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Substituted Pyridine N-Oxide Complexes. VI
Spectral and Magnetic Properties of Some 4-Substituted Pyridine N-Oxide Complexes with Transition Metal Perchlorates

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Visible spectra, infrared spectra and magnetic properties of 4-substituted pyridine N-oxide complexes of the general formula $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$, *where* $R = OCH_3, CH_3, H, Cl$ *and* NO_2; $M = Cr(III), Fe(III), Co(II)$ *and* $Ni(II)$; *and* $n = 2$ *or* 3, *are reported. For* $M = Cu(II)$, *tetrakis derivatives are formed for all R substituents and the hexakis complex is additionally isolated with* $R = H$. *The magnetic and spectral data indicate that the six coordinate complexes are high-spin octahedral species and that the four coordinate copper(II) complexes are probably square planar. From infrared spectral measurements nitrogen-oxygen and metal-oxygen stretching vibrations are assigned and the former are found to correlate with the* σ^+ *values of the ligands. Crystal field parameters are evaluated from diffuse reflectance and mull spectra and differences and trends discussed.*

Introduction

Considerable interest in the donor properties of pyridine N-oxides has recently been evident and in addition to investigations of the magnetic and spectral properties of complexes with copper(II) halides,[1,2] performed in this laboratory, several workers have studied pyridine N-oxide derivatives with other metals.[3-14] These investigations include the infrared and visible spectral properties of complexes with transition metal perchlorates, of the general formula $[M(C_5H_5NO)_6](ClO_4)_n$, where M = Cr(III), Mn(II), Fe(III), Fe(II), Co(II), Ni(II) and Cu(II), and n = 2 or 3.[3-5,7,9-11] With the exceptions of 3 and 4-acetylpyridine N-oxide derivatives[11] and a brief report of 4-methylpyridine N-oxide complexes with cobalt(II) and nickel(II) perchlorates,[6] no compounds of the above type containing substituted pyridine N-oxides have been examined. An investigation of the effect of the introduction of substituents into the ring upon the properties of the complexes was therefore initiated and the results of these studies are reported herein.

Additionally, earlier work on the unsubstituted pyridine N-oxide complexes included the calculation of crystal field parameters from solution spectral measurements of the compounds.[7] It has since become evident that several of the derivatives decompose in solution, one or more molecules of pyridine N-oxide being replaced by solvent molecules. An examination of the solid state spectra by diffuse reflectance and mull techniques therefore merited attention.

For this investigation a series of pyridine N-oxides substituted in the 4 position was chosen, the substituents being selected in such a manner as to provide a representative range of electron withdrawing and donating powers. Complexes of the general formula $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$, where R = OCH_3, CH_3, H, Cl and NO_2, M = Cr(III), Fe(III), Co(II) and Ni(II) have been prepared. Room temperature magnetic moments, infrared spectral measurements in the region 1300-250 cm^{-1} and diffuse reflectance and mineral oil mull spectra of the complexes are recorded.

During the course of this work a report of a similar study for nickel(II) complexes containing a range of six 4-substituted pyridine N-oxides appeared,[15] also drawing attention to inaccuracies in previous spectral assignments. The results obtained in our investigation of the nickel(II) complexes are generally consistent but small discrepancies arise owing to differing assignments of metal-oxygen stretching frequencies in the far infrared spectra.

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Experimental Section

Preparation of the Substituted Pyridine N-Oxides. Pyridine N-oxide, 4-methoxy- and 4-methylpyridine N-oxide were obtained commercially. The 4-nitro and 4-chloro substituted ligands were prepared from pyridine N-oxide by the method of Ochiai.[16] The melting points of the two products were consistent with literature values.

Preparation of the Complexes. In general a solution of the hydrated metal perchlorate in 2,2-dimethoxypropane and absolute ethanol was stirred for three hours at room temperature, a procedure which served to dehydrate the perchlorate. The complexes were then prepared by the addition of this mixture to an excess of an ethanolic solution of the ligand. A molar ratio, ligand: perchlorate, of 10: 1 was employed. The products, which generally crystallized immediately or upon standing for a short time, were filtered, washed with ethanol and dried in vacuo. For R = H, it was frequently found unnecessary to carry out the initial dehydration procedure and complexes were prepared simply by mixing warm methanol or ethanol solutions of the hydrated perchlorate and the ligand.

In the reaction with copper(II) perchlorate the use of the above conditions yielded a hexakis product for R = H, but tetrakis products with R = OCH_3, CH_3, Cl and NO_2. For the unsubstituted pyridine N-oxide, the tetrakis species was isolated by the use of stoichiometric quantities of the ligand and copper(II) perchlorate.

Analytical Data. Microanalyses for carbon, hydrogen and nitrogen were performed by Galbraith Laboratories, Inc., Knoxville, Tennesse. Metal analyses were carried out following the method reported by Guerrin *et al.*[17] The analytical data are presented in Table I.

Spectral Measurements. Infrared spectra in the region 1300-250 cm^{-1} were recorded on a Perkin Elmer, Model 521, grating spectrophotometer. The samples were measured as nujol mulls supported between caesium bromide plates.

Diffuse reflectance spectra of solid samples were obtained on a Beckman DU spectrophotometer fitted with the standard reflectance attachment and employing a block of magnesium carbonate as standard.

Visible spectra were also recorded as mineral oil mulls in the region 350-1500 mμ on a Cary 14 recording spectrophotometer. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in mineral oil.

Magnetic Measurements. Magnetic susceptibilities were determined by the Faraday method using equipment and procedures which have been described previously.[18] Mercury tetrathiocyanatocobaltate(II) was used as magnetic susceptibility standard[19] and diamagnetic corrections were estimated from Pascal's constants.[20]

Results and Discussion

The Complexes. For M = Fe(III), Co(II), Ni(II) and Cu(II), mixing ethanolic solutions of the ligand and

Table I. Analytical Data

Complex $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$			Analyses							
			C		H		N		M	
M	R	n	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Cr(III)	OCH_3	3	39.19	39.23	3.88	3.82	7.19	7.63	—	4.72
Cr(III)	CH_3	3	42.94	43.03	4.42	4.21	8.52	8.37	—	5.18
Cr(III)	H	3	38.91	39.12	3.44	3.28	8.91	9.13	—	5.65
Cr(III)	Cl	3	31.82	31.95	2.30	2.14	7.23	7.45	—	4.61
Fe(III)	OCH_3	3	39.35	39.13	3.99	3.80	7.41	7.61	5.04	5.06
Fe(III)	CH_3	3	42.73	42.86	4.19	4.20	8.08	8.33	5.76	5.54
Fe(III)	H	3	38.35	38.95	3.29	3.27	8.52	9.09	6.12	6.04
Fe(III)	Cl	3	31.68	31.85	2.05	2.14	7.48	7.42	5.05	4.94
Fe(III)	NO_2	3	30.09	30.15	2.20	2.02	13.84	14.07	4.78	4.67
Co(II)	OCH_3	2	42.72	42.86	4.20	4.17	8.45	8.34	5.86	5.85
Co(II)	CH_3	2	47.56	47.39	4.67	4.64	9.09	9.21	6.50	6.46
Co(II)	H	2	43.78	43.50	3.85	3.65	9.96	10.15	7.11	7.11
Co(II)	Cl	2	34.64	34.81	2.20	2.34	8.00	8.12	5.69	5.69
Co(II)	NO_2	2	32.70	32.82	2.32	2.20	15.16	15.31	5.37	5.37
Ni(II)	CH_3	2	47.53	47.40	4.59	4.64	9.10	9.21	6.24	6.43
Ni(II)	H	2	43.47	43.51	3.88	3.65	9.97	10.15	7.16	7.09
Ni(II)	Cl	2	35.01	34.81	2.30	2.34	7.98	8.12	5.60	5.67
Ni(II)	NO_2	2	32.86	32.82	2.36	2.20	15.10	15.31	5.36	5.35
*Cu(II)	OCH_3	2	37.79	37.77	3.81	3.67	7.12	7.34	8.21	8.33
*Cu(II)	CH_3	2	41.03	41.23	3.94	4.04	7.95	8.02	8.99	9.09
Cu(II)	H	2	43.75	43.26	3.78	3.63	10.20	10.09	7.71	7.63
*Cu(II)	H	2	37.17	37.38	3.12	3.14	8.60	8.72	9.90	9.89
*Cu(II)	Cl	2	30.71	30.77	2.16	2.07	6.87	7.18	8.08	8.14
*Cu(II)	NO_2	2	29.44	29.19	2.04	1.96	13.85	13.62	7.73	7.72

* Empirical formula $[Cu(4\text{-}RC_5H_4NO)_4](ClO_4)_2$.

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dehydrated metal perchlorate in 10:1 molar ratio afforded the complexes as crystalline materials. The chromium(III) compounds were more difficult to isolate and only the unsubstituted pyridine N-oxide derivative (R = H) appeared crystalline. For the remaining four ligands the products separated as dark green oils from the reaction mixture and only solidified on prolonged standing under ether. Although rather sticky in nature, the complexes with R = OCH_3, CH_3 and Cl analyzed correctly for the six coordinate species. For R = NO_2 several preparations of a pale green product gave unsatisfactory and inconsistent elemental analyses. Consequently no physical measurements on the chromium(III)-4-nitro-pyridine N-oxide complex were undertaken.

For M = Cu(II) the formation of four coordinate derivatives seemed to be preferred since these were obtained for all values of R and the six coordinate species was isolated only with R = H. The use of a large excess of the ligands R = OCH_3, CH_3, Cl and NO_2 in the preparations yielded only the four coordinate species. The formation of copper(II) complexes with both four and six molecules of pyridine N-oxide has been reported previously.[4,9]

Magnetic Data. Room temperature magnetic data for the complexes prepared in this study are presented in Table II. For the six-coordinate complexes the values of the magnetic moments are within the accepted range for high-spin octahedral species. Magnetic susceptibilities of several compounds with pyridine N-oxide have been reported previously and our measurements are consistent with the earlier work. However, magnetic moments of 1.62[3] and 2.09 BM[9] have been reported for the four coordinate pyridine N-oxide-copper(II) perchlorate complex and the former re-

Table II. Room temperature (25°C) magnetic moments (BM)

M	n	$[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$				
		R				
		OCH_3	CH_3	H	Cl	NO_2
Cr(III)	3	3.84	3.82	3.88	3.87	—
Fe(III)	3	6.04	6.04	5.97	6.07	5.97
Co(II)	2	4.79	4.71	4.84	4.82	4.79
Ni(II)	2	—	3.32	3.32	3.34	3.30
Cu(II)	2	—	—	1.91	—	—
*Cu(II)	2	1.86	1.89	1.89	2.02	2.05

* Four coordinate complexes.

Table III. Far infrared spectra in the region 550-250 cm^{-1}. Maxima which are in italic type are tentatively assigned as metal-oxygen stretching frequencies

4-methoxy-pyridine N-oxide		522 m		463 m			407 w		372 vw			
Cr(III)	554 m		490 s	460 m,sh			410 m		366 m	*340* s		
Fe(III)		527 w	480 s	463 m		437 s	410 m,sh				*311* vs	
Co(II)		529 m		473 s		426 m,sh	415 m	398 m				*282* s,sh
*Cu(II)		537 w	485 s	462 m.sh			410 m				*327* s	
4-methyl-pyridine N-oxide		523 m	481 m	468 m						337 m	320 w	
Cr(III)	552 m		503 s	461 m	*445 m*					332 w		
Fe(III)		527 m	497 s	461 m		*412* s,sh	*403 s*			320 w,sh		
Co(II)		530 m	488 m.sh	476 s				*392* s,sh	*384* s	322 w		
Ni(II)		532 m	489 m,sh	473 s				*393* s		322 w		
*Cu(II)	550 w		503 s	462 m	*438 s*					318 w,sh		
pyridine N-oxide	540 m	518 m		462 s								
Cr(III)	541 w			453 s		*428* s	*405* m,sh					
Fe(III)	523 w	509 w	478 w,sh	460 s				*385* s				
Co(II)	530 w			470 s			410 w			*340* m,sh	*330* s	
Ni(II)	534 w			468 s		420 w	410 w			*340* s	*328* m,sh	
Cu(II)	520 w			465 s		418 w	410 w		*366* s			
*Cu(II)	550 w,sh			452 s			*417* vs	*385* m,sh				
4-chloro-pyridine N-oxide		519 m	484 m			430 vw	420 vw	410 w			332 m	275 m
Cr(III)	543 w		491 s	*481* s,sh	*460* m,sh	435 m	405 w	391 w			322 m	
Fe(III)	525 vw	513 w	492 w	478 m	468 s	*442* s		395 m		358 w		
Co(II)	536 m	527 w,sh	500 s				420 w	400 w	*362* s,sh	*355* s		
Ni(II)	540 m	528 w,sh	500 s				418 w	400 w	*367* s,sh	*355* s		
*Cu(II)	545 w		503 w		469 s	*447* s,sh		400 m			306 m	
4-nitro-pyridine N-oxide	541 w	518 w		466 s			400 w,sh		367 vw		300 vw,sh	
Fe(III)		519 w		448 s,sh		*424* s	409 m,sh		370 m		308 w,sh	
Co(II)	542 w	511 m	477 m	459 s			411 w	385 m	*367* m,sh	*354* s	305 w	
Ni(II)	547 w	517 m	480 m	453 s			415 w	389 m	*370* s	*360* s	306 w	
*Cu(II)	555 w	532 w		447 s		*420* s		384 w	375 w		305 w,sh	

* Four coordinate complexes. w = weak, m = medium, and s = strong intensity, v = very.

presents a marked discrepancy from the value of 1.89 BM obtained in this study. The explanation for this is not clear, but since the other four coordinate complexes prepared here exhibit magnetic moments in the range 1.86-2.05 BM, our result, or that of Harris *et al.* appears preferable.

The configuration of the four coordinate copper(II) compounds cannot be determined solely on the basis of magnetic properties due to the small differences predicted between tetrahedral and square planar species. However, the diffuse reflectance spectra of the complexes, discussed in detail later, are typical of square planar configurations.

Infrared Spectra. The infrared spectra were measured as nujol mulls in the range 1300-250 cm^{-1} and the observed bands in the low frequency region (550-250 cm^{-1}) are recorded in Table III. Comparison of the spectra of the complexes with those of the free ligands facilitated the assignment of infrared-active nitrogen-oxygen and metal-oxygen stretching modes of vibration, and these are summarized in Table IV. For the unsubstituted pyridine N-oxide complexes, some of these frequencies have been assigned previously.[10,11]

Table IV. Infrared spectra (cm^{-1}) - Infrared-active nitrogen-oxygen [ν(NO)] and metal-oxygen [ν(MO)] stretching modes of vibration for the complexes $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$

	R				
	OCH_3	CH_3	H	Cl	NO_2
ν(NO)					
$4\text{-}RC_5H_4NO$	1210	1225	1243	1243	1269
Cr(III)	1198	1200	1199	1199	—
Fe(III)	1207	1205	1209	1209	1213
Co(II)	1201	1207	1217	1220	1237
Ni(II)	—	1206	1218	1220	1239
Cu(II)	—	—	1211, 1227	—	—
*Cu(II)	1200	1210	1200, 1213	1210	1212, 1234
ν(MO)					
Cr(III)	340	445	428, 405	481, 460	—
Fe(III)	311	412, 403	385	442	424
Co(II)	282	392, 384	340, 330	362, 355	367, 354
Ni(II)	—	393	340, 328	367, 355	370, 360
Cu(II)	—	—	366	—	—
*Cu(II)	327	438	417, 385	447	420

* Four coordinate complexes.

Table IV includes the nitrogen-oxygen stretching frequencies of the free ligands and the customary decrease in this value upon coordination is observed. The spectra of complexes containing different metal ions but with the same oxidation state and stereochemistry are very similar; thus the spectra of Cr(III) and Fe(III), Co(II) and Ni(II) derivatives with the respective ligands resemble each other very closely. For complexes with similar stereochemistries but different oxidation states, the strength of the coordinative metal-oxygen bond is expected to be greater the higher the oxidation state. Thus the values of metal-oxygen stretching frequencies for compounds containing trivalent metal ions should be higher than for those of divalent oxidation states. The observed ranges of frequencies for each series of derivatives containing one ligand are consistent with this suggestion. The increase from 366 to 417 cm^{-1} in the metal-oxygen vibrations of the copper(II) complexes containing six and four pyridine N-oxide ligands respectively, is noteworthy. A shift in this direction may be anticipated and it presumably reflects the increase in bond strength and reduced steric interaction consequent upon the presence of a smaller number of ligands in the coordination sphere of the metal ion.

Assuming O_h and D_{4h} symmetry, one infrared-active metal-oxygen stretching mode is predicted for both the octahedral six coordinate complexes, and four coordinate square planar species respectively. However, it is rather difficult to use symmetry considerations in discussing the metal-oxygen vibrations owing to the large number of absorptions found in this region of the spectrum, and the possibility of coupling with vibrations of similar symmetry properties. Thus the bands which have been tentatively assigned as metal-oxygen stretching frequencies are frequently fairly broad and asymmetric. Indeed, it is very difficult to make a definite assignment of these frequencies.

The values of the nitrogen-oxygen stretching modes lie in the order R = $OCH_3 < CH_3 < H < Cl < NO_2$ and thus correlate quite well with the σ^+ values of the substituents in the 4-position on the pyridine ring. Plots of ν(NO) as a function of σ^+ are exhibited in the Figure. The dependency on R is most marked for complexes with divalent ions and with M = Cr(III) the frequency is virtually independent of R.

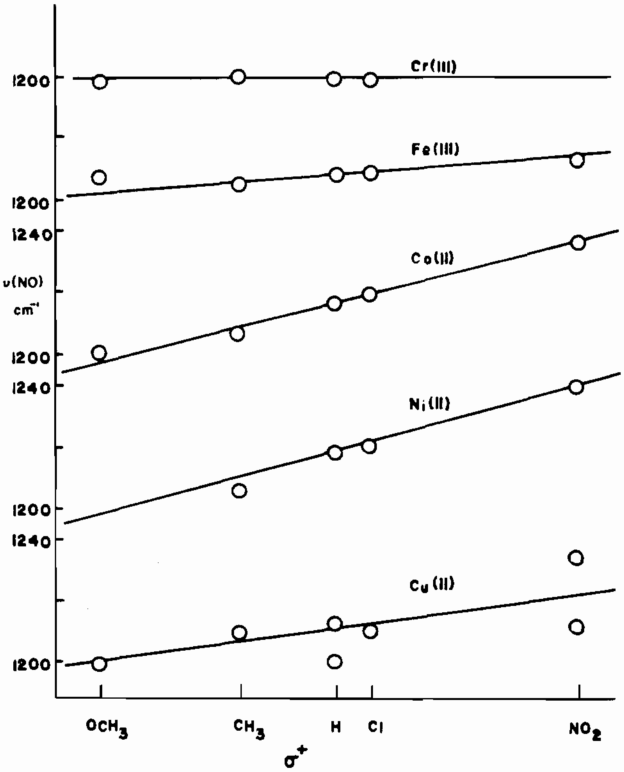

Figure 1. Nitrogen-oxygen stretching frequencies, ν(NO), as a function of σ^+

In contrast to the work of Herlocker, Drago and Meek[15] for the nickel(II) complexes, we do not find that the correlation with σ^+ extends to the metal-oxygen stretching frequencies. The discrepancy arises mainly from the different assignments of ν(MO) for R = CH_3 in the two studies. We assign a peak of relatively strong intensity at 393 cm^{-1} to this mode of vibration, whereas the earlier work reported a value of 325 cm^{-1}. Comparison with the spectra of the pyridine N-oxide complexes (R = H) reported previously indicates that the metal-oxygen stretching frequencies are relatively intense.[11] Whereas pyridine N-oxide is free of absorption in the range 450-250 cm^{-1}, 4-methylpyridine N-oxide shows maxima at 337 (m) and 320 (w) cm^{-1}. In the spectrum of the nickel(II) complex we prefer to associate the weak maximum at 322 cm^{-1} with internal vibrations of the ligand rather than the metal-oxygen vibration. In support of this conclusion a weak peak or shoulder at *ca.* 330-320 cm^{-1} is observed in the spectra of all the 4-methyl-pyridine N-oxide complexes considered here. Additionally, the peak at 393 cm^{-1} defies satisfactory alternative explanation. It is unlikely to be an internal vibration of the ring, infrared-inactive in the free ligand, but becoming activated in the complex, since 4-methylpyridine and its complexes do not show maxima in this range.[21]

Table V. Diffuse reflectance spectra of the complexes $[M(4\text{-}RC_5H_4NO)_6](ClO_4)_n$

M	Observed Maxima (cm^{-1}) R: OCH_3	CH_3	H	Cl	NO_2	Band Assignement
Cr(III)	16,130	15,270	15,150	15,750	—	$^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$
		16,810 sh	16,670 sh			
	22,990	22,730	22,730	22,220	—	$^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$
Co(II)	8,333	8,333	8,333	8,333	8,264	$^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$
	14,930 sh	15,150 sh	15,150 sh	15,380 sh	15,150 sh	
	18,180 sh	17,860	17,860	18,870	17,540 sh	$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$
	20,000 sh	20,000 sh	20,000 sh	20,000 sh	20,000 sh	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$
					20,410	ligand
	26,320 sh	25,000	25,000	25,000 sh	25,000	ligand or charge transfer
Ni(II)	—	8,333	8,264	8,230	8,230	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$
		12,350 sh	12,500 sh	12,990 sh	12,200 sh	$^3A_{2g}(F)\rightarrow{}^1E_g(D)$
		14,080	14,080	14,290	13,890	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$
		19,610 sh	19,610 sh	20,000 sh	—	$^3A_{2g}(F)\rightarrow{}^1A_{1g}(G)$
					21,740	ligand
		25,320	25,320	25,640	25,970	$^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$
Cu(II)	—	—	9,524 sh	—	—	*d* shell
			12,200			
			26,670			charge transfer
*Cu(II)	14,290 sh	13,510 sh	13,700 sh	13,160 sh	12,660 sh	*d* shell
	15,150	14,710	14,710	14,490	14,080	
					19,610	charge transfer
	25,640	25,640 sh	26,320 sh	25,320	21,280	
					24,390 sh	

* Four coordinate complexes. sh = shoulder. The numerical values are quoted to four significant figures since they are the reciprocals of the mμ scale readings on the spectrophotometer.

When plotted as a function of σ^+, the values of ν(MO) for the complexes with R = OCH_3, H and NO_2 generally fall on a straight line, whereas the frequencies for R = CH_3 and Cl are much higher and slightly higher, respectively, than anticipated from this line. However, the lack of a correlation is not too surprising in view of the obvious complexity of the vibrations in systems of this sort.

Visible Spectra. The visible spectra of the complexes were investigated by diffuse reflectance techniques, representative compounds being additionally examined as mineral oil mulls. In all cases the spectra, as measured by the two methods, were found to be identical.

For the six-coordinate complexes band assignments were made with the aid of Tanabe-Sugano diagrams for octahedral configurations. The assumption of octahedral symmetry was based both on the observed magnetic properties and on the similarity of the spectra to those of the corresponding hexaquo metal ions. The observed spectral data, together with the band assignments, are recorded in Table V. The spectral parameters Dq, P-F term splitting and β, for M = Cr(III), Co(II) and Ni(II) were calculated by the usual techniques[7] and are summarized in Table VI.

Table VI. Summary of the observed crystal field parameters

M	R	Dq (cm^{-1})	P-F term splitting (cm^{-1})	β (%)
Cr(III)	OCH_3	1613	10,520	23.58
	CH_3	1600	10,280	25.41
	H	1587	10,590	23.12
	Cl	1575	9,792	28.92
	NO_2	—	—	—
Co(II)	OCH_3	950	12,810	11.96
	CH_3	950	12,810	11.96
	H	950	12,810	11.96
	Cl	950	12,810	11.96
	NO_2	940	12,890	11.45
Ni(II)	OCH_3	—	—	—
	CH_3	833	14,240	10.09
	H	826	14,350	9.43
	Cl	823	14,760	6.85
	NO_2	823	15,100	4.68

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[21] C. W. Frank and L. B. Rogers, *Inorg. Chem.*, 5, 615 (1966).

Chromium(III) Complexes. For R = H, CH_3 the band which has been assigned to the ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition is asymmetric with a shoulder on the high energy side of the main band. In the calculations of spectral parameters the mean value of these two frequencies was taken as the energy of the transition since the mean energy gave a β value consistent with those found for R = OCH_3, Cl. Calculations based on these assignments predict the ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition to lie in the ultra-violet. Since the ligands themselves absorb in this region the use of mull techniques does not permit the observation of this third band.

The Dq values recorded in Table VI lie in the range 1575-1613 cm^{-1}. They are somewhat lower than that of 1740 cm^{-1} recorded for the hexaaquochromium(III) ion,[22] thus implying that pyridine N-oxides occupy a position below water in the spectrochemical series. Previous spectral measurements on the pyridine N-oxide derivative in acetone and acetonitrile[7] afford a still lower value of 1539 cm^{-1} for Dq and a β value of only 16.9%. However, since the nature of the species present in solution is uncertain, it is not possible to make a meaningful comparison.

Iron(III) Complexes. These spectra are characteristic of essentially octahedrally coordinated species in which the iron(III) ion is surrounded by six oxygen atoms, e.g., the tris-oxalato[23] and tris-malonato[24] complexes. The spectra consist of three main band systems, the first of which occurs as a very intense maximum at *ca.* 24,000 cm^{-1}, followed by two peaks of very weak relative intensity centered at *ca.* 14,000 and 9,000 cm^{-1} respectively. Two shoulders are included in the envelope of the most intense peak, one on the high energy side of the maximum and the second appearing as a barely discernible hump at *ca.* 18,000 cm^{-1}.

Unfortunately, the quality of the spectral data is not high enough to support a detailed crystal field analysis but is sufficient to confirm the presence of octahedral coordination, as was inferred from the room temperature magnetic data.

Cobalt(II) Complexes. Using Dq and P-F term splitting energies as parameters, the ${}^4T_{2g}(F)$ and ${}^4T_{1g}(P)$ assignments were fitted to the energy matrix for the two T_{1g} levels of a d^7 octahedral system. This calculation yielded Dq values of *ca.* 950 cm^{-1} with P-F term splitting energies of 12,800-12,900 cm^{-1}, thus affording β values in the order of 11-12%. In support of the assignments, this value of Dq gives very good agreement between the calculated and observed energies for the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition, as illustrated in Table VII. Now this transition is theoretically predicted to have a very small intensity[25] whereas in this analysis it has been assigned as one of the more intense peaks in the band system. However, alternative band assignments, e.g., with ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ placed at *ca.* 18,000 cm^{-1} give rise to clearly unacceptable β values (*ca.* 25%).

Table VII. Calculated and observed frequencies of the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transition for Co(II) complexes

R	Calculated (cm^{-1})	Observed (cm^{-1})
OCH_3	17,833	18,180
CH_3	17,833	17,860
H	17,833	17,860
Cl	17,833	18,870
NO_2	17,664	17,540

The assignment of the weak shoulder at *ca.* 15,000 cm^{-1} is uncertain. It is possibly the ${}^2E_g$ component of the ${}^2G$ state although this transition is predicted to occur at somewhat lower energies.

The maxima at 25,000 cm^{-1} occur as shoulders on the side of a more intense, presumably charge-transfer, transition in the ultraviolet. The former band may also be associated with a charge-transfer transition.

The assignment of the intense peak at 20,410 cm^{-1} for the complex with R = NO_2 is uncertain. Peaks of similar energy and intensity are noted in all the complexes with 4-nitropyridine N-oxide and it is probable that the maxima may be associated with a transition within the ligand. The diffuse reflectance spectrum of 4-nitropyridine N-oxide shows a maximum at 24,390 cm^{-1}.

Nickel(II) Complexes. The spectra of the nickel(II) compounds are characteristic of octahedrally coordinated d^8 systems.[26] The band assignments are substantiated by the good agreement between calculated and experimental values of the ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition, as demonstrated by the data in Table VIII. It was not possible to carry out this calculation for the chromium(III) complexes since the frequency of the highest energy band, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$, was unknown. The shoulder on the lower energy side of the middle band is assigned to the transition ${}^3A_{2g}(F) \rightarrow {}^1E_g(D)$. The intensity of this band is abnormally large for a spin-forbidden transition and is comparable to that of the main peak. The increased intensity may be explained by assuming that the upper singlet state mixes with the nearby triplet state *via* spin-orbit coupling. For R = H, CH_3 and Cl the very weak shoulder occurring at *ca.* 20,000 cm^{-1} is assigned to the transition ${}^3A_{2g}(F) \rightarrow {}^1A_{1g}(G)$, by analogy with the work of Dunn.[27]

Table VIII. Calculated and observed frequencies of the ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition for Ni(II) complexes

R	Calculated (cm^{-1})	Observed (cm^{-1})
CH_3	13,930	14,080
H	13,830	14,080
Cl	13,810	14,290
NO_2	13,850	13,890

Copper(II) Complexes. The main feature of interest in the spectra of the copper(II) derivatives, especially

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(22) C. K. Jørgensen, «Absorption Spectra and Chemical Bonding in Complexes», Permagon Press, Oxford, p. 110 (1962).
(23) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, *35*, 1809 (1961).
(24) W. E. Hatfield, *Inorg. Chem.*, *3*, 605 (1964).
(25) C. J. Ballhausen, «Introduction to Ligand Field Theory», McGraw Hill Book Co., Inc., New York, N. Y., p. 256 (1962).
(26) Ref. 25, p. 261.
(27) Ref. 20, p. 288.

the four coordinate complexes, lies in the assignment of the structural species present. As discussed previously, magnetic properties are not sufficient to distinguish between square planar and tetrahedral configurations.

The spectrum of the six-coordinate pyridine N-oxide derivative is very similar to that of the essentially octahedral hexaaquo copper(II) ion,[28] maxima due to transitions within the *d* shell occurring at 12,200 and 12,600 cm^{-1} respectively. In addition, a slight shoulder occurs on the low energy side of each maximum, indicative of a Jahn Teller distortion. Thus, the six-coordinate pyridine N-oxide complex contains a distorted octahedral configuration.

A square planar structure for the four coordinate pyridine N-oxide copper(II) complex has been suggested[13] on the basis of the similarity of the spectrum with those of $[Cu(Ph_3PO)_4](ClO_4)_2$ and $[Cu(Me_3PO)_4](ClO_4)_2$. Also the fact that the *d-d* transition occurs at a higher energy than in the octahedral species effectively rules out the possibility of a tetrahedral structure. The similarity of the spectra of the four coordinate derivatives indicates that they all possess analogous, possibly slightly distorted, square planar structures.

For the substituted pyridine N-oxide complexes with chromium(III), the Dq values are lower than that observed for hexaaquochromium(III) indicating that pyridine N-oxides occupy a position beneath water in the spectrochemical series. A similar order is found for complexes with divalent ions, but the tendency is less marked. Thus the Dq value for hexaaquonickel(II) is 850 cm^{-1},[22] and the corresponding values for the pyridine N-oxide complexes lie in the range 820-835 cm^{-1}.

It is difficult to effect a comparison with previously reported solution spectral data for pyridine N-oxide complexes with Cr(III), Co(II) and Ni(II)[7] since the composition of the absorbing species in acetonitrile, dimethylformamide and methanol is uncertain and possibly varies from solvent to solvent. However, for the recent and more refined investigation of the nitromethane solution spectra of a series of 4-substituted pyridine N-oxide complexes with nickel(II),[15] there is good agreement between the reported spectral bands and the reflectance spectra discussed here. For similar compounds studied, the order of Dq values, with respect to the substituent in the 4-position of the pyridine ring, is the same although the absolute numerical values are slightly higher (*ca.* 5%) in the solid state than in solution. Similarly, the values calculated for β (measured as a percentage) are also somewhat larger for the solid species.

Based on the electronic effects of the substituent in the 4-position, it is anticipated that the greater the electron density in the nitrogen-oxygen bond (of the N-oxide system), the greater the ligand field splitting and therefore the higher the value of Dq. Thus the Dq values for the complexes should lie in the order of increasing $-\sigma^+$, i.e. $OCH_3 > CH_3 > H > Cl > NO_2$, and reference to Table VI indicates that this is the generally observed trend of the values.

The β values for the chromium(III) complexes are considerably larger than the corresponding values with cobalt(II) and nickel(II). This is consistent with expectation since a trivalent ion might be anticipated to exert a stronger polarizing effect than a divalent ion upon the oxygen dipoles of the pyridine N-oxide ligands.

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(28) Ref. 20, p. 287.