	1.419	1.415	1.414	1.143	0.004	0.001	0.499	[30]
Type 3 $[Cu([14]aneN_4)](TCNQ)_3$									
$TCNQ_a$	1.370	1.419	1.410	1.416	1.144	0.009	−0.006	0.497	[47]
$TCNQ_b$	1.345	1.433	1.384	1.420	1.144	0.049	−0.036	0.485	[47]
Type 4 $[Ni(N_4\textit{trans}diene)](TCNQ)_3$									
$TCNQ_a$	1.35	1.429	1.400	1.434	1.135	0.029	−0.034	0.489	[37]
$TCNQ_b$	1.35	1.425	1.400	1.418	1.139	0.025	−0.018	0.492	[37]

[a] In all cases $TCNQ_a$ and $TCNQ_b$ represent crystallographycally different molecules.

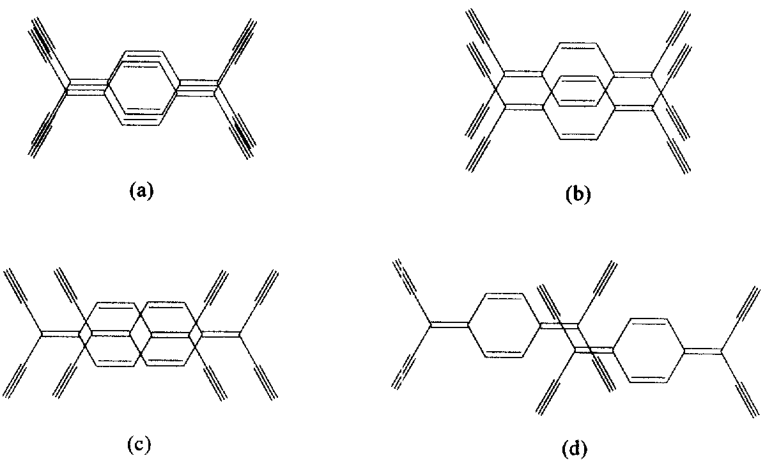


Fig. 13. Overlapping modes of TCNQ molecules (a) eclipsed ring over ring; (b) ring over ring slipped along the transverse axis; (c) ring over external bond; (d) external bond over external bond.

1. Uncoordinated dimers $(TCNQ)_2^{2-}$.
2. Coordinated dimers $(TCNQ)_2^{2-}$.
3. Coordinated dimers $(TCNQ)_2^{2-}$ plus neutral TCNQ between them.
4. Delocalized TCNQ stacks, approximately stacked trimers $(TCNQ)_3^{2-}$.

The oxidation state of the TCNQ and its overlapping mode can be related with the type of crystal arrangement. To exemplify this fact we will comment the structural data of a representative compound of each type (Table 1).

There has been a great deal of work relating the bond distances in every TCNQ to the degree of charge held on it. The reduced radical anion partially occupies an antibonding orbital and this is reflected in a shortening of the *b* and *d* bonds and a lengthening of *c* bonds. This implies that when the radical anion is formed the $b-c$ and $c-d$ differences are lowered. Flandrois and Chasseau [49] propose that these differences can be directly related to the degree of electronic density supported by the TCNQ molecule. Using a similar reasoning, Kistenmacher et al. [50] relate the degree of charge transfer to the TCNQ with the $c/(b+d)$ ratio.

The bond distances of the dimers $(TCNQ)_2^{2-}$ are characteristic of the radical anion, with independence of the dimer coordinative status, types 1 and 2. When the dimer is not coordinated the overlapping occurs in the ring over ring mode with both TCNQ eclipsed (Fig. 13(a)). On the contrary, the coordinated dimers also overlap in the ring over ring mode, but one TCNQ is slipped 0.5–1 Å along the transverse axis of the dimer (Fig. 13(b)). The intradimer distances are in the range 3.18–3.25 Å [30,31,33] but there was no relationship exhibited with the coordinative status or the physical properties the compounds.

In type 3 derivatives the coordinated TCNQ exhibited bond distances comparable to those of the dimers of type 2, i.e. typical of radical anions. The uncoordinated TCNQ is almost neutral although the overlap along the TCNQ stack favors a small degree of charge transfer from the radicals. The overlapping mode is also ring over ring, although the neutral TCNQ is shifted along the transverse axis (Fig. 13(b)). In these compounds the distances inside the coordinated dimer are smaller 3.09–3.20 Å [19,20,47] relative to derivatives of type 1 and 2, but the overlapping distances between neutral and anionic TCNQ are larger, in the range 3.26–3.35 Å.

Finally, the compounds belonging to type 4 show equivalent bond distances for the crystallographically different TCNQ units. This fact suggests a complete charge delocalization between the organic acceptors, each bearing 2/3 of negative charge [37]. The TCNQ are stacked, but there are two different intermolecular distances of 3.15 and 3.45 Å and the stack is best considered as formed by trimers $(TCNQ)_3^{2-}$ separated by the long intermolecular distances. The overlapping in the trimer is of the ring over external bond mode (Fig. 13(c)).

7. Physical properties

The properties related with the described compounds are also mainly dependent of the type of TCNQ arrangement found in the structure. Due to this fact we will comment the data of four derivatives each representative of one class of compounds.

7.1. Infrared spectra

The isolated TCNQ dimers, type 1, show the characteristic vibration modes of the organic group [53]. The compounds of type 2 show one extra ν(CN) band due to the activation of a new vibration mode on lowering of the symmetry by TCNQ coordination. In [Ni(trien)(TCNQ)$_2$], a compound of this type but with *cis* coordination of the TCNQ, one extra ν(CN) band is observed, a fact attributable to the additional lowering of the symmetry by the coordination mode of the organic acceptor.

Type 3 derivatives show the same bands of those of type 2, attributable to coordinated dimers plus extra bands (2217, 1539, 840 cm^{-1}) characteristic of neutral TCNQ [54].

The main characteristics in the IR spectra of type 4 compounds are the broadening of TCNQ bands, that appear at intermediate frequencies between those of neutral and those of anionic TCNQ and the superimposition of these bands on a background

Table 2
Characteristic IR bands of different types of TCNQ compounds

Compound		IR spectrum (cm^{-1})		
		ν(CN)	ν(CC)	δ(CH)
type 1	[Ni(N$_4$*cis*diene)](TCNQ)$_2$	2176, 2155	1579, 1500	824
type 2	[Ni([14]aneN$_4$)(TCNQ)$_2$]	2186, 2182, 2161	1584, 1504	825
type 3	[Ni([14]aneN$_4$)(TCNQ)$_3$]	2217, 2181, 2156	1578, 1539, 1497	840, 828
type 4	[Ni(N$_4$*trans*diene)](TCNQ)$_3$	2177, 2155	1566, 1508	829

absorption due to a low energy electronic transition characteristic of delocalized electronic states in TCNQ stacks [55], Table 2.

In spite of these conclusions the spectroscopical studies are not clear enough to establish without ambiguity the coordinative status of the TCNQ groups or the charge localization degree, due to the complexity and variety of supramolecular arrangements reported.

7.2. Electronic spectra

The electronic absorptions attributable to TCNQ molecules are mainly due to charge transfer processes between overlapping units. For the radical anion the locally excited levels absorb at about 12 000 and 25 000 cm^{-1} [56].

In the $(TCNQ)_2{}^{2-}$ dimers a charge transfer band attributable to the process:

$$TCNQ^{-}TCNQ^{-} \rightarrow TCNQ^{0}TCNQ^{2-}$$

appears between 11 000 and 8000 cm^{-1} [57]. Along with this band, the derivatives with TCNQ in different electronic states show a lower energy charge transfer [55] related to the process:

$$TCNQ^{-}TCNQ^{-}TCNQ^{0} \rightarrow TCNQ^{-}TCNQ^{0}TCNQ^{-}$$

In type 3 derivatives, with electronic localization on the TCNQ molecules, this band is observed at 6000 cm^{-1}, while in type 4 derivatives the delocalization shifts the band to lower energies, appearing around 4000 cm^{-1}. The tail of this band in background superimposition is observed in the IR spectra.

The electronic spectra in solution are less informative, since the compounds here reported are weakly soluble and they only dissolve in high donor solvents, such as acetonitrile or dimethylsulfoxide. In these solvents the metal–TCNQ interaction is always broken and the electronic spectra consist of independent absorptions due to the isolated cationic metal complex and the TCNQ groups.

The solution electronic spectrum of TCNQ is indicative of the electronic status of the acceptors in the solid, since the spectrum of the radical anion shows the two locally excited levels at 11 900 and 25 400 cm^{-1}, with an intensity ratio $\varepsilon(25\,400)/\varepsilon(11\,900) = 0.5$. The neutral TCNQ only absorbs at 25 400 cm^{-1} and an intensity ratio value higher of 0.5 would indicate the presence of both neutral and anionic TCNQ, thus this value is 1.25 for one neutral and two anionic TCNQ, and this is the observed value in type 3 and 4 derivatives [37,47]. In a similar way a value of 2.0 would indicate one neutral and one anionic TCNQ, equivalent to the monoanion $(TCNQ)_2{}^{-}$. It is possible to determine the relative quantities of neutral and anionic TCNQ, but the solution electronic spectra are not indicative of the electronic delocalization degree, due to the rupture of the interaction with the metals.

7.3. Electrical conductivity

Two prerequisites are necessary for obtaining a good low dimensional conductor from TCNQ derivatives [57]: formation of TCNQ stacks and partial reduction of the TCNQ molecules, which must adopt non integer oxidation estates.

The first condition predicts that solids of types 1 and 2 should behave as poor semiconductors or isolators and, in fact, room temperature conductivity values lower than 10^{-5} S cm^{-1} are observed in pressed powdered samples [27,38].

Compounds of type 3 show the stacks necessary for the electronic conductivity, but the coordination to the metal localizes the charges in the bonded TCNQ$^-$ and the second condition is not fulfilled, thus room temperature conductivity values of about 10^{-3} S cm^{-1} are observed [47].

In type 4 derivatives both conditions are accomplished, although the irregular stacking indicates that the electronic delocalization is not complete. The compounds are good semiconductors with single crystal conductivity values of 0.15 S cm^{-1} [32,37]. These values are between the higher found in TCNQ derivatives with transition metal centers.

The semiconducting behavior follows the normal exponential law, $\sigma = \sigma_0 \times \exp(-E_a/kT)$. The activation energy values vary with the type of stacking. The isolated dimers show values in the range 0.7–0.9 eV [31,37]. Lower activation energies are found for type 3 and 4 derivatives, due to the TCNQ stacking. Values of 0.12–0.35 eV have been found [32,47].

7.4. *Magnetic susceptibility*

Compounds of type 1 and 2 show magnetic susceptibility values corresponding to isolated metal ions. Their behaviors follow the Curie–Weiss law, indicating that the organic part of the molecule does not contribute to the total paramagnetism, since the π overlapping induces a strong antiferromagnetic coupling even at room temperature [30,31,36].

In type 3 derivatives the TCNQ derivatives are also antiferromagnetically coupled, but the overlapping with the neutral TCNQ weakens the coupling and the magnetic susceptibility variation is more complex. At very low temperatures, the magnetic moment can be attributable to the paramagnetic metal ions that follow the Curie–Weiss law, but on raising the temperature an increase in the magnetic moment is observed, indicating that a second paramagnetic contribution appears. This contribution is due to the presence of a thermally accessible triplet state ($S = 1$) for the TCNQ$^-$ dimer as a consequence of the weakening in the antiferromagnetic coupling. As the temperature increases the excited triplet state is populated and the contribution of the organic part to the total paramagnetism increases [47]. The reported coupling constants (J/k), i.e. the energy difference between the basal singlet and the excited triplet states, vary between -260 and -390 K [37,47].

An exception in the magnetic behavior of the TCNQ dimers is observed in the nickel and copper compounds with the macrocycle dh[14]aneN$_6$ [38,39]. Both compounds have only coordinated TCNQ dimers but, probably due to the hydrogen bond interactions with the hydroxo ends of the macrocycle, the antiferromagnetic coupling in the dimer is not as strong as in the rest of the derivatives of types 1 and 2. The coupling constant is -189 K for the nickel derivative and -382 K for the copper one.

Finally, in type 4 compounds the electronic delocalization favors the radical coupling and, again only the metal contribution to the paramagnetism is observed [32].

8. Final remarks

The diversity of stable nickel(II) and copper(II) coordination compounds with polyamine ligands has permitted one to design some synthetic strategies in hybrid solids containing TCNQ radicals. Concerning the metallic fragment, a stable metal environment favors the orientation of the TCNQ radical anions, either by direct σ bonding to the metal or by formation of hydrogen bonds with the auxiliary polyamine ligands. The σ coordination is favored by the existence of vacant positions and because of its formation, electronic localization on the TCNQ molecule is observed. The addition of neutral TCNQ favors the stacking of the organic acceptors, but electronic delocalization is only observed in the absence of direct metal–TCNQ bonds.

Adequate crystals for structural studies can only be obtained by the direct reaction of the fragments, since the attempts at recrystallization have not given good results. The compromise between solubility of the metallic complex, favored by the substitution of hydrogen atoms by other groups, and the formation of hydrogen bonds is a crucial aspect for every fragment.

Four main structural types have been obtained from solutions containing metallic fragments and selected $TCNQ^-/TCNQ^0$ relative concentrations. From the electronic perspective, coordinated or uncoordinated $(TCNQ)_2^{2-}$, stacks $(TCNQ)_2^{2-}$–$TCNQ^0$–$(TCNQ)_2^{2-}$, and $(TCNQ)_3^{2-}$ have been designed and obtained.

The electric and magnetic properties can be interpreted on the basis of the electronic state of both fragments. However, due to the subtle changes in the radical stacking, no quantitative correlation can be established. Less stable nickel and copper environments or changes in the solvents dramatically affect the supramolecular architecture finally obtained.

Acknowledgements

Support of this work has come from D.G.E.S. projects PB94-0240 and PB97-0236, and the COST action D4/0002/94. The authors gratefully acknowledge Dr C. Bellitto (Rome), Professor E. Coronado (Valencia) and Professor F. Palacio (Zaragoza), for help with the magnetic interpretations.

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