

CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY,
TULANE UNIVERSITY, NEW ORLEANS, LOUISIANA**2,6-Dimethylpyridine N-Oxide and 2,4,6-Trimethylpyridine N-Oxide Complexes of Divalent Cobalt**

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Cobalt(II) complexes of the type CoL_2X_2 where L = substituted pyridine N-oxides, X = Cl, Br, SCN, NO_3 , have been prepared and characterized. Infrared and visible spectra have been obtained. From the visible reflectance and absorbance spectra conclusions about the structural entities are drawn. Evidence for the bidentate nitrate ligand bonded to the metal ion is indicated. The effect of polar solvents on the solid halide complexes is discussed.

Many complexes containing ligands such as phosphine oxides, arsine oxides, dimethyl sulfoxide, and tetramethylene sulfoxide, in which bonding occurs through oxygen atoms, have recently been investigated.¹

As a logical extension of the study of copper(II) complexes of substituted pyridine N-oxides having subnormal magnetic moments,² this paper describes the investigations of several cobalt(II) complexes of substituted pyridine N-oxides. Quagliano³ and co-workers studied several cobalt(II) pyridine N-oxide complexes, but were reluctant to assign any structural entity based on color, magnetic properties, and spectral data.

Cobalt(II) complexes with aromatic as well as aliphatic N-oxides as ligands have also been reported.^{4,5}

ligand and the structural features of these cobalt(II) complexes.

Experimental

All the chemicals used were obtained commercially. Saturated absolute methanol solutions of cobalt(II) salts were added to absolute methanol solutions of the substituted pyridine N-oxides in 1:2 molar ratio. After adding acetone or ether, the solutions were kept in a refrigerator for a few hours and filtered. All the complexes were recrystallized from absolute methanol and dried in a desiccator over anhydrous calcium chloride.

Chemical analysis data, color, and melting points are shown in Table I.

Magnetic Susceptibility Determinations.—These determinations were made by the Gouy method using a semimicro analytical balance and an electromagnet at various temperatures, at a field strength of 6000 gauss. The effective magnetic moment was

TABLE I

Complex	Color	M.p., ^a °C.	% C		% H		% N	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
$\text{Co}(2,6\text{-DPNO})_2\text{Cl}_2$	Blue	265	45.14	44.70	4.82	4.82	7.46	7.54
$\text{Co}(2,4,6\text{-TPNO})_2\text{Cl}_2$	Blue	265	48.24	47.51	5.52	5.44	7.37	6.93
$\text{Co}(2,6\text{-DPNO})_2\text{Br}_2$	Blue	285	35.81	36.10	4.08	3.84	6.39	6.02
$\text{Co}(2,4,6\text{-TPNO})_2\text{Br}_2$	(greenish) Blue	dec. 285	40.03	39.02	4.57	4.46	5.87	5.61
$\text{Co}(2,6\text{-DPNO})_2(\text{SCN})_2$	Pink	178	45.58	45.62	4.28	4.27	13.74	13.29
$\text{Co}(2,4,6\text{-TPNO})_2(\text{SCN})_2$	Violet	194	48.33	48.12	5.27	4.89	12.71	12.46
$\text{Co}(2,6\text{-DPNO})_2(\text{NO}_3)_2$	Pink	205	39.78	39.10	4.40	4.19	13.16	13.05
$\text{Co}(2,4,6\text{-TPNO})_2(\text{NO}_3)_2$	Greenish yellow	245	42.16	42.06	5.17	4.82	12.22	12.28

^a Melting points were measured using a Thomas-Hoover capillary melting point apparatus.

However, cobalt(II) complexes of the type CoL_2X_2 (L = substituted pyridine N-oxides, X = Cl, Br, SCN, NO_3) seem not to have been investigated. The substituent group on the pyridine ring could produce some differences in the coordinating ability and properties of the complexes. We selected 2,6-dimethylpyridine N-oxide and 2,4,6-trimethylpyridine N-oxide (abbreviated as 2,6-DPNO and 2,4,6-TPNO, respectively) for this study in order to compare the donor properties of the

calculated by the formula $\mu_{\text{eff}} = 2.84\sqrt{\chi_{\text{M}}^{\text{cor}}T}$, where $\chi_{\text{M}}^{\text{cor}}$ is the corrected magnetic susceptibility per cobalt(II) ion. The diamagnetic corrections were estimated from Pascal's constants.^{6a}

Bulk susceptibilities were determined at the temperatures 297, 313, 354, and 403°K. These values were corrected for the diamagnetism of the ligands. The reciprocal values of $\chi_{\text{M}}^{\text{cor}}$ were plotted against absolute temperature and a straight line was obtained.

Spectrophotometric Measurements.—The infrared absorption spectra were obtained on a Beckman Model IR-8 recording spectrophotometer, using both Nujol and KBr disks (Tables III and IV).

The near-infrared and visible spectra were taken on a Cary Model 14 recording spectrophotometer. The absorption fre-

(1) (a) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960); *J. Phys. Chem.*, **65**, 1446 (1961); (b) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2275 (1960); *Inorg. Chem.*, **2**, 1162, (1963).

(2) M. Kato, H. B. Jonassen, and J. Fanning, *Chem. Rev.*, **64**, 103 (1964).

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TABLE II
 MAGNETIC SUSCEPTIBILITY DATA

Complex	$T, ^\circ\text{K.}$	$\chi_M \times 10^6$	Diam. cor.	χ_M^{cor}	μ_{eff}
L = 2,6-Dimethylpyridine N-oxide					
CoL_2Cl_2	301	22.10	182	8694	4.59
CoL_2Br_2	301	18.30	202	8712	4.61
$\text{CoL}_2(\text{SCN})_2$	301	22.41	204	9216	4.75
$\text{CoL}_2(\text{NO}_3)_2$	295	18.63	180	8130	4.41
L = 2,4,6-Trimethylpyridine N-oxide					
CoL_2Cl_2	301	21.28	204	8816	4.64
CoL_2Br_2	301	17.73	224	8994	4.68
$\text{CoL}_2(\text{SCN})_2$	301	21.66	226	9326	4.74
$\text{CoL}_2(\text{NO}_3)_2$	301	17.34	202	8028	4.40

TABLE III

ENERGIES OF THE CHARACTERISTIC INFRARED STRETCHING FREQUENCIES (cm.^{-1})

Complex	ν_1^a	ν_2^b	ν_3^c	ν_4^d
2,6-Dimethylpyridine N-oxide				
	1255 s	770		
CoL_2Cl_2	1200 s	780		
CoL_2Br_2	1200 s	792		
$\text{CoL}_2(\text{SCN})_2$	1195 s	825	2145 vs	782
$\text{CoL}_2(\text{NO}_3)_2$	1200 s	830		
2,4,6-Trimethylpyridine N-oxide				
	1247	839		
CoL_2Cl_2	1200 s	920		
CoL_2Br_2	1200 s	955 s		
$\text{CoL}_2(\text{SCN})_2$	1195 s	823	2145 vs	782
$\text{CoL}_2(\text{NO}_3)_2$	1200 s	878		

^a N-O stretching frequency. ^b C-H out-of-plane frequency. ^c SCN bridging. ^d C-S stretching.

TABLE IV

INFRARED BANDS OF NITRATE^a IONS IN THE COMPLEXES (cm.^{-1})

	ν_1^b	ν_2^c	ν_3^d	ν_4^e
$\text{Co}(2,6\text{-DPNO})_2(\text{NO}_3)_2$	1270	800	728	1020
$\text{Co}(2,4,6\text{-TPNO})_2(\text{NO}_3)_2$	1280	802	718	1020

^a B. O. Field and C. J. Hardy, *Quart. Rev.* (London), **18**, 361 (1964). ^b NO_2 sym. stretching. ^c Nonplane def. ^d NO_2 bending. ^e NO stretching.

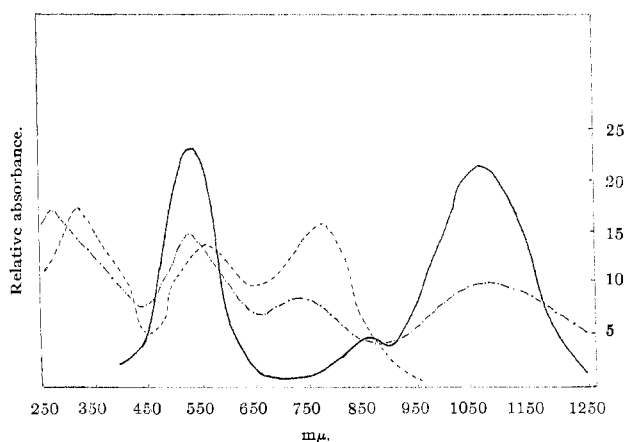


Figure 1.—Reflectance and absorption spectra: ———, $\text{Co}(2,4,6\text{-TPNO})_2(\text{NO}_3)_2$ in nitromethane (ϵ is shown on the right side); - - - - -, reflectance spectra in LiF; - - - - -, reflectance spectra of $\text{Co}(2,4,6\text{-TPNO})_2(\text{SCN})_2$ in LiF.

quencies and the extinction coefficients at the maxima are shown in Table IV and Figure 1.

The diffuse reflectance spectra of the complexes were measured using a Beckman DK reflectance spectrophotometer. Dry lithium

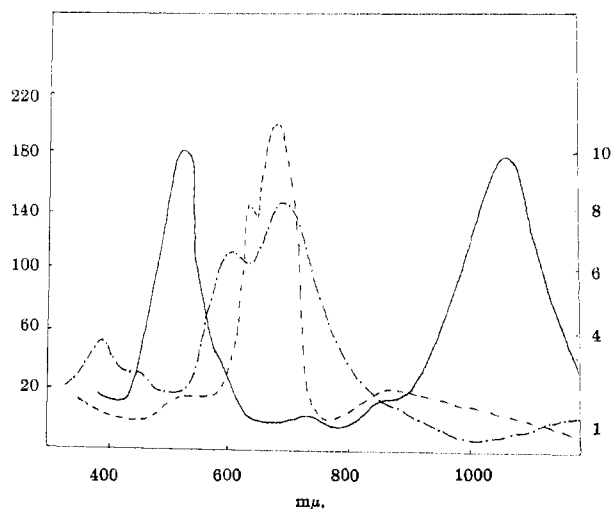


Figure 2.—Reflectance and absorption spectra of $\text{Co}(2,4,6\text{-TPNO})_2\text{Br}_2$: ———, in methanol; - - - - -, in DMF; - - - - -, in LiF. The molar absorptance at the left applies to the complex in DMF and the one at the right applies to the complex in methanol.

fluoride was used as a standard. The absorption frequencies are indicated in Table V and Figures 1 and 2.

Discussion

Magnetic Susceptibility Data.—The high magnetic moments of these cobalt(II) complexes (4.4–4.75 in this work) have been attributed to the incomplete quenching of the orbital contribution to the magnetic moment^{6b} or to mixing by means of spin-orbit coupling with the first and even the second excited states,⁷ since the energy difference involved is only around 3000 cm.^{-1} .

A determination of their magnetic moments at different temperatures from 280°K. to their melting points (approximately) discloses a Curie-Weiss temperature dependence, which rules out the possibility of co-existence of doublet and quartet states in these complexes.

Infrared Spectra.—As previously observed for pyridine N-oxide complexes⁸ these substituted pyridine N-oxide complexes, compared to the uncomplexed ligand, exhibit a lower N-O and a higher C-H (887 cm.^{-1}) frequency. These trends are consistent with coordination of the ligand to the metal ion which lowers the electron density of the ring⁹ and lowers the NO bond order.

Absorption Spectra.—A slight shift in the absorption frequency from the 2,6-DPNO to the 2,4,6-TPNO complexes is due to the difference in the number of the substituent groups on the ring.

The difference in the position of the absorption bands of the solid and the solution spectra of the complexes indicates a structural transformation of the complexes in solutions of polar organic solvents. The spectra of these complexes in polar solvents are the same in intensity and position as those reported.¹⁰

(7) S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(8) J. V. Quagliano, Y. Kakiuti, and S. Kida, *Spectrochim. Acta*, **19**, 208 (1963).

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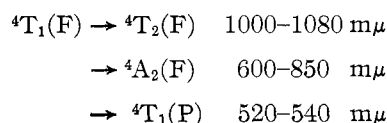
(10) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 288 (1962).

TABLE V
 ELECTRONIC ABSORPTION SPECTRA OF COBALT(II) COMPLEXES^a

Complex	Medium	$\lambda_1, m\mu$	$\lambda_2, m\mu$	$\lambda_3, m\mu$
Co(2,6-DPNO) ₂ Br ₂	Solid in LiF	...	375	650
			450 sh	
	Methanol	530 (16) 600 sh	620 (3)	1080 (12)
Co(2,4,6-TPNO) ₂ Br ₂	Solid in LiF	...	360	610
			410 sh	
	Methanol	520 (10)	820 (2) 710 sh	1060 (10)
Co(2,6-DPNO) ₂ (SCN) ₂	Solid in LiF	320 s 375 sh	560	775
			490 sh	
	Methanol	520 (22)	775 (3) 575 sh	1030 (23)
Co(2,4,6-TPNO) ₂ (SCN) ₂	Solid in LiF	325 s	510 sh 465 sh	610
			610 sh	
	Methanol	520 s (23)	825 (3) 610 sh	1020 (23) 975 sh
Co(2,6-DPNO) ₂ (NO ₃) ₂	Solid in LiF	525 s	710 b	1100
			825 (2)	1025 b (9)
	Methanol	500 (8) 455 sh		
Co(2,4,6-TPNO) ₂ (NO ₃) ₂	Solid in LiF	520 s	710	1100 b
			850 (4)	1075 (11)
	Nitromethane	535 (12)		

^a b, broad; s, sharp; sh, shoulder; the figures in parentheses indicate the molar extinction coefficients (ϵ) at band maxima. ϵ is given in l. mole⁻¹ cm.⁻¹ from the equation $\log I/I_0 = \epsilon cl$.

In line with the previous assignments, the following transitions can then be assigned for the solution spectra.



It can also be assumed that the distortion from true octahedral symmetry decreases as we go from dichloromethane to nitromethane to methanol.

Thiocyanate Complexes.—Chatt and co-workers¹¹ have shown that the CN stretching frequency is found at higher wave numbers for a bridging SCN group. The bis(*p*-toluidine)cobalt(II) thiocyanate complex in the solid state has a magnetic moment of 4.93 B.M., too high for a monomeric tetrahedral structure. Cotton and Holm¹² assigned a polymeric octahedral structure to this complex based on the color and ligand field spectra.

A pink color, indicative of the octahedral structure, is also observed for the 2,6-DPNO and 2,4,6-TPNO cobalt thiocyanate complexes. A weak band in the reflectance spectra at about 470 m μ characteristic of octahedral cobalt(II) complexes is also observed. Infrared spectra indicate a sharp band at 2145 cm.⁻¹, which is believed to be diagnostic of a bridging SCN group.¹¹

Three d-d transition bands predicted for the octahedral cobalt(II) complexes are also observed in the reflectance spectra of the solid complexes. Spectral data and color seem to indicate that these thiocyanate complexes have a dimeric or polymeric distorted octahedral structure. Similar thiocyanate bridging cobalt(II) complexes have been reported.¹³

(11) J. Chatt, L. A. Duncanson, F. A. Hart, and P. G. Owston, *Nature*, **181**, 43 (1958).

(12) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2984 (1960).

(13) M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografiya*, **A4**, 239 (1959).

An additional band around 310 m μ is not a d-d transition band but is due to the SCN group.¹⁴ A slight shift in absorption position of the solution seems to be due to the variation in the crystal field environment.

Halide Complexes.—The halide complexes of the type (CoX₄)²⁻¹⁵ appear to be very sensitive to solvent environment, even to chloroform. This has been ascribed to be due to solvolysis rather than mere distortion. The halide complexes of 2,4-DPNO and 2,4,6-TPNO exhibit a similar tendency to change their coordination number from four to six. This is reflected by marked changes in their reflectance and absorption spectra (Figure 2). The transition from tetrahedral to octahedral structure is demonstrated by the solution spectra, which are similar to those of regular octahedral species. In solution two molecules of the polar organic solvent coordinate to attain a coordination number of six for the complexes.

A multicomponent band around 650 m μ in the visible region for the solids and magnetic moments running between 4.3 and 4.7 B.M., however, indicate a tetrahedral structure in the solid state. The literature contains a disagreement as to the proper assignment of the spectra of the tetrahedral cobalt(II) complexes. Ballhausen and Jørgensen¹⁶ proposed three bands at 15,000 cm.⁻¹ (ν_3), 6300 cm.⁻¹ (ν_2), and ν_1 , in the infrared region at 3500 cm.⁻¹. This band has been observed at 3000–35,000 cm.⁻¹ as a broad band with Cs₃CoCl₅ crystals.¹⁷ Brubaker and Johnson¹⁸ have questioned the validity of the assignment of Jørgensen¹⁶ and Orgel.¹⁹ They feel

(14) L. I. Katzin, *J. Chem. Phys.*, **20**, 1165 (1952).

(15) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

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(17) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 791 (1958).

(18) C. H. Brubaker, Jr., and C. E. Johnson, *J. Am. Chem. Soc.*, **80**, 5037 (1958).

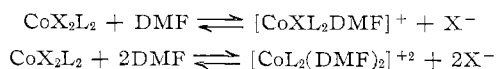
(19) L. E. Orgel, *J. Chem. Phys.*, **23**, 1006 (1955).

that the strong band in the visible region in $(\text{CoX}_4)^{-2}$ in the tetrahedral complexes may not be due to crystal field effects at all.

No attempt is therefore made to assign the spectral bands of the tetrahedral cobalt(II) complexes which seem to occur in chloride and bromide complexes only.

Two other possible structures are an oxygen or a chloride bridged structure similar to those found in copper(II) pyridine N-oxide complexes² and in $\text{Co}(\text{py})_2\text{Cl}_2$ (violet),²⁰ respectively. The infrared and magnetic susceptibility data, however, seem not to support these two types of bonding.⁴ Quite unexpectedly the halide complexes seem to maintain a tetrahedral structure in N,N-dimethylformamide²¹ (Figure 2).

This may be due to a mechanism similar to that observed by Buffagni and Dunn²² for CoCl_2 in dimethylformamide. It seems reasonable that a similar displacement occurs with the CoX_2L_2 complexes ($\text{X} = \text{Cl}, \text{Br}$).



This does not occur in methanol, since its coordina-

(20) J. N. Gill, R. S. Nyholm, G. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

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(22) S. Buffagni and T. M. Dunn, *J. Chem. Soc.*, 5105 (1961).

tion tendency is smaller than that of dimethylformamide.

Nitrate Complexes.—The single-crystal X-ray analysis²³ of $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ has established that the cobalt(II) ion is surrounded by an irregular arrangement of six oxygen atoms, with each nitrate ion acting as a bidentate ligand.

The spectra of the 2,6-DPNO and 2,4,6-TPNO cobalt(II) nitrate complexes are similar to the spectra of $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$. The absorption bands observed for these two nitrate complexes at 565 and 320 $m\mu$ were also observed for the above complex. The solids obey the Curie-Weiss law as shown by the determination of magnetic susceptibility at different temperatures, and the effective magnetic moments fall in the same range as those of the triphenylphosphine oxide complexes.^{1b} The spectra of the solid in lithium fluoride and in solution in nitromethane are superimposable except for the intensity, indicating that the complex does not change in the solvent (Figure 1). This seems to indicate that the 2,6-DPNO and 2,4,6-TPNO complexes also have distorted octahedral structures.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Coordination Compounds of Nickel(II) Salts with Substituted Pyridines. Complexes of 2-, 3-, and 4-Methylpyridine

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Complexes of 2-, 3-, and 4-methylpyridine (2-pic, 3-pic, and 4-pic) with a number of Ni(II) salts (chloride, bromide, iodide, nitrate, perchlorate, and tetrafluoroborate) were prepared and investigated. Three series of complexes were obtained, $\text{Ni}(\text{pic})\text{X}_2$ (pic = 2-pic, 3-pic; $\text{X} = \text{Cl}, \text{Br}$); $\text{Ni}(\text{pic})_2\text{X}_2$ (pic = 2-pic, 3-pic, 4-pic; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$); $\text{Ni}(\text{pic})_4\text{X}_2$ (pic = 3-pic, 4-pic; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4, \text{BF}_4$). The complex $\text{Ni}(\text{3-pic})_4\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) was obtained in two isomeric forms, identified as $[\text{Ni}(\text{3-pic})_4\text{X}_2]$ and $[\text{Ni}(\text{3-pic})_4]\text{X}_2$, respectively. The complexes of 4-aminopyridine, $\text{Ni}(\text{4-NH}_2\text{py})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4$), were also prepared and investigated. The stoichiometry and stereochemistry of the complexes were correlated with the properties of the anion and ligand, in particular with the basicity and steric requirements of the latter.

Introduction

This investigation is part of a study on the coordination compounds of substituted pyridines with Ni(II) salts, to establish a correlation between the stoichiometry and stereochemistry of Ni(II) complexes and the properties of the ligands and anions. Some previous results of this study have been published.¹⁻³ The

present paper describes the preparation and properties of the complexes of isomeric methylpyridines (picolines, abbreviated as 2-pic, 3-pic, and 4-pic) with a number of Ni(II) salts. The analogous complexes of 4-aminopyridine are also reported, as they are helpful in establishing a correlation between the stereochemistry of the NiL_4X_2 complexes and the basicity of the ligand L.

Experimental

Starting Materials.—The picolines (Brothers Chemical Co.) were dried over potassium hydroxide for 3 days, distilled under

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