Neutral Phosphonate and Phosphate Ethylesters as Preparation Media for Adducts of Metal Salts with Stronger Ligands

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Metal complexes with neutral phosphonate or phosphate alkylesters are generally difficult to precipitate as solids. Their preparation involves lengthy and tedious synthetic procedures [1–4], often requiring the use of dehydrating agents [1, 2], such as triethyl orthoformate [5]. Solutions of 3d metal salts (chlorides, perchlorates, nitrates, *etc.*) in neutral phosphonate or phosphate alkylesters are indefinitely stable at room temperature; these are, of course, solutions of the phosphoryl ester solvate of the metal salt, which does not, however, show any tendency to precipitate. On the other hand, these esters are generally fairly weak ligands; for instance, dimethyl methylphosphonate ($(CH_3O)_2CH_3P{=}O$) shows a Dq of 1440 cm^{-1} towards octahedral Cr^{3+} [1], while trimethyl phosphate ($(CH_3O)_3P{=}O$) exhibits an even lower Dq (1417 cm^{-1}) towards the same metal ion [2]; in addition, the Dq of $[Ni(tmp)_5(OH_2)](ClO_4)_2$ is only 770 cm^{-1} [2]. These observations suggested to us that neutral esters of the above types might be useful as solvents for the rapid precipitation of adducts of metal salts with stronger neutral ligands. Past experience with a variety of neutral phosphonate and phosphate alkylesters has shown that the synthesis of well-defined transition metal solvates with ethylesters of these types is among the most difficult to accomplish [6]. It was, therefore, felt that use of esters such as diethyl ethylphosphonate ($(C_2H_5O)_2C_2H_5P{=}O$; deep) and triethyl phosphate ($(C_2H_5O)_3P{=}O$; tep) as preparation media for metal complexes with stronger ligands than these phosphoryl esters would be advantageous. Research in this direction was undertaken and it was established that the instantaneous precipitation of a wide variety of adducts of 3d metal chlorides in excellent yields, from either a deep or a tep solution of the metal salt, occurs upon addition of the stronger ligand. It was also found that the same complexes precipitate, regardless of whether deep or tep is used as solvent. The present letter deals with our research in this direction.

The simple synthetic procedure was as follows: 2 mmol of metal chloride hydrate ($M^{n+} = Cr^{3+}, Co^{2+}, Ni^{2+}$ or Cu^{2+}) are dissolved in 20 ml deep or tep. Then, an excess of the stronger ligand (5–10 ml) is added, and precipitation of the adduct occurs immediately. All these operations are performed at room temperature, while stirring is usually not required after the complete dissolution of the metal chloride in deep or tep. The overall procedure (*i.e.*, dissolution of the metal salt followed by precipitation of the adduct) takes from 1 to 5 minutes. The precipitate is separated by filtration, washed with the appropriate washing agent (selected from the literature for each particular ligand) and stored *in vacuo* over anhydrous $CaSO_4$.

Initially, we attempted the preparation of pyridine (py) complexes (Dq of $Ni(py)_4Cl_2$ = 1087 cm^{-1} [7]) with Cr^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} chlorides. By employing the above synthetic procedure, $Cr(py)_3Cl_3$ (green), *trans*-$Co(py)_4Cl_2$ (pink), *trans*-$Ni(py)_4Cl_2$ (light blue) and $Cu(py)_2Cl_2$ (blue) were precipitated in *ca.* 100% yields. The dried, solid complexes are very pure, as suggested by analyses (*e.g.*, analysis of $Ni(py)_4Cl_2$, found (calc.)%: C 53.73(53.86); H 4.63 (4.52); N 12.46(12.56); Ni 13.27(13.16), Cl 16.03 (15.90); P 0.00; it should be noted here that none of the N-ligand complexes herein reported contains detectable amounts of phosphorus from deep or tep). The properties of the py complexes prepared are identical to those previously reported for these compounds [7–9]. Subsequently, we attempted the preparation of some $NiCl_2$ complexes with substituted pyridines. With *meta*- or *para*-substituted pyridines, we easily obtained the complexes described in the literature in yields of 80–100%, *viz.* light blue or green NiL_4Cl_2 (L = 3- or 4-picoline, 3,4- or 3,5-lutidine) [7, 10]. However, with *ortho*-substituted pyridines, pale green hydrated complexes of the $NiLCl_2 \cdot 3H_2O$ type were precipitated in low yields (L = 2-picoline, 2,4- or 2,6-lutidine, 2,4,6-collidine). This is presumably due to the fact that the isolation of anhydrous complexes with these sterically hindered ligands reportedly requires strictly anhydrous conditions [7]. Complexes of the types NiL_2Cl_2 (L = 2-picoline, 2,4- or 2,6-lutidine) [7, 11, 12], $Ni(2,4,6\text{-collidine})_4Cl_2$ [7] and $NiLCl_2$ (L = 2-picoline, 2,6-lutidine, 2,4,6-collidine) [7] were previously reported. We also explored the possibility of precipitating a $NiCl_2$ adduct with 2,6-di-tert-butylpyridine, but the light green precipitate we obtained was essentially hydrated $NiCl_2$, containing about 1.25% of the amine (C 1.02%, N 0.1%).

The next project concerned attempts at the precipitation of $NiCl_2$ complexes with N-ligands, containing exocyclic rather than ring nitrogen sites. The light blue or green NiL_2Cl_2 (L = aniline, *m*-toluidine, N,N-

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dimethylaniline) complexes were readily precipitated by our synthetic method in yields exceeding 90%. Analyses were again quite satisfactory (*e.g.*, Ni(aniline)$_2$Cl$_2$, found (calc.)%. C 45.91(45.63); H 4.52 (4.47); N 4.26(4.43); Ni 18.70(18.59); Cl 22.23 (22.45)), while the properties of our precipitates were identical to those reported in the literature [9, 13, 14]. Anilines are generally ligands of comparable strength to that of py (*e.g.*, Dq of Ni(aniline)$_4$Br$_2$ is 1064 cm^{-1}) [13].

We then investigated a relatively strong neutral oxygen ligand, namely, N,N-dimethylformamide (dmf) (Dq of 850–870 cm^{-1} towards octahedral Ni^{2+} [15, 16]). The light green Ni(dmf)$_2$Cl$_2$·3H$_2$O (analysis, found (calc.)%: C 22.08(21.85); H 5.96(6.11); N 8.59(8.49); Ni 18.10(17.80); Cl 21.20(21.49); P 0.00) was precipitated in 100% yield. The properties of this complex are analogous to those of the previously reported Ni(dmf)$_2$Br$_2$·3H$_2$O [17] and Ni(N,N-dimethylacetamide)$_2$Br$_2$·3H$_2$O [18]. The function of the carbonyl oxygen as the ligand site is obvious from shifts of both $\nu_{C=O}$ and $\delta_{N-C=O}$ to lower and higher wavenumbers, respectively ($\Delta\nu_{C=O} = -31$ cm^{-1}; $\Delta\delta_{N-C=O} = +26$ cm^{-1}) [15, 17, 18]. Since Ni(dmf)$_3$Cl$_2$ is a known compound [19], we attempted to precipitate this complex by using a solution of 2 mmol of triethyl orthoformate-pretreated [5] NiCl$_2$ hydrate in 7 ml deep, and adding a very large excess (*ca.* 30 ml) of dmf, however, Ni(dmf)$_2$Cl$_2$·3H$_2$O was obtained in this case too. Finally, attempts to precipitate a complex with a significantly weaker O-ligand, such as dimethyl sulfoxide (dmso, Dq towards octahedral Ni^{2+} = 773–805 cm^{-1} [16, 20]), resulted in mixed-ligand complex precipitates, *i.e.*, Ni(dmso)$_n$L$_{2-n}$Cl$_2$·xH$_2$O (L = deep or tep; $n > 1$) in low yields. This shows the limitations of the method reported when ligands of comparable strength to that of the solvent are used.

Current work in the field involves studies aimed at refinement of the method, so that complexes at various ligand to metal ratios can be isolated and conditions allowing operation at a strictly anhydrous environment are developed; work with P-, As-, Sb-, S-, Se-, Te-, *etc.* ligands is also in progress. It is also worth noting that, in addition to our synthetic experiments involving use of a large excess of the ligand, it was established that the metal chloride complexes with pyridine, aniline and dmf are also readily precipitated in good yields when the amount of ligand is only in slight excess over the stoicheiometrically required amount. Immediate, but only partial precipitation occurs in this case; completion of the precipitation is accomplished by brief stirring of the ester–metal salt–ligand mixture, and then allowing the mixture to stand still for a few minutes before filtering.

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