

## Spin-Free and Spin-Paired Transition Metal Perchlorate Complexes of 2,6-Lutidine N-Oxide

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Cationic transition metal complexes of 2,6-lutidine N-oxide (2,6-LNO) were synthesized and studied. For the monomeric tetra-coordinated cations of the type  $[M(2,6-LNO)_4]^{2+}$  ( $M=Fe, Co, Ni, Cu, Zn$ ), stabilization of an essentially planar configuration is interpreted in terms of a combination of steric and electronic effects. The  $MO_4$  grouping in the high-spin  $Cu^{II}$  and the low-spin  $Ni^{II}$  complex is assigned a  $D_{4h}$  symmetry. Evidence is presented in favor of a monomeric structure, with essentially planar  $MO_4$  groupings for the high-spin  $Co^{II}$  and the partially spin-paired  $Fe^{II}$  complex. Coordination of one monodentate  $OCIO_3$  group in  $[Mn(2,6-LNO)_4(OCIO_3)]^+$  is attributed to the anticipated instability of a planar configuration for the  $Mn^{II}$  ion.  $Cr^{III}$  forms a hexacoordinated cationic complex. Finally, the formation of tetra-coordinated  $Ni^{II}$  complexes with pyridine N-oxide and its monosubstituted derivatives is favored in triethyl orthoformate solution.

### Introduction

Numerous studies concerning the metal complexes of aromatic amine oxides have appeared in recent years.<sup>1,2</sup> The usual coordination number observed in 3d metal perchlorate complexes of pyridine N-oxides and quinoline N-oxides is six.<sup>3-6</sup> However,  $Cu(ClO_4)_2$  generally forms tetra-coordinated cationic complexes with pyridine N-oxides and only in the case of the unsubstituted pyridine N-oxide has a hexacoordinated  $Cu^{II}$  complex been prepared.<sup>4,7</sup>

Coordination numbers lower than six have been observed in  $[Co(2-PicNO)_5](ClO_4)_2$ ,<sup>8</sup>  $[Ni(2-PicNO)_4](ClO_4)_2$ ,<sup>9</sup> (2-PicNO = 2-picoline N-oxide),  $[M(EPNO)_5](ClO_4)_2$ <sup>10</sup> ( $M=Mn, Co, Ni, Zn$ ; EPNO = 4-ethoxy-pyri-

dine N-oxide) and  $[M(2,6-LNO)_4](ClO_4)_2^{11}$  ( $M=VO, Ni$ ; 2,6-LNO = 2,6-lutidine N-oxide(2,6-dimethylpyridine N-oxide)).  $[Ni(2-PicNO)_4](ClO_4)_2$  has been assigned a polynuclear oxygen-bridged structure on the basis of its electronic spectrum, which is indicative of an octahedral environment for  $Ni^{II}$ .<sup>9</sup> A similar structure should be assigned to the light green  $[Ni(2,6-LNO)_4](ClO_4)_2$ , reported by Schmauss and Specker,<sup>11</sup> which exhibits an electronic spectrum typical of hexacoordinated  $Ni^{II}$  compounds and a magnetic moment of 2.83BM.

Our preliminary studies on the interaction of 2,6-LNO with transition metal perchlorates in the presence of the dehydrating agent triethyl orthoformate, revealed that, under these conditions, complexes of a different type than those reported by Schmauss and Specker<sup>11</sup> are obtained. In fact, complexes of the formulae  $Cr(2,6-LNO)_6(ClO_4)_3$  and  $M(2,6-LNO)_4(ClO_4)_2$  ( $M$  = divalent 3d metal ion) were precipitated during our studies. In addition, the  $Ni^{II}$  complex is violet in color and diamagnetic and that of  $Fe^{II}$  exhibits a half-quenched spin (3.88BM). These properties are suggestive of a square planar configuration for the  $MO_4$  groupings. Since no square planar complexes of monodentate oxo-ligands (amine oxides, sulfoxides etc.) with 3d metal ions other than  $Cu^{II}$  have been reported, we were prompted to undertake characterization studies on these new compounds. The present paper deals with the syntheses and study of cationic 2,6-LNO complexes.

### Experimental Section

**Chemicals:** « Baker grade » 2,6-LNO and the purest commercially available metal perchlorates, triethyl orthoformate and solvents were utilized.

**Synthesis:** The hydrated metal perchlorate is mixed with a ten-fold excess of triethyl orthoformate, a dehydrating agent, and the minimum amount of acetone required for complete dissolution of the salt is added. The solution is stirred at 40° for 15 min. and an excess of ligand (molar ratio of ligand to salt >6:1) is subsequently added. In all cases studied, *i.e.*  $Cr^{III}$ ,  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ , and  $Zn^{II}$ , a copious precipitate is immediately formed. The complexes are filtered, washed with ether or triethyl orthoformate (in the case of  $Fe^{II}$ ) and dried over phosphorus pen-

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toxide in an evacuated desiccator. All syntheses were repeated several times with excellent reproducibility.  $\text{Cr}(\text{ClO}_4)_3$  forms a 1:6 complex and the divalent metal perchlorates 1:4 complexes. All the new complexes are stable in the atmosphere. The  $\text{Fe}^{\text{II}}$  complex starts decomposing at  $128^\circ$ , and the decomposition product melts at  $139.5\text{--}141^\circ$ . The  $\text{Zn}^{\text{II}}$  compound melts at  $154\text{--}156^\circ$  and decomposes at  $175^\circ$ . The other complexes decompose upon melting. Analyses of the compounds were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Analytical data and properties of the complexes are given in Table I.

**Magnetic Measurements:** Magnetic susceptibilities were measured at room temperature ( $297^\circ\text{K}$ ) by the Faraday method. Mercuric tetrathiocyanatocobaltate (II) was used as the magnetic susceptibility standard. Pascal's constants were utilized for diamagnetic corrections.<sup>12</sup> Magnetic moments were calculated by use of the equation  $\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}}}$ . T and are shown in Table IV.

**Conductance Measurements:** The conductivities of  $10^{-3} M$  nitromethane solutions of the complexes were measured at  $25^\circ$  by using a Wayne Kerr Universal bridge and a cell calibrated with aqueous 0.01N potas-

**Table I.** Properties and Analytical Data of 2,6-Lutidine N-oxide Metal Complexes

Complex	Color	M.p. and de-comp. temp $^\circ\text{C}$	Analytical Data							
			C%		H%		N%		Metal%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[\text{Cr}(2,6\text{-LNO})_6](\text{ClO}_4)_3$	Light green	167-169, m, dec.	46.31	45.60	5.00	5.40	7.72	7.12	4.77	4.59
$[\text{Mn}(2,6\text{-LNO})_4(\text{OClO}_3)](\text{ClO}_4)$	Very pale yellow	200-202, m, dec.	45.06	44.59	4.86	4.94	7.51	7.17	7.36	7.32
$[\text{Fe}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	Buff	128 dec., 139.5-141 m	45.00	44.75	4.86	5.22	7.50	7.17	7.47	6.88
$[\text{Co}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	Dark red	186-187.5, m, dec.	44.82	44.51	4.84	5.09	7.47	7.50	7.85	7.43
$[\text{Ni}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	Violet	206-207.5, m, dec.	44.83	44.31	4.84	5.11	7.47	7.22	7.83	7.96
$[\text{Cu}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	Greenish blue	223-224, m, dec.	44.54	44.20	4.81	4.91	7.42	7.32	8.42	8.27
$[\text{Zn}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	White	154-156 m, 175 dec.	44.43	43.84	4.79	4.82	7.40	7.22	8.64	8.36

m: melts; dec: decomposes.

**Table II.** Infrared Data of 2,6-Lutidine N-Oxide-Metal Perchlorate Complexes:  $\nu_{\text{NO}}$ ,  $\Delta\nu_{\text{NO}}$  and Perchlorate Bands in the  $1300\text{--}900 \text{ cm}^{-1}$  Region

Compound	$\nu_{\text{NO}}, \text{cm}^{-1}$	$\Delta\nu_{\text{NO}}, \text{cm}^{-1}$ <sup>b</sup>	$\nu_3$ of $\text{Td ClO}_4^-$ , $\text{cm}^{-1}$	$\nu_4, \nu_1$ and $\nu_2$ of $\text{C}_{3v}$ Perchlorate, $\text{cm}^{-1}$
2,6-LNO <sup>a</sup>				
as liquid film or in Nujol	1245 s			
in $\text{CS}_2$ solution	1255 s			
$[\text{Cr}(2,6\text{-LNO})_6](\text{ClO}_4)_3$	1188 s, b	-57	1076 vs, b	
$[\text{Mn}(2,6\text{-LNO})_4(\text{OClO}_3)](\text{ClO}_4)$	1203 s	-42	1076 vs, b	1133 s, 1024 s, 920 m
$[\text{Fe}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	1197 s	-48	1069 vs, b	
$[\text{Co}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	1212 sh, 1190 s	-44 (av)	1064 vs, b	
$[\text{Ni}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	1216 sh, 1191 s	-41.5 (av)	1070 vs, b	
$[\text{Cu}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	1215 sh, 1195 s	-40 (av)	1074 vs, b	
$[\text{Zn}(2,6\text{-LNO})_4](\text{ClO}_4)_2$	1190 s	-55	1060 vs, b	

vs: very strong; s: strong; m: medium; b: broad; sh: shoulder. <sup>a</sup> The spectrum of the free ligand in the  $4000\text{--}750 \text{ cm}^{-1}$  region is in good agreement with that reported by H. Shindo *Chem. Pharm. Bull.* (Tokyo) 4, 460 (1956). <sup>b</sup> The  $\nu_{\text{NO}}$  shifts reported are based on the NO stretch of the free ligand as liquid film or in a mixture with Nujol.

**Infrared Spectra:** IR spectra ( $4000\text{--}750 \text{ cm}^{-1}$ ) of the free ligand (liquid film, mixture with Nujol, and  $\text{CS}_2$  solution) and its metal complexes (Nujol mulls) were obtained between IRTRAN 2 (zinc sulfide) windows on a Perkin-Elmer 621 spectrophotometer. Calibration of the spectra was effected by means of known frequency absorptions of polystyrene. Table II gives the  $\nu_{\text{NO}}$  and the characteristic perchlorate bands of these compounds. The spectra of the complexes are characterized by the absence of water bands.

**Electronic Spectra:** Nujol mull<sup>3</sup> and solution spectra of the new complexes were obtained with a Cary Model 14 spectrophotometer and are given in Table III.

sium chloride. The results, shown in Table IV, indicate that the  $\text{Cr}^{\text{III}}$  complex is a uni-trivalent electrolyte and those of the divalent metal ions are uni-bivalent electrolytes in nitromethane solution.<sup>13</sup>

## Discussion

**IR Data.** In general, the IR spectra of the complexes show similar characteristics to those of the complexes of pyridine N-oxide.<sup>14</sup> Thus, in comparison to

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**Table III.** Electronic Spectra of 2,6-Lutidine N-Oxide Metal Complexes <sup>a</sup>

Complex	Medium	$\nu_{\max}$ , $\text{cm}^{-1}(\epsilon_{\max})$
[Cr(2,6-LNO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	Nujol mull	16,860, 25,320 sh, > 28,000
	1.3 × 10 <sup>-3</sup> M in CH <sub>3</sub> NO <sub>2</sub>	12,740 sh, 16,860 (58.6), 24,450 sh
[Mn(2,6-LNO) <sub>4</sub> (OCIO <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Nujol mull	25,000, > 28,000
	1.4 × 10 <sup>-3</sup> M in CH <sub>3</sub> NO <sub>2</sub>	13,620 sh, 17,640 sh, > 27,000 (> 650)
[Fe(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Nujol mull	10,400 sh, 27,700
	10 <sup>-3</sup> M in CH <sub>3</sub> NO <sub>2</sub>	10,400 (4.3), > 27,000 (> 2,600)
[Co(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Nujol mull	7200 sh, 8470, 13,020 sh, 19,420 sh, 27,930
	10 <sup>-2</sup> M in CH <sub>3</sub> NO <sub>2</sub>	8470 (20), 12,140 (16.3), 13,020 sh, 18,080 (115.7)
	10 <sup>-2</sup> M in acetone	10,020 sh, 11,900 (11.2), 17,540 (50.8), 18,350 sh
	10 <sup>-2</sup> M in 0.6 M solution of 2,6-LNO in CH <sub>3</sub> NO <sub>2</sub>	10,470 sh, 12,080 (17.8), 17,830 (164), 18,940 sh
[Ni(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Nujol mull	14,250 sh, 18,150 b, 28,170
	9 × 10 <sup>-3</sup> M in CH <sub>3</sub> NO <sub>2</sub>	9060 (5.9), 12,790 sh, 14,970 (10.0)
	9 × 10 <sup>-3</sup> M in 0.6 M solution of 2,6-LNO in CH <sub>3</sub> NO <sub>2</sub>	8730 (5.8), 12,740 (12.3), 13,510 (12.3)
[Cu(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Nujol mull	15,530, 25,510 sh, > 28,000
	1.8 × 10 <sup>-3</sup> M in CH <sub>3</sub> NO <sub>2</sub>	15,150 (113.0)

sh: shoulder, b: broad; <sup>a</sup>The spectra of the complexes are generally characterized by an intense charge-transfer band in the UV, which trails into the visible (*cf.* ref. 7).

**Table IV.** Magnetic Moments at 297°K and Molar Conductivities of 10<sup>-3</sup> M Nitromethane Solutions at 25°C of 2,6-Lutidine N-Oxide-Metal Perchlorate Complexes

Complex	$\chi_M^{\text{corr}} \times 10^6$	$\mu_{\text{eff}}$ , BM	$\Lambda_M$ , ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>
[Cr(2,6-LNO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	6,166	3.85	253.7
[Mn(2,6-LNO) <sub>4</sub> (OCIO <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	14,194	5.82	185.8
[Fe(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6,306	3.88	177.7
[Co(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	9,341	4.73	181.9
[Ni(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		Diamagnetic <sup>a</sup>	170.2
[Cu(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1,498	1.89	185.3
[Zn(2,6-LNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		Diamagnetic	182.7

<sup>a</sup>No EPR signal was observed for the Ni<sup>II</sup> complex.

the free ligand, the 2,6-LNO complexes exhibit negative  $\nu_{\text{NO}}$  shifts and positive shifts of the CH-out-of-plane vibrations (*e.g.* the CH-band occurring at 762 cm<sup>-1</sup> in the free ligand is observed at 780 cm<sup>-1</sup> or higher in the metal complexes). These shifts are due to decrease of the NO bond order and lowering of the electron-density of the aromatic ring, as a result of coordination of the ligand to the metal ion through the NO oxygen.<sup>14</sup>

All the complexes exhibit a very strong, broad band at 1076-1060 cm<sup>-1</sup>, which is assigned as the  $\nu_3$  mode of ionic T<sub>d</sub> ClO<sub>4</sub><sup>-</sup>.<sup>15</sup> In the IR spectrum of the Mn<sup>II</sup> complex two additional strong bands at 1133 and 1024 cm<sup>-1</sup> and one medium intensity band at 920 cm<sup>-1</sup>, assigned, respectively as the  $\nu_4$ ,  $\nu_1$ , and  $\nu_2$  modes of coordinated OCIO<sub>3</sub> (C<sub>3v</sub> symmetry),<sup>15</sup> are observed. This complex has, obviously, one ionic perchlorate group and one OCIO<sub>3</sub> group acting as a monodentate ligand, and is, therefore, formulated as [Mn(2,6-LNO)<sub>4</sub>(OCIO<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. In nitromethane solution the complex cation is decomposed, as indicated by the fact that the compound behaves as a 2:1 electrolyte (Table IV). The absence of splittings of the  $\nu_3$  mode in the other complexes does not necessarily exclude the

presence of coordinated perchlorate.<sup>16</sup> Since strong coordinated perchlorate bands are observed in the Mn<sup>II</sup> complex spectrum, some indication of splitting of the  $\nu_3$  mode should appear in the spectra of analogous 3d metal complexes. Further, the solid state electronic spectrum of the Co<sup>II</sup> complex does not resemble those of pentacoordinated pyridine N-oxide complexes of this ion.<sup>8,10</sup> The coordination of perchlorate in these complexes is, thus, considered as unlikely and they are formulated as [M(2,6-LNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (M=Fe, Co, Ni, Cu, Zn) and [Cr(2,6-LNO)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> (Tables II, IV).

**The Cr<sup>III</sup> Complex.** It should be noted at this point that cationic complexes of the types [ML<sub>6</sub>]<sup>2,3+</sup> and [CuL<sub>4</sub>]<sup>2+</sup> (L=pyridine N-oxide and its substituted derivatives) have been recently shown to have a symmetry lower than O<sub>h</sub> or D<sub>4h</sub>, respectively, on the basis of a detailed study of their vibrational and electronic (at -196°) spectra and magnetic moments.<sup>8</sup> A pure O<sub>h</sub> or D<sub>4h</sub> symmetry can be assigned only to the MO<sub>6</sub> or CuO<sub>4</sub> moieties, respectively, but the effective symmetry influencing the metal ion is lower.<sup>8</sup> In [Cr(2,6-LNO)<sub>6</sub>](ClO<sub>4</sub>)<sub>3</sub> the characteristic pyridine N-oxide complexes metal to ligand ratio<sup>4</sup> is observed. The rather broad  $\nu_{\text{NO}}$  in the IR spectrum of this complex

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(15) B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 4586 (1963); W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, 26, 21 (1964).

(16) A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, 2, 195 (1968).

(Table II) is indicative of splitting of this band, which has been interpreted in terms of symmetry lowering.<sup>8</sup> Nujol mull and nitromethane solution electronic spectra of the Cr<sup>III</sup> complex are in satisfactory agreement and show great resemblance to those of the corresponding trimethylamine N-oxide(TMNO) complex.<sup>17</sup> If a pure O<sub>h</sub> symmetry was assumed for this compound and the band at 16,860 cm<sup>-1</sup> was considered as the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> transition, a Dq value of 1686 cm<sup>-1</sup> would result for 2,6-LNO toward Cr<sup>III</sup>. The position of 2,6-LNO, in relation to other amine oxides, in the spectrochemical series for Cr<sup>III</sup> would be: TMNO(1710)<sup>17</sup> > 2,6-LNO(1686) > 4-CH<sub>3</sub>OC<sub>5</sub>H<sub>4</sub>NO(1613)<sup>4</sup> > 4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>NO(1600)<sup>4</sup> > C<sub>5</sub>H<sub>5</sub>NO(1587<sup>4</sup>, 1539<sup>18</sup>).

**The Ni<sup>II</sup> and Cu<sup>II</sup> Complexes.** X-ray powder diffraction patterns of the tetracoordinated cationic complexes revealed that only those of Ni<sup>II</sup> and Cu<sup>II</sup> are almost identical. The Cu<sup>II</sup> complex has been reported<sup>8,11</sup> and assigned a monomeric structure, involving a square planar CuO<sub>4</sub> grouping, on the basis of its electronic spectrum.<sup>8</sup> Further, a recent crystal structure determination of [Cu(C<sub>5</sub>H<sub>5</sub>NO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> established a square planar configuration for the CuO<sub>4</sub> moiety and a «swastika»-like arrangement of the four pyridine N-oxide molecules around Cu<sup>II</sup>, giving an effective symmetry close to C<sub>4h</sub><sup>8</sup> to the complex cation.<sup>19</sup>

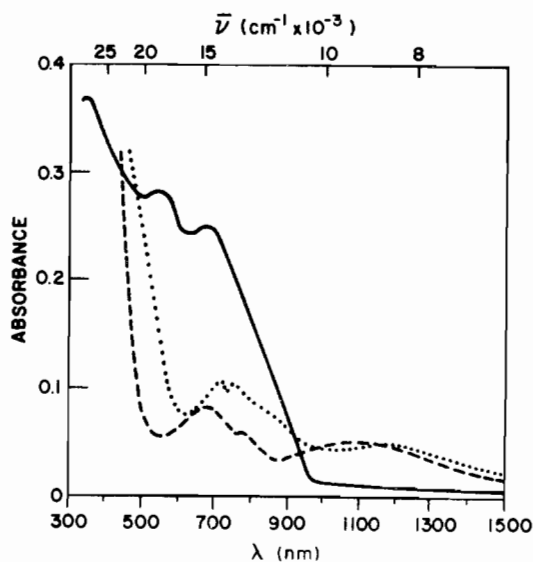


Figure 1. Electronic spectra of [Ni(2,6-LNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>. (—), Nujol mull (absorbance, arbitrary scale); (---), 8.6 × 10<sup>-3</sup> M in CH<sub>3</sub>NO<sub>2</sub>; (····) 8.6 × 10<sup>-3</sup> M in 0.6 M solution of 2,6-LNO in CH<sub>3</sub>NO<sub>2</sub>.

The Ni<sup>II</sup> complex is diamagnetic and shows similarity in its solid state electronic spectrum (Figure 1, Table III) and color to those of bis-(O,O'-diethyldithiophosphato)Ni<sup>II</sup>, which is, reportedly, monomeric, diamagnetic and planar.<sup>20</sup> In addition, it is isomorphous

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(20) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962); Q. Fernando and C. D. Green, *ibid.*, **29**, 647 (1967).

to the Cu<sup>II</sup> complex and quite different in properties from the polymeric and paramagnetic 1:4 complexes of Ni(ClO<sub>4</sub>)<sub>2</sub> with 2-picNO and 2,6-LNO.<sup>9,11</sup> These facts provide definitive evidence for a monomeric, square planar configuration of the NiO<sub>4</sub> grouping. This complex is one of the rare examples of a stable low-spin Ni<sup>II</sup> compound, containing the NiO<sub>4</sub> moiety. Other examples of NiO<sub>4</sub> low-spin complexes are the monomeric Ni<sup>II</sup> β-ketoenolates.<sup>21</sup> It is also noteworthy that the stabilization of a planar configuration in complexes of the type [ML<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>] (L=aryl group with two ortho-substituents or one bulky ortho-substituent; M=Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>), has been attributed to a combination of electronic and steric effect.<sup>22</sup> Thus, both electronic and steric effects<sup>19,21,22</sup> provide a satisfactory explanation for the stability of the diamagnetic [Ni(2,6-LNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> in the solid state.

The Ni<sup>II</sup> complex is insoluble in ether, triethyl orthoformate and 2,2-dimethoxypropane. It dissolves in many organic solvents, producing green or yellow solutions, which exhibit similar electronic spectra (Figure 1, Table III) to those of [Ni(TMNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> solutions.<sup>17</sup> Thus, both the distorted tetrahedral [Ni(TMNO)<sub>4</sub>]<sup>2+</sup> (μ<sub>eff</sub> = 3.86BM)<sup>17</sup> and the planar [Ni(2,6-LNO)<sub>4</sub>]<sup>2+</sup> ions form solvation products of the same type in solution. By addition of excess ligand to a nitromethane solution of [Ni(2,6-LNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> the color changes to orange-yellow and the electronic spectrum (Figure 1, Table III) shows considerable similarity to that of [Ni(EPNO)<sub>5</sub>](ClO<sub>4</sub>)<sub>2</sub> in CH<sub>3</sub>NO<sub>2</sub>,<sup>10</sup> and is thus indicative of the formation of [Ni(2,6-LNO)<sub>5</sub>]<sup>2+</sup>. Ni(ClO<sub>4</sub>)<sub>2</sub> yields in the presence of triethyl orthoformate the yellow [NiL<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> with pyridine N-oxide and its 3- or 4- substituted derivatives and the polymeric [NiL<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> with 2-picNO. If these complexes are suspended in a large amount of triethyl orthoformate and allowed to stand at room temperature, the supernatant liquid becomes a deep red or mauve color in a few minutes in the case of 2-picNO and after 48-72 hours in all other cases. Spectra of these deeply colored solutions are characteristic of planar Ni<sup>II</sup> complexes<sup>20,21</sup> and some examples are shown in Figure 2. Moderate heating (60-70°) or addition of organic solvents (acetone, nitromethane) to these solutions destroy the red or mauve coloration. This behavior and the spectral evidence lead to the conclusion that monomeric analogs of [Ni(2,6-LNO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> with these ligands exist, at least in solution, under anhydrous conditions.

**The Mn<sup>II</sup>, Fe<sup>II</sup>, Co<sup>II</sup>, and Zn<sup>II</sup> Complexes.** [Mn(2,6-LNO)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>]<sup>+</sup> is an analog of the recently reported pentacoordinated cationic complexes of phosphine and arsine oxides and probably has a symmetry close to square pyramidal.<sup>16</sup> In [Cu(C<sub>5</sub>H<sub>5</sub>NO)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> the perchlorate anions lie in an approximately octahedral position to the copper, but no atoms are close enough to be involved in coordination.<sup>19</sup> In the case of the Mn<sup>II</sup> complex of 2,6-LNO the anticipated instability of a planar configuration for this metal ion<sup>22b</sup> in combination with the absence of a Jahn-Teller effect<sup>23</sup>

(21) F. A. Cotton and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **83**, 2818 (1961).

(22) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (a) 1718 (1960); (b) 285 (1961).

(23) L. E. Orgel and J. D. Dunitz, *Nature*, **179**, 462 (1957).

leads, presumably, to the stabilization of a pentacoordinated configuration, involving four 2,6-LNO and one  $\text{OClO}_3$  groups. Coordination of the second perchlorate group is obviously sterically hindered.

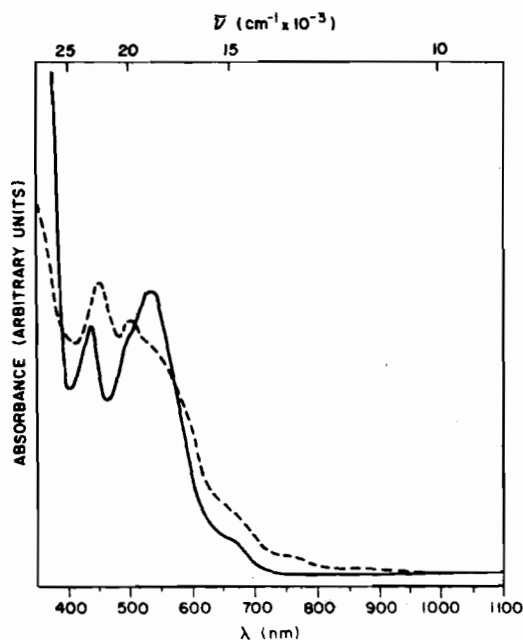


Figure 2. Electronic spectra of triethyl orthoformate solutions of the deeply colored reaction product of  $\text{Ni}(\text{ClO}_4)_2$  with (—), 4-nitropyridine N-oxide; (---), 2-picoline N-oxide (see text). No apparent absorption is observed in the 800-1700 nm region.

Various arrangements of the aromatic rings around the metal ion are possible in tetraordinated pyridine N-oxide complexes, leading to effective symmetries of the point groups  $C_{4h}$ ,  $D_{2d}$ ,  $C_{4v}$  or lower.<sup>8</sup> Thus, the fact that the X-ray powder diffraction patterns of the  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Zn}^{\text{II}}$  complexes differ from each other and from those of the  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  complexes, does not necessarily exclude essentially planar  $\text{MO}_4$  groupings for these compounds. The buff color and the presence of apparent (d-d) transitions at  $10,400\text{ cm}^{-1}$  in the solid state electronic spectrum of the  $\text{Fe}^{\text{II}}$  complex (Table III) rule out a tetrahedral configuration for the complex cation.<sup>24</sup> The possibility of a hexacoordinated polymeric structure for  $[\text{Fe}(\text{2,6-LNO})_4]^{2+}$ , involving two bridging and two terminal 2,6-LNO molecules can also be excluded. If this was the case the complex should exhibit a magnetic moment typical of a  $S=2$  spin configuration (ca.  $5.40\text{ BM}$ ), which is generally observed in complexes of the type  $[\text{FeL}_6]^{2+}$  ( $L = \text{pyridine N-oxide and derivatives}$ ).<sup>1</sup> This is also substantiated by the fact that the polymeric  $[\text{Ni}(\text{2-pic-NO})_4](\text{ClO}_4)_2$  is of the high-spin type ( $\mu_{\text{eff}} = 3.16\text{ BM}$ ).<sup>9</sup> The magnetic moment of the  $\text{Fe}^{\text{II}}$  complex ( $3.88\text{ BM}$ ) suggests a  $S=1$  spin configuration.  $\text{Fe}^{\text{II}}$  complexes with half-quenched spin appearing in the literature are the square planar  $\text{Fe}^{\text{II}}$  phthalocyanine ( $\mu_{\text{eff}} = 3.85\text{ BM}$ )<sup>25</sup> and  $[\text{Fe}(\text{Et}_2\text{PhP})_2(\text{C}_6\text{Cl}_5)_2]$  ( $\mu_{\text{eff}} = 3.60\text{ BM}$ ),<sup>22b</sup> and a number of cis-octahedral complexes of the type

$[\text{Fe}(\text{diimine})_2\text{X}]$  ( $\text{X} = \text{oxalate or malonate ion}$ ) ( $\mu_{\text{eff}} = 3.80\text{--}4.18\text{ BM}$ ).<sup>26</sup> The above discussion leads to the conclusion that, as in the case of  $[\text{Fe}(\text{Et}_2\text{PhP})_2(\text{C}_6\text{Cl}_5)_2]$ ,<sup>22b</sup> the  $\text{Fe}^{\text{II}}$  complex has an essentially planar configuration, with the planes of the aromatic rings lying approximately perpendicular to that of  $\text{FeO}_4$ , and stabilized by a combination of steric and electronic effects.

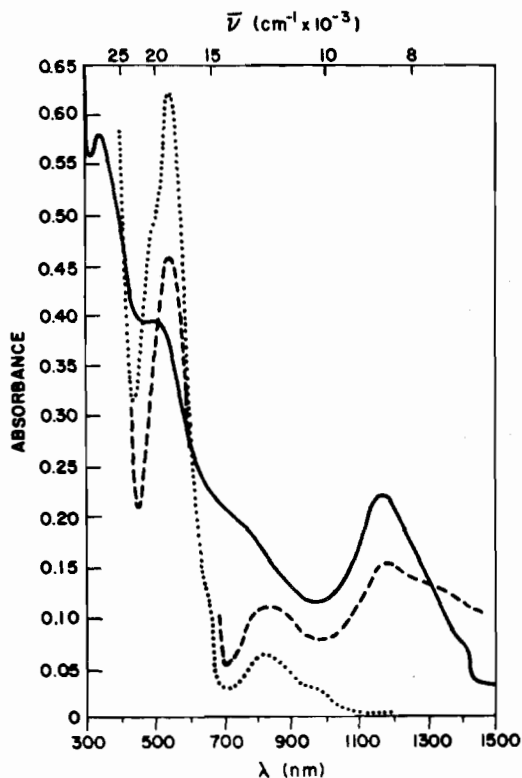


Figure 3. Electronic spectra of  $[\text{Co}(\text{2,6-LNO})_4](\text{ClO}_4)_2$ . (—), Nujol mull (absorbance, arbitrary scale); (---), 450-600 nm:  $4.3 \times 10^{-3}\text{ M}$  in  $\text{CH}_3\text{NO}_2$ , 700-1500 nm:  $7 \times 10^{-3}\text{ M}$  in  $\text{CH}_3\text{NO}_2$ ; (....),  $4 \times 10^{-3}\text{ M}$  in  $0.6\text{ M}$  solution of 2,6-LNO in  $\text{CH}_3\text{NO}_2$ .

The  $\text{Co}^{\text{II}}$  complex is solvated in nitromethane to yield a mixture of tetra- and penta-coordinated species and in acetone to yield a pentacoordinated solvation product (Figure 3, Table III).<sup>8,10</sup> Nitromethane solutions of the  $\text{Co}^{\text{II}}$  complex containing excess ligand, indicate the presence of  $[\text{Co}(\text{2,6-LNO})_5]^{2+}$  (Figure 3, Table III).<sup>8,10</sup> No solvents in which this complex is not solvated or dissociated were found. Thus, the only data available for characterization of this compound are its solid state electronic spectrum and magnetic moment. The magnetic moment ( $4.73\text{ BM}$ ) is in the « tetrahedral » region for  $\text{Co}^{\text{II}}$ . The solid state spectrum, however, with the visible band appearing as a shoulder at  $19,400\text{ cm}^{-1}$  rules out a pure or distorted tetrahedral symmetry. In fact, bis-(2,2,6,6-tetramethyl-3,5-heptanediono) $\text{Co}^{\text{II}}$ , which has been assigned an essentially tetrahedral (strictly  $D_{2d}$ ) symmetry, shows

(24) N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

(25) A. B. P. Lever *ibid.*, 1821 (1965).

(26) E. König, S. Hüfner, E. Steichele, and K. Madeja, *Z. Naturforsch.*, 22A, 1543 (1967); E. König and K. Madeja, *Inorg. Chem.*, 7, 1848 (1968).

the visible band at some  $1400\text{ cm}^{-1}$  lower in energy (ca.  $18,000\text{ cm}^{-1}$ ).<sup>27</sup> Thus, the spectrum of the  $\text{Co}^{\text{II}}$  complex can be interpreted in terms of either a polymeric hexacoordinated structure or a monomeric essentially planar configuration. It has been established<sup>22b,28</sup> that when  $\text{Fe}^{\text{II}}$  is stabilized in a planar configuration imposed by steric and electronic factors,  $\text{Co}^{\text{II}}$  will also be expected to form a more stable planar complex.

The solid state electronic spectrum of the  $\text{Co}^{\text{II}}$  complex (Table III, Figure 3) shows some similarity to those of hexacoordinated  $\text{Co}^{\text{II}}$ -2,6-LNO complexes.<sup>11,29,30</sup> Nevertheless, the quite sharp character of the maximum at  $8470\text{ cm}^{-1}$  (Figure 3) and the fact that the absorption is continuous up to about  $5000\text{ cm}^{-1}$  indicate a much greater similarity of the pattern of the spectrum of  $[\text{Co}(2,6\text{-LNO})_4]^{2+}$  to those of a number of low-spin square planar bis-( $\beta$ -ketoimino) $\text{Co}^{\text{II}}$  chelates reported by Everett and Holm.<sup>31</sup> Further, if the  $\text{Co}^{\text{II}}$  complex had a polymeric oxygen-bridged structure, attack by solvent molecules should be seriously hindered due to steric factors and, in any case, it should be less severe than that occurring with 2-picNO analogs. It has already been stated that  $[\text{Co}(2,6\text{-LNO})_4]^{2+}$  is solvated by acetone or nitromethane. Comparison of the acetone solution spectra of the polymeric  $[\text{Ni}(2\text{-picNO})_4]^{2+}$  and the monomeric  $[\text{Ni}(2,6\text{-LNO})_4]^{2+}$  provides indirect evidence in favor of a monomeric configuration for  $[\text{Co}(2,6\text{-LNO})_4]^{2+}$ .  $[\text{Ni}(2\text{-picNO})_4]^{2+}$  exhibits almost identical spectra in acetone ( $26,460, 20,050, 13,510, 12,660, 8400\text{ cm}^{-1}$ ) and in the solid state,<sup>9</sup> but the solvated species of  $[\text{Ni}(2,6\text{-LNO})_4]^{2+}$  in acetone exhibits a distinctly different spectrum ( $29,070, 24,390, 12,990, 8000\text{ cm}^{-1}$ ). Moreover, the split  $\nu_{\text{NO}}$  bands show identical patterns in the IR spectra of the  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  complexes. Unfortunately, molecular weight determinations for the new complexes do not seem possible, since no solvents in which they are stable were found.

A high-spin square planar anionic  $\text{Co}^{\text{II}}$  complex with 1,2-bis(mercapto)-*o*-carborane has been claimed<sup>32</sup> but no further discussion or spectral data have been presented thus far. No other high-spin square planar cobaltous complexes have been established. Cotton and Holm suggest that a donor set of four oxygens might produce a ligand-field of intensity insufficient to induce

spin-pairing in planar  $\text{Co}^{\text{II}}$  complexes.<sup>33</sup> Orbital contributions leading to moments higher than  $4.70\text{ BM}$  (spin-only value  $3.88\text{ BM}$ ) can be explained if the energy order  $d_{xz}, d_{yz} > d_z$ , which gives a  ${}^4E_g$  ground state, is assumed.<sup>33</sup>

Thus, both the  $\text{Fe}^{\text{II}}$  and  $\text{Co}^{\text{II}}$  complexes appear to have an essentially planar configuration. As in the case of the  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Ni}^{\text{II}}$  phosphine-*o*-substituted aryl complexes reported by Chatt and Shaw,<sup>22</sup> the accommodation of four 2,6-LNO molecules around the metal ion imposes an essentially planar configuration. Unambiguous characterization, especially for the  $\text{Co}^{\text{II}}$  complex, should be substantiated by a crystal structure determination, however. Further characterization studies, including detailed spectral and magnetic investigations and  ${}^{57}\text{Fe}$  Mössbauer spectra (for  $\text{Fe}^{\text{II}}$ ) are in progress and will be reported in a future publication. Finally, no structural assignments can be made for  $[\text{Zn}(2,6\text{-LNO})_4]^{2+}$  from the data available.

## Conclusion

The synthesis of square planar cationic 3d metal complexes of 2,6-LNO introduces a novel aspect to the chemistry of coordination compounds of monodentate oxo-ligands. Research in this direction with other monodentate heterocyclic oxo-ligands, substituted at the adjacent to the heteroatom ring positions (e.g. 1,3-disubstituted isoquinoline N-oxides, 2,5-disubstituted thiophene 1-oxides, 2,6-disubstituted phosphorine 1-oxides) should be rewarding.

$[\text{Ni}(2,6\text{-LNO})_4]^{2+}$  is the first example of a planar, diamagnetic complex of a first row transition metal ion with a monodentate oxo-ligand. The existence of planar  $\text{Ni}^{\text{II}}$  complexes of  $\text{C}_5\text{H}_5\text{NO}$  and monosubstituted derivatives in solution, leads to the conclusion that these ligands favor a planar  $\text{MO}_4$  configuration. Triethyl orthoformate is apparently a medium favoring the formation of monomeric tetraordinated pyridine N-oxide complexes.

2,6-LNO shows similar behavior to that of  $\text{TMNO}^{17}$  and hexamethylphosphoramide<sup>34</sup> in that it forms hexacoordinated complexes with  $\text{M}(\text{ClO}_4)_3$  and tetraordinated complexes with  $\text{M}(\text{ClO}_4)_2$  ( $\text{M} = 3\text{d}$  metal ion). It differs, however, from these ligands in the stereochemistry of its tetraordinated complexes.  $\text{TMNO}$  and hexamethylphosphoramide form tetrahedral cationic complexes of the type  $[\text{ML}_4]^{2+}$ .<sup>17,34</sup> It is evident that pyridine rings, particularly when 2,6-disubstituted, are effective in stabilizing a planar configuration.

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