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2,6-Lutidine N-oxide Complexes with Metal Chlorides[1]

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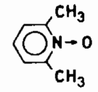
Complexes of 2,6-lutidine N-oxide (N-lutO or L) with a number of metal chlorides were prepared and characterized by means of spectral (ir and electronic), magnetic and conductance studies. Cr(III) and Al(III) yielded hexacoordinated complexes, which are most probably of the type $[ML_2Cl_2(OH_2)_2]Cl\cdot nH_2O$*, involving both coordinated and anionic Cl groups, aquo ligands and lattice water.* ML_2Cl_2 *complexes isolated appear to be binuclear, chloride-bridged, pentacoordinated, of the type* $[ClL_2MCl_2ML_2Cl]$ *for M = Mn, Ni, and monomeric, trans-square planar for M = Pd, Pt.* $FeCl_2$ *formed a 2:3 complex* ($Fe_2L_3Cl_4$)*, which seems to involve both terminal and bridging chloro ligands, and coordination number five. A* trans-*arrangement of the N-lutO ligands in the above complexes is considered as most likely, in view of the obvious steric interactions between ligands of this type, occupying coordination sites,* cis *to each other. Finally, a second* $NiCl_2$ *complex prepared, comprising coordinated methanol, is probably binuclear, chloride-bridged, hexacoordinated, of the type* $[ClL(CH_3OH)_2NiCl_2Ni(CH_3OH)_2LCl]$.

Introduction

Numerous studies of metal complexes with 2,6-lutidine N-oxide (N-lutO; I) have appeared in the literature [2–27].


(I)

The two *ortho*-methyl substituents of this ligand exert significant steric hindrance, during metal complex formation. This has been amply demonstrated during comparisons of the stoicheiometries and stereochemistries of the metal complexes of N-lutO and pyridine N-oxide (N-pyO). Thus, divalent 3*d* metal perchlorates form 1:4 and, in certain cases, 1:5 complexes with N-lutO, [11, 18, 20, 21] and 1:6 complexes with N-pyO [26, 28, 29]. Whereas Y(III) and lanthanide(III) perchlorates form cationic complexes of the type $[ML_5(OClO_3)]^{2+}$ with N-lutO [25], whilst $[ML_8]^{3+}$ cationic complexes are obtained during interaction of N-pyO with these metal(III) perchlorates or the corresponding iodides, under the same experimental conditions [30]. It should be noted that 1:8 Ln(III) perchlorate-N-lutO complexes can be obtained by treatment of the rare earth salts with a large excess of warm ligand [27].

The steric hindrance introduced by coordination of N-lutO was also demonstrated during studies of 3*d* metal nitrate [3, 22], nitrite [6], thiocyanate [3, 17, 21, 22], sulfate [24] and acetylacetonate [4] adducts with this ligand. Several M(II) (M = VO, Co, Cu, Zn, Cd, Hg) [3, 5, 7–9, 12, 13, 21], M(III) (M = Fe, Ru, Rh) [16, 23] and M(IV) (M = Ti, Zr, Hf, V, Pt, Te, Th) [10, 14, 19] halide complexes with N-lutO have been synthesized and adequately characterized. The steric effects introduced by this ligand have been discussed in several of these works. Thus, the steric hindrance is not severe enough as to preclude formation of binuclear, N-lutO-bridged, 1:1 Cu(II) halide complexes, exhibiting subnormal magnetic moments [5, 13]. However, in the case of TiL_2F_4 complexes with N-pyO and derivatives, the *cis*-octahedral configuration is normally stabilized, but in the case of N-lutO stabilization of the *cis*-isomer is sterically hindered, and the *trans*-octahedral complex is exclusively formed [10].

A series of 1:1 and 2:1 N-lutO complexes with divalent 3*d* metal halides (M = Mn, Co, Ni, Zn; halogen = Cl, Br, I) have been reported in a paper dealing mainly with the thermal decomposition of metal halide complexes with various aromatic amine N-oxides [12]. On the basis of limited (visible, far-ir) spectral and magnetic data presented, it appeared that the 1:1 complexes are generally polynuclear octahedral, while in the case of the 2:1 complexes the evidence favored a tetrahedral configuration for M = Co, Zn, and a polymeric octahedral structure for M = Mn, Ni [12]. During the course of our synthetic work on N-lutO metal complexes [11, 19, 20, 22–25] we have isolated a number of M(II) (M = Mn, Fe, Ni, Pd, Pt) and M(III) (M = Al, Cr) chloride complexes with this ligand. In view of the interesting coordination chemistry of N-lutO, it was felt that the characterization of these compounds was in order. Our work in this direction is presented in this paper.

TABLE I. Analytical Data for Metal Chloride Complexes with 2,6-Lutidine N-Oxide (L).

Complex	Color	C%		H%		N%		Cl%		Metal%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$AlL_2Cl_3 \cdot 3H_2O$	Off-white	38.77	39.12	5.58	5.42	6.46	6.28	24.52	24.83	6.22	5.89
$CrL_2Cl_3 \cdot 4H_2O$	Purple	35.27	34.85	5.50	5.37	5.88	5.49	22.31	21.91	10.91	11.27
MnL_2Cl_2	Pale Yellow	45.18	44.98	4.88	5.20	7.52	7.26	19.05	18.87	14.76	14.49
$Fe_2L_3Cl_4$	Brick Red–orange	40.81	40.55	4.37	4.44	6.75	6.51	22.76	22.97	17.93	18.07
NiL_2Cl_2	Blue	44.73	44.68	4.83	4.95	7.45	7.40	18.86	19.17	15.62	15.36
$NiLCl_2 \cdot 2CH_3OH$	Light Green	43.68	43.31	5.96	6.14	6.37	6.62	16.11	15.78	13.34	13.63
PdL_2Cl_2	Khaki	39.69	39.31	4.28	4.15	6.61	6.87	16.74	16.55	25.14	25.43
PtL_2Cl_2	Yellowish Beige	32.83	33.12	3.54	3.42	5.47	5.70	13.84	14.21	38.09	37.75

TABLE II. Pertinent Infrared Data for Metal Chloride Complexes with N-lutO (cm^{-1}).[a]

Compound	ν_{N-O}	δ_{N-O}	γ_{CH}	ν_{M-O} (N-lutO)	ν_{M-Cl}[b]	ν_{M-O} (aquo or methanol)	ν_{Ligand} (500–230 cm^{-1})
N-lutO = L	1245vs	844m	762vs	–	–	–	492m, 458sh, 372m–w, 300w, b, 286m, 267m, 250m, 240m
$AlL_2Cl_3 \cdot 3H2O$	1210vs	816vs,sh	787vvs	505m, 480m, 470m	375s,b, 350s, 298s	525m–s	440m,b, 398m–w, 311s,sh, 273s, 258s, 247s,b
$CrL_2Cl_3 \cdot 4H_2O$	1185vs,b	820m–s,sh	771m	490s, 470s	347m, 328m, 313m	520s,b	420m, 390m, 370w, 299m,sh, 288m,b, 272m–s, 251s, 246s
MnL_2Cl_2	1191vs, 1159s	822vs	773vs	376vs, 357s,sh	310vs, 300vs(t), 263vs,sh, 240vs, sh(b)	–	492s, 455w,sh, 396m, 283vs,sh, 274vs,sh, 250vs,sh
$Fe_2L_3Cl_4$	1203m,sh, 1188s	829s	780s	372s, 352s, 338vvs	310s, 307s(t), 289m,sh, 260w(b)	–	484m, 470m, 456m, 435w,b, 393w, 300s,sh, 268w,sh, 250w
NiL_2Cl_2	1217vs, 1197vs	823vs	774vs,b	374s	309s, 299s(t), 277s, 245s(b)	–	491vs, 460m,sh, 418w, 398w, 290m, 271s, 262m, 250m,sh
$NiLCl_2 \cdot 2CH_3OH$	1199vvs	824vvs	770vvs,b	340m–s,b	282s, 256s(t), 230s,b(b)	361m–s	496s, 459m, 430w,b, 270s,sh, 243s,sh
PdL_2Cl_2	1188vs, 1181vs, 1169vs	821vvs	788vvs	374m	330vs	–	493m, 460w,b, 418m–s, 350w, 327m, sh, 300w, 289vw, 273w, 261w, 250m,b
PtL_2Cl_2	1169vs,b	819vvs	792vvs	333s	323s	–	488w, 452m,b, 425m,b, 392m,sh, 372m–w, 341m, 313m, sh, 300m, 268m,vb, 247m

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder [b] In parentheses: (t), terminal, (b), bridging.

Experimental

Chemicals

N-lutO (Ennox Chemical Co.) was utilized after purification by vacuum distillation. The purest commercially available metal chlorides, triethyl orthoformate and organic solvents were used throughout this work.

Syntheses

MCl_3 (M = Al, Cr) complexes were prepared as follows. The hydrated metal chloride (1 mmol) was

TABLE III. Electronic Spectra, Magnetic Properties (at 294°K) and Molar Conductivities (10^{-3} *M* Nitromethane Solutions at 25 °C) of Metal Chloride Complexes with N-lutO (L).

Complex	Electronic Spectra[a]		$10^6\chi_M^{cor}$, cgsu	μ_{eff}, BM	Λ_M, Ω^{-1} cm^2 mol^{-1}
	Medium[b]	λ_{max}, nm(ϵ_{max})			
$AlL_2Cl_3\cdot 3H_2O$	Nujol	212vvs, 262vs	Diamagnetic		66
$CrL_2Cl_3\cdot 4H_2O$	Nujol	213vs, 221vs,sh, 258vs, 330sh, 400s, 560m, 600s,sh,	6,426	3.90	63
	3×10^{-3} *M* in CH_3NO_2	396(143)sh, 428(117)sh, 592(73)b			
MnL_2Cl_2	Nujol	218vvs, 225vvs, 259vs, 360vs,b, 453m,b, 551m–w, sh	14,320	5.84	17
	5×10^{-3} *M* in CH_3NO_2	<400, 522(18)sh, 612(2)			
$Fe_2L_3Cl_4$	Nujol	211vs, 222vs,sh, 261vs, 365vs,b, 760m,sh, 975m,sh, 1260w,sh, 1380w,b	10.452	4.98	22
	4×10^{-3} *M* in CH_3NO_2	<400, 990sh, 1250(8), 1400(7)b			
NiL_2Cl_2	Nujol	217vvs, 222vvs,sh, 269vs, 338sh, 435s,sh, 600s,b, 670s, 850m, 1130m,b, 1375m–w, 1925m–w	5.030	3.45	26
	2×10^{-3} *M* in CH_3NO_2	<400, 438(122), 596(57), 675(54), 833(18), 1160(19), 1400(12), 1937(9)			
	6×10^{-3} *M* in CH_3OH	<400, 412(58), 668(6), 1180(4)			
$NiLCl_2\cdot 2CH_3OH$	Nujol	218vs, 226vs, 271vvs, 360sh, 415m,sh, 680w,b, 1200w,b,	4.433	3.27	18
	7×10^{-3} *M* in CH_3NO_2	<400, 418(56), 677(7), 1200(5)b			
PdL_2Cl_2	Nujol	214vvs,sh, 223vvs,sh, 257vs,sh, 264vs, 269vs,sh, 320vs,sh, 430m,b	Diamagnetic		31
PtL_2Cl_2	Nujol	207vvs,sh, 212vvs,sh, 233vs,sh, 241vs,sh, 252vs,sh, 330vs,sh	Diamagnetic		27

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [b] Medium for electronic spectral measurements.

dissolved in 30 ml triethyl orthoformate, a dehydrating agent [31], mixed with about 10vol% acetone; the solution was warmed to 50 °C, 3 mmol N-lutO were then added and the resulting mixture was magnetically stirred for 15 min. In both cases, small amounts of precipitate were formed after this treatment. Addition of an excess of ligroin (boiling range 63–75 °C) induced the formation of a solid precipitate (Al(III)) or an oily product (Cr(III)). The latter product was solidified by decantation of the supernatant liquid and treatment of the oil with several portions of ligroin. A series of MCl_2 (M = Mn, Fe, Ni, Pd, Pt) complexes were prepared by dissolving the metal salt (1 mmol) in *ca.* 30 ml isopropyl alcohol, under stirring, adding 3 mmol N-lutO, warming to 60 °C , and then adding an excess of triethyl orthoformate (25–50 ml). Precipitation was immediate in the cases of Mn(II), Fe(II), Pd(II) and Pt(II); $NiCl_2$ yielded a blue precipitate, after reduction of the volume of the reaction mixture to 1/5 its original volume and subsequent cooling to ambient temperature.

The above complexes were filtered, washed on the filter with ligroin, and dried in an evacuated desiccator over P_2O_5. These complexes dissolve in various polar solvents (*e.g.*, nitromethane, acetonitrile, alcohols). The blue Ni(II) complex gives blue solutions in most of these solvents, but in methanol it affords a yellow solution. It was considered of interest to prepare a second $NiCl_2$ complex by following the above synthetic procedure, but substituting methanol for isopropyl alcohol. Under these conditions a green solution was obtained, and a light green solid was precipitated by addition of an excess of anhydrous diethyl ether. This complex, which was filtered, washed and dried as above, forms green solutions in polar solvents (*e.g.*, nitromethane). Analytical data for the new complexes (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) are given in Table I.

Spectral, Magnetic and Conductance Measurements

Infrared (Table II) and electronic (Table III) spectra and conductance measurements (Table III) were obtained by methods previously described [11, 22]. Magnetic susceptibility measurements at 294°K were obtained by the Faraday method by using a Cahn Magnetic Susceptibility System, Model 7600.

The magnetic susceptibility standard was mercuric tetrathiocyanatocobaltate(II). Diamagnetic corrections were effected by using Pascal's constants [32] and the magnetic moments (Table III) were calculated from the equation $\mu_{eff} = 2.84 \sqrt{\chi_M^{cor} \cdot T}$.

Discussion

Infrared and Conductance Data

The ir spectra of the N-lutO complexes at 4000–600 cm^{-1} (Table II) are characterized by negative ν_{N-O} and δ_{N-O} and positive γ_{CH} frequency shifts, relative to the spectrum of the free ligand. These features are common in metal complexes of N-pyO and derivatives, which coordinate through oxygen [2, 33]. The ν_{OH} (water) region in the spectra of the Al(III) and Cr(III) complexes exhibits a relatively sharp, strong maximum at 3400 cm^{-1}, indicative of the presence of aquo ligands [34], and a weaker, very broad absorption at 3550–3200 cm^{-1}, suggestive of the presence of several maxima and presumably associated with the concomitant presence of water of crystallization (lattice water) [35]. Ni(N-lutO)-$Cl_2 \cdot 2CH_3OH$ shows a single broad ν_{OH} band at 3350 cm^{-1}, attributable to coordinated methanol ligands [36].

Tentative metal–ligand band assignments, given in Table II, were based on similar assignments for N-pyO and N-lutO metal complexes [2, 12, 20, 22, 24, 26, 28, 29, 37–39], as well as transition metal chloro [12, 38–43] and aquo [44] complexes. The positions of the ν_{M-O} (N-lutO and aquo) and ν_{M-Cl} modes in the spectra of the Al(III) and Cr(III) complexes are typical for hexacoordinated compounds of these metal ions [20, 22, 24, 28, 29, 40, 44]. The two Ni(II) complexes exhibit the Ni–O stretch (N-lutO) at significantly differing frequency regions. The ν_{Ni-O} in the methanol-containing complex is suggestive of coordination number six [37], while the ν_{M-O} bands in Ni(N-lutO)$_2$Cl$_2$ and the Mn(II) and Fe(II) complexes are in favor of coordination number five [20, 22, 24]. Both Ni(II) complexes, and the Mn(II) and Fe(II) compounds show several absorptions attributable to ν_{M-Cl} modes (310–240 cm^{-1} region for the apparently penta- [42] and 282–230 cm^{-1} for the hexa- [40, 41] coordinated complexes). This may be interpreted in terms of the presence of both terminal and bridging chloro ligands [38]. The Pt(II) complex shows a very similar lower frequency ir-spectrum to those reported for *trans*-square planar complexes of the type $AMCl_2L$ (M = Pt, Pd; A = ethylene, CO, and analogous ligands; L = N-pyO and derivatives) [39, 45, 46], while the new Pd(II) complex also exhibits a spectrum of the same type. The apparent presence of single ν_{M-O} and ν_{M-Cl} (M = Pd, Pt) bands in the spectra of these complexes is consistent with *trans*-square planar configurations [39, 40, 43].

The electrolytic conductivity results (Table III) show that, in polar solvents, the Cr(III) and Al(III) complexes behave as 1:1 electrolytes, whereas the rest of the new complexes are non-electrolytes [47].

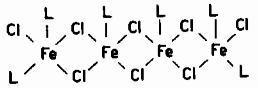
Electronic Spectra and Magnetic Moments

The UV spectrum of N-lutO in inert media (*e.g.*, cyclohexane) shows the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions at 274 and 319 nm, respectively [48]. At higher energies (200–230 nm), additional very strong bands, due to $\pi \rightarrow \pi^{**}$ and $n \rightarrow \pi^{**}$ transitions are observed [48, 49]. Upon metal complex formation, the $\pi \rightarrow \pi^*$ transition is generally shifted toward higher energies (252–271 nm; Table III). Similar hypsochromic shifts have been reported during metal complex formation with N-pyO and quinoline N-oxide [50, 51], which show the $\pi \rightarrow \pi^*$ transition at ca. 280 and 340 nm, respectively [48–50]. On the other hand, the $n \rightarrow \pi^*$ transition band is not observed in the spectra of metal complexes with aromatic amine N-oxides [50, 51]; this is also the case with the new metal complexes, as shown by the spectrum of the Al(III) complex (no maxima above 270 nm). In the case of the new 3*d* metal complexes, strong metal-to-ligand charge-transfer absorption, originating in the UV and trailing off into the visible region is observed, as would be expected [51]. The *d–d* transition spectra of the Cr(III) complex and the methanol-containing Ni(II) compound are suggestive of low symmetry hexacoordinated configurations [28] (band assignments for pure O_h symmetry, nm: Cr^{3+}, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$, 400, 430; $\rightarrow {}^4T_{2g}(F)$, 560, 600; Ni^{2+}, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, 360, 415; $\rightarrow {}^3T_{1g}(F)$, 680; $\rightarrow {}^3T_{2g}(F)$, 1200). However, the spectra of the Mn(II) and Fe(II) complexes and the Ni(N-lutO)$_2$Cl$_2$ compound are suggestive of pentacoordinated structures. In fact, these complexes exhibit several *d–d* bands (Ni(II) seven maxima at 400–1950 nm, Fe(II) four maxima at 760–1380 nm, Mn(II) several maxima up to 760 nm), as is also the case with various pentacoordinated complexes with these metal ions, reported in recent years [11, 22, 24, 52–54]. These complexes appear to remain pentacoordinated in their nitromethane solutions, while the Ni(II) complex is dissociated or solvated in methanol, yielding a hexacoordinated species, as suggested by the spectral changes observed (Table III), upon dissolution in this medium (the methanol solution spectrum of Ni(N-lutO)$_2$Cl$_2$ is very similar to that of Ni(N-lutO)Cl$_2 \cdot$ 2CH$_3$OH). The electronic spectrum of the Pt(II) complex is similar to that of 1-(pyridine N-oxide)-3-ethylene-2,4-dichloroplatinum(II) [55], with the lowest energy maximum occurring at 330 nm. The Pd(II) analog exhibits a maximum at 320 nm, and an additional band at lower energy (430 nm), as would be expected [56, 57]. In the 200–300 nm region, considerable overlaps between ligand, charge- transfer (probably of the ligand-to-metal class) and high energy *d–d* bands are presumably occurring in the case of the new Pd(II) and Pt(II) complexes [55–58], which show richer spectra in this region than the rest of the complexes.

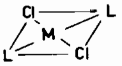
The magnetic moments of the Cr(III), Mn(II), Fe(II) and Ni(II) complexes (Table III) are normal for high-spin compounds of these metal ions, while the Pd(II) and Pt(II) complexes are diamagnetic, as is generally the case with square planar compounds of d^8 systems [59]. The methanol-comprising Ni(II) complex shows a μ_{eff} value consistent with a hexacoordinated configuration, but that of Ni $(N\text{-lutO})_2Cl_2$ is well above the "octahedral" region for Ni^{2+} (2.83–3.30 BM) [59]. Magnetic moments of 3.40–3.51 BM have been reported for several high-spin pentacoordinated Ni(II) compounds [22, 53, 54, 60–62].

Likely Structures for the New Complexes

On the basis of the overall evidence, the Al(III) and Cr(III) complexes appear to be of the type $[M(N\text{-lutO})_2Cl_2(OH_2)_2]Cl \cdot nH_2O$ (n = 1 for Al; n = 2 for Cr), involving both coordinated and ionic chloride groups, as is the case with several metal trichloride complexes [63, 64], as well as both coordinated and lattice water. The $M(N\text{-lutO})_2Cl_2$ (M = Mn, Ni) complexes seem to be characterized by coordination number five and by the presence of both terminal and bridging chloro ligands. A likely binuclear structure for these compounds is $[Cl(N\text{-lutO})_2MCl_2M(N\text{-lutO})_2Cl]$ (M = Mn, Ni). The ferrous complex appears to be also pentacoordinated and containing both terminal and bridging chloro ligands. The tetrameric structure (II) (L = N-lutO) is probable for this complex.



(II)



(III)

Alternative possibile structures considered, involving both chloro and N-lutO bridges, are less likely than (II), in view of the steric features of N-lutO.

For the methanol-comprising Ni(II) complex, a binuclear hexacoordinated structure, characterized by the presence of terminal N-lutO, chloro and methanol ligands and bridging chloride groups, *i.e.*, $[Cl(N\text{-lutO})(CH_3OH)_2NiCl_2Ni(CH_3OH)_2(N\text{-lutO})Cl]$, is considered as most likely. Finally, the evidence concerning the Pd(II) and Pt(II) compounds is clearly in favor of *trans*-square planar configurations (III; M = Pd, Pt; L = N-lutO). The *trans*-arrangement of two N-lutO ligands relative to each other is generally expected to be favored, not only in the Pd(II) and Pt(II) complexes, but also in the rest of the new metal complexes involving the coordination of two N-lutO molecules per metal ion (*i.e.*, all the new complexes with the exception of the hexacoordinated Ni(II) compound), in view of the steric effects exerted by this ligand discussed in the Introduction.

Finally, it is worth noting that the Mn(II) complex is photosensitive, as is the case with most amine N-oxide complexes with this metal ion; recently, it was shown that the darkening of the color of these complexes is due to partial oxidation of Mn^{2+} to Mn^{3+} [65]. When the new Mn(II) compound was stored in a small evaporating dish in a desiccator without taking any precautions for protection of the surface from daylight, a very thin brown surface layer was formed after 1–2 months. The amounts of the Mn(II) complex used for characterization work were protected from the light by wrapping the container (vial) in aluminum foil.

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