$\Delta^{2,2'}$-Bis-(4,5-dicyano-1,3-dithiolidene)

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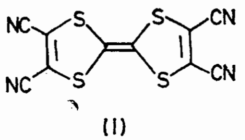
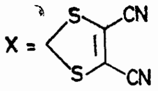
Summary $\Delta^{2,2'}$-Bis-(4,5-dicyano-1,3-dithiolidene) is prepared quantitatively by the reaction of trimethyl phosphite with 4,5-dicyano-1,3-dithiol-2-one.

$\Delta^{2,2'}$-BIS-(1,3-DITHIOLIDENES) are generally prepared by the action of a tertiary amine on the appropriate 1,3-dithiolium salt.[1,2] However, this method cannot be applied to the formation of $\Delta^{2,2'}$-bis-(1,3-dithiolidenes) substituted with strongly electron-withdrawing substituents owing to the failure to prepare the respective dithiolium salts.[3,4] Recent reports[5] of the preparation of alicyclic tetrathioethylenes by the desulphurization of trithiocarbonates with trivalent phosphorus compounds suggest an alternative approach, namely the desulphurization of 1,3-dithiol-2-thiones with trivalent phosphorus compounds. Indeed, Hartzler[6] has found that triphenylphosphine reacts with 4,5-bis(trifluoromethyl)-1,3-dithiol-2-thione giving the $\Delta^{2,2'}$-bis-(1,3-dithiolidene) (TTF) in high yield. We find, however, that the dicyano-substituted compound (II)[4] reacts with triphenylphosphine to give a mixture of products including less than 5% of (I). With trimethylphosphite in hot benzene, (II) gives (I) cleanly, but in less than 25% yield. We therefore decided to investigate the reaction of the dithiocarbonate, (III), with trimethyl phosphite.



(I)



(II) X = S
(III) X = O

When trimethyl phosphite and (III)[7] are heated under reflux in benzene for three hours, the solution slowly turns red, and on cooling, purple needles of (I) are obtained (> 95%). Recrystallization from methylene chloride gave monoclinic crystals,† m.p. 265—267: *Crystal data:* $a = 5{\cdot}52$, $b = 16{\cdot}49$, $c = 7{\cdot}08$ Å, $\beta = 109{\cdot}3$, space-group $P2_1/c$: $Z = 2$, D_c 1·67, $D_m = 1{\cdot}62$ g cm^{-3}.

A solution of (I) in dry acetonitrile containing 0·1 N $Et_4N^+ ClO_4^-$ as supporting electrolyte was analysed by cyclic voltammetry at a platinum button electrode in the manner previously described.[8] Two reversible oxidations occurred at $E_p = +1{\cdot}12$ and $+1{\cdot}22$ V, vs. s.c.e. and an irreversible reduction occurred at $E_p = -0{\cdot}87$ V. This surprising ease of oxidation in a compound with four strongly electron-withdrawing cyano substituents, emphasizes the stability of the dithiolium ion system.[1]

Compound (I) reacted with chlorine in methylene chloride to give a moisture-sensitive dichloro derivative† m.p. 170—172 (decomp.). The chlorine is removed quantitatively by reaction with 2 equiv. of silver ion in acetonitrile and a solution of the dication is thereby generated.

Treatment of this solution with 1 equiv. of (I) in CH_2Cl_2, followed by the addition of 2 equiv. of $Bu_4NNi(mnt)_2$[9] in CH_3CN gave a quantitative yield of black microcrystals of the salt $(I)^+ Ni(mnt)_2^-$. The electrical conductivity of a compacted sample of this salt was found to be 3×10^{-8} Ω^{-1} cm^{-1} [*cf* (TTF) $Ni(mnt)_2$].[10]

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† This compound gave a satisfactory elemental analysis, and mass and u.v. spectrum.

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