Tetracyanoquinodimethane Derivatives of Macrocyclic Nickel(II) Complexes. Synthesis and Crystal Structure of Bis(7,7,8,8-tetracyanoquinodimethanido)(1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II)

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The reactivity of the dichloro(1,8-disubstituted-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II) complex $[NiCl_2L^R]$ ($R = C_2H_4OH$, C_2H_5, $CH_2C_6H_5$) toward LiTCNQ leads to a complete replacement of the chloride groups by the anionic $TCNQ^{\bullet-}$ with formation of complexes of formulas $[NiL^R(TCNQ)_2]$. The crystal structure of the hydroxyethyl derivative has been solved. The nickel atom is hexacoordinated surrounded by four nitrogens of the macrocyclic ligand and two axial monodentate $TCNQ^{\bullet-}$ ligands, being the first nickel–TCNQ complex showing σ-bonds between the organic acceptor and the metal atom. Intermolecular interactions between TCNQ groups from adjacent molecules forming dimeric units and hydrogen bonds involving the hydroxo groups and one of the nitrogen atoms of a neighboring TCNQ unit are the most significant features of the crystal structure. These compounds behave virtually as insulators at room temperature.

Introduction

In the field of the charge-transfer compounds between transition metal complexes and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) the electronic and steric properties of the metal compound play an important role.[1] In order to design segregated stacked systems that would show the most interesting electric properties, the ability of TCNQ to interact as a σ-nitrile with the metal fragment has been proved to us to be one of the main factors to be considered. Recently, we have isolated a dimeric ruthenium–σ-bonded-TCNQ system in which the coordinative interaction ruthenium–nitrile favors the formation of dimeric stacked units of $[Ru(TCNQ)(PPh_3)_2]_2$.[2]

A few nickel–TCNQ complexes have been isolated by interaction of either neutral nickel(II) derivatives with TCNQ or cationic nickel(II) complexes with LiTCNQ or a LiTCNQ/$TCNQ^0$ mixture. Only the porphyrinate [Ni(TMP)(TCNQ)][3] and the tetraaza [14]annulene[Ni(hMedbtaa)(TCNQ)][4] complexes were fully characterized. In both cases the solid is formed by integrated stacks of metal complex and TCNQ molecules. The former presents short interplanar spacing between the metalloporphyrin and the TCNQ groups typical of 1:1 Mulliken π molecular compounds.

Macrocyclic nickel and copper complexes $[ML(TCNQ)_2]$ have been reported by Wang et al.[5] From magnetic and spectroscopic data they suggested that their crystal structures could be seen as segregated stacks of cationic metal complexes and TCNQ anions.

We have studied the reactivity of polyaza-saturated macrocyclic nickel(II) complexes. These compounds are very suitable species for use as reactive centers due to the high thermodynamic stability. This is an important condition in the reaction with TCNQ as we have proved in the reactivity studies with mono- and polynuclear nickel(II) complexes where these reactions take place with complete displacement of the ligands around the metal.[6] In addition the nickel atom in the tetraaza complexes is coordinatively unsaturated with two positions in the coordination sphere accessible for binding additional ligands.[7] In this case the equilibrium between planar and hexacoordinated environments is probably one of the main factors involved in the possibility of obtaining σ-bonded TCNQ complexes.

As a part of a project oriented to obtain stacked TCNQ metal complexes, we have studied the reactivity of (1,8-disubstituted-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II) complexes, $[NiCl_2L^R]$, toward LiTCNQ and now report here the preparation and full characterization of the first σ-bonded nickel–TCNQ complex.

Experimental Section

Preparation of Compounds. All reactions have been carried out under oxygen-free nitrogen using degassified solvents.

Dichloro(1,8-R_2-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II) ($R = C_2H_4OH, C_2H_5, CH_2C_6H_5$), $[NiCl_2L^R]$. These complexes were obtained by following the published method:[7] To a stirred solution of $NiCl_2{\cdot}6H_2O$ (11.5 g, 0.049 mmol) and ethylenediamine (6.8 mL, 0.10 mmol) in 50 mL of methanol was added dropwise a water solution of formaldehyde (20 mL, 36%) and the corresponding amine, RNH_2 ($R = C_2H_4OH$, C_2H_5, $CH_2C_6H_5$). The resulting solution was refluxed for 1 day. The pink precipitate that formed was filtered off and dried under vacuum over P_4O_{10}. Yield: 80–90%.

Anal. Calcd for $C_{12}H_{30}Cl_2N_6NiO_2$ ($R = C_2H_4OH$): C, 34.3; H, 7.1; N, 20.0. Found: C, 34.2; H, 7.0; N, 20.2. Calcd for $C_{12}H_{30}Cl_2N_6Ni$ ($R = C_2H_5$): C, 37.1; H, 7.7; N, 21.7. Found: C, 36.9; H, 7.7; N, 21.4. Calcd for $C_{22}H_{34}Cl_2N_6Ni$ ($R = CH_2C_5H_6$): C, 51.5; H, 6.6; N, 16.4. Found: C, 52.0; H, 6.4; N, 16.5.

Bis(7,7,8,8-tetracyanoquinodimethanato)(1,8-R_2-1,3,6,8,10,13-hexaazacyclotetradecane), $[NiL^R(TCNQ)_2]$. Dropwise addition of an ethanolic

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Table 1. Crystal and Refinement Data for $[NiL^R(TCNQ)_2]$, R = C_2H_4OH

formula	$NiO_2N_{14}C_{36}H_{38}$
fw	757.5
cryst system	triclinic
space group	$P\bar{1}$
a, Å	13.030(6)
b, Å	8.852(4)
c, Å	8.124(1)
α, deg	85.20(2)
β, deg	97.119(3)
γ, deg	73.23(4)
V, Å^3	3247.(2)
Z	1
ρ(calcd), g cm^{-3}	1.42
temp, °C	22
μ, cm^{-1}	6.03
λ(graphite-monochromated Mo Kα), Å	0.710 69
R_F,^{a} %	5.5
R_{wF},^{a} %	5.5

^{a} $R_F = \sum|\Delta^2F|/\sum|F_o|$; $R_{wF} = [\sum w\Delta^2F/\sum w|F_o|^2]^{1/2}$.

solution of LiTCNQ[8] to a stirred solution of the nickel dichloro complex in ethanol/water (25:1) in a molecular ratio nickel to TCNQ of 1:2 followed by stirring for 12 h affords a deep blue solid that was filtered off, washed with degassified water and diethyl ether, and dried under vacuum over P_4O_{10}. Yield: 90–95%. X-ray-quality crystals were obtained by slow diffusion of solutions of LiTCNQ in ethanol and the nickel complex in ethanol–water.

Anal. Calcd for $C_{36}H_{38}N_{14}NiO_2$ (R = C_2H_4OH): C, 57.1; H, 5.0; N, 25.9. Found: C, 57.0; H, 5.1; N, 26.0. Calcd for $C_{36}H_{38}N_{14}Ni$ (R = C_2H_5): C, 59.6; H, 5.2; N, 27.0. Found: C, 59.4; H, 5.0; N, 27.2. Calcd for $C_{46}H_{42}N_{14}Ni$ (R = $CH_2C_5H_6$): C, 65.0; H, 4.9; N, 23.1. Found: C, 64.9; H, 4.8; N, 23.1.

Physical Measurements. Elemental analyses were carried out by the Servicio de Microanalisis of the Universidad Complutense de Madrid. IR spectra were taken in KBr disks using a Perkin-Elmer 1300 or a Phillips PU9712 spectrophotometer. Electronic spectra were recorded in solid using an Uvikon 620 spectrophotometer equipped with diffuse reflectance accessories and in acetonitrile solution using a GBC 911 spectrophotometer. Cyclic voltammetric studies were carried out using an Autolab apparatus equipped with a PSTAT10 potentiostat using a three-electrode cell with platinum wire as working and auxiliary electrodes and a saturated calomel electrode as reference. The samples were dissolved in acetonitrile, and Et_4NBF_4 was used as the electrolyte. Magnetic measurements were carried out using a Faraday type susceptometer equipped with a helium continuous-flow cryostat. Electrical conductivities were measured at room temperature in condensed powders using a two-probe apparatus described elsewhere.[9]

X-ray Structure Determinations. A summary of the fundamental crystal data is given in Table I. 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 refections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for nickel were taken from ref 10. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinement.[11]

In order to prevent bias of *F* vs F_o or (sin θ)/λ, weights were assigned as $w = 1/(a + bF_o)^2$, with the following coefficients: $F_o < 12$, $a = 3.62$, $b = 0.228$; $12 < F_o < 170$, $a = 0.75$, $b = 0.011$. A final refinement was undertaken with fixed isotropic factors and coordinates for all hydrogen atoms. Final synthesis showed no significant residual electron density. Refined atomic coordinates are given in Table 2. Most of the calculations were carried out with the X-Ray 80 system.[12]

Table 2. Atomic Parameters and U_{eq} Values (Å^2) for $NiO_2N_{14}C_{36}H_{38}$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}^{a}
Ni	0.0000(0)	0.0000(0)	0.0000(0)	217(4)
O1	0.3624(4)	0.1191(6)	−0.3359(6)	613(21)
N1	0.1148(4)	−0.1654(5)	0.1987(6)	330(17)
N2	0.1465(4)	−0.6034(7)	0.5009(7)	581(24)
N3	0.7413(4)	−0.5692(6)	1.0257(7)	532(22)
N4	0.7017(5)	−0.1194(7)	0.7380(7)	578(24)
N5	0.0811(3)	−0.1262(5)	−0.1702(5)	280(15)
N6	0.1816(3)	0.0621(5)	−0.2213(5)	344(17)
N7	0.0951(3)	0.1490(5)	0.0190(5)	283(16)
C1	0.1683(4)	−0.2627(6)	0.3018(6)	283(18)
C2	0.2323(4)	−0.3838(6)	0.4301(6)	296(18)
C3	0.3315(4)	−0.3776(6)	0.5170(6)	274(17)
C4	0.3945(4)	−0.5015(6)	0.6439(6)	319(19)
C5	0.4898(4)	−0.4930(6)	0.7296(7)	327(19)
C6	0.5293(4)	−0.3616(6)	0.6963(6)	285(18)
C7	0.4665(4)	−0.2394(6)	0.5687(7)	320(19)
C8	0.3714(4)	−0.2458(6)	0.4842(6)	308(18)
C9	0.1856(4)	−0.5074(7)	0.4689(7)	365(20)
C10	0.6275(4)	−0.3558(6)	0.7877(7)	327(19)
C11	0.6906(4)	−0.4742(7)	0.9197(7)	358(20)
C12	0.6679(5)	−0.2242(7)	0.7575(7)	403(22)
C13	0.1148(4)	−0.0264(7)	−0.2974(7)	368(21)
C14	0.2921(5)	−0.0318(7)	−0.1433(8)	465(24)
C15	0.3713(5)	0.0606(8)	−0.1700(9)	552(28)
C16	0.1291(4)	0.1951(6)	−0.1415(7)	359(21)
C17	0.0357(4)	0.2835(6)	0.0998(7)	347(20)
C18	0.0115(4)	−0.2173(7)	−0.2423(7)	368(21)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j(10^4)$.

Results and Discussion

The synthetic procedure can be described according to Scheme 1. Similar compounds were obtained with the different R groups. As pointed out by Hay et al.,[7] the incorporation of the hydroxyethyl arms in place of the alkyl or benzyl groups does not influence the aqueous solution spectra, suggesting that, under these conditions, the hydroxyethyl groups do not interact with the nickel atom. However, under the structural point of view the hydroxo group can be involved in hydrogen bonds as noted below.

Crystal Structure of $[NiL^R(TCNQ)_2]$, R = C_2H_4OH. The compound crystallizes in the triclinic system, space group $P\bar{1}$. The atom-labeling scheme is indicated in the ORTEP view of the molecular unit shown in Figure 1. Relevant bond lengths and angles are summarized in Table 3. As can be seen, the crystal lattice is not formed by mixed stacks of planar macrocyclic nickel complex and TCNQ units, in contrast to the two other structurally characterized nickel(II) complexes, [Ni(TMP)(TCNQ)][3] and [Ni(hMebdtaa)(TCNQ)].[4]

The nickel atom which is located at a center of inversion is coordinated to four nitrogen atoms of the macrocyclic ligand. The nickel–nitrogen distances of 2.053(4) and 2.056(5) Å are similar to those found in other nickel(II) tetraaza macrocycles.[13] The ring adopts a chair conformation. Two nitrogens from two TCNQ units are axially bonded with nickel–nitrogen distances of 2.175(4) Å and complete the elongated octahedral coordination around the nickel atom. All the four C—C≡N groups in TCNQ are linear.

The TCNQ groups of neighboring molecular units interact along the cell diagonal in a ring–ring overlap with a shortest distance of 3.250(7) Å between the C7′ and C4 atoms (Figure 2). This distance corresponds to the formation of dimeric units $(TCNQ)_2^{2-}$ (Table 4).

A view of the arrangement of the molecules along the *b* axis is shown in Figure 3. The compound can be seen as parallel chains made of $[Ni(macrocycle)]^{2+}$ units held together by the

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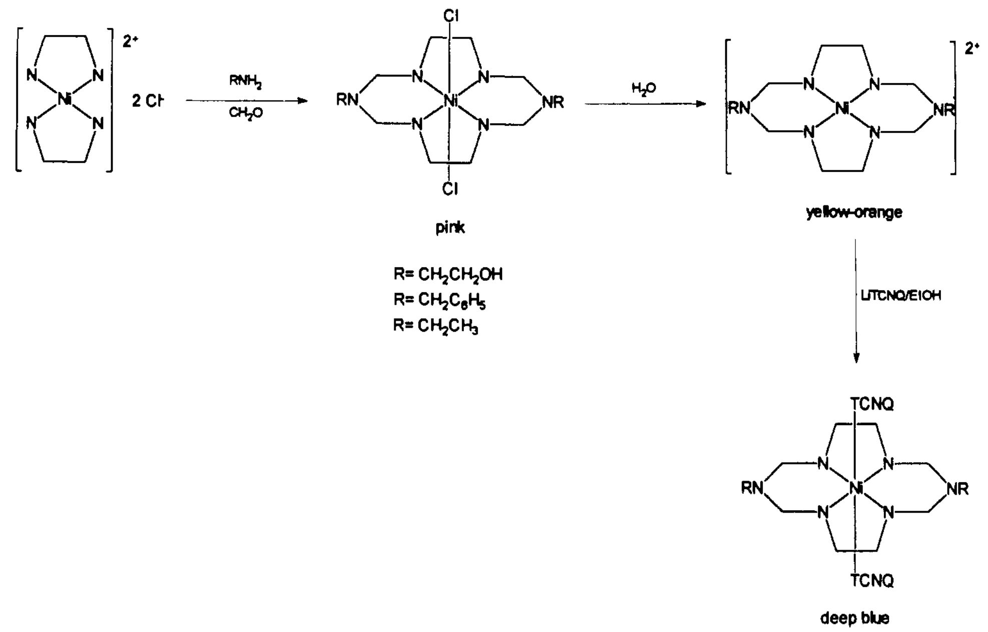
Scheme 1



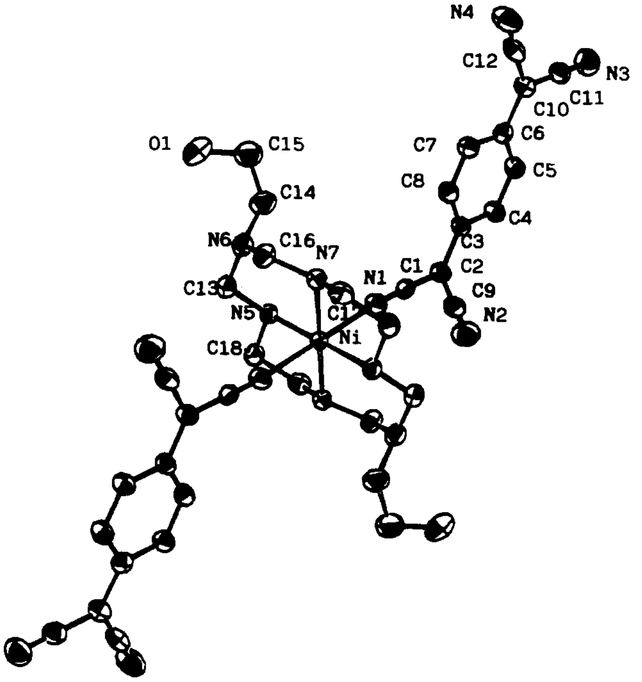


Figure 1. ORTEP plot of [NiL^R(TCNQ)$_2$], R = C_2H_4OH, with the atomic labeling scheme.

dimeric $(TCNQ)_2{}^{2-}$. These chains extend along the [111] direction of the crystal and interact with each other via hydrogen bonds formed between the hydroxo group and a nitrogen atom belonging to a TCNQ of a neighboring molecule: O1···N2′ = 2.950(5) Å, O1–H1···N2′ = 106.6(4)°.

Spectroscopic Studies. The number and intensity variations of the nitrile stretching bands in the IR spectra are highly indicative of the coordination status of the TCNQ ligand.[14]

The IR spectra of [NiL^R(TCNQ)$_2$] compounds present four bands in the $\nu(C{\equiv}N)$ stretching region (Table 5), the highest energy band being the weakest in an arrangement characteristic of σ-monodentate TCNQ.[15,16] Examining the 880–800-cm^{-1} region, it is also possible to have information about the electronic density and the intermolecular interactions that the TCNQ groups exhibit.[17] In our complexes the absorption observed at ca. 825 cm^{-1} is a clear indication that solely $TCNQ^{\bullet -}$ is present. Therefore the IR spectra of these compounds suggest a hexacoordinated environment for the nickel atom, four positions being occupied by the macrocyclic nitrogens and the other two by σ-monodentate radical anion TCNQ groups.

Table 3. Bond Lengths (Å) and Angles (deg) for [NiL^R(TCNQ)$_2$], R = C_2H_4OH

Ni–N1	2.175(4)	N7–C17	1.474(7)
Ni–N5	2.053(4)	C1–C2	1.419(6)
Ni–N7	2.056(5)	C2–C3	1.412(7)
O1–C15	1.381(8)	C2–C9	1.428(9)
N1–C1	1.148(6)	C3–C4	1.422(6)
N2–C9	1.138(9)	C3–C8	1.426(8)
N3–C11	1.141(7)	C4–C5	1.371(8)
N4–C12	1.144(9)	C5–C6	1.421(8)
N5–C13	1.491(7)	C6–C7	1.416(6)
N5–C18	1.478(8)	C6–C10	1.414(8)
N6–C13	1.447(8)	C7–C8	1.359(8)
N6–C14	1.470(6)	C10–C11	1.421(7)
N6–C16	1.431(7)	C10–C12	1.426(9)
N7–C16	1.490(7)	C14–C15	1.514(9)
N5–Ni–N7	94.7(2)	C4–C3–C8	117.3(5)
N1–Ni–N7	88.7(2)	C3–C4–C5	120.6(5)
N1–Ni–N5	88.5(2)	C4–C5–C6	121.9(5)
Ni–N1–C1	172.7(5)	C5–C6–C10	120.5(5)
Ni–N5–C18	106.6(3)	C5–C6–C7	117.1(5)
Ni–N5–C13	113.9(3)	C7–C6–C10	122.3(5)
C13–N5–C18	114.0(4)	C6–C7–C8	121.5(5)
C14–N6–C16	116.7(5)	C3–C8–C7	121.6(5)
C13–N6–C16	117.4(5)	N2–C9–C2	178.5(7)
C13–N6–C14	115.9(5)	C6–C10–C12	121.4(5)
Ni–N7–C17	106.2(4)	C6–C10–C11	123.6(5)
Ni–N7–C16	114.1(3)	C11–C10–C12	114.9(5)
C16–N7–C17	114.8(4)	N3–C11–C10	179.9(7)
N1–C1–C2	178.7(6)	N4–C12–C10	178.0(6)
C1–C2–C9	114.5(5)	N5–C13–N6	112.1(4)
C1–C2–C3	122.3(5)	N6–C14–C15	110.4(5)
C3–C2–C9	123.1(5)	O1–C15–C14	112.2(6)
C2–C3–C8	121.6(5)	N6–C16–N7	113.5(5)
C2–C3–C4	121.1(5)		

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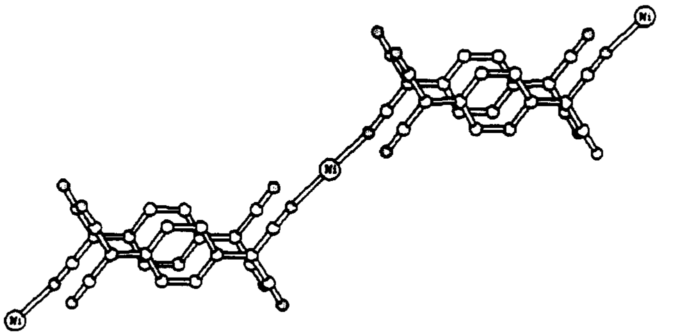

Figure 2. View of the overlapping of adjacent TCNQ units in the macrocyclic complex.

Table 4. Interplanar Distances for Selected TCNQ Dimeric Systems

compd	interplanar dist, Å	coord mode	ref
RbTCNQ	3.16	uncoordinated	22
(TPP)(TCNQ)$_2$	3.22	uncoordinated	22
[Cu(abpt)$_2$(TCNQ)$_2$]	3.22	monodentate	23
[Cu(pdto)(TCNQ)]	3.12	bidentate bridging	24
[NiL^R(TCNQ)$_2$]	3.25	monodentate	this work

The electronic spectra in solution of the TCNQ derivatives have been only studied in donor solvents such as DMSO or acetonitrile, due to the insolubility of the obtained compounds. These spectra show the well-defined transitions for the TCNQ groups[18,19] (locally excited levels of the TCNQ$^{\bullet-}$ anion, the lowest, LE$_1$, at ca. 800 nm and the second, LE$_2$, around 400 nm), and the complete spectra are clearly similar to that of free TCNQ$^{\bullet-}$ (i.e. RbTCNQ). The expected shifts to higher energies for these band systems upon coordination are not observed, indicating that only free TCNQ$^{\bullet-}$ is present.

The cyclic voltammograms of these complexes support the above affirmation. As a typical behavior, the [NiL^{R}Cl$_2$] (R = CH$_2$CH$_2$OH) complex shows one quasi-reversible process at 0.69 V in water (0.62 V in 20:1 DMSO/water solution) for the Ni^{III}/Ni^{II} couple in the square-planar [NiL^R]$^{2+}$ or octahedral [NiL^R(solvent)$_2$]$^{2+}$ that forms in solution after disociation of the chloride ligands (see Scheme 1).[7] This potential appears at values similar to those of other macrocyclic nickel derivatives.[20] A cathodic peak appearing at −0.99 V is attributed to the irreversible one-electron reduction to Ni^I.

The TCNQ derivative [NiL^R(TCNQ)$_2$] present three reversible or quasi-reversible waves in DMSO solution. The two waves at lower potentials appear at the same values (+0.12 and −0.43 V) as those for the couples TCNQ^0/TCNQ$^{\bullet-}$ and TCNQ$^{\bullet-}$/TCNQ^{2-} for free TCNQ, suggesting that the σ Ni–TCNQ interaction is broken in solution, since for coordinated TCNQ a shift to more positive values should be expected.[15] The third wave at 0.59 V can be attributed to the Ni^{III}/Ni^{II} process of the macrocyclic unit. The small shift relative to the starting complex could be attributed to the difference in the solvent nature since the dichloro complex only dissolves in the presence of a small quantity of water and the cyclic voltammograms measured in DMSO show lower potential values than those measured in water (*e.g.* 0.62 and 0.69 V for the dichloro derivative). Therefore, and in accordance with the results from the electronic spectra, the [NiL^R(TCNQ)$_2$] derivatives dissociate with breakage of the nickel–TCNQ bonds in TCNQ$^{\bullet-}$ and [NiL^R]$^{2+}$ and the redox processes observed correspond to those for the isolated species formed.

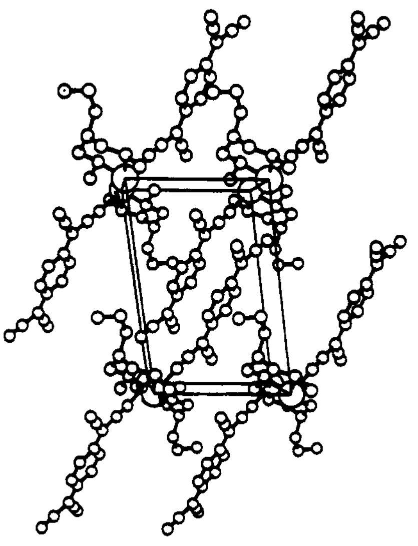

Figure 3. Crystal packing of [NiL^R(TCNQ)$_2$], R = C$_2$H$_4$OH, showing the cell unit projected along the *b* axis.

Table 5. Significant IR TCNQ Bands for the New Complexes[a]

compd	ν(C≡N)	ν(C=C)	δ(C—H)
TCNQ	2224 m	1545 m	862 s
TCNQ$^{\bullet-}$ [b]	2181 vs	1583 m	828 m
	2154 vs	1503 m	
[NiL^R(TCNQ)$_2$], R = C$_2$H$_4$OH	2212 w	1575 s	825 m
	2180 vs	1503 m	
	2168 s		
	2155s		
[NiL^R(TCNQ)$_2$], R = C$_2$H$_5$	2208 w	1578 s	825 m
	2180 vs	1501 s	
	2163 vs		
	2151 sh		
[NiL^R(TCNQ)$_2$], R = CH$_2$C$_6$H$_5$	2180 vs	1578 s	820 m
	2155 vs	1502 s	

[a] In KBr disks. [b] Free TCNQ$^{\bullet-}$ in Tl(18-crown-6)TCNQ.[25]

Conductivity and Magnetic Measurements. Two-probe conductivity measurements in powder at room temperature indicate that these compounds behave as insulators ($\sigma < 10^{-7}$ S cm^{-1}).

The magnetic susceptibility values of [NiL^4(TCNQ)$_2$] measured in the range 298–4 K correspond to hexacoordinated nickel(II) (μ_{eff} = 3.02 μ_B for R = C$_2$H$_4$OH and μ_{eff} = 2.95 μ_B for R = CH$_2$C$_6$H$_5$). No magnetic contribution from the TCNQ$^{\bullet-}$ radical is observed, suggesting that it is present as diamagnetic dimeric units in the measured range. This is possible due to the short TCNQ–TCNQ distance found in the crystal structure that allows the electron pairing of the radical species. In support of this interpretation of the magnetic behavior the derivative with R = C$_2$H$_4$OH is EPR silent at 80 K. This fact can be interpreted as a rapid relaxation of the S = 1 state for hexacoordinated Ni(II).[21] Since no signal for the radical could be observed, we do not expect a significant contribution of the TCNQ moieties to the magnetic moment. Nevertheless, more detailed magnetic studies are in progress.

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Concluding Remarks

The structure of [NiL^R(TCNQ)$_2$], R = C_2H_4OH, is the first example in which TCNQ groups are coordinated in a monodentate fashion to a nickel atom. The molecular parameters for TCNQ confirm that this molecule is coordinated as a formally anionic ligand. The strong trend shown by $TCNQ^{\bullet -}$ to delocalize the negative charge produces a molecular packing in which dimerization occurs. In accordance, these compounds behave virtually as insulators.

The thermodynamic stability given to the nickel environment and the trend to increase the metal coordination number in the macrocyclic complex play an important role in the stabilization of the reported complexes. This stabilization is lost in solution, where the nickel–TCNQ bonds break.

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Supplementary Material Available: Tables of complete crystal and refinement data, calculated atomic coordinates, anisotropic thermal parameters, and bond distances and angles (7 pages). Ordering information is given on any current masthead page.