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Chromium(III) Chloride Complexes with Purine and Adenine*

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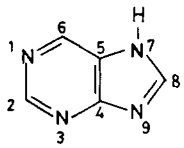
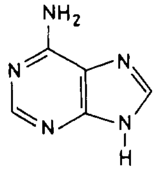
During the course of our synthetic studies of purine (puH; I) and adenine (adH; II) complexes with various metal chlorides [1–6], we isolated two Cr^{3+} complexes with the rather unusual stoichiometry $Cr_3L_5Cl_4 \cdot 2H_2O$ (L = pu^-, ad^-); analyses, found (calcd.)%: L = pu (light olive green): C 32.60(32.31); H 1.92(2.06); N 29.97(30.14); Cr 17.02(16.78); Cl 15.17(15.26); L = ad (dark olive green): C 30.17 (29.89); H 2.40(2.41); N 35.21(34.86); Cr 15.65 (15.53); Cl 13.97(14.12) (Cr to Cl weight ratios of *ca.* 1.1 were confirmed by means of repeated analyses). The new complexes are insoluble in all common organic solvents; this property, in combination with their stoichiometry, is suggestive of polymeric structures. Previous studies of Cr^{3+} complexes with purines include investigations of adH [7, 8], DNA and RNA [9, 10] complexes in aqueous media, and the syntheses of adenosine [11] and guanosine [12] 5′-triphosphate complexes, as well as an adduct of guanine (guH) with $Cr(ClO_4)_3$ [13]. The latter compound is apparently monomeric, of the $[Cr(guH)_2(EtOH)_2(OClO_3)_2](ClO_4)$ type, and, unlike the complexes herein reported, soluble in various organic solvents [13].



(I)



(II)

TABLE I. Spectral and Magnetic Properties of $Cr_3L_5Cl_4 \cdot 2H_2O$ Complexes.[a]

	puH	$Cr_3pu_5Cl_4 \cdot 2H_2O$	adH	$Cr_3ad_5Cl_4 \cdot 2H_2O$	Band assignment
IR data, cm^{-1}					
		3360mw,b		3410mw	ν_{OH}(aqua)
			1675vs	1667vs,sh	NH_2 sym in-plane def.
	1613vs	1630m,sh, 1600s	1600vvs,b	1647vs, 1600vs	A′ pym 8a
	1568s	1553vvs	1565m,sh	1567s	A′ pym 8b
	1499w	1492w	1510w	1494w	A′ im R_1
	1421s	1439m,sh	1419ms	1400s	A′ im R_3
	1398vs	1389m	1390w, 1370m	1382m,b	A′ pym 19a
			1252s	1248m	NH_2 as out-plane def.
		482m,b		490m,b	ν_{Cr-O}(aqua)
		319w, 300w		322w, 299w	ν_{Cr-Cl}
		287w,b		285w,b	ν_{Cr-N}
Electronic spectra, nm					
	188vs, 204vvs, 252vs, 267vs, 293s,sh, 345m, sh	205vvs, 222vvs, 254vvs, 282vs, 308vs, 355vs,sh, 471m,b, 497m,b, 562m,b, 589m,b, 604m,b, 638m,b	185vvs, 208 vvs, 260vs,vvb	207vs,vb, 239vs, sh, 275vvs, 292vs, 309vs, 353vs,sh, 468m,b, 492m,b, 564m,b, 585m,b, 606m,b, 641m,b	
Magnetic data at 298 K					
$10^6 \chi_A^{cor}$, cgsu[b]		5180		5355	
μ_{eff}, μB		3.53		3.59	

[a] IR band assignments after Lautié and Novak for free puH [15], and based on refs. 15–17 for free adH; solid-state (Nujol mull) UV spectra of the free ligands are in agreement with solution spectra reported by Clark and Tinoco [23]. [b] Magnetic susceptibility per Cr^{3+} ion.

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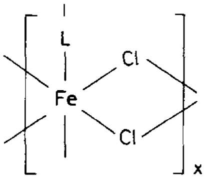
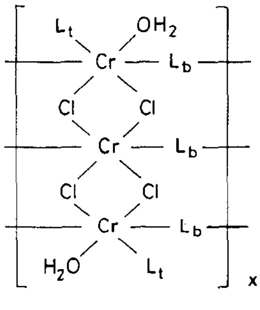
*Ref. 1.

0020-1693/83/$3.00

The syntheses of the new complexes were effected by dissolving 0.8 mmol $CrCl_3$ hydrate in a mixture of 35 ml absolute ethanol and 15 ml triethyl orthoformate (teof), then adding 2.4 mmol puH or adH, and refluxing the mixture for 72 h; subsequently, the volume of the supernatant was reduced to about one-half the original volume by heating, and the solid complexes were separated by filtration, washed with ethanol–teof and stored *in vacuo* over P_4O_{10}. Unlike $VOCl_2$ or $FeCl_3$, which, under the same synthetic conditions, yield adducts of the types $VO(LH)Cl_2$ [3] and $Fe(LH)_2Cl_3$ [5] (LH = puH, adH), $CrCl_3$ reacts with the same ligands to form $Cr_3L_5Cl_4 \cdot 2H_2O$ complexes with the corresponding monoanionic ligands. Characterization data for the new complexes are summarized in Table I. The infrared spectra of the complexes exhibit the characteristic ν_{OH} band of coordinated water at 3410–3360 cm^{-1} [14]. Bands associated with vibrational modes of the imidazole (im) and pyrimidine (pym) fragments of the ligands undergo significant shifts and occasional splittings upon Cr^{3+} complex formation, as would be expected for metal complexes involving coordination of pu^- or ad^- through ring nitrogens [15–17]. On the other hand, bands associated with deformation modes of the exocyclic NH_2 group of adenine are not very sensitive to Cr^{3+} complex formation; this indicates that the adenine ligands are not coordinated through the NH_2 nitrogen in the new ad^- complex [16, 17]. The tentative ν_{Cr-O}(aqua) and ν_{Cr-N} band assignments are consistent with coordination number six for the central Cr^{3+} ions [5, 13, 18, 19]. However, the bands tentatively assigned as ν_{Cr-Cl} occur at significantly lower wavenumbers relative to reported spectra of octahedral Cr^{3+} complexes with terminal chloro ligands (*e.g.*, Cr(pyridine)$_3$Cl$_3$ shows three ν_{Cr-Cl} absorptions at 364, 341 and 307 cm^{-1}) [20]. This may be interpreted in terms of the exclusive presence of bridging chloro ligands in the new complexes [21, 22]. The UV spectral bands of free puH or adH ($\pi \to \pi^*$ and $n \to \pi^*$ transitions) [23] undergo similar shifts and splittings upon Cr^{3+} complex formation to those previously observed for 3d metal chloride [3–5] or perchlorate [18, 24] complexes with the same ligands. Strong chromium-to-ligand charge-transfer absorption [25], originating in the UV and trailing off into the visible region, is also observed in the spectra of the complexes [3–5, 13, 18, 24]. The d–d transition bands in both new complexes appear as split, as follows: $^4A_{2g}(F) \to {}^4T_{1g}(F)$: two maxima at 468–497 nm; $^4A_{2g}(F) \to {}^4T_{2g}(F)$: four maxima at 562–641 nm. These splittings are presumably partly due to low symmetry hexacoordinated configurations [26] and partly due to the presence of at least two different chromophores in the polymeric complexes, *i.e.*, CrN_2Cl_4 and CrN_3OCl_2, on the basis of the proposed likely structural type (*vide infra*). Approximate Dq values are 1672 cm^{-1} for L = pu^- and 1669 cm^{-1} for L = ad^-; these compare to a Dq of 1644 cm^{-1} for $[Cr(guH)_2(EtOH)_2(OClO_3)_2](ClO_4)$ (CrN_2O_4 absorbing species) [13]. The room temperature magnetic moments of both new complexes are subnormal [27]. The magnetic properties of polymeric 3d metal complexes with purines depend on the type of bridging. Thus, Cu^{2+} or Cr^{2+} complexes with multiple purine bridges between adjacent metal ions show subnormal room temperature magnetic moments [18, 28–31]; whereas linear polymeric 3d metal complexes with single purine bridges usually exhibit normal or near-normal ambient temperature magnetic moments, showing evidence of magnetic exchange interactions only at lower temperatures [13, 24, 32]. The complexes under study differ from the latter linear complexes in that they apparently contain chloro-bridges (*vide supra*), in addition to the possible presence of pu^- or ad^- bridges. In this respect, they resemble the polymeric complex $[Fe(uridine)Cl_2]_x$ [33], which shows a decrease of its μ_{eff} from 5.24 μB at 298 K to 1.55 μB at 1.73, owing to strong antiferromagnetic interactions, and for which structural type (III) was proposed (L = uridine) [34]. A reasonable analogous structural type for the new Cr^{3+} complexes would be (IV), which also involves double chloro-bridges between adajcent Cr^{3+} ions ($CrCl_2CrCl_2Cr$ trimeric units), and single bridges of bidentate pu^- or ad^- (L_b) between Cr^{3+} ions of adjacent trimeric units; coordination number six for each of the two end-Cr^{3+} ions of each trimeric unit is attained by the presence of one terminal pu^- or ad^- (L_t) and one terminal aqua ligand. Studies of the temperature dependence of the paramagnetism of the new complexes are planned for the future.



(III)



(IV)

As regards the binding sites of bidentate bridging pu^- or ad^- in structure (IV), use of the N(7) and N(9) imidazole nitrogens is considered as most likely, in view of the recent crystal structure determination of the single-bridged chainlike polymeric $[Cu(puH)(OH_2)_4]SO_4 \cdot 2H_2O$ [35]. Terminal unidentate ad^- would be certainly N(9)-bonded [18, 36–38]. With respect to terminal unidentate pu^-, N(7) may be favored as the preferred binding site, since the site of protonation [28] of free crystalline puH is the N(7) nitrogen [39]; however, in view of the lack of crystal structure determinations of metal complexes with terminal puH or pu$^-$, it would not be advisable to speculate in connection with the most probable preferred binding site of these ligands.

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