

Polymorphism in [Cu(cyclam)(TCNQ)₂](TCNQ) Stacked Systems (cyclam = 1,4,8,11-Tetraazacyclotetradecane, TCNQ = 7,7,8,8-Tetracyanoquinodimethane)

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The compound [Cu(cyclam)(TCNQ)₂](TCNQ) (cyclam = 1,4,8,11-tetraazacyclotetradecane, TCNQ = 7,7,8,8-tetracyanoquinodimethane) has been obtained in two different crystallographic forms, isomers **1** and **2**. Crystal data for isomer **1**: triclinic, $P\bar{1}$, $a = 7.855(6)$ Å, $b = 10.267(2)$ Å, $c = 14.424(3)$ Å, $\alpha = 95.42(2)^\circ$, $\beta = 102.18(5)^\circ$, $\gamma = 109.74(3)^\circ$, $Z = 1$. Crystal data for isomer **2**: triclinic, $P\bar{1}$, $a = 8.165(1)$ Å, $b = 9.918(3)$ Å, $c = 13.278(3)$ Å, $\alpha = 83.91(2)^\circ$, $\beta = 78.31(2)^\circ$, $\gamma = 79.22(2)^\circ$, $Z = 1$. Both isomers show the same copper environment and oxidation states in the TCNQ molecules, and the only difference is observed in the stacking of the latter groups. The main common feature is the presence of parallel chains of copper macrocycle units linked by dimeric (TCNQ)₂²⁻, which coordinates to the metal. These chains are joined in isomer **1** by one neutral TCNQ molecule oriented parallel to the anionic TCNQ dimers and overlapping with two of them creating a bidimensional network. In contrast, the neutral TCNQ in isomer **2** is rotated about 70° relative to the anionic dimers and overlaps with four different chains, extending the interaction in a tridimensional way. The spectral and solid state conductivity data show electronic localization on the dimers (TCNQ)₂²⁻ in both isomers with a weak semiconducting behavior. The magnetic behavior of both isomers can be interpreted as the sum of contributions from the metal and a thermally activated triplet state for the dimerized anions. The latter contribution is favored by the π overlap of the neutral TCNQ molecules, since the analogous derivative [Cu(cyclam)(TCNQ)₂], only with anionic dimers, shows a strong antiferromagnetic coupling inside the dimers and no appreciable contribution to the bulk magnetic susceptibility is observed.

Introduction

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

The assemblage of organonitrile radicals with copper complexes has attracted special attention because of the wide possibilities of interaction that can be found. The first approach was directed toward the study of donor–acceptor interactions between planar copper complexes with π electron density, such as Schiff bases, and TCNQ (7,7,8,8-tetracyanoquinodimethane), with formation of integrated systems.³ When complexes with

the metal fully coordinated such as [Cu(phen)₃]²⁺ were used, new compounds, [Cu(phen)₃](TCNQ)₂, without direct interaction between the metal and the TCNQ were formed.⁴

The ability of reduced TCNQ⁻ units to coordinate to metallic fragments acting as σ -donor ligands can be used to build extended molecular assemblies, because transition metals offer the possibility of orienting the coordinated radicals in solids.⁵ Since the report of the interesting copper compounds with DCNQI (N,N'-dicyanoquinone diimine), metallic polymers,⁶ and with TCNQ, electrically bistable materials,⁷ great effort has been devoted to the study of molecular materials with σ interactions between metals and polynitriles. Cornelissen⁸ reported the compound [Cu(abpt)₂(TCNQ)₂] (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) with the copper atom octahedrally

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(1) See, for example: Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; Vol. 3, p 263.

(2) (a) Day, P. *Philos. Trans. R. Soc. London, Ser. A* **1985**, A314, 145. (b) Ogawa, M. Y.; Hoffman, B. M.; Lee, S.; Yudkowsky, M.; Halperin, W. P. *Phys. Rev. Lett.* **1986**, 57, 1177. (c) Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, 117, 12209. (d) Zhao, H.; Heintz, R. A.; Dunbar, K. R.; Rogers, R. D. *J. Am. Chem. Soc.* **1996**, 118, 12844.

(3) (a) Cassoux, P.; Gleizes, A. *Inorg. Chem.* **1980**, 19, 665. (b) Matsumoto, N.; Nonaka, Y.; Kida, S.; Kawano, S.; Ueda, Y. *Inorg. Chim. Acta* **1979**, 37, 27. (c) Matsumoto, N.; Miyazaki, T.; Sagara, Y.; Ohyoshi, A. *Inorg. Chim. Acta* **1982**, 63, 249. (d) Shiotsuka, M.; Okane, Y.; Matsumoto, N.; Okawa, H.; Isobe, T. *J. Chem. Soc., Dalton Trans.* **1994**, 2065. (e) Lacroix, P.; Kahn, O.; Gleizes, A.; Valade, L.; Cassoux, P. *Nouv. J. Chim.* **1984**, 8, 643.

(4) Bencini, A.; Midollini, S.; Zanchini, C. *Inorg. Chem.* **1989**, 28, 1963.

(5) Kaim, W.; Moscherosch, M. *Coord. Chem. Rev.* **1994**, 129, 157.

(6) Sinzger, K.; Hünig, S.; Jopp, M.; Bauer, D.; Bietsch, W.; von Shütz, J. U.; Wolf, H. C.; Kremer, R. K.; Metzenthin, T.; Bau, R.; Khan, S. I.; Lindbaum, A.; Lengauer, C. L.; Tillmanns, E. *J. Am. Chem. Soc.* **1993**, 115, 7696.

(7) Hoagland, J. J.; Wang, X. D.; Hipps, K. W. *Chem. Mater.* **1993**, 5, 54.

(8) Cornelissen, J. P.; van Diemen, J. H.; Groeneveld, L. R.; Hasnoot, J. G.; Spek, A. L.; Reedijk, J. *Inorg. Chem.* **1992**, 31, 198.

coordinated to six nitrogen atoms, four in the equatorial plane from the abpt ligands and two apical nitrogens belonging to the σ -monodentate TCNQ⁻ anion radicals. These coordinated TCNQ's are dimerized, resulting in diamagnetic dianions (TCNQ)₂²⁻, with each organic anion coordinated to a different copper atom, thus forming infinite linear chains.

We have also obtained a copper–TCNQ infinite chain in [Cu(N₄^{OH})(TCNQ)₂] (N₄^{OH} = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane), where the macrocycle stabilizing the copper environment allows two trans positions to be occupied by the radical anions.⁹ The nickel analogue also presents a similar structure,¹⁰ suggesting that the formation of infinite chains through dimerization of coordinated TCNQ⁻ is the usual outcome when all the TCNQ's are present as radical anions.¹¹ However, monocoordination of the anion radical or its dimer is not always observed, and we have previously obtained examples of double coordination to different metals as in [Ru(PPh₃)₂]₂(TCNQ)₂.¹²

Oshio¹³ obtained a related compound, [Cu(cyclam)]₂[2,5-DM-DCNQI]₅ (cyclam = 1,4,8,11-tetraazacyclotetradecane, 2,5-DM-DCNQI = *N,N'*-dicyano-2,5-dimethylquinone diimine), having a bidimensional array formed by [Cu(cyclam)(2,5-DM-DCNQI)₂] chains joined by the overlap of neutral 2,5-DM-DCNQI situated between them and extending the interactions of the organic radicals in a perpendicular direction. The structure of this compound prompted us to find a way to insert neutral TCNQ molecules between the metal–TCNQ chains to extend the monodimensional interaction in a second direction. These extra TCNQ molecules, loosely bound in the network, allow different arrays depending on the mutual orientations of the different building blocks. In this sense, we have obtained two different species, both of formula [Cu(cyclam)(TCNQ)₂](TCNQ), which, to our knowledge, are the first examples of 1:3 copper:TCNQ stoichiometry and are the first cases of supramolecular isomeric structures in systems with coordinated TCNQ. Only in the cases of hybrid materials containing [Fe(C₅Me₅)₂]⁺¹⁴ or [Cr(C₆Me₃H₃)]⁺¹⁵ has the formation of different phases been observed, although in these cases no direct interaction between the metallic center and the TCNQ units was found.

Experimental Section

All the reactions were carried out under oxygen-free nitrogen. [Cu(cyclam)](ClO₄)₂,¹⁶ LiTCNQ,¹⁷ and Et₃HN(TCNQ)₂¹⁷ were obtained by published methods, and their purities were checked by elemental analyses.

Warning! Perchlorate salts are potentially explosive and should be used in small amounts and handled with care.¹⁸

Bis(7,7,8,8-tetracyanoquinodimethanido)(1,4,8,11-tetraazacyclotetradecane)copper(II), [Cu(cyclam)(TCNQ)₂]. A solution of 0.22 g (1 mmol) of LiTCNQ in 15 mL of methanol was added dropwise to a solution of 0.24 g (0.5 mmol) of [Cu(cyclam)](ClO₄)₂ in 15 mL of methanol. After a few minutes of stirring, a dark blue microcrystalline solid appeared. The solid was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Yield: 62%. Anal. Calcd for CuC₃₄H₃₂N₁₂: C, 60.8; H, 4.8; N, 25.0. Found: C, 60.5; H, 4.7; N, 25.1. IR (cm⁻¹): 3225 m, 2182 vs, 2160 s, 1584 m, 1504 s, 1392 w, 1348 s, 1175 s, 825 w, 722 w.

Bis(7,7,8,8-tetracyanoquinodimethanido)(1,4,8,11-tetraazacyclotetradecane)copper(II) 7,7,8,8-Tetracyanoquinodimethane, [Cu(cyclam)(TCNQ)₂](TCNQ) (1). A solution of 0.51 g (1 mmol) of Et₃HN(TCNQ)₂ in 15 mL of acetonitrile was added to a solution of 0.24 g (0.5 mmol) of [Cu(cyclam)](ClO₄)₂ in 15 mL of methanol. After a few minutes of stirring, a dark blue microcrystalline solid appeared. The solid was filtered off, washed with methanol and diethyl ether, and dried under vacuum. Yield: 62%. Anal. Calcd for CuC₄₆H₃₆N₁₆: C, 63.0; H, 4.1; N, 25.6. Found: C, 63.3; H, 4.4; N, 25.4. IR (cm⁻¹): 3198 m, 2215 w, 2187 vs, 2175 vs, 2153 s, 1578 s, 1539 w, 1524 w, 1501 m, 1424 w, 1386 w, 1348 s, 1177 m, 1172 m, 840 w, 829 w, 722 w, 705 w.

[Cu(cyclam)(TCNQ)₂](TCNQ) (2). A solution of 0.1 g (0.4 mmol) of iodine in 25 mL of dichloromethane was added to a hot solution of 0.27 g (0.4 mmol) of [Cu(cyclam)(TCNQ)₂] in 50 mL of acetonitrile, and the mixture was left at room temperature. After 1 day, dark blue crystals of compound 2 appeared. The crystals were filtered off, washed with acetonitrile, and dried under vacuum. Yield: 28%. Anal. Calcd for CuC₄₆H₃₆N₁₆: C, 63.0; H, 4.1; N, 25.6. Found: C, 63.1; H, 4.1; N, 25.3. IR (cm⁻¹): 3198 m, 2215 w, 2187 vs, 2175 vs, 2153 s, 1578 s, 1539 w, 1524 w, 1501 m, 1424 w, 1386 w, 1348 s, 1177 m, 1172 m, 840 w, 829 w, 722 w, 705 w.

The filtered solution was slowly evaporated at room temperature; after 2 days, violet crystals of [Cu(cyclam)(I)₂] appeared. The crystals were collected, washed with diethyl ether, and dried. Yield: 21%. Anal. Calcd for CuC₁₀H₂₄I₂N₄: C, 23.2; H, 4.6; N, 10.8. Found: C, 23.1; H, 4.6; N, 11.0.

Physical Measurements. Elemental analyses were carried out by the Servicio de Microanálisis de la Universidad Complutense de Madrid. Infrared spectra were recorded as KBr pellets on a Nicolet Magna-550 FT-IR spectrophotometer. Electronic solution and diffuse-reflectance spectra were recorded on a Cary 5 spectrophotometer equipped with a praying mantis 3000–200 nm accessory. Magnetic experiments were made on polycrystalline samples using a SQUID MPMS-5S magnetometer manufactured by Quantum Design. Two kinds of measurements were carried out. Isothermal magnetization was measured at 1.8 and 3 K as a function of an external magnetic field of up to 5 T. The temperature dependence of the magnetization in the range between 1.8 and 250 K was recorded using a constant magnetic field of 0.5 T. The experimental data were corrected for the magnetization of the sample holder and for atomic diamagnetism as calculated from the known Pascal constants. X-band powder EPR spectra were obtained on a Bruker ESP 300 apparatus equipped with a Bruker ER035M gaussmeter and an Oxford JTC4 cryostat. Powder and single-crystal electrical conductivity measurements at variable temperatures were performed by the two- or four-point method, using an APD cryogenics INC HC2 helium cryostat.¹⁹

X-ray Structure Determinations. Good-quality single crystals of isomers 1 and 2 were obtained by slow diffusion of reactant solutions prepared as described in the Experimental Section. A summary of the fundamental crystal data is given in Table 1. In both cases, a deep-

- (9) Azcondo, M. T.; Ballester, L.; Gutiérrez, A.; Perpiñán, M. F.; Amador, U.; Ruiz-Valero, C.; Bellitto, C. *J. Chem. Soc., Dalton Trans.* **1996**, 3015.
- (10) Ballester, L.; Barral, M. C.; Gutiérrez, A.; Monge, A.; Perpiñán, M. F.; Ruiz-Valero, C.; Sanchez-Pélaez, A. *Inorg. Chem.* **1994**, *33*, 2142.
- (11) (a) Oshio, H.; Ino, E.; Mogi, I.; Ito, T. *Inorg. Chem.* **1993**, *32*, 5697. (b) Grossel, M. C.; Evans, F. A.; Hrijljac, J. A.; Morton, J. R.; Le Page, Y.; Preston, K. F.; Sutcliffe, L. H.; Williams, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 439. (c) Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Reiff, W. M.; Cittipediti, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496. (d) Humphrey, D. G.; Fallon, G. D.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1356. (e) Lacroix, P.; Kahn, O.; Gleizes, A.; Valade, L.; Cassoux, P. *New J. Chem.* **1984**, *8*, 643.
- (12) Ballester, L.; Barral, M. C.; Gutiérrez, A.; Jiménez-Aparicio, R.; Martínez-Muyo, J. M.; Perpiñán, M. F.; Monge, M. A.; Ruiz-Valero, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1396.
- (13) Oshio, H. *Inorg. Chem.* **1993**, *32*, 4123.
- (14) (a) Reis, A. H., Jr.; Preston, L. D.; Williams, J. M.; Peterson, S. W.; Candela, G. A.; Swartzendruber, L. J.; Miller, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 2756. (b) Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755. (c) Miller, J. S.; Reis, A. H., Jr.; Gebert, E.; Ritsko, J. J.; Salaneck, W. R.; Kovant, L.; Cape, T. W.; Van Duyne, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 7111. (d) Broderick, W. E.; Eichhorn, D. M.; Liu, X.; Toscano, P. J.; Owens, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3641.
- (15) O'Hare, D.; Ward, M. D.; Miller, J. S. *Chem. Mater.* **1990**, *2*, 758.
- (16) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2969.
- (17) Melby, L. R.; Herder, R. J.; Mahler, W.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374.
- (18) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335 and references therein.

- (19) (a) Wudl, F.; Brice, M. R. *J. Chem. Educ.* **1990**, *67*, 717. (b) van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, 1.

Table 1. Crystal and Refinement Data for [Cu(cyclam)(TCNQ)₂](TCNQ)

	isomer 1	isomer 2
empirical formula	CuC ₄₆ H ₃₆ N ₁₆	CuC ₄₆ H ₃₆ N ₁₆
mol wt	876.4	876.4
crystal system	triclinic	triclinic
space group	P1̄ (No. 2)	P1̄ (No. 2)
a, Å	7.855(6)	8.165(1)
b, Å	10.267(2)	9.918(3)
c, Å	14.424(3)	13.278(3)
α, deg	95.42(2)	83.91(2)
β, deg	102.18(5)	78.31(2)
γ, deg	109.74(3)	79.22(2)
Z	1	1
V, Å ³	1053(1)	1032(1)
ρ _{calcd.} , g cm ⁻³	1.38	1.25
temp, K	295	295
λ(Mo Kα), Å	0.710 69	0.710 69
μ(Mo Kα), cm ⁻¹	5.7	0.76
R ^a	0.054	0.045
R _w ^b	0.057	0.055

$$^a R = \sum |\Delta F| / \sum |F_o|, \quad ^b R_w = (\sum w \Delta^2 F / \sum w F_o^2)^{1/2}.$$

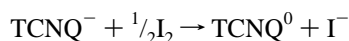
blue prismatic crystal was coated with resin epoxy and mounted in a κ diffractometer. The cell dimensions were refined by least-squares-fitting the θ values of 25 reflections within a 2θ range of 14–30°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu were taken from ref 20. The structure was solved by Patterson and Fourier methods. An empirical absorption correction was applied at the end of the isotropic refinements.²¹

Since no trend in ΔF vs F_o or $(\sin \theta)/\lambda$ was observed, a final refinement was undertaken with unit weights and anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system.²²

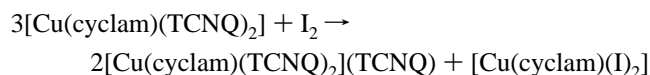
Results and Discussion

The synthesized TCNQ compounds were obtained by metathesis reactions from the parent perchlorate. When LiTCNQ (anionic TCNQ⁻) is added the bis derivative, [Cu(cyclam)(TCNQ)₂] is obtained, but if Et₃HN(TCNQ)₂ (consisting of one neutral and one anionic TCNQ per formula) is added the tris derivative, [Cu(cyclam)(TCNQ)₂](TCNQ) (isomer 1) is obtained.

The reaction of a solution of [Cu(cyclam)(TCNQ)₂] with iodine affords isomer 2 through the oxidation of anionic TCNQ⁻ by the iodine atoms:



This reaction takes place because the interactions between the TCNQ⁻s and the metal atoms, observed in the solid state, are always broken in solution.^{10,23} This solution behaves as though it is formed by independent [Cu(cyclam)]²⁺ cations and (TCNQ)₂²⁻ dianions, since the anion radical tends to dimerize in solution as in the solid state. After the redox reaction occurs, crystallization of the final compounds affords isomer 2 according to the global reaction



(20) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 72.

(21) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

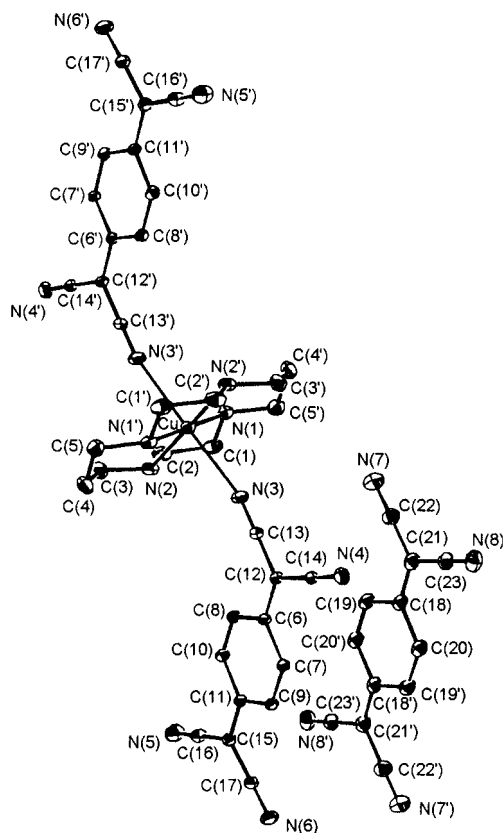


Figure 1. ORTEP view and labeling scheme of the molecular unit of isomer 1.

This process is supported by analytical and IR spectral characterization of [Cu(cyclam)(I₂)], which crystallizes from the reaction mixture.

Crystal Structures of [Cu(cyclam)(TCNQ)₂](TCNQ): Isomers 1 and 2. Both compounds show similar structural bases, with a unit cell consisting of a copper macrocyclic unit bonded to two TCNQ groups (type A) and a third crystallographically independent TCNQ (type B). The copper atoms and the TCNQ B lie on inversion centers. As commented below, the main difference between both structures is the orientation of this TCNQ B. Figures 1 and 2 show the ORTEP views and the atom-labeling schemes of isomers 1 and 2, respectively. Table 2 lists the more relevant bond distances and angles for both compounds.

The copper environment is common for both isomers, since the metal is surrounded by the four nitrogen atoms of the macrocycle at distances of 2.012(4) and 2.014(4) Å for isomer 1 and 2.006(3) and 2.011(3) Å for isomer 2. Two TCNQ units (type A) coordinate each copper ion as monodentate ligands through one nitrile group, occupying the trans positions of a distorted octahedron around the copper with distances of 2.537(5) and 2.598(3) Å for isomers 1 and 2, respectively. These copper–nitrogen distances are in the range usually found for related derivatives.^{8,9}

The equatorial plane around the copper atom and the quinoid TCNQ plane form angles of 74.9(2)° for isomer 1 and 79.1(1)° for isomer 2. These values deviate considerably more from perpendicularity than those found in related compounds such

(22) Stewart, J. M. *The X-RAY 80 System*; Computer Science Center, University of Maryland: College Park, MD, 1980.

(23) Azcondo, M. T.; Ballester, L.; Calderón, L.; Gutiérrez, A.; Perpiñán, M. F. *Polyhedron* **1995**, *14*, 2339.

(24) Azcondo, M. T.; Ballester, L.; Gutiérrez, A.; Perpiñán, M. F. *Inorg. Chem.*, in press.

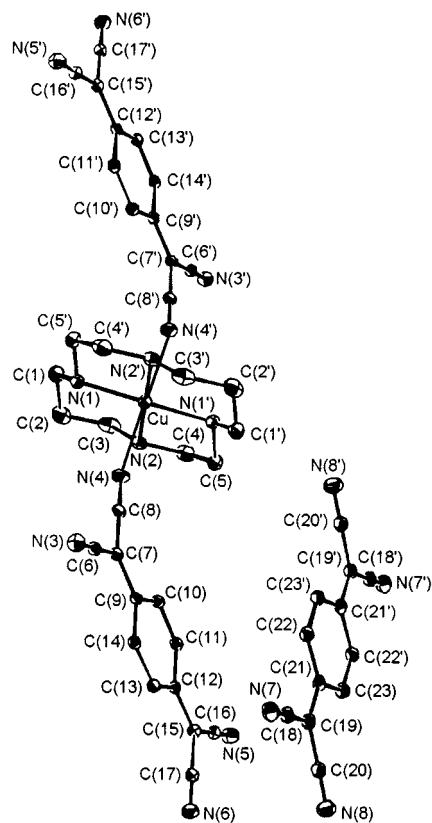


Figure 2. ORTEP view and labeling scheme of the molecular unit of isomer 2.

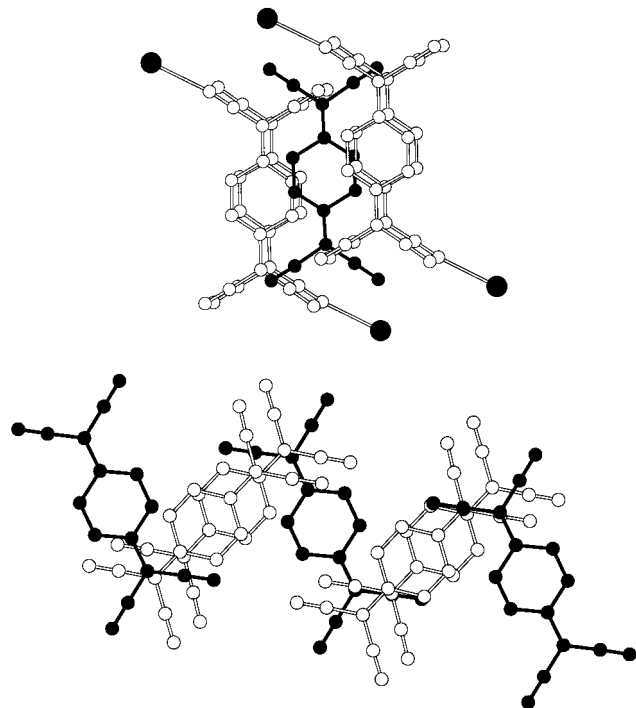


Figure 3. TCNQ overlapping in (a, top) isomer 1 and (b, bottom) isomer 2. In both cases, white circles correspond to TCNQ A and black circles to TCNQ B.

as $[\text{Cu}(\text{N}_4\text{OH})(\text{TCNQ})_2]^{10}$ and $[\text{Ni}(\text{cyclam})(\text{TCNQ})_2]^{24}$ where angles of $84.2(1)$ and $87.7(2)^\circ$ were respectively found. The coordination of the nitrile group also implies a deviation from linearity in the $\text{Cu}-\text{N}-\text{C}$ group with angles of $168.7(4)$ and $166.8(3)^\circ$ for isomers 1 and 2, respectively.

The TCNQ A groups are dimerized in the structure by overlapping with a second group related by an inversion center

Table 2. Bond distances (\AA) and Angles (deg) in $[\text{Cu}(\text{cyclam})(\text{TCNQ})_2](\text{TCNQ})$

isomer 1		isomer 2	
Cu–N1	2.014(4)	Cu–N1	2.011(3)
Cu–N2	2.012(4)	Cu–N2	2.006(3)
Cu–N3	2.536(5)	Cu–N4	2.598(3)
N3–C13	1.146(7)	N3–C6	1.144(5)
N4–C14	1.142(8)	N4–C8	1.142(5)
N5–C16	1.135(8)	N5–C16	1.145(5)
N6–C17	1.143(7)	N6–C17	1.147(5)
N7–C22	1.135(9)	N7–C18	1.142(5)
N8–C23	1.132(9)	N8–C20	1.146(5)
C6–C7	1.423(6)	C6–C7	1.423(5)
C6–C8	1.422(7)	C7–C8	1.415(5)
C6–C12	1.401(6)	C7–C9	1.411(4)
C7–C9	1.360(6)	C9–C10	1.420(5)
C8–C10	1.354(6)	C9–C14	1.420(4)
C9–C11	1.418(7)	C10–C11	1.372(4)
C10–C11	1.417(7)	C11–C12	1.419(4)
C11–C15	1.400(6)	C12–C13	1.417(5)
C12–C13	1.406(6)	C12–C15	1.409(4)
C12–C14	1.427(8)	C13–C14	1.369(4)
C15–C16	1.427(8)	C15–C16	1.414(5)
C15–C17	1.409(7)	C15–C17	1.414(5)
C18–C19	1.451(8)	C18–C19	1.427(5)
C18–C20	1.443(8)	C19–C20	1.414(5)
C18–C21	1.358(7)	C19–C21	1.384(5)
C19–C20'	1.324(7)	C21–C22	1.434(5)
C21–C22	1.428(9)	C21–C23	1.432(5)
C21–C23	1.448(9)	C22–C23'	1.345(5)

isomer 1		isomer 2	
N1–Cu–N2	86.1(2)	N1–Cu–N2	93.8(1)
N1–Cu–N3	92.2(2)	N1–Cu–N4	89.7(1)
N2–Cu–N3	88.6(2)	N2–Cu–N4	86.0(1)
Cu–N1–C1	107.0(3)	Cu–N1–C1	118.1(3)
Cu–N2–C3	116.9(4)	Cu–N2–C4	106.2(3)
Cu–N2–C2	104.6(3)	Cu–N2–C3	116.4(2)
Cu–N3–C13	168.7(4)	Cu–N4–C8	166.8(3)

situated between them. In isomer 1, the overlap is of the ring-over-ring mode¹ with a distance between the quinoid best planes of $3.096(4)$ \AA (Figure 3a). However, this overlapping is not complete since one TCNQ is shifted $1.052(5)$ \AA relative to the other along the TCNQ transverse axis. Every TCNQ A coordinates a different copper atom, creating an infinite chain of metallamacrocycles bridged by dimeric units, typical of $[\text{M}(\text{N}_4)(\text{TCNQ})_2]$ compounds:^{8,9}



The interactions of the TCNQ groups are completed by the formation of hydrogen bonds between some uncoordinated nitrile groups and the amine groups of the macrocycle. One hydrogen bond is found between the nitrogen opposite to that coordinated to the copper atom and one of the NH cyclam groups of the adjacent metallamacrocyclic unit, with bond distances of $\text{N1}-\text{H011} = 0.993(6)$ \AA and $\text{N6}\cdots\text{H011} = 2.170(6)$ \AA and an angle of $143.2(5)^\circ$. The existence of this hydrogen bond results in a double interaction between the $\text{Cu}(\text{cyclam})$ and the AA dimers, since each TCNQ is σ -bonded to one copper atom and hydrogen-bonded to the cyclam ligand that coordinates the opposite copper atom (Figure 4a).

The $\pi-\pi$ overlapping in the AA dimer for isomer 2 is of the ring-external bond type (Figure 3b) with a distance between the quinoid best planes of $3.057(3)$ \AA . The formation of the dimer also creates infinite chains, with the AA dimers acting as double bridges, by the σ -coordination of one nitrogen to the copper and the hydrogen bonding of the opposite nitrile with

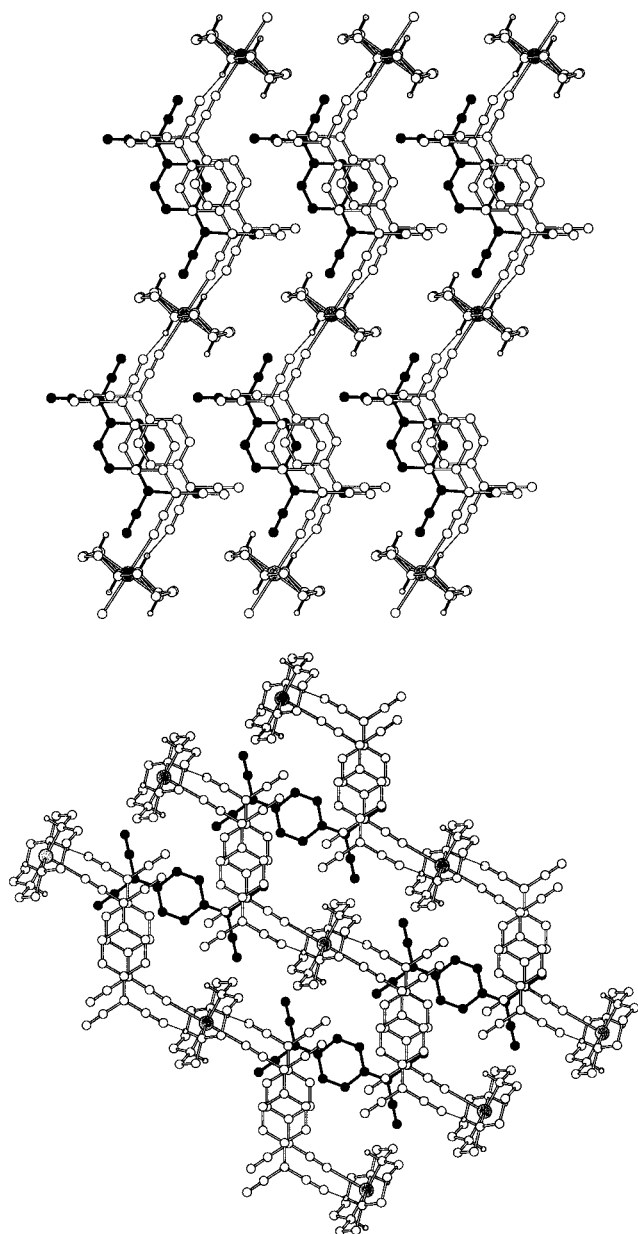


Figure 4. Views of the $-\text{Cu}(\text{cyclam})-\text{AA}-$ chains in the ac plane and the π -overlapping of TCNQ B in (a, top) isomer 1 and (b, bottom) isomer 2: TCNQ A, white circles; TCNQ B, black circles.

the cyclam of the second metallamacrocyclic unit: $\text{N1}-\text{H1} = 1.007(3) \text{ \AA}$ and $\text{N6}\cdots\text{H1} = 2.289(4) \text{ \AA}$, with an angle of $130.5(7)^\circ$.

The neutral TCNQ B is uncoordinated in both structures. Its only interaction is a $\pi-\pi$ overlapping with TCNQ A. The main differences between the two isomers arise from the orientation of TCNQ B relative to the AA dimers in the chains.

In isomer 1, the longitudinal axis of TCNQ B is oriented parallel to that of the AA dimer. The quinoid rings are also parallel, forming an angle of $1.8(2)^\circ$ between the best planes of A and B units. This orientation creates a ring-over-ring overlapping although shifted $0.64(3) \text{ \AA}$ along the transverse axis (Figure 3a). TCNQ B overlaps with two AA dimers belonging to different chains and produces a $\dots-\text{AA}-\text{B}-\text{AA}-\text{B}-\text{AA}-\text{B}-\dots$ stacking that forms an angle of 80° with the $\dots-\text{AA}-\text{Cu}(\text{cyclam})-\text{AA}-\dots$ chains. This overlap creates a bidimensional network with the chains oriented along the a crystal axis and the TCNQ's stack growing in the b direction (Figure 5a). Similar stacking modes have been found in $[\text{Fe}(\text{MeOH})_4(\text{TCNQ})_3]\cdot 2\text{MeCN}$,²⁵ in $[\text{Mn}(\text{tpa})(\text{TCNQ}(\text{MeOH}))](\text{TCNQ})_2\cdot$

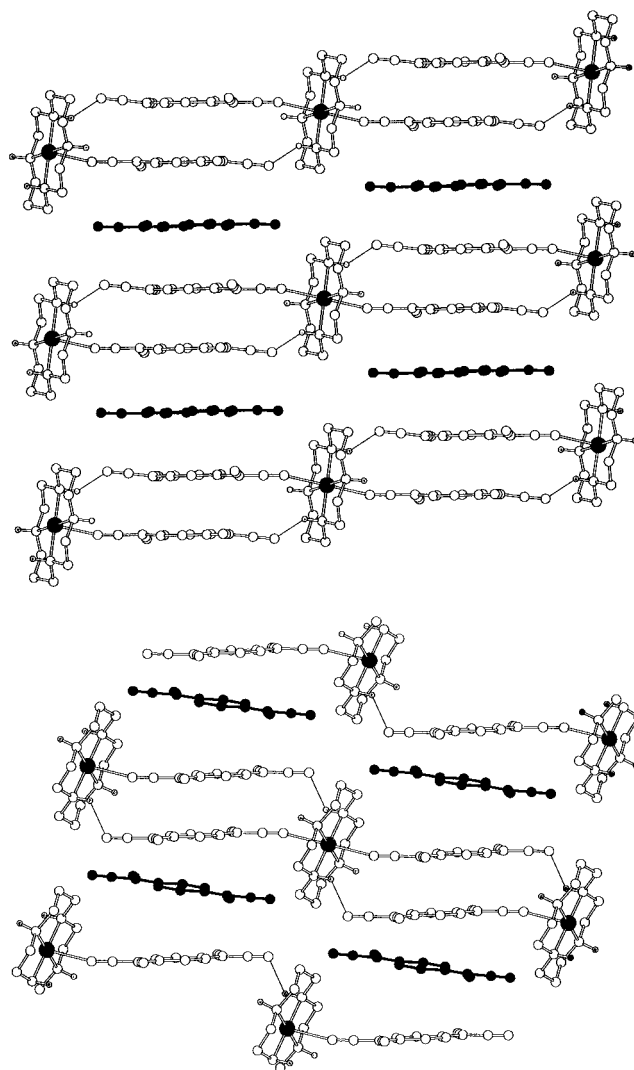


Figure 5. TCNQ stacking in the b direction for (a, top) isomer 1 and (b, bottom) isomer 2: TCNQ A, white circles; TCNQ B, black circles.

2MeCN ($\text{tpa} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$),^{11a} and in the related $[\text{Cu}(\text{cyclam})]_2[2,5\text{-DM-DCNQI}]_5$.¹³ The spacing in the TCNQ stacking is not uniform, since the intradimer AA distance is $3.096(5) \text{ \AA}$ whereas the AB distance is longer, $3.346(5) \text{ \AA}$. The different distances are expected because there is no electronic delocalization along the column.

The AB overlapping in isomer 2 is different, since the longitudinal axis of TCNQ B is rotated $72.2(8)^\circ$ relative to that of the AA dimer. Therefore the overlapping is of the external bond-external bond type (Figure 3b), with a distance of $3.155(4) \text{ \AA}$ between the exocyclic planes. As for isomer 1 this overlapping causes a $\text{TCNQ}\dots-\text{AA}-\text{B}-\text{AA}-\text{B}-\text{AA}-\dots$ stacking that forms an angle of 84° with the $-\text{AA}-\text{Cu}(\text{cyclam})-\text{AA}-$ chains, extending the interaction bidimensionally (Figure 5b). Due to the centrosymmetric nature of TCNQ B, both ends of the TCNQ overlap with different chains in the ac plane, giving rise to a tridimensional network of TCNQ interactions (Figure 4b). In conclusion, every TCNQ B is overlapping with four AA dimers belonging to four different $-\text{copper}-\text{AA}-$ chains.

There has been a great deal of work relating the bond distances in every TCNQ to the degree of charge held on it.²⁶ The reduced radical anion partially occupies an antibonding

(25) Oshio, H.; Ino, E.; Ito, T.; Maeda, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 889.

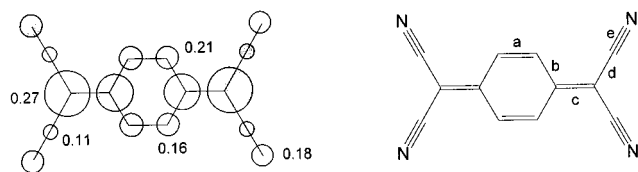


Figure 6. Plot of the TCNQ LUMO orbital and the bond labeling used in Table 3.

Table 3. Comparative Analysis of the TCNQ Intramolecular Bond Distances (Å) in [Cu(cyclam)(TCNQ)₂](TCNQ)

species	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 ^{-b}	1.374	1.423	1.420	1.416	1.153	0.003	0.004	0.500
isomer 1								
TCNQ A ^c	1.356	1.420	1.400	1.417	1.142	0.020	-0.017	0.494
TCNQ B ^c	1.324	1.447	1.358	1.438	1.133	0.089	-0.080	0.471
isomer 2								
TCNQ A ^c	1.370	1.419	1.410	1.416	1.144	0.009	-0.006	0.497
TCNQ B ^c	1.345	1.433	1.384	1.420	1.144	0.049	-0.036	0.485

^a Reference 27a. ^b Reference 27b. ^c The medium value of the different distances has been used.

orbital (the LUMO represented in Figure 6), 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 lessened. Flandrois and Chasseau^{26a} 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.^{26b} relate the degree of charge transfer to the TCNQ with the *c*/(*b* + *d*) ratio. We have, in our case, the additional distortion induced on TCNQ A by the coordination to the metal atom. Nevertheless we can see from Table 3 that TCNQ A shows *b* - *c* and *c* - *d* differences and a *c*/(*b* + *d*) ratio similar to those for the radical anions, TCNQ⁻, while the uncoordinated TCNQ B is more similar to neutral TCNQ⁰. This fact is related to the greater tendency for coordination found in the radical anion compared with the neutral TCNQ molecule.

Spectroscopic Studies. The IR spectrum of the TCNQ derivatives is frequently diagnostic of the formal oxidation state and the coordinative status of these organic acceptor molecules.²⁸ The neutral TCNQ shows the following characteristic vibration frequencies: $\nu(\text{C}\equiv\text{N}) = 2228 \text{ cm}^{-1}$, $\nu_{20}(\text{b}_{1u}) = 1530 \text{ cm}^{-1}$, $\nu_{34}(\text{b}_{2u}) = 1524 \text{ cm}^{-1}$, $\nu_4(\text{a}_g) = 1424 \text{ cm}^{-1}$, $\nu_{50}(\text{b}_{3u}) = 860 \text{ cm}^{-1}$, and $\nu_7(\text{a}_g) = 705 \text{ cm}^{-1}$. For the radical anion TCNQ⁻ these vibrational modes can be respectively observed at 2194/2177, 1577, 1507, 1386, 824, and 722 cm^{-1} .

For [Cu(cyclam)(TCNQ)₂], the observed bands at 2182, 2160, 1584, 1504, 1392, 825, and 722 cm^{-1} clearly indicate that all the TCNQ's are present in their reduced form. The $\nu(\text{CN})$ band pattern shows the characteristic features of σ -monodentate TCNQ⁻.^{28,29} This spectrum, similar to those exhibited by related compounds,^{9,10} suggests analogous structures for all these compounds, consisting of infinite chains of metallamacrocyclic units bridged by dimeric (TCNQ)₂²⁻. This is the same repeating

unit observed in the crystal structure of both isomeric forms of [Cu(cyclam)(TCNQ)₂](TCNQ). Both isomers show identical IR spectra in consonance with their structural similitudes. The bands found at 2215, 1539, 1524, 1424, 840, and 705 cm^{-1} suggest the presence of neutral TCNQ, while those at 2187, 2175, 2153, 1578, 1501, 1386, 829, and 722 cm^{-1} reveal the coordinated TCNQ⁻.

The solid state electronic spectra of isomers 1 and 2 are also identical. They show absorptions at 6100, 8900, 13 600, 17 800, 25 900, 34 000, and 39 500 cm^{-1} . The first two bands are broad and respectively result from a charge transfer between radical anionic and neutral species (CT₂), which appears around 6000 cm^{-1} , and from the intradimer charge-transfer transition (CT₁) between radical anions (TCNQ⁻TCNQ⁻ → TCNQ⁰TCNQ²⁻), usually observed in the 11 000–7500 cm^{-1} range.³⁰ The maxima at 13 600, 17 800, and 29 500 cm^{-1} can be attributed to locally excited levels of the anion radical, corresponding to the intramolecular transitions ²B_{2g} → ²B_{1u}, ²B_{2g} → ²A_u, and ²B_{2g} → ²B_{3u}, respectively.³¹ Finally, the bands at 34 000 and 39 500 cm^{-1} can be assigned to charge-transfer transitions involving the metallamacrocyclic unit.³² The bands corresponding to the copper(II) d → d transitions, which should appear in the 12 000–18 000 cm^{-1} region, are obscured by the more intense and broad charge-transfer bands previously mentioned. The compound [Cu(cyclam)(TCNQ)₂] shows the absorptions characteristic of the dimeric dianion (TCNQ)₂²⁻, the two locally excited intramolecular transitions at 12 000 and 25 500 cm^{-1} , respectively. Along with these bands attributable to the TCNQ's, the bands above 30 000 cm^{-1} involving the metallamacrocyclic unit are also observed.

The electronic spectra in acetonitrile solution of all the derivatives show the transitions characteristic of uncoordinated TCNQ⁻.³³ These spectra show two transitions, the two locally excited levels LE₁ and LE₂ that respectively appear at 11 900 and 25 400 cm^{-1} in the spectrum of the free anion radical. The intensity ratio for these two bands is a clear indicator of the oxidation state of the TCNQ groups present in solution, since neutral TCNQ only shows the band at 25400 cm^{-1} . As a reference, solutions having only TCNQ⁻ show a $\epsilon(25\ 400)/\epsilon(11\ 900)$ ratio of 0.5, while this value is higher when both neutral and anionic TCNQ groups are present: 1.25 for one neutral and two anionic TCNQ groups and 2.0 for one neutral and one anionic TCNQ group, that is, with the formation in concentrated solutions of the trimeric (TCNQ)₃²⁻ and the dimeric (TCNQ)₂⁻, respectively.^{11d} The ratio values for our compounds are 0.47 for [Cu(cyclam)(TCNQ)₂], as expected since only TCNQ⁻ is present, and 1.25 for both isomers of [Cu(cyclam)(TCNQ)₂](TCNQ), where one neutral and two anionic TCNQ's per copper atom are observed.

The EPR spectra of powdered samples show the axial pattern characteristic of tetragonally elongated octahedral copper(II).³⁴ The *g* values at room temperature for [Cu(cyclam)(TCNQ)₂] are *g*_{||} = 2.16 and *g*_⊥ = 2.03. The parallel signal appears as a quartet due to the hyperfine coupling with the copper (*I* = 3/2) nucleus, the coupling constant being *A*_{||} = 95 G (1 G = 10⁻⁴ T). For the isomeric [Cu(cyclam)(TCNQ)₂](TCNQ), the *g* values observed at room temperature are *g*_{||} = 2.20 and *g*_⊥ = 2.05, and there is also a very small signal at *g* = 2.004 attributable to a small quantity of nondimerized TCNQ⁻ radical

(26) (a) Flandrois, S.; Chasseau, D. *Acta Crystallogr., Sect. B* **1977**, *33*, 2744. (b) Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr., Sect. B* **1982**, *38*, 1193.

(27) (a) Kistenmacher, T. S.; Phillips, J. E.; Cowan, D. O. *Acta Crystallogr., Sect. B* **1974**, *30*, 763. (b) Hoeskstra, A.; Spoelder, T.; Vos, A. *Acta Crystallogr., Sect. B* **1972**, *28*, 14.

(28) Bozio, R.; Girlando, A.; Pecile, C. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1237.

(29) (a) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 539. (b) Inoue, M.; Inoue, M. B. *Inorg. Chem.* **1986**, *25*, 37. (c) Bell, S. E.; Field, J. S.; Haines, R. J.; Moscherosch, M.; Matheis, W.; Kaim, W. *Inorg. Chem.* **1992**, *31*, 3269.

(30) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(31) Schwartz, M.; Hatfield, W. E. *Inorg. Chem.* **1987**, *26*, 2823.

(32) (a) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730. (b) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p 356.

(33) Iida, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 673.

(34) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

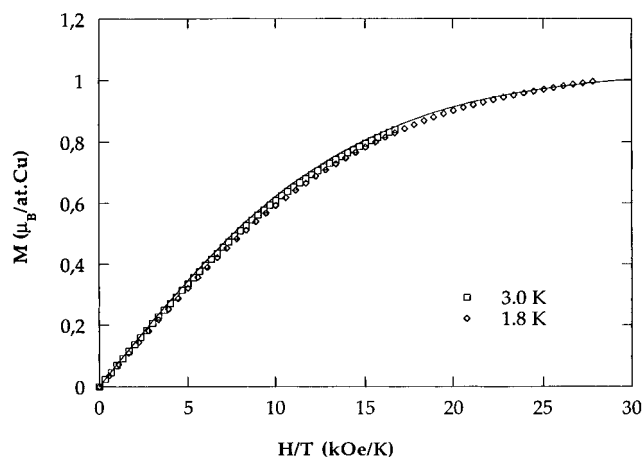


Figure 7. Isothermal magnetization of [Cu(cyclam)(TCNQ)₂](TCNQ), isomer **1**, at 3.0 and 1.8 K as a function of the magnetic field. The continuous line represents the fit of the data to the Brillouin function of an $S = 1/2$ paramagnet with $g = 2.11$.

anions. On lowering of the temperature, no significant changes in the spectrum are observed, except for a diminution in the intensity of the radical signal, in consonance with the behavior observed in the magnetic susceptibility (see below).

Electrical Conductivity. The conductivity in the solid state was measured in the temperature range 200–400 K for pressed powdered samples of [Cu(cyclam)(TCNQ)₂] and isomer **1**. [Cu(cyclam)(TCNQ)₂] behaves as an insulator ($\sigma < 10^{-7}$ S cm⁻¹) at room temperature, while isomer **1** shows semiconducting behavior [$\sigma = \sigma_0 \exp(-E_a/k_B T)$], with a room-temperature conductivity value of 1.4×10^{-4} S cm⁻¹ and values of $\sigma_0 = 4.1 \times 10^{-4}$ S cm⁻¹ and $E_a = 0.64$ eV.

No conductivity was detected in the measurements for single crystals of both isomers of [Cu(cyclam)(TCNQ)₂](TCNQ); this indicates for our apparatus a conductivity value lower than 10^{-7} S cm⁻¹. Since single-crystal conductivity values are usually a few orders of magnitude higher than powder values, the low value found by us should be explained in terms of the studied crystal habits. Single-crystal measurements were made on needles with approximate dimensions $4 \times 0.1 \times 0.05$ mm. Because of the needle form, the conductivity could only be measured along the long crystal direction. This direction corresponds to the *a* crystal axis, while the TCNQ stacking is observed along the *b* axis and along this direction the conductivity should be the highest.^{11e,35}

Magnetic Measurements. [Cu(cyclam)(TCNQ)₂] presents a magnetic susceptibility temperature dependence typical of a copper(II) compound having isolated metal atoms. In this sense, the susceptibility values follow the Curie–Weiss law [$\chi = C/(T - \Theta)$], with a Curie constant value of $C = 0.42$ emu K mol⁻¹ and a Weiss temperature of $\Theta = -0.14$ K. The Curie constant value corresponds to an effective magnetic moment of $1.83 \mu_B$ ($\mu_{\text{eff}} = 2.828C^{1/2}$) and a copper *g* value of 2.113, in good agreement with the medium *g* value obtained from the EPR spectrum. The low Θ value obtained in the fitting indicates that only a very weak interaction or no interaction at all must exist between neighboring copper atoms.

The magnetic properties of both isomers of [Cu(cyclam)(TCNQ)₂](TCNQ) are more complex. The field dependence of the isothermal magnetization at 1.8 and 3 K for isomer **1** is depicted in Figure 7. The magnetization values have been scaled to Bohr magnetons per Cu atom. The experimental points fit well to a Brillouin function corresponding to an $S = 1/2$

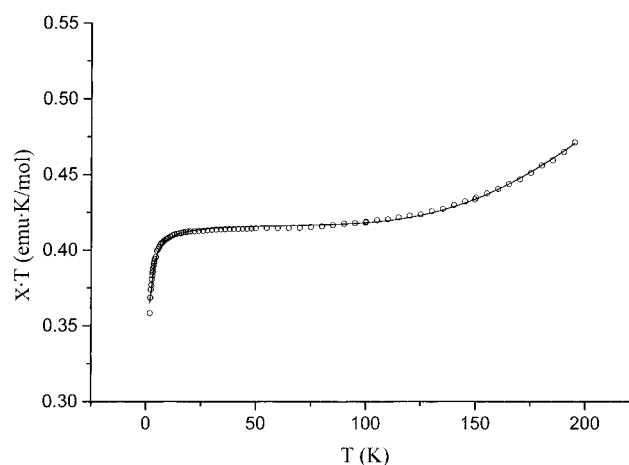
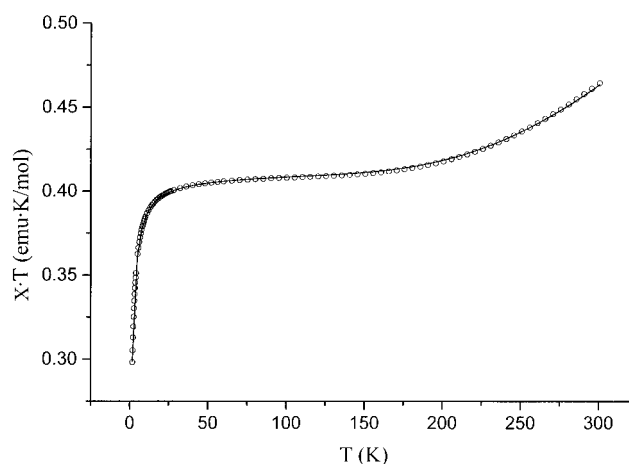


Figure 8. Temperature dependence of χT for [Cu(cyclam)(TCNQ)₂](TCNQ): (a, top) isomer **1**; (b, bottom) isomer **2**. The solid line in each panel represents a least-squares fit using eq 1 and the parameters described in the text.

paramagnet using a value of $g = 2.11$. The slight tendency of the theoretical magnetization values to be slightly higher than the experimental ones can be due to the presence of very weak antiferromagnetic interactions not included in the fit. These results are in excellent agreement with EPR determinations and suggest that in this temperature region only the Cu²⁺ ions contribute to the magnetism of the substance. In addition, there is no indication of magnetic interactions between the metallic atoms and the TCNQ radical units. The value of the magnetic dc susceptibility was determined from the magnetization experiments as a function of the temperature in the region from 1.8 to 300 K. A χT versus temperature plot is shown in Figure 8a. The experimental values of χT steadily decrease from 0.46 emu K mol⁻¹ at 300 K to 0.41 emu K mol⁻¹ at 70 K, where an inflection point is observed. This indicates that in the high-temperature region there is a small contribution from the dimers to the magnetic susceptibility. Below that temperature, the values of χT decrease more rapidly down to 0.30 emu K mol⁻¹ at 1.8 K. The molar magnetic susceptibility data were fit to the sum of the Curie and Bleaney–Bowers equations in the temperature range $40 \text{ K} < T < 250 \text{ K}$ ³⁶

$$\chi_{\text{tot}} = \frac{Ng_{\text{Cu}}^2\mu_B^2}{4k_B T} + \frac{Ng^2\mu_B^2}{k_B T} \left[\frac{2}{3 + \exp(-2J/k_B T)} \right] \quad (1)$$

where N , g_{Cu} , g , μ_B , k_B , and J represent respectively Avogadro's

(35) Goldberg, J. Z.; Eisenberg, R.; Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5173.

(36) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451.

number, the g value for copper, the g value for TCNQ, the Bohr magneton, the Boltzmann constant, and the exchange coupling constant for interacting TCNQ pairs. In order to reduce parameters, a value of $g = 2.003$ was kept fixed in the fitting process. The best fit to eq 1 was obtained with the following values: $J = -424(1) \text{ cm}^{-1}$ ($J/k_B = -610$) and $g_{\text{Cu}} = 2.092(3)$. The fitting process was then extended to the entire temperature range, and the Curie term was substituted by the Curie–Weiss law in eq 1. Using the Weiss temperature, Θ , as the only fitting parameter while keeping the others fixed at the fitted values given above, we obtained a value of $\Theta = -0.61(1) \text{ K}$, indicating the presence of small antiferromagnetic interactions between the Cu^{2+} ions. The fit is represented as a solid line in Figure 8a.

Isomer **2** shows a similar magnetic behavior. Figure 8b represents the experimental χT values measured in the 1.8–200 K region and the fitting curve obtained by following the same procedure as described for isomer **1**. The best fit of eq 1 was obtained with the following parameters: $g_{\text{Cu}} = 2.111(1)$, $J = -271(1) \text{ cm}^{-1}$ ($J/k_B = -390 \text{ K}$), and $\Theta = -0.26(1) \text{ K}$.

In conclusion, we believe that the magnetic properties of both isomers of $[\text{Cu}(\text{cyclam})(\text{TCNQ})_2](\text{TCNQ})$ are indicative of the presence of two independent magnetic subsystems in the compound, one organic and the other inorganic. Two TCNQ radical anions from the formula unit contribute to the magnetic organic subsystem, while the third TCNQ group remains neutral. The two radical anions interact antiferromagnetically quite strongly, forming a dimer that tends to $S = 0$ at low temperatures. The inorganic part of the compound is formed by the Cu^{2+} ions that behave as weakly interacting $S = 1/2$ paramagnetic units. No interactions are observed between electrons from the organic and the metallic subsystems.

This model is based in the existence of a thermally accessible triplet state for the dimers; this state is depopulated when the temperature decreases, as more dimers rest in the singlet state, in consonance with the lowering of the EPR signal intensity previously mentioned.

Concluding Remarks

Two different crystallographic forms of $[\text{Cu}(\text{cyclam})(\text{TCNQ})_2](\text{TCNQ})$ have been obtained. Both isomers show a crystal structure based on monodimensional chains built from alternating $[\text{Cu}(\text{cyclam})]^{2+}$ and $(\text{TCNQ})_2^{2-}$ units. These chains are characteristic of TCNQ derivatives having only σ -coordinated anion radicals. In these compounds, a strong antiferromagnetic coupling between the organic radicals is observed and the dimer $(\text{TCNQ})_2^{2-}$, formed by π -overlapping of two anion radicals, behaves diamagnetically below room temperature.^{11c,31}

The presence of a third TCNQ molecule in its neutral

oxidation state is responsible for the differences found in these isomers. Because this molecule remains uncoordinated, its stacking mode does not show the rigidity observed in the anion radicals and the weak interactions with the rest of the building blocks allow the possibility of different orientations in the structure. The parallel orientation found in isomer **1** permits the connection of the monodimensional chains in a second, perpendicular direction *via* a ring-over-ring π -overlapping between neutral and anionic TCNQ units, creating a bidimensional array. In isomer **2**, the rotated orientation of the neutral TCNQ allows the tridimensional connection of the $[\text{Cu}(\text{cyclam})(\text{TCNQ})_2]$ infinite chains through an external bond–external bond overlapping. The different orientation of this neutral TCNQ is reflected in the different degree of contribution of the TCNQ's to the total magnetic susceptibility of these compounds. Since the contribution of the dimeric dianion is usually negligible, the presence of a neutral TCNQ must weaken this antiferromagnetic coupling in the three TCNQ derivatives. The higher contribution in isomer **2** must be attributed to the different overlapping of this neutral TCNQ, which allows the simultaneous interactions with four different dimers. The weakening in the coupling inside the dianionic dimer cannot be related to the intradimer distance, since it is longer in isomer **1**, 3.096(5) Å, with stronger coupling than in isomer **2**, 3.057(3) Å. We must look for the cause of this weakening in the interaction between neutral and anionic TCNQ's, shorter in isomer **2**, 3.155(4) Å, relative to isomer **1**, 3.346(5) Å. This shorter and therefore stronger interaction in isomer **2** does not necessarily weaken the intradimer overlapping as its shorter distance suggests but is probably indicative of a slightly higher electronic delocalization between different TCNQ's, as can be observed from Table 3, where the structural parameters indicate that the neutral TCNQ is “less neutral” in isomer **2** than in isomer **1**. This delocalization would imply a lower antiferromagnetic coupling between the radicals as found in the magnetic susceptibility measurements.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (17 pages). Ordering information is given on any current masthead page.

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