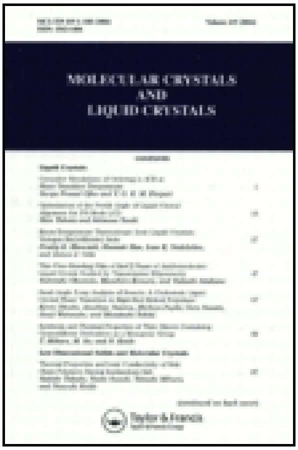

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Syntheses of 1,1′-Bicobaltocene Salts of Tetracyano-P-Quinodimethane, Tetrabromoquinone, and Tetrabromodiphenoquinone; and the Structure of 1,1′-Bicobaltocene[Co(III)Co(III)][TCNQ]$_3$

Chak-Po Lau [a], Phirtu Singh [a], Susan J. Cline [a], Reginald Seiders [a], Maurice Brookhart [a], Wayne E. Marsh [a], Derek J. Hodgson [a] & William E. Hatfield [a]

[a] Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27514

Version of record first published: 14 Oct 2011.

To cite this article: Chak-Po Lau, Phirtu Singh, Susan J. Cline, Reginald Seiders, Maurice Brookhart, Wayne E. Marsh, Derek J. Hodgson & William E. Hatfield (1982): Syntheses of 1,1′-Bicobaltocene Salts of Tetracyano-P-Quinodimethane, Tetrabromoquinone, and Tetrabromodiphenoquinone; and the Structure of 1,1′-Bicobaltocene[Co(III)Co(III)][TCNQ]$_3$, Molecular Crystals and Liquid Crystals, 86:1, 131-138

To link to this article: http://dx.doi.org/10.1080/00268948208073676

Mol. Cryst. Liq. Cryst., 1982, Vol. 86, pp. 131–138
0026-8941/82/8601-0131$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

SYNTHESES OF 1,1'-BICOBALTOCENE SALTS OF TETRACYANO-P-QUINODIMETHANE, TETRABROMOQUINONE, AND TETRABROMODIPHENOQUINONE; AND THE STRUCTURE OF 1,1'-BICOBALTOCENE[Co(III)Co(III)][TCNQ]$_3$*

CHAK-PO LAU, PHIRTU SINGH, SUSAN J. CLINE,
REGINALD SEIDERS, MAURICE BROOKHART, WAYNE E. MARSH,
DEREK J. HODGSON, AND WILLIAM E. HATFIELD
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Received for publication August 28, 1981

The reaction of 1,1'-bicobaltocene[Co(III)Co(III)]-$(PF_6)_2$, [BFDCo(III,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]$_3$. Reaction of [BFDCo(III,III)]$(PF_6)_2$ with excess tetrabromoquinone (bromanil, BA) and its sodium salt produces [BFD-Co(III,III)][BA]$_3$, while reaction with tetrabromodiphenoquinone (TBDQ) yields [BFDCo(III,III)][TBDQ]$_3$. The TCNQ units in the complex salt [BFDCo(III,III)][TCNQ]$_3$ 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 salts are diamagnetic and the electrical conductivities of pressed pellet samples range from 3.0×10^{-2} to 3.0×10^{-4} ohm^{-1} cm^{-1}.

---

*Supported in part by the Office of Naval Research

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 and related acceptors such as tetrabromoquinone (bromanil, BA) and tetrabromodiphenoquinone (TBDQ) 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, band filling, and electrical conductivities may be anticipated in bicobaltocene charge transfer salts. Results of our studies of the TCNQ, BA, and TBDQ salts of 1,1'-bicobaltocene are reported in this Article.

EXPERIMENTAL SECTION

Synthesis of TCNQ Salts of Bicobaltocene

The hexafluorophosphate salt of bicobaltocene(III,III) was prepared by the method of Davison and Smart,[4] and the mixed valence salt 1,1'-bicobaltocene[Co(III)Co(II)](PF$_6$) was prepared by the method described by Smart.[5]

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$_3$NH][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 has been described.[6] 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.

Synthesis of Bromanil Salts of Bicobaltocene

Sodium bromanil (0.48 g., 1.1 mmole) and bromanil (0.61 g., 1.43 mmole) were dissolved in 250 mL acetonitrile at room temperature. To this solution was added, drop by drop, a solution of [BFDCo(III,III)](PF$_6$)$_2$ in 20 mL acetonitrile. A shiny green precipitate formed immediately. After addition of [BFDCo(III,III)](PF$_6$)$_2$ was complete, the mixture was stirred for one hour, the green precipitate was collected, washed with acetonitrile and acetone, and dried in vacuo at 140° for two days. The yield was 0.61 g. Analyses: Calc'd for $[BFDCo(III,III)][BA]_3$ 27.72% C; 0.97% H; 58.30% Br; 5.84% O; and 7.17% Co. Found 27.50% C; 1.01% H; 58.73% Br; 5.91% O; and 7.23% Co.

Synthesis of Tetrabromodiphenoquinone Salts of Bicobaltocene

The complex salt $[BFDCo(III,III)][TBDQ]_3$ was prepared by the same experimental procedure used for the analogous bromanil complex. Analyses: Calc'd for $[BFDCo(III,III)][TBDQ]_3$ 35.88% C; 1.49% H; 51.20% Br; 6.23% Co; and 5.20% O. Found 35.81% C; 1.57%H; 51.31% Br; 6.15% Co; and 5.19% O.

Physical Characterizations

Electron paramagnetic resonance (EPR) spectra were recorded using a Varian E-3 spectrometer, and infrared spectra were collected using a Beckmann IR-4250 spectrophotometer. Electrical conductivities of pressed pellet samples were measured using four point contacts as necessary for the van der Pauw method[7]. A constant current of 10 microamperes 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.[8] The data were corrected for the diamagnetism of the constituent atoms.[9]

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. 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 using ORTEP-II.[10] Details of data collection and solution of the stucture have been given elsewhere.[6]

RESULTS

Description of the structure of 1,1'-bicobaltocene[Co(III)Co(III)]$[TCNQ]_3$

The central bond distance of 1.465(6) Å in the fulvalene moiety 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, but the two five membered rings of the fulvalene units are, however, slightly noncoplanar. The dihedral angle between the mean planes of the two five-membered rings is 1.3°. There is complete overlap of the corresponding atoms of the two fulvalene units in the cation. The distance between the planes of the fulvalene units 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 the fulvalene rings range from 2.012(5) Å to 2.041(5) Å.

There are two crystallographically independent TCNQ units, and one of these, TCNQ-2, lies on a crystallographic inversion center. The estimated standard deviations in the bond distances of the TCNQ ions 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. The six atom ring of both TCNQ-1 and TCNQ-2 are very nearly planar, but the TCNQ unit as a whole is slightly nonplanar in both cases.

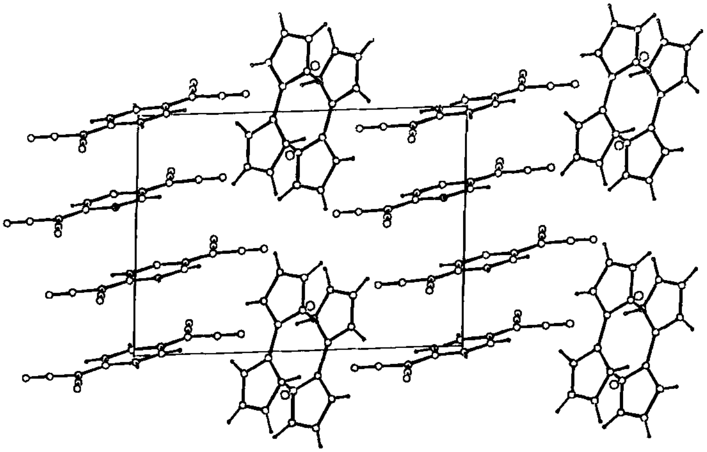

FIGURE 1 A view of the crystal packing along the a axis. The origin is in the center of the figure with b going down and c to the right.

TABLE 1. Electrical and Magnetic Properties

Compound	Electrical Conductivity, $ohm^{-1}\ cm^{-1}$, RT	EPR, RT g value
$[BFDCo(III,III)][TCNQ]_3$	3.0×10^{-2}	2.0023
$[BFDCo(III,III)][TCNQ]_2$	5.0×10^{-6}	2.0023
$[BFDCo(III,III)][BA]_3$	3.0×10^{-4}	2.0113
$[BFDCo(III,III)][BA]_2$	1.0×10^{-6}	2.0007
$[BFDCo(III,III)][TBDQ]_3$	5.3×10^{-3}	2.0132 2.0058
$[BFDCo(III,III)][TBDQ]_2$	2.0×10^{-6}	------

The packing of the ions in the crystal lattice is shown in a projection along the a-axis in Figure 1. It can be seen that the TCNQ anions form parallel stacks approximately along the b-axis at c = ± 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 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 are the so-called "ring external bond" type.[II] There is more direct atomic overlap between two centrosymmetrically related TCNQ-1 anions than between TCNQ-1 and TCNQ-2 anions, which may explain partly the smaller stacking distance (3.15 Å) in the latter case.

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 some of the compounds exhibited EPR signls. The g values which were observed are given in Table 1.

Room temperature electrical conductivities of pressed pellet samples of the charge transfer compounds and simple salts with the cation 1,1'-bicobaltocene$[Co(III)Co(III)]^{n+}$ were measured using the four point van der Pauw technique and the data are summarized in Table 1. Room temperature conductivities of the simple salts were several orders of magnitude smaller than those of the complex salts.

DISCUSSION

The reaction of 1,1'-bicobaltocene[Co(III)Co(III)] $(PF_6)_2$ with excess $[Et_3NH][TCNQ]_2$ 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 two. The complex salt also results from the reaction of the mixed valence compound 1,1'-bicobaltocene[Co(III)-Co(II)](PF_6) with excess $[Et_3NH][TCNQ]_2$ and TCNQ. In this latter reaction apparently the "cobalt(II) center" is oxidized to cobalt(III) by the TCNQ. Attempts to prepare salts of the mixed valence cobaltocene have not been successful.

Similar to the formation of the TCNQ salt, the reaction of [BFDCo(III,III)]$(PF_6)_2$ with excess bromanil and its sodium salt yields a complex salt with three molecules of bromanil per organocobalt moiety. The simple salt [BFDCo(III,III)]-$[BA]_2$ can be prepared by the reaction of [BFDCo(III,III)]-$(PF_6)_2$ with two moles of bromanil. The conductivity of the simple salt is about three orders of magnitude lower than that of the complex salt (Table 3). Attempts to prepare a complex salt of the mixed valence organocobalt cation [BFD-Co(III),II)]$^+$ were not successful, since reaction of [BFD-Co(III),II)](PF_6) with a mixture of excess bromanil and sodium bromanil led to oxidation of the cation and to the formation of [BFDCo(III,III)]$[BA]_3$.

The reaction of [BFDCo(III,III)]$(PF_6)_2$ with excess tetrabromodiphenoquinone and its sodium salt yields the complex salt [BFDCo(III,III)]$[TBDQ]_3$. The simple salt [BFD-Co(III,III)]$[TBDQ]_2$, which results from the reaction of [BFDCo(III,III)]$(PF_6)_2$ with two moles of NaTBDQ, is two orders of magnitude less conductive than the complex salt. Reaction of [BFDCo(III,II)]PF_6 with excess TBDQ and NaTBDQ did not give the complex salt of the mixed valence compound, but instead yielded [BFDCo(III,III)]$[TBDQ]_3$.

The TCNQ units in [BFDCo(III,III)]$[TCNQ]_3$ stack in the solid state to give an alternating chain which may be viewed as being formed by the 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 other chain systems. Distances are 3.091(2) Å (60 K)[12] and 3.168(2) Å (298 K)[13] in TTF-TCNQ, and range from 3.20 Å to 3.45 Å in other uniformly spaced cation TCNQ chain compounds.[14-18] Neutral TCNQ also crystallizes with a chain structure with an interplanar spacing of 3.45 Å.[19]

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. Particularly germane to this discussion are the alternating interplanar spacings of 3.162(5) and 3.423(10) Å in $[Fe(C_5H_4)_2(CH_2)_3][TCNQ]_2$.[20] The cation in this latter compound is the trimethyleneferrocenium ion. It is tempting to think of these compounds with large differences in the interplanar separations as being chains of non-interacting, tightly bound dimers. However, the semiconducting nature of the electrical conductivity of these materials indicates that there is some interaction between the dimers.

Trimeric units similar to those found in [bicobaltocene]$[TCNQ]_3$ have also been found in $Cs_2[TCNQ]_3$[21] and (morpholinium)$_2$$[TCNQ]_3$[22] although the alternation spacings in these two compounds are very similar, being 3.22-3.26 Å in the former and 3.24-3.25 in the latter. The alternation spacings in [bicobaltocene]$[TCNQ]_3$ vary much more widely.

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,[23] 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.

REFERENCES

1. D. O. Cowan, C. LeVanda, J. Amer. Chem. Soc., 94, 9271, (1972).
2. U. T. Mueller-Westerhoff, P. J. Eilbracht, J. Amer. Chem. Soc., 94, 9272, (1972).
3. L. Alcacer, R. J. H. Clark, W. E. Hatfield, K. Klabunde, J. S. Miller, G. D. Stucky, G. A. Toombs, F. Wudl, S. Yoshimura, S. In "Molecular Metals"; Hatfield, W. E., Ed.; Plenum Press: New York; 1979; pp. 517-525.
4. A. Davison, J. C. Smart, J. Organometal. Chem., 49, C43, (1973).

5. J. C. Smart, Ph. D. Dissertation, Massachusetts Institute of Technology, Cambridge, 1973.
6. C.-p. Lau, P. Singh, S. J. Cline, R. Seiders, M. Brookhart, W. E. Marsh, D. J. Hodgson, W. E. Hatfield, Inorg. Chem. in press.
7. L. J. van der Pauw, Philips Res. Rep., 13, 1, (1958). Philips Tech. Rev., 20, 320, (1958). See, also, D. Cahen, J. R. Hahn, J. R. Anderson, Rev. Sci. Instrum., 44, 1567, (1973).
8. P. J. Corvan, W. E. Estes, R. R. Weller, W. E. Hatfield, Inorg. Chem., 19, 1297, (1980).
9. R. R. Weller, W. E. Hatfield, J. Chem. Educ., 56, 652, (1979).
10. C. K. Johnson, ORTEP-II, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", ORNL-5138, National Technical Information Service, U. S. Department of Commerce, Springfield, VA 22161.
11. F. H. Herbstein, in "Perspectives in Structural Chemistry", Vol. II, pp. 166-395, J. D. Dunitz and J. A. Ibers, Editors, 1971. New York: John Wiley.
12. A. J. Schultz, G. D. Stucky, R. H. Blessing, P. Coppens, J. Amer. Chem. Soc., 98, 3194, (1976).
13. T. J. Kistenmacher, T. E. Phillips, D. O. Cowan, Acta Crystallogr., Sect. B, 30, 763, (1974).
14. K. Bechgaard, T. J. Kistenmacher, A. N. Bloch, D. O. Cowan, Acta Crystallogr., Sect. B., 33, 417, (1977).
15. C. J. Fritchie, Acta Crystallogr., 20, 892, (1966).
16. H. Kobayashi, F. Marumo, Y. Saito, Acta Crystallogr., Sect. B, 27, 373, (1971).
17. T. E. Phillips, T. J. Kistenmacher, A. N. Bloch, D. O. Cowan, J. Chem. Soc., Chem. Commun., 334, (1976).
18. S. R. Wilson, P. J. Corvan, R. Seiders, D. J. Hodgson, M. Brookhart, W. E. Hatfield, J. S. Miller, A. H. Reis, P. K. Rogan, E. Gebert, A. J. Epstein, In "Molecular Metals"; Hatfield, W. E., Ed.; Plenum Press: New York, 1979; pp. 407-414.
19. R. E. Long, R. A. Sparks, K. N. Trueblood, Acta Crystallogr., 18, 932, (1965).
20. C. Willi, A. H. Reis, Jr., E. Gebert, J. S. Miller, Inorg. Chem., 20, 313, (1981).
21. C. J. Fritchie, Jr., P. Arthur, Jr., Acta Crystallogr., 21, 139, (1966).
22. T. Sundaresan, S. C. Wallwork, Acta Crystallogr., Sect. B, 28, 491, (1972).
23. S. A. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D. M. Braitsch, J. S. Miller, M. Abkowitz, J. Amer. Chem. Soc., 99, 110, (1977).