Inorganica Chimica Acta, 218 (1994) 179–184

Note

Structural characterization of octahedral metal complexes of $[MX_3(py)_3]$ type with three pyridines as revealed by ^2H NMR spectra

Sumio Kaizaki*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

J. Ivan Legg**

Department of Chemistry, Washington State University, Pullman, WA 99164-4630 (USA)

(Received August 27, 1993, revised November 30, 1993)

Abstract

Deuterium NMR spectra of a series of *mer*-$[MX_3(py\text{-}d_5)_3]$ type complexes where M = Cr(III), Mo(III) and $X = Cl^-, Br^-, F^-, NCS^-$ have been measured to determine the geometrical structure. Most of them provided a decisive criteria for this purpose with only one exception of $[CrCl_3(py\text{-}d_5)_3]$ where the ^2H NMR and visible absorption spectra behave like the *fac* isomer. The previous assignments of 'fac'- and 'mer'-$[Cr(NCS)_3(py)_3]$ by DasSarma and DasSarma were found to be wrong; correctly *mer*-$[Cr(NCS)_3(py)_3]$ and (Hpy)-$[Cr(NCS)_4(py)_2]$, respectively.

Key words: Crystal structures; Chromium complexes; Molybdenum complexes; Octahedral complexes

Introduction

There is considerable interest in Cr(III) complexes of the ambidentate ligand nicotinic acid (niacin, 3-pyridine-carboxylic acid) due to the potential role of such a species in glucose metabolism [1]. Initially stabilization of a Cr(III)–nicotinic acid complex proved to be elusive, and indeed, it was reported that such complexes were unstable under physiological conditions [2] even though Cr(III) complexes of closely related pyridine are known to be stable. This apparent anomaly prompted us to investigate Cr(III) and other substitution inert d^3 and d^6 metal complexes of nicotinic acid and pyridine-like ligands. Recently we reported the first stable N- and O-coordinated nicotinic acid Cr(III) complexes [3].

We have established the identity and the stability of the complexes by a deuteron NMR technique recently developed in our laboratory [4]. This technique is a sensitive monitor of ligand coordination [5] and has been used to define the stereochemistry of paramagnetic chromium(III) complexes in solution [6, 7]. During the course of these studies, we discovered a number of inconsistencies in what had been published concerning the chemistry of Cr(III)–pyridine complexes. Reported structures were inconsistent with results obtained from ^2H NMR spectroscopy, a structural probe that has proved particularly valuable in elucidating Cr(III) chemistry. However, the ^2H NMR data proved to be ambiguous in several instances, and a more extensive investigation of d^3 and d^6 pyridine complexes was undertaken. We report here the characterization of a series of $[M(III)X_3(py)_3]$ complexes where M(III) can be Cr(III) and Mo(III) and X can be Br^-, Cl^-, F^- and NCS^-. The complex $[Cr(tpa)Cl_3]$ (tpa = tri(2-pyridyl)amine) was synthesized to help establish the structures of the species investigated. This study is the first report of the use of ^2H NMR to characterize a stable Mo(III) complex, though it has been reported that $[Mo(bpy\text{-}6,6'\text{-}d_2)_3]^{3+}$ (bpy = 2,2'-bipyridine) in solution gave a ^2H NMR spectrum of *cis*-$[Mo(bpy\text{-}6,6'\text{-}d_2)_2(solvent)_2]^{3+}$ due to its instability [8].

Experimental

Materials

Deuterium-labeled complexes were prepared from perdeutero pyridine (99 at.% ^2H, Sigma) and α-deutero pyridine obtained according to the literature method [9]. Tri(2-pyridyl)amine (tpa) was obtained by the method of Wibaut and La Bastide [10].

Preparation of thiocyanato-κN complexes

Patel's method was used to synthesize $[Cr(NCS)_3(py)_3]$ from $Cr(NCS)_3 \cdot xH_2O$ in pyridine [11]. The complex was recrystallized from acetone by the addition of ether. The procedure described by DasSarma and DasSarma [12] for the synthesis of so called 'fac'-$[Cr(NCS)_3(py)_3]$ from $NH_4[Cr(NCS)_4(py)_2]$ in pyridine yielded $(Hpy)[Cr(NCS)_4(py)_2]$. This complex and the potassium salt were synthesized independently as described in the literature [13]. When (Hpy)-$[Cr(NCS)_4(py)_2]$ was adsorbed on a preparative TLC

---

*Author to whom correspondence should be addressed

**Present address: Memphis State University, Memphis, TN, USA.

SSDI 0020-1693(93)03780-E

plate (Whatman PLK5 silica gel) and developed with CH_3NO_2, a single band was isolated and characterized as $H[Cr(NCS)_4(py)_2]$.

Preparation of halogeno complexes

Reported procedures were used to synthesize the following complexes: $[MoCl_3(py)_3]$ [14], $[CrF_3(py)_3]$ [15], $[CrCl_3(py)_3]$ [16], $[CrBr_3(py)_3]$ [17], $[CoCl_3(py)_3]$ [18], $[Co_2(OH)_3(py)_6]Cl_3$ [19], $[CoCl_2(py)_4]Cl$ [20], $[Co(CO_3)(py)_4]ClO_4$ [21].

Preparation of [CrCl₃(tpa)]

A solution of $CrCl_3 \cdot 6H_2O$ (0.26 g) dissolved in 10 cm^3 of *N*,*N*-dimethylformamide (dmf) was brought to boiling and the volume was reduced to 5 cm^3. To this solution 0.25 g of tri(2-pyridyl)amine was added whereupon green crystals precipitated. The product was recrystallized from dmf by the addition of ether to give 0.3 g of pure green product.

Measurements

Elemental analyses (C, H, N) were obtained from Galbraith Laboratories, Inc. and C, H and N from the Analytical Facility, Department of Chemistry, University of Idaho. Analytical results are reported in Table 1.

The 30.7 MHz ^{2}H spectra, 50.3 MHz ^{13}C spectra and 200 MHz ^{1}H spectra were recorded at room temperature on a Nicolet NT-200WB spectrometer. Instrumental parameters have been reported elsewhere [6]. UV–Vis absorption spectra were recorded on a Varian/Cary 219 spectrophotometer.

Results and discussion

Stereochemistry

In theory two isomers are possible for an $[MX_3(py)_3]$ complex, a facial (*fac*) isomer in which equivalent ligands define the face of an octahedron and a meridional (*mer*) isomer in which equivalent ligands define the edge (meridian) of an octahedron (see Fig. 1 for an example of a *mer* isomer). Assuming rapid rotation of the pyridines around the M–py bond, the effective symmetry for an NMR experiment in solution is C_{3v} for the *fac* isomer with all pyridines equivalent and C_{2v} for the *mer* isomer with the two *trans* pyridines equivalent and distinct from the remaining pyridine. A coordinated pyridine would give three signals for the nucleus under observation (^{1}H, ^{2}H, ^{13}C) for the α, β and γ positions integrating 2:2:1. Such a spectrum is expected in the absence of nuclear spin–spin coupling, a situation which obtains for the ^{2}H spectra (and natural abundance ^{13}C spectra). Thus, for a facial isomer a 2:2:1 spectrum would be observed and for a meridional isomer two sets of 2:2:1 spectra integrating 2:1 are expected in the absence of accidental degeneracy. A 2:2:1 spectrum was observed for *trans*-$[Cr(malonato)_2(py\text{-}d_5)_2]^+$ [4]. The α and β positions were differentiated by obtaining the ^{2}H NMR spectrum for the complex prepared with py-α-d. Although based on the results of this earlier study there is little doubt as to the specific assignment of the individual pyridine resonances in this study, py-α-d was employed to confirm the assignments for the Mo(III) and Cr(III) complexes investigated. It should be noted, as previously established, that the use of ^{2}H as an NMR probe makes possible the generation of useful NMR data for structural studies on Mo(III) and Cr(III) complexes due to the excessive broadening of resonances when ^{1}H is monitored.

Thiocyanato-κN complexes

DasSarma and DasSarma reported the characterization of both *mer* and *fac* isomers for $[Cr(NCS)_3(py)_3]$ [12]. Isomer assignment was based on an analysis of IR and visible spectra. Differences in complexity (IR)

TABLE 1. Elemental analysis

Complex	C (%)		H (%)		N (%)	
	Found	Calc.	Found	Calc.	Found	Calc.
$[CrCl_3(py\text{-}d_5)_3]$	43.61	43.78			9.78	10.21
$[CrF_3(py)_3]$	51.43	52.03	4 71	4.37	12.01	12.13
$[CrF_3(py\text{-}d_5)_3]$	49.47	49.84			11.45	11.64
$[CrBr_3(py)_3]$	33.79	34.06	2.99	2.86	7.53	7.94
$[CrBr_3(py\text{-}d_5)_3]$	32.60	33.13			7.41	7.73
$[Cr(NCS)_3(py)_3]$	46.94	46.65	3.39	3.24	17.47	18 14
$[Cr(NCS)_3(py\text{-}d_5)_3]$	44.82	45.19			17.06	17.57
$(Hpy)[Cr(NCS)_4(py)_2] \cdot H_2O$	43.62	42.21	3.37	3 36	18.15	18.13
$(Hpy\text{-}d_5)[Cr(NCS)_4(py\text{-}d_5)_2]$	42.68	42.46			17.98	18.24
$H[Cr(NCS)_4(py)_2] \cdot 4H_2O$	32.62	32.05	3 51	3.65	16.10	16.02
$[CrCl_3(tpa)] \cdot H_2O$	44.56	42.43	3.54	3.32	13.23	13.19

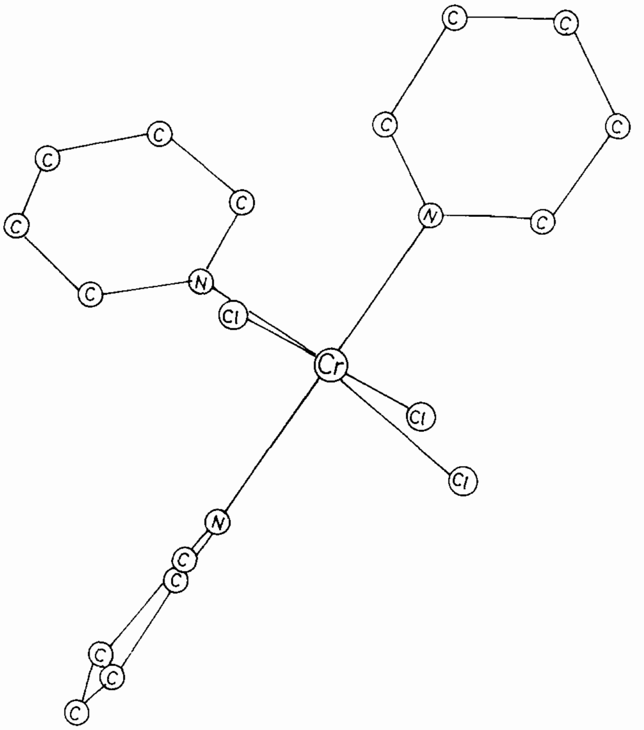

Fig. 1. Molecular structure of $[CrCl_3(py\text{-}d_5)_3]$.

and intensity (UV–Vis) of spectra as related to molecular symmetry were used to assign the isomers. The complex first prepared by Patel [11] was assigned as 'fac'-$[Cr(NCS)_3(py)_3]$ by DasSarma and DasSarma. Following Patel's procedure a complex with an IR spectrum identical to that previously reported was obtained in this study. However, a different visible absorption spectrum was obtained. When perdeutero pyridine was used in the synthesis, the ^2H NMR spectrum shown in Fig. 2 and summarized in Table 2 was obtained. Two resonances integrating 2:1 are seen for the β deuterons and the resonance for the γ deuterons is skewed to the high field side. These results show that the 'fac' isomer is *mer*-$[Cr(NCS)_3(py)_3]$ rather than the *fac*.

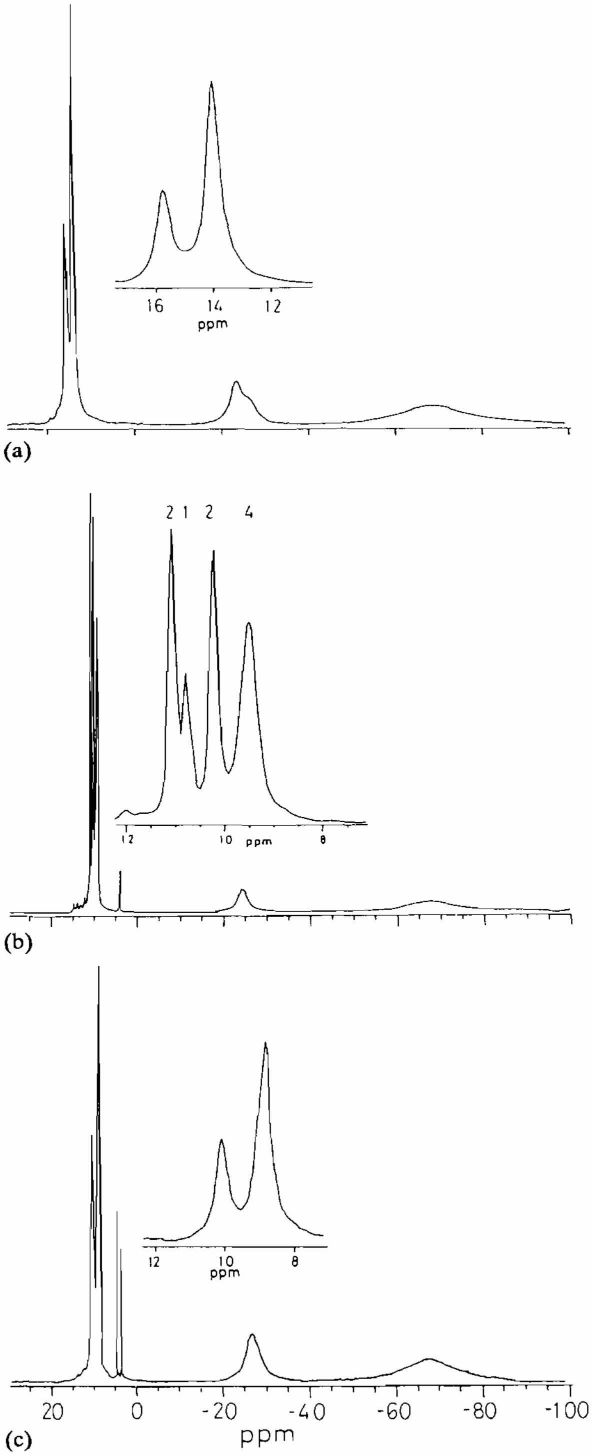

Fig. 2. ^2H NMR spectra of: (a) $[Cr(NCS)_3(py\text{-}d_5)_3]$, inset shows an expansion of the β deuteron signals; (b) $(Hpy\text{-}d_5)[Cr(NCS)_4(py\text{-}d_5)_2]$ in acetone, inset shows an expansion of the free pyridine signals (downfield) and a β deuteron signal; (c) $[CrF_3(py\text{-}d_5)_3]$ in $CHCl_3$, inset shows an expansion of the β deuteron signals.

The procedure described by DasSarma and DasSarma was used to prepare a complex that they characterized as 'mer'-$[Cr(NCS)_3(py)_3]$. The IR and visible absorption spectra of this complex were identical to those reported (Table 3) [12]. The ^2H NMR spectrum of the complex prepared with perdeutero pyridine is inconsistent with the structure formulated by DasSarma and DasSarma. The observed integration value for six peaks is found to be 2:1:2:4:2:4 from the downfield. This fact together with the relatively sharp linewidths of three peaks at 10.22, 10.77 and 11.06 ppm suggests that free pyridine is present in the ratio of 1:2 with respect to coordinated pyridines of which the peaks appeared at 9.55, −24.25 and −63.86 ppm with the integration of 4:2:4 (Fig. 2(b) and Table 2). This information, together with the chemical analysis (Table 1), is consistent with the formulation $(Hpy)[Cr(NCS)_4(py)_2]$. When the complex is developed on a preparative TLC plate, a product is

TABLE 2. ^{2}H NMR chemical shifts for the pyridine complexes[a]

Complexes	β	γ	α
$[Cr(NCS)_3(py\text{-}d_5)_3]$	10.11(2) 8 90(4)	$-26.08(3)$	$-66.69(6)$
$(Hpy\text{-}d_5)[Cr(NCS)_4(py\text{-}d_5)_2]$	9 55(4) 10 22(2)	$-24\ 25(2)$ 10.77(1)	$-63.86(4)$ 11 06(2)
$[MoCl_3(py\text{-}d_5)_3]$	37.25(2) 36 52(4)	$-67.66(2)$ $-73.48(1)$	$-83.54(4)$ $-85.85(2)$
$[CrF_3(py\text{-}d_5)_3]$	15.63(2) 14.00(4)	$-23.44(2)$ $-26.70(1)$	$-68\ 76(6)$
$[CrCl_3(py\text{-}d_5)_3]$[b]	8.60	$-26\ 18$	$-71\ 11$
$[CrBr_3(py\text{-}d_5)_3]$	8.67(2)	$-27\ 5(1)$	$-68\ 54(2)$

[a] The number in parentheses indicates the intensity ratio. [b] No reasonable intensity ratio was observed

obtained for which the free pyridine peaks are missing; only three signals appear at 9.55, −24.25 and −63.86 ppm. Chemical analysis of this product (Table 1) is consistent with the formulation $H[Cr(NCS)_2(py)_4]\cdot 4H_2O$. Addition of deuterated pyridine to this product gives a spectrum identical to that observed prior to TLC treatment and to the product assigned as 'mer'-$[Cr(NCS)_3(py)_3]$ by DasSarma and DasSarma. The syntheses of this product and the corresponding potassium salt have been reported previously [13]. The reported syntheses were repeated in this study with deuterated pyridine, and products were obtained that gave ^{2}H NMR spectra identical to the complex obtained from the DasSarma and DasSarma preparation.

It is unlikely, then, that the complex we obtained with their synthetic procedure is *mer*-$[Cr(NCS)_3(py)_3]$. We have assigned this structure to the $[Cr(NCS)_3(py)_3]$ complex prepared by Patel's method and assigned the *fac* configuration by DasSarma and DasSarma as previously discussed, *vide supra*. However, we cannot be certain that a product identical to what they reported was obtained, even though the IR spectra were the same, since their chemical analysis was somewhat different from ours.

Halogeno complexes

The ^{2}H NMR spectra obtained for $[MoCl_3(py\text{-}d_5)_3]$ (Fig. 3 and Table 2) clearly shows the complex to be the *mer* isomer. The relative positions of the resonances are the same as observed for Cr(III) pyridine complexes, but the resonances show larger isotropic shifts and are less broadened as reported for a decomposition complex, *cis*-$[Mo(bpy\text{-}6,6'\text{-}d_2)_2(solvent)_2]^{3+}$, from $[Mo(bpy\text{-}6,6'\text{-}d_2)_3]^{3+}$ [8]. The relatively high degree of resolution observed is a consequence of this behavior. This observation prompted us to look at the ^{1}H NMR spectrum of *mer*-$[MCl_3(py)_3]$. Some resolution was observed, but the ^{2}H NMR spectrum was clearly superior. This observation once again illustrates the advantage of using ^{2}H for NMR studies of complexes with paramagnetic metal ions having long electron spin relaxation times. The *mer* assignment in solution for $[MoCl_3(py\text{-}d_5)_3]$ agrees with the solid state geometry established by the crystallographic study [22].

The ^{2}H NMR spectrum obtained for $[CrF_3(py\text{-}d_5)_3]$ (Fig. 2) is consistent with the *mer* configuration. The spectrum is analogous to that observed for *mer*-$[Cr(NCS)_3(py\text{-}d_5)_3]$ except that the two resonances for the γ deuterons are definitely observable as evidenced by a well-defined shoulder on the high field side of the band at −23.4 ppm. The electronic absorption spectrum observed for *mer*-$[CrF_3(py)_3]$ definitely shows a large band splitting in the $^{4}T_1 \leftarrow {}^{4}A_2$ region (Fig. 4). The angular overlap model (AOM) was used to calculate

TABLE 3. UV–Vis absorption spectral data

Complexes (solvent)	Band I $\sigma(10^3\ cm^{-1})$ (ϵ (dm^3 mol^{-1} cm^{-1}))		Band II $\sigma(10^3\ cm^{-1})$ (ϵ (dm^3 mol^{-1} cm^{-1}))	
	Obs.	Calc[a]	Obs	Calc[a]
		16.47	21 74 (6 6)	21.24
$[CrF_3(py)_3]$ (MeOH)	17.73 (26.1)	17 55		24 04
		18 63	26.81 (15.5)	26.84
$[CrCl_3(py)_3]$ (dmf)	16 13 (33 6)		21 98 (51.8)	
(nujol)	16.50		22.32	
(reflectance)	16 78[b]		22.32[b]	
$[CrCl_3(tpa)]$	16.08 (56.0)		21.74 (83.0)	
$[CrBr_3(py)_3]$	15.95[b]		21.74[b]	
$[Cr(NCS)_3(py)_3]$ (acetone)	18 52 (143)		23.5(sh)	
$(Hpy)[Cr(NCS)_4(py)_2]$	18.28 (127)		25 00 (84)	
(acetone)	18.32 (121)[c]		25 06 (93)[c]	

[a] The calculated values for the fluoro complex were obtained neglecting the non-diagonal elements by using the following AOM parameters from ref 23; $e_\sigma(F) = 7400\ cm^{-1}$; $e_\pi(F) = 17\ 050\ cm^{-1}$, $e_\sigma(py) = 5800\ cm^{-1}$; $e_\pi(py) = -575\ cm^{-1}$; $B = 542\ cm^{-1}$ [b] Reflectance data from ref. 17b [c] Data from ref. 13

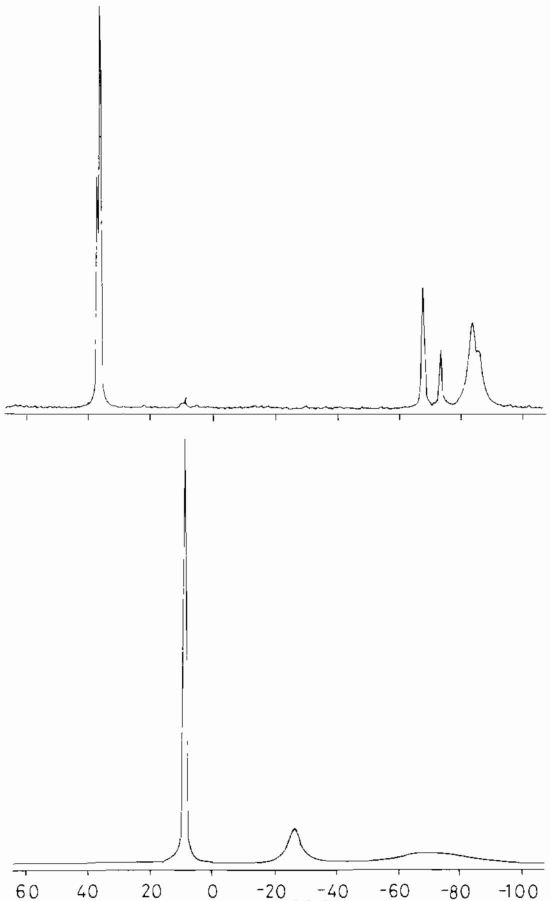

Fig. 3 ^{2}H NMR spectra of [$MoCl_3(py\text{-}d_5)_3$] (above) and [$CrCl_3(py\text{-}d_5)_3$] (below) in $CHCl_3$

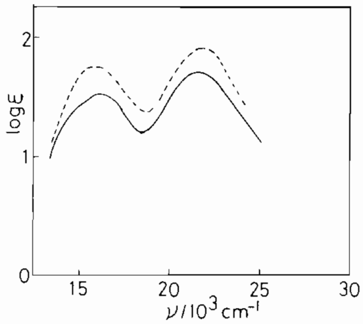

Fig 4 Absorption spectra of [$CrCl_3(py)_3$] (——), [$CrCl_3(tpa)$] (– – –) in dmf and [$CrF_3(py)_3$] (----) in methanol

the expected band positions by assuming the reported AOM parameter values [23]. The observed band positions are in fairly good agreement with the calculated ones for the *mer* isomer, but not for the *fac* one where no splitting is predicted, as shown in Table 3.

The ^{2}H NMR spectra observed for [$CrCl_3(py)_3$] and [$CrBr_3(py)_3$] (Fig. 3 and Table 2) show no band splitting or broadening that suggest more than one resonance for each of the distinct ring deuterons and, thus, is consistent with a *fac* configuration. Since no other *fac* isomer had been isolated and since the NCS^- and F^- analogues exhibited only small splitting for the resonances suggesting the possibility of accidental degeneracy in the ^{2}H NMR spectra of [$CrCl_3(py)_3$] and [$CrBr_3(py)_3$], we decided to synthesize [$CrCl_3(tpa)$] where a *fac* configuration is required. The tripod-like tpa can only coordinate on a face. The UV–Vis spectrum of *mer*-[$CrCl_3(tpa)$] is very similar to that obtained for [$CrCl_3(py)_3$] (Fig. 4 and Table 3), suggesting the *fac* configuration of the latter complex. This is inconsistent with the previous results on the basis of the far-IR spectrum [24] and the X-ray powder patterns of [$CrCl_3(py)_3$] and [$CrBr_3(py)_3$] as compared to that of *mer*-[$MoCl_3(py)_3$] for which the molecular structure was determined in the single crystal study [23]. The recent X-ray crystal structure analysis for [$CrCl_3(py)_3$] by Howard and Hardcastle [25] has definitely established the *mer* configuration and by Cordes's independent preliminary work [26] as shown in Fig. 1. The close similarity between the solid state (nujol mull and diffuse reflectance) and solution UV–Vis spectra (Table 3) confirmed that no structural change occurred on crystallization. Therefore, it is noted that the absorption spectra are not always a conclusive method to determine the structure for this type of complex.

The Co(III) analogue, [$CoCl_3(py)_3$], was also investigated. X-powder pattern comparisons with the corresponding Cr(III) and Mo(III) complexes were consistent with a *mer* configuration in the solid state [18]. Although ^{2}H and ^{1}H NMR spectra were not useful in assigning the solution structure, ^{13}C NMR data established the *mer* configuration. The data (Table 4) clearly show the 2:1 ratio of peaks in the α, β and γ regions expected for the *mer* isomer of [$CoCl_3(py)_3$]. Accordingly, no splitting for [$Co_2(OH)_3(py)_6$]$^{3+}$ and [$CoCl_2(py)_4$]$^+$ and the 1:1 intensity ratio for [$Co(CO_3)(py)_4$]$^+$ (Table 4) lend support to the assignment to *fac*, *trans* and *cis* configuration, respectively.

TABLE 4 ^{13}C NMR chemical shifts for the cobalt(III) pyridine complexes[a]

Complexes	β	γ	α
[$CoCl_3(py\text{-}d_5)_3$]	124 1(2)	139.1(1)	158.7(4)
	123.4(4)	138.4(2)	156 7(2)
[$Co_2(OH)_3(py)_6$]Cl_3	127.8(2)	141.9(1)	153.8(2)
[$CoCl_2(py\text{-}d_5)_4$]Cl	125.5(2)	140.9(1)	157.2(2)
[$Co(CO_3)_2(py\text{-}d_5)_4$]$ClO_4$	127.1(2)	140.7(1)	153.6(2)
	125.9(2)	140.4(1)	152.5(2)

[a] The number in parentheses indicates the intensity ratio.

Conclusions

It appears that for the +3 substitution inert metal ions Mo(III), Cr(III) and Co(III) of the type $[MX_3(py)_3]$ there is a strong preference for the *mer* configuration. Spectral analysis (UV–Vis and IR) has not proven particularly reliable in making structural assignments, and a combination of NMR and crystallographic analysis is required to make the definitive assignments.

Acknowledgements

We are grateful to Don Appel for obtaining ^{2}H NMR spectra at Washington State University and thank Dr W.D. Wheeler for his technical assistance. Professor W.A. Cordes of University of Arkansas is greatly appreciated for providing us with the molecular structure (Fig. 1) through his preliminary X-ray work.

References

1 J. Barrett, F. O'Brien and J.P. De Jesus, *Polyhedron 4* (1985) 1, and refs. therein.
2 E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, M. Sabat and J.A. Ibers, *Inorg Chim. Acta, 66* (1983) 115; J.C. Chang, L.E. Gerdom, N.C. Baenziger and H.M. Goff, *Inorg. Chem*, *22* (1983) 1739; L.E. Gerdom and H.M. Goff, *Inorg Chem*, *21* (1982) 3847.
3 C.A. Green, R.J. Bianchini and J.I. Legg, *Inorg. Chem., 23* (1984) 2713.
4 D.W. Wheeler, S. Kaizaki and J.I. Legg, *Inorg. Chem., 21* (1982) 3248.
5 C.A. Green, H. Place, R.D Willett and J.I. Legg, *Inorg Chem., 25* (1986) 4672; S. Kaizaki and M. Hayashi, *J Chem. Soc, Dalton Trans*, (1989) 1947; S. Kaizaki and H. Takemoto, *Inorg. Chem*, *29* (1990) 4960; S. Kaizaki, N. Hirota, C Tanaka, J. Tano, Liu Xi Lan and J.I. Legg, *Inorg Chim. Acta, 197* (1992) 185.
6 D.W. Wheeler and J.I. Legg, *Inorg. Chem., 23* (1984) 3798; *24* (1985) 1292
7 R.J. Bianchini, U. Geiser, H. Place, S. Kaizaki, Y. Morita and J.I. Legg, *Inorg. Chem., 25* (1986) 2129; S. Kaizaki, M. Byakuno, J.I. Legg, M Hayashi, K. Umakoshi and S. Ooi, *Inorg. Chem., 26* (1987) 2395; S. Kaizaki, N. Hirota, K. Segawa, M. Tanabe, A. Okumura, M. Yamamoto and J. I. Legg, *Inorg Chim. Acta, 191* (1992) 249
8 C. Cornioley-Deuschel and A. von Zelewsky, *Inorg Chem*, *26* (1987) 962.
9 J A. Zoltewicz, C.L. Smith and J.D. Meyer, *Tetrahedron, 24* (1968) 2269.
10 J.P. Wibaut and G.L.C. La Bastide, *Recl. Trav. Chim Pays-Bas, 52* (1933) 493.
11 S.J. Patel, *Bol Soc. Chil Quim., 16* (1970) 18.
12 S. DasSarma and B. DasSarma, *Inorg. Chem., 18* (1979) 3618.
13 Von R. Ripan, I. Ganescu and Cs. Varhelyi, *Z. Anorg. Allg. Chem., 357* (1968) 140.
14 H.B. Jonassen and L.T. Bailin, *Inorg Synth., 7* (1963) 140.
15 N. Costachescu, *J. Chem. Soc., 102* (1912) 493.
16 J.C. Taft and M.M. Jones, *Inorg Synth., 7* (1963) 132.
17 (a) F Hein and F. Pintus, *Berichte, 60* (1927) 2388; (b) D.H. Brown and R.T. Richardson, *J Inorg Nucl Chem., 35* (1973) 755.
18 T. Laier, C.E. Schäffer and J. Springborg, *Acta Chem Scand*, *Ser. A, 34* (1980) 343.
19 T. Laier and J. Springborg, *Acta Chem Scand*, *Ser. A, 35* (1981) 145.
20 J. Glerup, C E. Schaffer and J. Springborg, *Acta Chem Scand*, *Ser A, 32* (1978) 673.
21 J. Springborg and C.E. Schaffer, *Acta Chem Scand*, *27* (1973) 3312.
22 J.V. Brencic, *Z Anorg Allg Chem., 403* (1974) 218.
23 J. Glerup, O. Mønsted and C.E. Schaffer, *Inorg. Chem*, *15* (1976) 1399.
24 R.J.H. Clark and C.S. Williams, *Inorg. Chem., 4* (1965) 350.
25 S.A. Howard and K.I. Hardcastle, *J. Crystallogr. Spectrosc. Res*, *15* (1985) 643.
26 W A. Cordes, personal communication.