magnetochemistry

# New radical cation salts based on BDH-TTP donor: two stable molecular metals with a magnetic anion $[ReF_6]^{2-}$ and a semiconductor with an anion $[ReO_4]^-$

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## 1. X-ray Crystallography

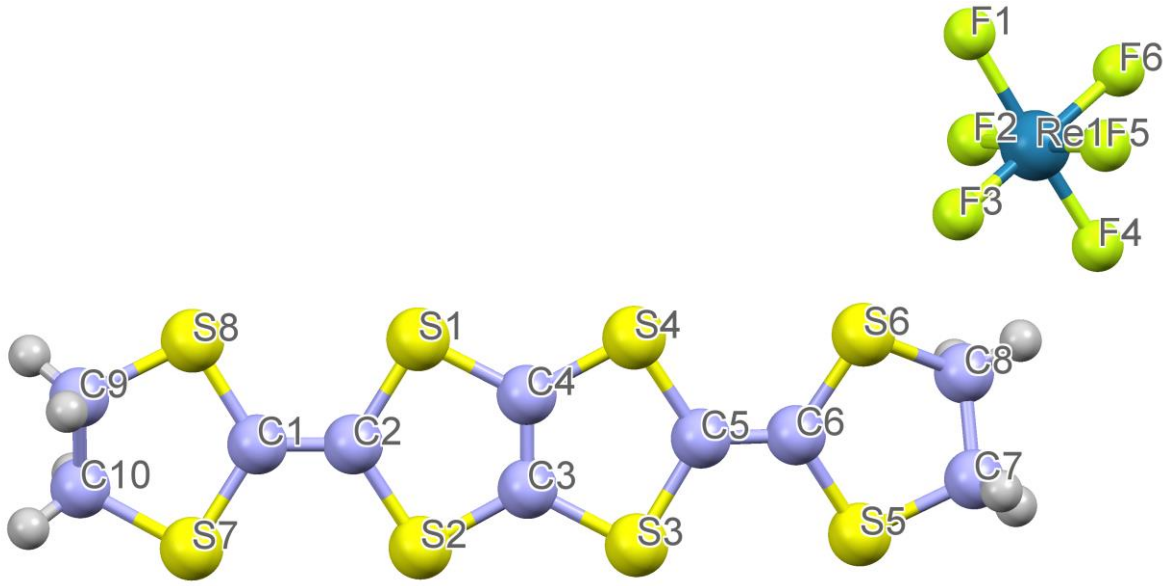


**Figure S1.** Asymmetric unit and the designations of the radical cation and anion in the crystals κ -(BDH-TTP)$_4$ReF$_6$ salt (**1**).

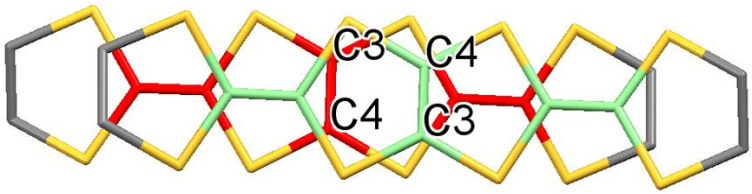


**Figure S2.** Mutual arrangement of the radical cations in the dimer and the designations of central C=C bond in the molecules κ -(BDH-TTP)$_4$ReF$_6$ salt (**1**).

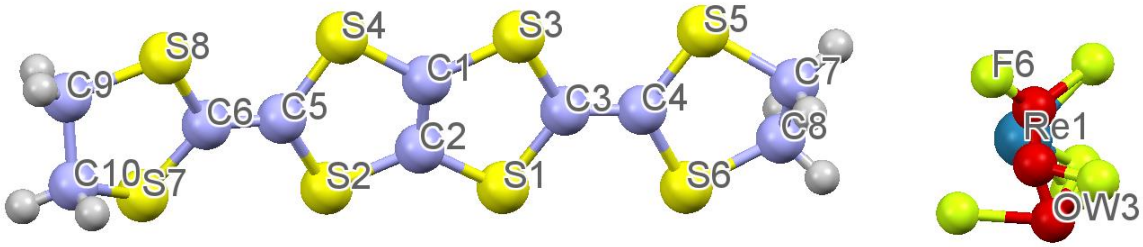


**Figure S3.** Asymmetric unit and the designations of the radical cation and anion in the crystals κ -(BDH-TTP)$_4$ReF$_6$·4.8H$_2$O (**2**).

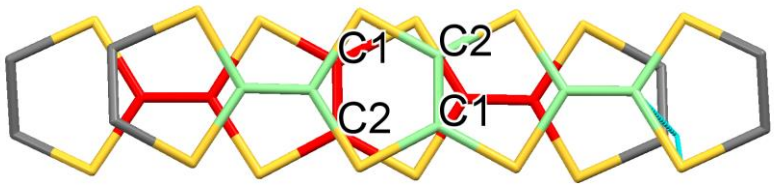


**Figure S4.** Mutual arrangement of the radical cations in the dimer and the designations of central C=C bond in the molecules κ -$(BDH\text{-}TTP)_4ReF_6 \cdot 4.8H_2O$ salt (**2**).

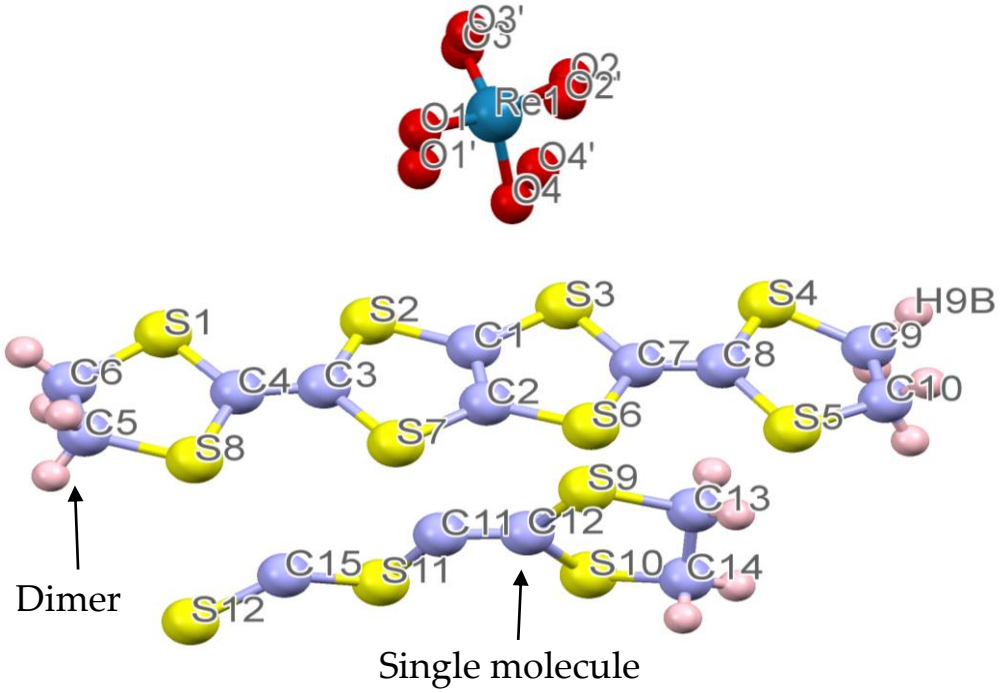


**Figure S5.** Asymmetric unit and the designations of the radical cations and anion in the crystals pseudo-κ" - $(BDH\text{-}TTP)_3(ReO_4)_2$ (**3**).

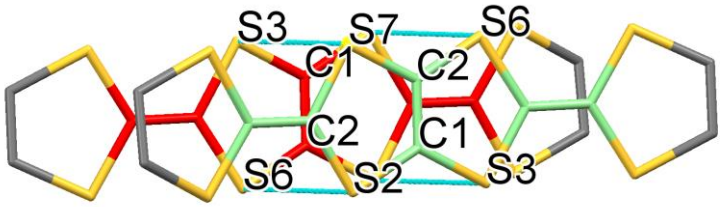


**Figure S6.** Mutual arrangement of the radical cations in the dimer and the designations of central C=C bond in the molecules of the pseudo-κ"-$(BDH\text{-}TTP)_3(ReO_4)_2$ salt (**3**). Dashed lines show shortened contacts designated as S2…S6 and S3…S7 between the radical cations in the dimer.

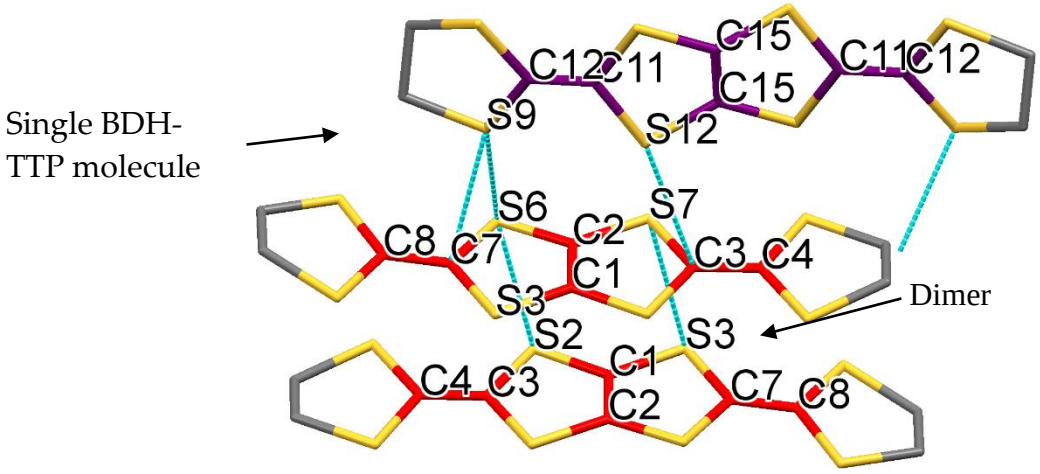


**Figure S7.** The short contacts between the radical cations inside the dimer and between the dimer and single BDH-TTP molecule.

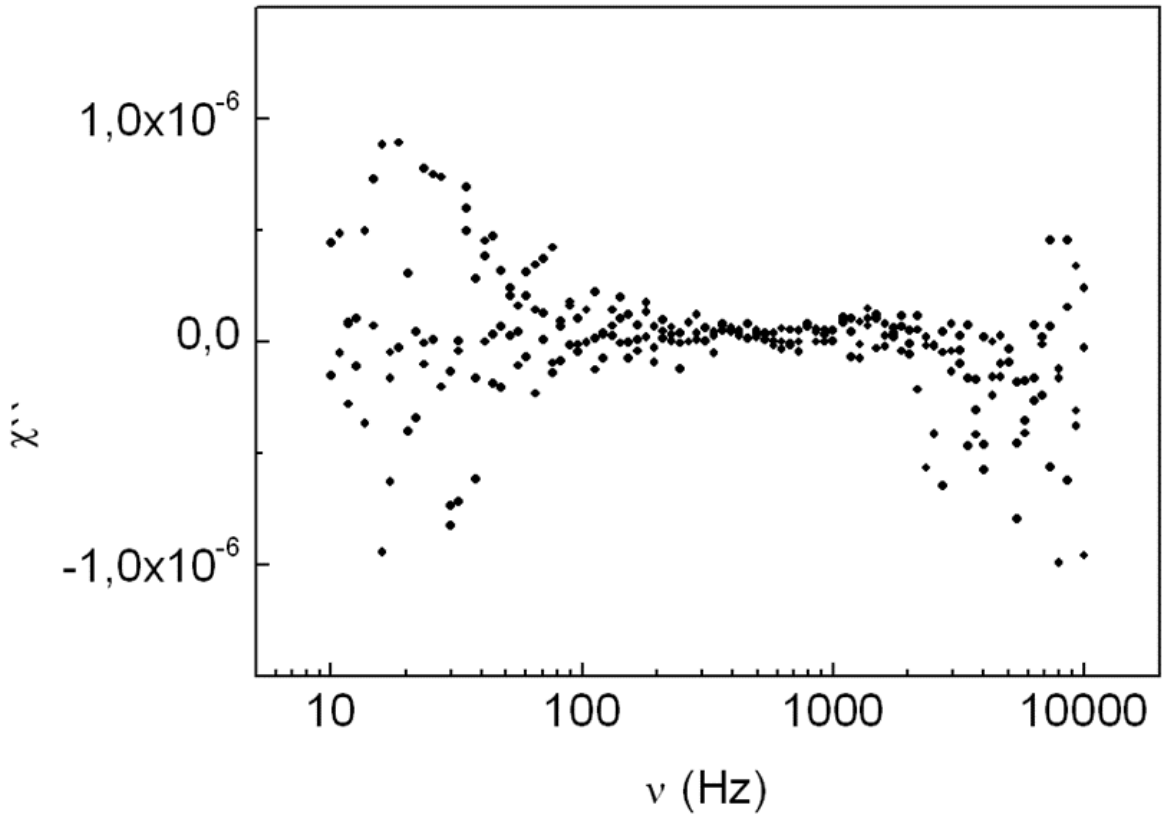


**Figure S8.** Frequency dependences of the out-of phase ($\chi''$) ac susceptibility for κ -(BDH-TTP)$_4$ReF$_6$ salt (**1**) at temperature of 2.0 K in a dc field of 0.4 Tesla

**Table S1.** Crystallographic data and refined structural parameters for the crystals **1-3**

| Identification code | 1 salt | 2 salt | 3 salt |
|---|---|---|---|
| Empirical formula | $C_{40}$ $H_{32}$ $F_6$ Re $S_{32}$ | $C_{40}$ $H_{32}$ $F_6$ $O_{4.80}$ Re $S_{32}$ | $C_{15}$ $H_{12}$ $O_4$ Re $S_{12}$ |
| Formula weight | 1838.78 | 1915.58 | 827.17 |
| Temperature | 150 K | 150 K | 100 K |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system, space group | Monoclinic, $P2_1/C$ | Monoclinic, C2/c | Triclinic, P/1 |
| a, Å | 20.0098(11) | 35.837(2) | 8.0239(4) |
| b, Å | 8.0568(4) | 7.9677(5) | 9.3028(5) |
| c, Å | 10.8367(5) | 10.8502(7) | 17.3930(10) |
| α, deg. | 90.00 | 90.00 | 96.935(5) |
| β, deg. | 92.795(5) | 99.028(9) | 97.999(5) |
| γ, deg. | 90.00 | 90.00 | 110.093(5) |
| Volume, $Å^3$ | 1744.96(15) | 3059.8(3) | 1187.41(11) |
| Calculated density, $Mg/m^3$ | 1.750 | 2.079 | 2.314 |
| Z | 4 | 2 | 2 |
| Absorption coefficient, $mm^{-1}$ | 2.746 | 3.142 | 6.210 |
| Crystal size, mm | 0.20 x 0.15 x 0.07 | 0.25 x 0.20 x 0.10 | 0.15 x 0.07 x 0.05 |
| Theta range for data collection, deg. | 3.15 to 34.07 | 3.09 to 26.07 | 2.76 to 29.07 |
| Reflections collected /unique | 27424 /7158/ [R(int) = 0.0583] | 10393 / 3028 [R(int) = 0.0568] | 10285 / 6338 [R(int) = 0.0404] |
| Data / restraints / parameters | 7158 / 7 / 226 | 3028 / 18 / 207 | 6338 / 44 / 302 |
| GOF | 1.100 | 1.005 | 1.047 |
| Final R indices [I>2sigma(I)] | R1 = 0.0929, wR2 = 0.2540 | R1 = 0.0702, wR2 = 0.1876 | R1 = 0.0468, wR2 = 0.0958 |
| R indices (All data) | R1 = 0.1182, wR2 = 0.2699 | R1 = 0.0783, wR2 = 0.1947 | R1 = 0.0620, wR2 = 0.1081 |

**Table S2.** Bond length of Re=O in a tetrahedron $[ReO_4]^-$

| Bond | Bond length, Å | Bond | Bond length, Å |
|---|---|---|---|
| Re-O1 | 1.786(7) | Re-O'1 | 1.700(9) |
| Re-O2 | 1.716(6) | Re-O'2 | 1.730(9) |
| Re-O3 | 1.732(7) | Re-O'3 | 1.734(10) |
| Re-O4 | 1.717(7) | Re-O4' | 1.771(9) |