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Zinc(II) Complexes of Adenine

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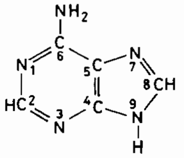
During our studies of adenine (adH; I) complexes with 3d metal perchlorates [1] and chlorides [2] we became interested in further studying the complexation of this ligand with various Zn^{2+} salts, in view of the fluorescent character of both $Zn(ad)(ClO_4)\cdot C_2H_5OH\cdot 3H_2O$ [1] and $Zn(ad)Cl\cdot 2H_2O$ [2]. Accordingly, complexation studies between adH and a wide variety of ZnX_n salts (X = Cl^-, Br^-, I^-, NO_3^-, NCS^-, BF_4^-, ClO_4^-, S^{2-}, CH_3COO^-; n = 2 or 1) were undertaken, and the present letter deals with the types of complexes obtained. Studies of the fluorescence of the new complexes are in progress and will be reported in a future paper.



(I)

Experimentally [1, 2], 1.4 mmol of the metal salt were treated with a mixture of 35 ml ethanol and 15 ml triethyl orthoformate (teof) at 50–60 °C, under stirring, for 2 h; subsequently, 2.5 mmol adH were added and the resultant suspension was refluxed for periods ranging from two to nine days. Immediately after refluxing, the solid complexes were separated by filtration, washed with ethanol–teof and stored *in vacuo* over P_4O_{10}. Characterization was based on elemental analyses and ir spectra (KBr pellets and Nujol mulls between IRTRAN 2 and high-density polyethylene windows, in conjunction with a Perkin-Elmer 621 spectrophotometer).

Zn Halides

The $ZnCl_2$–adH reaction was incomplete after 2 days of refluxing, the solid product consisting of a mixture of $Zn(adH)Cl_2$ and $Zn(ad)Cl$ hydrates; however, after 6 days of refluxing, $Zn(ad)Cl\cdot 2H_2O$ was isolated in pure state. In the cases of $ZnBr_2$ and ZnI_2, no exchange between halide and ad^- ions occurred, even after 9 days of refluxing. The complexes isolated were of the $Zn(adH)X\cdot 2H_2O$ type (X = Br, I). Pertinent ir data for the preceding three complexes and for free adH, cm^{-1}: adH [1–6] (pym: pyrimidine; im: imidazole): ν_{N-H}(im) 2690w,2600w; NH_2 deformation modes 1675vs,1252s,923s,722s; A′ pym 8a 1600vvs; A′ pym 8b 1565m,sh; A′ im R_3 1419ms, spectra of metal complexes [1–11]: $Zn(ad)Cl\cdot 2H_2O$. ν_{OH} 3340w; ν_{N-H}(im) absent; NH_2 def. 1669vs, 1263m,913w,722w; A′ pym 8a 1644vs,1597vs; A′ pym 8b 1558s,sh; A′ im R_3 1412m, 1398s; ν_{Zn-O}(OH_2) 431mw; ν_{Zn-Cl} 279m,259m; ν_{Zn-N} 252mw, 242m. $Zn(adH)Br_2\cdot 2H_2O$: ν_{OH} 3420s; ν_{N-H}(im) 2677m,2598mw,sh; NH_2 def. 1652vs,1244ms,910m, 717m; A′ pym 8a 1630vs,1593vs; A′ pym 8b 1560s, sh; A′ im R_3 1409s, ν_{Zn-O}(OH_2) 349 m; ν_{Zn-Br} 198w,b; ν_{Zn-N} 228w,209w. $Zn(adH)I_2\cdot 2H_2O$: ν_{OH} 3405ms,b; ν_{N-H}(im) 2680m,2602mw; NH_2 def. 1627vs,sh,1211vs,910m,722m; A′ pym 8a 1631vs, 1599vs; A′ pym 8b 1568s; A′ im R_3 1402s; ν_{Zn-O}(OH_2) 357m, 344m; ν_{Zn-N} 230m,213m (ν_{Zn-I} occurs well below 200 cm^{-1}). The Zn–ligand band assignments indicate coordination number five for the Zn chloride complex and six for the Zn bromide and iodide adducts [8–11]. Adenine is exclusively coordinated through ring (im and pym) nitrogens in the Zn chloride and bromide complexes [1–6, 12]. However, the spectrum of the ZnI_2 adduct shows significant shifts of two of the NH_2 deformation bands to lower wavenumbers (1627,122 cm^{-1}), relative to the spectrum of free adH; this is probably due to participation of the NH_2 nitrogen in coordination [1, 2, 5].

ZnS, Zn Acetate

No exchange between S^{2-} or CH_3COO^- and ad^- anions occurred even after nine days of refluxing. The adducts obtained were $Zn(adH)S\cdot 2H_2O$ and $Zn(adH)(CH_3COO)_2\cdot 2H_2O$. Ir spectral data [1–6, 8, 13–15]: ZnS complex: ν_{OH} 3340m,sh,3285s; ν_{N-H}(im) 2670s,b,2595s,sh; NH_2 def. 1655vs,1242vs,907s, 719s; A′ pym 8a 1630vs,sh,1590vs,b; A′ pym 8b 1564vs,sh; A′ im R_3 1409vs; ν_{Zn-O}(OH_2) 361w; ν_{Zn-S} 331ms,311s,273ms; ν_{Zn-N} 245w,207m. Zn acetate complex: ν_{OH} 3305s,vb; ν_{N-H}(im) 2682m, 2596m; NH_2 def. 1660vs,1234m,923m,720s; A′

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pym 8a + ν_{CO_2}, as (CH_3COO^-) 1628s,sh,1599vs; A′ pym 8b 1570s,b; A′ im R_3 1411ms,1391ms; ν_{CO_2}, sym (CH_3COO^-) 1327m; $\nu_{Zn-O}(OH_2)$ 353m; ν_{Zn-O}(CH_3COO^-) 326m,273m; ν_{Zn-N} 241m,210ms. Both of these complexes appear to be hexacoordinated, with adH coordinating through ring nitrogens [1–6, 8]. The acetato ligands act as monodentate, as suggested by the location of the ν_{CO_2} bands [14, 15].

$Zn(ClO_4)_2$, $Zn(BF_4)_2$, $Zn(NO_3)_2$, $Zn(NCS)_2$

In all these cases, complete substitution of one polyanion with one ad^- ligand occurred after refluxing for two days. The complex $Zn(ad)(ClO_4)\cdot C_2H_5OH\cdot 3H_2O$ was reported previously [1], but its pertinent ir bands are given also here, cm^{-1}: ν_{OH} 3415ms,3355ms; ν_{NH}(im) absent; NH_2 def. 1657vs,b, 1251m,sh,928m,b,740w,726w; A′ pym 8a 1635s,sh, 1605s; A′ pym 8b 1575ms,b; A′ im R_3 1406s; ν_3(ClO_4) 1100vvs, b; ν_4(ClO_4) 625ms; ν_{Zn-O}(OH_2 and EtOH) 365m, 333m; ν_{Zn-N}228s,215m. This complex was characterized as a linear polymeric species with bidentate bridging at ligands, coordinating through N(9) and either N(3) or N(7) (the latter designated as N(y)), *i.e.*, $\text{-}[Zn\text{-}N_9N_y\text{-}]_n$; coordination number six is attained by the presence of three aqua and one ethanol terminal ligands per Zn^{2+} ion [1]. The perchlorate group is ionic [1], as manifested by the single character of the ν_3 and ν_4(ClO_4) modes [16]. Similar types of complexes with both water and ethanol ligands were obtained in the remaining three cases, *viz.*: $Zn(ad)(BF_4)\cdot C_2H_5OH\cdot 3H_2O$, $Zn(ad)(NO_3)\cdot C_2H_5OH\cdot 3H_2O$ and $Zn(ad)(NCS)\cdot C_2H_5OH\cdot 2H_2O$. All three complexes are devoid of ν_{NH}(im) absorption, as would be expected. Single ν_3 and ν_4(BF_4) bands at 1062(vs) and 527(mw) cm^{-1}, respectively [17, 18], and ν_3(NO_3) at 1345(vs) cm^{-1} [19, 20], indicate that BF_4^- and NO_3^- are ionic in the respective complexes [17–20]. Evidently, these two compounds involve the same complex cation as the Zn perchlorate analog. Rest of pertinent ir bands, cm^{-1} [1–6, 8, 21, 22]: Zn tetrafluoroborate complex: ν_{OH} 3450s,3362s,b; NH_2 def. 1650vs,1235s,913m, 720w; A′ pym 8a 1628s,sh,1602s; A′ pym 8b 1572s, sh; A′ im R_3 1400s; ν_{Zn-O}(OH_2 and EtOH) 367m, 331m; ν_{Zn-N} 236s,b,211m. Zn nitrate complex: ν_{OH} 3435s,b,3340s,b; NH_2 def. 1642vs,1233s,911m, 717w; A′ pym 8a 1635vs,sh,1599vs; A′ pym 8b 1568s; A′ im R_3 1402s; ν_{Zn-O}(OH_2 and EtOH) 355m,334m; ν_{Zn-N} 239w,b,207s. Finally, the ir spectrum of the Zn thiocyanate complex shows the following pertinent ir absorptions, cm^{-1} [1–6, 8, 23, 24]: ν_{OH} 3435s,b,3345s,b; NH_2 def. 1639vs, 1210s,900w,b,705w,b; A′ pym 8a 1631s,sh,1600s; A′ pym 8b 1570s; A′ im R_3 1407s; ν_{CN} 2052vvs; ν_{CS} 833m; δ_{NCS} 473m; ν_{Zn-O}(OH_2 and EtOH) 357m,341m; ν_{Zn-N}(NCS) 289ms; ν_{Zn-N}(ad) 228m, 211m. The preceding data indicate that the complex involves a coordinated N-bond isothiocyanato ligand [23, 24] and NH_2 nitrogen-bonded ad (significant NH_2 deformation shifts for all four of the bands) [1, 2, 5]; the Zn–ligand band assignments favor coordination number six for the complex under discussion [1–6, 8, 23, 24].

Concluding Remarks

The work herein reported demonstrates that, from a synthetic viewpoint, complexes of purinic bases with metal salts, involving a wide variety of inorganic or organic anions, can be readily synthesized by refluxing mixtures of ligand and salt in ethanol–teof. Adduct formation or exchange between the anion of the salt and the anionic form of the purine apparently depend on the nature of the anionic ligand in the salt and the duration of the refluxing step. Studies currently underway are aimed at the isolation of the whole series of possible complexes, *i.e.*, $Zn(adH)_nX_m$, $Zn(ad)X$ and $Zn(ad)_2$, where X stands for all the anions studied. Our results in this direction, along with a more complete characterization of the complexes herein reported, will be published in the near future. It should be noted at this point that $Zn(adH)_2Cl_2$ has been previously isolated by Guichelaar and Reedijk [25]; also the complex of the adeninium cation, $Zn(adH_2)Cl_3$, has been prepared and its crystal structure determination revealed that adH_2^+ is coordinated through the N(7) nitrogen to Zn^{2+} [26].

Regarding the binding sites of adenine in the complexes reported, which appear to be generally polymeric (insoluble or sparingly soluble in organic media) with bidentate bridging adenine, it is most probable that the majority of the new complexes involve adenine bound through the N(9) and either the N(3) or the N(7) nitrogen [1, 2, 12, 27, 28]. In the cases of the Zn iodide and isothiocyanate complexes, the ir evidence favors coordination of the NH_2 (N(6)) nitrogen; coordination of this site of adenine, although rather rare, is conceivable and seems to occur in certain of its complexes [1, 28–31]; the second binding site in these latter cases would most likely be N(9) [1], as chelation through N(6), N(7) would result in monomeric species, probably soluble in organic media. Hence, the backbone of all the new Zn^{2+} complexes is most probably a linear chainlike polymeric species, involving bidentate bridging adenine ligands (binding sites discussed above; –Zn–L–Zn–L– sequences, where L = adH or ad). Coordination numbers five (Zn chloride complex) or six (rest of the new complexes) are attained by the presence of terminal aqua and ethanol, as well as (depending on the anionic group of the salt) chloro, bromo, iodo, acetato or isothiocyanato ligands. In the ZnS complex, each of the S^{2-} ligands would most likely act as a bridging group between Zn^{2+} ions located in two adjacent –Zn–(adH)–Zn–(adH)– linear chains, resulting in a highly cross-linked polymeric structure. Finally, in three cases ($X = ClO_4$, BR_4, NO_3) the anionic groups present are strictly ionic.

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