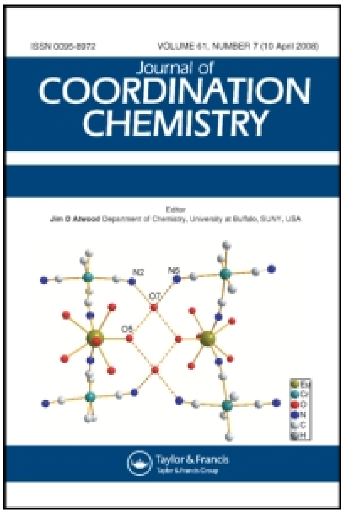

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PSEUDOTETRAHEDRAL COBALT(II) COMPLEXES OF C_{3v} and C_s SYMMETRIES

Theodoros F. Zafiropoulos[a]; Andreas G. Galinos[a]; Spyros P. Perlepes[b]
[a] Department of Chemistry, Laboratory of Inorganic Chemistry, University of Patras, Patras, Greece [b] Department of Chemistry, Laboratory of Inorganic and General Chemistry, University of Ioannina, Ioannina, Greece

To cite this Article Zafiropoulos, Theodoros F. , Galinos, Andreas G. and Perlepes, Spyros P.(1984) 'PSEUDOTETRAHEDRAL COBALT(II) COMPLEXES OF C_{3v} and C_s SYMMETRIES', Journal of Coordination Chemistry, 13: 3, 197 — 206

To link to this Article: DOI: 10.1080/00958978408073868

URL: http://dx.doi.org/10.1080/00958978408073868

J. Coord. Chem., 1984, Vol. 13, pp. 197-206
0095-8972/84/1303-0197 $18.50/0

PSEUDOTETRAHEDRAL COBALT(II) COMPLEXES OF C_{3v} and C_S SYMMETRIES

THEODOROS F. ZAFIROPOULOS and ANDREAS G. GALINOS†
Department of Chemistry, Laboratory of Inorganic Chemistry, University of Patras, Patras, Greece

and

SPYROS P. PERLEPES
Department of Chemistry, Laboratory of Inorganic and General Chemistry, University of Ioannina, Ioannina, Greece

(Received October 3, 1983)

New complexes of the general types $HCoX_3 \cdot nL$ and $HCoY_2X \cdot nL$ (X=Br, I; Y=Cl, Br, I; L=diethyl ether, pyridine, aniline; n=1, 2, 3 and 4) have been prepared and characterized by elemental analyses, molar conductance measurements, magnetic measurements, spectral (UV, visible, IR and far-IR) data and X-ray powder patterns. All the magnetic and spectroscopic results indicate that pseudotetrahedral $[CoX_3L]^-$ and $[CoY_2XL]^-$ anions are present in the solid pyridine and aniline complexes. The data for the solid compounds are compatible with, and lend support to, outer spheres comprising $(N — H- -N)^+$ groups.

INTRODUCTION

The study of halogen acids of metal ions is of special interest, because some of them have been proposed as intermediates in Friedel-Crafts reactions and chain polymerizations.[1] Two general classes of monomeric halogeno- tetrahedral cobalt(II) compounds are known. The first includes the truly tetrahedral $[CoL_4]^{2+}$ and $[CoX_4]^{2-}$ ions (where L=a neutral monodentate ligand and X^-=a halogen or pseudohalogen anion) and the second embraces those complexes which may be called pseudotetrahedral. In the second class two or more different kinds of ligands are present. Of the three cases involving two kinds of ligands, *viz* $[CoX_3L]^-$, $CoX_2 \cdot 2L$ and $[CoXL_3]^+$, only the second has previously been well realized. Salts containing $[CoX_3L]^-$ anions have been described.[2-4] Complexes with three kinds of monodentate ligands are quite rare.[5]

As a continuation of the interest of our laboratories in the metal halogen acids and their compounds[6-11] and since there is an absence of information on the ligand-mixed halide anionic complexes of Co(II), the present work deals with the preparation and characterization of new etherate, pyridine and aniline compounds of simple and mixed complex halogen acids of Co(II). The compounds chosen may be regarded as model systems for the $[CoX_3L]^-$ and $[CoY_2XL]^-$ anions.

EXPERIMENTAL

High purity chemicals were used for the preparation of the complexes. The solvents were purified and dried by standard methods. Ethanol, used for the UV spectra, was of spectroscopic grade. Pyridine and aniline were doubly distilled at atmospheric pressure. Cobalt(II) was estimated gravimetrically as cobalt(II) anthranilate. For the halide deter-

---

†Author to whom correspondence should be addressed.

mination the complexes were decomposed in 2M HNO_3. The total halogens were determined by the Volhard method, the iodides in the presence of chloride or bromide ions by the $PdCl_2$ method[12] and chlorides or bromides, in the presence of the other, potentiometrically with a standard 0.1 M $AgNO_3$ solution, using a Corning-Eel Model 12 potentiometer with calomel and sulfide-selective electrodes.[13] The acidic hydrogen was determined potentiometrically with a standard 0.1 M NaOH solution after decomposing the etherates in water and dissolving the pyridine and aniline complexes in DMSO.[14] The content of pyridine and aniline was determined by dissolving the complexes in glacial CH_3COOH and potentiometric titration with a standard 0.1 M $HC1O_4$ solution in CH_3COOH;[15] to the samples being analyzed were added 5-8 cm^3 of 6% $(CH_3COO)_2Hg$ solution in glacial CH_3COOH. For the potentiometric determinations of the acidic hydrogen and the organic bases a pH meter (Radiometer Copenhagen TV Type 26C) with glass and calomel electrodes was employed; in the case of the acidic hydrogen in the pyridine and aniline compounds the saturated aqueous KCl solution of the calomel electrode was replaced by a methanolic one.[14] Ether was estimated by weight difference.

Decomposition temperatures were obtained using a Buchi 510 apparatus. Conductance measurements were carried out with an Ehrhardt- Metzger Nachf. L21 conductivity bridge and a cell of standard design, previously calibrated with a 0.0200 M KCl solution; the conductances of the solutions were measured within 5 min of dissolution. The X-ray powder diffraction patterns of the solid complexes were obtained using a Philips diffractometer using Cu-K_a radiation; the spectra covered the region of the angle 2θ from 3° to 60°. Magnetic susceptibilities were measured at room temperature by the Faraday method, using a Cahn-Ventron RM-2 balance; mercuric tetrathiocyanatocobaltate(II) was used as the susceptibility standard. Diamagnetic corrections were made using Pascal's constants. The electronic solution spectra were recorded on an Optica CF-4R double beam spectrophotometer. Visible diffuse reflectance spectra, in the 13.30-25.00 kK region, were obtained with a Bausch and Lomb-Shimadzu Spectronic 210 spectrophotometer; spectroscopic grade MgO was used in the reference beam. Low frequency electronic spectra for some of the complexes were obtained with a Shimadzu MPS 50L and a Unicam SP 700 spectrophotometer. IR spectra, in the 4000-250 cm^{-1} region, were recorded on a Perkin-Elmer 577 spectrophotometer, calibrated with polystyrene. The samples were used in the form of KBr pellets or hexachlorobutadiene mulls between CsI plates. Far-IR spectra, as Nujol mulls supported between polyethylene sheets, were recorded on a Perkin Elmer-Hitachi FIS-3 and a Polytec FIR 30 spectrophotometer, at room temperature.

Preparation of the Complexes

The etherate compounds were prepared by the "etherohalogenosis" method.[8-10,16] To remove excess ether from the acid ether complexes they were evacuated at 4 Torr for 30 min under nitrogen.

For the preparation of the pyridine and aniline complexes *ca* 4 mmol of the freshly prepared corresponding etherate compound were suspended in 100 cm^3 of absolute diethyl ether. To the suspension was added a 50% excess of the organic base, dropwise and with continuous stirring. A vigorous and exothermic reaction took place; the oily etherate was dissolved, while simultaneously a precipitate formed. In the case of pyridine a mixture of pink and blue (or green) precipitates was obtained. The addition of 50 cm^3 of diethyl ether caused the formation of more precipitate. The solids were filtered off, washed with copious amounts of ether (the pink components of the pyridine products turned green or blue), dried in vacuum and obtained in powdered form.

RESULTS AND DISCUSSION

General

Colours, yields, analytical results and some physicochemical data for the prepared complexes are given in Table I.

For all three Co(II) halides, the proton acids $[(Et_2O)_nH][CoX_3]$ or $[(Et_2O)_nH][CoY_2X]$ (X=Br, I and Y=Cl, Br, I) have been isolated. Under the conditions employed, the value of n ranges from 1 to 3. The acids are viscous oils, fume in the air and are insoluble in nonpolar solvents. The vapour pressures of the evacuated ether complexes are about one order of magnitude below the vapour pressure of diethyl ether itself. These acids should be strong 1:1 electrolytes. However the Λ_M values for completely dissociated 1:1 electrolytes in CH_3NO_2 are larger than those found for the ether compounds considered here.[17] This suggests that either the ionic migration velocity of the compounds is low or that some ion-pair formation has taken place.

All the pyridine and aniline compounds, except $HCoCl_2I{\cdot}4Py$ (Py=pyridine), have the compositions $HCoX_3{\cdot}3L$ and $HCoY_2X{\cdot}3L$ and are formed by the complete replacement of the ether molecules in the etherates with pyridine or aniline, since the latter are stronger Lewis bases than ether. They are crystalline solids and stable in the atmosphere. The complexes are insoluble in nonpolar solvents, somewhat soluble in water and soluble in alcohols, acetone, CH_3NO_2, DMF and DMSO; they are also decomposed by dilute mineral acids. From the Λ_M values obtained it is concluded that they behave in CH_3NO_2 as 1:1 electrolytes.[17] The X-ray powder data show that the prepared Co(II) complexes are isomorphous with the corresponding pseudotetrahedral Zn(II) complexes.[8,9] All patterns suggest, by the multitude of the reflections, that the solids formed are not of high symmetry. It is worth noting that we are continually trying to obtain crystals suitable for full X-ray analysis, but have not so far been successful.

Magnetic Moments and Electronic Spectra

Table II gives the room temperature magnetic moments and details of the electronic spectra of the complexes.

A pseudotetrahedral configuration may be assigned to all the solid complexes described in this work on the basis of their magnetic moments and visible diffuse reflectance spectra.[2,4,5] The typical symmetry of the metal-ligand environment in the pyridine and aniline complexes is approximately C_{3v} and even lower (C_s) in those cases where two different halides are coordinated. The reduction of symmetry from T_d to C_{3v} and Cs should change the energy levels of the 3d electrons. It is expected that the orbital contribution to the magnetic moments should be smaller than for T_d and the d-d electronic transitions to T states should be split into two and three components for C_{3v} and C_s symmetries, respectively.

The observed μ_{eff} values at room temperature are lower than those for salts containing $T_d\,[CoX_4]^{2-}$ anions.[18] The trend of the μ_{eff} values, increasing in the sequence $Cl<Br<I$, is consistent with an increasing contribution to the spin-only value as the halide ligand field strength decreases.[2,18]

The visible diffuse reflectance spectra are characteristic of Co(II) atoms in pseudotetrahedral environments.[4,5] The complex maximum near 15.50 kK is basically associated with what would be a $^4A_2(F) \rightarrow {}^4T_1(P)$ transition for a species of full tetrahedral symmetry. The complexity of this band has been attributed to spin-orbit coupling effects, but in the present case splitting would also be expected because of the reduction of symmetry. So, the d-d multicomponent absorption appearing in the visible region prob-

TABLE I
Colours, Yields, Analytical Data and some Physicochemical Features of the Complexes.

	Complex[a]	Colour	Yield (%)	Analyses (%)						Density (g cm^{-3})	Decomp.temp.[d](°)	Λ_M^e (S cm^2 mol^{-1})
				H^{+b}	Co	Cl	Br	I	L^c			
1	$HCoCl_2Br \cdot 2Et_2O$	blue	86	(0.28) 0.27	(16.41) 16.33	(19.75) 20.01	(22.26) 22.11			1.26		30
2	$HCoCl_2Br \cdot 3Py$	blue	65	(0.22) 0.22	(13.15) 13.31	(15.83) 15.96	(17.83) 17.69		(52.96) 53.25		113–117	74
3	$HCoCl_2Br \cdot 3An$	blue	81	(0.21) 0.21	(12.02) 11.83	(14.47) 14.66	(16.30) 16.41		(57.00) 57.93		108–112	76
4	$HCoBr_3 \cdot Et_2O$	green	89	(0.27) 0.26	(15.77) 16.00		(64.13) 63.99			1.37		58
5	$HCoBr_3 \cdot 3Py$	dark blue	61	(0.19) 0.20	(10.97) 10.83		(44.64) 44.79		(44.19) 44.87		114–116	80
6	$HCoBr_3 \cdot 3An$	dark blue	79	(0.17) 0.17	(10.18) 10.30		(41.40) 41.53		(48.25) 48.76		103–107	70
7	$HCoI_2Br \cdot 3Et_2O$	dark green	83	(0.16) 0.16	(9.57) 9.66		(12.97) 13.11	(41.20) 41.44		1.46		55
8	$HCoI_2Br \cdot 3Py$	dark blue	71	(0.16) 0.15	(9.34) 9.40		(12.66) 12.41	(40.23) 40.71	(37.61) 37.88		95–98	103
9	$HCoI_2Br \cdot 3An$	blue	82	(0.15) 0.16	(8.75) 8.73		(11.87) 11.64	(37.71) 37.99	(41.51) 41.86		145–150	83
10	$HCoCl_2I \cdot 2Et_2O$	green	84	(0.25) 0.24	(14.51) 14.29	(17.47) 17.31		(31.26) 31.40		1.40		52
11	$HCoCl_2I \cdot 4Py$	blue-green	66	(0.17) 0.16	(10.26) 10.41	(12.35) 12.33		(22.10) 22.31	(55.11) 55.40		108–111	106
12	$HCoCl_2I \cdot 3An$	dark blue	81	(0.19) 0.20	(10.97) 10.91	(13.20) 13.11		(23.62) 23.79	(52.01) 52.12		80–85	82
13	$HCoBr_2I \cdot Et_2O$	green	96	(0.24) 0.23	(14.00) 13.88		(37.98) 37.66	(30.16) 30.40		1.40		44
14	$HCoBr_2I \cdot 3Py$	blue	79	(0.17) 0.16	(10.09) 9.90		(27.37) 27.21	(21.73) 21.88	(40.64) 40.79		75–80	99
15	$HCoBr_2I \cdot 3An$	blue	69	(0.16) 0.16	(9.41) 9.51		(25.53) 25.46	(20.27) 20.40	(44.63) 44.80		95–100	63
16	$HCoI_3 \cdot 3Et_2O$	green	87	(0.15) 0.15	(8.89) 8.91			(57.42) 57.49		1.41		45
17	$HCoI_3 \cdot 3Py$	dark green	76	(0.15) 0.14	(8.69) 8.41			(56.15) 55.88	(35.00) 35.71		200–205	64
18	$HCoI_3 \cdot 3An$	dark green	79	(0.14) 0.15	(8.18) 8.23			(52.87) 52.76	(38.80) 38.94		196–200	67

[a] Et_2O=diethyl ether, Py=pyridine, An=aniline. [b] This symbol refers to protons determined by sodium hydroxide titration.[14] Calculated values are given in parentheses. [c] L=Py, An. [d] Uncorrected. [e] Values of molar conductance for *ca.* 10^{-3} M solutions in CH_3NO_2 at 25°.

TABLE II
Magnetic Moments[a] and Visible Electronic (13.30–25.00 kK) Spectral Data.

Complex	μ_{eff}(B.M.)	Solution spectra[b]	Diffuse reflectance spectra	
			$^4A_2(F) \rightarrow {}^4A_2(T_1, P)$, $^4E(T_1, P)$	Other maxima
1	4.61	14.41,14.99sh,15.75sh,16.81,21.50		
2	4.52		14.64sh,15.31,16.18	18.52sh,21.23,22.93,24.33,24.81
3	4.59		15.27,15.97,16.86sh	19.16sh,20.37sh,22.42,23.58
4	4.74	14.37,14.81sh,15.36sh,15.70,16.15sh,21.32		
5	4.58		14.49,15.27,16.15sh	18.42,19.43sh,21.14,22.78,24.75
6	4.67		15.22,15.92,16.75sh	19.05sh,22.37,23.47
7	4.80	14.31,14.97sh,15.65,16.31		
8	4.67		14.04sh,14.58,15.31,16.30	18.59sh,19.19,20.37,21.32,23.70sh
9	4.78		14.75sh,15.22,15.97,16.78sh	21.74
10	4.74	13.40,13.93sh,14.58sh,15.22sh,18.62		
11	4.60		14.49,15.22,16.13sh	19.72,21.01sh,24.39sh
12	4.72		14.43,15.36,16.21sh,17.15	19.38sh,21.10,22.07
13	4.77	14.55,15.23sh,15.90,21.80		
14	4.63		14.33sh,15.43,16.08,16.81sh	18.94sh,20.32,22.67,23.58
15	4.74		15.20,15.92,16.78sh	19.05sh,21.69,22.42sh,23.58
16	4.80	13.80,15.10,16.05sh,22.01		
17	4.70		13.70,14.82,15.64sh	18.29,19.53,20.90,24.94sh
18	4.81		13.99,15.10,15.88sh	19.67,20.74,24.57sh

[a] At room temperature. [b] In CH_3NO_2.

ably arises as a result of both spin-orbit coupling and the trigonal potential. The spectra of the complexes $HCoX_3 \cdot 3L$ and $HCoY_2X \cdot 3L$ with the same organic ligand are nearly identical; this enables us to assign the spectra of $HCoY_2X \cdot 3L$ on the basis of C_{3v} symmetry, instead of the expected C_s symmetry.[5] This fact suggests that spin-orbit coupling effects are the principal factors responsible for the splitting of the T bands, prevailing over geometry effects. The bands in the 6.97-7.46 kK region in the spectra of the complexes $HCoX_3 \cdot 3Py$ and $HCoX_3 \cdot 3An$ (An=aniline) are assigned to the $^4A_2(F) \rightarrow {}^4E(T_1, F)$ transition and the 4.35-4.73 kK bands to the $^4A_2(F) \rightarrow {}^4A_2(T_1,F)$ transition[19] (only for the $HCoX_3 \cdot 3L$ are there spectral data at low energies). For a series of trigonally distorted pseudotetrahedral $[MX_3L]^-$ anions of the same metal ion, the magnitude of the crystal field parameter $D\tau$ is related to the difference in field strength between the unique ligand L and the three ligands X^-.[5,19] Our results (Table III) indicate that the ligand field strength of pyridine is slightly greater than that of aniline.

The UV spectra of the pyridine complexes in ethanol consist of a diffuse system near 41 kK which has been assigned to the $\pi \rightarrow \pi^*$ $^1A_1 \rightarrow {}^1B_1$ ($^1A_{1g} \rightarrow {}^1B_{2u}$ in benzene symmetry) transition,[20] and a weaker system of discrete maxima at slightly lower energies (39 kK) which has been assigned to a $n \rightarrow \pi^*$ $^1A_1 \rightarrow {}^1B_2$ transition of the pyridine molecule.[20] The absorption maxima near 35 and 42.50 kK in the UV spectra of the aniline compounds are assigned to the $^1A_{1g} \rightarrow {}^1B_{2u}$ and $^1A_{1g} \rightarrow {}^1B_{1u}$ transitions, respectively;[21] the shoulders at 38.50 kK are attributed to the presence of the AnH^+ ion in solution.[8,9] The spectra of **8**, **11**, **14** and **17** exhibit additional maxima at 27.8, 34.0 and 45.5 kK, which require some discussion. These maxima also appear in the spectra of the iodo- etherates, while the spectra of **9** and **12** show additional bands only at 27.8 and 45.5 kK. The 45.5 kK maximum is due to a charge-transfer transition between the iodide ion and the solvent,[22] indicating the existence of iodide ions in the ethanolic solutions. The two absorptions near 27.8 and 34.0 kK are assigned to the $\pi_g \rightarrow \sigma_u^*$ and $\sigma_g \rightarrow \sigma_u^*$ transitions of the I_3^- ion respectively,[23] which constitutes an autoxidation product. In the spectrum of a given etherate or pyridine iodo- complex the maximum at about 45.5 kK is much more intense than those at 27.8 and 34.0 kK; these maxima appear clearly reinforced when the spectrum is recorded many hours after the preparation of the solutions. It is believed that the very broad maxima near 35 kK in the spectra of **9** and **12** is a combination of absorptions due to aniline ($^1A_{1g} \rightarrow {}^1B_{2u}$) and $I_3^-(\sigma_g \rightarrow \sigma_u^*)$. The absence of these three maxima from the spectra of **15** and **18** (they begin to appear after 5 h for a 10^{-4} M solution) shows their greater stability in ethanol.

IR Spectral Studies

The spectra of the etherates in the 4000-350 cm^{-1} region are similar. The only absorp-

TABLE III
Low Energy Band Splittings (kK) in the Electronic Spectra of the Trigonally Distorted Pseudotetrahedral $[L_2H][CoX_3L]$ Complexes.

Complex	$^4T_1$ (F)[a]		Δ^b(kK)	$D\tau$(cm^{-1})
	A_2	E		
$[Py_2H][CoBr_3Py]$	4.68	7.46	2.78	278
$[Py_2H][CoI_3Py]$	4.35	7.02	2.67	267
$[An_2H][CoBr_3An]$	4.80	7.45	2.65	265
$[An_2H][CoI_3An]$	4.41	6.97	2.56	256

[a] The selected A_2 and E bands were obtained from the weighted center of the low energy bands. [b] $\Delta = {}^4E(T_1, F) - {}^4A_2(T_1, F)$.

TABLE IV

Far-IR[a] Assignments for Pyridine- and Anilinetrihalogenocobaltate(II) Anions in the 420-50 cm^{-1} region.

Assignment		$[CoX_3Py]^-$		$[CoX_3An]^-$	
A_1	E	X=Br	X=I	X=Br	X=I
	$\nu_d(CoX_3)$	247vs	217vs	248vs	214vs
$\nu_s(CoX_3)$		227s	196^bvsb	225vs	198vs
ν(Co–N)		231sh,189m	227sh,196^bvsb	415m,359m	413m,356m
sym.def.		126m	88m	123m	85m
	$\delta_d(CoX_3)$	96m,83w	69m	94m	71m,68sh
	ω_d	71m	56w	n.a.	61w
other bands		339w,330w,321w,307w	317w,137s,118m	320vw,296w,257sh,193m	317vw,263sh,190m
		261sh,157m,80m,57w	75w,53w	141w,133w,60m	156s,137m,126w,97w

[a] Data obtained at room temperature. [b] Overlapping. Abreviations: n.a.=not assigned, s=strong, m=medium, w=weak, sh=shoulder, v=very, b=broad.

tion bands without obvious counterparts in the spectrum of diethyl ether are a broad band at 3300 cm^{-1} and three others at 2910, 1810 and 1095 cm^{-1}.

The pyridine and aniline complexes have IR spectra (4000-350 cm^{-1}), in the solid state, indicative of the presence of coordinated organic base and of the existence of LH^+ ions involved in hydrogen bending;[8,9] the counterions appear to be the $[L - H- -L]^+$ cations. The extra pyridine molecule in **11** was shown by the presence of a sharp band at 604 cm^{-1} alongside a band of coordinated pyridine at 635 cm^{-1} and by its ease of removal, to be uncoordinated pyridine of crystallization.[24]

We have paid particular attention to the far-IR of the prepared compounds, as poor data are reported in the literature for complexes having these types of coordination. The far-IR spectra of the complex anions $[CoX_3L]^-$ (Table IV) and $[CoY_2XL]^-$ (Table V) give an insight into structure and bonding in the solid state. Only features below 420 cm^{-1} are listed, since it was clear that no fundamentals of the anions occured above this wavenumber. Since several sets of complexes of the same stereochemistry were available in which the anionic ligand varied from Cl to Br to I, the assignment of the cobalt-halogen stretching vibrations was made with a reasonable certainty. On the other hand, the assignment of the cobalt-nitrogen stretching vibration was rather tentative; this band was assigned on the assumption that for a series of complexes with the same stereochemistry, the ν(Co-N) modes would occur at approximately the same frequencies in the chloro-, bromo- and iodo- analogs, in the absence of significant coupling with ν(Co-X) vibrations, and by comparison with other pseudotetrahedral Co(II) complexes with pyridine[3,4] and aniline[25,26] for which the ν(Co-N) mode was found in the same spectral region.

The vibrational representation of a $[CoX_3L]^-$ ion is $\Gamma_v = 3A_1 + 3E$ and these ions should give rise to six IR-active skeletal vibrations.[3,27] Assuming that L acts as a point mass, the three A_1 modes are designated as $\nu_s(CoX_3)$, ν(Co-N) and the symmetric deformation, while the three E modes are $\nu_d(CoX_3)$, $\delta_d(CoX_3)$ (XCoX scissors) and the wagging of L perpendicular to the CoX_3 axis (where s=symmetric and d=degenerate). The C_2 axis of pyridine cannot, however, be reconciled with the C_3 axis of the CoX_3 group and, therefore, deviations from the predicted spectra are to be expected. In addition, since all the spectra were examined in the solid state, other interactions may give rise to additional splittings. The $\nu(Co\text{-}X)_t$ bands are observed to occur about 15 cm^{-1} lower than those of the corresponding diligand complexes $CoX_2 \cdot 2L$[3,28] and are in turn 15-20 cm^{-1} higher[29] than the cobalt-halide asymmetric stretch in the complex ions $[CoX_4]^{2-}$. It is clear that the positions of $\nu(Co\text{-}X)_t$ bands distinguish between a complex $[L_2H][CoX_3L]$ and an equimolar mixture of $CoX_2 \cdot 2L$ and $[L_2H]_2[CoX_4]$.

TABLE V
Far-IR[a] Stretching Bands (cm^{-1}) for the Pyridine and Aniline Compounds of Mixed Halogen Acids of Co(II).

Compound	$\nu(Co\text{-}Cl)_t$	$\nu(Co\text{-}Br)_t$	$\nu(Co\text{-}I)_t$	ν(Co-N)
2	314vs,308vs	246vs		228sh,195m
3	310s,303s	234sh,230m		416m,361s
8		243s	209m,197[b]mb	235sh,197[b]mb
9		237s	211sh,199mb	412m,358m
11	332vs,308m		219vs	239m,198w
12	311s,285s		210s	412m,351s
14		256sh,239vs	209m	234sh,201m
15		254sh,237s	212m	418m,360m

[a]Data obtained at room temperature. [b]Overlapping. For abbreviations see Table IV.

The main problem encountered in the study of the far-IR spectra of the aniline compounds is the identification of bands arising from internal vibrations of the aniline ligand itself or the $[An_2H]^+$ ion, and distinguishing these from ν(Co-N) modes. This is a problem recognised by other workers.[25,26,28] The region of particular difficulty is 420-300 cm^{-1}. In this region only one strong band appears in the spectra of aniline (390 cm^{-1}) and anilinium halides (*ca* 380 cm^{-1}). In the same region a system of three bands of medium to strong intensities is observed in the spectra of chlorine-free complexes. At least one of the additional bands must be that corresponding to ν(Co-N).

The $[L_2H]^+$ Counterion

The existence of the $[Py_2H]^+$ and $[An_2H]^+$ cations is proposed to account for the stoichiometry of the prepared complexes. Complexes comprising $[L_2H]^+$ counterions (where L=a monodentate heterocyclic organic base) with $(N - H- -N)^+$ bonding have attracted the attention of inorganic chemists comparatively recently.[30-33] The very strong hydrogen bonding in these systems causes[34] the N – H stretching vibration to appear as a very broad absorption centered at *ca* 2500 cm^{-1} with a half-width of 250 cm^{-1}. Our results are summarized as follows:

1) A broad band of medium to strong intensity, appears at *ca* 2800 cm^{-1} in the spectra of the pyridine and aniline complexes, which is attributed to the ν_s(NHN) mode.

2) The spectra of the pyridine compounds do include weak ν(N-H) bands in the 3220-3100 cm^{-1} region, which suggest that there are some non-associated $[PyH]^+$ groups present.

3) The inter-molecular ν_6 mode, which is characteristic of $[PyHPy]^+$ groups[35], was observed in our spectra as a well defined band at *ca* 135 cm^{-1}.

In conclusion, on the basis of the overall study presented, the formulae $[L_2H]$ $[CoX_3L]$ and $[L_2H]$ $[CoY_2XL]$ are proposed for the prepared complexes in the solid state. The anions possess pseudotetrahedral configurations.

REFERENCES

1. B. Chevrier and R. Weiss, *Angew. Chem. Internat. Edn.*, **13**, 1 (1974).
2. F.A. Cotton, O.D. Faut, D.M.L. Goodgame and R.H. Holm, *J. Amer. Chem. Soc.*, **83**, 1780 (1961).
3. J. Bradbury, K.P. Forrest, R.H. Nuttall and D.W.A. Sharp, *Spectrochim. Acta*, **23A**, 2701 (1967).
4. D.H. Brown, K.P. Forrest, R.H. Nuttall and D.W.A. Sharp, *J. Chem. Soc. (A)*, 2146 (1968).
5. G. Marcotrigiano, L. Menabue and G.L. Pellacani, *Inorg. Chim. Acta*, **26**, 57 (1978) and references therein.
6. A.G. Galinos, J.M. Tsangaris and A.A. Kouroumalis, *Inorg. Nucl. Chem. Lett.*, **14**, 87 (1978).
7. A.G. Galinos and S.P. Perlepes, *Bull. Soc. Chim. France*, I-46 (1979).
8. A.G. Galinos, J.K. Kouinis, P.V. Ioannou, Th.F. Zafiropoulos and S.P. Perlepes, *Z. Naturforsch. Sect. B*, **34**, 1101 (1979).
9. A.G. Galinos, S.P. Perlepes and J.K. Kouinis, *Monatsh.*, **111**, 829 (1980).
10. Th.F. Zafiropoulos, S.P. Perlepes, J.K. Kouinis and A.G. Galinos, *Inorg. Nucl. Chem. Lett.*, **16**, 377 (1980).
11. S.P. Perlepes, Th.F. Zafiropoulos, A.K. Anagnostopoulos and A.G. Galinos, *Z. Naturforsch. Sect. B*, **37**, 646 (1982).
12. A.I. Vogel, "A Text-Book of Quantitative Inorganic Analysis", 3rd ed., (Longmans, London, 1961), pp. 568, 569.
13. W.E. Bazzelle, *Analyt. Chim. Acta*, **54**, 29 (1971).
14. K.K. Barnes and C.K. Mann, *Anal. Chem.*, **36**, 2502 (1964).
15. J.S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents," (Allyn and Bacon Inc., Boston, 1973). pp. 122-127.
16. A.G. Galinos, *J. Amer. Chem. Soc.*, **82**, 3032 (1960).

17. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
18. F.A. Cotton, D.M.L. Goodgame and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 4690 (1981).
19. B.B. Garrett, V.L. Goedken and J.V. Quagliano, *J. Amer. Chem. Soc.*, **92**, 489 (1970).
20. U. Olsher, *Spectrochim Acta*, **34A**, 211 (1978).
21. M. Ballester and J. Riera, *Spectrochim, Acta*, **23A**, 1533 (1967).
22. M.J. Blandamer and M.F. Fox, *Chem. Rev.*, **70**, 59 (1970).
23. L. Andrews, E.S. Prochaska and A. Loewenschuss, *Inorg. Chem.*, **19**, 463 (1980).
24. I.J. McColm, *J. Inorg. Nucl. Chem.*, **32**, 1461 (1970).
25. M.A.J. Jungbauer and C. Curran, *Spectrochim. Acta*, **21**, 641 (1965).
26. I.S. Ahuja, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1105 (1965).
27. J.E. Drake, J.L. Hencher, L.N. Khasrou, D.G. Tuck and L. Victoriano, *Inorg. Chem.*, **19**, 34 (1980).
28. M. Goldstein and R.J. Hughes, *Inorg. Chim. Acta*, **40**, 229 (1980) and references therein.
29. A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, **86**, 17 (1964).
30. C. Glidewell and T.M. Shepherd, *J. Inorg. Nucl. Chem.*, **37**, 348 (1975).
31. P.C. Minshall and G.M. Sheldrick, *Acta Cryst.*, **B34**, 1378 (1978).
32. L.V. Kobets, N.N. Khod'Ko, I.M. Kopashova and D.S. Umreiko, *Russ. J. Inorg. Chem.*, **25**, 729 (1980).
33. J.V. Brencic, B. Ceh and P. Segedin, *J. Inorg. Nucl. Chem.*, **42**, 1409 (1980).
34. C. Glidewell and H.D. Holden, *Acta Cryst.*, **B38**, 667 (1982).
35. R. Clements, R.L. Dean, T.R. Singh and J.L. Wood, *Chem. Comm.*, 1125 (1971).