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Adenine N(1)-Oxide Complexes with Metal Chlorides

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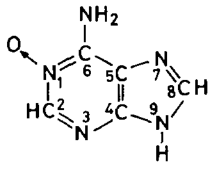
Abstract

$M(LH)_2Cl_3$ (M = Al, Fe), $VO(LH)Cl_2$ and $Dy(LH)_3Cl_3$ adducts and mixed neutral-monoanionic ligand complexes of the $M(LH)LCl_2$ (M = Cr, Fe) and $M(LH)LCl_3$ (M = Th, U) types are formed by boiling under reflux mixtures of adenine N(1)-oxide (LH) and the VO^{2+}, M^{3+} (M = Al, Cr, Fe, Dy) or M^{4+} (M = Th, U) chloride in ethanol–triethyl orthoformate. Characterization studies indicate significant differences in the ligand (LH or L^-) binding sites from complex to complex, *viz.*: Monomeric complexes: $[Al(LH)_2Cl_3]$ N(9) (unidentate); $[VO(LH)Cl_2]$ chelating through O(1), N(6); $[Fe(LH)_2Cl_3]$ one unidentate O(1)- and one bidentate chelating O(1), N(6)-bonded LH. Bi- or poly-nuclear linear complexes with single or double bridges of O(1), N(7)-bonded L^- or LH between adjacent metal ions involve the following binding sites for the terminal LH ligands: $[M(LH)LCl_2]_x$ (M = Cr, Fe; $x > 2$) chelating through O(1), N(6); $[Dy(LH)_3Cl_3]_2$ and $[M(LH)LCl_3]_x$ (M = Th, U) N(9) (unidentate).

Introduction

These laboratories have studied in the past 3d metal perchlorate complexes with adenine N(1)-oxide (adH-NO; LH; I) [1] and purine N(1)-oxide [2]. More recently, we prepared adH-NO complexes with a series of metal chlorides ($M^{n+} = Al^{3+}$, V^{3+}, VO^{2+}, Cr^{3+}, Fe^{3+}, Dy^{3+}, Th^{4+}, U^{4+}) [3], and reported on two $M(LH)_2Cl_3$ (M = Al, Fe) adducts in a preliminary communication [4]. The present paper deals with the syntheses and characterization of adenine N(1)-oxide complexes with the above metal chlorides. The metal complexes of purine N-oxides have attracted attention in view of the fact that these N-oxide ligands are highly active oncogens [5, 6] and have distinctly different coordination patterns from those of the parent purines [7]. During earlier studies of adH-NO–metal complexes the evidence available was interpreted in terms of bidentate chelation of this ligand through N(6), N(7) [8, 9]. Nevertheless, our characterization work indicated variation of the ligand coordination pattern from complex to complex, including terminal unidentate N(9)- or N(7)-bonded, bidentate chelating O(1), N(6)-bonded and bridging bidentate O(1), N(7)-bonded adenine N(1)-oxide [1, 4]. The latter two coordination patterns of this ligand were recently established by the crystal structure determinations of two complexes, *i.e.*: in dimeric $[Hg(LH)Cl_2]_2$ adH-NO acts as bridging bidentate O(1), N(7)-bonded [10], while in $Cu(L)_2Na_2(H_2O)_8$ the doubly deprotonated L^{2-} ligands function as bidentate chelating O(1), N(6)-bonded (CuO_2N_2 chromophore) [11]. The L^{2-} dianionic ligand in the latter complex is formed by deprotonation of the imidazole NH and the NH_2 group of adH-NO [11]. Finally, studies of adH-NO–Cu^{2+} salt systems in H_2O or D_2O revealed that at relatively low pH the ligand binds exclusively through N(9) to Cu^{2+} [7], whilst at pH < 0.3 adH-NO is degraded in the presence of the cupric cation, forming 4-aminoimidazole-5-carboxamidoxime by scission of the C(2)–N(1) and C(2)–N(3) bonds (removal of the C(2) carbon of the pyrimidine ring) [12]. In the ligand resulting by degradation of adH-NO, N(1) is placed in a *cis*-planar configuration to N(7) by rotation around the C(5)–C(6) bond, thus enabling N(1), N(7) equatorial chelation to Cu^{2+} [12].



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Experimental

The following synthetic method was employed: 0.65 mmol hydrated or anhydrous metal chloride are dissolved in a mixture of 35 ml ethanol and 15 ml

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TABLE I. Analytical Data for Adenine N(1)-oxide (LH) Complexes with Metal Chlorides

Complex	Color	Yield (%)	Analysis, found (calculated) (%)				
			C	H	N	M	Cl
$Al(LH)_2Cl_3$	pale pink	41	27.8(27.6)	2.3(2.3)	31.9(32.2)	6.5(6.2)	24.8(24.4)
$VO(LH)Cl_2$	green	43	20.4(20.8)	1.9(1.7)	23.8(24.2)	17.9(17.6)	24.1(24.5)
$Cr(LH)LCl_2$	gray green	40	27.8(28.3)	2.4(2.1)	32.6(33.0)	12.0(12.3)	16.7(16.7)
$Fe(LH)_2Cl_3$	brown	39	26.3(25.9)	2.0(2.2)	29.8(30.2)	11.9(12.0)	23.1(22.9)
$Fe(LH)LCl_2$	brown	44	28.1(28.3)	2.3(2.1)	32.7(32.5)	12.8(13.0)	16.2(16.6)
$Dy(LH)_3Cl_3$	khaki	73	25.3(25.0)	2.4(2.1)	29.7(29.9)	22.9(22.5)	15.0(14.7)
$Th(LH)LCl_3$	beige	56	18.3(18.8)	1.2(1.4)	22.5(21.9)	36.0(36.3)	16.3(16.6)
$U(LH)LCl_3$	golden yellow	60	18.9(18.6)	1.7(1.4)	21.2(21.7)	37.4(36.9)	16.8(16.5)

triethyl orthoformate and stirred at 40–50 °C for 2 h. Then, 1.3 mmol adH-NO are added and the resulting mixture is boiled under reflux for 2–5 days, depending on the speed of formation of the metal complex. Subsequently, the volume of the supernatant is reduced to about one-half by heating under reduced pressure, and the solid complex is separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. The complexes obtained under these conditions were either LH–metal chloride adducts (M = Al^{3+}, VO^{2+}, Fe^{3+}, Dy^{3+}) or mixed neutral-monodeprotonated adenine N(1)-oxide ligand (LH–L^-) complexes (M = Cr^{3+}, Th^{4+}, U^{4+}), as shown in Table I. We were also able to prepare a mixed LH–L^- Fe^{3+} complex with the same synthetic method, by employing a 3:1 (instread of 2:1) adH-NO to Fe^{3+} molar ratio. $AlCl_3$, $VOCl_2$ and $DyCl_3$ afford the same adducts at 2:1 or 3:1 ligand to metal ratios. Finally, VCl_3 formed a lavender complex with adenine N(1)-oxide under our standard preparative conditions; this product was, however, contaminated with substantial amounts of a VO^{2+} complex (green specks), even when the preparation was carried out in an atmosphere of dry deoxygenated nitrogen. Partial oxidation of V^{3+} by the N–O function of aromatic amine N-oxides has been observed in many occassions [13–16]. The V^{3+} complex was not studied any further. Among the new complexes, the $AlCl_3$, $VOCl_2$ and $FeCl_3$ adducts readily dissolve in various organic solvents. The remaining complexes are rather sparingly soluble in single organic solvents, but dissolve in some binary solvent mixtures, such as 1:1 (v/v) acetone–nitromethane. The new complexes behave as non-electrolytes in the latter medium (Λ_M values of 10^{-3} M solutions of the complexes ranged between 10–23 Ω^{-1} cm^2 mol^{-1}) [17]. IR spectra (Tables II, III) were recorded using KBr discs (4000–500 cm^{-1}) or Nujol mulls between NaCl (4000–700 cm^{-1}) and high-density polyethylene (700–200 cm^{-1}) windows, on a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements at 300 K (Table IV) were obtained by methods previously described [18].

Results and Discussion

Both simple adducts and mixed LH–L^- ligand complexes were isolated during the present work (Table I), as described in the Experimental section. Similar trends were observed in our corresponding synthetic work with 3d metal perchlorates, *i.e.*, Cr^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+} yielded LH adducts, while Fe^{3+}, Ni^{2+} and Cu^{2+} formed mixed LH–L^- complexes [1]. Actually, with Ni^{2+} and Cu^{2+} perchlorates, LH adducts were initially precipitated, but were subsequently redissolved during the progress of the refluxive step, which eventually resulted to precipitation of mixed ligand complexes [1]. It is also noteworthy that variation of the ligand to Fe^{3+} molar ratio in this work led to the formation of different products, *i.e.*, $Fe(LH)_2Cl_3$ at a 2:1 and $Fe(LH)LCl_2$ at a 3:1 molar ratio.

IR band assignments for adH-NO (Table II) were based on the corresponding assignments for adenine [19], IR studies of aromatic amine N-oxides [20, 21] and our earlier work [1]. The $\nu_{NH} + \nu_{CH}$ bands of the ligand at 3000–2600 cm^{-1} show only slight changes in the spectra of the new complexes, as expected, since all these compounds contain neutral LH ligands [1, 2, 22]. Quite interesting differences are observed in the δ_{NH_2} and ρ_{NH_2} regions in the spectra of the various new complexes. Thus, the free ligand δ_{NH_2} band at 1663 cm^{-1} remains virtually unchanged in the Th^{4+} and U^{4+} complexes or is shifted toward higher wavenumbers in the Al^{3+} and Dy^{3+} complexes. In addition, no significant spectral changes occur in the ρ_{NH_2} region (1020–960 cm^{-1}) in the spectra of the preceding compounds, in which apparently the N(6) nitrogen of the exocyclic amino group is not involved in binding [1, 9, 23, 24]. On the other hand, the new 3d metal complexes (M = VO^{2+}, Cr^{3+}, Fe^{3+}) exhibit substantial δ_{NH_2} shifts

TABLE II. Relevant Infrared Data for adH-NO and the New Metal Complexes (3500–950 cm^{-1} region)

adH-NO[a]	M = Al^{3+}	M = VO^{2+}	M = Cr^{3+}	M = Fe^{3+}[b]	M = Fe^{3+}[c]	M = Dy^{3+}	M = Th^{4+}	M = U^{4+}	Band assignment
3380m, 3310w, b	3380m, 3305m, 3250m, sh	3345m, 3275m, b	3340ms, 3280s, vb	3360m, 3275m, 3240m, sh	3350m, 3270ms, 3250ms	3380s, b, 3290s, vb	3400m, 3275s, 3230m, b	3385s, 3300s, vb	ν_{NH_2}
2960s, 2920s, 2800s, 2720m, 2670m	2980s, 2915s, 2800s, 2735m, 2690m, 2545m	2975s, 2910s, 2805s, 2725w, 2680w, 2560vw	2990s, 2900s, 2815s, 2725w, 2675w, 2550w	2980s, 2900s, 2795s, 2720w, 2675w, 2565w, sh	3000s, 2915s, 2810s, 2730w, 2680w, 2550w	2990s, 2920s, 2820s, 2725w, 2675w, 2555w	2995s, 2915s, 2825s, 2730w, 2670w, 2550w	2990s, 2920s, 2815s, 2725w, 2665w, 2555w	$\nu_{NH} + \nu_{CH}$
1663s	1700vs	1650s, sh, 1628vs	1663vs, 1641vs	1688s, 1640s	1676s, 1639s	1672vs	1664vs	1661vs	δ_{NH_2}
1608m, 1593m, 1560ms	1631w, 1607w, 1580s	1610w, 1561vs, 1539s	1602s, 1578m, 1548m	1605m, 1571ms, 1522m	1614s, 1580m, 1545m	1623w, 1583m, 1525w, sh	1612s, 1599s, 1580s, 1545m, b	1598s, 1576s, 1540mw	$\nu_{C5-C6} + \delta_{NH_2} + \nu_{C4-C5}$
1513w, 1487w	1520w, 1487ms	1508m, 1477mw, b	1485w, 1462mw	1485ms, b	1507m, 1482m	1510vw, 1483w	1490mw, b	1481mw, b	$\nu_{C4-N9} + \delta_{C8-H}$
1442w, 1411m	1443w, 1411ms, 1397ms,	1440w, 1412s, 1371s	1439w, 1419mw, 1383ms	1440w, 1411ms, 1395ms	1436w, 1414ms, 1386ms	1442w, 1416ms, 1383m	1443w, 1416s, 1382ms	1437w, 1410vs, 1399s	$\delta_{CH} + \nu_{C8-N9} + \nu_{N-C-N}$
1345w, 1321w, 1308w	1325m, 1303m	1340m, 1310s	1333mw, 1307m	1337m, 1305ms	1338m, 1309ms	1336m, 1303m	1329m, 1311mw	1332m, 1308mw	$\nu_{C3-C2} + \nu_{C-N-C} + \delta_{CH}$
1272m, 1264m, sh, 1240m, 1210w	1272w, 1251w, 1240s, 1205w	1233m, b, 1200vs	1231m, b, 1200vs	1270w, 1229m, b 1198vs	1234m, b, 1196vs	1274w, 1267w, 1240w, 1228s	1279m, 1241m, sh, 1229vs	1276m, 1242m, sh, 1226vs	$\nu_{N-O} + \delta_{N9-H} + \delta_{C8-H} + \nu_{N7-C8}$ + ring mode
1020w, 971m	1020w, b, 968mw	982w, sh,[d] 964s	1030w, b, 996w, sharp, 954w, b	1023w, 998w, sharp, 952w, b	1026w, 996w, sharp, 952w, b	1020w, 966m	1020w, 967m	1020w, 960m	$\rho_{NH_2} + \nu_{N1-C6}$
		1001svs							$\nu_{V=O}$

[a] Free adH-NO band assignments based on refs. 19–21. [b] $Fe(LH)_2Cl_3$. [c] $Fe(LH)LCl_2$. [d] The strong $\nu_{V=O}$ band at 1001 cm^{-1} masks the ligand absorptions at 1025–985 cm^{-1}.

TABLE III. Metal–Ligand Stretching Mode Band Assignments in adH-NO (LH) Complexes with Metal Chlorides (cm^{-1})[a]

Complex	ν_{M-N6}	ν_{M-Cl}	ν_{M-O1}	ν_{M-Nim}[b]
$Al(LH)_2Cl_3$		453m, 435m		352m, 324w
$VO(LH)Cl_2$	480ms	399ms	363m	
$Cr(LH)LCl_2$	472m	362m, 341mw	451m	286w, b
$Fe(LH)_2Cl_3$	467mw	355w, 326mw, 317mw	439m	
$Fe(LH)LCl_2$	463m	356m, 333mw	440m	280w, b
$Dy(LH)_3Cl_3$		317w	372mw	259m
$Th(LH)LCl_3$		286w, b	391m, 377m	258m
$U(LH)LCl_3$		289w, b	402m, 373m	256m

[a] Free adH-NO main IR bands at 550–230 cm^{-1}: 530m, 488m, b, 446w, sh, 422vw, 403vw, b, 382vw, 354vw, 330vw, 290vw, 281vw, 269vw, 247vw, 230vw, vb. [b] ν_{M-Nim}: ν_{M-N9} or ν_{M-N7}.

TABLE IV. Solid-State (Nujol mull) Electronic Spectra and Ambient Temperature (300 K) Magnetic Properties of the adH-NO (LH) Metal Complexes

Complex	λ_{max} (nm)[a,b]	$10^6\chi_M^{cor}$ (cgsu)	μ_{eff} (μ_B)
$Al(LH)_2Cl_3$	224vvs, 246s, 283s, sh, 308vs, 366m, sh	diamagnetic	
$VO(LH)Cl_2$	221vvs, 244vvs, 277vvs, b, 315vs, 363ms, b, 435m, 504mw, 693w, sh	1223	1.72
$Cr(LH)LCl_2$	240vs, 280vs, 294vs, 312vvs, 341vs, 447ms, 473ms, 566m, 612mw, 665w, b	5998	3.81
$Fe(LH)_2Cl_3$	219vs, 246vs, sh, 267s, sh, 281s, 311vs, sh, 358ms, b, 480m, vb	14,758	5.94
$Fe(LH)LCl_2$	221vs, 243vs, sh, 268s, sh, 284s, 313vs, sh, 361ms, b, 472m, vb	15,422	6.11
$Dy(LH)_3Cl_3$	217vvs, 247vs, 280s, sh, 309vs, 364m, sh, 425w, sh	47,987	10.78
$Th(LH)LCl_3$	222vvs, 244vs, 273s, sh, 290s, sh, 309vs, 360m, sh, 411w, vb	diamagnetic	
$U(LH)LCl_3$	224vvs, 243vs, 279vs, 294vs, 310vs, 361s, sh, 420s, sh, 443ms, b, 475ms, 500ms, 607m, b, 634m, 680m, 732m, 785mw, 871w, b, 916w, 940w, 962w, sh, 1080w, 1245w, sh, 1280w, sh, 1350w, b, 1400w, vb	3296	2.82

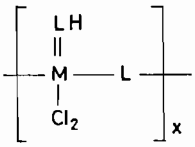
[a] Reported spectrum of the free ligand at pH 7: 231, 262.5 nm [46]. [b] The maxima at 962 and 1350 nm in the spectrum of the U^{4+} complex are due to ligand near-IR absorptions (vibrational overtones and combination bands), which occur at 960 and 1355 nm in free adH-NO [1].

toward lower wavenumbers and a new sharp band at 998–996 cm^{-1} (ρ_{NH_2}). These data favor participation of the N(6) nitrogen in coordination [1, 19, 22, 25, 26]. In $VO(LH)Cl_2$ the single adH-NO ligand coordinates through N(6), but in the Cr^{3+} and the two Fe^{3+} complexes one of the adenine N(1)-oxide ligands does not bind through this nitrogen site, as manifested by NH_2 bands at 1688–1663 and 1030–1020 cm^{-1}. Differences are also observed in the ν_{N-O} spectral region (1300–1190 cm^{-1}) of the complexes. The spectrum of the $AlCl_3$ adduct in this region is almost identical to that of the free ligand, so that it can be concluded that LH does not bind through the O(1) oxygen in this complex [1, 2, 13, 27]. The 3d metal complexes show a clearcut negative ν_{N-O} frequency shift (very strong band at 1200–1196 cm^{-1}), as well as a second band at 1234–1229 cm^{-1}, possibly due to ν_{N-O} splitting; the latter band is broad enough as to mask the ligand absorptions at 1280–1250 cm^{-1} in most of the 3d metal complexes. The preceding features suggest that all the LH and L^- ligands in the 3d metal complexes bind through O(1) [1, 2, 13, 27]. The Dy^{3+}, Th^{4+} and U^{4+} complexes show maxima at 1279–1267 and around 1240, as well as a strong ν_{N-O} band at 1229–1226 cm^{-1}. N-oxide complexes with 4f and 5f metal ions reportedly exhibit rather small negative ν_{N-O} frequency shifts relative to the spectrum of the free ligand [28, 29]. Hence, it appears that some adenine N(1)-oxide ligands bind through O(1) and some do not in the 4f and 5f metal complexes. It should be noted that negative ν_{N-O} frequency shifts in complexes of ligands with N-oxide and other potential binding sites do not always correspond to ligand binding through the N–O function. For instance, among several pyridinecarboxylate N-oxide complexes showing ν_{N-O} shifts to lower wavenumbers [30, 31], some were later found to involve exclusive coordination of the ligands through carboxylato oxygens [32]. However, the dramatic difference between the spectrum of the $AlCl_3$ adduct and those of the rest of the new complexes (ν_{N-O} region), and the identification of ν_{M-O1} maxima in the latter complexes (*vide infra*), provide sufficient evidence in favor of the participation of O(1) in coordination in these compounds.

Additional features in the IR spectra of Table II are shifts and occasional splittings of the ν_{CC}, ν_{CN} and ring vibrations of the ligand upon metal complex formation; these are typical for complexes with adH-NO binding through ring nitrogens or the O(1) oxygen [1, 2, 19, 22, 24, 25]. Finally, $\nu_{V=O}$ appears at 1001 cm^{-1} in $VO(LH)Cl_2$, indicating that this complex is pentacoordinated [33]. The tentative metal–ligand stretching mode assignments (Table III) show ν_{M-N6} ($M = VO^{2+}$, Cr^{3+}, Fe^{3+}) [34] and ν_{M-O1} ($M = VO^{2+}$, Cr^{3+}, Fe^{3+}, Dy^{3+}, Th^{4+}, U^{4+}) [28, 29, 35, 36] bands in the spectra of the complexes that exhibit significant δ_{NH_2} or ν_{N-O} negative frequency shifts. ν_{M-Nim} (im = imidazole) absorptions were identified in the spectra of all the LH–L^- mixed-ligand complexes and the $AlCl_3$ and $DyCl_3$ adducts [1, 2, 4, 37, 38], but were absent from the spectra of the $VOCl_2$ and $FeCl_3$ adducts. The combined evidence from the ν_{M-Cl} [4, 37–42], ν_{M-O}, ν_{M-N} and $\nu_{V=O}$ band assignments favors coordination number five for $M = Al^{3+}$, VO^{2+} [4, 15, 33, 34, 37, [39, 40] and six or seven (Dy^{3+}) for the rest of the new complexes [1, 2, 4, 34–36, 38, 39, 41, 42]. The overall IR evidence favors the presence of bridging O(1), N(7)-bonded [10] adenine N(1)-oxide ligands in the $M(LH)LCl_2$ (M = Cr, Fe), $Dy(LH)_3Cl_3$ and $M(LH)LCl_3$ (M = Th, U) complexes [1, 2, 4]. The location of the ν_{M-Cl} bands in the preceding complexes suggests that all the chloro ligands present are terminal [38–42].

The ambient temperature magnetic moments of the paramagnetic new complexes are normal for $3d^1$, high-spin $3d^3$ and $3d^5$ [43], Dy^{3+} and octahedral U^{4+} [44, 45] complexes (Table IV). The main $\pi \rightarrow \pi^*$ transition bands (231, 262.5 nm) in the UV spectrum of free adH-NO appear in most cases split and show a trend of being shifted to lower energies in the spectra of the new complexes [1]. A band at 300–315 nm in the spectra of the complexes is due to the $n \rightarrow \pi^*$ transition of the ligand [1, 47]. Charge-transfer bands originating in the UV and trailing off into the visible region are also observed, especially in the spectra of the 3d metal complexes [1]. The d–d transition spectrum of the Cr^{3+} complex (${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 447, 473; $\rightarrow {}^4T_{2g}(F)$ 566, 612, 665 nm) is consistent with low-symmetry hexacoordinated Cr^{3+}, and the approximate Dq value of 1628 cm^{-1} is compatible with a $CrO_2N_2Cl_2$ chromophore [1, 2, 40]. The d–d maxima in the $VOCl_2$ adduct (435, 504, 693 nm) are typical for oxovanadium(IV) complexes [40, 48, 49], but can not be used to distinguish between coordination numbers five or six [49]. Finally, the visible and near-IR spectrum of the U^{4+} complex is characterized by multiple and, in most cases, sharp maxima, as is typical for compounds of this metal ion [44, 50].

On the basis of the overall evidence discussed, including the solubilities of the new complexes in organic solvents (see Experimental), the $[M(LH)_2Cl_3]$ (M = Al, Fe) and $[VO(LH)Cl_2]$ adducts are characterized as monomeric. The $AlCl_3$ adduct involves exclusively terminal unidentate imidazole nitrogen-bound LH ligands and is pentacoordinated, but in the hexacoordinated $FeCl_3$ adduct one LH is bidentate chelating O(1), N(6)-bound and the other unidentate O(1)-bound. The single LH ligand in the $VOCl_2$ adduct is chelating O(1), N(6)-bound. Thus, the absorbing species in the preceding adducts are AlN_2Cl_3, FeO_2NCl_3 and $V(=O)ONCl_2$. The remaining new complexes are presumably bi- or poly-nuclear with bridging adenine N(1)-oxide ligands between adjacent metal ions [1, 2, 10, 51]. Most likely binding sites for the bridging LH or L^- ligands are O(1) and N(7) [10]. Probable structural types are **II** for $M(LH)LCl_2$ (M = Cr, Fe); **III** (dimeric) for $Dy(LH)_3Cl_3$ ($DyON_3Cl_3$ absorbing species); and **IV** for $M(LH)LCl_3$ (M = (M = Th, U; MON_2Cl_3 chromophores). LH is bidentate chelating O(1), N(6)-bound in **II**, while in **III** and **IV** the terminal LH ligands are unidentate imidazole nitrogen-bound. N(9) appears to be the preferred binding site for unidentate adH-NO [7]. With respect to the normal room temperature magnetic moments of the di- or poly-meric complexes of types **II**–**IV**, it should be pointed out that the separation between two adjacent metal ions in the linear polymer exceeds 8 Å, since the ligand bridges through O(1), N(7) [10]. Even Cu^{2+} single-bridged polymeric complexes with diazoles or diazines (including purine) and their N-oxides, with Cu–Cu separations of >6.5 Å, show normal ambient temperature magnetic moments and evidence of magnetic exchange only at lower temperatures [52–54]. Hence, no subnormal room temperature magnetic moments were anticipated for the complexes of types **II**–**IV**.

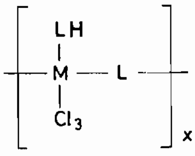


$$\left[\,-\overset{\overset{\text{LH}}{\|}}{\underset{\underset{\text{Cl}_2}{|}}{\text{M}}}-\text{L}-\,\right]_x$$

II

$$\left[(LH)_2Cl_3Dy-(LH)_2-DyCl_3(LH)_2\right]$$

III



$$\left[\,-\overset{\overset{\text{LH}}{|}}{\underset{\underset{\text{Cl}_3}{|}}{\text{M}}}-\text{L}-\,\right]_x$$

IV

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