Iron and Aluminum Trichloride Adducts with Adenine N(1)-Oxide

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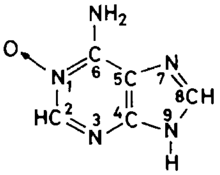
Previous work in these laboratories has dealt with 3d metal perchlorate complexes with adenine N(1)-oxide (I; adH-NO or LH) [1] and purine N(1)-oxide (puH-NO) [2]. Some of these complexes involve exclusively terminal N-oxide ligands, coordinating through one of the imidazole ring nitrogens (N(7) or N(9)), but several other complexes are polymeric with bridging N-oxide ligands, binding through the N–O oxygen (O(1)) and one imidazole ring nitrogen [1, 2]. Finally, in one case ($Fe(LH)_2L(ClO_4)_2$), the overall evidence pointed to a polymeric structural type, involving two bidentate chelating adenine N(1)-oxide ligands, binding through O(1) and the nitrogen of the exocyclic amino group (N(6)), and one bidentate bridging adenine N(1)-oxide group, coordinating through O(1) and one imidazole ring nitrogen [1]. It should be noted that, during earlier studies of adH-NO complexes with 3d metal(II) ions (M = Mn through Zn), the evidence available was interpreted in terms of bidentate chelation of the ligand through N(6) and N(7) [3, 4]. As most of the previously studied metal perchlorate complexes with the above N(1)-oxides contained ethanol ligands, and there was significant overlap between the IR spectral bands of adH-NO or puH-NO with those of the perchlorate group and the ethanol ligands at 1500–600 cm^{-1} [1, 2], we became interested in isolating and characterizing simpler, ethanol- or water-free complexes of these N(1)-oxides with metal salts, whose anionic group does not exhibit IR absorptions in the preceding region, as, for instance, the chloride ion. Accordingly, work in this direction was initiated, and several water- and ethanol-free adducts of metal chlorides with adH-NO were synthesized. The present letter deals mainly with differences, insofar as the apparent ligand binding sites are concerned, between two adducts of the same type, namely the pale pink $Al(LH)_2Cl_3$ and the brown $Fe(LH)_2Cl_3$.

The synthetic procedure employed was as follows: 0.65 mmol $MCl_3 \cdot 6H_2O$ (M = Al, Fe) is dissolved in a mixture of 15 ml triethyl orthoformate and 35 ml ethanol. Then, 1.3 mmol adH-NO is added, and the mixture is refluxed for 2–5 days. Following the refluxive step, the volume of the supernatant is reduced to about one-half its original volume by heating, and the solid complex formed (yield about 40% of the theoretical in both cases) is separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. The new complexes are somewhat soluble in organic media. At this time, the most suitable organic solvent or mixture of solvents for conductance and electronic spectral studies is being sought. The magnetic moment of the ferric complex at 298 K is 5.94 μB.



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Infrared spectra of the complexes, obtained on Nujol mulls between NaCl (4000–600 cm^{-1}) and high-density polyethylene (700–200 cm^{-1}) windows, in conjunction with a Perkin-Elmer 621 spectrophotometer, are generally of excellent quality, being characterized by substantially sharper absorption bands, relative to the adH-NO complexes with 3d metal perchlorates [1]. Pertinent data are given in Table I, in which band assignments were based on the corresponding assignments of Savoie *et al.* for adenine [5], a number of IR studies of aromatic amine N-oxides [6, 7], and our previous work on adH-NO metal complexes [1]. The spectra of both new complexes exhibit ν_{NH} bands, as expected for adducts of neutral adH-NO [1, 2, 8]. The spectrum of the Al^{3+} complex is fairly simple to interpret; in fact, the δ_{NH_2} band of the free ligand at 1663 cm^{-1} undergoes a positive frequency shift upon aluminum complex formation, whilst the ρ_{NH_2} band at 1020 cm^{-1} remains unchanged. These features indicate that the NH_2 nitrogen of the ligand does not participate in coordination [1, 5, 9, 10]. On the other hand, the spectrum of the Al^{3+} complex in the ν_{N-O} region (1300–1180 cm^{-1}) is very similar to that of free adH-NO, so that it can be concluded that the N–O oxygen is also not involved in coordination [1, 2, 11, 12]. Since none of the exocyclic potential ligand sites is involved in coordination in the $AlCl_3$ adduct, it follows that adH-NO uses ring nitrogens as binding sites [1, 2]. In contrast, the IR spectrum of the $FeCl_3$ adduct provides adequate evidence in favor of use of both the NH_2 group nitrogen and the N–O oxygen in coordination. Thus, the splitting of δ_{NH_2} and ρ_{NH_2} into two components at 1688, 1640 and at 1023, 998 cm^{-1}, respectively, is taken as indicative of use of the N(6) nitrogen

TABLE 1. Pertinent Infrared Data for adH-NO and its Adducts with $AlCl_3$ and $FeCl_3$ (cm^{-1}).

adH-NO	$Al(adH\text{-}NO)_2Cl_3$	$Fe(adH\text{-}NO)_2Cl_3$	Band assignment
3380m, 3310w,b	3380m, 3305m, 3250m,sh	3360m, 3275m, 3240m,sh	ν_{NH_2}
2720w, 2670w	2735m, 2690m, 2545m	2725w, 2675w, 2565w,sh	ν_{NH}
1663s	1700vs	1688s, 1640vs	δ_{NH_2}
1608m, 1593m	1631w, 1607w	1605ms,sh	$\nu_{C5-C6} + \delta_{NH_2}$
1560ms	1580s	1571ms	ν_{C4-C5} or $\nu_{N3-C4-C5}$
1513w, 1487m	1520w, 1487ms	1522m, 1485ms	$\nu_{C4-N9} + \delta_{C8-H}$
1345w, 1421w	1325m	1337m	$\nu_{C5-N7-C8}$
1308w	1303m	1305ms	$\nu_{N9-C8} + \nu_{N_3-C_2} + \delta_{CH}$
1272m, 1264m,sh, 1240m, 1210w	1272w, 1251w, 1240s, 1205w	1270w, 1229w, 1198svs	$\nu_{N-O} + \delta_{N9-H}$ + ring mode + $\delta_{C8-H} + \nu_{N7-C8}$
1020w,b	1020w,b	1023w, 998w, sharp	ρ_{NH_2}
		467m	ν_{M-N6}
		439m	ν_{M-O1}
	453m, 435w	355w, 326mw, 317mw	ν_{M-Cl}
	352m, 324m	[a]	ν_{M-Nim}

[a] See text.

in coordination by only a part of the adH-NO ligands present in the complex [1, 9, 13, 14]. Whereas, the appearance of a strong band at 1198 cm^{-1} is obviously due to a substantial shift of the ν_{N-O} mode to lower wavenumbers, and favors participation of the O(1) oxygen of all the adH-NO ligands present in the Fe^{3+} complex in coordination [1, 2, 11, 12]. It should be mentioned at this point that negative ν_{N-O} frequency shifts in metal complexes with N-oxide ligands containing additional potential binding sites, such as the nicotinate and isonicotinate N-oxides, have been attributed in the past to use of the N–O oxygen in coordination [15, 16]; however, crystal structure determinations, performed later, have established that only some of these nicotinate and isonicotinate N-oxide metal complexes involve ligand binding through the N–O oxygen, while in other cases coordination occurs exclusively through carboxyl group oxygens of the ligands [17–19]. This suggests that apparent negative ν_{N-O} frequency shifts for metal complexes with ligands bearing several types of potential binding sites, as, *e.g.*, adH-NO, should be generally interpreted with caution. Nevertheless, comparison of the location of the strongest absorption in the ν_{N-O} region in the spectra of the two new complexes leaves no doubt that ν_{N-O} is practically unaltered for M = Al^{3+} (1240 cm^{-1} band), but shows a $\Delta\nu_{N-O}$ of at least -42 cm^{-1} for M = Fe^{3+} (1198 cm^{-1} band). It is worth noticing, in this connection, that chelation of the N(1)-oxides of adenine and adenosine through O(1) and N(6) has been proposed for several of their metal complexes [1, 4, 11, 20, 21]. As regards metal–ligand stretching vibrations, the tentative band assignments of Table I are in agreement with the preceding conclusions, *viz.*: ν_{Fe-N6} at 467 [22], ν_{Fe-O} at 439 [1, 2, 23] and three ν_{Fe-Cl} bands at 355–317 [24–26] cm^{-1} are consistent with coordination number six and binding of adH-NO through the exocyclic potential ligand sites in the Fe^{3+} adduct. On the other hand, the ν_{Al-Cl} and ν_{Al-Nim} (Nim = imidazole ring nitrogen) absorptions appear at wavenumbers intermediate between those reported for tetra- [27] and hexa- [28] coordinated Al^{3+} complexes with chloro ligands and purines. Hence, coordination number five is most likely for the $AlCl_3$ adduct. It is of interest that in our previous studies of N(6)-bonded metal complexes of adH-NO [1] or adenine [29], we were unable to identify the ν_{M-N6} mode, owing to overlap with either the ν_{M-O}(N–O) [1] or the $\nu_2(ClO_4)$ and ν_{M-O} (aqua or ethanol) [29] absorptions. In the case of the new Fe^{3+} complex, the ν_{Fe-N6} and ν_{Fe-O}(N–O) bands are sufficiently sharp (due to the good resolution of the spectrum), and their maxima are clearly distinguishable, despite the significant overlap of these two absorptions.

The evidence presented suggests that the new metal complexes are probably monomers of the $[M(LH)_2Cl_3]$ type (M = Al, Fe). They differ, however, as far as coordination number and configuration (AlN_2Cl_3 *vs.* $FeNO_2Cl_3$ species) are concerned, because of the use of different adH-NO binding sites in each complex. In the case of the Al^{3+} complex, both adH-NO ligands are monodentate, imidazole nitrogen-bonded (with N(7) and N(9) being equally likely to act as the binding site, as discussed previously [1]). On the other hand, the Fe^{3+} complex seems to contain one bidentate chelating O(1), N(6)-bonded and one monodentate O(1)-bonded adH-NO. However, an alternative structural possibility exists for the $FeCl_3$ adduct: this involves two different bidentate adH-NO ligands (as was the case with the corresponding Fe^{3+} perchlorate complex [1]), *i.e.*, one chelating O(1), N(6)-bonded and one bridging O(1), N(7)-bonded, and a linear oligomeric structure of the $[Fe(LH)_2Cl_2]_nCl_n$ type ($FeN_2O_2Cl_2$ chromophore). Although no distinct $\nu_{\text{Fe–Nim}}$ maximum was detected at 290–270 cm^{-1} [1, 2, 26, 29], a weak, broad absorption is present in the spectrum of the complex in this region, in which free adH-NO shows three very weak maxima at 290, 281 and 269 cm^{-1} [1].

More detailed characterization work on the two complexes herein reported will be presented in a future publication, dealing with a series of metal chloride complexes with adH-NO. So far, we have synthesized complexes of this ligand with VCl_3, $CrCl_3$, $DyCl_3$, $ThCl_4$ and UCl_4, and are working on the isolation of some metal dichloride analogs. Of particular interest is probably the isolation of a lavender-colored VCl_3–adH-NO complex, in which 100% of the vanadium is in the +3 oxidation state. In fact, V^{3+} tends to be partially oxidized by the N–O function of aromatic amine N-oxides, yielding mixtures of V^{3+} and VO^{2+} complexes [11, 30–32]. The fact that V^{3+} does not undergo a redox reaction with adH-NO is probably due to non-direct interaction of this metal ion with tthe N–O function (*i.e.*, coordination of V^{3+} to nitrogen sites of this ligand).

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