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Purine and Adenine Adducts with Ferric Chloride

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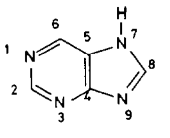
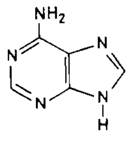
The syntheses and characterization of 3d metal(II) chloride adducts with purine (puH; I) were recently reported by these laboratories [1, 2]. Subsequent studies have dealt with adducts of both puH and adenine (adH; II) with $VOCl_2$ [3], complexes of $DyCl_3$ involving mixed neutral and anionic purine or adenine ligands (*i.e.*, $Dy(LH)LCl_2 \cdot H_2O$; L = puH, adH) [4], and ML_2Cl_2 (M = Th, U) [4] and $AlLCl_2 \cdot 2H_2O$ [5] complexes with anionic pu^- or ad^-. We are currently investigating the types of complexes obtained by analogous preparative interactions of puH or adH with 3d metal (III) chlorides (M = V, Cr, Fe) in ethanol–triethyl orthoformate (teof) [1–5]. It is quite interesting that these three metal trichlorides behave in a different manner under our synthetic conditions. Thus, VCl_3 and $CrCl_3$ clearly react with either puH or adH to yield complexes involving both neutral and anionic nucleobase ligands, *viz.*, $V(LH)_xL_2Cl \cdot 6EtOH$ (x = 1–2) and $Cr_2(LH)_xL_3Cl_3$ (x = 1–2); we are still working towards the isolation of these complexes in sufficiently pure form for characterization. In contrast, $FeCl_3$ easily produces well-defined adducts of the $Fe(LH)_2Cl_3$ type with both puH and adH. The present letter describes the preparation and characterization of these adducts.



(I)



(II)

The following synthetic procedure was employed: 0.8 mmol anhydrous $FeCl_3$ were dissolved in a mixture of 35 ml ethanol and 15 ml teof, and 2.4 mmol puH or adH were subsequently added. The resultant mixture was refluxed for 72 h, and then the volume of the supernatant was reduced to about one-half its original volume by heating, and the solid complex was separated by filtration, washed with ethanol–teof and stored *in vacuo* over P_4O_{10}. It was established later that the puH adduct with $FeCl_3$ can be more easily precipitated by mixing puH and $FeCl_3$ solutions in ethanol–teof, at a 2:1 molar ratio, and stirring the resulting mixture for 5–10 min at 30–40 °C. Analytical results: Found (Calc. for $Fe(LH)_2Cl_3$)%: LH = puH, light brown solid: C 29.72(29.85); H 1.97(2.00); N 27.80(27.85); Fe 13.70(13.88); Cl 26.54(26.43); LH = adH, golden brown solid: C 27.56(27.77); H 2.17(2.33); N 32.62(32.39); Fe 13.08(12.91); Cl 24.73(24.59). Both of the new complexes are only sparingly soluble in organic media.

Table I lists spectral and magnetic data for the complexes. Both these compounds show ν_{NH} absorptions at 2690–2595 cm^{-1}, as expected for complexes of neutral puH or adH [6]. IR ligand bands associated with vibrational modes of the pyrimidine (pym) or imidazole (im) fragments of the ligands undergo significant shifts, as well as occasional splittings, upon adduct formation with $FeCl_3$ [6–8]. These features are consistent with participation of ring nitrogens in coordination [2–8]. As regards the exocyclic (NH_2) nitrogen of adenine, the relatively small shifts of the 1675 and 1252 cm^{-1} NH_2 bands of free adH indicate that this potential binding site is not used for coordination in the $FeCl_3$ adduct [7–9]. The occurrence of two or three ν_{Fe-Cl} bands at 349–318 cm^{-1} is compatible with the exclusive presence of terminal chloro ligands in hexacoordinated configurations [10, 11], which are also supported by the appearance of ν_{Fe-N} at 287–286 cm^{-1} [9, 12]. The UV spectral bands of free puH or adH $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions) [13] exhibit similar types of shifts and splittings upon $FeCl_3$ adduct formation to those previously observed for 3d metal(II) chloride [2] or 3d metal perchlorate (M = Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) [9, 14] complexes with the same ligands. Strong iron-to-ligand charge-transfer absorption [15], originating in the UV and trailing off well into the visible region (absorption maxima at 411–532 nm) is present in the electronic spectra of the new complexes. The room temperature magnetic moments of the two adducts are normal for high-spin Fe^{3+}. This is of interest, as several Fe^{3+} complexes with purine derivatives have been found to exhibit low μ_{eff} values even at room temperature. These include monomeric mixed-ligand (adenine-2,2′-bipyridine) Fe^{3+} low-spin complexes, characterized by μ_{eff} values of 1.9–2.7 μB [16], and several polymeric ferric complexes with guanine [16], adenine [9] and adenosine 5′-monophosphate [17], which show magnetic moments in the 2.39–3.81 μB range, apparently due to spin–spin coupling [9, 16, 17].

Since the new complexes are surrounded by five ligands and the chloro groups appear to be exclusively terminal, it follows that coordination number six can

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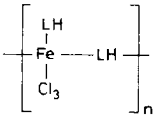
TABLE I. Spectral and Magnetic Data for $Fe(LH)_2Cl_3$ Complexes[a].

	puH	$Fe(puH)_2Cl_3$	adH	$Fe(adH)_2Cl_3$	Band assignment
IR data, cm^{-1}	2725s, b	2675m, vb	2690w, 2600w	2690w, 2595m	ν_{NH}
			1675vs	1673vvs	NH_2 sym in-pl. def.
	1613vs	1603vs, 1581vs	1600vvs, b	1648vs, 1600vs	A′ pym 8a
	1568s	1552vvs	1565m, sh	1570s, sh	A′ pym 8b
	1499w	1483w	1510w	1500w	A′ im R_1
	1421s	1441w, sh	1419ms	1401m, 1392m	A′ im R_3
	1398vs	1399vs	1390w, 1370m	1378m, b	A′ pym 19a
			1252s	1239m	NH_2 as out-pl. def.
		349m, b, 318m		337m, 333m, 321m	ν_{Fe-Cl}
		287w, b		286w, b	ν_{Fe-N}
Electronic spectra, nm	188vs, 204vvs, 252vs, 267vs, 293s, sh, 345m, sh	206vvs, 222vvs, 255vs, 283vs, 304vs, 352vs, sh, 411m, b, 532m, vb	185vvs, 208vvs, 260vs, vvb	208vs, vb, 242vs, sh 274vvs, 289vs, 308vs, 354vs, sh, 420m, b, 525m, vb	
Magnetic data (298 K)					
$10^6\chi_M^{cor}$, cgsu		15,024		16,036	
μ_{eff}, μ_B		6.01		6.21	

[a]Free puH IR band assignments after Lautié and Novak [6]; free adH IR band assignments based on refs. 6–8; ligand Nujol mull UV spectra are in agreement with solution spectra reported by Clark and Tinoco [13].

be attained only if one of the nucleobase ligands acts as bidentate; it is also well established that purines have a pronounced tendency to function as bidentate bridging rather than chelating ligands [18]. It should be noted here that the possibility of the presence of additional ligands, such as water or ethanol, was carefully examined. However, neither the analytical data nor the IR spectra of the complexes at 3600–3100 cm^{-1} (ν_{OH} band region) provided any indication favoring the presence of such ligands. The IR spectrum of the puH adduct is practically absorption-free at 3600–3200 cm^{-1}, whilst that of the adH complex exhibits only the characteristic ν_{NH_2} bands at 3290 and 3120 cm^{-1} [7, 8]. In view of the preceding facts and the very limited solubility of the new complexes in organic solvents, it is considered as most likely that the $FeCl_3$ adducts are linear polymeric species, involving single puH or adH bridging ligands between adjacent Fe^{3+} ions, as shown in III, which also contains three terminal chloro and one terminal puH or adH ligand per ferric ion. Similar structural types have been previously proposed for several 3d metal complexes with puH and adH [2, 3, 9, 14], and were recently substantiated by the crystal structure determination of $[Cu(puH)(OH_2)_4]SO_4 \cdot 2H_2O$, which is indeed a linear chainlike polymer with single bridges of N(7), N(9)-bonded puH [19]. The fact that the new complexes show normal room temperature magnetic moments does not contradict our structural assignment. In fact, linear, chainlike, single-bridged polymeric puH complexes of the $[M(puH)_2(OH_2)_3](ClO_4)_2$ type (M = Co, Ni, Cu) were found to exhibit normal ambient temperature magnetic moments, showing evidence of magnetic exchange interactions only at temperatures below about 110 K [14]. The most likely binding sites of bidentate bridging puH or adH in the new adducts are N(7) and N(9), in view of the recent structural elucidation of the analogous $[Cu(puH)(OH_2)_4]SO_4 \cdot 2H_2O$ [19]. The terminal adH ligand in $Fe(adH)_2Cl_3$ would be certainly N(9)-bonded [9, 20–22]. Regarding the terminal puH ligand in $Fe(puH)_2Cl_3$, it is known that the most likely binding site of unidentate purine derivatives is the imidazole nitrogen protonated in the free base [18]. However, although free puH is protonated at N(7) in the crystal [23], it is established from ^{13}C nmr studies that the N(7)-H and N(9)-H tautomers of this compound are of comparable energies [24]. No complexes with unidentate neutral puH have been structurally characterized thus far; nevertheless, the purinium cation (puH_2^+) has been found to coordinate as unidentate through the N(3) nitrogen in its complex with $CuCl_2$ [25] and through the N(7) nitrogen in $[Zn(puH_2)Cl_3]$ [26]; whereas in the case of complexes with terminal unidentate adH_2^+, a $CuBr_2$ complex was found to involve N(9)-bonded adenium [27] and $[Zn(adH_2)Cl_3]$ N(7)-bonded adH_2^+ [28].


$$\left[-Fe(LH)(Cl_3)-LH- \right]_n$$
(III)

These comparisons might be taken as suggesting that unidentate puH is probably less prone than unidentate adH to use N(9) as its binding site. In light of the preceding discussion, it would be tempting to propose N(7) as the likely binding site of the terminal puH ligand in $Fe(puH)_2Cl_3$, but such a proposal is considered as somewhat *risqué* at this point.

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