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Synthesis of 1,1′-Bicobaltocene Salts of Tetracyano-*p*-quinodimethanide and the Structure of 1,1′-Bicobaltocene[$Co^{III}Co^{III}$] Tris(tetracyano-*p*-quinodimethanide)

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The reaction of 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$(PF_6)_2$ or the analogous mixed-valence compound [$Co^{III}Co^{II}$] with excess $[(C_2H_5)_3NH][TCNQ]_2$ and TCNQ yields the complex salt 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$[TCNQ]_3$. The complex salt crystallizes in the triclinic system: space group $P\bar{1}$ with unit cell dimensions a = 7.475 (4) Å, b = 10.113 (5) Å, c = 14.306 (3) Å, α = 92.51 (3)°, β = 98.84 (3)°, and γ = 92.64 (4)°. The conventional and weighted R factors for 1979 reflections for which I was greater than $3\sigma(I)$ are R = 0.047 and R_w = 0.044. The TCNQ units stack to form an alternating chain with two short, adjacent interplanar spacings of 3.15 Å, followed by a longer interplanar spacing of 3.45 Å. The interplanar spacing of the fulvalene moieties in the cation is 3.270 Å, and the cobalt–carbon bond distances range from 2.012 (5) to 2.041 (5) Å. The complex salt is diamagnetic, and the electrical conductivity of a pressed pellet sample is 0.03 Ω^{-1} cm^{-1}.

Introduction

The relatively high electrical conductivities of pressed pellet samples of the mixed-valence compound 1,1′-biferrocene-[$Fe^{II}Fe^{III}$]$[TCNQ]_2$,[1,2] where $[TCNQ]_2^-$ is the tetracyano-*p*-quinodimethanide radical anion dimer, continues to attract attention[3] since the mechanism of the conductivity process is unknown. The analogous 1,1′-bicobaltocene salts of TCNQ are of interest in this regard since it is well-known that bicobaltocene is much more easily oxidized than the iron compound, and a different degree of charge transfer, TCNQ band filling, and electrical conductivities may be anticipated in bicobaltocene salts of TCNQ. Results of our studies of the TCNQ salts of 1,1′-bicobaltocene are reported in this paper.

Experimental Section

Synthesis of Salts of Bicobaltocene. The hexafluorophosphate salt of bicobaltocene[$Co^{III}Co^{III}$] was prepared by the method of Davison and Smart,[4] and the orange product was purified by elution with acetone from a Florisil column. The purified copper red compound gave two well-separated, equally intense triplets at τ = 5.5 and 7.5 in the NMR spectrum.

Tetracyano-*p*-quinodimethane (TCNQ) was obtained from Pfaltz and Bauer, Inc., and purified by recrystallization from tetrahydrofuran. The lithium salt of TCNQ was prepared by adding a boiling solution of lithium iodide in acetonitrile to a boiling solution of TCNQ in acetonitrile. The reaction mixture was allowed to stand for 4 h, and the purple solid was separated from the brown solution. The purple solid was washed with acetonitrile until the washing was bright green, and then it was washed with a large volume of diethyl ether.

The triethylammonium salt of TCNQ was prepared by adding triethylamine to a very hot solution of TCNQ in THF. After several hours, black shiny crystals of $[Et_3NH][TCNQ]_2$ separated from the intensely green colored solution. The black crystals were collected, washed with THF, and purified by recrystallization from acetonitrile.

The mixed-valence salt 1,1′-bicobaltocene[$Co^{III}Co^{II}$](PF_6) was prepared by the method described by Smart[5] by reducing 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$(PF_6)_2$ in acetonitrile with hydrazine hydrate. The initial dark orange solution turned green immediately, and dark green microcrystals separated upon cooling. The product was collected, washed with absolute ethanol, anhydrous diethyl ether, and dried in vacuum at room temperature.

The new compound 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$[TCNQ]_3$ resulted from the reaction of the mixed valence hexafluorophosphate salt with a mixture of $[Et_3NH][TCNQ]_2$ and neutral TCNQ. However, it was later found that this compound is more conveniently prepared from 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$(PF_6)_2$, and this procedure is given here. $[Et_3NH][TCNQ]_2$ (0.262 g) and TCNQ (1.046 g) were dissolved in a minimum amount of hot acetonitrile (about 200 mL) in a closed flask under nitrogen, and a solution of the cobalt(III,III) hexafluorophosphate compound (0.170 g) in acetonitrile (20 mL) was added dropwise through a dropping funnel. After the addition of cobalt compound, the mixture was refluxed for 1 h. The black precipitate which had formed was collected, and washed thoroughly with distilled water until the washing was colorless. The precipitate was then washed with acetonitrile until the washing was no longer yellow and dried in a vacuum at room temperature. The yield was 0.225 g (89%). Anal. Calcd for $C_{56}Co_2H_{28}N_{12}$: C, 68.16; H, 2.86; N, 17.04. Found: C, 68.02; H, 2.92; N, 17.15.

Table I. Crystallographic Data

formula: $Co_2C_{56}H_{28}N_{12}$	fw = 986.79
λ(Mo Kα) = 0.709 26 Å	
a = 7.475 (4) Å	α = 92.51 (3)°
b = 10.113 (5) Å	β = 98.84 (3)°
c = 14.306 (3) Å	γ = 92.64 (4)°
V = 1066.1 $Å^3$	triclinic, $P\bar{1}$
D_c = 1.54 g cm^{-3}	Z = 1
D_o = 1.54 g cm^{-3} by flotation in $CHBr_3/CHCl_3$	
intensity data collected by ω-θ scan between $2 < \theta < 30°$	
no. of reflctns with $I > 3\sigma$ = 1979	
R = 0.047	R_w = 0.044

The simple salt 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$[TCNQ]_2$ was prepared by the reaction of 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$(PF_6)_2$ with a stoichiometric amount of LiTCNQ in refluxing acetonitrile.

Physical Characterizations. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-3 spectrometer, and infrared spectra were collected with a Beckman IR-4250 spectrophotometer. Electrical conductivities of pressed pellet samples were measured with the use of four-point contacts as necessary for the van der Pauw method.[6] A constant current of 10 μA was supplied by a Keithley Model 227 constant-current source, and the voltage drop was measured with a Keithley Model 180 nanovoltmeter. Magnetic susceptibilities were measured as a function of temperature using procedures which have been described previously.[7] The data were corrected for the diamagnetism of the constituent atoms.[8]

X-ray Crystallographic Studies. Deep red crystals of 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$[TCNQ]_3$ were obtained by slowly cooling a hot saturated solution of the compound in dimethylformamide. The crystals were thin and did not diffract well. A crystal of dimensions 0.30 × 0.20 × 0.06 mm was mounted on a glass fiber and used for all data collection at 19 °C on an Enraf-Nonius CAD-4 computer-controlled diffractometer equipped with a molybdenum X-ray tube and a graphite monochromator. The cell constants were determined

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Table II. Fractional Coordinates

atom	*x*	*y*	*z*
Co	0.4856 (1)	0.31552 (7)	0.03517 (5)
N1	−0.0394 (7)	−0.0695 (5)	0.1081 (3)
N2	0.5127 (7)	−0.0185 (5)	0.2632 (4)
N3	0.1159 (7)	−0.2340 (5)	0.7597 (3)
N4	−0.4221 (6)	−0.2674 (5)	0.6035 (3)
N5	0.4788 (6)	0.6325 (5)	0.3323 (3)
N6	−0.0536 (7)	0.5786 (5)	0.1739 (3)
C1	0.1116 (7)	−0.1163 (5)	0.3477 (3)
C2	−0.0746 (7)	−0.1451 (5)	0.3510 (4)
C3	−0.1397 (7)	−0.1781 (5)	0.4298 (3)
C4	−0.0167 (7)	−0.1845 (5)	0.5167 (3)
C5	0.1715 (7)	−0.1550 (5)	0.5157 (3)
C6	0.2314 (7)	−0.1214 (5)	0.4350 (3)
C7	0.1744 (7)	−0.0795 (5)	0.2656 (4)
C8	0.0552 (8)	−0.0738 (5)	0.1769 (4)
C9	0.3621 (8)	−0.0469 (5)	0.2645 (4)
C10	−0.0843 (6)	−0.2179 (5)	0.5980 (3)
C11	0.0307 (7)	−0.2268 (5)	0.6881 (4)
C12	−0.2725 (7)	−0.2450 (5)	0.6001 (4)
C13	0.0730 (6)	0.5359 (4)	0.4175 (3)
C14	−0.1161 (6)	0.5062 (4)	0.4153 (3)
C15	−0.1863 (6)	0.4730 (5)	0.4933 (3)
C16	0.1449 (6)	0.5726 (5)	0.3361 (3)
C17	0.3310 (7)	0.6049 (5)	0.3355 (3)
C18	0.0316 (7)	0.5748 (5)	0.2470 (3)
C19	0.3607 (6)	0.4705 (5)	0.0888 (3)
C20	0.2306 (7)	0.3681 (5)	0.0470 (4)
C21	0.2689 (7)	0.2502 (5)	0.0948 (4)
C22	0.4215 (8)	0.2770 (5)	0.1648 (3)
C23	0.4810 (7)	0.4098 (5)	0.1615 (3)
C24	0.3709 (6)	0.6083 (5)	0.0618 (3)
C25	0.2544 (7)	0.6667 (5)	−0.0112 (4)
C26	0.3106 (7)	0.8019 (5)	−0.0133 (4)
C27	0.4626 (8)	0.8282 (5)	0.0586 (4)
C28	0.4999 (8)	0.7095 (5)	0.1053 (3)
HC2	−0.155 (4)	0.865 (3)	0.306 (2)
HC3	−0.267 (5)	−0.189 (4)	0.427 (3)
HC5	0.248 (5)	−0.159 (4)	0.569 (3)
HC6	0.347 (6)	−0.122 (4)	0.437 (3)
HC14	−0.193 (5)	0.517 (4)	0.359 (3)
HC15	−0.306 (5)	0.453 (4)	0.488 (3)
HC20	0.143 (6)	0.386 (4)	−0.005 (3)
HC21	0.192 (6)	0.161 (5)	0.076 (3)
HC22	0.482 (5)	0.209 (4)	0.207 (2)
HC23	0.569 (5)	0.462 (4)	0.200 (3)
HC25	0.158 (6)	0.615 (4)	−0.055 (3)
HC26	0.259 (5)	0.860 (4)	−0.064 (3)
HC27	0.555 (6)	0.906 (5)	0.075 (3)
HC28	0.594 (5)	0.701 (3)	0.156 (2)

by a least-squares refinement of the setting angles of 25 high-angle reflections. Pertinent crystallographic data are presented in Table I. Data reduction and all other calculations, except those for the drawings, were done with the CAD-4 SDP set of programs on a PDP 11/34 computer. Drawings of the structure were made with the use of ORTEP-II.[9] The structure was solved by locating the cobalt atom from an origin-removed, sharpened Patterson function, and the remaining atoms were located from successive difference Fourier maps. The refinement was carried out by the full-matrix least-squares procedure with the function minimized being $\sum w[|F_o| - |F_c|]^2$. The weights, *w*, were taken to be $4F_o^2/\sigma\text{-}(F_o^2)$. All atoms except hydrogens were refined with anisotropic temperature factors. The hydrogen atoms were refined with isotropic temperature factors. The final discrepancy indices

$$R = \sum||F_o| - |F_c||/\sum|F_o|$$

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

are 0.047 and 0.044, respectively. The largest shift/error in the last cycle of refinement was 0.28, and the estimated standard deviation

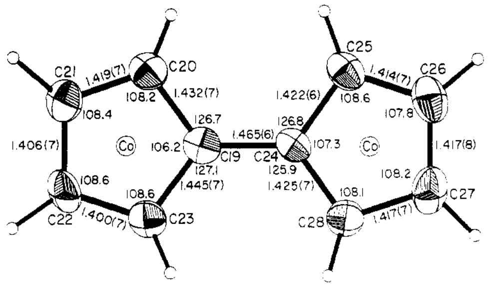

Figure 1. Bond distances and bond angles in the fulvalene moiety. The estimated standard deviations in the bond angles are 0.5°. The view is approximately normal to the molecular plane with atoms drawn as thermal ellipsoids at the 40% probability level. Hydrogen and cobalt atoms are drawn as open circles of arbitrary size.

Table III. Deviations (×10³, Å) of Atoms from Least-Squares Planes through Various Moieties

TCNQ Planes

atom	I	II	atom	III^a	IV^a
C1	29	7	C13	−3	−1
C2	11	−3	C14	3	−32
C3	8	−2	C15	−3	−40
C4	15	2	C16		−15
C5	22	2	C17		−7
C6	17	−7	C18		8
C7	1		N5		−12
C8	12		N6		21
C9	−23				
C10	5				
C11	14				
C12	−29				
N1	19				
N2	−62				
N3	13				
N4	−52				

Bis(fulvalene) Planes

atom	V	VI	VII	atom	V	VI	VII
C19	1	−9	-5^b	C24	4	-17^b	2
C20	−2	6	-23^b	C25	11	-6^b	−1
C21	−14	−1	-35^b	C26	3	-28^b	−1
C22	−5	−5	-10^b	C27	−9	-55^b	2
C23	24	9	27^b	C28	−13	-53^b	−2

[a] Each atom in this plane has a corresponding atom related by a center of inversion, the latter being also included in the plane calculation. [b] Atom not included in the plane calculation.

of an observation of unit weight was 1.3. The positional parameters are given in Table II. A list of structure factors and a table of thermal parameters are deposited as supplementary material.

Results

Description of the Structure of 1,1′-Bicobaltocene-[Co^{III}Co^{III}][TCNQ]$_3$. The bond distances and angles in the fulvalene C_5H_4–C_5H_4 moiety are shown in Figure 1. The central bond, C19–C24, of 1.465 (6) Å is somewhat longer than the carbon–carbon bond distances in the rings, the latter having a mean value of 1.420 Å. The fulvalene ring bonds thus have more double-bond character than the central bond connecting the two rings. The mean value of the ten ring angles in the fulvalene moiety is 108.0°. Each five-membered ring of the fulvalene moiety is planar (Table III, planes VI and VII). The two five-membered rings of the fulvalene moieties are, however, slightly noncoplanar (Table III, plane V). The dihedral angle between the mean planes of the two five-membered rings is 1.3°. Two cobalt atoms related by an inversion center are sandwiched between two centrosymmetrically related fulvalene molecules, thus forming the complex cation, bicobaltocene, as shown in Figure 2. There is complete overlap of the corresponding atoms of the two fulvalene

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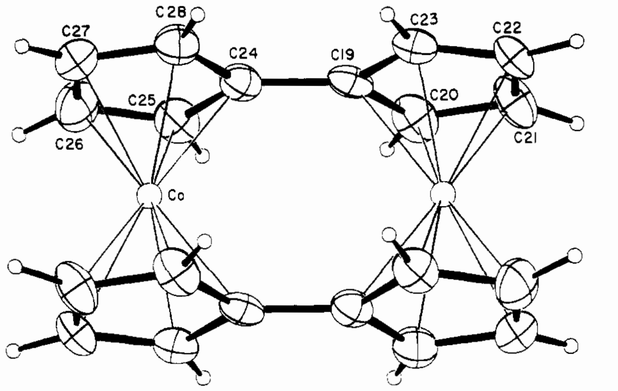

Figure 2. View of the centrosymmetric 1,1′-bicobaltocene[$Co^{III}Co^{III}$]$^{2+}$ cation with the atoms drawn as thermal ellipsoids at the 40% probability level. Hydrogen atoms and cobalt atoms are drawn as open circles of arbitrary size.

moieties in the cation. The distance between the planes of the fulvalene moieties is 3.270 Å, and that between the two cobalt atoms is 3.912 (1) Å. The distances between the cobalt atom and the carbon atoms of fulvalene range from 2.012 (5) to 2.041 (5) Å.

The bond distances and the bond angles for the TCNQ moiety are given in Figure 3a for TCNQ-1 and in Figure 3b for TCNQ-2. The latter TCNQ entity lies on a crystallographic inversion center. These values are consistent with the usual quinonoid structure for this molecule. The estimated standard deviations in the bond distances are unfortunately too high (~0.007 A) for any reasonable estimate to be made of the amount of negative charge associated with the TCNQ molecule.[10] The six-atom rings of both TCNQ-1 and TCNQ-2 are very nearly planar (Table III, planes II and III, respectively), but the TCNQ unit as a whole is slightly nonplanar in both cases (Table III, planes I and IV).

The packing of the ions in the crystal is shown in the stereoview in Figure 4. It can be seen that the TCNQ anions form parallel stacks approximately along the *b* axis at $c = \pm^1/_2$. The bicobaltocene cations are situated in between the TCNQ anion stacks, and these cations do not form parallel planar stacks. All of the TCNQ anions along a stack are parallel to each other, the dihedral angle between the least-squares planes of TCNQ-1 and TCNQ-2 (Table III, planes II and III, respectively) being only 0.2°. The stacking distances between two centrosymmetrically related TCNQ-1 anions is 3.45 Å, which is a normal distance for the van der Waals separation between such units. The stacking distance between TCNQ-1 and TCNQ-2 anions, however, is 3.15 Å, which is an extremely short interplanar separation in stacks of TCNQ anions. The modes of molecular overlap, as shown in Figure 5, a and b, are the so-called "ring external bond" type.[10] There is more direct atomic overlap between two centrosymmetrically related TCNQ-1 anions, Figure 5a, than between TCNQ-1 and TCNQ-2 anions, Figure 5b, which may explain partly the smaller stacking distance (3.15 Å) in the latter case.

There are a number of short contacts between atoms in the two TCNQ units in the stack. The shortest distance is 3.17 Å between C1 in TCNQ-1 and C16 in TCNQ-2. Owing to the large stacking distance of 3.45 Å between the two centrosymmetric TCNQ-1 anions, there are no short contacts between atoms in the two units. In addition to those mentioned above, there are only two other nominally short contacts: C9–C27 = 3.36 Å and N6–HC20 = 2.45 Å.

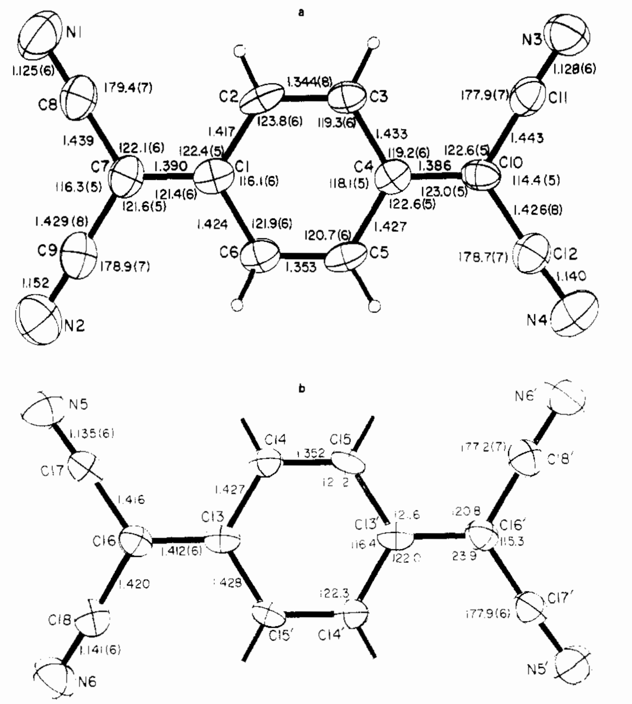

Figure 3. Bond distances and bond angles (a) for TCNQ-1 and (b) for TCNQ-2. The estimated standard deviations in the bond distances, if not shown, are 0.007 Å. Thermal ellipsoids are drawn at the 40% level except for hydrogens which are drawn as circles of arbitrary size.

The TCNQ stack exhibits an unusual alternation in the interplanar stacking distances. Essentially the stack may be considered to be a chain of trimers with two short interplanar distances of 3.15 Å followed by a longer interplanar distance of 3.45 Å. A crude model for the electronic structure of the compound involves dicationic bicobaltocene[$Co^{III}Co^{III}$]$^{2+}$ and dianionic $[TCNQ]_3^{2-}$ units. However, as discussed below, the magnetic and electrical conductivity properties of the compound argue against such a simple localized description of the electronic structure.

Magnetic and Electrical Properties. The magnetic properties of all of the compounds prepared in this study were measured with a vibrating-sample magnetometer. All of the compounds were diamagnetic, although 1,1′-bicobaltocene[$Co^{III}Co^{III}$]-[TCNQ]$_3$ exhibited a sharp singlet at $g = 2.0033$ in the EPR spectrum.

The room-temperature electrical conductivity of a pressed pellet sample of 1,1′-bicobaltocene[$Co^{III}Co^{III}$][TCNQ]$_3$ was measured with use of the four-point van der Pauw technique and found to be 0.03 Ω^{-1} cm^{-1}. The room-temperature conductivity of the simple salt 1,1′-bicobaltocene[$Co^{III}Co^{III}$]-[TCNQ]$_2$ was several orders of magnitude smaller, being 5.0×10^{-6} Ω^{-1} cm^{-1}.

Discussion

The reaction of 1,1′-bicobaltocene[$Co^{III}Co^{III}$](PF$_6$)$_2$ with excess [Et$_3$NH][TCNQ]$_2$ and TCNQ yields the complex salt 1,1′-bicobaltocene[$Co^{III}Co^{III}$][TCNQ]$_3$. The formation of this complex salt was not expected since the reaction had been designed to form a compound with a TCNQ to cobalt ratio of 2. The complex salt also results from the reaction of the mixed-valence compound 1,1′-bicobaltocene[$CO^{III}Co^{II}$](PF$_6$) with excess [Et$_3$NH][TCNQ]$_2$ and TCNQ. In this latter reaction, apparently the "cobalt(II) center" is oxidized to cobalt(III) by the TCNQ. Attempts to prepare salts containing the mixed-valence cobaltocene have not been successful.

The TCNQ units stack in the solid state to give an alternating chain which may be viewed as being formed by the

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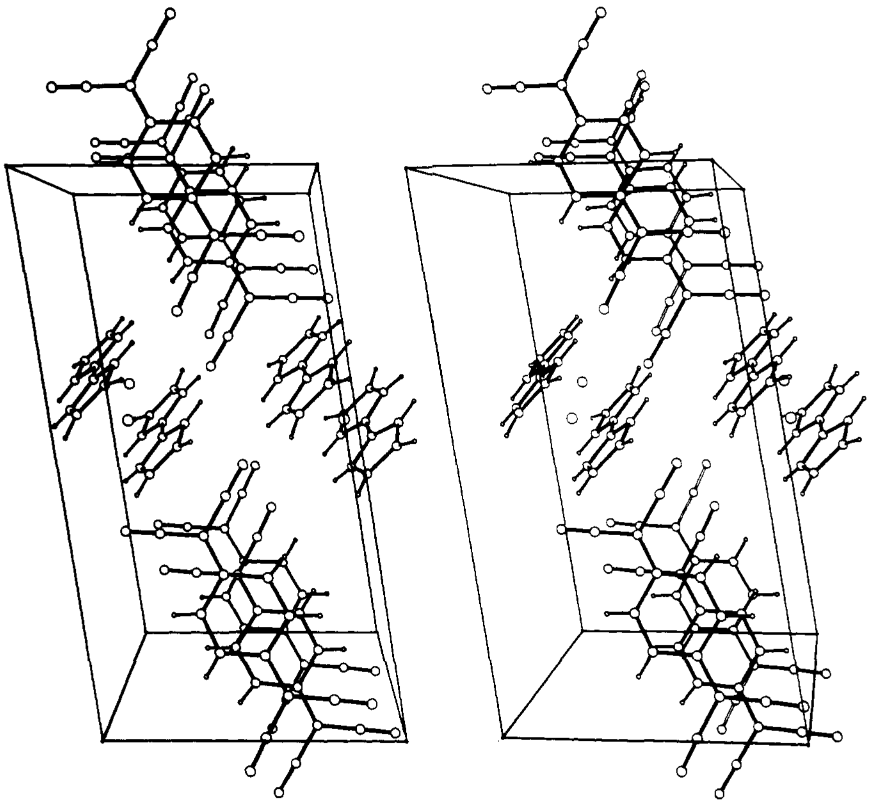

Figure 4. Stereoview of the contents of the unit cell viewed approximately along *b*.

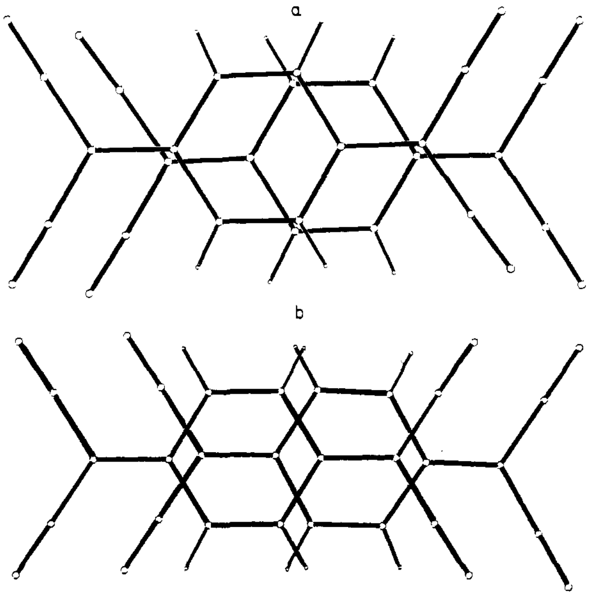

Figure 5. Modes of molecular overlap in pairs of TCNQ: (a) overlap between centrosymmetrically related TCNQ-1 anions; (b) overlap between TCNQ-1 and TCNQ-2 anions.

stacking of $[TCNQ]_3^{2-}$ units. The repeat distance in the trimer is 3.15 Å, and the distance between trimers is 3.45 Å. It is of value to compare the distance between the centers of $TCNQ^{n-}$ in electrically conducting $TCNQ^{n-}$ chain systems. The TCNQ–TCNQ distance is 3.091 (2) Å in [TTF][TCNQ] at, and below, the metal–insulator transition of approximately 60 K,[12] while the separation is 3.168 (2) Å at 295 K.[13] TCNQ–TCNQ distances in other uniformly spaced cation TCNQ chain compounds include the following: the interplanar stacking distance is 3.26 Å in [TMTSF][TCNQ] (where TMTSF is the cation of 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bis-1,3-diselenole)[14] and [NMP][TCNQ] (where NMP is the cation of *N*-methylphenazine),[15] 3.22 Å in [quinolinium][TCNQ],[16] 3.20 Å in [HMTSF][TCNQ] (where HMTSF is the cation of $\Delta^{2,2'}$-bis(4,5-trimethylene)-1,3-diselenole),[17] and 3.45 Å in [1,1′-dimethylferrocenium]$[TCNQ]_2$.[11] Neutral TCNQ also crystallizes with a chain structure. In the neutral compound, the TCNQ–TCNQ interplanar spacing is 3.45 Å.[18]

A vast array of alternatingly spaced TCNQ chains exists. The simplest of these are a series of compounds in which there is pairwise alternation of the interplanar separations. Alternating interplanar spacings of 3.15 and 3.27 Å have been observed in [MEM]$[TCNQ]_2$ (where MEM is the cation of *N*-methyl-*N*-ethylmorpholine),[19] while alternating interplanar spacings of 3.162 (5) and 3.423 (10) Å have been determined in $[Fe(C_5H_4)_2(CH_2)_3][TCNQ]_2$.[20] The cation in this latter compound is the trimethyleneferrocenium ion. The alternating interplanar spacings are 3.149 and 3.484 Å in the chains found in [Rb(TCNQ)].[21] It is tempting to think of these latter compounds with large differences in the interplanar separations as being chains of noninteracting, tightly bound dimers. However, the semiconducting nature of the electrical con-

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ductivity of these materials indicates that there is some interaction between the dimers.

Alternating chains of TCNQ which contain tetrameric units are found in $[(C_2H_5)_3NH][TCNQ]_2$,[22] the isomorphous methyltriphenylarsonium and methyltriphenylphosphonium salts of $[TCNQ]_2^-$,[23] the *N*-propylquinolinium salt of $[TCNQ]_2^-$,[24] the *N,N'*-dibenzyl-4,4'-bipyridinium salt of $[TCNQ]_4^{2-}$,[25] and the 1,3,3-trimethyl-2-(*p*-methyl-(β-chloroethyl)styryl)indolinium salt of $[TCNQ]_2^-$, although the spacings in the last compound are consistent with a pair of dimers.[26] In the triethylammonium compound, the TCNQ–TCNQ interplanar separations do not differ greatly and range from 3.24 to 3.32 Å. In the other three compounds, however, there are much larger differences between the interplanar spacings within the tetrameric unit and those between tetrameric units. For example, the interplanar spacings within the tetrameric units in methyltriphenylphosphonium bis(tetracyano-*p*-quinodimethanide) are 3.20 Å while the spacing between tetrameric units is 3.58 Å.[23]

The alternating chains which exist in the 5:1 compounds formed between 1,2-bis(1-benzyl-4-pyridyl)ethane or 1,2-bis(1-benzyl-4-pyridinio)ethylene and TCNQ[27,28] may be thought of as stacks of pentamers with TCNQ–TCNQ spacings within the pentameric unit being 3.23–3.25 Å and the TCNQ–TCNQ spacings between pentamers being 3.36–3.41 Å. The alternating chain compounds have electrical conductivities on the order of 0.03 Ω^{-1} cm^{-1}, values which are comparable to that observed for [bicobaltocene]$[TCNQ]_3$.

Trimeric units similar to those found in [bicobaltocene]$[TCNQ]_2$ have also been found in $Cs_2[TCNQ]_3$[29] and (morpholinium)$_2[TCNQ]_3$[30] although the alternation spacings in these two compounds are very similar, being 3.22–3.26 Å in the former and 3.24–3.25 Å in the latter. The alteration spacings in [bicobaltocene]$[TCNQ]_3$ vary much more widely than these two examples.

The interplanar TCNQ–TCNQ spacings in discrete dimers are germane to this discussion. The interplanar spacing is 3.26 Å in $[(CH_3)_3NH]_2[TCNQ]_2[TCNQ]_3$,[31] 3.12 Å in [benzimidazolinium][TCNQ],[32] and 3.10 Å in $[Nb_3(\mu\text{-}Cl)_6(C_6(CH_3)_6)_3][(TCNQ)_2]$.[33] The intratrimer interplanar spacing of 3.15 Å in [bicobaltocene]$[TCNQ]_3$ is among the shortest TCNQ–TCNQ contacts that has yet been observed.

There has been considerable discussion concerning the charge distribution within TCNQ clusters based on differences in bond distances, and attention is usually focused on the exocyclic carbon–carbon double bond. In neutral TCNQ, the exocyclic carbon–carbon bond distance is 1.374 (4) Å,[34] and the bond distance increases in the radical anion. Depending on the counterion, the exocyclic bond distance in $TCNQ^-$ ranges from 1.401 (6)[35] to 1.418 Å,[36] and the bond distance in $TCNQ^{1/2}$, that is, in $[TCNQ]_2^-$, is usually taken to be about 1.395.[10] It is clear that caution must be exercised in the analysis of these data since the estimated standard deviations are within the range of the calculated differences in bond distances. Our structural data do not permit a conclusion concerning the charge distribution.

A first approximation to the bonding in the TCNQ chain involves the trimeric unit and the lowest unoccupied molecular orbital on each TCNQ molecule. Assuming D_{2h} symmetry for TCNQ,[33] the LUMO is B_{2g}, and in the trimeric unit of idealized point symmetry C_{2h}, the three LUMOs combine to give one bonding level, one antibonding level, and an intermediate level which is largely nonbonding. The two electrons associated with the charge transfer in the formulation $[TCNQ]_3^{2-}$ are accommodated in the bonding level, thereby accounting for the short interplanar spacing and the diamagnetism of the compound. This picture is incomplete since the intertrimer, interplanar TCNQ–TCNQ separation is relatively small, being 3.45 Å, and a refined description of the electronic structure must take interactions between trimers in the chain into consideration. The interactions between the trimers lead to the relatively high electrical conductivity of this semiconductor.

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Registry No. 1,1'-bicobaltocene$[Co^{III}Co^{III}][TCNQ]_3$, 79102-47-9; 1,1'-bicobaltocene$[Co^{III}Co^{III}][TCNQ]_2$, 79102-46-8; 1,1'-bicobaltocene$[Co^{III}Co^{III}](PF_6)_2$, 39333-80-7; 1,1'-bicobaltocene$[Co^{III}Co^{II}](PF_6)$, 69365-59-9; $[Et_3NH][TCNQ]_2$, 12261-33-5.

Supplementary Material Available: A table of thermal parameters (Table IV) and a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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