

NEW REACTIONS OF PHENOTHIAZINE GREEN CATIONS
AND THEIR METAL COMPLEXES¹

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Summary: New reactions of phenothiazine green cations and their complexes with copper and iron chlorides of both ionic and radicalic type leading to C- and N-derivatives of 3,10'-diphenothiazine are described.

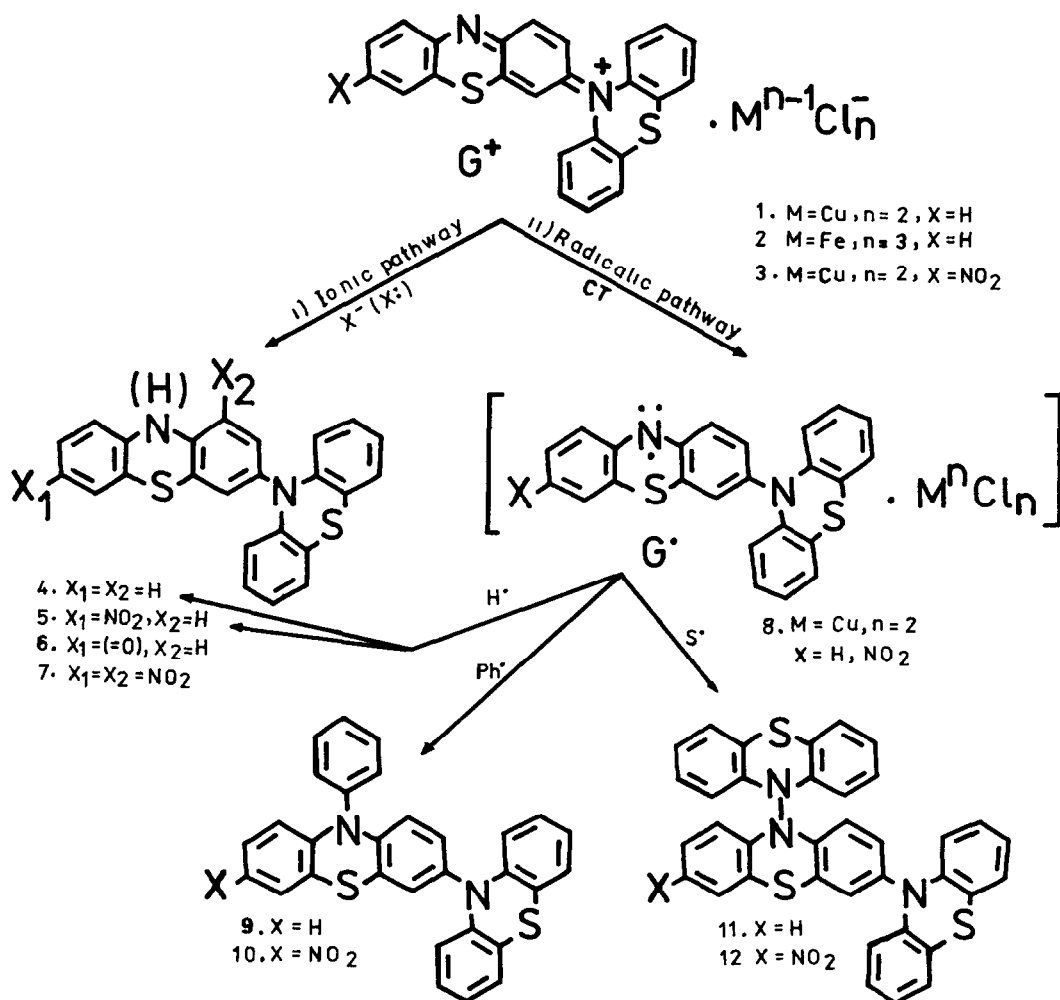
The controversy about the phantomatic "green product" (denoted by us G⁺) in the phenothiazine chemistry was relatively recently elucidated by the isolation² in solid state of 10-(3-phenothiazinylidene)-phenothiazinium perchlorate (G⁺ClO₄⁻) and the unambiguous synthesis³ of 3,10'-diphenothiazine and subsequent oxidation with Tl(III)-acetate in acetonitrile. The spectral data (visible spectrum: 450 and 630 nm²⁻⁴, for G⁺; esr-consistent with a triplet state⁴, for GH⁺⁺) and the hydrolysis (with isolating of phenothiazine 3%, phenothiazin-3-one 5%, 3,10'-diphenothiazine 40% and 3,10'-diphenothiazin-7-one 30%) were however the single reported data for G⁺.

We succeeded in isolating, for the first time, some solid metal complexes of G⁺, with general formula $X-G^+M^{n-1}Cl_n^- \leftrightarrow X-G_nM^nCl_n$, X=H, NO₂, M=Cu, Fe, n=2,3 (m.p.(decomp.)°C: 1, 143-4; 2, 231-3 and 3, over 198; visible spectrum (CHCl₃)nm: 1, 457.8, 469.3 and 3, 432.5, 453.9, 646.4; ir-no NH band-see scheme) by oxidizing phenothiazine (or its 3,10'-dimers) with corresponding metal halides (in alcohol at room temperature-see also⁵). The esr signals of 1 and 2 (polycrystalline samples) are of isotropic type ($\Delta H=15.0$ Gauss, $g=2.0069082$, for 1 and $\Delta H=116.5$ Gauss, $g=2.0150502$, for 2) and suggest a radicalic state for G⁺(G⁺↔G⁺.) in such complexes and also the existence of Cu(I) and Fe(II) ions. The cations of type G⁺ can participate to reactions in which they manifest both ionic and radicalic characteristics, the last ones formed by charge transfer, in their metal complexes: $G_n^+M^{n-1}Cl_n^- \xrightarrow{CT} G_nM^nCl_n$, transfer "at

demand" in the presence of radicalic partners.

1) Ionic pathway. At neutral or alkaline pH, in polar solvent, the G^+ cations support the attack of nucleophiles X^- (or $X:$) in the positions 7(3) and 1(9) of 10-unsubstituted phenothiazine nucleus, forming C-substituted 3,10'-dimers (see scheme) or splitting the bond C_3-N_{10}' (little favoured because of steric hindrance, cf. hydrolysis, $X:=H_2O$)⁶. Thus we performed the nitration of G^+ -complexes 1 and 3 ($NaNO_2$, DMF, room temperature, chromatography on alumina) obtaining the compounds 5 (m.p. 135-7°C from benzene, 31.32%)⁷ and 7 (m.p. 143°C; mass spectrum: $m/e=486(M^+)$, 469, 440, 394, 198, 196; ir (KBr, cm^{-1}): $\nu(NH)$, 3330). By hydrolysing 1 (in the presence of hydrazine) we isolated⁶ the compounds 4 (27.95%) and 6 (26.70%).

11) Radicalic pathway. The spin density being maximum in atom N_{10} (cf. $S\cdot$)⁸, we succeeded, for the first time, to couple the radical $G\cdot$ (3,10'-diphenothiazin-10-yl, from 8) with radical $Ph\cdot$ (by melting a mixture of 1 or 3 and $SnPh_4$, at 150-70°C, 30-45 min., followed by chromatography on alumina) to obtain the 10-phenyl-3,10'-diphenothiazines 9 (white powder, m.p. 230-1°C, 26.70%, ir-no NH band) and 10 (orange powder, m.p. 235°C, 42.19%, ir-no NH band). In chromatographic separation of 9 and 10 we revealed also the dimers 4 and 5 (by TLC) compounds resulting from coupling of radicals $S\cdot$ (phenothiazin-10-yl) and $H\cdot$ (scheme). Taking into account the ability of radicalic coupling of $G\cdot$ as well as the existence and reactivity of monomeric neutral radical $S\cdot$ 3,9,10 we succeeded to couple these two radicals (generated "in situ" by stirring a mixture of phenothiazinyl tetrachlorocuprate(II)¹¹ and $NaHCO_3$ in acetone, subsequent oxidation of the green solution with $KMnO_4$ at room temperature, when the colour turns blue) and to obtain a metal complex 11a (10,10',3',10''-triphenothiazinyl-tetrachlorocuprate(II), dark blue powder, m.p.(decomp.) about 194°C, 35.44%, visible spectrum($CHCl_3$): 686.3 nm, ir-no NH band). Its reduction with hydrazine led to 10,10',3',10''-triphenothiazine, 11, $X=H$ (white powder, m.p. about 230°C, 26.7%, ir-no NH band), a new class of oligo-phenothiazines. By nitrating 11a with $NaNO_2$ (DMF, room temperature) we obtained 7'-nitro-10,10',3',10''-triphenothiazine, 12, $X=NO_2$ (brownish-violet powder, m.p.(resin.) 194°C, 17.76%, mass spectrum: $m/e=638(M^+)$, 592, 394, 198, 196, ir-no NH band), the subsequent oxidation



with $CuCl_2$ (acetone- CCl_4 , room temperature, dilution with ligroine) leading to a complex 12a (dark blue powder, m.p.(decomp.) about $210^\circ C$, 43.87%, visible spectrum ($CHCl_3$): 693.0 nm, ir-no NH band) analogous with 11a. The nitroderivatives 10 and 12 do not yield aci-nitro colours^{6,12} pointing out the absence of iminic proton (the NH band absent in ir).

The complex 11a shows an esr signal ($\Delta H=36.2$ Gauss, $g_1=2.0102191$, $g_2=-2.0068008$, $g_3=1.9941198$, polycrystalline sample) consistent with a radical state-triphenothiazinyl, and interactions between the organic radical and copper(II) ion. The electronic spectra of 11a, 12a and also of 1 and 3 show a solvatochromism, proving the existence of the intimate pair ions stabilized by intramolecular charge transfer.

These reactions of the green cations provide that they are not final compounds but reactive intermediates in phenothiazine chemistry.

References and footnotes

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 13. Satisfactory elemental analyses were obtained for all new compounds (e.g. for 1, $C_{24}H_{15}Cl_2CuN_2S_2$ (calcd/found): C 54.39/55.87, H 2.85/3.28, N 5.28/5.44, Cl 13.38/13.59, Cu 11.98/11.61 and for 2, $C_{24}H_{15}Cl_3FeN_2S_2$: C 51.69/49.91, H 2.71/2.39, N 5.02/5.33, Cl 19.07/19.45, Fe 10.01/10.42).
 14. Mass spectra were recorded on a Varian-MAT 111 spectrometer and esr spectra on a JEOL spectrometer.
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