

## Reactions of Triethyl Phosphorothionate with Nickel (II) and Copper(II) Perchlorates

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Previous work at these and other laboratories established that interactions of metal halides with trialkyl phosphates or dialkyl alkylphosphonates, at moderately elevated temperatures, lead invariably to precipitation of polynuclear dialkyl phosphato or alkyl alkylphosphonato metal complexes and a concomitant elimination of alkyl halide [1-6]. With certain metal halides (e.g., those of the alkali metal ions,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Zr^{4+}$ ,  $Sn^{4+}$ ,  $Te^{4+}$ ), further dealkylation of the neutral phosphoryl ester, resulting in the precipitation of polynuclear metal monoalkyl- or pyro-phosphates or -phosphonates, may occur [1, 7, 8]. In contrast, during interactions of the above neutral phosphoryl esters with metal perchlorates, no dealkylation reactions are observed; in fact, numerous adducts of these neutral esters with metal perchlorates have been isolated and characterized [1, 9, 10].

More recently, we have been studying the corresponding interactions of trialkyl phosphorothionates with metal salts, and have already reported on the formation of polynuclear dialkyl thiophosphato [11] or alkyl pyrothiophosphato [12] metal complexes, during reactions of these esters with metal halides; these reactions are identical to those occurring with the neutral phosphate and phosphonate esters [11, 12]. However, during attempts at the isolation of 3d metal perchlorate adducts with triethyl phosphorothionate (teptn), it was observed that reactions leading to partial elimination of alkyl and perchlorate groups may occur. Many teptn- $M(ClO_4)_2$  ( $M = Mn, Fe, Co, Zn$ ) reactions led to the formation of soft very deliquescent solids, whose exact stoichiometries could not be deduced from analytical data. Nevertheless, Ni(II) and Cu(II) perchlorates yielded characterizable products, which are discussed in this communication.

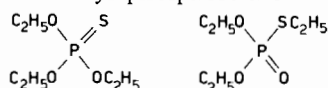
Experimentally, we followed a synthetic approach similar to that previously employed for the preparation of metal perchlorate complexes with neutral phosphate or phosphonate alkylesters [9, 10], viz.:

the hydrated metal perchlorate was treated with triethyl orthoformate (teof) at 40-50 °C for ca. 1 hr, under stirring, and then an eightfold (mol/mol of metal salt) excess of teptn (Aldrich) was added. The resulting solution was stirred for 1-2 hr at 40-50 °C and then the stirring was continued overnight at ambient temperature in a dry-box ( $N_2$  atmosphere), for evaporation of most of the supernatant liquid. The  $Ni(ClO_4)_2$  reaction product is a very hygroscopic, gelatinous, deep greenish yellow solid, analyzing (A. Bernhardt, W. Germany) as  $NiClO_4[(C_2H_5O)_2-POS] \cdot 3H_2O$  (found(calc.)%: Ni 15.81(15.39); C 12.82(12.60); H 4.46(4.23); P 7.82(8.12); S 8.10(8.41); Cl 8.94(9.30)). This complex seems to partially decompose upon washing with anhydrous diethyl ether or ligroin on the filter, and was treated as follows. After filtration, the solid was suspended in cold (0-5 °C) teof, stirred for 1-2 min, quickly filtered and transferred in a desiccator over  $CaCl_2$ .  $Cu(ClO_4)_2$ , on the other hand, formed a pale green-blue powder, insensitive to the atmospheric moisture and very sparingly soluble in polar organic solvents, analyzing as  $Cu_2(ClO_4)_3[(C_2H_5O)_2POS] \cdot 4H_2O$  (found(calc.)%: Cu 19.42(19.06); C 7.57(7.21); H 2.82(2.72); P 4.48(4.65); S 5.05(4.81); Cl 16.02(15.95)).

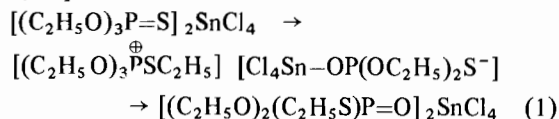
Characterization studies were performed by methods described elsewhere [9]. Electronic spectra (on Nujol mulls) and magnetic susceptibility measurements (300 °K) are suggestive of coordination numbers six for the  $Ni^{2+}$  ( $10^6 \chi_A^{cor}$  4201 cgsu;  $\mu_{eff}$  3.19  $\mu_B$ ; (d-d) spectrum, nm: 385s, b, 410s, sh, 597m, 683m, 1150w, b) and four (square-planar) for the  $Cu^{2+}$  ( $10^6 \chi_A^{cor}$  1413 cgsu;  $\mu_{eff}$  1.84  $\mu_B$ ; (d-d) spectrum, nm: 588vs, b, 657vs, sh, 816m, sh, 995w-m, sh) complex [7, 9, 10]. A  $10^{-3} M$  solution of the  $Ni^{2+}$  complex in nitromethane shows a molar conductivity of 43  $\Omega^{-1} cm^2 mol^{-1}$  at 25 °C, indicative of a behavior intermediate between those of a non- and a 1:1-electrolyte [13]. However, this  $\Lambda_M$  value is apparently due to some dissociation of the complex in nitromethane, since the ir spectrum of the solid  $Ni^{2+}$  complex suggests that it comprises exclusively coordinated perchlorato [14, 15] and diethylthiophosphato (detp) [11, 16-18] groups, viz. ( $cm^{-1}$ ):  $ClO_4$  modes:  $\nu_3$  1137vs, 1043vs;  $\nu_1$  923m;  $\nu_4$  644s, 626s;  $\nu_2$  471m, b; detp modes:  $\nu_{P-O}$  1167vs,  $\nu_{P-S}$  592vs,  $\nu_{P-O-(C)}$  1027s, sh. The spectrum of the Ni(II) complex does not show any evidence in favor of the presence of ionic  $ClO_4$  (e.g., very strong absorption at 1120-1060  $cm^{-1}$  ( $\nu_3$  region) is not observed). In contrast, the Cu(II) complex comprises both ionic and coordinated perchlorate, i.e. ( $cm^{-1}$ ):  $ClO_4$  modes:  $\nu_3$  1176vs, 1137vs, 1090vs, vb, 1041vs, sh;  $\nu_1$  935m-s;  $\nu_4$  655s, sh, 634s, 621vs, 604s, sh;  $\nu_2$  458m, b; detp modes:  $\nu_{P-O}$  1163vs,  $\nu_{P-S}$  597s,

$\nu_{\text{P-O-C}}$  1026s, sh. The ir spectra of both new complexes exhibit also bands demonstrating the presence of aqua ligands ( $\nu_{\text{OH}}$  at ca. 3350,  $\delta_{\text{H-O-H}}$  at ca. 1625  $\text{cm}^{-1}$ ) [19], and are devoid of absorptions associated with unidentate (P=O oxygen or P=S sulfur) coordinated detp ( $\nu_{\text{P=O}}$  region 1250–1190 [1, 10, 11, 16, 20];  $\nu_{\text{P=S}}$  regions 830–790 and 650–600  $\text{cm}^{-1}$  [1, 11, 16, 18, 20–22]). As regards the fundamental vibrational modes of the  $\text{ClO}_4$  group, the Ni(II) complex appears to contain unidentate ( $-\text{OClO}_3$ ) ligands, and the Cu(II) compound ionic  $\text{ClO}_4$  and bidentate, most probably bridging ( $-\text{OCl}(\text{O}_2)\text{O}-$ ; *vide infra*) perchlorato groups [14, 15]. Finally, the ir spectra of both complexes at 450–200  $\text{cm}^{-1}$  are characterized by very poorly resolved weak to medium absorptions, which make even tentative metal–ligand band assignments practically impossible.

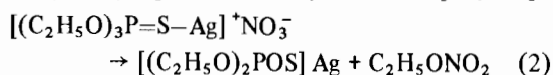
The neutral thiophosphate ethylester may exist in either of two tautomeric forms, namely teptn(I) and triethyl phosphorothiolate (teptl; II). It is well



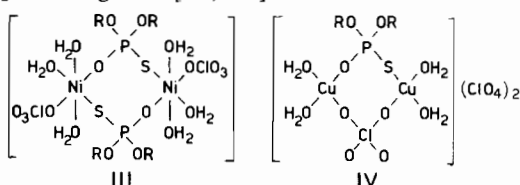
established that, whereas teptn behaves as a sulfur ligand in its adducts with salts of soft (class b) metal ions ( $[(\text{C}_2\text{H}_5\text{O})_3\text{P}=\text{S}]_n\text{MX}_m$ ; M =  $\text{Pt}^{4+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Hg}^{2+}$ ; X = Cl,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{BF}_4$ ) [23–26], it is invariably converted to the thiol tautomer (teptl), upon adduct formation with salts of hard (class a) metal ions, behaving as an oxygen ligand ( $[(\text{C}_2\text{H}_5\text{O})_2(\text{C}_2\text{H}_5\text{S})\text{P}=\text{O}]_n\text{MX}_m$ ; M =  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Sb}^{5+}$ ; X = Cl, Br) [23, 26, 27]. Reaction (1) was proposed for this tautomerism in presence of  $\text{SnCl}_4$  [23, 27]:



Another interesting aspect of the chemistry of the ligand is that, in addition to numerous examples of dealkylation in the presence of metal halides [11, 12, 23, 25], the silver nitrate complex can decompose, yielding  $\text{Ag}(\text{detp})$  and methyl nitrate [23, 24]:



The overall evidence suggests that, in both new complexes, detp is exclusively bidentate bridging, O, S-bonded, as is quite common with coordinated  $\text{R}_2\text{POS}^-$  ligands [11, 28]. The binuclear structures



(III) and (IV) appear to be most likely for the Ni(II) and Cu(II) complexes, respectively (R =  $\text{C}_2\text{H}_5$ ). In connection with the mechanism of formation of these compounds, the initial step undoubtedly involves coordination of the neutral ester as a unidentate S-ligand. Whether subsequent tautomerization of teptn to teptl, and formation of an O-bonded intermediate complex, as in (1), occurs is not clear from the evidence available. In fact, neither the nature of the final products obtained, which comprise bidentate O, S-bonded detp, nor the hard or soft acid character of the  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions, which are borderline cases with maybe slightly greater affinity for S- rather than O-ligands [29], allow any predictions in this connection. Whichever is the case, the next step presumably involves formation of a second bond between the neutral ester and a neighboring metal ion, leading to a dimeric intermediate (*i.e.*,  $\text{M}-[\text{S}-\text{P}(\text{OC}_2\text{H}_5)_2-\text{O}(\text{C}_2\text{H}_5)]_n-\text{M}$  or  $\text{M}-[\text{S}(\text{C}_2\text{H}_5)-\text{P}(\text{OC}_2\text{H}_5)_2-\text{O}]_n-\text{M}$  ( $n = 2$  for M = Ni;  $n = 1$  for M = Cu), respectively) [1, 6, 30]. The final dealkylation reaction is analogous to (2) resulting in the formation of the new complexes (III) or (IV) and elimination of one ethyl perchlorate per neutral ester molecule. It should be noted at this point that the rather uncommon alkyl perchlorates have been also observed as products of reactions between  $\text{AgClO}_4$  and alkyl halides [31] or alcohols and anhydrous  $\text{HClO}_4$  [32].

Prior to concluding, it is worth mentioning that the fact that neutral phosphoryl esters do not undergo any dealkylation in the presence of 3d metal perchlorates, while their thiophosphoryl analogs are dealkylated under the same, relatively mild, experimental conditions, may be implying that the teptn to teptl tautomerization takes place, since it is established that P–S–C bonds are more labile than P–O–C bonds [1, 33]. On the other hand, the fact that elimination of ethyl nitrate occurs in reaction (2), which undoubtedly involves C–O bond scission, since the ligand is S-bonded to the soft  $\text{Ag}^+$  ion, makes the preceding statement somewhat questionable. These laboratories consider the clarification of this aspect of the reactions herein reported as interesting enough as to justify the continuation of the present work to include reactions of teptn with the perchlorate salts of selected hard, soft and borderline metal ions in the immediate future.

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