Tris(pyridine)cobalt(III) Complexes. Synthesis, Chemical and Spectroscopic Properties, and Angular Overlap Model Considerations

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Seven new cobalt(III) complexes have been synthesized from $[Co(py)_3(CO_3)Cl]$. The complex $[Co(py)_3Cl_3]$, its acetonitrile adduct and the perchlorate salts of the five cations: $[Co(py)_3(CO_3)(H_2O)]^+$, $[Co(py)_3Cl_2(H_2O)]^+$, $[Co(py)_3(H_2O)_3]^{3+}$, $[Co(py)_3FCl(H_2O)]^+$ and $[Co(py)_3F(H_2O)_2]^{2+}$ were isolated. The formation of $[Co(py)_3Cl(H_2O)_2]^{2+}$ was characterized in solution.

$[Co(py)_3Cl_3]$ and $[Co(py)_3(H_2O)_3]^{3+}$ were shown, and the other cations inferred, to possess the meridional configuration. The ion $[Co(py)_3(CO_3)(H_2O)]^+$ reacts slowly with perchloric acid ($t_{\frac{1}{2}} = 99$ s, 4 M $HClO_4$, 20 °C) and $[Co(py)_3(CO_3)Cl]$ forms a fairly inert adduct with mercury(II) in acid solution.

The assumption of equal participation of the t_{2g} electrons in π-bonding leads, by a new application of the angular overlap model formalism, to a fixation of the rotational positions of the pyridine molecules with respect to the Co–N bond direction. A simultaneous interpretation of the absorption spectra of $trans$-$[Co(py)_4Cl_2]^+$ and mer-$[Co(py)_3Cl_3]$ leads to $\Delta_{py} = 21.3$ kK and $\Delta_{Cl} = 11.9$ kK. Further, a discussion of the π-contribution to Δ_{py} is given.

Very few cobalt(III) complexes containing more than two pyridine ligands have been described in the literature. Only four tetrakis(pyridine)cobalt(III) complexes[1,2] have been isolated and no complexes containing more than four pyridines have been described. Four tris(pyridine)cobalt(III) complexes are known, $[Co(py)_3(SCN)_2Cl]$,[4] $[Co(py)_3(CO_3)Cl]$,[1] $[Co(py)_3(NO_2)_3]$,[3] and $[Co(py)_3F_2$-$(H_2O)]ClO_4$.[2] The difluoro complex was synthesized from $[Co(py)_3(CO_3)Cl]$, which has been used in the present work as starting material for the synthesis of seven new tris(pyridine)cobalt(III) complexes. The tris(pyridine) series is a potential source for the synthesis of the spectroscopically more interesting tetrakis(pyridine) series, as recently illustrated by the synthesis of $[Co(py)_4(CO_3)]ClO_4$.H_2O and $trans$-$[Co(py)_4F_2](ClO_4).H_2O$ from $[Co(py)_3(CO_3)Cl]$ and $[Co(py)_3F_2(H_2O)]ClO_4$.H_2O, respectively.[1,2]

Our interest in this type of complexes lies in two particular properties of pyridine as a ligand. It is non-linearly ligating, $i.e.$ the symmetry of the metal to ligand bond is not $C_{\infty v}$ (but actually C_{2v}) and pyridine is potentially a π-acceptor (π-acid). When we started this investigation, we had hoped to find complexes whose ligand field spectra had a high information content[10] like, for example, those of the difluorotetraamminechromium(III) ion for which the first and the second spin-allowed cubic parentage transitions, $^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$ and $^4A_{2g} \rightarrow a^4T_{1g}(O_h)$, both show pronounced tetragonal splittings. Our hope has not been fulfilled regarding the second absorption band, $^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$, in these cobalt(III) complexes, but yet we have obtained some information about the π-accepting property of pyridine as a ligand by analyzing the splittings of the first band, $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$, simultaneously for two different complex ions, using the Angular Overlap Model.
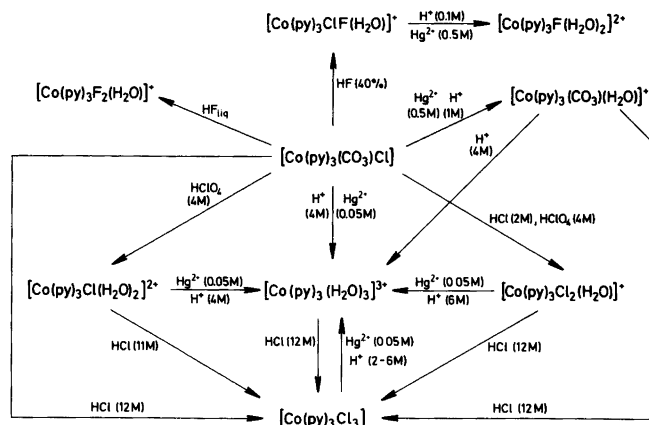
Scheme 1.

RESULTS AND DISCUSSION

Preparations. The preparative procedures and some chemical properties of the compounds are summarized in Scheme 1. With concentrated hydrochloric acid, $[Co(py)_3(CO_3)Cl]$ gives green *mer*-$[Co(py)_3Cl_3]$, which can be reprecipitated from acetonitrile as a yellowish green mono acetonitrile solvate. At lower hydrochloric acid concentrations, $[Co(py)_3(CO_3)Cl]$ reacts to form a mixture of chloroaqua species, from which $[Co(py)_3Cl_2(H_2O)]$-$(ClO_4).H_2O$ was isolated as a green salt. $[Co(py)_3(CO_3)Cl]$ dissolves rapidly in 4 M perchloric acid to give the blue cation $[Co(py)_3Cl(H_2O)_2]^{2+}$. Several attempts were made to isolate salts of this cation, but well-defined products could not be obtained.

$[Co(py)_3(CO_3)Cl]$ is hydrolyzed rapidly in 0.5 M $Hg(ClO_4)_2$, 1.0 M $HClO_4$, to give the purple cation $[Co(py)_3(CO_3)(H_2O)]^+$, which is a Brønsted acid at H_2O and a base at CO_3.[1] This cation and the other cations mentioned in the following were all isolated as their perchlorate salts. With 12 M perchloric acid $[Co(py)_3(CO_3)(H_2O)]ClO_4.H_2O$ reacts rapidly to give the cation *mer*-$[Co(py)_3-(H_2O)_3]^{3+}$. The complex $[Co(py)_3(CO_3)Cl]$ dissolves in 40 % hydrofluoric acid at room temperature with the formation of the purple ion $[Co(py)_3-ClF(H_2O)]^+$, and this ion reacts with mercury(II) in perchloric acid to give the purple ion $[Co(py)_3F-(H_2O)_2]^{2+}$.

As reported recently,[2] $[Co(py)_3(CO_3)Cl]$ reacts with anhydrous liquid hydrogen fluoride to give the purple cation $[Co(py)_3F_2(H_2O)]^+$.

Attempts to substitute bromide failed because of a rapid reduction to cobalt(II). Thus, addition of ice-cold concentrated hydrobromic acid to $[Co(py)_3(CO_3)Cl]$ yielded, within 5 min, the intensely blue solution of tetrahedral cobalt(II) bromo complexes.

For each compound it was shown that the visible absorption spectrum did not change upon further recrystallization or reprecipitation, and this suggests that the compounds are pure isomers. Furthermore, identical spectra were obtained for different samples of $[Co(py)_3(CO_3)Cl]$, purified either by recrystallization from methanol or by reprecipitation from dichloromethane, and this strongly indicates that this compound is also a pure isomer. Finally the same pure isomer of $[Co(py)_3(H_2O)_3]^{3+}$ is obtained from several different initial materials.

Assignment of configurations. Each of the complexes in Scheme 1 can, in principle, exist as one facial (for $[Co(py)_3ClF(H_2O)]^+$ a racemate) and up to three meridional isomers. The meridional configuration for the complex $[Co(py)_3Cl_3]$ was established by the observation that the X-ray powder diffraction pattern* of this compound

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* On the basis of its far IR spectrum, the green isomer of $[Cr(py)_3Cl_3]$ has been assigned the meridional geometry.[6] This assignment has recently been confirmed by a comparative study of $[Cr(py)_3Cl_3]$ and *mer*-$[Mo(py)_3Cl_3]$.[7] The *mer*-configuration of the latter was shown by X-ray structure analysis, and $[Cr(py)_3Cl_3]$ and *mer*-$[Mo(py)_3Cl_3]$ were both shown to crystallize in the space group $P2_1/c$ with almost identical lattice dimensions.

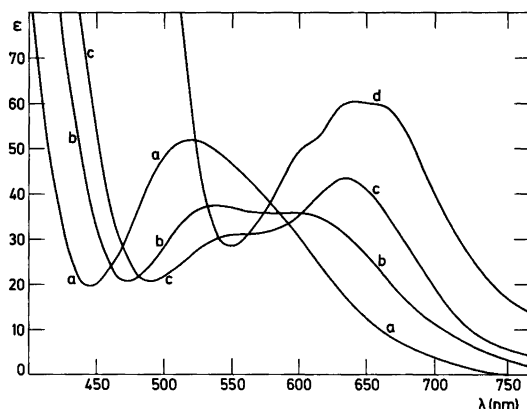*Fig. 1.* Visible absorption spectra of the (supposedly) meridional isomers of the cations $[Co(py)_3$-$(H_2O)_3]^{3+}$ (a), $[Co(py)_3Cl(H_2O)_2]^{2+}$ (b), $[Co(py)_3Cl_2(H_2O)]^+$ (c) and of the complex $[Co(py)_3Cl_3]$ (d), measured at room temperature in 6 M $HClO_4$ (a), 4 M $HClO_4$ (b), 4 M HCl (c) and chloroform (d), respectively.

was nearly identical with that of *mer*-$[Cr(py)_3Cl_3]$. It may be noted that the two complexes both form adducts with nitriles.[5] The meridional assignment is in agreement with the observed splitting of the first cubic parentage ligand field band of *mer*-$[Co(py)_3Cl_3]$ into three components (Fig. 1). The cation $[Co(py)_3(H_2O)_3]^{3+}$ exhibits a less-pronounced splitting, as expected from the spectrochemical parameters of the ligands. These splittings indicate that the holohedrized[8,9] symmetry of the complexes is D_{2h} as expected for meridional complexes, rather than O_h as expected for a facial[8] complex, provided that the pyridine ligand behaves

as approximately linearly ligating.[10] We therefore assign the configuration as meridional. The spectra of the remaining compounds (Figs. 1 and 2) do not allow an assignment of configuration by similar clear-cut, qualitative arguments, but a reasonable semiquantitative analysis of the spectra can be made on the basis of assumed meridional configurations. Further, the chemical evidence outlined below suggests that the other complexes also have the meridional configuration.

Only one isomer, *mer*-$[Co(py)_3(H_2O)_3]^{3+}$, is obtained by the reactions taking place when tris-(pyridine) complexes of the types carbonatochloro,

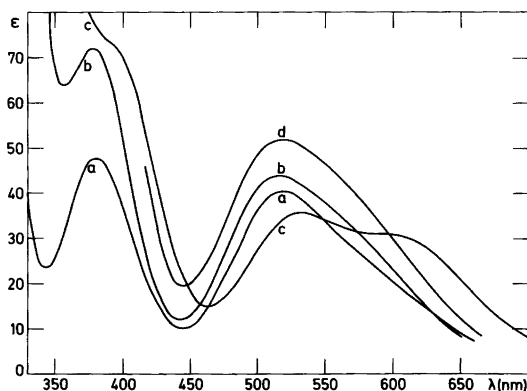*Fig. 2.* Visible absorption spectra of the (supposedly) meridional isomers of the cations $[Co(py)_3F_2(H_2O)]^+$ (a), $[Co(py)_3F(H_2O)_2]^{2+}$ (b), $[Co(py)_3ClF(H_2O)]^+$ (c) and $[Co(py)_3(H_2O)_3]^{3+}$ (d), measured at room temperature in 0.1 M HCl (a), 4 M $HClO_4$ (b), 0.1 M HCl (c) and 6 M $HClO_4$ (d), respectively.

trichloro, aquadichloro, and diaquachloro species are dissolved in 2 – 6 M $HClO_4$, 0.05 M $Hg(ClO_4)_2$. Further, the same isomer is obtained by the reaction of the aquacarbonato species with 6 M $HClO_4$. The identity of the *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ in all cases was shown by absorption spectral studies. Similarly only one isomer, *mer*-$[Co(py)_3Cl_3]$, is obtained by the reaction of the aquadichloro, diaquachloro, carbonatochloro and aquacarbonato species with concentrated hydrochloric acid (Scheme 1). These results strongly support the assumption that the compounds are pure isomers and indicate that they all have the same configuration, *i.e.* meridional. However, no definite conclusions can be drawn since it is well-known that cobalt(III) complexes often undergo rapid isomerization reactions.

On the basis of the frequency of occurrence, *trans*-tetrakis(pyridine) complexes would seem to be more stable than their corresponding *cis* isomers. If this is due to steric hindrance between the coordinated pyridine molecules, it is worth noting that a *trans* complex can be described as containing four *mer* pyridine relationships, while a *cis* complex has two *mer* and two *fac* relationships. Therefore, a greater stability of *trans* than *cis* would sterically correspond to a greater stability of *mer* than *fac*.

Cobalt-carbonate bond-breaking. As mentioned above, the cation $[Co(py)_3(CO_3)(H_2O)]^+$ reacts slowly with acid to give *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ quantitatively. The reaction is slow even in 4 M perchloric acid, with a half-life of 99 s at 20 °C. The cation $[Co(py)_4(CO_3)]^+$ is known to react very slowly with acid,[1,11] and the half-life for this reaction in 4 M $HClO_4$ at 20 °C is at least several hours long. This means that the cation $[Co(py)_4(CO_3)]^+$ reacts at least fifty times more slowly than $[Co(py)_3(CO_3)(H_2O)]^+$.

The reaction of $[Co(py)_3(CO_3)(H_2O)]^+$ with 12 M hydrochloric acid gives *mer*-$[Co(py)_3Cl_3]$ within 12 h at −15 °C (yield 47 %). The reaction of *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ under identical conditions is slow, and no formation of the trichloro complex was observed within 48 h. After two weeks, however, *mer*-$[Co(py)_3Cl_3]$ was obtained in low yield (10 %). This means that *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ can be excluded as an intermediate in the former reaction. The initial product, therefore, has to be a chloro substituted complex, presumably the cation $[Co(py)_3(H_2O)_2Cl]^{2+}$. The latter, as well as the aquadichloro cation, was found to give *mer*-$[Co(py)_3Cl_3]$

in high yields (70 − 80 %) within 12 h under these conditions. This result is in agreement with previous results which show that cobalt(III) carbonato complexes are hydrolyzed by cobalt − oxygen bond-breaking followed by carbon − oxygen bond-breaking.[12]

Complex formation between $[Co(py)_3(CO_3)Cl]$ *and Hg(II)*. The acid hydrolysis of $[Co(py)_3(CO_3)Cl]$ in 4 M $HClO_4$, 0.05 M $Hg(ClO_4)_2$ is remarkably slow. The estimated half-life of the overall reaction yielding *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ is 30 ± 5 min (22 °C), and the reaction is thus much slower than hydrolysis in 4 M $HClO_4$ in the absence of mercury(II) ($t_{\frac{1}{2}} < 10$ s) to give the diaquachloro ion. Since the latter ion and the aquacarbonato ion rapidly give the triaqua ion in 4 M $HClO_4$, 0.05 M $Hg(ClO_4)_2$ ($t_{\frac{1}{2}} < 1$ s and $t_{\frac{1}{2}} = 99$ s, respectively), it is concluded that mercury-(II) assisted[13,14] chloride hydrolysis of $[Co(py)_3(CO_3)Cl]$ must be slow and that the reaction of $[Co(py)_3(CO_3)Cl]$ with hydrogen ions is inhibited by the presence of mercury(II).

These results suggest rapid formation of a strong complex between $[Co(py)_3(CO_3)Cl]$ and mercury-(II), giving a chloro-bridged cation which is inert with respect to acid hydrolysis and with respect to cobalt − chloro bridge cleavage. An obvious candidate for such a chloro-bridged ion is $[(py)_3(CO_3)-CoClHg]^{2+}$, and this cation should clearly react much more slowly with hydrogen ions than $[Co(py)_3(CO_3)Cl]$ for purely electrostatic reasons. Since $HgCl^+$ will be the leaving group, it is also understandable that the cobalt − chloride bond-breaking within the bridge is inhibited due to the low charge on the cobalt caused by the two negative charges furnished by the carbonato ligand. Hydrolysis of the chloro-bridged complex can occur *via* several paths. One reaction path is cleavage of the cobalt − chloro bond giving the aquacarbonato ion, and we can say, as shown above (see also preparation No. 4), that this is the predominant reaction path in 1 M $HClO_4$, 0.5 M $Hg(ClO_4)_2$ (0 °C).

Bonding considerations

The Angular Overlap Model[9,15] allows a discussions of *d* electron participation in bonding based upon the assumption that each bonding energy contribution is proportional to the square of a suitably chosen overlap integral.[16] We want to discuss here the ligand field spectra of the *trans*-dichlorotetrakis(pyridine)cobalt(III) ion and the
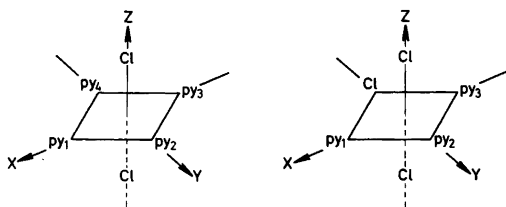
Fig. 3. Coordinate systems used to define the components of the transitions $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$.

trichlorotris(pyridine)cobalt(III), but first we shall discuss the π-bonding arising from the pyridine ligands alone.

We assume that the directional coordinates of the coordinated chloride ions as well as of the nitrogen ligators (*i.e.* coordinating atoms) of the pyridine are such that they describe a regular octahedron. We further assume that the carbon atoms in the 4-position in the pyridine ring lie on the central ion to nitrogen vector. These assumptions have the consequence that of the d orbitals only d_{yz}, d_{zx} and d_{xy} can overlap with ligand π-orbitals.

Using the coordinate systems and pyridine ligand numbering of Fig. 3, the angular overlap *energy* matrix is given in Table 1. The angles associated with each of the numbered pyridine molecules, with the "active" π-orbitals on the nitrogen ligators (*i.e.* those π-orbitals having their nodal planes coinciding with the plane of the pyridine molecule) chosen as πc, are (given as $(\phi_i,\ \theta_i,\ \psi_i)$), py_1 $(0,\pi/2,\ \psi_1)$; py_2 $(\pi/2,\ \pi/2,\ \psi_2)$; py_3 $(\pi,\ \pi/2,\ \psi_3)$; py_4 $(3\pi/2,\ \pi/2,\ \psi_4)$, where ψ_i is the angle between the pyridine plane and the XY-plane. In applying the angular overlap matrix in the form of table 3b of Ref. 15, the reference position of the pyridine molecule is that in which the nitrogen ligator is placed on the

positive Z-axis (Cartesian coordinates $(0,0,1)$) and the pyridine molecular plane is in the YZ-plane.

It is seen that the trace of the angular overlap *energy* matrix (Fig. 3) is 4, which is in accordance with the sum rule[16] since there are four π-orbitals (one on each nitrogen ligator). The chloride perturbations do not give rise to any non-diagonal contributions. Therefore on the condition that pyridine molecules *trans* to each other have the same ψ-angles, the functions $t_2(x)$, $t_2(y)$, and $t_2(z)$ are eigen-functions in the *trans* case. In the *mer* case the conditions that they are eigen-functions are that $\psi_2 = 0$ or $90°$ and $\psi_1 = \psi_3$ (see text to Table 2).

In crystal structures *trans*-tetrakis(pyridine) complexes are usually found to have all four ψ-angles the same and equal to $45°$. For this angle the energy matrix of Table 1 is diagonal with the diagonal elements 1, 1 and 2, respectively. If π-backbonding from central ion to pyridine is predominant compared with π-backbonding to chloride ion, this gives an unsymmetrical contribution from the three d orbitals to the bonding. However, if it is assumed that the ψ-angles are the same for *trans*-pyridine ligands, the condition $2\cos^2 \psi = 4/3$ for all angles gives a diagonal energy matrix with elements 4/3, 4/3 and 4/3 corresponding to equal participation* of the three d orbitals in π-bonding for $\psi = 35.26°$.

It is interesting to compare this result with the angle $\psi = 38°.1$ found[10] solely on the basis of ligand field spectral data for a series of *trans*-tetrakis-(pyridine)chromium(III) complexes for which the equiparticipation conditions are the same but for which the number of π-bonding d electrons is only half (t_{2g}^3) that for the cobalt(III) (t_{2g}^6) complexes.

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* This assumption of equiparticipation is not required by the Angular Overlap Model but, using the assumption, the model leads to definite restraints on the geometry.

Table 1. Angular Overlap Model *Energy* Matrix[15] representing the π-interaction between a d set and either three or four coordinated pyridine molecules (Fig. 3). ψ_i is for each of the numbered pyridine molecules the angle between the pyridine plane and the XY-plane. The matrix applies as it reads to the *trans*-tetrakis(pyridine) case and when the terms involving ψ_4 are omitted it applies to the *mer*-tris(pyridine) case.

$$\mathbb{A}_{\pi py} \text{ (units of } e_{\pi py})$$

		d_{yz}	d_{zx}	d_{xy}
$t_2(x)$	d_{yz}	$\cos^2\psi_2 + \cos^2\psi_4$	0	$\sin\psi_2\cos\psi_2 - \sin\psi_4\cos\psi_4$
$t_2(y)$	d_{zx}	0	$\cos^2\psi_1 + \cos^2\psi_3$	$\sin\psi_3\cos\psi_3 - \sin\psi_1\cos\psi_1$
$t_2(z)$	d_{xy}	$\sin\psi_2\cos\psi_2 - \sin\psi_4\cos\psi_4$	$\sin\psi_3\cos\psi_3 - \sin\psi_1\cos\psi_1$	$\sin^2\psi_1 + \sin^2\psi_2 + \sin^2\psi_3 + \sin^2\psi_4$

Table 2. Ligand field part of transition energies $\sigma(\psi_1=\psi_3$ and $\psi_2=\psi_4$, Table 1) for $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ in $t_{2g}^6\rightarrow t_{2g}^5 e_g$ approximation. $\Delta_{py}\equiv 3\ e'_{\sigma py}-2\ e'_{\pi py}$ and $\Delta_{Cl}\equiv 3\ e'_{\sigma Cl}-4\ e'_{\pi Cl}$ are the usual spectrochemical parameters which using an additive ligand field are the single ligand parameters which apply to the parameterization also of non-cubic complexes. For the mer-complex a non-diagonal element caused by the pyridine ligand numbered 2 is $\langle{}^1T_{1g}(z)|\mathbb{A}_{\pi py}|^1T_{1g}(x)\rangle=1/8\ \sin(2\ \psi_2)\Delta_{\pi py}$.

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trans-dichlorotetrakis(pyridine)cobalt(III) ion

$[T_1(z)]$: $\Delta_{py}+\frac{1}{4}\left[\cos(2\ \psi_1)+\cos(2\ \psi_2)+\cos(2\ \psi_3)+\cos(2\ \psi_4)\right]\Delta_{\pi py}$

$[T_1(y)]$: $\frac{1}{2}\Delta_{py}+\frac{1}{2}\Delta_{Cl}-\frac{1}{4}\left[\cos(2\ \psi_1)+\cos(2\ \psi_3)\right]\Delta_{\pi py}$

$[T_1(x)]$: $\frac{1}{2}\Delta_{py}+\frac{1}{2}\Delta_{Cl}-\frac{1}{4}\left[\cos(2\ \psi_2)+\cos(2\ \psi_4)\right]\Delta_{\pi py}$

mer-trichlorotris(pyridine)cobalt(III)

$[T_1(z)]$: $\frac{3}{4}\Delta_{py}+\frac{1}{4}\Delta_{Cl}+\frac{1}{4}\left[\cos(2\ \psi_1)+\cos(2\ \psi_2)+\cos(2\ \psi_3)\right]\Delta_{\pi py}$

$[T_1(y)]$: $\frac{1}{2}\Delta_{py}+\frac{1}{2}\Delta_{Cl}-\frac{1}{4}\left[\cos(2\ \psi_1)+\cos(2\ \psi_3)\right]\Delta_{\pi py}$

$[T_1(x)]$: $\frac{1}{4}\Delta_{py}+\frac{3}{4}\Delta_{Cl}-\frac{1}{4}\left[\cos(2\ \psi_2)\right]\Delta_{\pi py}$

It may be added here that if π-backbonding to the chloride ions is established using the empty d orbitals on the halide, this will by symmetry involve only the d_{yz} and d_{zx} orbitals in a *trans*-tetrakis(pyridine) complex. In this case equiparticipation of all three π-bonding d orbitals can be established with a ψ-angle greater than 35.26° and for good π-acceptor ligands on the Z axis, even a $\psi>45°$ may arise. For $\psi=45°$ equiparticipation leads to the relation $2e_{\pi Cl}=e_{\pi py}$. This relation can be intuitively understood by noting that the chloride provides two vacant $d\pi$ orbitals whereas the nitrogen ligator only provides the π orbital whose nodal plane coincides with the pyridine molecular plane.

Let us now look at the *mer*-tris(pyridine) complex and ask about the ψ-angle conditions for equiparticipation of the d orbitals in π-bonding here. This means in this case that the energy matrix should be a unit matrix since each of the three pyridine ligands contributes $e_{\pi py}$. The condition then leads to $\psi_2=0$ and $\psi_1=\psi_3=45°$ which is easy to visualize since it means that pyridine ligand number 2 has an orientation which is symmetry-wise perfect for π-interaction with d_{yz} while the two other pyridine ligands divide their π capacity symmetry-wise equally between the orbitals d_{zx} and d_{xy}.

If the chloride acts as a π-acceptor in the *mer*-complex and all ψ-angles are equal to 45°, equiparticipation again leads to the relation $2e_{\pi Cl}=e_{\pi py}$.

Ligand field spectra

Still with the assumption of *trans* pyridine ψ-angles being equal, we now look at the transition energies for the components of the first spin-allowed cubic parentage absorption band $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ of our cobalt(III) systems. In the pure cubic-subconfiguration approximation, i.e. $t_{2g}^6\rightarrow t_{2g}^5 e_g$, the wave number, σ, of the first spin-allowed transition has the expression $\sigma=\Delta-C$. In a forthcoming paper we shall show how this approximation for $^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$ is very good as far as the ligand field terms are concerned, but C should be replaced by $C'=cC$, where c for the present complexes can be expressed by the approximate equation,

$$c=0.417+0.00890\Sigma-0.0008522\Sigma^2 \qquad (1)$$

where $\Sigma=\Delta/B$ and the ratio between the Racah parameters, C/B, has been taken as 4, as usual.

Again using Fig. 3, the components of the transitions can for both *trans*-tetrakis(pyridine) and *mer*-tris(pyridine) complexes be characterized as $T_1(z)$, $T_1(x)$, and $T_1(y)$, where spin-multiplicity and parity indices have been dropped and where the symbols refer to the direct product of the irreducible representations of the ground state $A_1(O)$ and the excited states $T_1(O)$.

The transition energies for the two types of complexes are given in Table 2 in such a way that one has the corresponding results for linearly ligating ligands when the terms involving the ψ-angles are omitted. It is seen that in this case the spectrochemical parameters of pyridine and chloride are
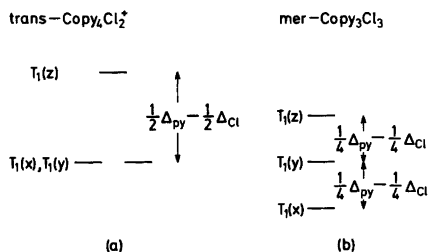
trans—Copy$_4$Cl$_2^+$ mer—Copy$_3$Cl$_3$

Fig. 4. Illustration of the situation when pyridine is assumed to be linearly ligating ((cos(2 ψ)=0) in Table 2). Splitting of the first spin-allowed cubic parentage transition $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ in the $t_{2g}^6 \rightarrow t_{2g}^5 e_g$ approximation. Note that the transitions $T_1(x)$, $T_1(y)$, $T_1(z)$ can be associated with the YZ-, ZX- and XY-planes, respectively, in the sense that the spectrochemical parameters (Δ_{py} and Δ_{Cl}) influencing, for example, the $T_1(y)$ transition refer to the ligands whose ligating atoms are in the ZX-plane. Actually the ligand field energies of $T_1(x)$ and $T_1(y)$ within the *trans*-complex are equal to that of $T_1(y)$ of the *mer*-complex (Fig. 3). However, this energy coincidence is not expected to be found experimentally because of small differences in the repulsion terms C'. C' depends, even for a fixed C/B ratio, upon two independent parameters, Δ_{average} and B_{Racah}, but seems to take on the same value in the *mer*- and the *trans*-complex as seen from the fact that $T_1(y)$ takes on the same value for the *trans*- and the *mer*-complex.

alone responsible for the energy differences within $^1T_{1g}(O_h)$. In Fig. 4 this situation is illustrated, and at the same time it is noted (Table 2) that even in the general case of non-linear ligation, the terms involving the deviation from linear ligation vanish in the average of the transition energies $(1/3)[T_1(x) + T_1(y) + T_1(z)]$.

We now look at the experimental results (in units of 1000 cm^{-1}=1 kK) which for *mer*-[Co(py)$_3$Cl$_3$] were obtained by a Gaussian analysis made with the analogue computer of Erik Pedersen.[17] Referring to Fig. 3 and Table 2 and with assignments based upon the qualitatively known relative positions of Cl$^-$ and pyridine in the spectrochemical series, the results are

trans-Co(py)$_4$Cl$_2^+$ *mer*-Co(py)$_3$Cl$_3$

$T_1(z)$	19.7 kK	$T_1(z)$	17.0 kK
$T_1(x), T_1(y)$	15.8 kK	$T_1(y)$	15.8 kK
		$T_1(x)$	14.6 kK

One observes that the energy difference between the highest and the lowest level is 3.9 kK in the *trans*-complex but only 2.4 kK in the *mer*-complex. This fact shows (Fig. 4) that our model cannot account for the spectra without considering the deviations from linear ligation.

However, from the sum of the transition energies the values of $\sigma = \Delta - C'$ [see eqn. (1)] can be found as $\sigma_{py} = 19.7$ kK and $\sigma_{Cl} = 11.9$ kK where (Ref. 18, Table 1) C' is approximately equal to 1.6 kK for our present complexes, so that $\Delta_{py} = 21.3$ and $\Delta_{Cl} = 13.5$.

The fact that $T_1(y)$ is equidistant from $T_1(z)$ and $T_1(x)$ in the *mer*-complex requires that $\psi_1 = \psi_3 = 45°$ as seen from $\sigma[T_1(z)] + \sigma[T_1(x)] - 2\sigma[T_1(y)] = 0$, which by Table 2 $\Rightarrow \frac{3}{2} \Delta_{\pi py} \cos(2 \psi_1) = 0.0$ kK $\Rightarrow \psi_1 \cong 45°$ for $\Delta_{\pi py} \neq 0$. Similarly for the *trans*-complex, assuming now all the ψ to be equal,

$$\sigma[T_1(z)] - \sigma[T_1(x)] - \sigma[T_1(y)] + \sigma_{Cl} = 0.0 \text{ kK}$$
$$\Rightarrow 2\Delta_{\pi py} \cos(2 \psi) = 0.0 \Rightarrow \psi \cong 45° \text{ for } \Delta_{\pi py} \neq 0.$$

For the *mer*-complex, one further obtains

$$\sigma[T_1(z)] + \sigma[T_1(y)] - \sigma[T_1(x)] - \sigma_{py} = -1.5 \text{ kK}$$
$$\Rightarrow 1/2 \, \Delta_{\pi py} \cos(2 \psi_2) = -1.5 \text{ kK}$$

which for $\cos(2\psi_2) > 0$, *i.e.* $\psi_2 < 45°$, gives an upper limit (lower limit to the absolute value) of -3.0 kK for $\Delta_{\pi py}$, corresponding to $\psi_2 = 0$. This limiting value for $\Delta_{\pi py}$ is not uninteresting since a value of -2.0 kK was found for a series of *trans*-tetrakis(pyridine)chromium(III) complexes[10] and since arguments have been offered[18] (for 2,2'-bipyridine and 1,10-phenanthroline) in favour of values of $\Delta_{\pi bipy}$ and $\Delta_{\pi phen}$ which are (at most) 1.4 kK lower for cobalt-(III) complexes than for chromium(III) complexes.

The results obtained can be summarized as follows: $\Delta_{Cl} = 13.5$ and $\Delta_{py} = 21.3$, consisting of $\Delta_{\sigma py} = 18.3$ (upper limit) and $\Delta_{\pi py} = -3.0$ (upper limit).

In conclusion, we may say that new evidence has been presented for the non-linear ligation character of pyridine to complement previous evidence. However, the uncertainties here in the energy parameters as well as in the assumed values for the ψ-angles are difficult to assess.

The main purpose of the discussion given here is therefore to show how the additive ligand field and, in particular, the Angular Overlap Model, with the transferability assumption, can be used to extract single ligand parameters from the combined applica-

tion of spectra of different complexes involving the same ligands.

It is difficult to design experiments which with certainty will elucidate the non-linear ligation and π-back-bonding problems. But it is almost certain that one needs systems similar to those studied here and, preferentially, ones which at the same time are geometrically well-defined and enable the components of the second spin-allowed absorption band $^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$ to be observed.

EXPERIMENTAL

Materials. [Co(py)$_3$(CO$_3$)Cl] and *mer*-[Cr(py)$_3$-Cl$_3$] were prepared according to the literature.[1,19] All other chemicals were of analytical grade.

Spectra and identification methods. Absorption spectra in the 300−800 nm region, recorded using either a Cary Model 14 or a Zeiss DMR 21 spectrophotometer, were used as a check of purity and as characterization of the compounds. Data for maxima, minima and shoulders are given below as (ε,λ), with the molar decadic absorption coefficient ε in l mol^{-1} cm^{-1} and the wavelength λ in nm.

When it is stated in the following that a sample is pure, this means that the positions of the maxima and minima of the spectrum remained constant upon a further reprecipitation and that a deviation of less than 1 % in the ε values (for both maxima and minima) was found between the two crops. In a few cases, deviations in the ε_{min} values of 1.5 % were observed.

Also the spectra of most of the compounds showed small changes with time. In all cases the spectrum was run the first time after a few minutes. The spectrum, run the second time after 5−15 min, was always sufficiently little different from the first one (*i.e.* ∼4 % at most) to make it reasonable to obtain the spectral data by linear extrapolation to the time of dissolution. This method obviously does not account for any fast reactions that may have taken place immediately after the dissolution. There may be various reasons for these inconstancies of the spectra. Pyridine ligands may split off, hydrolysis, anation or isomerization reactions may take place, or cobalt(III) may be reduced to cobalt(II). It appears, however, from the interdependence of most of our results (Scheme 1) that our extrapolations, in general, are reasonable.

Infrared spectra of the compounds in potassium bromide discs were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer.

Guinier powder diffraction diagrams were obtained using a Guinier powder camera with Cu$K\alpha$ radiation.

Preparative procedures

Properties of and measurements on the individual compounds. 1. Carbonatochlorotris(pyridine)cobalt-(III). [Co(py)$_3$(CO$_3$)Cl]. Reprecipitation from dichloromethane. Crude [Co(py)$_3$(CO$_3$)Cl] (1.4 g) was dissolved in dichloromethane (200 ml) at room temperature. The solution was immediately filtered and the complex precipitated with ether (200 ml). Within half a minute precipitation of microscopic blue-grey crystals began and after a further half minute the precipitate was filtered off and washed once with ether. Yield 1.1 g (78 %). A further reprecipitation yielded a pure product. $(\varepsilon,\lambda)_{max}$: (124,577); (145,409); $(\varepsilon,\lambda)_{min}$: (21.7,481); (122,382). Medium: 80 % v/v acetonitril in water. $(\varepsilon,\lambda)_{max}$: (113,582); (142,401); $(\varepsilon,\lambda)_{min}$: (21,476); (109,373). Medium: water.

The (ε,λ) values found for the product recrystallized from methanol are $(\varepsilon,\lambda)_{max}$: (124,577); (145,409); $(\varepsilon,\lambda)_{min}$: (24.5,481); (123.0,382). Medium: 80 % acetonitril in water. Because of a miscalculation in Ref. 1, the ε values given there are 2.5 times too small.

The infrared spectra and the Guinier powder diffraction diagrams of the reprecipitated and the recrystallized samples were identical.

Properties. The reprecipitated product dissolves more rapidly in water than does the product obtained by recrystallization from methanol. In the latter case dissolution is so slow that measurements of the visible absorption spectrum are difficult. Thus, using the product reprecipitated from dichloromethane, however, it was possible to obtain the spectrum in water. When the product reprecipitated from dichloromethane was thoroughly ground in a mortar, it dissolved just as slowly in water as did the product recrystallized from methanol.

When [Co(py)$_3$(CO$_3$)Cl] was dissolved in 4 M HClO$_4$, 0.05 M Hg(ClO$_4$)$_2$ at 20 °C, an almost constant visible absorption spectrum was attained within 10 h. The half-life of the overall reaction was estimated to be 30 min. The final spectrum showed $(\varepsilon,\lambda)_{max} = (53.3,521)$ and $(\varepsilon,\lambda)_{min} = (18.8,446)$, in reasonable agreement with the extremum values found for the cation *mer*-[Co(py)$_3$(H$_2$O)$_3$]$^{3+}$ (see prep. No. 5).

[Co(py)$_3$(CO$_3$)Cl] dissolved at room temperature in 4 M perchloric acid with evolution of carbon dioxide to give a solution of the bluish-purple cation [Co(py)$_3$Cl(H$_2$O)$_2$]$^{2+}$ within 1 min. The half-life of the reaction under these conditions is then estimated to be less than 10 s. Addition of mercury(II) perchlorate to the solution of the cation [Co(py)$_3$Cl(H$_2$O)$_2$]$^{2+}$ led to the instantaneous formation of the cation *mer*-[Co(py)$_3$(H$_2$O)$_3$]$^{3+}$. The half-life for this reaction was estimated to be less than 1 s.

On adding 12 M hydrochloric acid (5 ml, -15 °C) to a concentrated, ice-cold solution (0.5 ml) of the cation $[Co(py)_3Cl_2(H_2O)]^+$ and keeping the mixture at -15 °C for 12 h, a green precipitate was formed which was identified by its infrared spectrum in the region $4000-250$ cm^{-1} as mer-$[Co(py)_3Cl_3]$. Yield 70 %.

2. *Trichlorotris(pyridine)cobalt(III)*. $[Co(py)_3$-Cl$_3]$. Carbonatochlorotris(pyridine)cobalt(III) (5 g, 12.8 mmol) was treated with 12 M hydrochloric acid (40 ml) at room temperature. The complex dissolved with evolution of carbon dioxide gas, giving a green solution from which green crystals of mer-$[Co(py)_3$-Cl$_3]$ immediately precipitated. The mixture was allowed to stand for 10 min at room temperature and then filtered. The mother liquor was blue due to the presence of Co(II) species. The precipitate was washed thoroughly with water and then with 96 % ethanol (10 ml) and dried with ether. Drying in the air yielded 2.6 g (50 %). This was reprecipitated from chloroform: 1.0 g was dissolved in chloroform (40 ml) and to the filtered solution was added dry ether (160 ml). Green crystals of mer-$[Co(py)_3Cl_3]$ precipitated, and were isolated by filtration, washed with dry ether and dried in air. Yield 0.88 g (88 %). The product reprecipitated three times was pure. Anal. $[Co(py)_3Cl_3]$: Co, N, C, H, Cl. $(\varepsilon,\lambda)_{max}$: (60.2,640); $(\varepsilon,\lambda)_{shoulder}$: (57.7,670); (49.3,600); $(\varepsilon,\lambda)_{min}$: (28.4,550). Medium: Chloroform.

Properties. mer-$[Co(py)_3Cl_3]$ is sparingly soluble in water. The Guinier powder diffraction diagram of the complex is almost identical to that of mer-$[Cr(py)_3Cl_3]$. When treated with acetonitrile, dissolution occurs, followed by rapid precipitation of a green acetonitrile adduct. Anal. $[Co(py)_3Cl_3]$.-CH$_3$CN: C, N, H, Cl. The analyses were made within 4 h after the compound had been isolated. The adduct was found to lose acetonitrile quantitatively within two weeks at room temperature, giving pure mer-$[Co(py)_3Cl_3]$ identified by its visible absorption spectrum and its Guinier powder diffraction pattern. The loss in weight was found to be 10.5 % compared to 9.3 % calculated for $[Co(py)_3Cl_3]$.CH$_3$CN. On dissolving in $2-6$ M HClO$_4$, 0.05 M Hg(ClO$_4$)$_2$, a red solution of the cation mer-$[Co(py)_3(H_2O)_3]^{3+}$ was instantaneously formed as shown spectrophotometrically.

3. *Aquadichlorotris(pyridine)cobalt(III) perchlorate monohydrate.* $[Co(py)_3Cl_2(H_2O)]ClO_4$.-H$_2$O. Crude $[Co(py)_3(CO_3)Cl]$ (20 g, 0.051 mol) was added to a mixture of 12 M perchloric acid (50 ml), 4 M hydrochloric acid (75 ml) and water (25 ml), and the mixture was stirred at room temperature for 50 min. After 10 min all the solid had dissolved, giving a blue-green solution from which green crystals of $[Co(py)_3Cl_2(H_2O)]ClO_4$.H$_2$O began to precipitate. The precipitate was filtered off, washed with 4 M perchloric acid (2×40 ml) and 80 v/v %

ether in methanol (3×40 ml), and dried in air. Yield 17.9 g (70 %). The crude product (3 g) was dissolved in acetone (100 ml), and the complex was reprecipitated from the filtered solution with ether (200 ml) as quickly as possible. The precipitate was filtered off, washed with ether and dried in air. Yield 1.5 g (50 %). After a further two reprecipitations (yields 80 and 85 %, respectively) a pure product was obtained. Anal. $[Co(py)_3Cl_2(H_2O)]$-ClO$_4$.H$_2$O: Co, C, N, Cl, H. $(\varepsilon,\lambda)_{max}$: (43.5,636). $(\varepsilon,\lambda)_{shoulder}$: (31.0,550). $(\varepsilon,\lambda)_{max}$: (21.0,489). Medium: 2 M HCl. $(\varepsilon,\lambda)_{max}$: (43.3,636). $(\varepsilon,\lambda)_{shoulder}$: (31.0,550). $(\varepsilon,\lambda)_{min}$: (21.0,489). Medium: 4 M HCl.

Properties. $[Co(py)_3Cl_2(H_2O)]ClO_4$.H$_2$O dissolved in $2-4$ M hydrochloric acid to give a green solution. With 6 M HClO$_4$, 0.05 Hg(ClO$_4$)$_2$, a red solution of the cation mer-$[Co(py)_3(H_2O)_3]^{3+}$ formed instantaneously as shown spectrophotometrically. Treatment with 12 M hydrochloric acid at -15 °C for 12 h gave a green precipitate which was identified by its infrared spectrum in the region $4000-250$ cm^{-1} as mer-$[Co(py)_3Cl_3]$. Yield 80 %.

4. *Aquacarbonatotris(pyridine)cobalt(III) perchlorate monohydrate.* $[Co(py)_3(CO_3)(H_2O)]$-ClO$_5$.H$_2$O.* To crude $[Co(py)_3(CO_3)Cl]$ (39.1 g, 100 mmol) in acetone ice-cold 1 M HClO$_4$, 0.5 M Hg(ClO$_4$)$_2$ (200 ml). The suspension was cooled in ice with stirring for 5 min during which time most of the carbonato salt dissolved. Precipitation of purple crystals of $[Co(py)_3(CO_3)(H_2O)]ClO_4$.H$_2$O began almost instantaneously. To complete the precipitation a saturated solution of sodium perchlorate (100 ml) was added dropwise with stirring over a period of 5 min. After a further 5 min, the precipitate was filtered off and washed with ice-cold water (2×10 ml). Drying in air yielded 34 g (70 %) of a rather impure product. The crude product (34 g) was dissolved in 0.001 M HClO$_4$ (1500 ml) at room temperature and a saturated solution of sodium perchlorate (500 ml) was added to the filtered solution with stirring and cooling in ice. After 1 h the precipitate was filtered off and washed and dried as above. Yield 24 g (71 %). The sample reprecipitated once more was pure. Anal. $[Co(py)_3(CO_3)(H_2O)]ClO_4$.H$_2$O: Co, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (119,540); (138,380). $(\varepsilon,\lambda)_{min}$: (20,453); (113,358). Medium: water.

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* We actually first prepared this compound directly from cobalt(II). The preparative procedure given[1] for $[Co(py)_3(CO_3)Cl]$ was essentially followed, but with the following changes. Cobalt(II) nitrate hexahydrate, sodium hydrogen carbonate and nitric acid were substituted for cobalt(II) chloride hexahydrate, potassium hydrogen carbonate and hydrochloric acid, respectively. Further, charcoal was added in order to minimize the formation of polynuclear peroxo complexes and the final reaction mixture was evaporated *in vacuo* at 20 °C. The yield of crude $[Co(py)_3(CO_3)(H_2O)]ClO_4$.H$_2$O was 20 %.

Properties. The aquacarbonato ion reacts very slowly with acid. In 4 M perchloric acid (20 °C), a constant spectrum was obtained within 15 min. The final extremum ε,λ values were in good agreement with the values obtained for the triaqua ion (see prep. No. 5). A plot of $\log(A_t - A_\infty)$ against t yielded a straight line from which a value of $k_{obs} = 7.0 \times 10^{-3}$ s^{-1} ($t_{\frac{1}{2}} = 99$ s) was calculated. Addition of mercury(II) produced no effect. The final spectrum in 4 M HClO$_4$, 0.05 M Hg(ClO$_4$)$_2$ (20 °C) was identical to that in 4 M HClO$_4$ and a value of $k_{obs} = 7.0 \times 10^{-3}$ s^{-1} was also obtained in this case from the logarithmic plot.

[Co(py)$_3$(CO$_3$)(H$_2$O)]ClO$_4$.H$_2$O dissolved in 12 M hydrochloric acid at -15 °C to give a violet solution from which a green solid was precipitated within 12 h. This was identified by its infrared spectrum in the region 4000−250 cm^{-1} as mer-[Co(py)$_3$Cl$_3$]. The yield was 47 %.

A comparison of the infrared spectrum of [Co(py)$_3$(CO$_3$)(H$_2$O)]ClO$_4$.H$_2$O with that of mer-[Co(py)$_3$Cl$_3$] clearly revealed the bands[1,20] of the bidentately bound carbonate ion v_1 (1650(sharp), 1625(broad) cm^{-1}) and v_5 (1250(sharp) cm^{-1}).

5. Triaquatris(pyridine)cobalt(III) perchlorate dihydrate. [Co(py)$_3$(H$_2$O)$_3$](ClO$_4$)$_3$.2H$_2$O. Pure [Co(py)$_3$(CO$_3$)(H$_2$O)]ClO$_4$.H$_2$O (0.75 g, 1.53 mmol) was treated with 12 M HClO$_4$ (1 ml) at room temperature in a small Erlenmeyer flask. The complex dissolved within 5 min with evolution of carbon dioxide and after a further 5 min precipitation of purple crystals began. The flask was stoppered and allowed to stand for 12 h at room temperature in order to complete the precipitation. The crystals were then isolated by filtration and washed with ether (6 × 2 ml). Yield 0.755 g (75 %). Anal. [Co(py)$_3$(H$_2$O)$_3$]ClO$_4$.2H$_2$O: Co, C, N, H and Cl. $(\varepsilon,\lambda)_{max}$: (52.2,518); $(\varepsilon,\lambda)_{min}$: (16.1,445). Medium: 4 M perchloric acid.

Properties. The perchlorate salt is very soluble even in 12 M perchloric acid. Solutions of mer-[Co(py)$_3$(H$_2$O)$_3$](ClO$_4$)$_3$.2H$_2$O in 2−6 M perchloric acid at room temperature were found to be very stable. Thus, the visible absorption spectrum of a solution in 4 M perchloric acid remained almost unchanged within 24 h.

Dissolution of mer-[Co(py)$_3$(H$_2$O)$_3$](ClO$_4$)$_3$.-2H$_2$O in 12 M hydrochloric acid at -15 °C yielded a purple solution. After two days the purple solution had become more bluish and the visible absorption spectrum showed the presence of the cobalt(II) chloride system and mer-[Co(py)$_3$(H$_2$O)$_3$]$^{3+}$ ions only. However, after a further two weeks a low yield of a green precipitate, identified as mer-[Co(py)$_3$Cl$_3$] by its infrared spectrum, was obtained.

6. Aquachlorofluorotris(pyridine)cobalt(III) perchlorate. [Co(py)$_3$ClF(H$_2$O)](ClO$_4$). Finely powdered [Co(py)$_3$(CO$_3$)Cl] (10 g, 25.5 mmol) was added in portions to a mixture of 40 % hydrofluoric acid (30 ml) and 6 M perchloric acid (5 ml) at room temperature in a polyethylene beaker with manual stirring. The complex dissolved with evolution of carbon dioxide and grey crystals of [Co(py)$_3$ClF-(H$_2$O)](ClO$_4$) were precipitated. After 5−10 min the reaction was complete and the precipitate was collected on a polyethylene Büchner funnel. Most of the hydrofluoric acid was then removed by washing with 0.012 M perchloric acid (3 × 20 ml), and the sample was then transferred to a sintered glass filter and washed with three further portions (20 ml) of 0.012 M perchloric acid and then with 96 % ethanol. Drying in air yielded 10.4 g (85 %). The pure product was obtained by reprecipitation from dilute acid: 3 g was dissolved in 0.1 M hydrochloric acid (1700 ml), and 70 % perchloric acid (300 ml) was added to the filtered solution with stirring and cooling in ice. After cooling for 1 h the precipitate was filtered off and washed with 0.1 M hydrochloric acid (10 ml), 96 % ethanol (2 × 10 ml) and finally with ether. Drying in air yielded 1.82 g (62 %). The sample reprecipitated twice was pure. Anal. [Co(py)$_3$ClF(H$_2$O)]ClO$_4$: Co, C, N, H, Cl, F. $(\varepsilon,\lambda)_{max}$: (35.7,532); $(\varepsilon,\lambda)_{shoulder}$: (30.9,600); (72.6,395); $(\varepsilon,\lambda)_{min}$: (14.9,462.5). Medium: 0.1 M hydrochloric acid.

7. Diaquafluorotris(pyridine)cobalt(III) perchlorate dihydrate. [Co(py)$_3$F(H$_2$O)$_2$](ClO$_4$)$_2$.-2H$_2$O. Pure [Co(py)$_3$ClF(H$_2$O)]ClO$_4$ (4.6 g, 9.8 mmol) was added to a solution of 0.5 M Hg(ClO$_4$)$_2$, 0.1 M HClO$_4$ (11 ml). The suspension was cooled in ice with stirring for 4 h, after which all the complex had dissolved and a small amount of mercury(II) chloride had precipitated. The solution was filtered, ice-cold 12 M perchloric acid (11 ml) was added, and the solution was then cooled in an ice-salt bath (-10 °C) for $\frac{1}{2}$ h. After a few minutes, precipitation of purple [Co(py)$_3$F(H$_2$O)$_2$](ClO$_4$)$_2$.-2H$_2$O began. The product was filtered off and was sucked as dry as possible, and it was then washed with 66 % v/v ether in ethanol (20 ml), and finally with ether (3 × 20 ml). Drying in air yielded 3.5 g (63 %) of almost pure [Co(py)$_3$F(H$_2$O)$_2$](ClO$_4$)$_2$.-2H$_2$O. The crude product (3.5 g) was dissolved in 0.012 M perchloric acid (7 ml), and ice-cold 12 M perchloric acid (7 ml) was added to the filtered solution. After cooling in an ice-salt bath for *ca.* 15 min, the mixture was filtered and the product washed as described above. Yield 2.25 g (64 %) of a pure product. Anal. [Co(py)$_3$F(H$_2$O)$_2$](ClO$_4$)$_2$-.2H$_2$O. Co, C, N, H, Cl, F. $(\varepsilon,\lambda)_{max}$: (44.0,516); (72.2,376); $(\varepsilon,\lambda)_{min}$: (12.0,442); (63.7,357). Medium: 4 M perchloric acid.

Properties. The perchlorate salt is very soluble even in 6 M perchloric acid. It is relatively robust in acid solution, but when dissolved in pure water at room temperature it hydrolyzes to give a brownish solution within a few minutes.

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