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Preparation and Isolation of Amine(organo)chromium(III) Complexes in Alcoholic Media

KAREN CROUSE and LAI-YOONG GOH*

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

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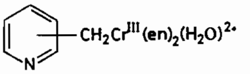
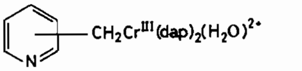
σ-Bonded organochromium complexes are prepared by the reaction of the 2- and 3-pyridylmethyl chlorides (picolyl chlorides) with bis(amine)chromium(II) ions, where amine = en, ethylenediamine; dap, 1,3-diaminopropane and trien, triethylenetetramine, in alcoholic media. The air-stable species are isolated as hydrated chlorides of the pyridylmethyl complexes, 2- and 3-$NC_5H_4CH_2Cr(amine)_2(H_2O)_m^{2+}$ *and the N-protonated pyridiomethyl complexes 2- and 3-*$H\overset{+}{N}C_5H_4CH_2Cr(amine)_2(H_2O)_m^{2+}$ *(m = 1 for amine = en and dap and m = 0 for amine = trien). Characterisation was by elemental analysis, absorption spectra and product analyses of their decomposition in dilute aqueous solution.*

Introduction

σ-Bonded chromium–carbon complexes have been a subject of continuing research interest. Since the first report of monoalkylchromium(III) complexes by Anet and Leblanc [1], a large number of such complexes have been prepared via different synthetic routes [2]. The most extensively studied have been the pentaaquo series of the $RCr(H_2O)_5^{2+}$ family [1, 3–7] followed by the (alkyl)ethylenediaminechromium(III) complexes [8, 9]. Generally, these complexes have been isolated as aquated species in dilute solution. The isolation of the first solid species was reported by one of us for the monoaquobis(ethylenediamine)(pyridylmethyl)chromium(III) complexes, $2\text{-}NC_5H_4CH_2Cr(en)_2(H_2O)^{2+}$ and $3\text{-}NC_5H_4CH_2Cr(en)_2(H_2O)^{2+}$, as their perchlorates, albeit in impure form [9]. Very recently, two reports of the isolation of similar alkylchromium complexes in solid form have also been published. Samuels and Espenson [10] reported the isolation of complexes containing a macrocyclic tetradentate ligand, namely [*trans*-n-PrCr([15]aneN_4)H_2O]$(ClO_4)_2\cdot H_2O$ and [*trans*-EtCr([15]aneN_4)NCS]ClO_4. Petrou, Vrachnou-Astra and Katakis described the isolation as a highly hygroscopic unstable solid of an uncharacterized organochromium(III) species from the reaction of Cr^{II} with 3- and 4-pyridineacrylic acid [11].

This paper reports the preparation and characterization of pure ethylenediamine complexes (*1a*) and (*1b*) and related monoalkylchromium(III) complexes as their chlorides resulting from the reaction of 2- and 3-pyridylmethyl (or picolyl) chloride hydrochloride with Cr^{II} complexes of 1,3-diaminopropane and triethylenetetraamine.





(*1a*) 2-pyridylmethyl complex (*2a*) 2-pyridylmethyl complex
(*1b*) 3-pyridylmethylcomplex (*2b*) 3-pyridylmethyl complex

Experimental

General

UV–VIS spectra were recorded in 1 *M* $HClO_4$ on a Varian Superscan, a Cary 17 or a Beckman 5270 instrument. I.R. spectra were recorded on a Beckman IR 4240. C, H, N analyses were carried out by Pascher's Microanalytisches Laboratorium of Bonn, Germany and/or Australian Microanalytical Service, Melbourne and recently with a Hewlett-Packard 135B CHN Analyser at Universiti Pertanian Malaysia. Chromium was analysed either as CrO_4^{2-} [12] or as Cr_2O_3 [13] and chloride was analysed as AgCl [14] or by means of a chloride ion electrode Model 94-17 on the Orion Model 901 Ionalyser.

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

Materials and Reagents

Hydrochloric acid was Hopkin and Williams analytical grade. Chromium metal was Koch-Light 99.99% pure. Picolyl chloride hydrochlorides were obtained from Aldrich. The amines, ethylenediamine and triethylenetetraamine of B.D.H. reagent grade and 1,3-diaminopropane of ROC/RIC reagent grade, were

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*Author to whom correspondence should be addressed.

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TABLE I. Analytical Data of n-Pyridylmethylbis(amine)chromium(III) Complexes.

Complex			C	H	N	Cl	Cr
$[n\text{-}pyCH_2Cr(en)_2(H_2O)]Cl_2 \cdot 2H_2O$		Calc:	30.85	7.25	17.99	18.21	13.35
$[n\text{-}pyCH_2Cr(en)_2(H_2O)]Cl_2 \cdot 1/7HCl \cdot 2H_2O$		Calc:	30.44	7.19	17.75	19.26	13.18
	n = 3	Found:	30.63[a]	7.29[a]	17.69[a]	19.5[b]	12.8[c] (12.8[b])
	n = 2	Found:	[d]	[d]	[d]	[d]	13.6[c]
$[n\text{-}pyCH_2Cr(dap)_2)H_2O)]Cl_2 \cdot 1\frac{1}{2}H_2O$		Calc:	35.30	7.65	17.15	17.37	12.73
$[n\text{-}pyCH_2Cr(dap)_2(H_2O)]Cl_2 \cdot \frac{1}{4}HCl \cdot 1\frac{1}{2}H_2O$		Calc:	34.53	7.55	16.78	19.11	12.46
	n = 3	Found:	35.01[e]	7.47[e]	15.36[e]	19.2[e]	12.3[c]
			36.11[f]	7.80[f]	16.31[f]	19.4[b]	12.3[c]
	n = 2	Found:	[g]	[g]	[g]	[g]	12.2[c]
$[n\text{-}pyCH_2Cr(trienHCl)_2]Cl_2$		Calc:	37.25	7.64	21.72	24.43	8.96
$[n\text{-}pyCH_2Cr(trienHCl)_2]Cl_2 \cdot 1/3HCl$		Calc:	36.48	7.54	21.27	25.92	8.77
	n = 3	Found:*	37.91[f]	8.86[f]	20.51[f]	26.21[e]	8.6[c] (8.7[b])
	n = 2	Found:	[d]	[d]	[d]	[d]	8.5[c] (8.6[b])

[a] Analysis performed on a fresh sample on a Hewlett-Packard 135B CHN Analyser. [b] By precipitation methods. [c] By spectroscopic determination as chromate. [d] Decomposed during transit to Germany. [e] C.S.I.R.O. Analytical Laboratory, Australia. [f] Microanalitisches Laboratorium, Dr. F. Pascher, Bonn, Germany. [g] Observed to decompose on standing one week at room temperature. Not sent for analysis. *Sum of percentages = 102.11%.

distilled over powdered KOH and stored over molecular sieves before use. All solvents used were of analytical grade and were stringently dried and, with the exception of acetone, were stored over molecular sieves [14, 15].

Chromium(II) chloride was obtained as the blue crystalline 4-hydrate, $CrCl_2 \cdot 4H_2O$, upon concentration of an approximately 1 *M* solution prepared by dissolving chromium metal in 2 *M* HCl under N_2. The hydrated crystals were washed thoroughly with acetone and dried under vacuum at room temperature to give pale blue crystalline $CrCl_2 \cdot 4H_2O$. These solids can be stored unchanged under dry nitrogen for indefinate periods of time. They can be used directly for reactions with ethylenediamine and triethylenetetraamine. For reaction with 1,3-diaminopropane, it was necessary to dehydrate $CrCl_2 \cdot 4H_2O$ completely by refluxing for several hours with an excess of 2,2-dimethoxypropane, whereupon a greenish-white methanolate $CrCl_2 \cdot nMeOH$ was obtained.

Reaction of $Cr^{II}(en)_2Cl_2$ with Picolyl Chloride Hydrochlorides

With 2-picolyl chloride hydrochloride

Earnshaw, Larkworthy and Patel [16] have reported that tris(ethylenediamine)chromium(II) chloride readily loses the third amine ligand. This observation is utilized to make a solution of bis(ethylenediamine)chromium(II) chloride as follows: deoxygenated, redistilled ethylenediamine (1.5 cm^3, *ca.* 25 mmol) was added to a solution of $CrCl_2 \cdot 4H_2O$ (1.1 g, *ca.* 6 mmol) in absolute ethanol (*ca.* 10 cm^3). The solution turned purple with evolution of heat, followed by precipitation of the pale blue tris(en) complex. The addition of less than 1 cm^3 deoxygenated water caused these pale blue solids to dissolve and give a deep purple solution of the bis(ethylenediamine)chromium(II) complex. This solution reacted immediately with a solution of 2-picolyl chloride hydrochloride (0.9 g, *ca.* 6 mmol) in absolute ethanol (*ca.* 5 cm^3) to give a blood-red solution which had UV spectrum (1) in 1 *M* $HClO_4$ shown in Fig. 1. After standing for about 15 min at room temperature, this was poured into acetone (*ca.* 40 cm^3) precipitating a magenta-red oil (see UV spectrum (2) in Fig. 1). Addition of ether (*ca.* 50 cm^3) to the supernatant ethanol–acetone mixture precipitated out a blood-red oil (see UV spectrum (3) in Fig. 1). Both oils were pumped to dryness at room temperature and each separately dissolved in ethanol (*ca.* 15 cm^3) to leave insoluble purplish solid residues (1.65 g and 0.05 g, respectively). These were predominantly non-organometallic solids, presumably of the type $[Cr(en)_2Cl(H_2O)]Cl_2$ as previously reported [9]. (Refer to UV spectrum (4) in Fig. 1). The red mother liquors were combined and poured into ether (*ca.* 100 cm^3) to precipitate out a pale pink-orange, fluffy, extremely hygroscopic solid (0.60 g, 60%

TABLE II. Absorption Spectra of n-Pyridylmethylchromium(III) Complex Ions in 1 *M* $HClO_4$.

n-	Complex	Formula	λ_{max}, nm ($\epsilon_{max} \times 10^{-3}$, M^{-1} cm^{-1})	λ_{min}, nm ($\epsilon_{min} \times 10^{-3}$, M^{-1} cm^{-1})
2	en	*1a*	487 (0.15), 326 (7.0), 267 (4.4), 235 (3.0)	448 (0.14), 283 (3.4), 240 (2.9), 230 (2.9)
			[520 (0.22), 331 (4.8), 265.5 (4.5) in H_2O][a]	[452 (0.14), 295 (2.3), 251 (4.0) in H_2O][a]
	dap	*2a*	505(0.19), 322 (6.9), 263 (5.0)	452 (0.16), 286 (3.7), 244 (3.7)
	trien	*3a* or *4a*	505 (0.22), 329 (7.8), 266 (4.8)	460 (0.19), 290 (3.9), 245 (3.7)
	pentaaquo	*5a*	[550 (0.073), 318 (10.4), 262 (6.2) at pH 1][b]	
3	en	*1b*	326 (3.8), 285 (6.8), 222 (5.2)	244 (2.3)
			[515 (0.23), 290–291 (7.5) in 0.1 *M* $HClO_4$][a]	[455 (0.17), 251 (5.3) in 0.1 *M* $HClO_4$][a]
	dap	*2b*	515 (0.11), 328sh (3.7), 285 (7.5)	460 (0.08), 246 (3.9)
	trien	*3b* or *4b*	505 (0.14), 330 (3.9), 283 (6.9), 225 (5.6)	465 (0.12), 244 (2.7)
	pentaaquo	*5b*	[534 (0.049), 320 (9.6), 285 (15) at pH 1][b]	

[a] From ref. [9]. [b] From ref. [4].

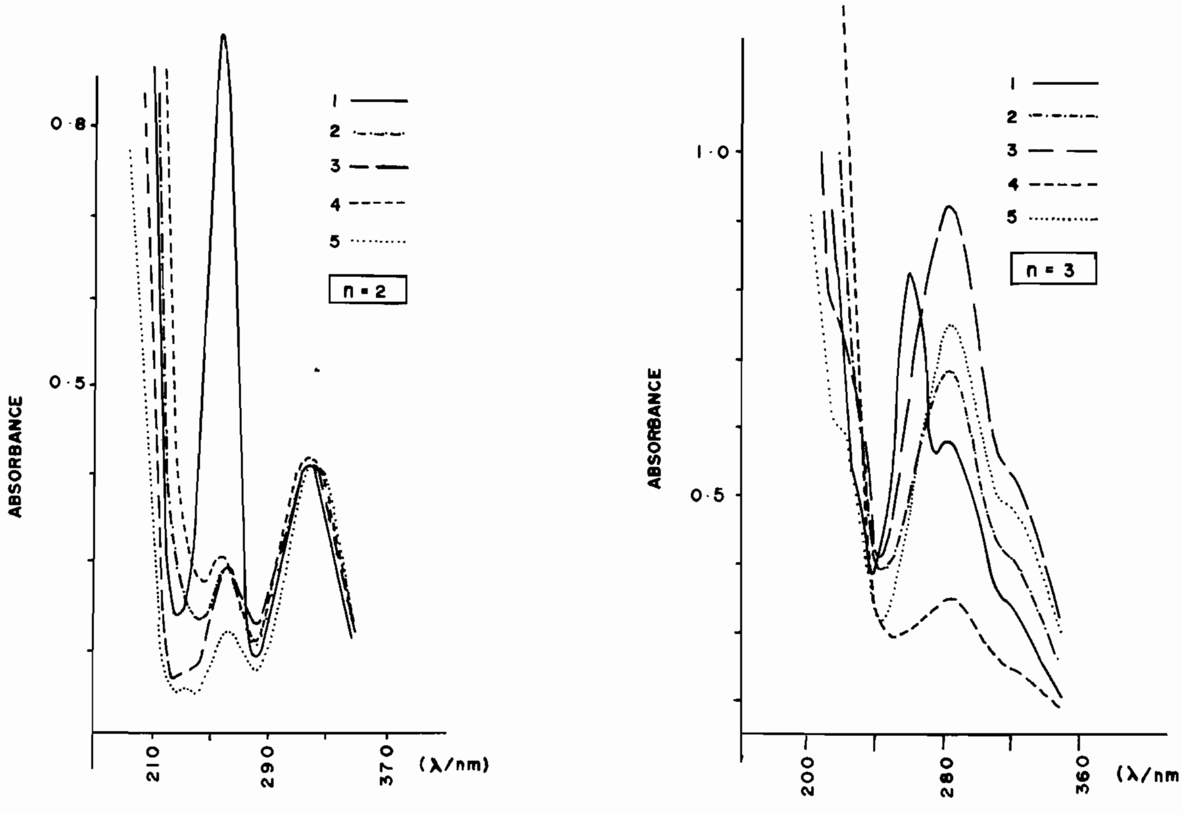


Fig.1. UV spectra in 1 *M* $HClO_4$ of products from the reaction of $Cr^{II}(en)_2Cl_2$ with n-picolylchloride hydrochloride: (1), product solution immediately after reaction; (2) and (3), subsequent precipitated oils; (4), precipitated inorganic solids; (5), pure organometallic solids.

yield based on $CrCl_2 \cdot 4H_2O$) which had a UV spectrum (5) as shown in Fig. 1. This solid was shown to contain one chromium atom to one picolyl group as a result of the analysis of Cr as CrO_4^{2-} [12] and the UV spectral estimation of the organic group as 2-picoline ($\epsilon_{max}^{262.5\,nm}$ 6.63 × 10^3 in 0.1 *N* HCl) [17] formed by decomposition in dilute aqueous acid in the presence of air. The results of the chromium and other elemental analyses are given in Table I. Based on the formula proposed, *i.e.* $[NC_5H_4CH_2Cr(en)_2(H_2O)]Cl_2 \cdot 1/7HCl \cdot 2H_2O$, the extinction coefficients of the absorption bands are given in Table II.

With 3-picolyl chloride hydrochloride

The 3-picolyl isomer (*1b*) was prepared in the same manner as the 2-isomer above (yield, *ca.* 60%). The spectra of fractions obtained in the process of isolation are given in Fig. 1. Like the 2-isomer above, the extremely hygroscopic pale pink-orange, fluffy organochromium complex was found to contain one chromium atom to one picolyl group. Data from the analysis of this complex are given in Table I. The formula proposed is $[NC_5H_4CH_2Cr(en)_2(H_2O)]Cl_2 \cdot 1/7HCl \cdot 2H_2O$. The IR spectrum of the compound in KBr showed among other bands, broad and weak absorbances at 800, 548 and 465 cm^{-1}, respectively.

With 4-picolyl chloride hydrochloride

4-picolyl chloride hydrochloride reacted immediately with $Cr(en)_2Cl_2$ to give a red solution like the 2- and 3-isomers. However, this solution rapidly turned purple. Only purple solids could be isolated. These solids had no absorption in the UV, as is characteristic of inorganic chromium(ethylenediamine) complexes.

Reaction of 1,3-Diaminopropane Complexes of Cr^{II} with Picolyl Chloride Hydrochlorides

The mono and bis(1,3-diaminopropane) complexes of chromium(II), $Cr(dap)Cl_2$ and $Cr(dap)_2Cl_2$ respectively, were prepared according to the procedure reported by Larkworthy [18].

With 3-picolyl chloride hydrochloride

Purple crystalline $Cr(dap)_2Cl_2$ (5.8 g, *ca.* 21 mmol) was suspended in dried absolute ethanol (*ca.* 40 cm^3) containing 0.5 cm^3 dap, which was added to enhance the solubility of the Cr^{II} complex. Into this was injected a solution of 3-picolyl chloride hydrochloride (1.8 g, *ca.* 11 mmol) in ethanol (10 cm^3). A red coloration which slowly deepened was observed. The reaction was allowed to proceed with stirring for 4 h at room temperature. This was found to be the optimum reaction time for maximum yield with minimal decomposition of the product. After this time, the unreacted $Cr(dap)_2Cl_2$ (3.0 g, *ca.* 11 mmol) was filtered off and washed with ethanol. The intensely red filtrate (see UV spectrum (1) in Fig. 2) was poured into acetone (*ca.* 100 cm^3) to precipitate out pale purple, predominantly inorganic solids (0.38 g) which had a UV spectrum (2) as given in Fig. 2. Addition of more acetone (*ca.* 100 cm^3) precipitated out more purplish solids (0.92 g) (UV spectrum (3)). A third additional lot of acetone (100 cm^3), followed by addition of ether (*ca.* 50 cm^3), gave a purplish brown precipitate (0.32 g) (UV spectrum (4)), suspended in an orange-coloured solution. A final addition of ether (100 cm^3) to this caused pink-orange solids (UV spectrum (5)) to precipitate out on shaking. On drying, this was found to

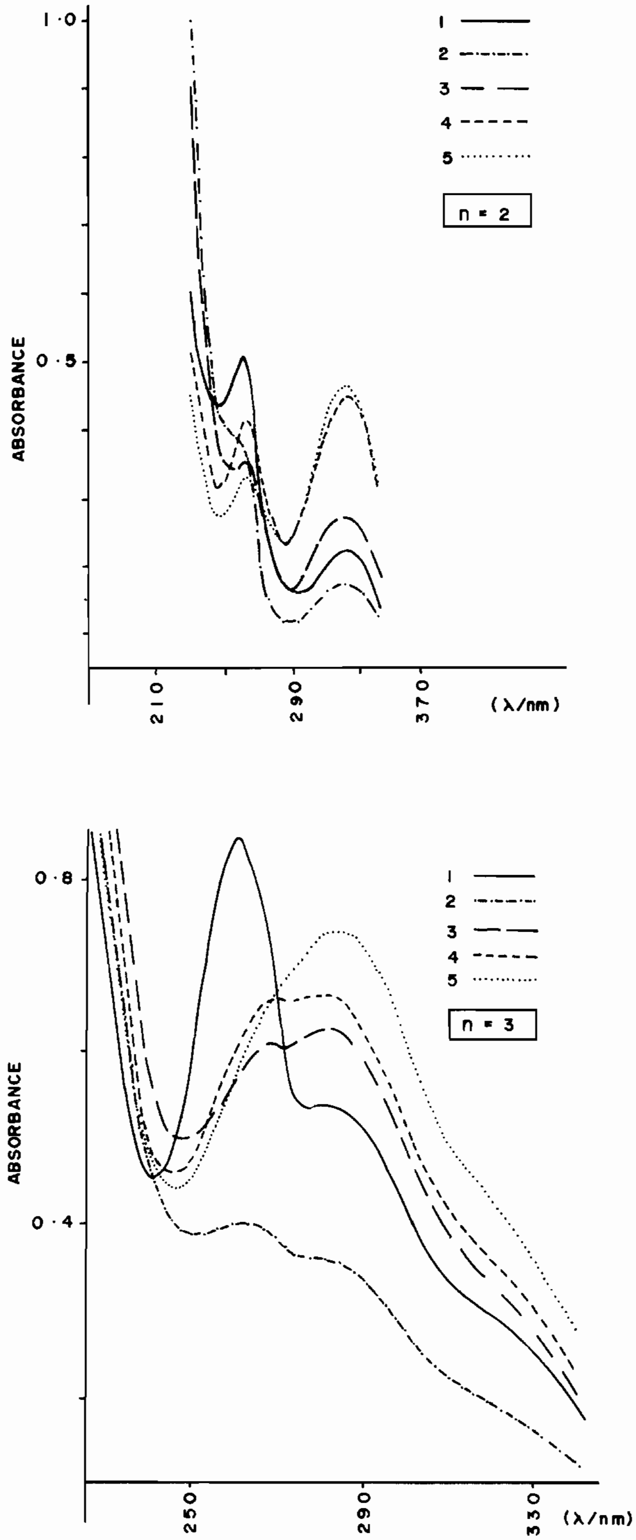


Fig. 2. UV spectra in 1 *M* $HClO_4$ of products from the reaction of $Cr(dap)_2Cl_2$ with n-picolylchloride hydrochloride: (1), product solution immediately after reaction; (2), precipitated inorganic solids; (3) & (4), precipitated solids; (5), pure organometallic solids.

be a fluffy, highly hygroscopic, air-stable solid (1.18 g, 2.8 mmol, 56% yield, based on reacted $Cr(dap)_2Cl_2$). The solid was found to contain one chromium atom to one picolyl group. The data for the elemental analyses as given in Table I supports the formula $[3\text{-}NC_5H_4CH_2Cr(dap)_2(H_2O)]Cl_2 \cdot \frac{1}{4}HCl \cdot 1\frac{1}{2}H_2O$. UV–VIS spectral data are given in Table II. The IR spectrum of the organometallic complex in KBr showed broad and weak bands at 805, 525 and 425 cm^{-1} respectively.

An ionic chloride and total chloride content was performed on a solution of the organometallic complex containing 0.2858 g/dm^3. The chloride content was measured, using the chloride ion electrode Model 94-17 in conjunction with the Orion Model 901 Ionalyser standardised against a NaCl solution. Measurements were made (a) immediately after dissolution of the complex for the determination of ionic chloride; (b) after 24 h at room temperature, (c) after heating for several hours at 100 °C and (d) after basifying followed by heating for several hours at 100 °C, for the determination of ionic plus coordinated chloride. In all cases the same chloride content of 60 ppm in the prepared solution, equivalent to 20.8% by weight of the solid complex was obtained.

With 2-picolyl chloride hydrochloride

The 2-picolyl isomer (*2a*) was prepared similarly with a similar yield. A chromium to picolyl group ratio of 1:1 was obtained. Elemental analysis is reported in Table I. The spectral characteristics are given in Table II whilst the spectra of the various solids isolated are illustrated in Fig. 2.

The reaction of 2- and 3-picolyl chloride hydrochloride with $Cr(dap)Cl_2$ did not produce any organometallic compound.

With 4-picolyl chloride hydrochloride

This organic chloride reacted with $Cr(dap)_2Cl_2$ to give an initial red coloration, but this rapidly decomposed to purple, and all which could be isolated were deep purple inorganic solids with no UV absorption, as in the reaction of $Cr(en)_2Cl_2$.

Like the 2- and 3-isomer, this organic halide also did not react with $Cr(dap)Cl_2$.

Reaction of the Triethylenetetramine Complex of Cr^{II} with Picolyl Chloride Hydrochlorides

With 2-picolyl chloride hydrochloride

To a solution of $CrCl_2 \cdot 4H_2O$ (1.7 g, *ca.* 9 mmol) in absolute ethanol (10 cm^3) was added an excess of triethylenetetramine (trien) (25. cm^3, *ca.* 18 mmol). The solution turned blue, then purple with precipitation of some purple solids. No attempt was made to isolate these solids. Into this was injected a solution of 2-picolyl chloride hydrochloride (0.9 g,

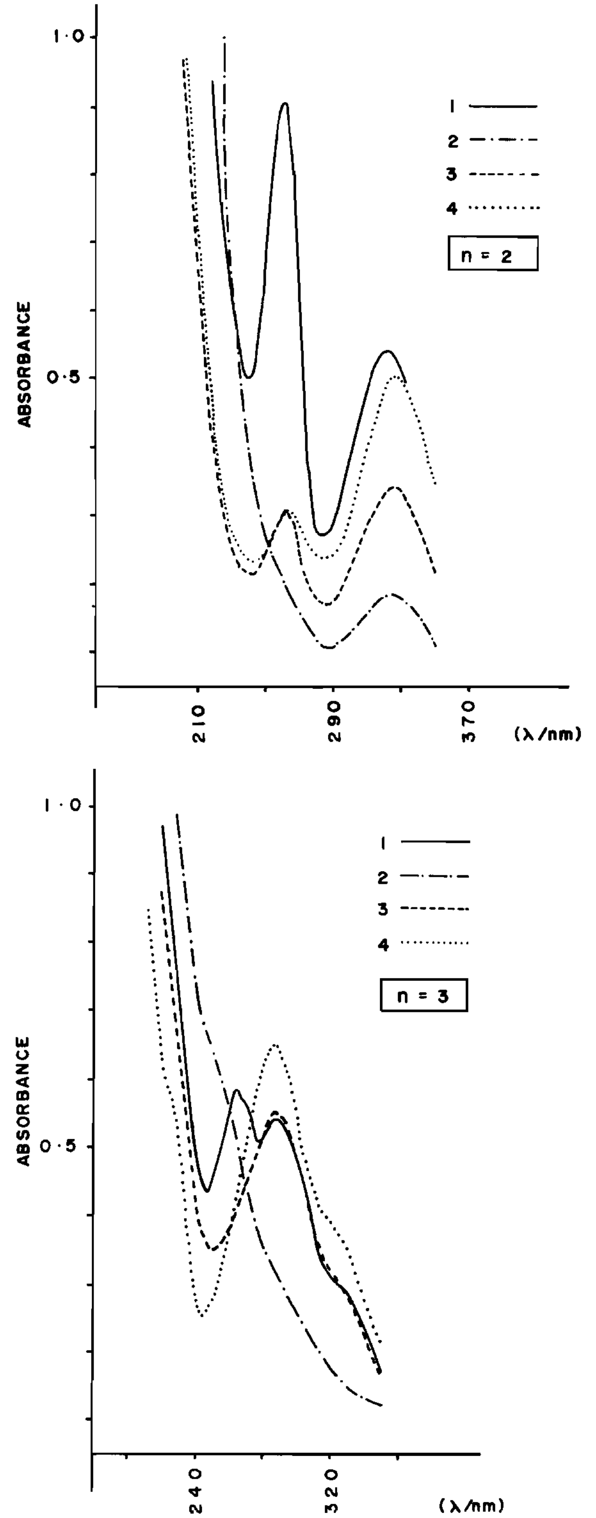


Fig. 3. UV spectra in 1 *M* $HClO_4$ of products from the reaction of the triethylenetetramine complex of Cr^{II} with n-picolylchloride hydrochlorides: (1), product solution immediately after reaction; (2), precipitated inorganic solids; (3), impure organometallic solids; (4), pure organometallic solids.

ca. 5.5 mmol) in ethanol (5 cm^3) whereupon the solution turned deep red (UV spectrum (1) in Fig. 3). The solution was then poured into acetone (*ca.* 40 cm^3) from which purple solids (UV spectrum (2)) were precipitated. The acetone–ethanol filtrate was added into ether (*ca.* 50 cm^3), precipitating pinkish solids (UV spectrum (3)) which when dried were fluffy. Further addition of ether (50 cm^3) precipitated out buff-coloured solids, fluffy when dried (0.7 g, 1.2 mmol, 26% yield, based on analytical data reported in Table I) and had UV spectrum (4) given in Fig. 3. Spectral data are given in Table II.

With 3-picolyl chloride hydrochloride

The 3-picolyl isomer was likewise isolated with a similar yield: Cr/picolyl group, 1.0/1.0. Analytical data are reported in Table I. Spectral data are given in Table II, and illustrated in Fig. 3.

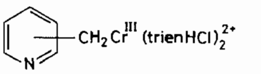
Results and Discussion

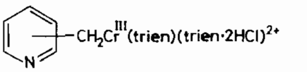
Bis(ethylenediamine) Organochromium Complexes

Our earlier work in aqueous solution [9] has shown that bis(ethylenediamine)chromium(II) chloride reacted with picolyl chlorides according to the following stoichiometric equation (i):

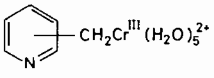
$$pyCH_2Cl + 2Cr(en)_2^{2+} \rightarrow pyCH_2Cr(en)_2^{2+} + ClCr(en)_2^{2+} \qquad (i)$$

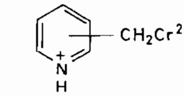
and we have isolated the perchlorate salts of the pyridylmethyl complexes (*1a*) and (*1b*) in admixture with the inorganic $ClCr^{III}(en)_2^{2+}$ complexes. After the successful isolation from a non-aqueous medium of the pure chloride salts of the analogous dap complexes (*2a*) and (*2b*) described below, it occurred to us that purification of the en complexes could be effected by carrying out the synthesis and separation in a non-aqueous medium. This would obviate problems, including a slow decomposition in the moist state, associated with the extremely hygroscopic nature of these complexes. It would be desirable to isolate out the $Cr^{II}(en)_2Cl_2$ complex in solid form before reaction with the organic substrates, like in the case of the dap complexes described below. However, whilst the solid pale blue $Cr^{II}(en)_3Cl_2$ was readily isolated, the purple solid $Cr^{II}(en)_2Cl_2$ was only capable of transient existence as a suspension [16]. It was also reported that the third en ligand in $Cr^{II}(en)_3^{2+}$ could be readily removed by washing the complex with solvent, in agreement with earlier findings by Pecsok and Bjerrum [19] which showed an extremely low stability constant K_3 *ca.* 0.1, compared with K_1 1.4 × 10^5 and K_2 1 × 10^4 for the $Cr^{II}(en)^{2+}$ and the $Cr^{II}(en)_2^{2+}$ complexes, respectively. To overcome these difficulties we therefore prepared the $Cr^{II}(en)_3Cl_2$ complex in absolute ethanol by reacting $CrCl_2 \cdot 4H_2O$ with excess ethylenediamine, and immediately converted the pale blue suspension to a purple solution of $Cr^{II}(en)_2Cl_2$ by addition of a small amount of water. Following this the organometallic complexes were readily obtained by addition of the appropriate organic substrates. The deep red product solution was worked up as quickly as possible, as it tended upon standing to change to a purple colour and to give only purple inorganic solids as a result of decomposition. Successive precipitations in alcohol–acetone–ether mixtures were used to finally give hydrated chlorides of the monoaquobis(ethylenediamine) organochromium complexes (*1a*) and (*1b*), as fluffy, highly hygroscopic, orange-pink powders. The oily nature of the first precipitate could be attributed to the presence of the added water and it was important to remove this rapidly under vacuum to minimise water-induced decomposition. Subsequent purification steps were then carried out under dry conditions. The relatively low yields obtained, *ca.* 60%, indicate that water-induced decomposition in the initial stages of the preparation still occurred. The UV spectral characteristics are shown in Fig. 1 and Table II, where they can be compared with those of analogous complexes.





(*3a*) 2-pyridylmethyl complex (*4a*) 2-pyridylmethyl complex
(*3b*) 3-pyridylmethyl complex (*4b*) 3-pyridylmethyl complex





(*5a*) 2-pyridylmethyl complex (*6*) n-pyridiomethyl chromium
(*5b*) 3-pyridylmethyl complex complex

Elemental analyses (Table I) indicate a mixture of the pyridylmethyl complex (*1a*) or (*1b*) and their pyridiomethyl forms (*6*) in a molar ratio of 6:1. The occurrence of the pyridiomethyl form points to a resemblance to the picolyl chloride hydrochlorides themselves which readily precipitate or crystallise out of ethanol. However it is noted that despite the fact that picolyl chloride hydrochlorides were used in the preparation, not all but only a minor fraction (1/7) of the complex molecules was obtained in the pyridiomethyl form. This is not unexpected because the more strongly basic ethylenediamine (pK_a 10.7), used in excess in the preparation, will certainly abstract most of the protons attached to the heterocyclic nitrogen of the pyridine ring ($pK_a \sim 6$). This same finding is again observed in the complexes containing 1,3-diaminopropane (pK_a 10.6) discussed below.

Bis(1,3-diaminopropane) Organochromium Complexes

The purple crystalline $Cr(dap)_2Cl_2$ was isolated before reaction with the organic substrate. A crude spectral titration of the reaction of $Cr(dap)_2Cl_2$ with 3-picolyl chloride, coupled with an estimation of unreacted reagents on a preparative scale demonstrated that the reaction follows the normal stoichiometric pattern of other Cr(II) complexes with RX [2], [9] *viz.*,

$$3\text{-}pyCH_2Cl + 2Cr(dap)_2Cl_2 \rightarrow$$
$$3\text{-}pyCH_2Cr(dap)_2Cl_2 + Cr(dap)_2Cl_3 \qquad \text{(ii)}$$

The reaction was much slower than that of Cr^{II} or Cr^{II}(en) complexes. After 4 h, only about 50% of the $Cr(dap)_2Cl_2$ had reacted under the conditions of the reaction. It was not advantageous to allow the system to react longer because decomposition of the organochromium product began to set in. Dried solvents have to be used at all stages of the preparation and isolation, which was slightly more difficult than for the en complexes. The spectra of successive lots of precipitates obtained in the isolation procedure for the 3-isomer are illustrated in Fig. 2. It is apparent that the purity was improved with each successive precipitation. Finally the pure organometallics were obtained as fluffy, pink-orange, highly hygroscopic and air-stable solids, having elemental and decomposition product analyses conforming to hydrated chlorides of complexes representated by (*2a*) and (*2b*) in the mixed pyridylmethyl-pyridiomethyl forms (in molar proportion of 3:1, Table I), as in the case of the analogous en complexes. The assignment of coordinated water in these complexes was based on IR studies of (*2b*) as well as (*1b*). The broad and fairly weak absorbances at 805, 525 and 425 cm^{-1} for (*2b*) and 800, 548 and 465 cm^{-1} for (*1b*) could be attributed to the ρ_r and ρ_w modes of vibration and ν_{Cr-O}, respectively, of coordinated water. These absorbances compare very well with the corresponding frequencies of 800, 541 and 490 cm^{-1} of hexaaquochromium(III) chloride [20]. This conclusion is supported by the apparent absence of any ν_{Cr-Cl} at 400–200 cm^{-1} in the IR region and by the experiment on ionic-*versus*-total chloride content which indicated that there was no coordinated chloride.

The failure of $Cr(dap)Cl_2$ to react with the picolyl chlorides was not unexpected since Larkworthy has reported that the $Cr(dap)X_2$ (X = Cl, Br, I) complexes were polymeric chloride-bridged species, on the basis of their stoichiometry, reflectance spectra and magnetic behaviour [18].

Bis(triethylenetetramine) Organochromium Complexes

Based on Pecsok's findings [21] that the ion $Cr(trien)^{2+}$ exists in solution in the presence of excess trien, we prepared this ion *in situ* and allowed it to react directly with the picolyl chlorides, rather than attempt to isolate the solid Cr^{II}(trien) species first. This was because, according to Larkworthy's report [22], these have eluded complete characterisation apparently existing as partly-hydrolysed polymeric species in which magnetic interaction occurred. The species, prepared *in situ*, consisting of a suspension of purple solids in a blue ethanolic solution, reacted immediately with both 2- and 3-picolyl chloride to give deep red solutions, resembling those of the en and dap complexes. It has been observed that this red coloration is characteristic of the formation of a σ C–Cr bond between alkyl or aralkyl groups and chromium, whether bonded to H_2O [1, 4], en [9] or dap. The buff-coloured solids isolated have elemental analysis (Table I) conforming to the chlorides of a mixture of 2 pyridylmethyl to 1 pyridiomethyl complex ions represented by (*3a*) and (*3b*) or (*4a*) and (*4b*). The presence of 2 trien:1 Cr seems to be in contrast to Pecsok's findings that only one species $Cr(trien)^{2+}$ is formed between Cr^{II} and trien [21]. However, the suggestion of the presence of terdentate $trienH^+$ or bidentate $trienH_2^{2+}$ ligands is not without precedent. It is known [23] that steric constraints sometimes force facultative ligands like trien to behave as terdentate rather than tetradentate ligands. Thus the pH-dependent terdentate nature of the trien ligand in Cu^{II} systems has been widely demonstrated [24, 25], and the isolation of complexes of the type $[Ni_2(trien)_3]X_4$, though structurally undetermined, also supports the tendency of trien to deviate from its expected quadridentate nature [26].

UV–VIS Absorption Spectra

The very striking characteristic resemblance between the UV–VIS absorption spectra of the en, dap and trien chromium complexes of each of the n-pyridylmethyl isomers, and their close similarity to those of the analogous pentaaquo complexes, as evident in Table II, provides evidence for the presence of the $NC_5H_4CH_2$–Cr bond in these complexes.

Stability of Complexes

All the complexes isolated were found to be air-stable, extremely hygroscopic and unstable in the moist state. Generally they were thermally unstable with a tendency to decompose even at room temperature, but the dry complexes could be kept unchanged for extended periods at temperatures below 0 °C. The formation of the 4-picolyl complexes could only be detected spectrometrically in all cases, as they were found to decompose almost immediately after their formation. These preliminary observations seem to indicate a stability order, 3- > 2- ≫ 4-, for the pyridylmethyl isomers.

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