

Isotrithionedithiolatoferrates of alkali metals

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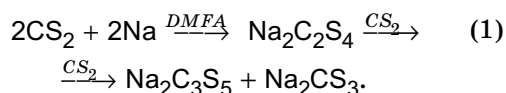
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Received July 25, 2002

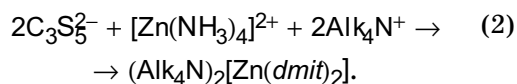
Isotrithionedithiolate iron complexes $Kt_n[Fe(dmit)_2]$ (Kt — Li, Na, K, Rb, or Cs; $0 \leq n \leq 2$) have been synthesized for the first time. It is found that mixed valence salts can be obtained basing on the isotrithionedithiolates of iron, thus, a high conductivity can be expected in those complexes. The complexes have been studied by IR spectroscopy, the electron structure thereof has been calculated using the $SW X_\alpha$ quantum chemistry method. Novel conductive synthetic materials have been concluded to can be obtained basing on isotrithionediolates of alkali metals.

Впервые синтезированы изотритиондителилатные комплексы железа $Kt_n[Fe(dmit)_2]$ (Kt — Li, Na, K, Rb, Cs; $0 \leq n \leq 2$). Обнаружена возможность получения солей смешанной валентности на основе изотритиондителилатоферратов, в результате чего можно ожидать наличие высокой проводимости в данных комплексах. Проведены ИК спектроскопические исследования и квантовохимические расчеты электронной структуры комплексов в рамках метода $PB X_\alpha$. Сделан вывод о возможности получения новых проводящих синтетических материалов на основе изотритиондителилатоферратов щелочных металлов.

In 1974, it was revealed that a carbon sulfide is reduced electrochemically in *DMF*, a mixture comprising of isotrithionedithiolate ions, $C_3S_5^{2-}$, and trithiocarbonate ones, CS_3^{2-} , is formed instead of the expected tetrathiooxalate ion $C_2S_4^{2-}$ [1]. The same result was obtained by Steinmecke when reducing carbon sulfide by sodium in the presence of dimethylformamide [2]:



The $C_3S_5^{2-}$ ion is denoted as *dmit*²⁻. The *dmit*²⁻ anions are oxidized easily in air, however, its complexes with zinc salts are stable in air and are easy to separate from the solution by tetraalkylammonium salts:



Zincate was found to be a convenient material to synthesize new tetrathiofulvalene (TTF) derivatives. For example, isotrithionedithiolate zincate with dibromoethane results in formation of 4,5-ethylenethiolo-1,3-dithiol-2-thione. Treating the latter with triethylphosphite gives bisethylenedithiolo-tetrathiofulvalene (ET). Basing on this compound, organic superconductors were obtained in 1983 with the superconducting transition temperature T_c attaining 13.5 K [3, 4].

Superconductors have been synthesized also basing on isotrithionedithiolatometalates with both "open-shell" cations (TTF-based cation-radicals) and "closed-shell" type ones (tetraalkylammonium cations). The T_c values for those materials attain 6.5 K [5], the critical current densities and magnet field ones are strongly anisotropic. So, in $\beta'-(Et_2Me_2P)[Pd(dmit)_2]_2$ complex with $T_c = 4.0$ K, the $B_{c2\parallel}/B_{c2\perp} \approx 25$ at 6.9 kbar pressure, evidencing a substan-