The spectrum of $[\mathrm{Cr}\{\mathrm{CH_3CON(CH_3)_2}\}_3\mathrm{Cl_3}]$ was determined immediately after preparation of the solution and again, in the regions of maximum and minima, after 24 hr. Except for an increase in the short wave length minimum, little change had occurred. Since the solution of $[\mathrm{Cr}\{\mathrm{HCON(CH_3)_2}\}_3\mathrm{Cl_3}]$ had turned green, an indication of hydrolysis, its spectrum was not redetermined.

The spectra of dimethylformamide and dimethylacetamide solutions of $[\mathrm{Cr(H_2O)_4Cl_2}]\mathrm{Cl}$ (0.02 M solutions) were obtained by the procedure described immediately after preparation of the solutions and again after 24 hr. The difference in absorption spectra of aqueous and dimethylformamide solutions of $\mathrm{CrCl_3{\cdot}6H_2O}$ also was observed by Pflaum and Popov.[13] The results of the present investigation confirm their conclusion that the effect is attributable to displacement of water molecules by amide molecules.

The curves for the dimethylacetamide–water solutions of $[\mathrm{Cr}\{\mathrm{CH_3CON(CH_3)_2}\}_3\mathrm{Cl_3}]$ (Fig. 3) were plotted from data taken 24 hr. after preparation of the solutions; the blank in each case was dimethylacetamide containing the same amount of water as the solution. Composition of the solutions is shown in Table I, which also shows some features of the spectra in comparison with those of $[\mathrm{Cr(H_2O)_3Cl_3}]$ and $[\mathrm{Cr(H_2O)_4Cl_2}]\mathrm{Cl}$.

Infrared Spectra.—The infrared spectra of five chromium–amide compounds were determined with Nujol mulls; spectra of the corresponding amides were determined with thin films. The spectra obtained for dimethylformamide and dimethylacetamide were in good agreement with those previously reported.[14] We are indebted to Mr. W. Feairheller of this Department for obtaining these spectra.

Coördination of the amide caused no great change in its spectrum except for a considerable shift of the carbonyl band. This is split into two bands in the triamide compounds. The single peak observed for the carbonyl band in the 2-pyrrolidinone complex is in accord with the highly symmetrical structure of the *trans* isomer.[15]

In the following the pertinent data are given in the order: $\tilde{\nu}$ (cm.$^{-1}$) of the carbonyl band of the amide; $\tilde{\nu}$ of the carbonyl band of the amide in the complex compound; shift (wave numbers) of strong band due to coördination (s indicates the strong absorption band): tris-(N,N-dimethylformamide)-trichlorochromium(III): 1670 s; 1665, 1630 s; 40; tris-(N,N-dimethylacetamide)-trichlorochromium(III): 1655 s; 1620, 1585 s; 70; tris-(N-methyl-2-pyrrolidinone)-trichlorochromium(III): 1685 s; 1660, 1615 s; 70; tris-(ε-caprolactam)-trichlorochromium(III): 1670 s; 1660, 1615 s; 55; *trans*-dichlorotetra-(2-pyrrolidinone)-chromium(III) chloride: 1690 s; 1620 s; 70.

Acknowledgment.—The authors are indebted to the Mutual Chemical Division, Allied Chemical and Dye Corporation, for financial assistance which facilitated this investigation; and to Prof. Ellis Lippincott of this Department for assistance in obtaining and interpreting the infrared spectra.

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Spectrochemical Studies of Dimethyl Sulfoxide, Tetramethylene Sulfoxide, and Pyridine N-Oxide as Ligands with Nickel(II), Chromium(III), and Cobalt(II)

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A comparison of the values of the crystal field parameter, Dq, for octahedral complexes of Ni(II) and Co(II) with water, dimethyl sulfoxide, tetramethylene sulfoxide, and pyridine N-oxide produces the spectrochemical series: $\mathrm{H_2O} > \mathrm{C_5H_5NO} > \mathrm{DMSO} \sim \mathrm{TMSO}$. Toward Cr(III) a different series is obtained: $\mathrm{H_2O} > \mathrm{DMSO} \sim \mathrm{TMSO} > \mathrm{C_5H_5NO}$. The larger Dq values for the sulfoxides toward Cr(III), compared to pyridine N-oxide, are attributed to the greater polarizability of the S–O bond. The decrease of the P–F term splittings for the complexes, compared to the gaseous ion values, has been interpreted to indicate some covalency in the metal ion–ligand bond. This interaction produces the nephelauxetic series: $\mathrm{DMSO} \sim \mathrm{TMSO} > \mathrm{H_2O} > \mathrm{C_5H_5NO}$.

Introduction

Recently, we have discussed the preparation and properties of coördination complexes of dimethyl sulfoxide with first row transition metal halides.[3,4] The current interest in this area is indicated by the appearance of several other

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[1] Abstracted in part from the Ph.D. Thesis of D. W. Meek, University of Illinois, 1961; General Electric Foundation Fellow.

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papers on the preparation of sulfoxide complexes[5-8] and on the preparation of complexes of ligands containing oxygen bonded to P,[9,10] As,[11] and N.[12]

The ligands of interest, having an oxygen atom bonded to a non-metal atom, are quite polar molecules, as indicated by their dipole moments: 3.9 D. for dimethyl sulfoxide[6] and 4.24 and 4.28 D. for pyridine N-oxide[13] and triphenylphosphine oxide,[14] respectively. In each case, the oxygen atom is the negative end of the dipole. The phosphine oxides can bond only through the oxygen atom,[15] and it has been shown by infrared spectra[3,4,7,8,16,17] that the sulfoxides bond through the oxygen atom in most complexes.

Our original studies on complexes of this type have been extended to a consideration of the *Dq* values of dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), and pyridine N-oxide. In general, *Dq* values for a given transition metal ion usually correlate with coördinating ability. Since oxygen is employed for coördination in each of the above complexes, it is of interest to compare the *Dq* values obtained for these three ligands with that for water in the six-coördinate complexes of Ni(II), Cr(III), and Co(II). Furthermore, the lowering of the P–F term splittings should indicate the covalency of the metal ion–ligand interactions.

Experimental

Tetramethylene sulfoxide (Wateree Chemical Company, Lugoff, South Carolina) was dried with barium oxide for two days. It was refluxed *in vacuo* for 1 hr. over lump barium oxide and then distilled slowly through an insulated Vigreux column. Dimethyl sulfoxide was purified as described previously.[3]

Purification of acetonitrile was accomplished as described by Lewis and Smyth.[18] The fraction boiling at 81.5° was collected. Dimethylformamide was dried and fractionated under vacuum from barium oxide. Pyridine N-oxide was purified by vacuum distillation after extracting an aqueous solution of the crude material with chloroform.[19]

The metal sulfoxide complexes were prepared by the following general procedure. The aquated metal perchlorates were dehydrated with 2,2-dimethoxypropane[20] by stirring with a magnetic stirrer for 2 hr. at 30°. The resulting solutions then were treated with a slight excess of the respective sulfoxide. Addition of an equal volume of ether resulted in the nearly quantitative precipitation of the nickel, cobalt, manganese, copper, and iron(III) complexes. In the case of Cr(III), an oil formed initially on treatment of the solution with several solvents. The complex was obtained in 40% yield by dissolving the oil in a minimum amount of hot acetone and cooling to 0°. All of the complexes were washed with acetone and ether and dried with a stream of dry air.

Anal. Calcd. for $[Co(C_4H_8SO)_6](ClO_4)_2$: C, 32.65; H, 5.48; Co, 6.68. Found: C, 32.80; H, 5.61; Co, 6.67.

Anal. Calcd. for $[Ni(C_4H_8SO)_6](ClO_4)_2$: C, 32.66; H, 5.48; Ni, 6.65. Found: C, 33.22; H, 5.89; Ni, 6.47.

Anal. Calcd. for $[Cr(C_4H_8SO)_6](ClO_4)_3$: C, 29.55; H, 4.96; Cr, 5.33. Found: C, 28.54; H, 5.06; Cr, 5.94.

Anal. Calcd. for $[Mn(C_4H_8SO)_6](ClO_4)_2$: C, 32.80; H, 5.51; Mn, 6.25. Found: C, 33.48; H, 5.48; Mn, 6.40.

Anal. Calcd. for $[Co(C_2H_6SO)_6](ClO_4)_2$: C, 19.83; H, 4.99. Found: C, 20.07; H, 5.16.

Anal. Calcd. for $[Ni(C_2H_6SO)_6](ClO_4)_2$: C, 19.84; H, 5.00. Found: C, 20.07; H, 5.16.

Anal. Calcd. for $[Cr(C_2H_6SO)_6](ClO_4)_3$: C, 17.59; H, 4.43. Found: C, 17.72; H, 4.53.

Anal. Calcd. for $[Mn(C_2H_6SO)_6](ClO_4)_2$: C, 19.94; H, 5.02. Found: C, 19.84; H, 5.03.

The pyridine N-oxide complexes were prepared easily by adding a warm methanolic solution of pyridine N-oxide to a similar solution of the hydrated metal perchlorate. Crystals of the respective complex precipitated on cooling.[12]

Anal. Calcd. for $[Ni(C_5H_5NO)_6](ClO_4)_2$: C, 43.50; H, 3.65; N, 10.14. Found: C, 42.77; H, 3.78; N, 9.73.

Anal. Calcd. for $[Co(C_5H_5NO)_6](ClO_4)_2$: C, 43.49; H, 3.65; N, 10.14; Co, 7.11. Found: C, 44.09; H, 3.80; N, 10.35; Co, 7.06.

Spectrophotometric Measurements.—Near infrared, visible, and ultraviolet absorption spectra were obtained with a recording Cary spectrophotometer, Model 14 M.

Solutions of the sulfoxide complexes were prepared by dissolving a weighed quantity of the appropriate complex in the respective sulfoxide as a solvent. This eliminates the possibility of a polar solvent replacing some of the coördinated sulfoxide from the coördination sphere of the cation.

The pyridine N-oxide complexes were dissolved in polar solvents because of their insolubility in non-polar ones. The spectra in acetonitrile are shifted with respect to the position of λ_{max} obtained in dimethylformamide and nitro-

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methane. The parameters for the pyridine N-oxide complexes were calculated from the spectra obtained in the latter two solvents.

The spectra of the solutions were measured in matched quartz cells of 0.1, 1.0, 5.0, and 10.0 cm. path length, against the solvent as a reference.

Calculations.—The secular equations for Ni(II)(d^8), Cr(III)(d^3), and Co(II)(d^7) were solved in the weak field formalism; the crystal field matrices have been reported by Orgel.[21] For Cr(III) and Ni(II) the values of *Dq* were taken directly from the wave numbers of the first (lowest energy) spin allowed absorption band. Orgel diagrams were constructed by solving the resulting equations, assuming a gas phase value for the term splittings. Attempts to fit the observed absorption bands to the predicted energy values using this ionic model resulted in systematic discrepancies.

In order to fit the experimental bands for the measured values of *Dq*, it is necessary to decrease the F–P term splitting in the complexes from the known values for the gaseous ions.

Using the experimental values for *Dq* and for the position of the second band for the Cr(III) complexes, we have calculated $E(^4P)$ from the secular equation. In the Ni(II) complexes, the strongest band at ~24,000 cm.$^{-1}$ is identified as the transition $^3A_2(^3F) \rightarrow {}^3T_1(^3P)$. Thus, the position of this band was used with the equation to calculate the parameter $E(^3P)$.[22] The second absorption band for Ni(II) provides an independent check on the values of *Dq* and $E(^3P)$.

The third band of Cr(III) complexes, corresponding to the transition $^4A_2 \rightarrow {}^4T_1(P)$, is predicted far in the ultraviolet and it could not be observed in our spectra due to the absorption of the ligands in this region. We, therefore, fitted $E(^4P) - E(^4F)$ to the second band, but we do not have a further independent check on the parameters for Cr(III) as with Ni(II). In addition, Schäffer[23] has demonstrated that the third band of Cr(III) complexes often deviates from the predicted position contrary to the analogous d^8 case. This effect may result from charge transfer interactions.

Fitting the Co(II) spectra to the parameters was more difficult because (1) the ground state $^4T_1$ is not a linear function of *Dq*, and (2) there was some doubt as to the position of the transition to $^4A_2$. The best fit was found graphically by constructing several Orgel diagrams with 10, 12.5, 15, and 17.5% lowering of the term value.

Results and Discussion

The spectral data for the complexes are summarized in Table I and illustrated in Fig. 1, 2, and 3. The band assignments also are indicated. For the Ni(II) complexes, these assignments are substantiated by the excellent agreement between the calculated and experimental values for the λ_{max} of the second band (Table II). Also these assignments are supported by the constancy of the intensity ratio of the $^3A_2(F) \rightarrow {}^3T_1(P)$ to $^3A_2(F) \rightarrow {}^3T_1(F)$ transition. This feature of Ni(II) spectra has been reported.[24,25]

The values for *Dq* and for the P–F term splitting for the complexes are indicated in Table III. The quantity β is defined as the percentage lowering of the F–P term splitting in the complex compared to the value of the gaseous ion with no crystalline field.

The data summarized in Table III permit the following observations: (1) The *Dq* values of pyridine N-oxide are larger than those of the sulfoxides for Ni(II) and Co(II) but the order is reversed for Cr(III); (2) the S–O bond is more nephelauxetic than the N–O bond.

Pyridine N-oxide has a larger net dipole than dimethyl sulfoxide and exerts a stronger field on the Ni(II) and Co(II) ions than the sulfoxides. However, the trivalent chromium ion would be expected to exert a stronger polarizing effect on a dipole than divalent ions, and may explain why the sulfoxides possess a larger *Dq* value toward Cr(III) than pyridine N-oxide, which is less polarizable than the sulfoxides.

The nephelauxetic effect has been correlated with the polarizability or covalency of the ligands.[26–28] The most convincing evidence for partial covalent bonding, as derived from the absorption spectra, is the decrease of the F–P term splittings from that of the gaseous ion value. The effect of covalency is to delocalize the 3d electronic distribution over the entire complex; thus, on the average the distance between the metal electrons increases. Therefore, the mutual repulsions of the electrons decrease, in turn decreasing the term splittings.

Both of the sulfoxide ligands have much larger values of β than water and pyridine N-oxide and, thus, are the most nephelauxetic of the series

$$\text{DMSO} \sim \text{TMSO} > H_2O > C_5H_5NO$$

The large increase in the value of β in going from the divalent to the trivalent ions further demonstrates the effect of polarization on the oxygen dipoles of both pyridine N-oxide and the sulfoxides. The larger *Dq* for the sulfoxides toward Cr(III), compared to pyridine N-oxide, is attributed to the greater polarizability of the S–O bond.

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TABLE I

SPECTRAL BANDS FOR Ni(II), Co(II), AND Cr(III) COMPLEXES OF DIMETHYL SULFOXIDE, TETRAMETHYLENE SULFOXIDE, AND PYRIDINE N-OXIDE

Compound	Solvent	λ_{max} cm.$^{-1}$	ϵ_{max}[a]	$\Delta\nu$,[b] cm.$^{-1}$	Band assignment[c]
$[Ni(DMSO)_6](ClO_4)_2$	DMSO	7,728	3.48	2300	$^3A_2(F) \rightarrow {}^3T_2(F)$
		12,970	3.68		$\rightarrow {}^3T_1(F)$
		(14,286)[d]	~2.54		
		24,038	10.15	2900	$\rightarrow {}^3T_1(P)$
$[Ni(TMSO)_6](ClO_4)_2$	TMSO	7,752	3.70	2300	$^3A_2(F) \rightarrow {}^3T_2(F)$
		12,987	3.83		$\rightarrow {}^3T_1(F)$
		(14,286)	~2.70		
		24,010	10.75	2900	$\rightarrow {}^3T_1(P)$
$[Ni(C_5H_5NO)_6](ClO_4)_2$	DMF	8,403	6.75	2400	$^3A_2(F) \rightarrow {}^3T_2(F)$
		14,124	5.99		$\rightarrow {}^3T_1(F)$
		25,840	124	5300	$\rightarrow {}^3T_1(P)$
$[Cr(DMSO)_6](ClO_4)_3$	DMSO	15,773	33.4	3100	$^4A_2(F) \rightarrow {}^4T_2(F)$
		22,523	34.6	4100	$\rightarrow {}^4T_1(F)$
$[Cr(TMSO)_6](ClO_4)_3$	TMSO	15,748	30.5	3300	$^4A_2(F) \rightarrow {}^4T_2(F)$
		22,523	34.2	4700	$\rightarrow {}^4T_1(F)$
$[Cr(C_5H_5NO)_6](ClO_4)_3$	Acetone	15,385	83.4	4200	$^4A_2(F) \rightarrow {}^4T_2(F)$
		22,548	125.7	4100	$\rightarrow {}^4T_1(F)$
$[Co(DMSO)_6](ClO_4)_2$	DMSO	7,273	2.38	2100	$^4T_1(F) \rightarrow {}^4T_2(F)$
		14,535	0.49	2600	$\rightarrow {}^4A_2(F)$
		18,622	11.40	2700	$\rightarrow {}^4T_1(P)$
		(20,833)	~2.67	1600	
$[Co(TMSO)_6](ClO_4)_2$	TMSO	7,353	2.32	2000	$^4T_1(F) \rightarrow {}^4T_2(F)$
		14,771	0.48	2600	$\rightarrow {}^4A_2(F)$
		18,587	11.14	2900	$\rightarrow {}^4T_1(P)$
		(20,833)	~2.6	1500	
$[Co(C_5H_5NO)_6](ClO_4)_2$	DMF	7,813	5.16	2400	$^4T_1(F) \rightarrow {}^4T_2(F)$
		15,625	0.90		$\rightarrow {}^4A_2(F)$
		18,975	27.81	3600	$\rightarrow {}^4T_1(P)$

[a] ϵ is given in l. mole^{-1} cm.$^{-1}$ from the equation $\log I/I_0 = \epsilon cl$. [b] $\Delta\nu$ is the band half-width at one-half the maximum absorbance. [c] The spectra of Ni(II), Co(II), and Cr(III) complexes of these ligands are very similar to the spectra of the corresponding hexaaquo complexes except for the wave length of λ_{max}. [d] The parentheses designate a shoulder on a main peak of the spectrum.

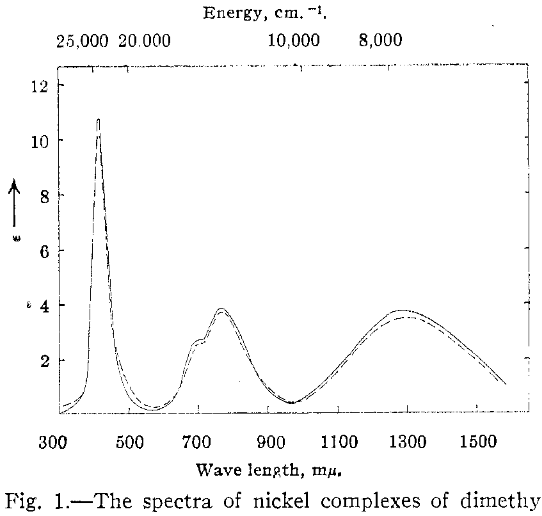

Fig. 1.—The spectra of nickel complexes of dimethylsulfoxide and tetramethylene sulfoxide. The solid line is for $[Ni(TMSO)_6](ClO_4)_2$ in TMSO solvent and the dashed line is for $[Ni(DMSO)_6](ClO_4)_2$ in DMSO solvent.

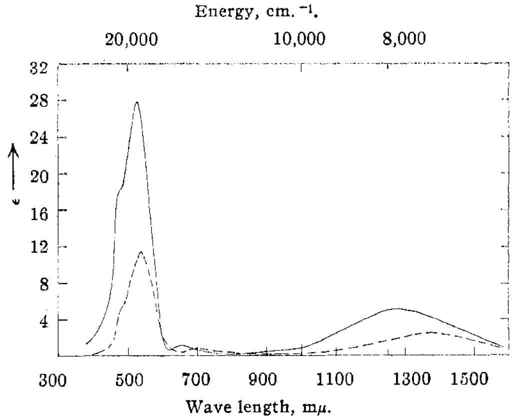

Fig. 2.—The spectra of cobalt complexes of pyridine N-oxide and DMSO. The solid line is for $[Co(C_5H_5NO)_6](ClO_4)_2$ in DMF and the dashed line is for $[Co(DMSO)_6](ClO_4)_2$ in DMSO.

The Dq values for Ni(II) and Co(II) produce the spectrochemical series

$$H_2O > C_5H_5NO > DMSO \sim TMSO$$

The reduction of the F–P term splittings in the Co(II) sulfoxide complexes by 15% is in good

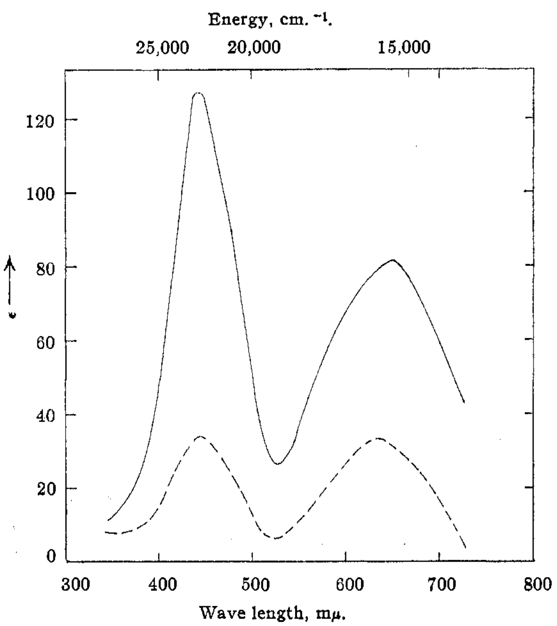

Fig. 3.—The spectra of chromium complexes of pyridine N-oxide and DMSO. The solid line is $[Cr(C_5H_5NO)_6](ClO_4)_3$ in the solvent acetonitrile and the dashed line is for $[Cr(DMSO)_6](ClO_4)_3$ in DMSO solvent.

TABLE II

CALCULATED AND EXPERIMENTAL FREQUENCIES OF THE SECOND BAND OF Ni(II) COMPLEXES

Compound	Solvent	Position of ν_2 ($^3T_1(F)$), cm.$^{-1}$ Predicted	Observed
$[Ni(DMSO)_6](ClO_4)_2$	DMSO	12,970	12,970
$[Ni(TMSO)_6](ClO_4)_2$	TMSO	12,995	12,987
$[Ni(C_5H_5NO)_6](ClO_4)_2$	DMF	14,066	14,124

TABLE III

SUMMARY OF THE CALCULATED CRYSTAL FIELD PARAMETERS

Compound	Solvent	E(P) − E(F), cm.$^{-1}$	Dq, cm.$^{-1}$	β, %
$[Ni(DMSO)_6](ClO_4)_2$	DMSO	13,820	773	12.7
$[Ni(TMSO)_6](ClO_4)_2$	TMSO	13,760	775	12.7
$[Ni(C_5H_5NO)_6](ClO_4)_2$	DMF	14,710	840	7.15
$[Cr(DMSO)_6](ClO_4)_3$	DMSO	10,390	1577	24.58
$[Cr(TMSO)_6](ClO_4)_3$	TMSO	10,390	1575	24.58
$[Cr(C_5H_5NO)_6](ClO_4)_3$	CH_3CN	11,433	1539	16.90
	Acetone	11,433	1539	16.90
$[Co(DMSO)_6](ClO_4)_2$	DMSO	12,400	830	14.9
$[Co(TMSO)_6](ClO_4)_2$	TMSO	12,400	830	14.9
$[Co(C_5H_5NO)_6](ClO_4)_2$	DMF	12,400	900	14.9

NOTE ADDED IN PROOF: Subsequent to our study, spectrochemical data on the dimethyl sulfoxide complexes were reported: H. L. Schläfer and H. P. Opitz, *Z. Elektrochem.*, **65**, 372 (1961). Both studies are in excellent agreement.

agreement with the 12.7% lowering observed in the case of nickel. However, the best fit for the three bands of the Co(II) pyridine N-oxide complex also requires $E(^4P)$ to be reduced by 15%. This is to be contrasted to the analogous complexes of Cr(III) and Ni(II), where the value of β is much less for pyridine N-oxide than for the sulfoxide complexes.

In all three Co(II) complexes the second band is predicted to be 800–1200 cm.$^{-1}$ higher than is observed. The assignment of Dq and $E(^4P)$ values is based on the assumption that the most intense band is due to the transition $^4T_1(F) \rightarrow {}^4T_1(P)$. This band has a shoulder on the high energy side which can be resolved into a Gaussian curve. This absorption may result from spin-orbit splitting or from a transition to a doublet level, *e.g.*, $^2A_1(G)$. The transition $^4T_1(F) \rightarrow {}^4A_2$ is assigned to the weak band which appears on the low energy side of the strongest band. If one assigns the most intense band or its shoulder to the transition $^4T_1 \rightarrow {}^4A_2$, the Dq values are unreasonably high, and as a consequence the first observed transition does not fit the predicted position.

Since the position of $^4A_2$ is not well fitted, the parameters for Co(II) are not as reliable as for Ni(II). Nevertheless, they are reasonable in comparison to those obtained for Ni(II) and also in comparison to experience with other Co(II) spectra which indicate that Dq of Co(II) is always a bit larger than that of Ni(II) for the same ligand. Part of the difficulty in fitting the spectra may be due to spin-orbit splitting of the ground state, as well as a possible Jahn–Teller distortion from octahedral symmetry.

In the case of Ni(II), it has been demonstrated that the individual positions of the two $^3T_1$ levels for d^8 are in excellent agreement with the predicted positions; thus, the deviations from cubic symmetry in solution must not be large.

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