Inorganica Chimica Acta, 107 (1985) 269–274

Preparation and Characterization of some Cr(III) Chloro-complexes with Nicotinic Acid Esters

J. BARRETT*‡, M. K. KORMOH*‡ and P. O'BRIEN‡

Department of Chemistry, Chelsea College, Manresa Road, Chelsea, London SW3 6LX, U.K.

Received February 23, 1985

Abstract

The preparation and characterisation of the trichlorotris(alkylnicotinate)chromium(III) complexes of general formula $CrCl_3(py \cdot 3COOR)_3 \cdot nH_2O$, where R = Me, Et, Pr and Bu are reported, n being 3.5, 1.0, 0 and 0 respectively. It is concluded that the ligation of the three chloride ions and that of the three nitrogen atoms is consistent with a C_{2v} arrangement in each case.

Introduction

Until recently, Cr(III) was not regarded as an essential micronutrient even though early research had shown some usefulness of the metal in biological processes [1–3]. However, and as a direct consequence of the discovery of Mertz *et al.* [4–7] of its importance in glucose metabolism, some renewed interest in the Cr(III) complexes of these ligands, especially with nicotinic acid, has resulted. The chromium containing compound became known as the Glucose Tolerance Factor (GTF). The compound is considered to behave as a cofactor to insulin potentiation.

The structure of the GTF molecule is unknown but has been suggested to possess two nicotinic acid molecules in a *trans* coordination to Cr(III) through the nitrogen atoms of the pyridine rings. The ligand has an additional carboxylate oxygen through which ligation is possible and a survey of the literature has shown that complexation through this oxygen with Cr(III) is more frequently encountered [8–10]. In addition to the nicotinic acid ligand, GTF is also considered to incorporate glycine, cysteine and glutamic acid.

Consequently, systematic syntheses of Cr(III) complexes with the esters of nicotinic acid, which bind exclusively through the pyridine nitrogen, have been undertaken. It was hoped that from spectroscopic studies of these complexes, an assessment of the effects of coordination on the ligands could be made. The chloro-complexes have been chosen especially for the infra-red studies.

Experimental

Materials

Methyl- and ethyl- nicotinate were purchased from BDH chemicals and were used directly in the preparations. Propyl- and butyl nicotinates were prepared by the reaction of nicotinic acid with thionylchloride and the respective alcohols according to the method of Clark-Lewis and Thompson [11]. The green $CrCl_3 \cdot 6H_2O$ salt – laboratory grade – was also used.

Analyses

The elements C, H and N were analysed by Butterworth Laboratories Ltd., Middlesex, U.K.

Chromium(III) was determined after decomposition of the complex and on oxidation to the chromate ion with alkaline peroxide according to the method of Haupt [12].

Preparations

All the complexes were prepared from anhydrous $CrCl_3$ which was obtained by the standard method from the green $CrCl_3 \cdot 6H_2O$ [13].

Trichlorotris(methylnicotinate)chromium(III) hydrate, $CrCl_3(py \cdot 3COOCH_3)_3 \cdot 3.5H_2O$

Five grams (5 g) of anhydrous $CrCl_3$ (0.03 mol) and 27.7 g of methylnicotinate (0.16 mol) were placed in a round-bottomed flask and refluxed, with stirring, over a water bath for 2 h to give a green solution. The solution was transferred into a beaker, cooled to room temperature, and 100 cm^3 ether added to remove the excess ester. The resulting light-green mass was crushed and extracted with methanol in a Soxhlet extractor. The complex was obtained on

*Authors to whom correspondence should be addressed.

‡Present addresses: J.B., Dept. of Chemistry, Queen Elizabeth College, Campden Hill, Kensington, London W8 7AH; M.K.K., Dept. of Chemistry, Fourah Bay College, University of Sierra Leone, Freetown, Sierra Leone, W. Africa; P.O'B., Dept. of Chemistry, Queen Mary College, Mile End Road, London E1 4NS.

0020-1693/85/$3.30

evaporation of the methanol. The product was insoluble in water but dissolved in chloroform and acetone. The final yield was 17 g (86%). *Anal.* Found: Cr, 7.87; C, 39.89; H, 4.69; N, 6.93; H_2O, 10 (by TG). Calcd. for $CrCl_3(py{\cdot}3COOCH_3)_3{\cdot}3.5H_2O$: Cr, 8.23; C, 39.87; H, 4.45; N, 6.65; H_2O, 10.02%.

Trichlorotris(ethylnicotinate)chromium(III) Hydrate, $CrCl_3(py{\cdot}3COOEt)_3{\cdot}H_2O$

The complex was prepared as above but with 24 g of ethylnicotinate (0.16 mol). A precipitate was obtained by the addition of 100 cm^3 ether to the green solution after refluxing. The precipitate was washed further with more of the ether until the ester smell disappeared completely. The extraction process was carried out with chloroform. The complex was also insoluble in water but dissolved in alcohols and was slightly soluble in ether. The final yield was 16 g (80%). *Anal.* Found: Cr, 8.50; C, 45.78; H, 4.51; N, 6.77; H_2O, 3 (by TG). Calcd. for $CrCl_3(py{\cdot}3COOET)_3{\cdot}H_2O$: Cr, 8.27%; C, 45.79; H, 4.61; N, 6.68; H_2O, 2.86%.

Trichlorotris(propylnicotinate)chromium(III), $CrCl_3(py{\cdot}3COOPr^n)_3$ and trichlorotris(butylnicotinate)chromium(III), $CrCl_3(py{\cdot}3COOBu^n)_3$

These complexes were prepared by the above method, from a 1:5 molar ratio of the anhydrous $CrCl_3$ and the esters respectively. An exothermic reaction was observed with the butyl ester. The resulting green liquids were poured into 100 cm^3 ether and eluted through a silica column to remove the excess esters. After evaporation of the ether, the viscous products were analysed for Cr(III). *Anal.* Found: Cr, 7.65. Calcd. for $CrCl_3(py{\cdot}3COOPr)_3$, 7.96%. Found: Cr, 7.25. Calcd. for $CrCl_3(py{\cdot}3COOBu)_3$, 7.48%.

Trichlorotris(pyridine)chromium(III), $CrCl_3(py)_3$

The complex was prepared by the method of Taft and Jones [14], for purposes of comparison.

Apparatus

The visible and infra-red absorption spectra were measured with Perkin-Elmer 402 and 457 Grating spectrophotometers respectively. The thermal and magnetic-susceptibility measurements were carried out with Stanton Red-Croft Type 750 and the Stanton Type Gouy Balance respectively.

Results and Discussion

Thermal Analysis

Analysis of the methyl ester complex was carried out on 4.8 mg of the sample at a heating rate of 10 °C min^{-1}. The results were consistent with the loss of three and a half molecules of water at 100 °C followed by the loss of the chlorides (3 mol) and the methoxyl groups of the ester at *ca.* 280 °C. The residue of the ligands, including the pyridine group plus the attached CO after the loss of the OMe group, were given off at 420 °C with the formation of Cr_2O_3. The amount of Cr_2O_3 remaining gave 7.87% Cr as the Cr content of the original material. No conclusive deduction on the thermogram for the ethyl ester could be made, except for the loss of 3% H_2O – one molecule – at *ca.* 100 °C.

Infra-red Absorption Spectra

The major absorption frequencies are shown in Table I. The band assignments have been made by comparison with the spectra of the ligands [15–18] and with the Cr(III) complexes of other 3-substituted pyridines [19]. Spectral assignments for the propyl and butyl esters were carried out by analogy with the methyl- and ethyl- esters. A striking feature of the infra-red spectra of the lower homologues is the high resolution of the aromatic (CH) stretching frequencies of the complexes.

In the infra-red spectra of the complexes, additional peaks were observed at $\bar{\nu}_{max}$ of 1090m, 840m, 730s, 712m, 675s and 370 m cm^{-1} for the methyl ester complex and at 1140s, 870w, 845m, 830w and 705w cm^{-1} for the ethyl ester complex. Generally, such additional bands are due to lattice modes – intermolecular interactions resulting from the lowering of the molecular symmetry in the crystalline state. Bands due to this mode occur below 300 cm^{-1} but can occur at higher frequencies as combination bands with other internal vibrations. However, due to the appearance of some of these bands in both the complexes and the ligands of the higher homologues – bands at $\bar{\nu}_{max}$ of 1090 and 840 cm^{-1} (in the methyl complex) and at 845 and 830 cm^{-1} (in the ethyl complex) – they are less likely to be due to lattice modes. The band at 1090 cm^{-1} is probably due to the in-plane (symmetric) CH stretching vibrations (A_1). Some of these bands have been observed by Greenwood and Wade in pyridine and the pyridine adducts of BCl_3 [20]. Most of the bands were assigned to CH stretching and deformation modes.

In addition to the appearance of additional peaks in the complexes, coordination of the esters resulted in band shifts from 1592s to 1605s and shifts from 1420s, 1022s and 620m to 1435s, 1055m and 655m respectively in the methyl complex. Band shifts from 1592s, 1420m, 1040m and 620m cm^{-1} to 1610s, 1425m, 1058s and 655m respectively were observed for the ethyl ester complex; similar shifts were seen for the propyl- and butyl-ester complexes (Table IC and ID). These band shifts are due to the (C=C) and (C=N) stretching modes resulting from the coordination of the esters through the pyridine nitrogen atom. The ring vibrational frequencies are most affected with spectral band displacements of about 33 cm^{-1}.

TABLE I. Infrared Frequencies and the Comparative Band Assignments for the Esters and their respective Chloro Complexes of the type: $CrCl_3(py \cdot 3COOR)_3$.

py·3COOR	$CrCl_3(py \cdot 3COOR)_3$	Assignments
A. The Methyl Complex (R = Me)		
	3420m	ν(OH)
	3205w, 3160w	ν(CH)
	3120w, 3100m	
	3070m, 3020m	
2960m(2970)	2950m, 2890m	
1725vs(1730)	1742vs, 1730sh	ν(C=O)
1592m(1595)	1605m	ν(C=C), (C=N); (A1)
(1580sh)	1595w	ν(C=N), (C=C); (B1)
1440s (1438)	1440s	s Me bend, OMe
1420s (1421)	1435s	ν(C=N), (C=C); (A1)
	1360	ν(CH)
1328m(1328)	1325m	ν(CCO)
1290vs(1285)	1295vs	
(1205)		
1190s (1188)	1192m	ν(CCO), β(CH)
1125s (1122)	1125s	B1, β(CH)
1115vs(1112)	1110s	ν(CCO)
	1090m*	A1, β(CH)
(1036)		B1, β(CH)
1022vs(1025)	1055m	A1 ring
(1005)		
960w(955)	960w	γ(CH), OMe
	840m*	(HC=CH)?
825m(825)	825m	(CCO)
750vs(750)	750s	δ(COO)
	735s*, 712m*	γ(CH) out-of-plane
700s (700)	693s	ν4, ring
	675s*	
620m(625)	655s	ν6b, ring
(480)	470b, w	ν6a, ring
(430)		ν16a, ring
	370m*	
	360s	ν(Cr–Cl)
330m	340m	
	335s	ν(Cr–Cl)
	290s	ν(Cr–Cl)
B. The Ethyl Complex (R = Et)		
	3430m	ν(OH)
	3120w, 3100w	ν(CH)
	3080w, 3050w	
2985m(2990)	3020w, 2990m	
	2940w, 2900	
1725vs(1724)	1725vs	ν(C=O) ester
1592s (1598)	1610s	ν(C=N), (C=C); (A1)
	1595m	ν(C=N), (C=C); (B1)
1475w(1470)	1475m	ethyl CH_2 scissor
(1447)		ethyl CH_3 asy. bend
1420m(1422)	1425s	ν(C=C), (C=N); (A1)
1392w(1392)	1392m	ethyl CH_3 sy. bend
1370m(1370)	1368s	ethyl CH_2 wag
1328w(1328)	1325m	ν(CCO)
1285vs(1284)	1295vs	
1195w(1193)	1192m	
1173w(1167)	1173w	
	1140s*	
1130s (1128)	1125s	β(CH) (A1)

(continued overleaf)

TABLE I *(continued)*

py·3COOR	$CrCl_3(py \cdot 3COOR)_3$	Assignments
1110s (1110)	1113vs	β(CH) (B1)
(1086)		
1040m(1039)	1058s	B1 ring, (CH)
1027s (1027)	1020s	A1 ring
(853)	870m*, 845w*, 830w*	B2 γ(CH)
742s	745vs	δ(COO)?
	705w*	γ(CH) out-of-plane
702vs	692vs	γ(CH) out-of-plane
620m(618)	655m	ring in-plane
(490)	470b, w	ring in-plane
(388)		ring out-of-plane
	370s	
	320s	ν(Cr–Cl)
	290s	
C. The Propyl Complex (R = Pr^n)		
3450m	3450m	ν(C=O) overtone
3080w, 2050w	3120w, 3090w, 3065w	
3040mw, 3020mw	3045w, 3020w	ν(CH)
2968vs, 2932s(2980)	2970s, 2930m	
2892s, 2878s	2900m, 2880m	
1730-1720vs	1725vs	ν(C=O) ester
1595vs(1595)	1610vs	ν(C=C), (C=N)
1576sh(1578)	1585sh	
1470s, 1460sh	1470s, 1460sh	ν(CH)
1420s (1419)	1430ms	ν(C=C), (C=N)
1390s	1390s	CH_3 sym. bend
1380sh, 1348ms	1350m	CH_2 wag
1326s, 1310s	1327s, 1312s	
1300-1270vs	1280s	ν(CCO)
1236s		
1193s (1191)		
1110vs, b	1112s	B1 β(CH)
1090ms	1090m	A1 β(CH)
1038ms(1037)	1038mw	B1 β(CH)
1024vs(1024)	1055s	A1 ring
965m, 948m	965mw, 948m	γ(CH)
912ms, 892mw	912m	
845w, 832m	845w, 832m	B1 γ(CH)?
740vs	740s	δ(COO)?
702vs	690vs	ring out-of-plane
620s	655ms	ring in-plane
	370s	
	320s	ν(Cr–Cl)
	290s	
D. The Butyl Complex (R = Bu^n)		
3445ms	3450m	ν(C=O) overtone
3090w	3120w, 3090w	
3060w, 3040w	3070w, 3050w	
3020w, 2960s	2960ms	ν(CH)
2932ms	2935m, 2900sh	
2870ms	2870m	
1730-1720vs	1726vs	ν(C=O) ester
1592vs(1594)	1610ms	ν(C=C), (C=N)
1570sh(1578)	1600m	
1466ms	1470m	ν(CH)
1418s (1420)	1430ms	ν(C=C), (C=N)
1390sh		CH_3 sym. bend
1385ms	1386m	

(continued overleaf)

TABLE I *(continued)*

py·3COOR	$CrCl_3$(py·3COOR)$_3$	Assignments
1356mw	1357w	CH_2 wag.
1327s	1328ms	
1295sh	1292vs	
1282vs, b	1267sh	ν(CCO)
1237ms		
1193ms(1190)	1192m	
1110vs, b	1130ms*, 1112s	B1 β(CH)
	1095m	A1 β(CH)
1025vs	1057m	A1 ring
963mw, 942m	955w, 945w	γ(CH)
905w	905vw	
845m, 832m	845w, 832mw	B2 γ(CH)?
742vs	745s	δ(COO)?
705vs	690s	ring out-of-plane
620ms	652m	ring in-plane
	367s	
	318s	ν(Cr–Cl)
	290s	

Similar shifts were observed for the ethyl-, propyl- and the butyl-ester complexes. These two properties – the appearance of additional peaks in the spectra and the shift in the spectra – are exhibited by pyridine and its derivatives on coordination [19, 21]. The spectral modification is the result of donation of the non-bonding electron pair on the pyridine nitrogen atom into the d orbitals of the metal ion.

Three (Cr–Cl) stretching modes were observed between 370 and 290 cm^{-1} [22], indicating C_{2v} local symmetry of ligand atoms around the chromium rather than C_{3v} which would allow only two bands.

The band at 3450 cm^{-1} in both the propyl- and butyl nicotinates and their chromium complexes have been assigned to the first overtone band of the carbonyl stretching frequency [23].

Visible Absorption Spectra

The absorption spectra of the ester complexes were obtained in acetone solution and are presented together with that of the pyridine complex in Table II. As expected, the ϵ_{max} values for the esters are lower than those of the pyridine complex due to the ring deactivating effect of the carboxylate group.

The absorption bands in the region of 630 nm of all the complexes are considerably broader than would be expected for a symmetrical arrangement of ligands around a regular octahedral chromium atom. The observation is consistent with there being a lower than octahedral symmetry around the chromium atom. The magnetic susceptibilities are exactly as expected for chromium(III) complexes.

TABLE II. Magnetic-susceptibility and Visible Spectra for the $CrCl_3L_3$ Complexes.

Complex	η(BM)	ϵ_{max}	(nm)	Solvent
$CrCl_3(py)_3$	3.78	456	623	Acetone
$CrCl_3$(py·3COOMe)$_3$·3.5H_2O	3.84	462	628	Acetone
$CrCl_3$(py·3COOEt)$_3$·H_2O	3.81	460	630	Acetone

Conclusions

The complexes prepared are shown to have C_{2v} ligation of the three chloride ions and the three nitrogen atoms of the nicotinic acid esters. The infrared assignments will be useful in deciding the ligation in a further series of complexes under consideration.

Acknowledgement

M.K.K. thanks The Association of Commonwealth Universities, U.K. Branch, for the fellowship support through the British Council.

References

1 L. H. Stickland, *Biochem. J., 44,* 190 (1949).
2 A. M. Baetjer, in M. J. Udy (ed.), 'Chromium, Vol. 1', Reinhold New York, 1956, p. 80.
3 B. L. Horecker, E. Stotz and T. R. Hogness, *J. Biol. Chem., 128,* 251 (1939).
4 W. Mertz and K. Schwarz, *Arch. Biochem. Biophys., 72,* 515 (1957).
5 W. Mertz, *Physiol. Rev., 49,* 163 (1969).
6 R. A. Anderson and W. Mertz, *Trends Biochem. Sci. (Ref. Ed.), 2,* 277 (1977).
7 W. Mertz, E. W. Toepfer, E. E. Roginski and M. M. Polanski, *Fed. Proc., Fed. Am. Soc. Exp. Biol., 33,* 2275 (1974).

8 L. E. Gerdom and H. M. Goff, *Inorg. Chem, 21,* 3847 (1982).
9 E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat and J. A. Ibers, *Inorg. Chim. Acta, 66,* 115 (1982).
10 C. L. Sharma, P. K. Jain and T. K. De, *J. Inorg. Nucl. Chem., 42,* 1681 (1980).
11 J. W. Clark-Lewis and M. J. Thompson, *J. Chem. Soc.,* 442 (1957).
12 G. E. Haupt, *J. Res. Nat. Bur. Stand., 48,* 414 (1952).
13 A. R. Pray, *Inorg. Synth., 5,* 154 (1957).
14 J. C. Taft and M. M. Jones, *Inorg. Synth., 7,* 132 (1965).
15 A. R. Katritzky, A. M. Munro, J. A. T. Beard, D. P. Dearnaley and N. S. Earl, *J. Chem. Soc.,* 2182 (1958).
16 A. R. Katritzky, A. R. Hands, R. A. Jones, *J. Chem. Soc.,* 3165 (1958).
17 R. Isaac, F. F. Bentley, H. Strenglanz, W. C. Coburn, C. V. Stephenson and W. S. Wilcox, *Appl. Spectrosc., 17,* 90 (1963).
18 A. R. Katritzky, *Q. Rev., Chem. Soc., 13,* 353 (1959).
19 J. C. Change, M. A. Haile and G. R. Keith, *J. Inorg. Nucl. Chem., 34,* 360 (1972).
20 N. N. Greenwood and K. Wade, *J. Chem. Soc.,* 1130 (1960).
21 J. Burgess, *Spectrochim. Acta, 24,* 227 (1968).
22 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 358 (1965).
23 S. D. Ross, personal communication.