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[1−4] 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,[5] has been used as the starting material. It has been shown that by the use of silver complexes of strong π-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[6,7] 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[8] 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 $[AgL_2]^+$ as a synthon (L = neutral bidentate ligand). The silver compound $[AgL_2]^+$ 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), 1,-10-phenanthroline (phen, L^2), 2-(phenylazo)pyridine (pap, L^3), and 2-(*m*-tolylazo)pyridine (tap, L^4), have been chosen for the present work. All of them form stable tetracoordinated compounds[9,10] with silver(I) of type the $[AgL_2]^+$. 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

$$CrCl_3{\cdot}6H_2O + AgL_2^+ \xrightarrow[\substack{L = L^1, L^2:\ n = 1\\ L = L^3, L^4:\ n = 0}]{EtOH/MeCN} CrCl_2L_2^{n+} + AgCl$$

Scheme 2

$$CrCl_3{\cdot}6H_2O + 3AgL_2^+ \xrightarrow[\substack{L = L^1, L^2:\ n = 3\\ L = L^3, L^4:\ n = 1}]{EtOH/MeCN} CrL_3^{n+} + 3AgCl + 3L$$

Scheme 3

$$CrCl_2L_2^3 + 2AgL_2^+ \xrightarrow[L = L^1-L^3]{EtOH} CrL^3{}_2L^+ + 2AgCl + 3L$$

The syntheses of dichlorocomplexes from $CrCl_3{\cdot}6H_2O$ requires removal of one Cl^- associated with coordination of 2 mol of L to the metal ion. Thus, the reaction of $CrCl_3{\cdot}6H_2O$ with an equimolar amount of $[AgL_2]^+$ led to the formation of $CrCl_2L_2^{n+}$ (L = L^1, L^2 and $n = 1$ and L = L^3, L^4 and n = 0). In the cases of L^3 and L^4, it is believed that the reduction of chromium(III) to chromium(II) is accomplished by the reducing solvent. The syntheses of the dichloro complexes of L^1-L^3 are reported[11,12] 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 $CrCl_3{\cdot}6H_2O$ (Scheme 2), complete removal of Cl^- is necessary. Thus, in these cases the reactions were carried out with the reagent ratio $CrCl_3{\cdot}6H_2O$:$[AgL]_2^+$ = 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 complexes is the syntheses of chromium(I) com-

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plexes $[CrL^3_3]^+$ and $[CrL^4_3]^+$ 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 π-acidic nature of L^3 and L^4 no doubt plays an effective role in the stabilization of +1 state in $[CrL_3]^+$ ($L = L^3$, 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[13] multiple steps: (i) initial reduction of Cr^{3+} to Cr^{2+}, (ii) ligand addition, and (iii) reoxidation of the product. There is a recent report[14] 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 $[CrCl_2L^3_2]$ 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 mixed triscomplexes of general formula, $[CrL^1_nL^3_{3-n}]^{z+}$ ($n = 1-3$; $z = 3, 1$) could easily be achieved by this route and by the selection of appropriate reactants. For example, the reaction of $[CrCl_2L^3_2]$ with 2 mol of $[AgL^3_2]^+$ yields $[CrL^3_3]^+$ whereas a similar reaction using 2 mol of $[AgL^1_2]^+$ or $[AgL^2_2]^+$ in place of $[AgL^3_2]^+$ affords a mixed ligand complex, $[CrL^3_2L]^+$ ($L = L^1$, L^2). It may be relevant to mention here that the starting material $CrCl_2L^3_2$, used for the syntheses of mixed ligand complexes, is unusually substitutionally inert[11] 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[11,14-16] data and thus confirm that the compounds isolated by us are the same as those described before.

All the chromium compounds are paramagnetic. While the magnetic moments (μ_{eff} values) of chromium(I) complexes fall in the range 1.80 to 1.97 μ_B corresponding to a single unpaired electron, those of chromium(II) complexes lie in the range 2.81 to 2.90 μ_B, confirming[17] a low spin chromium(II) ground state. The IR spectra of the compounds display a pattern typical of coordinated ligands under consideration.

Some observations on the redox potentials (Experimental Section) of the chromium complexes are in order. The dihalocomplex $[CrCl_2L_2]$ ($L = L^3$, L^4) displays one oxidative process and one reductive reversible process at ca. 0.40 and ca. −0.30 V versus SCE which have been attributed to Cr(III)/Cr(II) and Cr(II)/Cr(I) couple, respectively. Hence, in the corresponding trischelated complexes it was anticipated that those processes would shift to more positive potentials. Thus, for CrL_3^+ three waves which are observed at −0.15 (reductive), 0.56 (oxidative) and 1.09 V (oxidative) are attributed[14] to Cr(I)/Cr(0), Cr(II)/Cr(I), and Cr(III)/Cr(II) couples. Interestingly, all these three processes also occur in $[CrL_2(bpy)]^+$ ($L = L^3$, L^4) but at lower potentials. This is surely due to the better stabilization of lower valent chromium by pap over bpy. The voltammetric behavior of the two known complexes, viz. $[Cr(bpy)_3]^{3+}$ and $[Cr(phen)_3]^{3+}$, correspond to those reported earlier.

Conclusions

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 are in progress.

Experimental Section

Materials. Chromium trichloride hexahydrate, $CrCl_3 \cdot 6H_2O$ received from Thomas Baker and Co., Bombay, India, was dried before use. The silver complexes, $[AgL_2]X \cdot nH_2O$ ($X = ClO_4$, NO_3) were prepared[9,10] as before. All other chemicals and organic solvents used in synthesis were reagent grade commercial materials. For electrochemical and spectral data, spectrograde CH_3CN was used. Commercial tetrabutylammonium bromide was converted to tetrabutylammonium perchlorate (TBAP) by following an available procedure.[18]

Measurements. 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 82T 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.[19] Microanalyses (CHN) were done by using an elemental analyzer, Heraous CHN-0-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, $[CrCl_2(bpy)_2]ClO_4 \cdot 2H_2O$. $CrCl_3 \cdot 6H_2O$ (267 mg, 1 mmol) was dissolved in acetonitrile (25 mL), and to it was added $[Ag(bpy)_2]ClO_4.2H_2O$ (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 $NaClO_4$ (5 mL) was added. When the mixture was kept at room temperature overnight, a dark brown crystalline compound was obtained; yield 55%. Anal. Calcd for $CrC_{20}H_{20}N_4O_6Cl_3$: C, 42.06; H, 3.50; N, 9.82. Found: C, 42.15; H, 3.65; N, 10.10. λ_{max}, nm (0.1 M HCl) (ϵ, M^{-1} cm^{-1}): 552 (45), 475 (22), 444 (88). Λ_M (CH_3CN): 155 ohm^{-1} cm^2 M^{-1}.

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The complex **$[CrCl_2(phen)_2]ClO_4.H_2O$** was prepared similarly using $[AgL^2_2]ClO_4.2H_2O$ instead of $[AgL^1_2]ClO_4.2H_2O$. Yield 50%. Anal. Calcd for $CrC_{24}H_{20}N_4O_6Cl_3$: C, 46.56; H, 3.23; N, 9.05. Found: C, 46.68; H, 3.42; N, 9.21. λ_{max}, nm (0.1 M HCl) (ϵ, $M^{-1}cm^{-1}$): 560(42), 476(18). $\Lambda_M(CH_3CN)$: 160 $ohm^{-1}cm^2M^{-1}$.

Dichlorobis(2-phenylazopyridine)Chromium(II), $[CrCl_2(pap)_2]$. A mixture of $CrCl_3.6H_2O$ (267 mg, 1 mmol) and $[Ag(pap)_2]ClO_4$ (575 mg, 1 mmol) in dry ethanol (25 mL) was heated to reflux for 2 h. The dark solution thus obtained was cooled and filtered through a quantitative filter paper to remove insoluble AgCl. The filtrate was then concentrated to 5 mL, whereupon dark crystals were obtained. It was filtered and washed with ether (3 × 5 mL). The compound was recrystallized from 1:1 acetone−water; yield 55%. Anal. Calcd for $CrC_{22}H_{18}N_6Cl_2$: C, 53.99; H, 3.68: N, 17.18. Found: C, 54.15; H, 3.75; N, 17.31. λ_{max}, nm (CH_3CN) (ϵ, M^{-1} cm^{-1}): 725 (17 800), 380 (14 800), 374 (1000), 332 (1180). μ_{eff}(298 K) : 2.85 μ_B. ν_{max}, cm^{-1} (KBr): 412^{sh} (M−N(azo)), 370 (M−N(py)). $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr(II), 0.42 (120); Cr(II)/Cr(I), −0.31 (120).

Dichlorobis(2-*m*-tolylazopyridine)chromium(II), $[CrCl_2(tap)_2]$. This was prepared similarly with the exception that $[Ag(tap)_2]ClO_4$ (1 mmol) was taken instead of $[Ag(pap)_2]ClO_4$; yield 55%. Anal. Calcd for $CrC_{24}H_{22}N_6Cl_2$: C, 55.70; H, 4.25; N, 16.25. Found: C, 55.82; H, 4.38; N, 16.41. λ_{max}, nm (CH_3CN) (ϵ, $M^{-1}cm^{-1}$) : 725 (18 100), 375 (15 100), 370 (960), 330 (2150). μ_{eff}(298 K) : 2.88 μ_B. ν_{max}, cm^{-1} (KBr) : 415^{sh} (M - N(azo)), 370(M-N(py)). $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/CR(II), 0.49 (110); Cr(II)/Cr(I), −0.23 (110).

Tris(2,2′-bipyridine)chromium(III) Perchlorate Monohydrate, $[Cr(bpy)_3](ClO_4)_3·H_2O$. $CrCl_3·6H_2O$ (267 mg, 1 mmol) was dissolved in acetonitrile (25 mL), and to it was added $[Ag(bpy)_2]ClO_4·2H_2O$ (1.7 g, 3 mmol) and the resulting mixture heated to reflux for 5 h. The mixture was then cooled and filtered through a quantitative filter paper to remove insoluble AgCl. The filtrate was concentrated to 5 mL and left for crystallization overnight. A yellow crystalline compound was obtained. It was filtered and dried in vacuo over P_4O_{10}; yield 60%. Anal. Calcd for $CrC_{30}H_{26}N_6O_{13}Cl_3$: C, 43.04; H, 3.25; N, 10.04. Found: C, 43.12; H, 3.25; N, 10.22. λ_{max}, nm (0.1 M HCl) (ϵ , M^{-1} cm^{-1}): 458 (274), 430 (670), 402 (940). Λ_M (CH_3CN): 350 ohm^{-1} cm^2 M^{-1}. $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr-(II), −0.26 (100; Cr(II)/Cr(I), −0.78 (110); Cr(I)/Cr(0), −1.35 (100).

The complex $[Cr(phen)_3](ClO_4)_3·2H_2O$ was prepared similarly using $[Ag(phen)_2]ClO_4·2H_2O$ instead of $[Ag(bpy)_2]ClO_4·2H_2O$; yield 55%. Anal. Calcd for $CrC_{36}H_{28}N_6O_{14}Cl_3$: C, 46.63; H, 3.02; N, 9.07. Found: C, 46.69; H, 3.15; N, 9.15. λ_{max}, nm (0.1 M HCl) (ϵ, M^{-1} cm^{-1}): 455 (320), 434 (600), 405 (880). Λ_M (CH_3CN): 355 ohm^{-1} cm^2 M^{-1}. $E°_{298}$, V (CH_3CN, TBAP, vs SCE (ΔE_p, mV): Cr(III)/Cr-(II), −0.29 (100); Cr(II)/Cr(I), −0.90 (110); Cr(I)/Cr(0), −1.37 (110).

Tris(2-phenylazopyridine)chromium(I) Perchlorate Monohydrate, $[Cr(pap)_3]ClO_4·H_2O$. $CrCl_3·6H_2O$ (267 mg, 1 mmol) was dissolved in absolute ethanol (25 mL), and to it was added a solution of $[Ag(pap)_2]ClO_4$ (1.72 g, 3 mmol in 15 mL absolute ethanol) and the solution heated to reflux for 5 h in dinitrogen atmosphere. The brown solution was then cooled and filtered through a quantitative filter paper to remove insoluble AgCl. The solution was then concentrated to 10 mL and left in the refrigerator for 6h. A dark colored crystalline compound, thus obtained, was filtered and washed thoroughly with diethylether and finally dried in vacuo over P_4O_{10}; yield 70%. Anal. Calcd for $CrC_{33}H_{29}N_9O_5Cl$: C, 55.11; H, 4.03; N, 17.54. Found: C, 55.25; H, 4.12; N, 17.82. λ_{max}, nm (CH_3CN) (ϵ, M^{-1} cm^{-1}): 630^{br} (3025), 515 (8634), 380^{sh} (22 185), 335 (30 250). Λ_M (CH_3CN): 135 ohm^{-1} cm^2 M^{-1}). μ_{eff}(298 K): 1.89 μ_B (t_2^5). $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr(II) 1.06 (260); Cr(II)/Cr(I), 0.52 (110); Cr(I)/Cr(0), −0.18 (100).

$[Cr(tap)_3]ClO_4·H_2O$ was prepared similarly using $[Ag(tap)_2]ClO_4$ instead of $[Ag(pap)_2]ClO_4$; yield 70%. Anal. Calcd for $CrC_{36}H_{35}N_9O_5Cl$: C, 56.80; H, 4.60; N, 16.57. Found: C, 57.01; H, 4.82; N, 16.88. λ_{max}, nm (CH_3CN) (ϵ, M^{-1} cm^{-1}): 625^{br} (3150), 514 (8800), 378^{sh} (23 000), 330 (31 200). Λ_M (CH_3CN): 130 ohm^{-1} cm^2 M^{-1}). μ_{eff}-(298 K): 1.85 μ_B (t_2^5). $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr(II), 1.09 (170); Cr(II)/Cr(I), 0.57 (110); Cr(I)/Cr(0), −0.14 (100).

Synthesis of $[CrL_3]ClO_4·H_2O$ Starting from $[CrCl_2L_2]$ (L = pap, tap). The syntheses were performed by using a general procedure given below: $[CrCl_2L_2]$ (1 mmol) was dissolved in absolute ethanol (25 mL) and to it a solution of $[AgL_2]ClO_4$ (2 mmol) in absolute ethanol (15 mL) was added and the mixture was heated to reflux for 2h. The rest of the procedure is similar to that described above.

$[Cr(pap)_3ClO_4·H_2O$: yield 75%. **$[Cr(tap)_3ClO_4·H_2O$:** yield 75%. The analytical, spectral and electrochemical data of the complexes correspond to those described above.

(2,2′-Bipyridine)bis(2-phenylazopyridine)chromium(I) Perchlorate Monohydrate, $[Cr(pap)_2(bpy)]ClO_4·H_2O$ $[CrCl_2(pap)_2]$ (490 mg, 1 mmol) was dissolved in absolute ethanol (25 mL), and to it was added $[Ag(bpy)_2]ClO_4.2H_2O$ (1.10 g, 2 mmol) and the mixture heated to reflux for 4 h. It was then cooled and filtered through a quantitative filter paper to remove insoluble AgCl. The filtrate was concentrated to 5 mL and left for crystallization overnight in the refrigerator. A dark colored crystalline compound was obtained which was filtered, washed with diethyl ether, and finally dried in vacuo over P_4O_{10}: yield 60%. Anal. Calcd for $CrC_{32}H_{28}N_8O_5Cl$: C, 55.53; H, 4.05; N, 16.20. Found: C, 55.75; H, 4.15; N, 16.35. λ_{max}, nm (CH_3CN) (ϵ, M^{-1} cm^{-1}): 770 (1235), 645 (3185), 530 (7145), 485 (9000). Λ_M (CH_3CN): 140 ohm^{-1} cm^2 M^{-1}. μ_{eff}(298 K) : 1.85 μ_B. $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr(II), 0.87 (90); Cr(II)/Cr(I), 0.41 (100); Cr(I)/Cr(0), −0.88 (130).

(1,10-Phenanthroline)bis(2-phenylazopyridine)chromium(I) Perchlorate Monohydrate, $[Cr(pap)_2(phen)]ClO_4·H_2O$. This was prepared similarly as above with the exception that $[Ag(phen)_2]ClO_4·2H_2O$ (2 mmol) was used instead of $[Ag(bpy)_2]ClO_4·2H_2O$; yield 50%. Anal. Calcd for $CrC_{36}H_{32}N_8O_5Cl$: C, 58.10; H, 4.30; N, 15.06. Found: C, 58.25; H, 4.35; N, 15.15 λ_{max}, nm (CH_3CN) (ϵ, M^{-1} cm^{-1}): 768 (1310), 644 (3210), 530 (8985), 487 (9230). Λ_M (CH_3CN): 135 ohm^{-1} cm^2 M^{-1}. μ_{eff}(298 K): 1.82 μ_B. $E°_{298}$, V (CH_3CN, TBAP, vs SCE) (ΔE_p, mV): Cr(III)/Cr(II), 0.88 (100); Cr(II)/Cr(I), 0.45 (110); Cr(I)/Cr(0), −0.90 (120).

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