Convenient Approach to the Direct Syntheses of Chromium Complexes from Chromium(III) Chloride

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Introduction

In the last few years we have been actively engaged in developing direct and general procedures for the syntheses of transition metal complexes based on silver(I)-assisted metal exchange reactions. In this respect we have reported successful synthesis of some compounds of acknowledged importance from the corresponding metal chloride salts. The success in this area has led us to extend our strategy to the syntheses of chromium complexes of some N,N donors. In this report we describe the syntheses of bis- and trischelated chromium complexes of bidentate polypyridyl and related ligands (L). In these syntheses chromium(III) chloride, an unusually substitutionally inert compound, has been used as the starting material. It has been shown that by the use of silver complexes of strong n-acceptors it is also possible to achieve the direct syntheses of unusual chromium(I) complexes. It may be noted here that the chromium complexes of polypyridines are important because of their potential applicability as photosensitizers for solar energy conversion. But until now, no direct procedures starting from commercially available chromium(III) chloride are available. Moreover, examples of chromium(I) complexes are rare and syntheses of these complexes lack synthetic versatility and incapable of yielding complexes of desired composition.

Results and Discussion

The problems encountered in the syntheses of chloride-free chromium compounds from commercially available chromium(III) chloride is largely due to its unusual inertness to chloride substitution reaction. In cognizance of our recent experience, it was anticipated that this problem could be overcome by the use of [AgL₂]+ as a synthon (L = neutral bidentate ligand). The silver compound [AgL₂]+ possesses some special qualities as a reagent, as it can not only act as a source of Ag⁺ required for halide abstraction even from an inert metal chloride but it also is a source of L required for the formation of the complex. An important issue in this context is the selection of an appropriate solvent for carrying out the synthetic reactions. Thus, for the synthesis of chromium(III) complexes, redox-inert acetonitrile may be a good solvent, whereas, for the syntheses of lower valent compounds, a reducing solvent like ethanol is a better choice.

The four N,N donors (L) viz. 2,2'-bipyridine (bpy, L'), 1-10-phenanthroline (phen, L²), 2-(phenylazo)pyridine (pap, L³), and 2-(m-tolylazo)pyridine (tap, L⁴), have been chosen for the present work. All of them form stable tetracoordinated compounds with silver(I) of type the [AgL₂]⁺. They were reacted with hydrated chromium(III) chloride for the syntheses of chromium complexes. The synthetic reactions which have been studied are shown in Schemes 1–3. In the Scheme 1, the syntheses of dichlorobisligated complexes have been elaborated whereas Schemes 2 and 3 describe the syntheses of trischelated compounds.

Scheme 1

\[
\text{CrCl}_3\cdot 6\text{H}_2\text{O} + \text{AgL}_2^{+} \rightarrow \text{EOH} \text{MeCN} \rightarrow \text{CrCl}_2\text{L}_2^{2+} + \text{AgCl}
\]

Scheme 2

\[
\text{CrCl}_3\cdot 6\text{H}_2\text{O} + 3\text{AgL}_2^{+} \rightarrow \text{EOH} \text{MeCN} \rightarrow \text{CrL}_3^{n+} + 3\text{AgCl} + 3\text{L}
\]

Scheme 3

\[
\text{CrL}_2^{3+} + 2\text{AgL}_2^{+} \rightarrow \text{EOH} \rightarrow \text{CrL}_3^{2+} + 2\text{AgCl} + 3\text{L}
\]

The syntheses of dichlorocomplexes from CrCl₃6H₂O requires removal of one Cl⁻ associated with coordination of 2 mol of L to the metal ion. Thus, the reaction of CrCl₃6H₂O with an equimolar amount of [AgL₂]⁺ led to the formation of CrCl₂L₂⁺ (L = L², and n = 1 and L = L¹, L² and n = 0). In the cases of L³ and L⁴, it is believed that the reduction of chromium(III) to chromium(II) is accomplished by the reducing solvent. The syntheses of the dichlorocomplexes of L¹-L₃ are reported previously using different procedures. The advantages of our route are as follows: (i) the procedure is a general one for all four ligands, (ii) the reactions occur at a much faster rate, (iii) yields are better as compared to the yields in the existing synthetic procedures, and (iv) no additional reducing agent is required.

In order to obtain trischelated complexes directly from CrCl₃6H₂O (Scheme 2), complete removal of Cl⁻ is necessary. Thus, in these cases the reactions were carried out with the reagent ratio CrCl₃6H₂O:[AgL₂]⁺ = 1:3. These reactions are fast and proceed smoothly, and the yields of the compounds are also high (60–75%).

The most remarkable amongst the syntheses of present trischelated compounds are the syntheses of chromium(I) compounds.

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1 Dedicated to Professor Animesh Chakravorty on the occasion of his 60th birthday.
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plexes [CrL3]3+ and [CrL4]3+ from chromium(III) chloride. To the best of our knowledge this is the first ever example of syntheses of chromium(I) compounds directly from chromium-
(III) chloride and without addition of any external reducing agent. The very high \( \pi \)-acidic nature of \( \text{L}^3 \) and \( \text{L}^4 \) no doubt plays an effective role in the stabilization of +1 state in [CrL3]3+ (\( \text{L} = \text{L}^3, \text{L}^4 \)). It may be noted, in the present context, that examples of chromium(I) complexes are rare, and this may be due to a lack of suitable preparative methods. The new method of preparation, described above, is straight forward and much more convenient than those reported previously. For example, the synthesis of [Cr(bpy)3]3+ or [Cr(phen)3]3+ involves multiple steps: (i) initial reduction of Cr3+ to Cr2+, (ii) ligand addition, and (iii) reoxidation of the product. There is a recent report on the synthesis of [Cr(pap)3], starting from [Cr(CO)6]. Although it has been reported that [Cr(pap)3] is air stable, the electrochemical oxidation of the Cr(0) complex occurs at a negative potential (−0.21 V) versus SCE (saturated calomel electrode). This clearly explains the better stability of [Cr-
pap]3]+ over [Cr(pap)3]. Thus the formation of [Cr(pap)3]+ from our reaction conditions is not surprising; rather, it is as expected. Moreover, we note here that the complete substitution of CO form [Cr(CO)6] by 3 mol of pap is very slow (20 h) and the yield of [Cr(pap)3] is also low (48%).

Our concern for obtaining mixed ligand tris chromium complexes led us to use substitutionally inert [CrCl2L32] as the starting material. The reactions are described in Scheme 3. The optimum ratio of the reagents required for the above reactions is 1:2 as expected. In fact, the syntheses of triscomplexes of general formula, [CrL1,L33-,,lZ+] (\( n = 1–3; \ z = 3, 1 \)) could easily be achieved by this route and by the selection of appropriate reactants. For example, the reaction of [CrCl2L2] with 2 mol of [AgL2]+ yields [CrL3]3+ whereas a similar reaction using 2 mol of [AgL3]3+ or [AgL2]+ in place of [AgL2]3+ affords a mixed ligand complex, [CrL3-L]+ (\( \text{L} = \text{L}^1, \text{L}^2 \)). It may be relevant to mention here that the starting material CrCl2L2 used for the syntheses of mixed ligand complexes, is unusually substitutionally inert and also the syntheses of such mixed ligand complexes are otherwise very difficult. The reactions described in Scheme 3 occur even at a much faster rate as compared to the reactions described in Scheme 2.

Characterization and Properties. The chromium complexes, thus synthesised, gave satisfactory elemental (CHN) analyses. Selected characterization data of the complexes are depicted in Experimental Section. The spectra of the reported compounds agree well with the reported as before. All other chemicals and organic solvents used in synthesis were reagent grade commercial materials. For electrochemical and spectral data, spectrophotometer CHN-CAN was used. Commercial tetrabutylammonium bromide was converted to tetrabutylammonium perchlorate (TBAP) by following an available procedure. Silver assisted trans-metalation strategy has been demonstrated to be useful to achieve the syntheses of chromium complexes starting from unusually inert chromium(III) chloride. Furthermore, this strategy allows the syntheses of mixed-ligand chromium complexes of predetermined composition by the controlled insertion of the ligands to the metal ion. The synthetic strategy reported in this paper should also be useful for the synthesis of new building blocks of bridging ligands for the synthesis of polynuclear systems. Our research on the syntheses of transition metal complexes of bridging ligands is in progress.

Experimental Section

Materials. Chromium trichloride hexahydrate, CrCl3•6H2O received from Thomas Baker and Co., Bombay, India, was dried before use. The silver complexes, [AgL2]XnH2O (\( X = \text{ClO}_4, \text{NO}_3 \)) were prepared as before. All other chemicals and organic solvents used in synthesis were reagent grade commercial materials. For electrochemical and spectral data, spectrophotometer CHN-CAN was used. Commercial tetrabutylammonium bromide was converted to tetrabutylammonium perchlorate (TBAP) by following an available procedure. IR spectra were recorded on KBr disks (4000-300 cm\(^{-1}\)) by using a Perkin-Elmer IR-983 spectrophotometer. Solution electrical conductivity measurements were performed on an Elico CM 827 conductivity bridge with a solution concentration of 10\(^{-3}\) M. The magnetic susceptibilities of the samples were measured on a PAR 155 vibrating sample magnetometer fitted with a walker scientific L75 FBAL magnet. Electrochemical measurements were done by using the PAR Model 370-4 electrochemistry system as described before. Microanalyses (CHN) were done by using an elemental analyzer, Heraeus CHN-O-RAPID.

Preparation of Complexes. Caution! Perchlorate salts of metal complexes are potentially explosive. Care should be taken in handling such samples.

Dichlorobis(2,2'-bipyridine)chromium(III) Perchlorate Dihydrate, [CrCl2(bpy)2]ClO4•2H2O. CrCl3•6H2O (267 mg, 1 mmol) was dissolved in acetonitrile (25 mL), and to it was added [Ag(bpy)]-ClO4•2H2O (556 mg, 1 mmol) and the mixture heated to reflux for 6 h on a water bath. The light brown solution was cooled and filtered through a quantitative filter paper to remove insoluble AgCl. The filtrate was concentrated to 10 mL and an aqueous saturated solution of NaClO4 (5 mL) was added. When the mixture was kept at room temperature overnight, a dark brown crystalline compound was obtained; yield 5%. Anal. Calcd for Cr3Cl2H2N4O12Cl: C, 42.06; H, 3.50; N, 9.82. Found: C, 42.15; H, 3.65; N, 10.10. \( \delta_{\text{max}} \) (cm\(^{-1}\)): 542 (45), 475 (22), 444 (88). \( \chi_{\text{M}} \) (CHN-CAN): 155 \( \mu\text{m}^{-1}\) cm\(^{-1}\).

Notes

(13) Reference 8, p 817.
(17) Reference 8, p 718.
The complex \([\text{Cr(Cl}_{2}\text{(phen)}_{2})\text{ClO}_{4}]\cdot\text{H}_{2}\text{O}\) was prepared similarly using \([\text{Ag(phen)}_{2}]\text{ClO}_{4}\cdot\text{H}_{2}\text{O}\) instead of \([\text{Ag(pap)}_{2}]\text{ClO}_{4}\cdot\text{H}_{2}\text{O}\). Yield 50%. Anal. Caled for \(\text{C}_{24}\text{H}_{18}\text{N}_{6}\text{Cl}_{2}: \text{C}, 53.99; \text{H}, 3.68; \text{N}, 17.18. \lambda_{\max}, \text{nm} (\text{CH}_{3}\text{CN}): 455 (320), 434 (600), 405 (880). \lambda_{\max}, \text{nm} (\text{CH}_{3}\text{CN}, \text{TBAP}, \text{vs SCE}): 455 (320), 434 (600), 405 (880). \Lambda_{\max}, \text{mM}^{-1} \text{cm}^{-1} (\text{KBr}): 412 (\text{M} = \text{N(azo)}), 370 (\text{M} = \text{N(py)}). E'_{\text{298}} \text{V} (\text{CH}_{3}\text{CN}, \text{TBAP}, \text{vs SCE}) (\Delta E_{\text{p}} \text{mV}): \text{Cr(III)/Cr(II)}, 0.12 (120); \text{Cr(II)/Cr(I)}, -0.31 (120).---

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**Notes**

**11,14-Phenanthroline bis(2-phenylazoipyridine)chromium(II) perchlorate Monohydrate, \([\text{Cr(pap)}_{2}\text{(phen)}_{2}]\text{ClO}_{4}\cdot\text{H}_{2}\text{O}\).** This was prepared similarly as above with the exception that \([\text{Ag(phen)}_{2}]\text{ClO}_{4}\cdot\text{H}_{2}\text{O}\) was used instead of \([\text{Ag(pap)}_{2}]\text{ClO}_{4}\cdot\text{H}_{2}\text{O}\). Yield 50%. Anal. Caled for \(\text{C}_{36}\text{H}_{32}\text{Cl}_{10}\text{N}_{5}\text{O}_{5}: \text{C}, 55.75; \text{H}, 4.05; \text{N}, 16.20. \lambda_{\max}, \text{nm} (\text{CH}_{3}\text{CN}): 455 (320), 434 (600), 405 (880). \Lambda_{\max}, \text{nm} (\text{CH}_{3}\text{CN}, \text{TBAP}, \text{vs SCE}) (\Delta E_{\text{p}} \text{mV}): \text{Cr(III)/Cr(II)}, 0.87 (90); \text{Cr(II)/Cr(I)}, -0.52 (110); \text{Cr(I)/Cr(0)}, -1.37 (110).---

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