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Facilitation of the Syntheses of Metal Perchlorate Complexes with Purines from Non-aqueous Suspensions by Substituting Ethyl Acetate for Ethanol in the Interaction Medium

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Complexes of metal perchlorates with purine (puH), adenine (adH) or guanine (guH) were relatively easily prepared in good yields by these laboratories, by allowing mixtures of ligand and salt to interact in a 7:3 (v/v) mixture of ethanol and triethyl orthoformate (teof) [1–3]. The complexes of puH were precipitated immediately upon mixing solutions of ligand and salt in this medium [1], while in the cases of adH and guH solid complexes gradually formed by refluxing the reaction mixture for several days [2, 3]. The same procedure was successful in isolating the corresponding complexes between $Cu(ClO_4)_2$ and xanthine (xnH), hypoxanthine (hxH) [4], theophylline (tpH), theobromine (tbH) and caffeine (caf) [5]. When we attempted, however, to obtain the complexes of the latter five ligands with other 3d metal perchlorates ($M = Cr^{3+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}), we encountered difficulties in isolating precipitates in sufficient yields or even at all. Thus, with L = xnH or hxH, solid products were obtained only after long refluxive treatment in ethanol–teof, ranging from 5 days to 2 months, while the yields were generally low (less than 10–20% of the theoretical). The xnH complexes prepared in this way were reported recently in a letter [6]. On the other hand, with L = tpH, tbH or caf, the same procedure failed to produce solid complexes, regardless of the length of the refluxive step [7].

It was of interest to us to complete our synthetic and characterization work on the complexes formed by interaction of xnH, hxH or substituted xanthines with metal perchlorates. Accordingly, alternative interaction media were sought for our preparative method. Following screening studies of several organic solvents or diluents, including aliphatic and aromatic esters, higher alcohols, ketones and ethers, we concluded that best results are obtained when ethyl acetate is used. This ester has been used successfully in the past for the preparation of metal complexes with biologically important pyrimidines (uracil, thymine, cytosine) and their nucleosides [8]. The new synthetic procedure developed is much simpler than our previous preparative method [1–6], and can be also used for the faster preparation of adH or guH complexes with metal perchlorates in higher yields, relative to those obtained when ethanol-teof is used as the interaction medium. The new method is as follows: 1.2 mmol hydrated metal perchlorate is dissolved in a mixture of 35 ml ethyl acetate and 15 ml of the dehydrating agent [9] teof, 2.5 mmol ligand (xnH, hxH, tpH, tbH, caf, adH or guH) are added, and the resultant mixture is refluxed for 6 h or until no further significant change in appearance is noted. After cooling to ambient temperature, 15–20 ml anhydrous diethyl ether are added to the mixture and the volume is then reduced to *ca.* 20 ml by heating under reduced pressure. At this point, with the exception of L = caf, solid precipitates in good yields are generally obtained (these precipitates were separated by filtration, washed with diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$). With L = caf, the solid residues obtained were apparently unreacted mixtures of ligand and salt, with the exception of $Cu(ClO_4)_2$ which yielded the previously reported [5] $Cu(caf)_2(ClO_4)_2$ complex in 90% yield. Some of the tpH adducts obtained by the new method were already reported in a preliminary communication [7]. They are of the $M(tpH)_2(ClO_4)_2\cdot xH_2O$ ($M = Mn$, Zn, $x = 0$; M = Ni, $x = 2$) type and were isolated in yields ranging between 47–75% [7]. 2:1 tpH to metal salt adducts were also isolated for $M = Co^{2+}$ (purple solid), Fe^{2+}, Fe^{3+} (brown oils) and Cr^{3+} (khaki green solid) in yields ranging between 60–97%. The corresponding tbH 2:1 adducts with metal perchlorates are generally solids, as follows (color-yield in parentheses): M = Cr^{3+} (light green-78%), Mn^{2+} (cream white-59.2%), Fe^{2+} (mustard yellow-69.2%), Fe^{3+} (mustard yellow-90.6%), Co^{2+} (light purple to grayish-90.1%), Ni^{2+} (light green-100%), Zn^{2+} (white-69.2%). Characterization studies of the preceding complexes are nearing completion and will be reported in forthcoming publications. Solid metal complexes of xnH or hxH with metal perchlorates were relatively recently prepared from ethyl acetate–teof. Analyses of these complexes are pending, but it can be stated that in all cases investigated (*i.e.*, $M = Cr^{3+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}), both xnH and hxH afforded crystalline precipitates in yields ranging between 60–100%. Finally, we were also successful in isolating the previously prepared from ethanol–teof complexes $Cu(gu)_2\cdot H_2O$ [4], $Fe(adH)_2(ad)(ClO_4)_2$ [2] and $CuL_2(ClO_4)_2$ (L = tpH or tbH) [5] in better yields (exceeding 90%) by using ethyl acetate-teof as the

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preparation medium. In conclusion, ethyl acetate-teof is a substantially more advantageous interaction medium than ethanol–teof for the syntheses of complexes of purines with metal perchlorates, as far as both yields and speed of complex precipitation are concerned. We plan to investigate the use of the ethyl acetate–teof system for the preparation of the complexes of the same purines with various metal salts (halides, nitrates, thiocyanates, etc.) in the near future.

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