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New Pr and Nd complexes containing TCNQ radicals

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Abstract

New compounds formed by reaction of TCNQ lanthanide complexes containing N-donor ligands have been obtained. By controlling the reaction conditions, different compounds of formulae Ln(N–N)$_x$(TCNQ)$_3$ (Ln=Pr, Nd; N–N=1,10-phenanthroline, dipyridylamine; x=2, 4) and Ln(N–N)$_4$(TCNQ)$_4$ are isolated. The former have only TCNQ anions neutralizing the lanthanide charge, while the latter exhibit electronic delocalization, as reflected by their semiconducting behavior.

Keywords: Lanthanide; Charge transfer; Organic radical salts

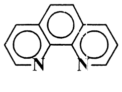
1. Introduction

The coordination chemistry of the lanthanide ions is characterized by their big size, combined with the mainly electrostatic nature of the metal–ligand bond, which gives rise to high coordination numbers [1].

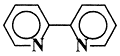
With N-donor ligands like phenanthroline (phen) or 2,2′-bipyridyne (bpy), the lanthanide ions form compounds of stoichiometry Ln(N–N)$_z$X$_3$ (X=NCS$^-$, NO$_3^-$, ClO$_4^-$, z=2, 3) with the metal ion nine-coordinated but showing a large tendency to dissociate in solution [2].

The reactions of the planar organic radical-anion TCNQ (TCNQ=7,7,8,8-tetracyanoquinodimethane) with transition metal complexes show that the coordination of the former orientates the organic molecules favoring the formation of infinite stacks and stabilizing the supramolecular arrangement [3,4].

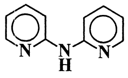
In this sense, the presence of lanthanide ions and TCNQ radicals can afford new materials with interesting magnetic properties by interaction of the corresponding spins. In order to look for such new derivatives, we have studied the reactions of anionic TCNQ with compounds of the general formula Ln(N–N)$_2$(NO$_3$)$_3$, where Ln=Pr, Nd and N–N is one of the following ligands:-



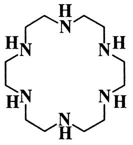
phen



bpy



dpa



N$_6$

2. Experimental

The compounds Ln(N–N)$_2$(NO$_3$)$_3$, with Ln=Pr or Nd, and N–N=phen, bpy or dpa (dipyridylamine), have been obtained from the corresponding nitrates following the method described previously [5,6]. Elemental CHN analyses have been carried out by the CAI of Microanálisis of the Universidad Complutense of Madrid. IR spectra were recorded in KBr pellets on a Nicolet Magna-550 FT-IR spectrometer. Electronic spectra were recorded on a Cary-5 spectrometer, either in DMF solution or with a solid sample rubbed on optical glass. Magnetic susceptibilities were measured in the 2–300 K temperature range, using a SQUID magnetometer MPMS XL-5 manufactured by Quantum Design, at a constant magnetic field of 0.5 T. Electrical conductivity measurements were performed by the four-points method.

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2.1. Reactions with LiTCNQ

Synthesis of Pr(phen)$_2$(TCNQ)$_3$·7H$_2$O (**1**), *Pr(dpa)$_4$(TCNQ)$_3$* (**2**) *and Nd(dpa)$_4$(TCNQ)$_3$* (**3**): These compounds were obtained by the addition of a solution of 0.6 mmol LiTCNQ in methanol to a DMF solution of $Ln(N–N)_2(NO_3)_3 \cdot xH_2O$ in a metal-to-TCNQ molar ratio of 1:3. The resulting solution was cooled and a dark blue solid appeared. The solid was filtered off, washed with methanol and dried under vacuum.

$Pr(phen)_2(TCNQ)_3 \cdot 7H_2O$: Anal. Calcd. for $C_{60}H_{42}N_{16}O_7Pr$: C, 58.1; H, 3.4; N, 18.1. Found: C, 57.6; H, 3.4; N, 17.8. IR TCNQ bands (cm^{-1}): 2185, 2159, 1579, 1505, 1344, 1176, 814, 725. Yield, 40%.

$Pr(dpa)_4(TCNQ)_3$: Anal. Calcd. for $C_{76}H_{48}N_{24}Pr$: C, 63.5; H, 3.4; N, 23.4. Found: C, 63.0; H, 3.1; N, 23.8. IR TCNQ bands (cm^{-1}): 2198, 2166, 1560, 1384, 1116, 823, 720. Yield, 28%.

$Nd(dpa)_4(TCNQ)_3$: Anal. Calcd. for $C_{76}H_{48}N_{24}Nd$: C, 63.3; H, 3.4; N, 23.3. Found: C, 63.1; H, 3.4; N, 23.4. IR TCNQ bands (cm^{-1}): 2188, 2168, 1560, 1384, 831, 719. Yield, 33%.

Synthesis of Nd(N$_6$)(TCNQ)$_3$·3H$_2$O (**4**): The compound was obtained by the addition of a solution of 0.6 mmol LiTCNQ in methanol to a methanolic solution containing a mixture of 0.2 mmol $Nd(NO_3)_3 \cdot 6H_2O$ and 0.2 mmol of the macrocycle (N_6). The final solution was stirred for 2 h and cooled for two days. A dark blue solid was obtained. Anal. Calcd. for $C_{48}H_{48}N_{18}NdO_3$: C, 53.9; H, 4.5; N, 23.6. Found: C, 52.8; H, 4.7; N, 23.2. IR TCNQ bands (cm^{-1}): 2176, 2156, 1575, 1501, 1360, 832, 719. Yield, 62%.

2.2. Reactions with LiTCNQ/TCNQ^0

Synthesis of Pr(phen)$_4$(TCNQ)$_4$ (**6**), *Pr(dpa)$_4$(TCNQ)$_4$* (**7**) and *Nd(dpa)$_4$(TCNQ)$_4$* (**8**): These compounds were obtained by addition of a mixture of 0.6 mmol LiTCNQ and 0.6 mmol TCNQ in acetonitrile to a stirred solution of 0.2 mmol of the corresponding $Ln(NN)_2(NO_3)_3 \cdot xH_2O$ in a 1:1 DMF–acetonitrile solution. A black solid appeared immediately and was filtered off, washed with methanol and acetonitrile and dried.

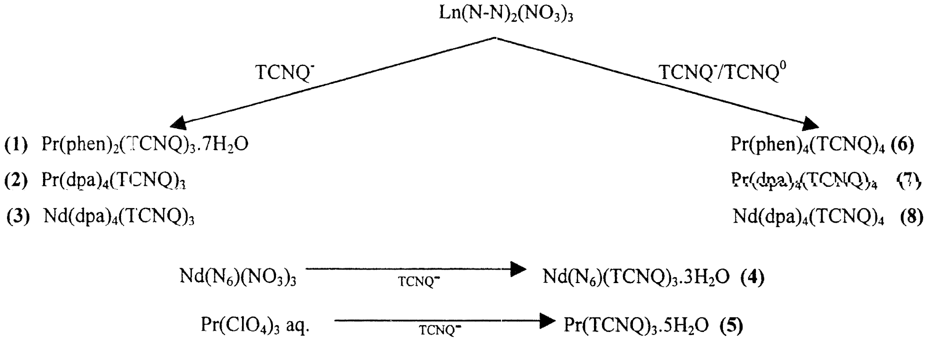
$Pr(phen)_4(TCNQ)_4$: Anal. Calcd. for $C_{96}H_{48}N_{24}Pr$: C, 68.7; H, 2.9; N, 20.0. Found: C, 68.4; H, 3.2; N, 19.6. IR TCNQ bands (cm^{-1}): 2210, 2200, 2185, 2160, 1597, 1514, 1335, 1146, 845, 710. Yield, 34%.

$Pr(dpa)_4(TCNQ)_4$: Anal. Calcd. for $C_{88}H_{52}N_{28}Pr$: C, 64.4; H, 3.2; N, 23.9. Found: C, 64.3; H, 3.4; N, 24.0. IR TCNQ bands (cm^{-1}): 2220, 2198, 2122, 1562, 1514, 1384, 1095, 845, 720. Yield, 41%.

$Nd(dpa)_4(TCNQ)_4$: Anal. Calcd. for $C_{88}H_{52}N_{28}Nd$: C, 64.2; H, 3.2; N, 23.8. Found: C, 64.7; H, 3.2; N, 24.2. IR TCNQ bands (cm^{-1}): 2210, 2198, 2130, 1560, 1520, 1304, 1099, 835, 769. Yield, 31%.

3. Results and discussion

The compounds $Ln(N–N)_2(NO_3)_3$ react with anionic TCNQ, either as LiTCNQ or mixed with neutral TCNQ, with displacement of the nitrate anions by the organic radicals. The reactions carried out are summarized in the following scheme:



Synthesis of Pr(TCNQ)$_3$·5H$_2$O (**5**): This compound was obtained by slow diffusion of a methanolic solution of 0.6 mmol LiTCNQ into an aqueous solution of 0.2 mmol $Pr(ClO_4)_3$. A dark blue microcrystalline solid was formed after three days. The solid was filtered off, washed with methanol and dried under vacuum. Anal. Calcd. for $C_{32}H_{22}N_{12}O_5Pr$: C, 51.3; H, 2.6; N, 19.9. Found: C, 51.0; H, 2.5; N, 19.4. IR TCNQ bands (cm^{-1}): 2195, 2168, 1579, 1502, 1355, 837, 720. Yield, 75%.

The tendency of the parent reagents, $Ln(N–N)_2(NO_3)_3$ to dissociate in polar solvents makes the isolation of well defined species difficult and explains the formation of salt-like derivatives between free N–N ligand and the TCNQ, such as $(Hphen^+)(TCNQ^-) \cdot H_2O$ or $(Hdpa^+)(TCNQ^-)$, isolated from some of the reaction mixtures.

With the macrocyclic ligand, 1,4,7,10,13,16-hexaazacyclooctadecane, a more stable environment for

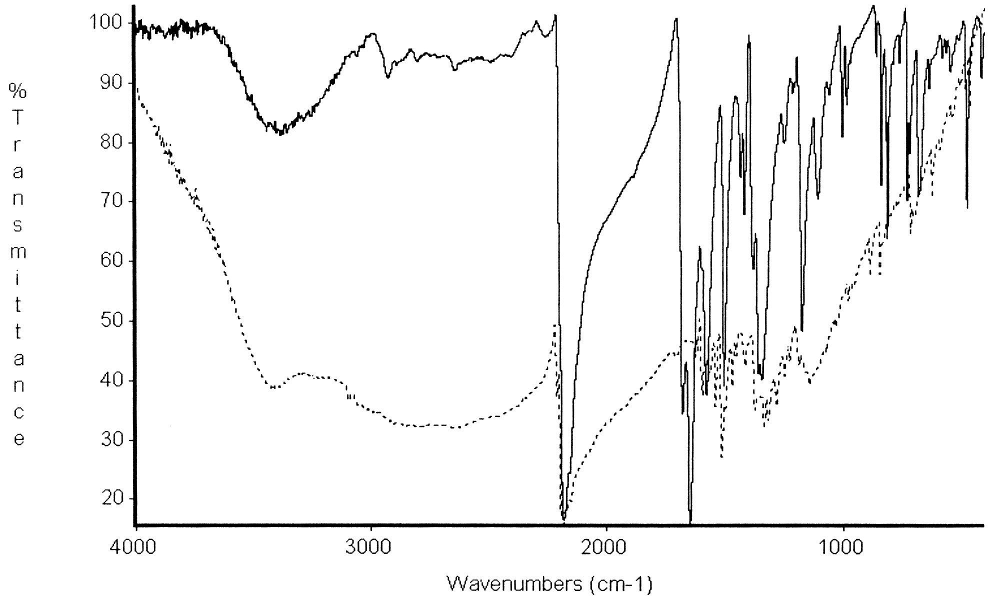


Fig. 1. IR spectra of $Pr(phen)_2(TCNQ)_3$ (solid line) and $Pr(phen)_4(TCNQ)_4$ (dotted line).

neodymium is obtained, favoring the formation of compound (**4**).

The IR spectra of (**1–8**) offer a convenient diagnosis of the formal oxidation state and the coordinative status of the TCNQ groups [7]. Neutral TCNQ shows the following characteristic vibration frequencies: $\upsilon(C{\equiv}N)=2228\ cm^{-1}$, $\upsilon_{20}(b_{1u})=1530\ cm^{-1}$, $\upsilon_{34}(b_{2u})=1524\ cm^{-1}$, $\upsilon_4(a_g)=1424\ cm^{-1}$, $\upsilon_{50}(b_{3u})=860\ cm^{-1}$ and $\upsilon_7(a_g)=705\ cm^{-1}$. For the anionic $TCNQ^-$, these vibrational modes are observed at 2194/2177, 1577, 1507, 1386, 824 and 722 cm^{-1}, respectively.

Compounds (**1–5**) show the $\upsilon(C{\equiv}N)$ and υ_{50} vibration modes in the ranges 2190–2150 and 840–810 cm^{-1}. These frequencies clearly indicate that the TCNQ groups are present in the radical-anion form. For compounds (**6–8**), the IR spectra are characteristic of a delocalized, mixed-valence state with intermediate frequencies between the neutral and ionic molecules of TCNQ. The a_g modes show broad bands and they are displaced to lower energies due to electron–molecular vibration coupling. The most characteristic feature is the presence of an electronic transition that appears as a broad absorption in spectra localized around 3100 cm^{-1} (Fig. 1) [8].

The electronic spectra of solid samples of (**1–5**) show broad and intense absorption bands that are characteristic of the formation of dimeric dianions, $(TCNQ)_2^{2-}$, and are centered around 2200, 1200, 860, 650 and 400 nm. The band at 2200 nm results from the intradimer charge-transfer transition (CT_1) between radical-anions ($TCNQ^-TCNQ^- \rightarrow TCNQ^0TCNQ^{2-}$) [9]. The other maxima can be attributed to locally excited levels of the anion radical, corresponding to the usual intramolecular transitions [10]. In contrast, compounds (**6–8**) show significant differences in the low-energy region. The existence of a broad band centered around 3000 nm, and seen in the IR spectrum, corresponds to a charge-transfer transition (CT_2) between neutral and anionic units ($TCNQ^-TCNQ^0 \rightarrow TCNQ^0TCNQ^-$). Spectra of representative samples are shown in Fig. 2.

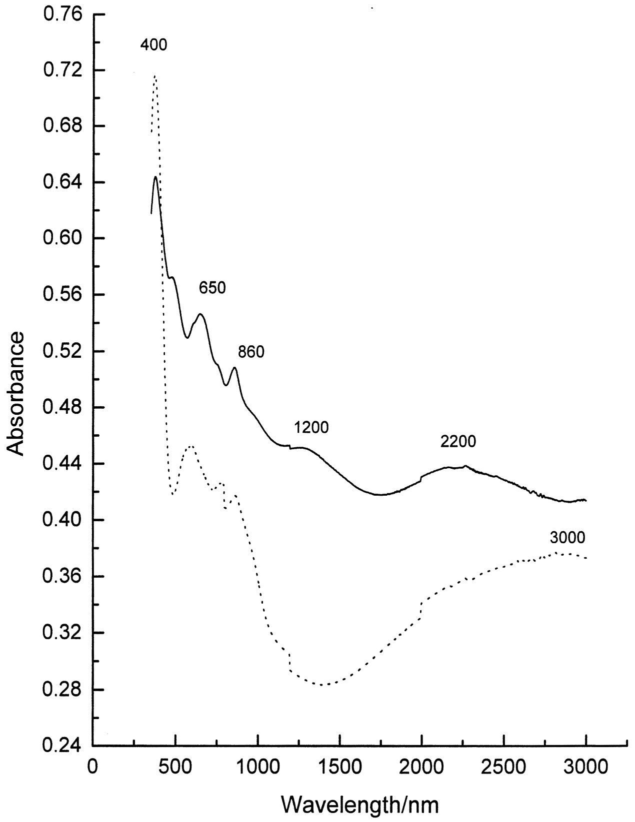


Fig. 2. Electronic spectra in the solid state of $Pr(phen)_2(TCNQ)_3$ (solid line) and $Pr(phen)_4(TCNQ)_4$ (dotted line).

The electrical conductivities of (**1–5**) are lower than 10^{-7} Scm, indicating that these compounds behave as insulators, whereas compounds (**6–8**) show room-temperature conductivity values around 10^{-3} Scm, in the range of similar derivatives showing semiconducting behavior due to electronic delocalization along the TCNQ stacks [11].

Finally, the static magnetic susceptibilities of these compounds show that they follow the Curie law above 50 K and give typical magnetic moment values, 3.8–4.0 BM, for the $S=\frac{3}{2}$ lanthanide ions. This fact indicates that the spins from the organic radicals do not contribute to the magnetic susceptibility and, therefore, the $TCNQ^-$ units should be dimerized forming diamagnetic $(TCNQ)_2^{2-}$ dianions with strong antiferromagnetic coupling between the corresponding spins. The formation of these diamagnetic dimers is typical of TCNQ derivatives having only the anionic form present [12,13].

These spectroscopic and magnetic data suggest that the $Ln(N–N)_x(TCNQ)_3$ derivatives can have the lanthanide ion coordinated to the N–N ligands and some nitrile groups of the TCNQ anions. The expected coordination number of nine implies that some TCNQ groups must be bridging different lanthanide ions in order to fulfill their coordinative requirements. In fact, preliminary structural data in $Ln(TCNQ)_3 \cdot xH_2O$ derivatives indicate that some TCNQ anions are coordinated in a monodentate fashion but others bridge two or even three lanthanide ions. It is not possible to generalize the ways of coordination due to the tendency to polymorphism found in the TCNQ derivatives [14].

In the derivatives $Ln(N–N)_4(TCNQ)_4$, every TCNQ has a formal oxidation state of -0.75, as expected from the electronic delocalization that the spectral data suggest. In previous works, this delocalization is related to the formation of monodimensional TCNQ stacks by overlap of the π clouds of adjacent units and is responsible for the semiconducting behavior found in these compounds [15].

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