Magnetic Behavior and Crystal Structure of [Fe(cyclam)(NCS)$_2$](TCNQ)$_2$: An Unusual One-Dimensional (TCNQ)$_2^-$ Radical-Ion System

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The compound [Fe(cyclam)(NCS)$_2$](TCNQ)$_2$, where cyclam is 1,4,8,11-tetraazacyclotetradecane and TCNQ is a partially reduced 7,7,8,8-tetracyanoquinodimethane fragment, has been obtained from the corresponding thiocyanate by metathesis reaction. The compound crystallizes in the triclinic system, space group $P\bar{1}$, $a = 7.832(3)$ Å, $b = 8.008(2)$ Å, $c = 15.501(3)$ Å, $\alpha = 79.85(2)°$, $\beta = 85.11(2)°$, $\gamma = 74.18(3)°$, $Z = 1$. The crystalline lattice consists of one-dimensional TCNQ units, stacked along the a direction, and it is stabilized by interactions with the Fe(III) hexacoordinated complex cations. All of the TCNQ's are crystallographically equivalent, with bond parameters typical of partially reduced acceptors with a formal charge of 0.5 electron. Two different distances between adjacent TCNQ units are observed, i.e., 3.29 and 3.42 Å, indicating the presence of dimeric (TCNQ)$_2^-$ in the chains. The temperature dependence of the magnetic susceptibility was described as due to two contributions: the first one comes from the Curie contribution of the Fe(III) complex while the second arises from the magnetic exchange interactions between the nearest neighbor TCNQ anions. The latter is typical of one-dimensional antiferromagnetic chains of $S = {}^1/_2$ spins, localized on (TCNQ)$_2^-$ units, and it could be fitted according to a one-dimensional Heisenberg antiferromagnet model.

Introduction

The synthesis of molecular-based solids obtained by assembling two different supramolecular systems, by combining organic radicals and open-shell transition metal fragments, has provided in the recent past an interesting series of structurally characterized systems.[1] Among the variety of organic radicals, those containing the acceptor TCNQ have been proved to offer special structural features due to the possibility of forming σ-bonds with the transition ions.[2] The existence of σ-bonds between TCNQ$^{\bullet-}$ and transition metal ions can affect the supramolecular architecture and the stabilization of different electronic states in systems with low $M^{(n+1)+}/M^{n+}$ redox potentials.

Compounds containing Fe(III) ions and TCNQ have been widely studied since Miller et al. in 1979 reported the synthesis ot the first ferrocenyl derivative [Fe(C$_5$Me$_5$)$_2$]$^+$(TCNQ)$^-$.[3] From these first results, notable structures and different magnetic behaviors have been obtained, but only in the past decade have compounds with common transition metal fragments and Fe(II) been reported. In 1996 Haasnoot et al. reported the interesting [Fe^{II}(abpt)(TCNQ)$_2$], abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole, showing spin crossover.[4] H. Oshio et al. reported in 1995 the formation of [Fe(CH$_3$OH)$_4$(TCNQ)$_2$]-TCNQ·2CH$_3$CN obtained from the reaction between Fe(NO$_3$)$_3$·9H$_2$O, H$_2$salen, and LiTCNQ. A similar reaction with Mn(III) afforded the Mn(III) compound [Mn(salen)(TCNQ)$_{0.5}$][Mn(salen)(TCNQ)$_{0.5}$(MeOH)], H$_2$salen = *N,N'*-disalicylidene-ethylenediamine, and the significative differences with the iron compound have been interpreted in terms of the corresponding redox potentials.[5] Finally, Dunbar et al. have recently reported the characterization of [Fe(TCNQ)$_2$(L)$_2$], L = H$_2$O, MeOH.[6]

From these results and from our knowledege about the possibilities of controlling the formation of σ-bonds in Ni−

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TCNQ and Cu−TCNQ systems[7] we have tried to assemble in the lattice mixed-valence TCNQ stacks, in an attempt to avoid the tendency of this molecule to di- or trimerize. For this reason only very few examples of compounds with segregated uniform chains of $(TCNQ)_2^-$ anions have been isolated and, to our knowledge, only one structurally characterized.[8] To accomplish this objective a transition metal fragment with a heteroleptic hexacoordinated iron(III), $[Fe(cyclam)(NCS)_2]^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), was chosen, because it contains a stable six-coordinated environment around the metal ion, thus preventing the formation of σ-bonds with the TCNQ. In order to favor the formation of mixed-valence derivatives and therefore the delocalization of the electronic charge on the acceptor molecules, the triethylammonium salt of the TCNQ, which contains both neutral and radical-anionic molecules, was used as reagent.

Experimental Section

$[Fe(cyclam)(NCS)_2](SCN)$[9] and $(Et_3NH)(TCNQ)_2$[10] were prepared by following the published methods, and the purity was checked by elemental analysis.

$[Fe(cyclam)(NCS)_2](TCNQ)_2$. This compound was obtained by slow diffusion of an acetonitrile solution of 0.1 mmol of $(Et_3NH)(TCNQ)_2$ into a methanol solution containing 0.1 mmol of $[Fe(cyclam)(NCS)_2]$-(SCN). After 1 day, dark blue crystals of the title compound had been obtained. Yield: 45%. Anal. Calcd for $FeC_{36}H_{32}N_{14}S_2$: C, 55.5; H, 4.1; N, 25.1. Found: C, 55.8; H, 4.1; N, 25.2. IR (cm^{-1}): 3170m, 2881w, 2184s, 2150s, 2051vs, 1557s, 1539w, 1501s, 1445m, 1302s, 1116s, 1093s, 1055s, 951m, 841m, 695m.

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. Solid state electronic spectra were recorded on a Cary-5 spectrophotometer, the sample being rubbed on optical glass. Magnetic experiments were made on polycrystalline samples using a SQUID magnetometer MPMS-5S manufactured by Quantum Design. The temperature dependence of the magnetization in the range between 5 and 250 K was recorded using a constant magnetic field of 0.5 T. The experimental data have been corrected for the magnetization of the sample holder and for atomic diamagnetism as calculated from the known Pascal's constants. X-band powder EPR spectra have been obtained on a Bruker ESP 300 apparatus equipped with a Bruker ER035M gaussmeter and an Oxford JTC4 cryostat. Single-crystal electrical conductivity measurements at variable temperature were performed by the two points method, using an APD cryogenics INC HC2 helium cryostat.[11]

Table 1. Crystal and Refinement Data for $[Fe(cyclam)(NCS)_2](TCNQ)_2$

empirical formula	$C_{36}H_{32}FeN_{14}S_2$
fw	780.73
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	7.833(1)
b, Å	8.008(1)
c, Å	15.507(1)
α, °	79.84(1)
β, °	85.10(1)
γ, °	74.14(1)
Z	1
V, Å^3	920.3(2)
ρ_{calcd}, Mg m^{-3}	1.41
T, K	293
λ(Mo Kα), Å	0.71073
μ, cm^{-1}	5.72
R^a	0.035
$R_w{}^a$	0.088

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

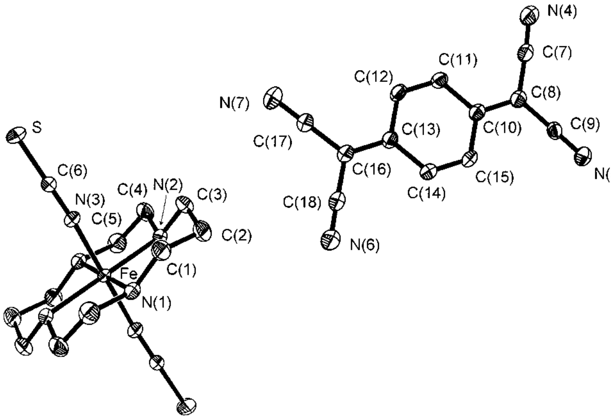

Figure 1. ORTEP view (50% probability thermal ellipsoids) and atom labeling of $[Fe(cyclam)(NCS)_2](TCNQ)_2$.

X-ray Structure Determination. Good quality crystals have been obtained by the synthetic method. A deep blue prismatic crystal was coated with resin epoxy and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensity data were collected by the $\omega-2\theta$ technique and corrected for Lorentz and polarization effects. Atomic scattering factors were taken from ref 12.

The structure was solved by Patterson and Fourier methods and refined by applying full-matrix least squares on F^2 with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located on a Fourier difference synthesis and their positions refined with fixed isotropic contributions. The calculations were carried out with the SHELXL93 software package.[13] A summary of the fundamental crystal data is given in Table 1.

Results and Discussion

Crystal Structure of $[Fe(cyclam)(NCS)_2](TCNQ)_2$. This compound crystallizes in the triclinic system, space group $P\bar{1}$. An ORTEP view of the cationic unit is shown in Figure 1. Selected bond lengths and angles are listed in Table 2.

The iron atom is located on an inversion center and is coordinated to the four macrocyclic nitrogen atoms with distances of 1.993(3) and 1.996(3) Å. The quasi-regular octahedral environment is completed by two isothiocyanate groups bonded in trans positions at 1.896(2) Å, a distance somewhat shorter as corresponds to an sp nitrogen.

All of the TCNQ groups in the crystal are crystallographically equivalent, and therefore they must bear the same electronic

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Fe(cyclam)(NCS)_2](TCNQ)_2$

Fe−N(1)	1.993(3)	C(8)−C(10)	1.383(6)
Fe−N(2)	1.997(3)	C(10)−C(11)	1.432(5)
Fe−N(3)	1.897(3)	C(10)−C(15)	1.428(6)
S−C(6)	1.602(4)	C(11)−C(12)	1.346(6)
N(3)−C(6)	1.161(5)	C(12)−C(13)	1.431(6)
N(4)−C(7)	1.137(6)	C(13)−C(14)	1.424(5)
N(5)−C(9)	1.145(5)	C(13)−C(16)	1.390(6)
N(6)−C(18)	1.136(6)	C(14)−C(15)	1.341(6)
N(7)−C(17)	1.134(5)	C(16)−C(17)	1.416(6)
C(7)−C(8)	1.421(6)	C(16)−C(18)	1.425(6)
C(8)−C(9)	1.420(5)		
N(3)−Fe−N(2)	90.36(13)	Fe−N(3)−C(6)	171.7(3)
N(3)−Fe−N(1)	90.83(14)	N(3)−C(6)−S	179.5(4)
N(2)−Fe−N(1)	94.15(14)		

charge. This charge has been related to the variation of the intramolecular C−C distances of the organic molecule on reduction.[14] Table 3 lists the TCNQ bond distances of our compound and those of neutral and monoanionic TCNQ for comparison. The observed distances clearly indicate that the acceptor is present as $TCNQ^{0.5-}$.

The TCNQ molecules form one infinite stack (Figure 2) along the a direction, with two different short-contact distances between neighboring groups. The shortest distance, 3.29(1) Å, corresponds to the C(12)−C(12) contact between adjacent TCNQ units (Figure 3a). The other contact distance is 3.42(1) Å and corresponds to the overlap of the π clouds of six of the carbon atoms of adjacent TCNQ's (Figure 3b). In conclusion the TCNQ's form an alternate stack made of $TCNQ^{0.5-}$ units, and these stacks are separated in the crystal by rows of metal cations in correspondence to the anion units. Thus, the charge modulation in the crystal should be the responsibility of this packing.

Although a poor π overlap is observed between the nearest TCNQ molecules along the chains, the chain itself can be considered as formed by $(TCNQ)_2^-$ dimers. This type of packing has been previously observed in $(MEM)(TCNQ)_2$, where MEM is the *N*-methyl-*N*-ethylmorpholinium cation,[8,16] but in our case the shorter interdimeric distance corresponds to a poorer overlap between adjacent TCNQ units.

The cations $[Fe(cyclam)(NCS)_2]^+$ interact with the TCNQ with formation of hydrogen bonds between the cyclam amino groups and two nitriles of the TCNQ molecule. The structural data for these H bonds are N(5)⋯H(2), 2.33(3) Å, H(2)−N(2), 0.78(3) Å, angle N(5)⋯H(2)−N(2), 163(3)°; N(7)⋯H(1), 2.25(4) Å, H(1)−N(1), 0.87(3) Å, N(7)⋯H(1)−N(1), 149(3)°. Every TCNQ is then bonded to two different $[Fe(cyclam)(NCS)_2]^+$ cations by opposite nitrile groups, and the metallomacrocyclic cation is bonded to four TCNQ units belonging to two adjacent stacks (Figure 2). In this way the formation of these hydrogen bonds confers some rigidity to the solid structure favoring the TCNQ stacks, but simultaneously it could be responsible for the alternate intermolecular distances in the stack since every pair of TCNQ's is hydrogen bonded to the same metallomacrocycles, a fact that could keep the TCNQ at fixed distances.

Spectroscopic Studies. Vibrational spectroscopy has been used for detailed characterization of the TCNQ derivatives to give infomation on the formal oxidation state and the coordinative status of these organic acceptor molecules.[17] Table 4 reports the characteristic vibration frequencies of TCNQ for the title compound and those of the neutral acceptor and the radical monoanion for comparison.

Typical TCNQ vibrations in our derivative show intermediate frequencies between neutral and radical-anionic TCNQ although others appear out of range. Furthermore, because several authors have reported deviations from the expected linear dependence of the CN frequencies with the charge held on the TCNQ, we have used the C−C stretching mode b_{1u}, ν_{20}, as indicative of the degree of charge. This frequency occurs at 1529 cm^{-1}, thus confirming an average charge of 0.5.[18] The same result is observed by using the out of plane bend b_{3u}, ν_{50}, whose frequency also shows a linear variation with the charge on the uncoordinated TCNQ molecule.

Along with the TCNQ absorptions, the bands at 2051 and 951 cm^{-1} are characteristic of a N-coordinated isothiocyanate.

The main feature of the IR spectrum is, however, the presence of the tail centered around 4200 cm^{-1}, with the vibronic TCNQ bands superimposed on it. This band is due to a CT electronic transition and is a characteristic feature of derivatives showing electronic delocalization along the TCNQ stack.[19]

Electronic spectra provide more evidence for the origin and the magnitude of the charge transfer observed here. The solid state electronic spectrum of this compound shows absorption bands centered at 26 200, 17 300, 11 600, 7100, and 4200 cm^{-1}. The first two bands are characteristic of TCNQ derivatives and correspond to the two first locally excited levels of the anion radical, while the band at 11 600 cm^{-1} has been assigned to a charge transfer involving radical anions.[20] The two lower frequency bands are very broad and characteristic of mixed-valence TCNQ compounds.[21] The band centered at 4200 cm^{-1} results from a charge transfer between radical-anionic and neutral species (CT_2), that frequently appears around 6000 cm^{-1} and shifts to lower frequencies when the charge delocalization increases. It is worth noticing the close relation between the energy of the intermolecular charge transfer transition and the activation energy, E_a, obtained from the electrical conductivity measurements.

Electrical Conductivity. The conductivity has been measured in a single crystal of dimensions 0.16 × 0.44 × 0.8 mm, in the temperature range 293−8 K. The compound shows a semiconducting behavior with room temperature conductivity of 3.4×10^{-3} S cm^{-1}. In the temperature range 170−293 K the conductivity follows an exponential variation with the temperature ($\sigma = \sigma_0 \exp[-E_a/kT]$) giving an activation energy of 0.21 eV. Below 170 K the behavior is no longer linear.

Magnetic Measurements. The single-crystal EPR spectrum of the title compound shows one single signal, corresponding to a low-spin iron(III) atom, in the three orientations with values of $g_x = 2.07$, $g_y = 2.06$, $g_z = 2.09$, giving an average isotropic

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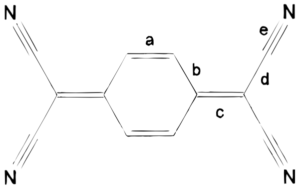
Table 3. Comparative Analysis of the TCNQ Intramolecular Bond Distances (Å) in $[Fe(cyclam)(NCS)_2](TCNQ)_2$



compound	a	b	c	d	e	b − c	c − d	c/(b + d)
TCNQ[a]	1.345	1.448	1.374	1.441	1.140	0.074	−0.067	0.476
$TCNQ^{-}$ [a]	1.373	1.423	1.420	1.416	1.153	0.003	0.004	0.500
$TCNQ^{0.5-}$ [a]	1.354	1.434	1.396	1.428	1.141	0.040	−0.032	0.488
$[Fe(cyclam)(NCS)_2](TCNQ)_2$	1.343	1.429	1.386	1.420	1.139	0.043	−0.034	0.486

[a] Reference 15.

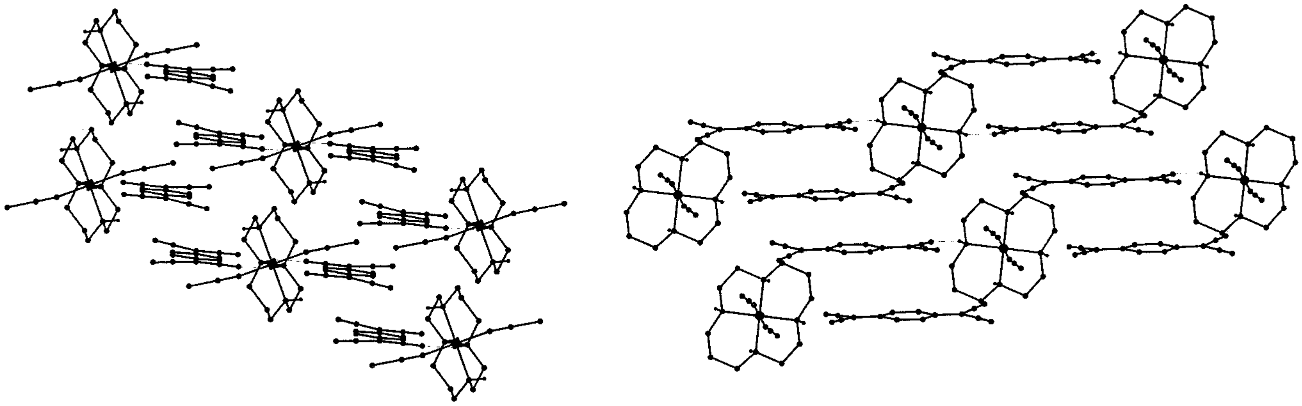


Figure 2. Two views of the TCNQ stacking mode in the crystal of $[Fe(cyclam)(NCS)_2](TCNQ)_2$.

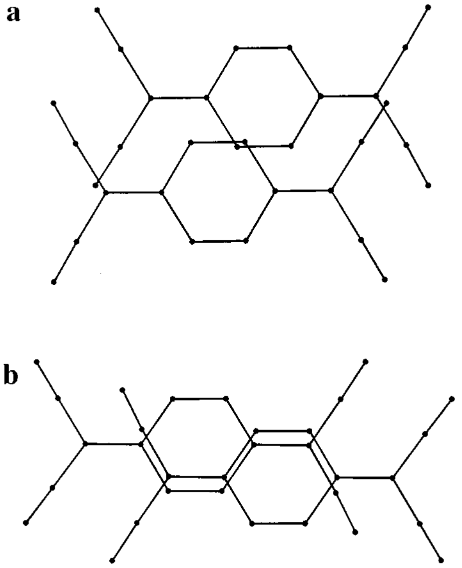


Figure 3. The two different close contacts of every TCNQ in the stack.

value of $g = 2.07$. No free radical signal is observed, suggesting the existence of antiferromagnetic interactions between the spins located on the TCNQ anions.

The dc magnetic susceptibility, χ_M, of $[Fe(cyclam)(NCS)_2](TCNQ)_2$, corrected for the diamagnetic contributions, was measured in the temperature range 5−250 K at an applied field of 500 G. The temperature dependences of the $1/\chi_M$ values obey the Curie−Weiss law above 70 K, and the Curie constant, C, and the Weiss constant, θ, as obtained from the fit of the data, are estimated to be 1.157 emu K mol^{-1} and −57 K, respectively. The value of C corresponds to an effective magnetic moment of 3.04 μ_B, which is higher than the value expected for a spin system containing Fe(III) ion in the low-spin d^5 configuration ($S = {}^1/_2$) and that from the dimeric $(TCNQ)_2^-$ ions ($S = {}^1/_2$). The magnetic moment, as calculated from the equation $\mu_{eff} = 2.828(\chi T)^{1/2}$, decreases from 2.85 μ_B, at 250 K, to 1.9 μ_B at 5 K (see Figure 4). The latter value can be identified as due to the low-spin Fe(III) ion contribution. This result, together with the large negative value of the Weiss constant, suggests that antiferromagnetic interactions should arise from the spins residing on the organic $(TCNQ)_2^-$ ions. A simple attempt at extracting from the total susceptibility, χ_M, the contribution of the TCNQ chains was accomplished by subtracting both the temperature independent paramagnetism, χ_{tip}, and the Curie susceptibility of the iron(III) complex, and the results are reported in Figure 5. The value of χ_{tip} was estimated by plotting χ vs $1/T$ and taking the susceptibility value for $T \rightarrow \infty$, i.e., 9.6×10^{-4} emu mol^{-1}. The temperature dependent chain susceptibility estimated in this way shows a broad maximum centered at ∼75 K. This is a typical magnetic behavior expected for a $S = {}^1/_2$ spin 1D system or for a dimeric $S = {}^1/_2$ system. On the basis of the crystal structure, the magnetic data above 30 K were fitted to the Heisenberg linear chain model[22] with the equation derived from Hatfield et al.:[23]

$$\chi_{org} = [Ng^2\mu_B{}^2/kT]\{[A + Bx + Cx^2]/[1 + Dx + Ex^2 + Fx^3]\}$$

where A, B, C, D, E, and F are parameters which take into account the possible distortion of the chain and have been computed for values of $0 < \alpha < 1$ ($\alpha = 0$ corresponds to the dimeric $(TCNQ)_2^-$ isolated unit, while $\alpha = 1$ is for the uniform

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Table 4. Most Significative Vibration Frequencies (cm^{-1}) of the TCNQ Units

compound	ν(C≡N)	$\nu_{20}(b_{1u})$	$\nu_{34}(b_{2u})$	$\nu_4(a_g)$	$\nu_{50}(b_{3u})$	$\nu_7(a_g)$
[Fe(cyclam)(NCS)$_2$](TCNQ)$_2$	2184/2150	1557	1501	1445	841	695
TCNQ^0	2228	1545	1524	1424	860	705
TCNQ$^-$	2194/2177	1577	1507	1386	824	722

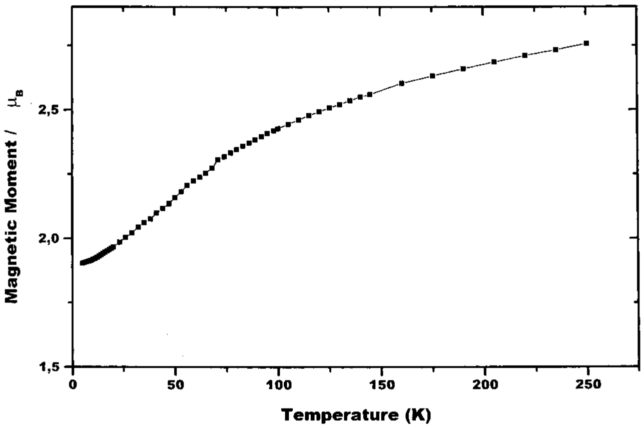

Figure 4. Plot of the variation of the total magnetic moment with the temperature.

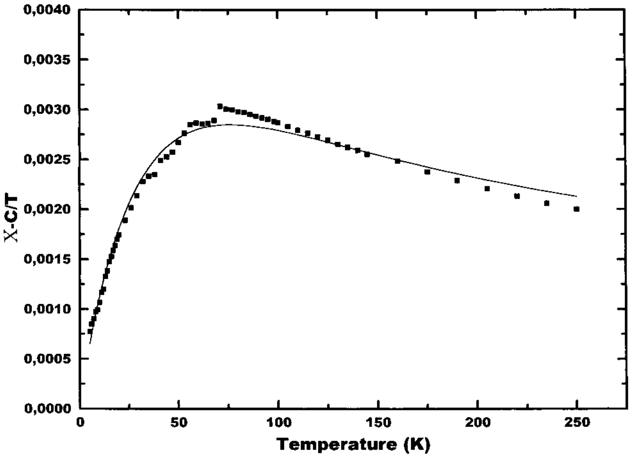

Figure 5. Plot of the magnetic susceptibility located in the organic stack as a function of the temperature. The solid line corresponds to the fit of the experimental data to a Heisenberg linear chain model (see text).

chain) and $x = |J|/kT$. This model is based on the assumption that the $S = {}^1/_2$ spins are localized on every TCNQ dimer.

The computed curve for χ_{org} vs T, with $g = 2$, and varying J/k and the parameter α, are compared with the experimental curve in Figure 5. It is apparent that the curve with $\alpha = 0.85$ and $J = -62$ K is reproducing the experimental data. Below 30 K no sign of a sudden drop in the magnetic susceptibility plot is observed, thus suggesting an absence of a spin-Peierls distortion at low temperatures.

Conclusion

We have obtained a novel 1D stable iron(III)−TCNQ derivative with electronic delocalization in the organic part. The TCNQ's are stacked, forming a nonuniform chain with alternatively short contacts and long π overlaps. This asymmetry in the overlap is probably responsible for the relatively low conductivity and high activation energy of this compound, and it is in contrast with the expectation that the 1D TCNQ compound with this degree of charge should behave as a metal. The magnetic behavior could be described as due to the Curie contribution of the iron(III) complex cation and to the antiferromagnetic exchange interaction between the organic acceptors along the chain; this interaction can be fitted by using the Bonner−Fisher one-dimensional Heisenberg model with an antiferromagnetic exchange of −62 K between neighboring spins. From our data we cannot ascertain if a spin-Peierls distortion is present at low temperatures, a transition observed in the structurally related (MEM)(TCNQ)$_2$;[24] probably the stack stabilization produced by the hydrogen bonds between TCNQ and the metallomacrocyclic cations precludes this distortion.

In conclusion, the semiconducting behavior of the title compound is likely attributable to an electron localization, caused by the combined effect of the presence of strong electron correlation and the interactions with localized charge and spins of the cations.[25]

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

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