Inorganica Chimica Acta, 99 (1985) 199–205

σ-Bonded Organochromium(III) Complexes.
Part 2*. Preparation and Isolation of Pyridylmethylchromium(III) Complexes Containing Dien, [15]aneN_4 and Aquo Ligands

KAREN CROUSE and LAI-YOONG GOH**

Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

Received August 4, 1984

Abstract

σ-Bonded organochromium complexes were prepared by the reaction of the 2-, 3- and 4-pyridylmethyl chlorides (picolyl chlorides) with L_n-chromium(II) ions, where L = dien, diethylenetriamine; 15[ane]N_4, tetraazacyclopentadecane; and aquo, H_2O. Reactions were carried out in alcoholic, partially alcoholic or aqueous media. The air-stable species were isolated as hydrated chlorides of the pyridylmethyl complexes and the N-protonated pyridiomethyl complexes by precipitation or in solution by purification on a Sephadex C-25 ion exchange column. Characterization was by elemental analysis, absorption spectra and product analyses of their decomposition in aqueous solution.

Introduction

σ-bonded organochromium(III) complexes are a subject of continuing research interest. In part 1 of this series we reported the preparation and isolation of amine(organo)chromium(III) complexes in alcoholic media [1]. 2- and 3-pyridylmethylchloride (picolylchlorides) reacted with bis(amine)chromium(II) ions, where amine = en, ethylenediamine; dap, 1,3-diaminopropane and trien, triethylenetetraamine, to produce air-stable hydrated chlorides of the corresponding pyridylmethyl and the N-protonated pyridiomethyl complexes as isolated solids. This work is extended herein to other systems in which pyridylmethylchlorides were reacted with $L_n$chromium(II) ions, where L = dien, diethylenetriamine; 15[ane]N_4, tetraazacyclopentadecane and aquo, H_2O.

Experimental

General

UV–Vis spectra were recorded in 1 M $HClO_4$ on a Cary 17 or a Beckman 5270 instrument. CHN analyses were carried out on a Hewlett-Packard 135B CHN analyser.

Chromium was analysed spectrophotometrically as CrO_4^{2-} [2], gravimetrically as Cr_2O_3 [3] or by atomic absorption using an IL651 aa/ae Spectrophotometer with a chromium lamp at 357.9 nm. Chloride was analysed gravimetrically as AgCl [3].

Manipulations were generally carried out under a wet or dry nitrogen atmosphere as appropriate, using Schlenk or modified Schlenk apparatus.

Materials and Reagents

Hydrochloric acid was Hopkin and Williams or May and Baker analytical grade. Chromium metal was Koch-Light 99.99% or BDH 99.5% electrolytically pure. Picolylchlorides were obtained from Aldrich. Diethylenetriamine, of BDH reagent grade, was distilled over powdered KOH and stored over molecular sieves. Solvents were dried using standard techniques and, with the exception of acetone, were stored over activated molecular sieves [4]. Tetraazacyclopentadecane was obtained from Strem Chemicals and was used as supplied. C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane dihydrate, Me_6[14]ane$N_4 \cdot 2H_2O$, was prepared by the method of Curtis [5].

Chromium(II) chloride tetrahydrate, $CrCl_2 \cdot 4H_2O$, was prepared as previously described [1]. The method of Holah and Fackler [6] was used to produce the acetonitrile adduct of the Cr(II) salt. The hydrated salt (*ca.* 50 mmol) was dissolved in a minimum amount of boiling ethanol and filtered directly into a large excess of boiling acetonitrile (*ca.* 200 cm^3). The blue-green crystals which precipitated were collected by suction filtration, washed with cold acetonitrile and then dried under vacuum.

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*Ref. [1] is considered to be Part 1 in this series.

**Author to whom correspondence should be addressed.

0020-1693/85/$3.30

TABLE I. Absorption Maxima of n-Pyridylmethylchromium(III) $[L]_x$ Ions in 1 M $HClO_4$.

n	L	λ_{max}, nm ($\epsilon_{max} \times 10^{-3}$, M^{-1} cm^{-1})
2	dien	576(0.11), 323(4.8), 263(3.3), 235(2.9)
	[15]aneN_4	527(0.1), 323(7.9), 262(5.0)
	H_2O	580(0.1), 322(9.0), 262(7.0), 235(4.8)[a]
		550(0.8), 318(8.3), 262(6.2), 235(4.0)[b]
	pentaaquo	550(0.073), 318(10.4), 262(6.2)[c]
3	dien	553.2(0.1), 330(2.8), 285(7.6)
	[15]aneN_4	494(0.09), 330(5.32), 285(9.29)
	H_2O	544, 320sh, 285[a]
	pentaaquo	534(0.049), 320(9.6), 285(15)[c]
4	[15]aneN_4	535(0.1), 318(11.62), 255(5.8)
	pentaaquo	550(0.92), 308(15.6), 225(6.75)[c]

[a] Viscous oil. [b] Viscous oil dissolved in 1 M $HClO_4$ and after standing at ~30 °C for ½ h. [c] Ions in solution separated by ion exchange, data from Ref. [12].

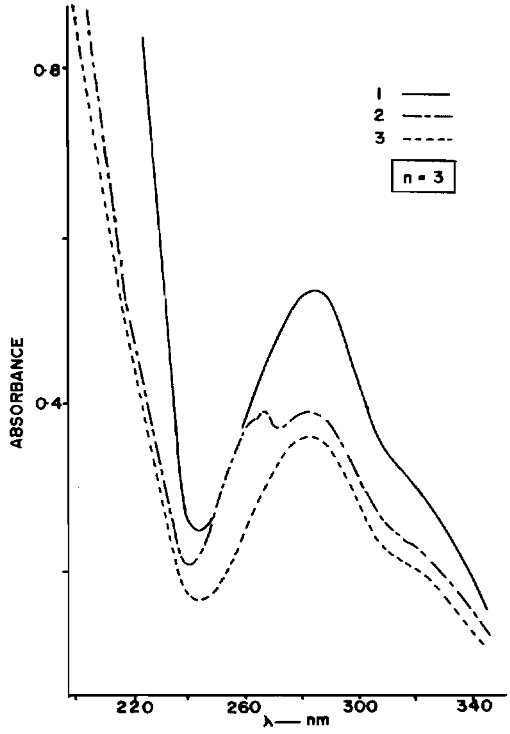


Fig. 1. UV spectra in 1 M $HClO_4$ of products from the reaction of $Cr^{II}(dien)Cl_2$ with n-picolylchloride hydrochloride in absolute ethanol (*ca.* 5×10^{-5} M): (1) product solution immediately after reaction; (2) brown solids; (3) buff solids.

Reaction of $Cr^{II}(dien)Cl_2$ Complex

With 3-picolylchloride hydrochloride

The mono(dien) complex, $Cr(dien)Cl_2$ was prepared in alcoholic media using a modification of the method of Earnshaw *et al.* [7]. A stoichiometric amount of deoxygenated diethylenetriamine (0.6 cm^3, 5.5 mmol) was added to $CrCl_2 \cdot 4H_2O$ (1.0 g, 5.5 mmol) in ethanol (5 cm^3), followed by the addition of a few drops of conc. HCl to produce the blue mono(dien) complex, $Cr(dien)Cl_2$. This reacted immediately on an injection of 3-picolylchloride hydrochloride (0.5 g, 3 mmol) dissolved in absolute ethanol (2 cm^3). The blood-red reactant solution (see UV spectrum (1) in Fig. 1), which contained fine solids, was centrifuged and the supernatant liquid was poured into acetone (*ca.* 30 cm^3) whereupon fluffy solids were precipitated. These solids were washed with three additional portions of acetone (each *ca.* 30 cm^3), and then dried *in vacuo* at room temperature.

The spectrum indicated the presence of some free organic compound, suggesting that the complex had undergone some decomposition (spectrum (2), Fig. 1). These solids had a Cr:picolyl group ratio of 1:0.8, *i.e.* they were initially ~80% pure on a molar basis. The golden coloured acetone-ethanol solution was combined with dry ether (*ca.* 100 cm^3) and buff, fluffy solids (*ca.* 0.2 g, 0.4 mol, 15% yield) were precipitated (spectrum 3, Fig. 1). The Cr: picolyl group ratio was 1:1. The formula $\{[3\text{-}pyCH_2\text{-}Cr(dien)]Cl_2 \cdot 2.3HCl\}$ was proposed on the basis of the elemental analysis. Spectral data are given in Table I.

The reaction was also carried out in a partially aqueous medium. $CrCl_2 \cdot 4H_2O$ (1.4 g, 8 mmol) in absolute ethanol (10 cm^3) was combined with H_2O (3 cm^3) and a slight excess of diethylenetriamine (1 cm^3, 9.3 mmol). The pH was adjusted to ~7 by addition of HCl to ensure the formation of the mono(dien) complex, in accordance with the find-

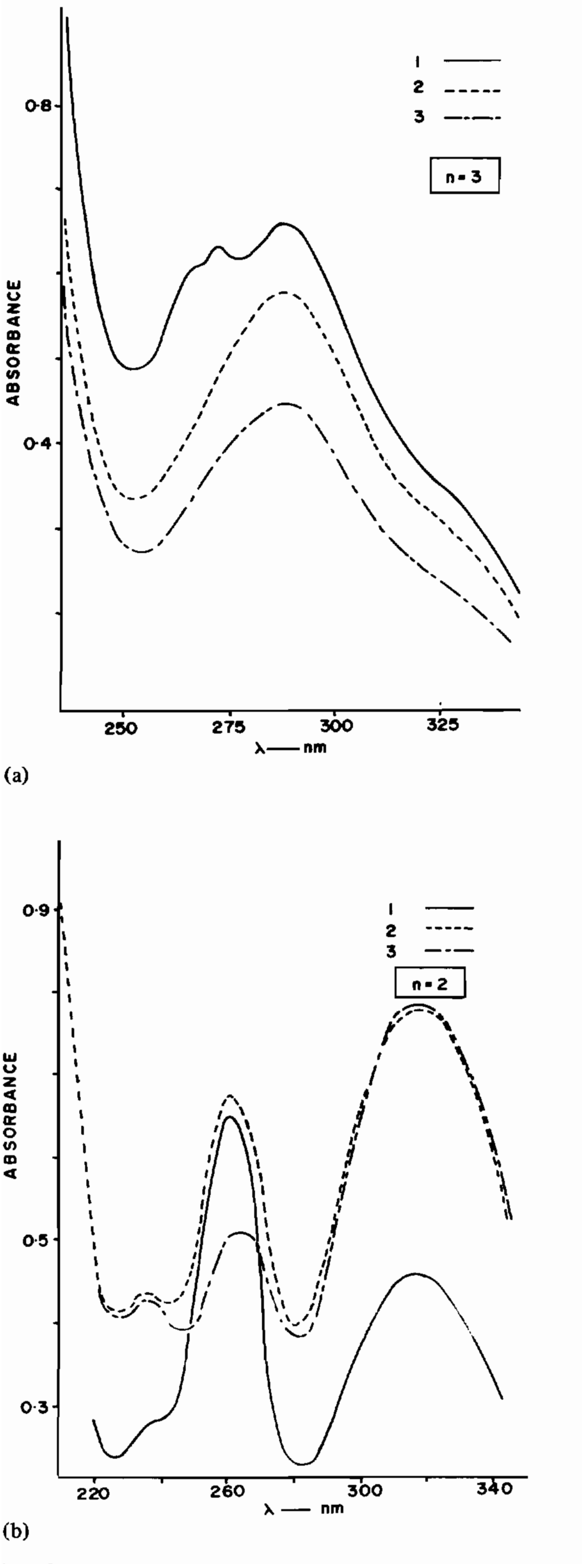


Fig. 2. UV spectra in 1 M $HClO_4$ of products from the reaction of $Cr^{II}(dien)Cl_2$ with n-picolylchloride hydrochloride in (a) aqueous ethanol (*ca.* 8 × 10^{-5} M) and (b) aqueous media (*ca.* 1 × 10^{-4} M): (1) product solution immediately after reaction; (2) oil; (3) brown solids.

ings of Pecsok *et al.* [8] that for a totally aqueous medium at pH 6.5–7.5 the stable species is the mono(dien)Cr(II) complex ($\epsilon_{max}^{614\,nm}$ = 32.3), while at pH 8–11 the bis(dien) complex is formed ($\epsilon_{max}^{587\,nm}$ = 38.8). An ethanolic solution of 3-picolylchloride hydrochloride (*ca.* 0.6 g, 4 mmol) was injected and there was an immediate colour change to olive-red. The solution was stirred at room temperature for 1 h (spectrum (1), Fig. 2a). To the stirred reactant solution was then added acetone (*ca.* 100 cm^3) resulting in the separation of two layers. Approximately half the greenish-brown lower layer containing the organochromium complex was washed with three portions of acetone (each *ca.* 100 cm^3), causing it to become very viscous (spectrum (2), Fig. 2a). Brown solids were precipitated when this viscous layer was combined with ether (*ca.* 100 cm^3). The solids upon drying *in vacuo* were found to have a Cr:picolyl group ratio of 1:0.6, *i.e.* they consisted of ~60% organometallic complex (spectrum (3), Fig. 2a).

With 2-picolylchloride hydrochloride

The 2-isomer was prepared in aqueous solution in a manner similar to the 3-isomer. The spectra of the crude product solution, separated oils and the final brown organometallic solids (yield ~15%) are given in Fig. 2b. The Cr:picolyl group ratio of the organochromium species isolated was 1:1. The elemental analyses support the formulation $\{[2\text{-}pyCH_2Cr(dien)]Cl_2(2.3HCl)(0.5H_2O)\}$. The spectral data are given in Table I.

Reaction of $Cr^{II}(dien)_2Cl_2$ Complex

With 3-picolylchloride hydrochloride

The bis(dien) complex was prepared by the method of Earnshaw *et al.* [6]. Neat ligand (1.8 cm^3, 16 mmol) was added to a solution of $CrCl_2 \cdot 4H_2O$ (1 g, 5 mmol) in ethanol (5 cm^3) in an ice bath. To this suspension of the bis(dien) complex was added a solution of 3-picolylchloride hydrochloride (0.45 g, 2.7 mmol) in ethanol (3 cm^3). The solution was stirred under nitrogen for ~2 h but no formation of any organochromium species was observed.

Reaction of $Cr^{II}(H_2O)_n$ Complex

With 2-picolylchloride hydrochloride

On addition of 2-picolylchloride hydrochloride (3.3 g, 20 mmol) in ~5 cm^3 water to an aqueous solution of Cr(II) ions (40 cm^3, 40 mmol) in 1 M HCl, a blood-red solution was produced (spectrum (1), Fig. 3a). The reactant solution was poured into acetone (1 dm^3) and ether (200 cm^3) to precipitate a deep red oil (spectrum (2), Fig. 3a). The supernatant acetone solution retained its green

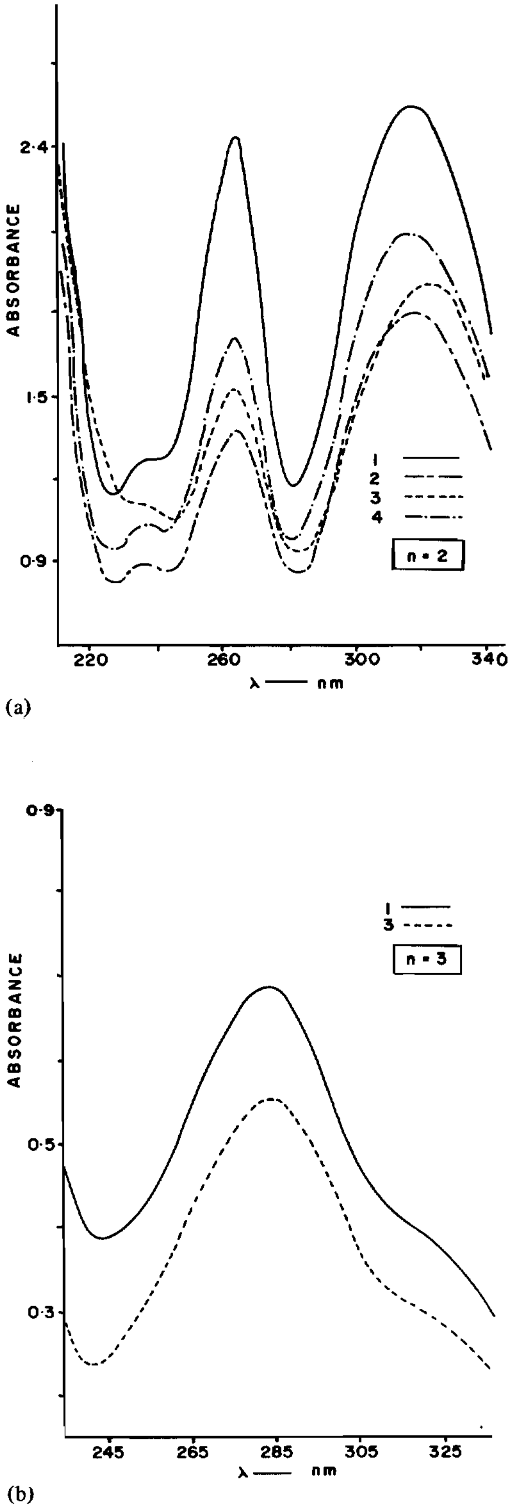


Fig. 3. UV spectra in 1 M $HClO_4$ of products from the reaction of $[Cr^{II}(H_2O)_6]^{2+}$ with n-picolylchloride hydrochloride in (a) aqueous medium (*ca.* 2×10^{-4} M) and (b) aqueous ethanol (*ca.* 4×10^{-5} M): (1) product solution immediately after reaction; (2) red oil; (3) viscous oil; (4) sample (3) after ½ h at 30 °C.

colour on standing. The oil on trituration with two more 200 cm^3 portions of acetone gave an olive-coloured supernatant layer and a viscous, deep brown oil (spectrum (3), Fig. 3a), but failed to produce any solids even on further treatment with acetone and ether. The latter supernatant acetone layer changed colour from olive to plum on standing overnight. The absorption maximum of the viscous oil in 1 M $HClO_4$ had shifted to 322 nm but reverted to 318 nm after some time at room temperature (compare spectra (3) and (4), Fig. 3a). Further evacuation of this apparently pure oil caused its colour to change from deep brown, finally giving plum-coloured solids. The spectra of these solids in 1 M $HClO_4$ merely indicated that they were inorganic complexes contaminated with organic decomposition products. The plum solids gave a green solution in acid but a purple solution in acetone.

With 3-picolylchloride hydrochloride

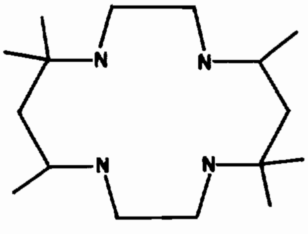
Cr(II) chloride (40 cm^3, 40 mmol) in 1 M HCl reacted with an ethanolic solution (10 cm^3) of 3-picolylchloride hydrochloride (3.3 g, 20 mmol) to produce an olive-green solution (spectrum (1), Fig. 3b). A very viscous oil (spectrum (2), Fig. 3b) was precipitated by acetone (2 dm^3). The 1:1 ratio for Cr:picolyl group showed that the oil contained a pure organochromium species. This oil redissolved in ethanol and added to ether precipitated a fluffy, green-brown powder which was extremely hygroscopic. The solids collapsed to oily drops on drying under vacuum, and the spectrum showed that the sample had undergone extensive decomposition.

The spectrum of the crude product solution obtained for the reaction carried out on the same scale in absolute ethanol confirmed the presence of the pyridylmethyl-chromium species; however, its rapid decomposition prevented isolation.

Reactions of $Cr^{II}(Me_6[14]aneN_4)$ Complex

With 2- and 3-picolylchloride hydrochloride

The $Cr(Me_6[14]aneN_4)Cl_2$ complex was prepared using a technique similar to that outlined in [9]. $CrCl_2{\cdot}2CH_3CN$ (5 mmol) was dissolved in 'superdry' ethanol (10 cm^3) and combined with an ethanolic solution (5 cm^3) of the ligand, (1), (5 mmol). The purple form of the complex for which a planar configuration of the ligand was proposed was used to react with stoichiometric amounts of 2- and 3-picolylchloride hydrochloride to give solutions which contained the desired organochromium complexes. These complexes, however, were very unstable and attempts to isolate them by addition of acetone and ether resulted in rapid decomposition.



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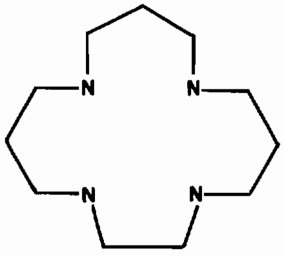

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Reaction of $Cr^{II}([15]aneN_4)$ Complex

With 3-picolylchloride hydrochloride

In an attempt to isolate the solid organochromium complex, [15]aneN$_4$, (2), (0.65 g, 3 mmol) was added to $CrCl_2 \cdot 4H_2O$ (0.6 g, 3 mmol) in absolute ethanol (20 cm^3). The solution immediately became the royal purple colour characteristic of the macrocyclic complex. 3-picolyl chloride hydrochloride (0.25 g, 1.5 mmol) in ethanol (1 cm^3) was then added. The solution became olive-brown. However neither the green solids which precipitated nor the mother liquor had any absorption in the UV which was characteristic of an organochromium complex.

A stoichiometric amount of $CrCl_2 \cdot 4H_2O$ (0.09 g, 0.47 mmol) was added to an aqueous solution (5 cm^3) of the ligand (0.1 g, 0.47 mmol) giving the purple macrocyclic $[15]aneN_4Cr^{2+}$ complex. Addition of an excess of 3-picolylchloride hydrochloride (0.1 g, 0.6 mmol) caused an immediate colour change to blood-red (spectrum (1), Fig. 4). About 3 cm^3 of the reactant solution was loaded on to a Sephadex C-25 column (1 cm × 10 cm) which had been washed with water. Bands comprising the excess organic halide, the inorganic Cr(III) macrocyclic complexes and the organochromium complex were eluted with 0.2 M $NaClO_4$ adjusted to pH 5 (spectra (2), (3), (4) and (5), Fig. 4). The Cr:picolyl group ratio of the organochromium complex was found to be 1:1. The spectral data are given in Table I.

With 2- and 4-picolylchloride hydrochlorides

The 2- and 4-picolylchloride hydrochlorides were reacted in aqueous medium and the products were separated as described above for the 3-isomer. In each case the fraction containing the organochromium complex had a Cr:picolyl group ratio of 1:1. Spectral data are given in Table I.

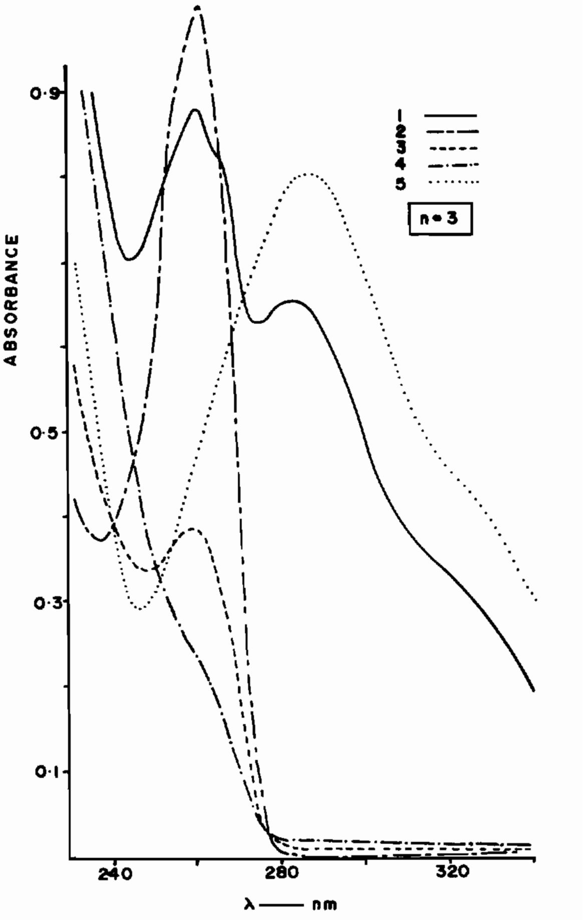

Fig. 4. UV spectra in 1 M $HClO_4$ of products from the reaction of $[Cr^{II}(15[ane]N_4)]^{2+}$ with n-picolylchloride hydrochloride in aqueous medium (*ca.* 8 × 10^{-5} M): (1) product solution immediately after reaction; (2) fraction 1 from Sephadex C-25; (3) fraction 2; (4) fraction 3; (5) fraction 4.

Results and Discussion

Mono(dien)organochromium Complexes

The mono(dien) complexes, $Cr(dien)X_2$ (X = Cl, Br, I), which were isolated from ethanol or n-butanol were assigned a halide-bridged, binuclear structure on the basis of their magnetic moments and the reflectance spectra of their solids [7]. Such species would be expected to be unreactive towards organic halides. Although the $Cr(dien)Cl_2$ complex has been reported to be "insoluble in all solvents tried", the bromide and iodide complexes were reported to be slightly soluble in DMF. Conductance measurements of dilute solutions of these halides in DMF indicated the presence of 2:1 electrolytes, which implied a dissociation of the binuclear species on dissolution.

Pecsok *et al.* [8] also found evidence for the existence of the monomeric species ($\epsilon_{\max}^{614\,\mathrm{nm}} = 32.3$) in aqueous solution between pH 6.5–7.5. They proposed that the nitrogen atoms lie in a plane at right angles to the distortion axis.

The stepwise aquation of 1, 2, 3- and 1, 2, 6-triaquodiethylenetriaminechromium(III) cations to the hexaaquochromium cation has been reported to proceed through the 'partially unwrapped' singly and doubly protonated intermediates, $\mathrm{Cr(dienH)(OH_2)_4}^{4+}$ and $\mathrm{Cr(dienH_2)(OH_2)_5}^{5+}$, both of which were isolated in aqueous medium [10].

It was found in this study that a few drops of HCl helped to partially solubilize the $\mathrm{Cr(dien)Cl_2}$ suspended in ethanol, perhaps through a combination of the factors discussed above, enabling its reaction with the organic halides to proceed readily. The yield of pure complex (15%) was reduced because of the co-precipitation of the residual inorganic complex and the picolylchromium species by acetone.

Elemental analyses indicate mixtures of the pyridylmethyl complex and the pyridiomethyl form. This has been observed previously [1] and may be understood in the same manner. $\{[\mathrm{2\text{-}pyCH_2Cr(dien)}]\mathrm{Cl_2(2.3HCl)(0.5H_2O)}\}$ found (calc.): C 30.5(30.2), H 5.5(5.7), N 10.2(10.6), Cl 38.0(38.4), Cr 13.6 (13.4). $\{[\mathrm{3\text{-}pyCH_2Cr(dien)}]\mathrm{Cl_2(2.3HCl)}\}$ found (calc.): C 31.0(30.8), H 5.5(5.7), N 10.7(10.8), Cl 39.0(39.2), Cr 13.2(13.4).

Bis(dien)chromium Complexes

The bis(dien) complex, $\mathrm{Cr(dien)_2Cl_2}$, was reported to contain terdentate ligands both in the solid [7] and in solution [8]. On the basis of such a structure this complex was not expected to react with the organic halide, and indeed this was found to be the case.

Aquo(organo)chromium Complexes

The pentaaquo(pyridylmethyl)Cr(III) ions (prepared by the reaction of picolylbromide hydrobromide with chromous sulphate and purified by chromatography on Zeocarb 225SRC-10 ion exchange resin) were the first air-stable monoalkyl chromium ions isolated, albeit in solution [11, 12]. It was hoped that the techniques which resulted in the isolation of the various amine(pyridylmethyl)Cr(III) complexes as solid salts might be successfully applied to these aquo complexes.

The attempt to isolate the solid salt from a totally aqueous solution was not successful. The very viscous oil precipitated by acetone and ether analysed for a pure organochromium species as indicated by the 1:1 Cr:picolyl group ratio. Its spectrum (spectrum (3), Fig. 4) showed it to be free of organic picolyl compounds and inorganic by-products. The reversible shift in the UV absorption maximum was conceivably due to removal of aquo ligands during the purification process in which dry solvents were used. These aquo ligands were possibly replaced by acetone or chloride. The attempt to dry the oil under vacuum caused rapid decomposition of the oil, accompanied by colour changes through olive to plum. The plum-coloured inorganic decomposition products gave a green solution in acid and a purple solution in dry acetone which became green on mixing with aqueous acid, which further supported the conclusion that aquo ligands had been lost.

Acetone and ether were added to the crude reaction solution to obtain a viscous oil from the reaction of Cr(II) chloride with 3-picolylchloride in 1:4 ethanol–water. This oil was free of organic and inorganic contaminants and had a chromium: picolyl group ratio of 1:1. The oil dissolved in ethanol precipitated out as an olive-brown powder on addition of acetone and ether. However, due to the extreme hygroscopic nature of the isolated solids and the rapid decomposition induced by evacuation, no quantitative measurements could be made.

The spectrum of the crude product solution from the reaction in absolute ethanol confirmed the presence of the pyridylmethyl-chromium species; however, its rapid decomposition prevented isolation.

Hexamethyl-tetraaza[14]ane Complex

The purple, planar complex having the formula $\mathrm{Cr(Me_6[14]aneN_4)Cl_2}$ which was prepared by the method of Dei and Mani [9] was sensitive to moisture as well as oxygen. It reacted with 2- and 3-picolylchloride hydrochloride in absolute ethanol. A shoulder at 295 nm in the crude reaction solution confirmed the presence of the pyridylmethyl-Cr complex. The spectrum of the purple solid precipitated by acetone showed that the relative proportion of organic picolyl compound had increased over that in the crude solution, which was evidence of decomposition. These solids were dissolved in ethanol and were re-precipitated by ether, but the spectra of the solids thus obtained still showed contamination by organic picolyl compounds. Decomposition of the isolated solids in absolute ethanol was essentially complete after ½ h at 27 °C.

A similar pattern was observed for the reaction and work-up of the 3-picolyl isomer. The spectra showed that the desired organochromium complex did form but, due to rapid decomposition, no pure sample could be isolated.

Tetraaza[15]ane Complex

The picolylchloride hydrochlorides did react with the $\mathrm{Cr([15]aneN_4)}$ complex in absolute ethanol,

TABLE IIa. Reaction of 2-$pyCH_2Cl \cdot HCl$ with $Cr([15]aneN_4)^{2+}$. Fractions Eluted from Sephadex C-25.

Fractions	λ_{max} (nm)[a]	Colour[b]	Content[c]
1	262	Colourless	$pyCH_2Cl$
2	590, 470, 412, 262	Yellow-green	X_2CrL^+, $pyCH_2Cl$
3	564, 462, 393	Pink	$XCr(H_2O)L^{2+}$
4	527, 323, 262	Orange	$pyCH_2Cr(H_2O)L$

[a] L is $[15]aneN_4$. [b] In 1 M $HClO_4$. [c] In 0.2 M $NaClO_4$.

TABLE IIb. Absorption Maxima $XCr(H_2O)([15]aneN_4)^{n+}$ Complexes.*

X	λ_{max} (nm)
Cl	564, 462, 393
Br	560, 460, 393
I	562, 462, 394
H_2O	(sh) 540, 454, 377

*All data presented in this table were taken from Ref. 12.

however the organochromium complex which was formed was unstable and could not be isolated.

The preparation of a series of mono(alkyl)chromium complexes containing the $[15]aneN_4$ ligand in aqueous medium has been reported [13, 14]. All were synthesized by the reaction of the chromous macrocyclic complex with organic halides. The complexes were purified on columns of Sephadex C-25, a strong acid ion exchange resin.

A method of preparation and isolation similar to that outlined above was employed in this work. The purple, macrocylic complex was prepared in aqueous medium by the reaction of free ligand with $CrCl_2 \cdot 4H_2O$. The picolylchloride hydrochlorides reacted with $Cr([15]aneN_4)^{2+}$ to produce blood-red solutions. For the reaction with the 2-isomer the fractions described below, Table IIa, were readily eluted from the Sephadex C-25 column with 0.2 M $NaClO_4$ at pH 5. The last fraction contained the pyridylmethylchromium species. The Cr:picolyl group ratio which was found to be 1:1 confirmed the purity of the complex. Spectral data for the complex are given in Table I.

Since fraction 3 has a visible spectrum identical to that reported for the chloro complex, it can be concluded that it contains only this species in solution. The inorganic complex eluted in fraction 2 is expected to be of lower charge. Also the shift in its absorption maxima to higher wavelengths is consistent with the replacement of an aquo ligand with a halide ion, as shown in Table IIb. Hence this species has been assigned the formula $Cl_2Cr([15]aneN_4)^+$.

The 3- and 4-isomers reacted in the same manner as the 2-isomer and the crude reaction solutions were purified in the same way giving similar fractions. Cr:picolyl group ratio for the organochromium complexes 1:1 in each case. Spectral data are given in Table I. It will be noted that this macrocyclic amine ligand is the only amine ligand for which the 4-isomer is capable of more than transient existence. The reasons for this will be examined in a subsequent paper.

Acknowledgements

The authors thank the University of Malaya and University Pertanian Malaysia (K. C.) for financial support.

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