

Complexation of 4-N,N-dimethylaminopyridine with Tin(II), Uranium(IV) and Thorium(IV)

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The reactions of 4-N,N-dimethylaminopyridine with SnCl_2 , UCl_4 and $\text{Th}(\text{NO}_3)_4$ result in the formation of complexes in which coordination occurs through heterocyclic nitrogen.

INTRODUCTION

4-N,N-dimethylaminopyridine (DMAP) is a versatile reagent and finds wide applications in organic synthesis¹. Only a few metal complexes of DMAP like $\text{CoCl}_2\cdot\text{DMAP}$ and $\text{CoBr}_2\cdot\text{DMAP}$ ² are known. In this paper, we present the preparation and characterization of the complexes of DMAP with SnCl_2 , UCl_4 and $\text{Th}(\text{NO}_3)_4$ which can be employed for the preparation of bimetallics. The latter are considered to possess catalytic activity³. Tin(II) halides form numerous complexes with amines. The lone pair of electrons on tin in such complexes can be made to coordinate to Lewis acids resulting in donor-acceptor complexes⁴. $\eta^5\text{-C}_5\text{H}_5\text{UCl}$ had been shown to form unstable green complexes with aluminium chloride⁵. Nitrate ion can act as a bridging ligand⁶. Thus Sn(II), U(IV) and NO_3^- derivatives are suitable for the formation of bimetallics. In order to prepare stable bimetallics we obtained the complexes of these metals with DMAP as a first step.

EXPERIMENTAL

Tin(II) chloride was obtained by dehydration of $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ using acetic anhydride as published⁷. The amount of tin was estimated by titration with potassium iodate⁸ and the amount of chlorine was found by back titration with ammonium thiocyanate employing Volhard's method⁸. Anal. calc. for SnCl_2 : Sn 62.6, Cl 37.4%. Found: Sn 61.9, Cl 37.3%. The IR spectrum of anhydrous SnCl_2 contained no peak in the region of 3500 cm^{-1} , indicating the absence of H_2O . UCl_4 was obtained by the reaction of uranyl nitrate by hexachloropropene as reported⁹. It was analyzed for chlorine by Volhard's method and uranium by titration with cerium(IV) sulphate⁸. Anal. calc. for UCl_4 : U 62.7, Cl 37.4%. Found: U 62.3, Cl 36.4%. The solvents were dried using standard methods¹⁰. DMAP (Fluka) was used without further purification. The IR spectra were recorded as KBr pellets using Shimadzu infrared spectrophotometer, IR-435. The ¹H NMR and UV-Vis spectra were obtained using Hitachi R-600 (60 MHz) instrument and UVIDEC-430 B double beam spectrophotometer respectively. Samples for UV and visible spectra were prepared in methanol and water respectively and immediately used. Conductivity data were obtained using ELICO MHOS pH meter (Model PE-133).

Preparation of Complexes

(1) $\text{SnCl}_2 \cdot \text{DMAP}$: To a solution of SnCl_2 (0.5093 g, 2.69 mmol) in dry tetrahydrofuran (THF), DMAP (0.3288 g, 2.70 mmol) was added in a current of nitrogen. The mixture was kept stirring for 2 h. The solvent was removed *in vacuo*. The resulting solid was then washed with petroleum ether and dried in high vacuum to give a colourless product. Yield 0.8 g (96%). The amounts of tin and chlorine were estimated following the procedure used for SnCl_2 .

Anal: Calc. for $\text{SnCl}_2 \cdot \text{DMAP}$ (311.8): Sn 38.1, Cl 22.7%; Found: Sn 37.7, Cl 21.2%.

IR ν_{max} (cm^{-1}): 3080(m), 2910(m), 1644(s), 1560(s), 1440(m), 1390(s), 1215(s), 1080–1065(w), 994(s), 938(m), 744(w), 504(b).

(2) $\text{UCl}_4 \cdot \text{DMAP}$: To a solution of UCl_4 (1.034 g, 2.72 mmol) in 10 mL dry THF, 0.3242 g (2.65 mmol) of DMAP was added. The mixture was kept stirring for 3 h. The solvent was then removed *in vacuo* and the product washed with petroleum ether and dried in high vacuum to give a pale green solid. Yield 0.98 g (95%). The amount of uranium and chloride were estimated as mentioned previously for UCl_4 .

Anal: Calc. for $\text{UCl}_4 \cdot \text{DMAP}$ (501.8): U 47.4, Cl 28.3%; Found: U = 47.4, Cl = 28.2%.

IR ν_{max} (cm^{-1}): 3275(m), 2900(b), 1645(s), 1560(b), 1460(b), 1378(s), 1210(s), 1115(b), 1055(b), 998(s), 830(w), 770(w), 735(m), 505(m).

(3) $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O} \cdot \text{DMAP}$: To a solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (1.0084 g, 1.77 mmol) in 10 mL THF, 0.2159 g (1.77 mmol) of DMAP dissolved in THF was added in small aliquots. A milky-white precipitate was formed instantaneously. It was then stirred for 10 minutes. The solvent was decanted out and the product was washed thrice with petroleum ether. The compound was dried in vacuum [yield 1.2 g (98%)]. The amount of thorium in the product was estimated titrimetrically⁸ using EDTA. A known weight of the product (0.2811 g) was dissolved in distilled water. The pH of the solution was adjusted between 2 and 3 by adding few drops of 2N HCl. A drop of xylenol orange indicator was added and the solution was titrated against standard EDTA. The end point was the colour change from pink to yellow.

Anal: Calcd. for $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O} \cdot \text{DMAP}$: Th 33.5; Found: Th 33.0%.

IR ν_{max} (cm^{-1}): 3280(s), 3149(w), 1650(s), 1562(s), 1510(s), 1382(s), 1280(s), 1218(s), 1057(w), 1027(s), 998(m), 938(w), 838(w), 807(s), 740(s), 505(m).

RESULTS AND DISCUSSION

In the IR spectra of all the three products the C—C and C—N stretching frequencies are shifted to higher frequencies when compared to the corresponding frequencies observed in DMAP (1600, 1535, 1515, 1445 cm^{-1}). The ^1H NMR of $\text{SnCl}_2 \cdot \text{DMAP}$ in dimethyl sulfoxide contains peaks at 8.24(d) [$J = 9.6$ Hz], 6.89(d) [$J = 9.6$ Hz], 3.13(s) and shows downfield shifts with respect to the signals of the free ligand 8.17(d) [$J = 6$ Hz], 6.64(d) [$J = 6$ Hz], 2.69(s). The conductivity of 10^{-4}M solution of $\text{SnCl}_2 \cdot \text{DMAP}$ in DMF was found to be $216.3 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$. This is comparable to the value $240 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ predicted for the

equivalent conductance of an electrolyte of the type MX_2 at infinite dilution¹¹, but differs from the value $8\text{--}10 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ noted for the chelates of SnCl_2 with semicarbazones¹² and 1,10-phenanthroline¹³.

The UV spectrum of the ligand (λ_{max} : 255 nm) shows marked changes upon complexation with UCl_4 . The UV absorption shows a bathochromic shift to 263 nm with broadening. This effect is similar to that observed in bipyridyl complexes of many metals¹⁴. The visible spectrum of $\text{UCl}_4 \cdot \text{DMAP}$ in water [$\lambda_{\text{max}} = 464, 540, 624(\text{s}), 648, 668$] resembles that of $\eta^5\text{-Cp}_3\text{UCl}^{15}$ [$\lambda_{\text{max}} = 475, 600(\text{s}), 650, 750$] also in water. Accordingly, the presence of U(IV) in this complex is indicated.

In the ^1H NMR spectrum of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O} \cdot \text{DMAP}$, two broad signals appear at 6.63 and 7.87 ppm downfield to the corresponding signals observed for DMAP itself. The presence of coordinated water molecules is also indicated by the signal at 4.80(s) ppm. In the UV spectrum the absorption of DMAP at 255 nm is shifted to 285 nm. The shift of $\text{C}=\text{C}/\text{C}=\text{N}$ stretching frequencies, downfield shift in ^1H NMR and bathochromic shift in UV spectrum are all ascribed to complexation of the ligand to the metal. All the three complexes are non-hygroscopic, unlike the starting metal salts and can be handled in air.

Conclusion

The reaction of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O} \cdot \text{DMAP}$ with SnCl_2 gave rise to a product whose ^1H NMR spectrum showed downfield shift with respect to the corresponding signals in the starting thorium complex. Further study is in progress to ascertain the nature of interaction between the complex and SnCl_2 .

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