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Adenine Complexes with Divalent 3d Metal Chlorides

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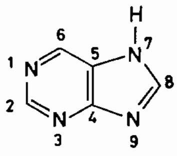
Abstract

Upon refluxing 2:1 mixtures of adenine (adH) and divalent 3d metal chloride hydrates in a 7:3 (v/v) mixture of ethanol–triethyl orthoformate for several days, partial substitution of ad^- for Cl^- ligands occurs, and solid complexes of the $M(ad)Cl \cdot 2H_2O$ (M = Mn, Zn), $Fe_2(ad)(adH)_2Cl_3 \cdot 2H_2O$, $M(ad)(adH)Cl \cdot H_2O$ (M = Co, Cu) and $Ni_2(ad)_3Cl \cdot 6H_2O$ types are eventually isolated [1]. It is probably of interest that during analogous previous synthetic work, involving interaction of ligand and salt in refluxing ethanol, no substitution reactions between Cl^- and ad^- took place, and MCl_2 adducts with neutral adH were reportedly obtained. Characterization studies suggest that the new complexes reported are linear chainlike polymeric species, involving single adenine bridges between adjacent M^{2+} ions. Terminal chloro, adenine and aqua ligands complete the coordination around each metal ion. The new Ni^{2+} complex is hexacoordinated, whilst the rest of the complexes are pentacoordinated. Most likely binding sites are considered to be N(9) for terminal unidentate and N(7), N(9) for bridging bidentate adenine [1].

Introduction

During earlier synthetic work in these laboratories, purine (puH; **I**) [2], adenine (adH; **II**) [3] and guanine (guH; **III**) [4, 5] complexes with divalent 3d metal perchlorates, and puH complexes with the corresponding metal chlorides [6] were prepared by using a mixture of absolute ethanol and triethyl orthoformate (teof) as the medium for interaction of ligand and salt. Purine is soluble in this solvent mixture, and adducts of the types $M(puH)_2(ClO_4)_2 \cdot 3H_2O$ and $M(puH)Cl_2 \cdot nH_2O$ (n = 0–2; M = Mn, Fe, Co, Ni, Cu, Zn) are easily precipitated upon combining ethanol–teof solutions of puH and metal salt [2, 6]. However, neither adenine nor guanine readily dissolve in ethanol–teof, and the synthetic procedure used for the preparation of their 3d metal perchlorate complexes involved refluxing of mixtures of ligand and salt in this medium for several days [3–5]. Under these conditions, Mn^{2+} and Cu^{2+} perchlorates afforded neutral adH adducts, while Fe^{2+}, Ni^{2+} and Zn^{2+} perchlorates yielded complexes with the monodeprotonated ad^- ligand; in the case of Co^{2+} perchlorate, both an adH adduct and an anionic ad^- complex were isolated, under differing synthetic conditions [3]. Likewise, during the corresponding preparative work with guanine, a number of neutral guH adducts (M = Ni, Cu, Zn), gu^- complexes (M = Mn, Fe, Cu) and a mixed-ligand ($guH–gu^-$) Co^{2+} complex were obtained [4, 5]. During subsequent studies, it was established that when a mixture of puH, adH or guH with a metal chloride (M = Al^{3+}, V^{3+}, VO^{2+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Pd^{2+}, Pt^{4+}, Dy^{3+}, Th^{4+}, U^{4+}) in ethanol–teof is refluxed for several days, in some cases adducts of the neutral ligand are formed, and in other cases complexes of the monodeprotonated anionic ligand are isolated [7–11]. In all these cases adducts of the neutral ligand are presumably formed initially, and their stability in ethanol–teof at the reflux temperature determines whether they will be isolated intact or they will be eventually replaced by complexes of the corresponding monoanionic ligand [3–5, 7–11]. It is noteworthy, in this connexion, that during the syntheses of adenine N(1)-oxide complexes with 3d metal perchlorates, the Ni^{2+} and Cu^{2+} salts yielded initially solid adducts of the neutral ligand, which were gradually replaced by complexes of the corresponding monoanionic ligand [12].



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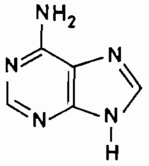

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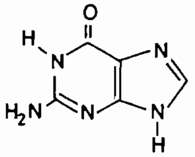

III

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TABLE I. Analytical Data for the New Adenine Metal Complexes.

Complex	Color	C%		H%		N%		Metal%		Cl%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Mn(ad)Cl \cdot 2H_2O$	Cream white	22.53	22.70	3.03	2.94	26.27	25.93	20.61	20.44	13.30	13.52
$Fe_2(ad)(adH)_2Cl_3 \cdot 2H_2O$	Brownish orange	27.36	27.12	2.76	2.77	31.91	32.05	16.96	17.20	16.15	16.31
$Co(ad)(adH)Cl \cdot H_2O$	Violet	31.47	31.76	2.91	3.08	36.70	36.44	15.44	15.25	9.29	9.55
$Ni_2(ad)_3Cl \cdot 6H_2O$	Pale yellow	27.16	26.97	3.65	3.83	31.67	31.34	17.70	17.28	5.34	4.99
$Cu(ad)(adH)Cl \cdot H_2O$	Turquoise	31.10	31.36	2.87	2.80	36.26	36.09	16.45	16.62	9.18	8.89
$Zn(ad)Cl \cdot 2H_2O$	White	21.68	21.75	2.91	2.78	25.28	25.50	23.60	23.84	12.80	13.00

It was of interest to us to isolate and characterize the complexes produced by employing our synthetic procedure [1–12] on mixtures of adH and 3d metal(II) chlorides (M = Mn, Fe, Co, Ni, Cu, Zn). Accordingly, research in this direction was undertaken, and our results are reported in the present paper. It should be mentioned that several studies dealing with the preparation of complexes of adenine or 9-substituted adenines with the same metal chlorides, from either aqueous or non-aqueous media, have been reported previously [13–23]. However, the complexes isolated during the present work differ from those previously reported.

Experimental

Synthetic Procedure

0.8 mmol hydrated metal chloride were dissolved in a mixture of 35 ml absolute ethanol and 15 ml teof. After allowing the metal salt solution to stir at 50 °C for 1 h, 1.6 mmol adH were added and the resultant mixture was refluxed for 6–9 days (until a sufficient quantity of the final solid product was precipitated). During the early stages of refluxing (1–2 days), solids consisting of mixtures of the adH adduct with MCl_2 and products of partial substitution of ad^- for Cl^- groups began forming (as previously reported for the reaction between $ZnCl_2$ and adH [10]). Continuation of the refluxive step led to the eventual replacement of the initial solid products by complexes produced by partial substitution of chloro by ad^- ligands. At this point the refluxive step was discontinued, the mother liquor was condensed to about one-half its original volume by heating under reduced pressure, and the solid complexes were separated by filtration, washed with ethanol–teof, and stored *in vacuo* over P_4O_{10}. Analytical data (Table I) indicate that the metal to Cl atomic ratios range from 2:1 to 2:3; some of the new complexes contain exclusively anionic ad^- ligands (M = Mn, Ni, Zn), while the remaining complexes involve both neutral adH and anionic ad^- ligands (M = Fe, Co, Cu). Coordinated water ligands are present in all of the new complexes, which are generally very sparingly soluble in organic media.

Spectral and Magnetic Measurements

Infrared spectra of the new complexes (Table II) were recorded on KBr discs (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. Solid-state (Nujol mull) electronic spectra and room temperature (298 K) magnetic measurements (Table III) were obtained by methods described elsewhere [24].

Discussion

Several well-defined adducts of adH with 3d metal(II) chlorides, of the $M(adH)Cl_2$ (M = Co, Cu, Zn), $M(adH)_2Cl_2$ (M = Co, Ni, Cu, Zn) and $Cu(adH)_2Cl_2 \cdot 3H_2O$ types were prepared in the past by refluxing mixtures of adenine and metal salt in ethanol for 4–70 h [15, 17]. In contrast, our synthetic procedure led invariably to the isolation of metal complexes involving partial substitution of ad^- for Cl^- ligands (Table I), even after a few hours of refluxing [10] the adH and MCl_2 mixture in ethanol–teof. It appears that inclusion of teof in the interaction medium enhances the tendency for substitution reactions at the expense of simple adduct formation. Another noticeable feature of the present work is that the six new complexes are not characterized by similar stoichiometries, *viz.*: with respect to the M:Cl atomic ratio, most common is the 1:1 ratio (M = Mn, Co, Cu, Zn); nevertheless for M = Fe or Ni, Cl^- substitution by ad^- proceeded, respectively, to a lesser (Fe:Cl = 2:3) or larger (Ni:Cl = 2:1) extent. As regards the nature of the adenine ligands present, the Mn, Ni and Zn complexes are simply substitution products, containing exclusively

TABLE II. Pertinent Infrared Spectral Data for adH and Its 3d Metal(II) Chloride Complexes (cm^{-1}).

adH[a]	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn	Band assignment
	3440ms,sh	3415m,sh	3400ms,sh	3390m,sh	3470m	3400m,sh	ν_{OH}(aqua)
3350sh, 3295s, 3118s	3340vs, 3135vs	3350vs,sh, 3280vs, 3100vs	3360vs,sh, 3300vs, 3110vs	3310vs,b, 3105vs	3360vs,sh, 3310vs, 3115vs	3330vs,b 3100vs,b	ν_{NH_2} region
2985s	2990s,sh	3000s,sh	3000vs	3000s,sh	2990vs	3000s,sh	ν_{CH}
2900m, 2800m, 2690m, 2600m	2870w, 2640w	2915s,sh, 2800s, 2700s, 2580s	2920s,sh, 2790s, 2690s, 2610s	2640w,b	2930s,sh, 2790s, 2680s, 2590s	2660w,b	ν_{NH} region[b]
1675vs	1688vvs	1665vvs	1667vvs	1662vvs	1672vvs	1660vvs	δ_{NH_2}
1600vvs,b, 1565 m,sh, 1508w, 1449m, 1419s, 1369s, 1334s, 1308s	1625vs, 1611vvs, 1565s,sh, 1530m, b, 1455m, 1430m, 1406ms, 1348s, 1295ms	1642vs, 1598vvs, 1560s,sh, 1535m, b, 1460m, 1440m, 1401m, 1392m, 1350m, 1305ms	1646s, 1603vvs, 1563s,sh, 1540m, sh, 1450m, 1411m, 1402m, 1363mw, 1331m, 1305s	1648s, 1606vs, 1570s,b, 1540m, sh, 1440m, 1397m, b, 1350m, 1300s	1650vs, 1608vvs, 1562s,sh, 1538m, 1450m, 1416m, 1403m, 1360mw, 1331m, 1304ms	1644vs, 1597vvs, 1558s, 1533m, 1489m, 1439s, 1398s, 1339s, 1303ms	$\nu_{C=C} + \nu_{C=N}$ + ring vibrations + δ_{HOH}
1252s	1235s	1241m	1247m	1254m	1250m	1244mw	$\nu_{C-NH_2} + \nu_{C-N}$ [21] or δ_{N9-H} + ring mode [26]
1025m	1083m, 1020m	1085w, 1022m	1090w, 1020m	1085w, 1022m	1090w, 1018m	1085w, 1021m	ρ_{NH_2} region
546m, 450m,sh, 330m, 267mw,sh, 225m,b	536m, 450m,sh, 326m, 220w,sh	538m, 450m,sh, 330m,b, 225w,b	532m, 440mw,sh, 318m, 230m,b	530m, 445m,b 340w, 322w, 266w,sh	535m, 440m,sh, 327m, 225w,b	527m, 450m,sh, 348w, 319w, 220w,b	main adH bands at 600–200 cm^{-1}
	436m	440m	445mw	407m,b	460m	431m	ν_{M-O}(aqua)
	286m, 268m,	289m,vvb	291m, 278m	255m, 244m	303m, 286mw	279m, 259m	ν_{M-Cl}
	255w, 243w	263w, 248w	274m, 257m	240w, 221w	280mw, 261mw	252w, 242w	ν_{M-N}

[a] Band assignments for free adH based on refs. 21 and 26. [b] Includes ν_{CH} and combination modes [26, 34].

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of the New Adenine Metal Complexes.

Complex	λ_{max}, nm[a,b]	$10^6 \chi_A^{cor}$, cgsu[c]	μ_{eff}, μB
Mn(ad)Cl·$2H_2O$	192vvs, 207vvs, 241vs,sh, 248vs,sh, 270vs, 311vs,sh, 385s,b, 437m,sh, (960w,b, 1300w,b)	14,822	5.97
Fe_2(ad)(adH)$_2Cl_3$·$2H_2O$	191vs,b, 211vvs, 222vvs,sh, 245vvs,sh, 279vvs,b, 291vvs,sh, 308vs,sh, 420s, 500ms,b, 765ms,sh, 897m,sh, 940w,b, (965m,sh, 1290mw,b), 1400vw,b	12,011	5.37
Co(ad)(adH)Cl·H_2O	196vs,sh, 205vvs, 220vs,sh, 244s, 273vs, 289vs, 310vs, 362s,sh, 540m,b, 635m,sh, 752m,sh, 865w,b, (950w,sh), 995w,b, (1310w,b), 1855w,vb	10,692	5.07
Ni_2(ad)$_3$Cl·$6H_2O$	192vvs, 201vvs, 223vvs,sh, 250vs,sh, 277vs,b, 307s,sh, 392ms,sh, 425ms,b, 641m,b, 745m,sh, 825w,b, (955w,b), 1021w,b, 1233w,b, (1310w,sh)	3938	3.08
Cu(ad)(adH)Cl·H_2O	200vvs,b, 219vvs,sh, 254s,sh, 276vvs, 293vvs, 311s,sh, 393s,sh, 664ms,vb, 782ms,sh, (960w,sh), 1000w,sh, (1300w,b)	1887	2.13
Zn(ad)Cl·$2H_2O$	188vvs, 211vvs, 219vvs,b, 250vs,sh, 279vs, 286vs, 313s,sh, 352w,b, (945vw,b, 1295vw,b)	Diamagnetic	

[a] Solution UV spectrum of adH in trimethyl phosphate, nm: 185, 208 ($A_{1g} \rightarrow E_{1u}$), 260 ($A_{1g} \rightarrow B_{2u}$); the third $\pi \rightarrow \pi^*$ ($A_{1g} \rightarrow B_{1u}$) and the $n \rightarrow \pi^*$ transition, which occur at 240 and 290 nm, respectively, in the spectrum of unsubstituted purine, are masked in the spectrum of adH [46]. [b] The bands shown in parentheses are common in the spectra of adenine metal complexes and presumably arise from vibrational overtones and combination modes originating from adH [15]. [c] Magnetic susceptibility per M^{2+} ion.

monodeprotonated ad$^-$ ligands, but the Fe, Co and Cu compounds contain both neutral adH and anionic ad$^-$ and can be considered as adducts of adH with the Fe_2(ad)Cl_3·xH_2O and M(ad)Cl·yH_2O (M = Co, Cu) substitution products. Finally, aqua ligands are present in all the new complexes, despite the use of teof, a usually effective dehydrating agent [25], during their preparation.

The infrared spectra of adH and its metal complexes have been studied by several research groups 21, 26–28]. Certain band assignments (especially those concerning absorptions with possible contribution of NH_2 modes at 1260–1020 cm^{-1}) differ from work to work [21, 26–28]. We decided to base our assignments in Table II on the two most recent works, *i.e.*, those of Shirotake [21] and Savoie *et al.* [26]. Our data indicate that in no case does the exocyclic NH_2 nitrogen (N(6)) coordinate to the metal ion in the new complexes reported. In fact, the δ_{NH_2} mode of free adH at 1675 cm^{-1} does not undergo shifts as large as those corresponding to N(6)-bonded complexes of this ligand [3, 10, 21, 26–28]. Regarding the 1260–1000 cm^{-1} region, relatively small shifts to lower wavenumbers are observed for the band occurring at 1252 cm^{-1} in free adH, whilst all the complexes exhibit two maxima at 1090–1083 and 1022–1018 cm^{-1}, as was also the case with several complexes (*e.g.*, Zn(adH)Cl_2 and Ca(adH)$_2Cl_2$) involving adH ligands binding exclusively through ring nitrogens [21]. In complexes with N(6)-bonded adenine, no absorption is observed at 1040–1020 cm^{-1}, but a new band appears at 1120–1115 cm^{-1} [26]. It should be noted here that coordination of adenine and derivatives through N(6) is rather uncommon, but it was suggested on certain occasions by spectral evidence or even established by crystal structure determination [3, 10, 26, 29–33]. In the cases under study, adenine presumably coordinates through ring nitrogens. Appreciable shifts and occasional splittings of $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of the ligand at 1650–1300 cm^{-1} are observed in the spectra of the new metal complexes, as would be expected [3, 10, 21, 26–28, 34].

In the 3500–3000 cm^{-1} region, all the new complexes show the ν_{OH} mode of coordinated water at 3470–3390 cm^{-1} [35], and the various ν_{NH_2} bands slightly shifted [21, 26–28]. In the ν_{NH} region (2900–2500 cm^{-1}), the presence or absence of neutral adH ligands is easily detectable. Thus, the Fe^{2+}, Co^{2+} and Cu^{2+} complexes, which contain neutral adH ligands, show four strong ν_{NH} absorption bands [21, 26–28, 34], whereas the Mn^{2+}, Ni^{2+} and Zn^{2+} complexes, which contain only monodeprotonated anionic ad$^-$, exhibit one or two weak maxima in this region. The latter maxima are obviously due to ν_{CH} and combination modes; in fact, purine deuterated at N(7) (the protonation site of puH) reportedly exhibits several weak bands at 2900–2600 cm^{-1} [34].

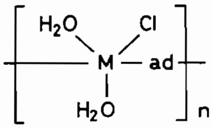
The lower frequency IR spectrum of adH is characterized by several bands of medium to weak intensity at 600–200 cm^{-1} [36, 37], the most prominent of which are shown in Table II. Despite the presence of these absorptions, metal-sensitive bands in the same region were clearcut and readily detectable. Tentative ν_{M-O}(aqua), ν_{M-Cl} and ν_{M-N} band assignments were based on our previous studies of purine and adenine 3d metal(II) complexes [2, 3, 6, 10], and various IR studies of 3d metal complexes with purines [15–17], diazines [38, 39], chloro [6, 15–17, 38–43] and aqua [35, 44, 45] ligands. These assignments are in favor of coordination numbers six for M = Ni and five for the rest of the new complexes [2, 3, 6, 10, 15–17, 35, 38–45]. The metal-sensitive IR bands of the pentacoordinated complexes follow the Irving–Williams series trends of wavenumber increase with metal ion variation, *i.e.*, $Zn^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Cu^{2+}$, as was also the case with puH adducts with 3d metal(II) chlorides [6]. Finally, the location of the ν_{M-Cl} bands detected in the spectra of the complexes favors the presence of terminal chloro ligands [6, 15–17, 38–43].

The $\pi \rightarrow \pi^*$ transition bands of adH at 185, 208 and 260 nm [46] appear shifted and split in the spectra of the complexes, with the overall effect being a trend of shifting to lower energies upon metal(II) complex formation (Table III). Bands corresponding to the $A_{1g} \rightarrow B_{1u}$ and the $n \rightarrow \pi^*$ transitions, which are masked in the UV spectrum of free adH [46], are observed at 244–254 and 307–313 nm, respectively, in the spectra of the metal complexes. UV spectra with similar features were previously observed for adenine complexes with 3d metal perchlorates [3], as well as Co^{3+} [27] and Pt^{2+} [47] salts. Metal-to-ligand charge-transfer absorption [48], originating in the UV and trailing off well into the visible region occurs in the spectra of all the paramagnetic new complexes. In addition to the d–d transition bands, which are discussed below, the spectra of the new complexes show common near-IR absorptions at 945–960 and 1290–1310 nm (given in parentheses in Table III), which are presumably due to vibrational overtones and combination modes originating from the ligand [3, 15].

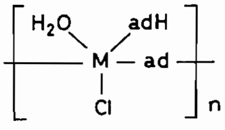
The d–d transition spectrum of the Ni^{2+} complex is compatible with a low symmetry hexacoordinated configuration: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 392, 425; $\rightarrow {}^3T_{1g}(F)$, $^1E_g(D)$ 641, 745, 825; $\rightarrow {}^3T_{2g}(F)$ 1021, 1233 nm [6, 49]. An approximate *Dq* value of 887 cm^{-1}, calculated from this spectrum, is considered as consistent with the presence of alternating NiN_3O_3 and NiN_2O_3Cl chromophores (*vide infra*) in the complex [6, 15]. The d–d spectrum of the Co^{2+} complex is characterized by six maxima at 540–1855 nm and suggestive of coordination number five [6, 49, 50]. The same coordination number is also favored by the presence of at least four maxima at 765–1400 nm in the spectrum of the ferrous complex [6, 51, 52], and the occurrence of the most intense d–d transition maximum at 644 nm in the case of the Cu^{2+} compoumd [3, 6, 15, 53].

The magnetic moments of the metal complexes at 298 K are generally normal for high-spin $3d^5$–$3d^8$ compounds or the $3d^9$ configuration [54]. This does not rule out polymeric structures, which are strongly suggested by the very poor solubility of the complexes in organic media, combined with the pronounced tendency of purines to act as bridging ligands [55]. In fact, linear chainlike polymeric single-bridged purine complexes with 3d metal perchlorates, exhibiting normal ambient temperature magnetic moments, reportedly show evidence in favor of magnetic exchange interactions at lower temperatures (below 120 K) [2]. Similar trends were observed in analogous linear polymeric Cu^{2+} complexes with diazines (including purines) and related ligands [19, 56].

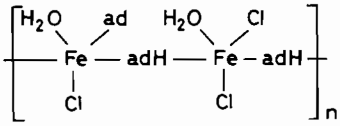
The overall evidence presented favors linear chainlike polymeric structures for the new complexes [2–12]. Likely structural types are as follows: for the pentacoordinated Mn^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} complexes, which involve 1:1 M to Cl atomic ratios, a linear single-bridged backbone (–M–ad–M–ad– sequences) is considered as probable [2–12]; coordination number five is attained by the presence of terminal aqua, chloro and, for M = Co, Cu, adH ligands. Structural type IV would apply for M = Mn, Zn (MN_2O_2Cl absorbing species) and type V for M = Co, Cu (MN_3OCl chromophores). The Fe^{2+} and Ni^{2+} complexes would, of necessity, involve two different absorbing species, in view of their stoichiometries. Most likely structural types for these complexes are **VI** and **VII**, respectively. **VI** involves alternating FeN_3OCl and FeN_2OCl_2 and **VII** alternating NiN_3O_3 and NiN_2O_3Cl chromophores:



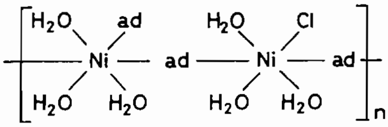
IV



V



VI



VII

As regards the probable binding sites of adenine in the new complexes, it is well established that this ligand tends to bind through the N(9) imidazole nitrogen when acting as terminal unidentate [55, 57–59] (the sole reported exception being Zn(adH_2)Cl_3, in which the adeninium cation coordinates through N(7) to Zn^{2+} [22]). N(9) is also the protonation site of free adH [55]. Thus, the terminal adenine ligands in the new Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes should be binding through N(9). As far as bidentate bridging adenine is concerned, N(9) would again be one of the binding sites, while the second binding site would be either the N(7) imidazole or the N(3) pyrimidine nitrogen (the N(1) pyrimidine nitrogen, although not improbable as a binding site of adenine [21], would be less likely than N(7) or N(3) to function as the second binding site of bidentate bridging adenine). Both the N(3), N(9) [60–62] and N(7), N(9) [32, 63] combinations have been established for Cu^{2+} or CH_3Hg^+ complexes with bidentate bridging adenine or purine, while in the case of a methylmercury(II) complex with tridentate bridging adenine coordination occurs through N(3), N(7) and N(9) [64]. Use of N(7) rather than N(3) as the second binding site of the bidentate bridging ligand in the new metal complexes is considered as most likely, in view of the postulated presence of single adenine bridges between adjacent M^{2+} ions in the polymeric structures **IV–VII**. In fact, N(7), N(9)-bonding was recently established for [Cu(puH)(OH_2)$_4$]$SO_4 \cdot 2H_2O$, which is a linear chainlike polymeric complex with single puH bridges between adjacent Cu^{2+} ions [63]; the same type of bonding is applicable for several 3d metal complexes with purines, which, although polymeric, are characterized by normal or near-normal room temperature magnetic moments [2–6, 8, 9]. In contrast, N(3), N(9)-bonded bidentate bridging adenine has been found so far only in quadruple-bridged dimeric Cu^{2+} complexes [60–62], which are characterized by subnormal magnetic moments even at ambient temperature [3, 5, 18–20, 65–67].

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