Inorganica Chimica Acta, 67 (1982) 173–175

Aluminum Chloride Complexes with Purine, Adenine and Guanine

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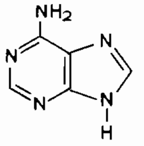
Received June 15, 1982

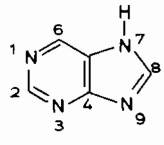
$AlCl_3$ reacts with purines to yield complexes of the $AlLCl_2 \cdot 2H_2O$ type (LH = purine, adenine, guanine). The complexes appear to be polymeric, probably characterized by a linear chain-like $\{Al-L\}_x$ backbone, with coordination number six being attained by the presence of two chloro and two aqua terminal ligands in the first coordination sphere of each Al^{3+} ion.

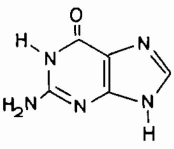
Introduction

Relatively limited information is available on Al^{3+} complexes with purine free bases and their derivatives. The stability constants of Al^{3+} complexes with adenine (adH; *I*) has been correlated to those of the corresponding complexes with other metal ions, as follows: $Fe^{3+} > Cr^{3+} > Al^{3+} > UO_2^{2+} > Be^{2+} > Cu^{2+} > Ni^{2+}$ [1]. It has also been established by means of nmr and i.r. studies that Al^{3+} complexation with adenosine triphosphate (ATP) takes place at neutral or acidic pH [2, 3], but not at alkaline pH [4]. These laboratories have previously reported on synthetic and characterization studies of 3d metal, lanthanide and actinide chloride complexes with purine (puH; *II*) and adH [5–7], as well as 3d metal perchlorate complexes with puH [8], adH [9] and guanine (guH; *III*) [10]. Our studies in this direction were recently extended to include complexes of these ligands with main group metal salts, and the present paper reports on the complexes derived by reaction of $AlCl_3$ with puH, adH and guH. It should be mentioned here that, quite recently, a study of adenine and cytosine complexes with another main group metal chloride ($SnCl_2$) was reported [11].

Experimental


(I)


(II)


(III)

The new complexes were synthesized by a procedure similar to those employed in our previous synthetic work [6, 7, 9, 10], *i.e.*. 0.8 mmol $AlCl_3 \cdot 6H_2O$ is dissolved in a mixture of 35 ml absolute ethanol and 15 ml triethyl orthoformate (teof), and the resultant solution is warmed to 50–60 °C for 2h, under stirring. Then, 1.6 mmol puH, adH or guH is added, and the mixture is refluxed for 2–5 days (depending on the speed of accumulation of the off-white solid complex). Subsequently, the volume of the supernatant is reduced to about one-half its original volume by heating, and the solid complex is separated by filtration, washed with ethanol-teof and stored *in vacuo* over P_4O_{10}. Analytical data show that the three new complexes have analogous stoichiometries, being of the $AlLCl_2 \cdot 2H_2O$ type (L = monodeprotonated purines, *i.e.*, pu^-, ad^-, gu^-); found (calcd.)%:

$Al(pu)Cl_2 \cdot 2H_2O$: C, 24.03(23.74); H, 2.83(2.79); N, 22.37(22.14); Al, 10.37(10.66); Cl, 27.74 (28.02)%.

$Al(ad)Cl_2 \cdot 2H_2O$: C, 22.27(22.41); H, 2.86(3.01); N, 25.95(26.13); Al, 9.77(10.07); Cl, 26.72(26.45)%.

$Al(gu)Cl_2 \cdot 2H_2O$: C, 21.32(21.14); H, 3.06(2.84); N, 24.51(24.66); Al, 9.22(9.50); Cl, 25.13(24.96)%.

The new complexes are generally insoluble in common organic solvents. Their infrared spectra were obtained on KBr pellets (4000–500 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Pertinent IR bands were as follows, cm^{-1} (the corresponding free ligand absorptions are shown in parentheses):

$Al(pu)Cl_2 \cdot 2H_2O$: ν_{OH}(aqua) 3340s,b; A′ pym 8a 1606vs (1613vs); A′ pym 8b 1552vs (1568s); A′ im

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R_1 1486m(1499w); A′ im R_3 1420m,sh(1421s), A′ pym 19a 1394vs(1398vs), ν_{Al-O}(aqua) 528m,b; ν_{Al-Cl} 432w, 415m; ν_{Al-N} 308w, 280w.

$Al(ad)Cl_2 \cdot 2H_2O$: ν_{OH}(aqua) 3330s; NH_2 sym in-plane def. 1662vs,sh(1675vs); A′ pym 8a 1635vvs,b (1600vvs); A′ pym 8b 1557s(1565m,sh); A′ im R_3 1393m(1419ms); NH_2 as out-of-plane def. 1250s (1252s); ν_{Al-O}(aqua) 525w,b, ν_{Al-Cl} 432w, 407w, ν_{Al-N} 304w,b, 279w.

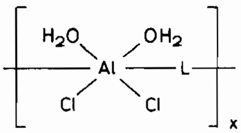
$Al(gu)Cl_2 \cdot 2H_2O$: ν_{OH}(aqua) 3350s,b; ν_{NH} 2880s,b (2900s, 2850s); $\nu_{C=O}$ 1702vs(1705vs); δ_{NH_2} scissoring 1677vs(1680s); ν_{CC} + ν_{CN} and ring vibrations 1600s,sh, 1565s, 1478s, 1470s,sh, 1419m, 1371s (1587m, 1578m, 1477m, 1464m, 1418m, 1375m); δ_{NH_2} rocking 1107m(1100sh); ν_{Al-O}(aqua) 530w,b, ν_{Al-Cl} 435w, 390m; ν_{Al-N} 313w,b, 281w,b.

Discussion

The IR evidence indicates that the new complexes are, in addition to being isostoichiometric, structurally similar. Thus, ν_{OH}(aqua) appears as a well-defined single band, indicative of the exclusive presence of coordinated water [12], in the spectra of all of the new complexes. The various ν_{CC} + ν_{CN} and ring vibrations of puH [13], adH [13–15] and guH [16] undergo significant shifts upon Al^{3+} complex formation; these shifts are suggestive of participation of ring nitrogens of the ligands in coordination [5–10, 13–16]. As far as potential exocyclic ligand sites (*i.e.*, NH_2 (N(6)) nitrogen in adH and C=O (O(6)) oxygen and NH_2 (N(2)) nitrogen in guH) are concerned, it is clear that none of these sites is involved in coordination, as demonstrated by the relative insensitivity of the NH_2 modes of both adH and guH and the $\nu_{C=O}$ mode of guH to Al^{3+} complex formation [14–16]. The presence of anionic monodeprotonated pu^- and ad^- ligands is manifested by the absence of ν_{NH} absorptions at 3000–2500 cm^{-1} in the spectra of the complexes with these ligands [7, 9]; on the other hand, coordinated gu^- shows ν_{NH} bands, since it is the monodeprotonation product of neutral guH, which contains two labile protons at N(1) and N(9). The tentative identification of ν_{Al-O}(aqua) at 530–525 cm^{-1} is consistent with coordination number six for the new complexes [17]; it is worth noticing that all three complexes also show bands at 840–830 and 600–590 cm^{-1}, which can be attributed to the rocking and wagging modes (respectively) of coordinated H_2O [12, 18]. The occurrence of the ν_{Al-Cl} modes at 437–390 cm^{-1} can be interpreted in terms of the presence of exclusively terminal chloro ligands, in hexacoordinated structures. In fact, terminal ν_{Al-Cl} was observed at 502–485 and bridging ν_{Al-Cl} at 396–345 cm^{-1} in tetracoordinated $RAlCl_2$ (R = CH_3, C_2H_5) dimers [19]; hence, the location of the ν_{Al-Cl} bands in the spectra of the new complexes is only compatible with terminal chloro ligands, since the coordination number in these compounds is definitely higher than four. The tentative ν_{Al-N} band assignments at 313–279 cm^{-1} are also in favor of a high coordination number, such as six, for the new complexes. The approximate ν_{Al-N} range for hexacoordinated Al^{3+} complexes with heterocyclic N-ligands can be estimated by comparisons such as the following. The ν_{M-N} mode in $[(CH_3)_2MN{=}P(CH_3)_3]_2$ occurs at 655 cm^{-1} for M = Al and 536 cm^{-1} for M = In [20], while ν_{In-N} appears at 195, 184 cm^{-1} in py_3InCl_3 (py = pyridine) [21]; thus, ν_{Al-N} would be expected to occur at around 300 cm^{-1} in analogs of the latter compound, as well as in the new complexes.

In view of the insolubility of the new Al^{3+} complexes in organic media and the definite tendency of purines to function as bidentate bridging ligands [5–10, 22–24], a linear chain-like polymeric structure with bidentate bridging L groups (L = pu^-, ad^-, gu^-) and exclusively terminal chloro and aqua ligands (*i.e.*, (IV)) is considered as reasonable for these compounds. As regards the actual binding sites of the bridging purines, ad^- and gu^- would certainly be coordinating through N(9) [22, 25, 26], whilst in the case of pu^- N(9) and N(7) are equally likely to function as the primary binding site [5, 7, 8, 24, 26]; usually, the imidazole nitrogen, which is protonated in the neutral free base, is the preferred binding site of the purine ligands [22]. In the case of puH, a crystal structure determination revealed that the solid compound is protonated at N(7) [27], but ^{13}C NMR studies have shown that the N(7)-H and N(9)-H tautomers are of comparable energies [28]; consequently, the actual primary binding site of pu^- or puH is still unknown, since no crystal structure determinations of metal complexes with unidentate pu^- or puH ligands are available. With respect to the second binding site of the ligands, although the coordination of bidentate bridging purines through one imidazole and one pyrimidine nitrogen (N(3), N(9) or N(1), N(7) combinations) has been established for a number of binuclear [22, 23, 29] or oligomeric [22, 30] metal complexes, the only available crystal structure for a single-bridged, linear, chain-like polymeric complex ($[Cu(puH)(H_2O)_4] \cdot SO_4 \cdot 2H_2O$), which is of a similar structural type to that proposed for the new Al^{3+} complexes, reveals that the bridging ligand coordinates through the two imidazole nitrogens, N(7) and N(9), to adjacent Cu^{2+} ions [24]. Hence, it is considered as most likely that the binding sites of the bridging pu^-, ad^- and gu^- ligands in the Al^{3+} complexes herein reported are the N(7), N(9) imidazole nitrogens.

A final point of interest is that the hard Al^{3+} ion coordinates exclusively to ring nitrogens not only in the pu^- and ad^- complexes, but also in the



(IV)

complex with gu$^-$, which contains an exocyclic C=O oxygen potential ligand site. Past experience on complexes of purine or pyrimidine derivatives with oxygen ligand sites indicates that hard metal ions have a greater affinity for oxygen rather than nitrogen potential binding sites (*e.g.*, coordination to phosphate oxygens rather than ring nitrogens in nucleotide metal complexes [31] or the preferential coordination of alkaline earth metal ions to the exocyclic C=O oxygen rather than the ring nitrogen of cytidine [32]). The ligand under discussion (gu$^-$) could conceivably function as a chelating agent for a hard metal ion, showing affinity for oxygen sites, by coordinating through the O(6), N(7) guanine clip [33, 34], but this is not the case, at least for Al^{3+}.

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