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Adenine Complexes with 3d Metal Perchlorates from Ethanol–Triethyl Orthoformate*

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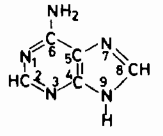
Most of the previously reported metal complexes with adenine (I; 6-aminopurine) and substituted derivatives were prepared from aqueous media, at various pH levels, in order to simulate real-life conditions [2–4]. Quite recently, Guichelaar and Reedijk prepared a series of adenine (AH) and 9-methyladenine (MA) complexes with transition metal salts, by using absolute ethanol as the reaction medium; ethanol was used instead of water, in order to minimize the influence of the solvent upon hydrogen-bonding, which is observed in many AH or MA complexes isolated from aqueous media [5]. During these studies, complexes of the following types were prepared, by refluxing ethanolic solutions of the metal salts with the ligand, at 1:2 (L = AH) or 1:1 (L = MA) ligand to metal molar ratios, for 70 hr: $M(AH)_2Cl_2$ (M = Ni, Zn, Cd), $Cu(AH)_2X_2 \cdot nH_2O$ (X = Cl, Br, NO_3, ClO_4; n = 0–3), $M(MA)X_2$ (M = Co, Ni, Cu, Zn, Cd; X = Cl, Br) and $M(MA)_2(NO_3)_2 \cdot nH_2O$ (M = Co, Ni, Cu; n = 1 or 2) [5]. Similar synthetic attempts at higher ligand to metal ratios than the above invariably resulted in the isolation of products consisting of mixtures of the preceding complexes with uncomplexed ligand. Guichelaar and Reedijk mention that, despite several attempts, they were unable to obtain well-defined manganese complexes with either of these ligands, while it is also obvious that well-defined cobalt complexes with AH could not be isolated [5]. On the other hand, several 1:1 and 2:1 MA complexes with MX_2 (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg; X = Cl, Br, NO_3) were recently prepared either from hot ethanol or by evaporating MA–metal salt aqueous mixtures to dryness and boiling the solid residue with ethanol [6].



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We have been interested in synthetic and characterization studies of purine and adenine metal complexes since 1970, when we prepared most of the complexes herein reported; these studies had to be temporarily discontinued and were resumed less than one year ago. The recent paper of Guichelaar and Reedijk [5] prompts us to report a synthetic procedure by which well-defined complexes of AH or the monodeprotonated adenine anion (A) with all common metal(II) perchlorates (M = Mn, Fe, Co, Ni, Cu, Zn) are rather easily obtained. Under our synthetic conditions, 1.4 mmol hydrated metal perchlorate is dissolved in a mixture of 15 ml triethyl orthoformate (teof), a dehydrating agent [7], and 35 ml ethanol, and warmed at 50–60 °C for 2 hr, under stirring. Then, 2.5 mmol AH (ligand to metal ratio *ca.* 1.8:1) is added to the metal salt solution, and the resultant mixture is refluxed for 48 hr. Subsequently, the supernatant is concentrated to about one-half its original volume, and the solid complexes are separated by filtration, washed with ethanol–teof, and stored *in vacuo* over P_4O_{10}. The above preparations and subsequent handling of the complexes can be performed either under N_2 or in the presence of air, in most cases; however, with Fe^{2+} all these operations were made under dry N_2 and deoxygenated solvents were used, in order to prevent possible oxidation of this metal ion. Under our synthetic procedures, 2:1 adducts of AH with $M(ClO_4)_2$, also containing ethanol, were obtained for M = Mn, Co, Cu; whereas Fe^{2+}, Ni^{2+} and Zn^{2+} perchlorates yielded complexes with anionic A^-, of the $M(A)(ClO_4)$ type, comprising also both ethanol and water. None of these complexes seems to be contaminated with free, uncomplexed AH, as demonstrated by complete elemental analyses (Table I). Since our procedure differs from that of Guichelaar and Reedijk in that teof is used in the solvent mixture and that the supernatant is reduced to half its volume after the refluxing step, it follows that these differences are of key importance in facilitating the formation of metal complexes free of uncomplexed AH.

We are currently continuing our synthetic studies in an attempt at preparing the rest of the $M(AH)_2(ClO_4)_2$ (M = Fe, Ni, Zn) and $M(A)(ClO_4)$ (M = Mn, Co, Cu) complexes of the two series, as well as isolating water- and ethanol-free species, if possible. So far we have succeeded in obtaining a tan-colored compound of the $Co(A)(ClO_4) \cdot xC_2H_5OH \cdot yH_2O$ type, by using a 3:1 AH to Co ratio; this complex,

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*See ref. 1.

TABLE I. Metal Perchlorate Complexes with AH and A.

Complex	Color	μ_{eff}, μ_B[c]	Analysis, % Found (Calc.)				
			C	H	N	Metal	Cl
$Mn(AH)_2(ClO_4)_2\cdot2C_2H_5OH$	Off white[a]	5.72	27.34 (27.28)	3.77 (3.60)	22.88 (22.73)	8.80 (8.92)	11.83 (11.51)
$Fe(A)(ClO_4)\cdot C_2H_5OH\cdot2H_2O$	Tan	4.86	22.14 (22.63)	3.47 (3.53)	19.15 (18.85)	15.32 (15.03)	9.33 (9.54)
$Co(AH)_2(ClO_4)_2\cdot3C_2H_5OH$	Golden brown-orange	5.07	27.76 (28.17)	4.31 (4.14)	20.27 (20.53)	8.89 (8.64)	10.12 (10.39)
$Ni(A)(ClO_4)\cdot C_2H_5OH\cdot2H_2O$	Yellow-green	3.14	22.94 (22.46)	3.59 (3.77)	18.98 (18.71)	15.32 (15.68)	9.09 (9.47)
$Cu(AH)_2(ClO_4)_2\cdot C_2H_5OH$	Violet	1.66	25.19 (24.90)	2.66 (2.79)	23.81 (24.20)	10.70 (10.98)	12.51 (12.25)
$Zn(A)(ClO_4)\cdot C_2H_5OH\cdot3H_2O$	Light yellow[b]	Diamagnetic	20.83 (21.07)	3.69 (3.79)	17.70 (17.54)	16.75 (16.38)	9.07 (8.88)

[a] Photosensitive solid [15a], turning to light grey-green when exposed to light. [b] Fluorescent compound. [c] Magnetic properties determined at 298 K.

TABLE II. Pertinent Spectral Data for the New Metal Complexes.

Compound	NH_2 Deformation Modes, cm^{-1}[a,b]	$\nu_{M-O}(X)$, cm^{-1}		ν_{M-N}, cm^{-1}	d–d transition[d] Spectra λ_{max}, nm
		X = ROH[c]	$X = OClO_3$		
Adenine	1675vs, 1252s, 917s, 722s				
$Mn(AH)_2(ClO_4)_2\cdot2C_2H_5OH$	1672vvs,b, 1247m, 912m, 724m	330m	303m	231s, 220s	
$Fe(A)(ClO_4)\cdot C_2H_5OH\cdot2H_2O$	1661vs, 1252m,sh, 924m, 718m	350m, 321m	306m	244s, 228s	1030mw,b, 1245mw,b
$Co(AH)_2(ClO_4)_2\cdot3C_2H_5OH$	1663vs,b, 1260mw, 927m, 715w,b	345m		251s, 234s	471m, 502m, 611w,sh, 1205w,b
$Ni(A)(ClO_4)\cdot C_2H_5OH\cdot2H_2O$	1637s, 1225m, 902m, 700w,b	387m, 340m	305m	262ms, 227vs	420ms, 720m,b, 1200w,b[e]
$Cu(AH)_2(ClO_4)_2\cdot C_2H_5OH$	1659vs, 1258m, 930m, 731m		343m, b	290s, 280s, 259m	540s,vb
$Zn(A)(ClO_4)\cdot C_2H_5OH\cdot3H_2O$	1657vs,b, 1251m, sh, 920m,b, 726w	365m, 333m		228s, 215s	

[a] NH_2 sym in-plane, asym out-of-plane, sym out-of-plane and asym in-plane deformation modes, respectively [23]. [b] NH_2 deformation bands for $Zn(AH_2)Cl_3$: 1680vs, 1240s, 910s, 718s [9]; and for the recently prepared $Co(A)(ClO_4)\cdot xC_2H_5OH\cdot yH_2O$ product: 1638s, 1230m, 900m, 692w,b. [c] R = H, C_2H_5 or both. [d] Solid-state (Nujol mull) spectra. [e] Dq for Ni^{2+} complex = 833 cm^{-1}.

which is presently under study, shows an ir spectrum (4000– 500 cm^{-1}) almost identical to that of the Ni^{2+} analog (*vide infra*). Our complete study on adenine–3d metal perchlorate complexes will appear in a future publication. Meanwhile, a brief account of the pertinent characterization data for the already available complexes of Table I is given here. Magnetic moments (298 K) are shown in Table I and d–d transition and some infrared spectral data in Table II. The new complexes are generally very sparingly soluble in polar organic solvents, so that molar conductivity determinations could not be performed.

The complexes with the AH ligand exhibit the characteristic ν_{NH} absorption at 2700–2600 cm^{-1} [8], whereas those with the deprotonated anionic A^- ligand do not show absorption maxima in this region, as expected. All of the new complexes show the usual, for adenine metal complexes, shifts and splittings of various ring vibrations at 1610–1300 cm^{-1}, corresponding to both the pyrimidine and imidazole fragments of the ligand [9, 10], as well as ν_{OH} (ethanol and/or water) bands at 3500–3250 cm^{-1} [11, 12]. Tentative ν_{M-O} and ν_{M-N} band assignments (Table II) favor coordination number six in most cases, with the exception of the Cu^{2+} complex, which obviously involves a lower coordination number (probably five) [5, 6, 12–15]. Some clearcut infrared spectral differences between sets of new complexes are as follows. The Co^{2+} and Zn^{2+} complexes show single ν_3 and $\nu_4(ClO_4)$ bands at *ca.*

1080 and 620 cm^{-1}, respectively, and involve, therefore, exclusively ionic perchlorate. The Fe^{2+} and Ni^{2+} complexes show doublets in both of these regions (*ca.* 1110, 1050 and 645, 625 cm^{-1}) and appear to contain exclusively coordinated $-OClO_3$ ligands, whereas the Mn^{2+} and Cu^{2+} complexes exhibit triply split ν_3 and $\nu_4(ClO_4)$ bands, indicative of the presence of both ionic and coordinated perchlorate. The latter four complexes also show ir-active $\nu_2(ClO_4)$ bands at 480–460 cm^{-1} (the ν_1 region is masked by the NH_2 symmetric out-of-plane absorption of the ligand (Table II)) [16, 17]. NH_2 deformation modes: as shown in Table II, the spectra of most of the new complexes exhibit small shifts of these absorptions, relative to the spectrum of free AH. This is normal for metal complexes involving N(9)- or N(3), N(9)-nitrogen-bonded AH or A [9, 10], *i.e.*, the most common modes of coordination of these ligands [2–5, 9, 10, 18–22]. However, the spectrum of the new Ni^{2+} complex (and that of the recently prepared Co^{2+} analog) shows sizeable shifts of all four NH_2 deformation modes to lower wavenumbers. This type of ir behavior may be suggestive of participation of the amino nitrogen in coordination in the Ni^{2+} complex [23], while it might also be that deprotonation of the NH_2 group of AH, resulting in the formation of a NH= group, occurred in this case [24, 25]. In fact, neither coordination of A through the N(9) and N(3) nitrogen nor coordination through the N(1) or N(7) nitrogen with involvement of NH_2 nitrogens in H-bonding to the perchlorato, ethanol or aqua ligands (as in the case of $Zn(AH_2)Cl_3$, which contains N(7)-coordinated adeninium cationic ligand, and involves strong H-bonding between NH_2 hydrogen and a chloro group [26]; the NH_2 deformation bands for this complex [9] given in footnote b of Table II) can account for the ir spectrum of the Ni^{2+} complex.

The Cu^{2+} complex shows a somewhat low magnetic moment (1.66 μB) and its color and d–d transition spectrum are very similar to those of complexes involving the well characterized binuclear, square pyramidal $[(H_2O)Cu(AH)_4Cu(OH_2)]^{4+}$ cation, in which four bidentate N(3), N(9)-bonded AH ligands (protonated at N(7)) act as bridging groups between two Cu^{2+} ions [5, 20, 27]; compounds of this type, as well as other bi- or poly-nuclear adenine-bridged Cu^{2+} complexes, are characterized by antiferromagnetic coupling between cupric ions and exhibit subnormal room temperature magnetic moments [5, 27–29]. The new complex apparently differs from the above cationic complex in that it contains perchlorato instead of aqua ligands, being of the type $[(O_3ClO)Cu(AH)_4Cu(OClO_3)](ClO_4)_2 \cdot 2C_2H_5OH$ (with lattice ethanol). The rest of the new complexes are evidently hexacoordinated, as suggested by the far-ir spectra and the d–d transition spectra of the Fe^{2+}, Co^{2+} and Ni^{2+} compounds [5]. The Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} complexes show normal magnetic moments for high-spin compounds of these metal ions. The stoichiometries of these complexes, combined with their very poor solubility in organic media, may be taken as indicative of bi- or poly-nuclear structures with bidentate bridging AH or A ligands, N(3), N(9)-bonded in most cases, with the possible exception of the Ni^{2+} complex, in which it is conceivable that A is bonded through the NH_2 [10, 23–25] and one of the ring nitrogens (*e.g.*, N(1) [30] or N(7) [10, 24, 31]); although the ir evidence for this complex clearly favors the participation of the NH_2 nitrogen in coordination [10, 23–25], it would be rather naive to make such a structural assignment with any degree of confidence, solely on the basis of this evidence, in view of many similar assignments for adenine metal complexes made in the past, that were later proved wrong when their crystal structures were determined [2, 3, 18]. The few crystal structures reported for AH or A complexes with 3d metal ions other than Cu^{2+}, involve coordination of these ligands as unidentate N(9)-bonded [2–4, 19, 22]; however, it is obvious that they can also function as bidentate toward the metal ions of interest; in fact, in addition to their established function as bidentate briding in many Cu^{2+} [18–21] and organoHg(II) [30] complexes, their coordination as bidentate chelating [10, 23, 24, 31, 32] or bridging [33] has been quite frequently postulated, in order to explain the properties of some of their complexes with transition metal ions. Hence, binuclear AH- or A-double-bridged structures of the $[(C_2H_5OH)_2(O_3ClO)(AH)Mn(AH)_2Mn(AH)(OClO_3)(C_2H_5OH)_2](ClO_4)_2$, $[(C_2H_5OH)(H_2O)_2(O_3ClO)M(A)_2M(OClO_3)(OH_2)_2(C_2H_5OH)]$ (M = Fe, Ni), $[(C_2H_5OH)_3(AH)Co(AH)_2Co(AH)(C_2H_5OH)_3](ClO_4)_4$ and $[(C_2H_5OH)(H_2O)_3Zn(A)_2Zn(OH_2)_3(C_2H_5OH)](ClO_4)_2$ types (with the two AH complexes containing both bridging and terminal (unidentate) adenine), which are compatible with the overall evidence available, can be considered as likely for the new complexes. As regards the insolubility of the complexes reported in organic media, it should be pointed out that it does not necessarily indicate that these compounds are not monomeric. We have considered it as providing positive evidence in favor of bi- or poly-nuclear structures when we recently isolated a ferric perchlorate complex with A^-, which appears to be monomeric of the $[Fe(A)(OClO_3)_2(C_2H_5OH)_3]$ type and dissolves readily in binary mixtures of some polar organic solvents (*e.g.*, acetone–nitromethane). In contrast, no solvent combinations were found for the 3d metal(II) perchlorate complexes, which dissolve with dissociation (color changes) in water and show limited solubility in boiling ethanol, but are insoluble in all other organic solvents examined (including dimethylsulfoxide, N,N-dimethylformamide and hexamethylphosphoramide) and mixtures thereof.

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