crystals

MDPI

Communication

New Radical-Cation Salts Based on the TMTTF and TMTSF Donors with Iron and Chromium Bis(Dicarbollide) Complexes: Synthesis, Structure, Properties †

Denis M. Chudak [1], Olga N. Kazheva [2,3,*], Irina D. Kosenko [4], Gennady V. Shilov [2], Igor B. Sivaev [4,5], Georgy G. Abashev [6], Elena V. Shklyaeva [6], Lev I. Buravov [2], Dmitry N. Pevtsov [2], Tatiana N. Starodub [7], Vladimir I. Bregadze [4] and Oleg A. Dyachenko [2]

[1] Chemistry Department, V. N. Karazin Kharkiv National University, 4 Svoboda Sq., 61077 Kharkiv, Ukraine; chudakdenis@gmail.com
[2] Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 Semenov Av., 142432 Chernogolovka, Moscow Region, Russia; genshil@icp.ac.ru (G.V.S.); buravov@icp.ac.ru (L.I.B.); pevtsovdm@gmail.com (D.N.P.); doa@rfbr.ru (O.A.D.)
[3] Institute of Experimental Mineralogy, Russian Academy of Sciences, 4 Academician Osypyan Str., 4, 142432 Chernogolovka, Moscow Region, Russia
[4] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia; kosenko@ineos.ac.ru (I.D.K.); sivaev@ineos.ac.ru (I.B.S.); bre@ineos.ac.ru (V.I.B.)
[5] Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stremyannyi Line, 117997 Moscow, Russia
[6] Organic Chemistry Department, Perm State University, 15 Bukirev Str., 614990 Perm, Russia; gabashev@psu.ru (G.G.A.); EV_Shklyaeva@psu.ru (E.V.S.)
[7] Institute of Chemistry, Jan Kochanowski University, 15G Swietokrzyska Str., 25-406 Kielce, Poland; tstarodub@ujk.edu.pl
* Correspondence: koh@icp.ac.ru
† Dedicated to Professor Alan J. Welch in recognition of his outstanding contribution to the chemistry of carboranes.

Citation: Chudak, D.M.; Kazheva, O.N.; Kosenko, I.D.; Shilov, G.V.; Sivaev, I.B.; Abashev, G.G.; Shklyaeva, E.V.; Buravov, L.I.; Pevtsov, D.N.; Starodub, T.N.; Bregadze, V.I.; Dyachenko, O.A. New Radical-Cation Salts Based on the TMTTF and TMTSF Donors with Iron and Chromium Bis(Dicarbollide) Complexes: Synthesis, Structure, Properties. *Crystals* **2021**, *11*, 1118. https://doi.org/10.3390/cryst11091118

Academic Editors: Georgina Rosair and Marina Yu. Stogniy

Received: 11 August 2021
Accepted: 09 September 2021
Published: 14 September 2021

Materials and Methods

1. Synthesis of donors and anions

Tetramethyltetrathiafulvalene (TMTTF) was synthesized as described in [1, 2]. Tetramethyltetraselenafulvalene (TMTSF) was used as received. The supporting electrolytes - $(Me_4N)[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ [3] and $(Me_4N)[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{10})_2]$ [4] were prepared as described in the literature.

2. Synthesis of radical-cation salts

Radical-cation $(TMTTF)[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{11})_2]$ (**1**), $(TMTTF)[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{11})_2]$ (**2**), and $(TMTSF)_2[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{11})_2]$ (3) salts were grown by anodic oxidation the corresponding electron donors in the presence of a supporting electrolyte at ambient temperature under argon atmosphere in standard two-electrode H-cell with platinum electrodes separated by glass frit under galvanostatic conditions. The black crystals were grown on the anode. Crystals of (**1**) and (**3**) were obtained from the $(Me_4N)[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{10})_2]$ ($1.5\cdot10^{-3}$ M) – TMTTF for (**1**) or TMTSF for (**3**) (2×10^{-3} M) system using 1,1,2-trichloromethane - acetonitrile (12 : 1) mixture as a solvent. The current applied was changed discretely on 0.05 μA per day from 0.3 to 1.7 μA. The period of crystal growth was 4 weeks. Crystals of (**2**) were obtained from the $(Me_4N)[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{10})_2]$ ($7.5\cdot10^{-3}$ M) – TMTTF (2×10^{-3} M) system using dichloromethane – acetonitrile (6 : 1) mixture as a solvent. The period of crystal growth was 3 weeks. The current applied was changed discretely on 0.1 μA per day from 0.15 to 2.25 μA.

3. X-Ray diffraction study

X-ray diffraction study of $(TMTTF)[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{11})_2]$ (**1**), $(TMTTF)[3,3'\text{-}Fe(1,2\text{-}C_2B_9H_{11})_2]$ (**2**), and $(TMTSF)_2[3,3'\text{-}Cr(1,2\text{-}C_2B_9H_{11})_2]$ (3) was carried out with a Bruker APEX II CCD diffractometer (Mo-K_α-radiation, graphite monochromator, ω-scan technique). The experiment for (**2**) was carried out at room temperature, while for (**1**) and (**2**) - at 173 K. The structures were solved by direct methods followed by Fourier difference syntheses and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms using SHELX software [5, 6]. An absorption correction using the APEX2 was applied [7]. Coordinates of hydrogen atoms were defined experimentally and refined isotropically or were fixed in positions of ideal geometry. In (**2**) C(2) and B(2) atoms are disordered over two sites with the populations of 0.5 by the symmetry conditions.

4. Electric resistivity measurements

The temperature dependence of electric resistivity of single crystals was measured using four-contact-probe technique. The crystals were glued on the module with platinum thin wire of diameter 15 μkm using conducting graphite paint. The module was mounted inside of stainless-steel thin-wall tube (diameter ~ 11 mm), and the tube was slowly inserted to the transport helium jar with gradual cooling.

Table S1. Bond lenghts (Å) and selected angles (°) in.

(TMTTF)[3,3′-Cr(1,2-$C_2B_9H_{10})_2$] (**1**)

Cr(1)-C(1')	2.1731(15)
Cr(1)-C(2)	2.1755(15)
Cr(1)-C(1)	2.1785(15)
Cr(1)-C(2')	2.1801(16)
Cr(1)-B(4')	2.2319(17)
Cr(1)-B(4)	2.2381(16)
Cr(1)-B(7)	2.2433(17)
Cr(1)-B(7')	2.2434(16)
Cr(1)-B(8')	2.2765(16)
Cr(1)-B(8)	2.2794(16)
S(1)-C(5)	1.7180(15)
S(1)-C(3)	1.7424(16)
S(2)-C(5)	1.7168(16)
S(2)-C(4)	1.7419(16)
S(3)-C(6)	1.7151(16)
S(3)-C(7)	1.7327(15)
S(4)-C(6)	1.7095(15)
S(4)-C(8)	1.7306(16)
C(3)-C(4)	1.350(2)
C(3)-C(9)	1.499(2)
C(4)-C(10)	1.496(2)
C(5)-C(6)	1.394(2)
C(7)-C(8)	1.357(2)
C(7)-C(11)	1.498(2)
C(8)-C(12)	1.499(2)
C(1)-C(2)	1.603(2)
C(1)-B(4)	1.680(2)
C(1)-B(5)	1.708(2)
C(1)-B(6)	1.718(2)
C(2)-B(7)	1.683(2)
C(2)-B(11)	1.702(2)
C(2)-B(6)	1.714(2)
B(4)-B(9)	1.778(2)
B(4)-B(5)	1.778(2)
B(4)-B(8)	1.782(2)
B(5)-B(9)	1.766(2)
B(5)-B(10)	1.767(2)
B(5)-B(6)	1.772(3)
B(6)-B(10)	1.759(3)
B(6)-B(11)	1.773(3)

B(7)-B(12)	1.770(2)
B(7)-B(11)	1.771(3)
B(7)-B(8)	1.782(3)
B(8)-B(12)	1.787(2)
B(8)-B(9)	1.789(2)
B(9)-B(12)	1.779(3)
B(9)-B(10)	1.783(3)
B(10)-B(11)	1.777(3)
B(10)-B(12)	1.789(3)
B(11)-B(12)	1.775(3)
C(1')-C(2')	1.595(2)
C(1')-B(4')	1.678(2)
C(1')-B(5')	1.703(2)
C(1')-B(6')	1.715(3)
C(2')-B(7')	1.682(2)
C(2')-B(11')	1.696(2)
C(2')-B(6')	1.717(2)
B(4')-B(9')	1.767(2)
B(4')-B(5')	1.773(3)
B(4')-B(8')	1.776(3)
B(5')-B(9')	1.775(3)
B(5')-B(10')	1.776(3)
B(5')-B(6')	1.776(3)
B(6')-B(10')	1.757(3)
B(6')-B(11')	1.778(3)
B(7')-B(12')	1.771(2)
B(7')-B(11')	1.776(3)
B(7')-B(8')	1.780(2)
B(8')-B(12')	1.785(2)
B(8')-B(9')	1.785(3)
B(9')-B(12')	1.780(3)
B(9')-B(10')	1.790(3)
B(10')-B(11')	1.774(3)
B(10')-B(12')	1.786(3)
B(11')-B(12')	1.767(3)

C(1')-Cr(1)-C(2)	138.93(6)
C(1')-Cr(1)-C(1)	177.58(6)
C(2)-Cr(1)-C(1)	43.21(6)
C(1')-Cr(1)-C(2')	42.98(6)
C(2)-Cr(1)-C(2')	176.98(6)
C(1)-Cr(1)-C(2')	134.95(6)
C(1')-Cr(1)-B(4')	44.74(6)
C(2)-Cr(1)-B(4')	104.50(6)

C(1)-Cr(1)-B(4')	137.47(6)
C(2')-Cr(1)-B(4')	75.67(6)
C(1')-Cr(1)-B(4)	133.15(6)
C(2)-Cr(1)-B(4)	75.87(6)
C(1)-Cr(1)-B(4)	44.70(6)
C(2')-Cr(1)-B(4)	104.14(6)
B(4')-Cr(1)-B(4)	176.70(6)
C(1')-Cr(1)-B(7)	105.06(6)
C(2)-Cr(1)-B(7)	44.74(6)
C(1)-Cr(1)-B(7)	76.00(6)
C(2')-Cr(1)-B(7)	138.28(6)
B(4')-Cr(1)-B(7)	99.09(6)
B(4)-Cr(1)-B(7)	78.82(6)
C(1')-Cr(1)-B(7')	75.86(6)
C(2)-Cr(1)-B(7')	132.32(6)
C(1)-Cr(1)-B(7')	103.23(6)
C(2')-Cr(1)-B(7')	44.67(6)
B(4')-Cr(1)-B(7')	78.77(6)
B(4)-Cr(1)-B(7')	103.46(6)
B(7)-Cr(1)-B(7')	176.00(6)
C(1')-Cr(1)-B(8')	76.28(6)
C(2)-Cr(1)-B(8')	101.79(6)
C(1)-Cr(1)-B(8')	104.78(6)
C(2')-Cr(1)-B(8')	76.09(6)
B(4')-Cr(1)-B(8')	46.40(7)
B(4)-Cr(1)-B(8')	136.87(6)
B(7)-Cr(1)-B(8')	129.83(6)
B(7')-Cr(1)-B(8')	46.38(6)
C(1')-Cr(1)-B(8)	102.74(6)
C(2)-Cr(1)-B(8)	76.28(6)
C(1)-Cr(1)-B(8)	76.36(6)
C(2')-Cr(1)-B(8)	105.97(6)
B(4')-Cr(1)-B(8)	130.33(6)
B(4)-Cr(1)-B(8)	46.44(6)
B(7)-Cr(1)-B(8)	46.40(6)
B(7')-Cr(1)-B(8)	137.43(6)
B(8')-Cr(1)-B(8)	175.93(6)
C(5)-S(1)-C(3)	96.01(7)
C(5)-S(2)-C(4)	96.33(7)
C(6)-S(3)-C(7)	96.36(7)
C(6)-S(4)-C(8)	96.35(7)
C(4)-C(3)-C(9)	127.00(15)
C(4)-C(3)-S(1)	116.60(12)
C(9)-C(3)-S(1)	116.40(12)

C(3)-C(4)-C(10)	127.31(15)
C(3)-C(4)-S(2)	116.04(12)
C(10)-C(4)-S(2)	116.65(12)
C(6)-C(5)-S(2)	122.80(12)
C(6)-C(5)-S(1)	122.23(12)
S(2)-C(5)-S(1)	114.86(9)
C(5)-C(6)-S(4)	122.85(12)
C(5)-C(6)-S(3)	122.36(12)
S(4)-C(6)-S(3)	114.79(9)
C(8)-C(7)-C(11)	126.42(14)
C(8)-C(7)-S(3)	115.97(12)
C(11)-C(7)-S(3)	117.44(11)
C(7)-C(8)-C(12)	126.18(15)
C(7)-C(8)-S(4)	116.40(12)
C(12)-C(8)-S(4)	117.26(12)
C(2)-C(1)-B(4)	111.45(11)
C(2)-C(1)-B(5)	111.45(11)
B(4)-C(1)-B(5)	63.30(10)
C(2)-C(1)-B(6)	62.04(10)
B(4)-C(1)-B(6)	115.13(12)
B(5)-C(1)-B(6)	62.31(10)
C(2)-C(1)-Cr(1)	68.29(7)
B(4)-C(1)-Cr(1)	69.53(8)
B(5)-C(1)-Cr(1)	128.71(10)
B(6)-C(1)-Cr(1)	127.94(10)
C(1)-C(2)-B(7)	111.89(12)
C(1)-C(2)-B(11)	112.11(12)
B(7)-C(2)-B(11)	63.09(10)
C(1)-C(2)-B(6)	62.28(10)
B(7)-C(2)-B(6)	115.13(12)
B(11)-C(2)-B(6)	62.53(10)
C(1)-C(2)-Cr(1)	68.50(7)
B(7)-C(2)-Cr(1)	69.77(8)
B(11)-C(2)-Cr(1)	128.97(11)
B(6)-C(2)-Cr(1)	128.35(10)
C(1)-B(4)-B(9)	104.63(12)
C(1)-B(4)-B(5)	59.10(9)
B(9)-B(4)-B(5)	59.54(10)
C(1)-B(4)-B(8)	105.51(12)
B(9)-B(4)-B(8)	60.34(9)
B(5)-B(4)-B(8)	108.57(12)
C(1)-B(4)-Cr(1)	65.77(7)
B(9)-B(4)-Cr(1)	122.35(10)
B(5)-B(4)-Cr(1)	121.39(10)

B(8)-B(4)-Cr(1)	68.00(7)
C(1)-B(5)-B(9)	104.01(11)
C(1)-B(5)-B(10)	104.37(12)
B(9)-B(5)-B(10)	60.60(10)
C(1)-B(5)-B(6)	59.13(10)
B(9)-B(5)-B(6)	108.21(12)
B(10)-B(5)-B(6)	59.57(10)
C(1)-B(5)-B(4)	57.59(9)
B(9)-B(5)-B(4)	60.24(10)
B(10)-B(5)-B(4)	108.36(12)
B(6)-B(5)-B(4)	107.78(12)
C(2)-B(6)-C(1)	55.68(9)
C(2)-B(6)-B(10)	104.26(12)
C(1)-B(6)-B(10)	104.31(12)
C(2)-B(6)-B(5)	103.40(12)
C(1)-B(6)-B(5)	58.56(10)
B(10)-B(6)-B(5)	60.07(10)
C(2)-B(6)-B(11)	58.39(10)
C(1)-B(6)-B(11)	103.52(12)
B(10)-B(6)-B(11)	60.42(10)
B(5)-B(6)-B(11)	107.99(13)
C(2)-B(7)-B(12)	104.79(12)
C(2)-B(7)-B(11)	58.98(10)
B(12)-B(7)-B(11)	60.18(10)
C(2)-B(7)-B(8)	105.15(11)
B(12)-B(7)-B(8)	60.39(10)
B(11)-B(7)-B(8)	109.03(12)
C(2)-B(7)-Cr(1)	65.49(7)
B(12)-B(7)-Cr(1)	122.37(11)
B(11)-B(7)-Cr(1)	121.21(10)
B(8)-B(7)-Cr(1)	67.86(8)
B(7)-B(8)-B(4)	105.95(11)
B(7)-B(8)-B(12)	59.48(10)
B(4)-B(8)-B(12)	106.93(12)
B(7)-B(8)-B(9)	106.62(12)
B(4)-B(8)-B(9)	59.74(9)
B(12)-B(8)-B(9)	59.68(10)
B(7)-B(8)-Cr(1)	65.73(7)
B(4)-B(8)-Cr(1)	65.56(7)
B(12)-B(8)-Cr(1)	119.65(11)
B(9)-B(8)-Cr(1)	119.65(10)
B(5)-B(9)-B(4)	60.22(10)
B(5)-B(9)-B(12)	108.03(13)
B(4)-B(9)-B(12)	107.39(12)

B(5)-B(9)-B(10)	59.74(10)
B(4)-B(9)-B(10)	107.67(12)
B(12)-B(9)-B(10)	60.28(10)
B(5)-B(9)-B(8)	108.78(12)
B(4)-B(9)-B(8)	59.92(9)
B(12)-B(9)-B(8)	60.09(10)
B(10)-B(9)-B(8)	108.72(12)
B(6)-B(10)-B(5)	60.36(10)
B(6)-B(10)-B(11)	60.20(10)
B(5)-B(10)-B(11)	108.04(12)
B(6)-B(10)-B(9)	108.08(12)
B(5)-B(10)-B(9)	59.66(10)
B(11)-B(10)-B(9)	107.56(12)
B(6)-B(10)-B(12)	108.04(12)
B(5)-B(10)-B(12)	107.55(12)
B(11)-B(10)-B(12)	59.72(10)
B(9)-B(10)-B(12)	59.77(10)
C(2)-B(11)-B(7)	57.93(9)
C(2)-B(11)-B(6)	59.08(10)
B(7)-B(11)-B(6)	108.01(12)
C(2)-B(11)-B(12)	103.78(12)
B(7)-B(11)-B(12)	59.89(10)
B(6)-B(11)-B(12)	107.99(13)
C(2)-B(11)-B(10)	103.99(12)
B(7)-B(11)-B(10)	108.05(13)
B(6)-B(11)-B(10)	59.38(10)
B(12)-B(11)-B(10)	60.47(10)
B(7)-B(12)-B(11)	59.93(10)
B(7)-B(12)-B(9)	107.56(12)
B(11)-B(12)-B(9)	107.78(12)
B(7)-B(12)-B(8)	60.13(10)
B(11)-B(12)-B(8)	108.62(12)
B(9)-B(12)-B(8)	60.22(10)
B(7)-B(12)-B(10)	107.56(12)
B(11)-B(12)-B(10)	59.81(10)
B(9)-B(12)-B(10)	59.95(10)
B(8)-B(12)-B(10)	108.55(12)
C(2')-C(1')-B(4')	111.60(12)
C(2')-C(1')-B(5')	112.07(12)
B(4')-C(1')-B(5')	63.25(11)
C(2')-C(1')-B(6')	62.37(10)
B(4')-C(1')-B(6')	115.34(12)
B(5')-C(1')-B(6')	62.61(11)
C(2')-C(1')-Cr(1)	68.75(8)

B(4')-C(1')-Cr(1)	69.49(8)
B(5')-C(1')-Cr(1)	129.02(11)
B(6')-C(1')-Cr(1)	128.79(11)
C(1')-C(2')-B(7')	111.91(12)
C(1')-C(2')-B(11')	112.15(12)
B(7')-C(2')-B(11')	63.42(10)
C(1')-C(2')-B(6')	62.25(11)
B(7')-C(2')-B(6')	115.78(12)
B(11')-C(2')-B(6')	62.79(11)
C(1')-C(2')-Cr(1)	68.28(8)
B(7')-C(2')-Cr(1)	69.66(8)
B(11')-C(2')-Cr(1)	129.09(10)
B(6')-C(2')-Cr(1)	128.24(11)
C(1')-B(4')-B(9')	104.89(13)
C(1')-B(4')-B(5')	59.07(10)
B(9')-B(4')-B(5')	60.18(11)
C(1')-B(4')-B(8')	105.45(12)
B(9')-B(4')-B(8')	60.50(10)
B(5')-B(4')-B(8')	109.30(13)
C(1')-B(4')-Cr(1)	65.77(7)
B(9')-B(4')-Cr(1)	122.80(11)
B(5')-B(4')-Cr(1)	121.70(11)
B(8')-B(4')-Cr(1)	68.13(8)
C(1')-B(5')-B(4')	57.68(10)
C(1')-B(5')-B(9')	103.50(12)
B(4')-B(5')-B(9')	59.75(11)
C(1')-B(5')-B(10')	103.69(13)
B(4')-B(5')-B(10')	107.79(13)
B(9')-B(5')-B(10')	60.55(11)
C(1')-B(5')-B(6')	59.03(10)
B(4')-B(5')-B(6')	107.77(13)
B(9')-B(5')-B(6')	108.01(13)
B(10')-B(5')-B(6')	59.30(11)
C(1')-B(6')-C(2')	55.38(9)
C(1')-B(6')-B(10')	103.98(13)
C(2')-B(6')-B(10')	103.80(13)
C(1')-B(6')-B(5')	58.36(10)
C(2')-B(6')-B(5')	103.11(13)
B(10')-B(6')-B(5')	60.35(11)
C(1')-B(6')-B(11')	102.87(12)
C(2')-B(6')-B(11')	58.04(10)
B(10')-B(6')-B(11')	60.24(11)
B(5')-B(6')-B(11')	107.94(13)
C(2')-B(7')-B(12')	104.12(12)

C(2')-B(7')-B(11')	58.68(10)
B(12')-B(7')-B(11')	59.77(10)
C(2')-B(7')-B(8')	105.02(12)
B(12')-B(7')-B(8')	60.35(10)
B(11')-B(7')-B(8')	108.70(12)
C(2')-B(7')-Cr(1)	65.67(7)
B(12')-B(7')-Cr(1)	122.06(10)
B(11')-B(7')-Cr(1)	121.03(10)
B(8')-B(7')-Cr(1)	67.79(8)
B(4')-B(8')-B(7')	105.97(12)
B(4')-B(8')-B(12')	106.58(12)
B(7')-B(8')-B(12')	59.58(10)
B(4')-B(8')-B(9')	59.49(10)
B(7')-B(8')-B(9')	107.02(12)
B(12')-B(8')-B(9')	59.80(10)
B(4')-B(8')-Cr(1)	65.48(7)
B(7')-B(8')-Cr(1)	65.83(7)
B(12')-B(8')-Cr(1)	119.65(10)
B(9')-B(8')-Cr(1)	119.55(11)
B(4')-B(9')-B(5')	60.06(11)
B(4')-B(9')-B(12')	107.21(12)
B(5')-B(9')-B(12')	107.82(13)
B(4')-B(9')-B(8')	60.01(10)
B(5')-B(9')-B(8')	108.81(12)
B(12')-B(9')-B(8')	60.10(10)
B(4')-B(9')-B(10')	107.41(13)
B(5')-B(9')-B(10')	59.75(11)
B(12')-B(9')-B(10')	60.03(11)
B(8')-B(9')-B(10')	108.58(12)
B(6')-B(10')-B(11')	60.46(11)
B(6')-B(10')-B(5')	60.35(11)
B(11')-B(10')-B(5')	108.12(12)
B(6')-B(10')-B(12')	108.14(12)
B(11')-B(10')-B(12')	59.53(10)
B(5')-B(10')-B(12')	107.51(13)
B(6')-B(10')-B(9')	108.16(13)
B(11')-B(10')-B(9')	107.41(13)
B(5')-B(10')-B(9')	59.70(11)
B(12')-B(10')-B(9')	59.70(11)
C(2')-B(11')-B(12')	103.70(12)
C(2')-B(11')-B(10')	103.93(13)
B(12')-B(11')-B(10')	60.56(11)
C(2')-B(11')-B(7')	57.90(9)
B(12')-B(11')-B(7')	59.99(10)

B(10')-B(11')-B(7')	108.27(13)
C(2')-B(11')-B(6')	59.17(10)
B(12')-B(11')-B(6')	108.04(13)
B(10')-B(11')-B(6')	59.30(11)
B(7')-B(11')-B(6')	108.21(12)
B(11')-B(12')-B(7')	60.24(10)
B(11')-B(12')-B(9')	108.17(13)
B(7')-B(12')-B(9')	107.66(12)
B(11')-B(12')-B(8')	108.87(12)
B(7')-B(12')-B(8')	60.08(9)
B(9')-B(12')-B(8')	60.10(10)
B(11')-B(12')-B(10')	59.91(11)
B(7')-B(12')-B(10')	107.95(12)
B(9')-B(12')-B(10')	60.28(11)
B(8')-B(12')-B(10')	108.78(13)

Table S2. Bond lenghts (Å) and selected angles (°) in (TMTTF)[3,3′-Fe(1,2-$C_2B_9H_{10})_2$] (**2**).

Fe(1)-C(1)	2.0790(9)
Fe(1)-C(1)#1	2.0790(9)
Fe(1)-C(2)#1	2.1000(8)
Fe(1)-C(2)#2	2.1000(8)
Fe(1)-C(2)#3	2.1000(8)
Fe(1)-C(2)	2.1001(8)
Fe(1)-B(8)	2.1494(8)
Fe(1)-B(8)#2	2.1494(8)
Fe(1)-B(8)#1	2.1494(8)
Fe(1)-B(8)#3	2.1494(8)
S(1)-C(3)	1.7140(6)
S(1)-C(4)	1.7363(8)
C(1)-C(2)	1.6505(9)
C(1)-C(2)#2	1.6506(9)
C(1)-B(5)	1.7140(12)
C(1)-B(5)#2	1.7140(12)
C(2)-B(8)	1.7434(11)
C(2)-B(9)	1.7453(12)
C(2)-B(5)	1.7494(12)
B(9)-B(12)	1.7728(12)
B(9)-B(5)	1.7734(12)
B(9)-B(10)	1.7835(12)
B(9)-B(8)	1.7941(12)

B(10)-B(5)#2	1.7704(14)
B(10)-B(5)	1.7704(14)
B(10)-B(12)	1.7867(17)
B(5)-B(5)#2	1.7765(19)
B(8)-B(12)	1.7906(13)
B(8)-B(8)#2	1.7910(17)
C(3)-C(3)#4	1.397(2)
C(4)-C(4)#5	1.3514(17)
C(4)-C(5)	1.4992(12)

C(1)-Fe(1)-C(1)#1	180.0
C(1)-Fe(1)-C(2)#1	133.48(2)
C(1)#1-Fe(1)-C(2)#1	46.52(2)
C(1)-Fe(1)-C(2)#2	46.52(2)
C(1)#1-Fe(1)-C(2)#2	133.48(2)
C(2)#1-Fe(1)-C(2)#2	99.06(4)
C(1)-Fe(1)-C(2)#3	133.48(2)
C(1)#1-Fe(1)-C(2)#3	46.52(2)
C(2)#1-Fe(1)-C(2)#3	80.94(4)
C(2)#2-Fe(1)-C(2)#3	180.00(4)
C(1)-Fe(1)-C(2)	46.52(2)
C(1)#1-Fe(1)-C(2)	133.48(2)
C(2)#1-Fe(1)-C(2)	180.0
C(2)#2-Fe(1)-C(2)	80.94(4)
C(2)#3-Fe(1)-C(2)	99.06(4)
C(1)-Fe(1)-B(8)	81.46(3)
C(1)#1-Fe(1)-B(8)	98.54(3)
C(2)#1-Fe(1)-B(8)	131.57(3)
C(2)#2-Fe(1)-B(8)	82.95(3)
C(2)#3-Fe(1)-B(8)	97.05(3)
C(2)-Fe(1)-B(8)	48.43(3)
C(1)-Fe(1)-B(8)#2	81.46(3)
C(1)#1-Fe(1)-B(8)#2	98.54(3)
C(2)#1-Fe(1)-B(8)#2	97.05(3)
C(2)#2-Fe(1)-B(8)#2	48.42(3)
C(2)#3-Fe(1)-B(8)#2	131.58(3)
C(2)-Fe(1)-B(8)#2	82.95(3)
B(8)-Fe(1)-B(8)#2	49.24(5)
C(1)-Fe(1)-B(8)#1	98.54(3)
C(1)#1-Fe(1)-B(8)#1	81.46(3)
C(2)#1-Fe(1)-B(8)#1	48.42(3)
C(2)#2-Fe(1)-B(8)#1	97.05(3)
C(2)#3-Fe(1)-B(8)#1	82.95(3)
C(2)-Fe(1)-B(8)#1	131.58(3)

B(8)-Fe(1)-B(8)#1	180.0
B(8)#2-Fe(1)-B(8)#1	130.76(5)
C(1)-Fe(1)-B(8)#3	98.54(3)
C(1)#1-Fe(1)-B(8)#3	81.46(3)
C(2)#1-Fe(1)-B(8)#3	82.95(3)
C(2)#2-Fe(1)-B(8)#3	131.58(3)
C(2)#3-Fe(1)-B(8)#3	48.42(3)
C(2)-Fe(1)-B(8)#3	97.05(3)
B(8)-Fe(1)-B(8)#3	130.76(5)
B(8)#2-Fe(1)-B(8)#3	180.00(5)
B(8)#1-Fe(1)-B(8)#3	49.24(5)
C(3)-S(1)-C(4)	96.66(4)
C(2)-C(1)-C(2)#2	111.34(8)
C(2)-C(1)-B(5)	62.62(5)
C(2)#2-C(1)-B(5)	113.34(7)
C(2)-C(1)-B(5)#2	113.33(7)
C(2)#2-C(1)-B(5)#2	62.63(5)
B(5)-C(1)-B(5)#2	62.43(7)
C(2)-C(1)-Fe(1)	67.41(4)
C(2)#2-C(1)-Fe(1)	67.41(4)
B(5)-C(1)-Fe(1)	125.90(5)
B(5)#2-C(1)-Fe(1)	125.90(5)
C(1)-C(2)-B(8)	108.77(6)
C(1)-C(2)-B(9)	108.04(6)
B(8)-C(2)-B(9)	61.90(5)
C(1)-C(2)-B(5)	60.46(5)
B(8)-C(2)-B(5)	112.01(6)
B(9)-C(2)-B(5)	60.99(5)
C(1)-C(2)-Fe(1)	66.07(4)
B(8)-C(2)-Fe(1)	67.27(4)
B(9)-C(2)-Fe(1)	123.12(5)
B(5)-C(2)-Fe(1)	122.68(5)
C(2)-B(9)-B(12)	105.74(6)
C(2)-B(9)-B(5)	59.62(5)
B(12)-B(9)-B(5)	107.91(6)
C(2)-B(9)-B(10)	106.17(6)
B(12)-B(9)-B(10)	60.32(6)
B(5)-B(9)-B(10)	59.70(6)
C(2)-B(9)-B(8)	59.00(5)
B(12)-B(9)-B(8)	60.26(5)
B(5)-B(9)-B(8)	108.52(6)
B(10)-B(9)-B(8)	108.84(6)
B(5)#2-B(10)-B(5)	60.23(7)
B(5)#2-B(10)-B(9)#2	59.87(5)

B(5)-B(10)-B(9)#2	107.81(7)
B(5)#2-B(10)-B(9)	107.81(7)
B(5)-B(10)-B(9)	59.87(5)
B(9)#2-B(10)-B(9)	107.25(8)
B(5)#2-B(10)-B(12)	107.43(7)
B(5)-B(10)-B(12)	107.43(7)
B(9)#2-B(10)-B(12)	59.54(5)
B(9)-B(10)-B(12)	59.54(5)
C(1)-B(5)-C(2)	56.91(4)
C(1)-B(5)-B(10)	104.59(6)
C(2)-B(5)-B(10)	106.57(6)
C(1)-B(5)-B(9)	104.02(6)
C(2)-B(5)-B(9)	59.39(5)
B(10)-B(5)-B(9)	60.43(5)
C(1)-B(5)-B(5)#2	58.79(4)
C(2)-B(5)-B(5)#2	105.75(4)
B(10)-B(5)-B(5)#2	59.89(4)
B(9)-B(5)-B(5)#2	107.99(4)
C(2)-B(8)-B(12)	105.06(6)
C(2)-B(8)-B(8)#2	105.56(4)
B(12)-B(8)-B(8)#2	59.99(3)
C(2)-B(8)-B(9)	59.11(5)
B(12)-B(8)-B(9)	59.28(5)
B(8)#2-B(8)-B(9)	107.53(4)
C(2)-B(8)-Fe(1)	64.31(4)
B(12)-B(8)-Fe(1)	118.33(5)
B(8)#2-B(8)-Fe(1)	65.38(2)
B(9)-B(8)-Fe(1)	118.02(5)
B(9)#2-B(12)-B(9)	108.19(8)
B(9)#2-B(12)-B(10)	60.14(5)
B(9)-B(12)-B(10)	60.14(5)
B(9)#2-B(12)-B(8)#2	60.46(5)
B(9)-B(12)-B(8)#2	108.49(7)
B(10)-B(12)-B(8)#2	108.85(7)
B(9)#2-B(12)-B(8)	108.49(7)
B(9)-B(12)-B(8)	60.46(5)
B(10)-B(12)-B(8)	108.85(7)
B(8)#2-B(12)-B(8)	60.01(7)
C(3)#4-C(3)-S(1)	122.81(3)
C(3)#4-C(3)-S(1)#5	122.81(3)
S(1)-C(3)-S(1)#5	114.37(7)
C(4)#5-C(4)-C(5)	127.31(6)
C(4)#5-C(4)-S(1)	116.14(3)
C(5)-C(4)-S(1)	116.55(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 x,-y,z #3 -x,y,-z

#4 -x,-y-1,-z #5 x,-y-1,z

Table S3. Bond lenghts (Å) and selected angles (°) in (TMTSF)[3,3'-Cr(1,2-$C_2B_9H_{10}$)$_2$] (**3**).

Cr(1)-C(1)#1	2.175(7)
Cr(1)-C(1)	2.175(7)
Cr(1)-C(2)	2.176(7)
Cr(1)-C(2)#1	2.176(7)
Cr(1)-B(4)#1	2.226(8)
Cr(1)-B(4)	2.226(8)
Cr(1)-B(7)	2.244(8)
Cr(1)-B(7)#1	2.244(8)
Cr(1)-B(8)	2.277(8)
Cr(1)-B(8)#1	2.277(8)
Se(1)-C(7)	1.877(7)
Se(1)-C(4)	1.900(7)
Se(2)-C(7)	1.867(7)
Se(2)-C(5)	1.891(7)
Se(3)-C(8)	1.882(7)
Se(3)-C(10)	1.899(7)
Se(4)-C(11)	1.884(7)
Se(4)-C(8)	1.879(7)
C(2)-C(1)	1.619(10)
C(2)-B(7)	1.698(10)
C(2)-B(11)	1.699(11)
C(2)-B(6)	1.730(11)
C(1)-B(4)	1.676(11)
C(1)-B(5)	1.718(11)
C(1)-B(6)	1.722(11)
C(3)-C(4)	1.513(10)
C(4)-C(5)	1.344(9)
C(5)-C(6)	1.490(10)
C(7)-C(8)	1.366(11)
C(9)-C(10)	1.498(10)
C(10)-C(11)	1.352(10)
C(11)-C(12)	1.502(10)
B(4)-B(8)	1.764(12)
B(4)-B(9)	1.777(11)

B(4)-B(5)	1.789(12)
B(5)-B(6)	1.783(12)
B(5)-B(10)	1.769(11)
B(5)-B(9)	1.771(11)
B(6)-B(10)	1.762(12)
B(6)-B(11)	1.784(12)
B(7)-B(11)	1.781(12)
B(7)-B(8)	1.793(11)
B(7)-B(12)	1.792(11)
B(8)-B(12)	1.783(12)
B(8)-B(9)	1.798(12)
B(9)-B(12)	1.771(12)
B(9)-B(10)	1.780(12)
B(10)-B(11)	1.763(13)
B(10)-B(12)	1.779(11)
B(11)-B(12)	1.774(11)

C(1)#1-Cr(1)-C(1)	180.0
C(1)#1-Cr(1)-C(2)	136.3(3)
C(1)-Cr(1)-C(2)	43.7(3)
C(1)#1-Cr(1)-C(2)#1	43.7(3)
C(1)-Cr(1)-C(2)#1	136.3(3)
C(2)-Cr(1)-C(2)#1	180.0
C(1)#1-Cr(1)-B(4)#1	44.7(3)
C(1)-Cr(1)-B(4)#1	135.3(3)
C(2)-Cr(1)-B(4)#1	103.8(3)
C(2)#1-Cr(1)-B(4)#1	76.2(3)
C(1)#1-Cr(1)-B(4)	135.3(3)
C(1)-Cr(1)-B(4)	44.7(3)
C(2)-Cr(1)-B(4)	76.2(3)
C(2)#1-Cr(1)-B(4)	103.8(3)
B(4)#1-Cr(1)-B(4)	180.0
C(1)#1-Cr(1)-B(7)	103.2(3)
C(1)-Cr(1)-B(7)	76.8(3)
C(2)-Cr(1)-B(7)	45.1(3)
C(2)#1-Cr(1)-B(7)	134.9(3)
B(4)#1-Cr(1)-B(7)	100.9(3)
B(4)-Cr(1)-B(7)	79.1(3)
C(1)#1-Cr(1)-B(7)#1	76.8(3)
C(1)-Cr(1)-B(7)#1	103.2(3)
C(2)-Cr(1)-B(7)#1	134.9(3)
C(2)#1-Cr(1)-B(7)#1	45.1(3)
B(4)#1-Cr(1)-B(7)#1	79.1(3)
B(4)-Cr(1)-B(7)#1	100.9(3)

B(7)-Cr(1)-B(7)#1	180.0
C(1)#1-Cr(1)-B(8)	103.5(3)
C(1)-Cr(1)-B(8)	76.5(3)
C(2)-Cr(1)-B(8)	76.6(3)
C(2)#1-Cr(1)-B(8)	103.4(3)
B(4)#1-Cr(1)-B(8)	133.9(3)
B(4)-Cr(1)-B(8)	46.1(3)
B(7)-Cr(1)-B(8)	46.7(3)
B(7)#1-Cr(1)-B(8)	133.3(3)
C(1)#1-Cr(1)-B(8)#1	76.5(3)
C(1)-Cr(1)-B(8)#1	103.5(3)
C(2)-Cr(1)-B(8)#1	103.4(3)
C(2)#1-Cr(1)-B(8)#1	76.6(3)
B(4)#1-Cr(1)-B(8)#1	46.1(3)
B(4)-Cr(1)-B(8)#1	133.9(3)
B(7)-Cr(1)-B(8)#1	133.3(3)
B(7)#1-Cr(1)-B(8)#1	46.7(3)
B(8)-Cr(1)-B(8)#1	180.0
C(7)-Se(1)-C(4)	93.8(3)
C(7)-Se(2)-C(5)	94.3(3)
C(8)-Se(3)-C(10)	93.9(3)
C(11)-Se(4)-C(8)	94.6(3)
C(1)-C(2)-B(7)	111.7(5)
C(1)-C(2)-B(11)	111.2(6)
B(7)-C(2)-B(11)	63.2(5)
C(1)-C(2)-B(6)	61.8(5)
B(7)-C(2)-B(6)	115.7(6)
B(11)-C(2)-B(6)	62.7(5)
C(1)-C(2)-Cr(1)	68.1(4)
B(7)-C(2)-Cr(1)	69.5(4)
B(11)-C(2)-Cr(1)	128.3(5)
B(6)-C(2)-Cr(1)	127.6(5)
C(2)-C(1)-B(4)	111.0(5)
C(2)-C(1)-B(5)	111.8(5)
B(4)-C(1)-B(5)	63.6(5)
C(2)-C(1)-B(6)	62.3(5)
B(4)-C(1)-B(6)	115.2(5)
B(5)-C(1)-B(6)	62.5(5)
C(2)-C(1)-Cr(1)	68.2(4)
B(4)-C(1)-Cr(1)	69.2(4)
B(5)-C(1)-Cr(1)	129.0(5)
B(6)-C(1)-Cr(1)	128.1(5)
C(5)-C(4)-C(3)	127.3(7)
C(5)-C(4)-Se(1)	118.6(5)

C(3)-C(4)-Se(1)	114.2(5)
C(4)-C(5)-C(6)	127.2(7)
C(4)-C(5)-Se(2)	118.5(5)
C(6)-C(5)-Se(2)	114.3(5)
C(8)-C(7)-Se(2)	122.6(6)
C(8)-C(7)-Se(1)	122.5(6)
Se(2)-C(7)-Se(1)	114.9(4)
C(7)-C(8)-Se(3)	123.1(6)
C(7)-C(8)-Se(4)	122.5(6)
Se(3)-C(8)-Se(4)	114.4(4)
C(11)-C(10)-C(9)	127.2(7)
C(11)-C(10)-Se(3)	118.7(6)
C(9)-C(10)-Se(3)	114.1(5)
C(10)-C(11)-C(12)	126.5(7)
C(10)-C(11)-Se(4)	118.4(5)
C(12)-C(11)-Se(4)	115.1(6)
C(1)-B(4)-B(8)	106.5(6)
C(1)-B(4)-B(9)	105.1(6)
B(8)-B(4)-B(9)	61.0(5)
C(1)-B(4)-B(5)	59.3(4)
B(8)-B(4)-B(5)	109.5(6)
B(9)-B(4)-B(5)	59.5(4)
C(1)-B(4)-Cr(1)	66.0(4)
B(8)-B(4)-Cr(1)	68.5(4)
B(9)-B(4)-Cr(1)	123.4(5)
B(5)-B(4)-Cr(1)	122.1(5)
C(1)-B(5)-B(6)	58.9(5)
C(1)-B(5)-B(10)	103.4(6)
B(6)-B(5)-B(10)	59.5(5)
C(1)-B(5)-B(9)	103.6(6)
B(6)-B(5)-B(9)	108.2(6)
B(10)-B(5)-B(9)	60.3(5)
C(1)-B(5)-B(4)	57.0(4)
B(6)-B(5)-B(4)	106.9(6)
B(10)-B(5)-B(4)	107.0(6)
B(9)-B(5)-B(4)	59.9(5)
C(1)-B(6)-C(2)	56.0(4)
C(1)-B(6)-B(10)	103.6(6)
C(2)-B(6)-B(10)	103.4(6)
C(1)-B(6)-B(5)	58.7(5)
C(2)-B(6)-B(5)	103.8(6)
B(10)-B(6)-B(5)	59.9(5)
C(1)-B(6)-B(11)	102.7(6)
C(2)-B(6)-B(11)	57.8(5)

B(10)-B(6)-B(11)	59.6(5)
B(5)-B(6)-B(11)	107.3(6)
C(2)-B(7)-B(11)	58.4(4)
C(2)-B(7)-B(8)	104.5(5)
B(11)-B(7)-B(8)	107.6(6)
C(2)-B(7)-B(12)	103.8(6)
B(11)-B(7)-B(12)	59.6(5)
B(8)-B(7)-B(12)	59.6(5)
C(2)-B(7)-Cr(1)	65.3(3)
B(11)-B(7)-Cr(1)	120.1(5)
B(8)-B(7)-Cr(1)	67.6(4)
B(12)-B(7)-Cr(1)	121.1(5)
B(4)-B(8)-B(12)	106.6(6)
B(4)-B(8)-B(9)	59.9(5)
B(12)-B(8)-B(9)	59.3(5)
B(4)-B(8)-B(7)	106.3(5)
B(12)-B(8)-B(7)	60.1(5)
B(9)-B(8)-B(7)	107.3(6)
B(4)-B(8)-Cr(1)	65.4(4)
B(12)-B(8)-Cr(1)	119.8(5)
B(9)-B(8)-Cr(1)	119.7(5)
B(7)-B(8)-Cr(1)	65.7(3)
B(12)-B(9)-B(4)	106.6(6)
B(12)-B(9)-B(5)	108.3(6)
B(4)-B(9)-B(5)	60.6(5)
B(12)-B(9)-B(10)	60.1(5)
B(4)-B(9)-B(10)	107.1(6)
B(5)-B(9)-B(10)	59.8(5)
B(12)-B(9)-B(8)	59.9(5)
B(4)-B(9)-B(8)	59.1(5)
B(5)-B(9)-B(8)	108.8(6)
B(10)-B(9)-B(8)	108.1(6)
B(11)-B(10)-B(6)	60.8(5)
B(11)-B(10)-B(5)	108.8(6)
B(6)-B(10)-B(5)	60.7(5)
B(11)-B(10)-B(12)	60.1(5)
B(6)-B(10)-B(12)	109.1(6)
B(5)-B(10)-B(12)	108.0(6)
B(11)-B(10)-B(9)	108.0(6)
B(6)-B(10)-B(9)	108.8(6)
B(5)-B(10)-B(9)	59.9(5)
B(12)-B(10)-B(9)	59.7(5)
C(2)-B(11)-B(10)	104.7(6)
C(2)-B(11)-B(12)	104.5(6)

B(10)-B(11)-B(12)	60.4(5)
C(2)-B(11)-B(6)	59.5(5)
B(10)-B(11)-B(6)	59.6(5)
B(12)-B(11)-B(6)	108.3(6)
C(2)-B(11)-B(7)	58.4(4)
B(10)-B(11)-B(7)	109.0(6)
B(12)-B(11)-B(7)	60.5(5)
B(6)-B(11)-B(7)	109.1(6)
B(9)-B(12)-B(8)	60.8(5)
B(9)-B(12)-B(10)	60.2(5)
B(8)-B(12)-B(10)	108.8(5)
B(9)-B(12)-B(11)	107.9(5)
B(8)-B(12)-B(11)	108.3(5)
B(10)-B(12)-B(11)	59.5(5)
B(9)-B(12)-B(7)	108.5(5)
B(8)-B(12)-B(7)	60.2(4)
B(10)-B(12)-B(7)	107.8(5)
B(11)-B(12)-B(7)	59.9(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Reference

1. Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. 1.3-dithiol-2-thion-4.5-dithiolat aus schwefelkohlenstoff und alkalimetall. *Phosphorus and Sulfur* **1979**, *7*, 49-55 [doi: 10.1080/03086647808069922]
2. Simonsen, K.B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mork, P.; Kristensen, G.J.; Becher, J. Sequential functionalisation of bis-protected tetrathiafulvalene-dithiolates. *Synthesis* **1996**, 407-418 [doi: 10.1055/s-1996-4216]
3. Hawthorne, M. F.; Yong, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. π-Dicarbolyl derivatives of the transition metals. Metallocene analogs. *J. Am. Chem. Soc*. **1968**, *90*, 879-896. [doi: 10.1021/ja01006a008]
4. Ruhle, H. W.; Hawthorne, M. F. π-Dicarbolyl derivatives of chromium. Metallocene analogs. *Inorg. Chem*. **1968**, 7, 2279-2282. [doi: 10.1021/ic50069a021]
5. Sheldrick, G. M. A short history of SHELX. *Acta Cryst. A* **2008**, *64*, 112–122 [doi: 10.1107/S0108767307043930]
6. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015**, *71*, 3–8 [doi: 10.1107/S2053229614024218]
7. *APEX2 Software Package*, Bruker AXS, Madison, (Wisconsin, USA). **2005**