Inorganica Chimica Acta, 46 (1980) 235–241

Purine Complexes with Divalent 3d Metal Chlorides*

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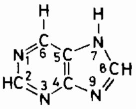
Received April 23, 1980

A series of purine (puH) complexes with 3d metal(II) chlorides were prepared by interaction of ligand and metal salt in ethanol–triethyl orthoformate. 1:1 complexes of the general type $M(puH)Cl_2 \cdot nH_2O$ *(*$n = 0$ *for* $M = Zn$*;* $n = 1$ *for* $M = Fe, Co, Cu$*;* $n = 2$ *for* $M = Mn, Ni$*) were isolated. Spectral evidence favors a tetrahedral configuration for* $Zn(puH)Cl_2$*, and coordination numbers five for* $M(puH)Cl_2 \cdot H_2O$ *(M = Fe, Co, Cu) and six for* $M(puH)Cl_2 \cdot 2H_2O$ *(M = Mn, Ni). The new paramagnetic metal ion complexes are characterized by normal ambient temperature magnetic moments for high-spin* $3d^5$*–*$3d^8$ *compounds or the* $3d^9$ *configuration. A linear oligomeric structural type, involving single-bridged –M–puH–M–puH–sequences and exclusively terminal chloro, and wherever applicable, aqua ligands was considered as most likely for the new complexes. Probable bonding sites of the bidentate bridging puH ligands are the N(3) and N(9) nitrogens.*

Introduction

Metal complexes with various substituted purines of biological interest (*e.g.*, adenine, guanine, hypoxanthine, xanthine, theophylline, 6-mercaptopurine, 8-azapurines and their alkyl derivatives, nucleosides and nucleotides) have been the subject of numerous synthetic and characterization studies in recent years [2, 3]. In contrast, only a few well-defined metal complexes with unsubstituted purine (puH; I) or the monodeprotonated anionic pu^- species have been isolated and characterized, *viz.*: Na(pu) [4], Tl(pu) [5], $Hg(puH)X_2$ (X = Cl, Br) [6], $[Cu(puH)Cl_2] \cdot HCl$, $[Cu(puH)(OH_2)_2]SO_4 \cdot 3H_2O$ [7], $[Cu(pu)_2(NH_3)(OH_2)] \cdot 3H_2O$ [8], $W(CO)_5(puH)$, $[W(CO)_5(pu)]^-$ and $M(CO)(PPh_3)_2(pu)$ (M = Rh, Ir) [9]. The precipitation of solid Co^{2+} and Ni^{2+} complexes with purine was also reported [10], while several species of the $[M(puH)(solvent)_n]^{2+}$ and/or $[M(pu)(solvent)_n]^+$ (M = Co, Ni, Zn) types were identified by means of ^1H NMR spectroscopy of solutions of purine–metal salt mixtures in various solvents [11–13]. Formation constants for metal complexes of purine were determined for various metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) [13–15]; the stabilities of the Cu^{2+} complexes of a number of purines were found to decrease along the series: 6-diethylaminopurine > 2,6-diaminopurine > adenine > purine > hypoxanthine > 7-methylhypoxanthine > 9-methylhypoxanthine > xanthine ⩾ 1,3-dimethylxanthine [15].



(I)

It was felt that synthetic and characterization studies of adducts of puH with 3d metal salts (*e.g.*, chlorides, perchlorates, nitrates) would be worthwhile. Accordingly, research in this direction was undertaken, and the present paper reports on divalent 3d metal (Mn, Fe, Co, Ni, Cu, Zn) chloride complexes with puH.

Experimental

Synthetic Method: Reagent grade puH (Aldrich), hydrated or anhydrous metal chlorides and organic

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*Ref. 1.

TABLE I. Analytical Data for puH Complexes with Metal Chlorides.

Complex	Color	C%		H%		N%		Metal%		Cl%		Water%[a]	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Mn(puH)Cl_2 \cdot 2H_2O$	Cream white	21.30	21.55	2.86	2.83	19.87	20.15	19.48	19.22	25.14	25.40	12.78	12.90
$Fe(puH)Cl_2 \cdot H_2O$	Brownish yellow	22.67	22.98	2.28	2.47	21.15	20.89	21.08	21.38	26.77	27.12	6.80	6.50
$Co(puH)Cl_2 \cdot H_2O$	Violet	22.41	23.02	2.26	2.43	20.91	21.08	21.99	22.24	26.46	26.87	6.72	7.00
$Ni(puH)Cl_2 \cdot 2H_2O$	Yellow green	21.02	21.36	2.82	3.17	19.61	19.77	20.55	20.17	24.81	25.30	12.61	12.20
$Cu(puH)Cl_2 \cdot H_2O$	Turquoise	22.03	21.74	2.22	2.19	20.55	20.49	23.31	23.18	26.01	26.43	6.61	6.90
$Zn(puH)Cl_2$	White	23.42	23.93	1.57	1.82	21.85	22.08	25.50	25.23	27.66	28.15		

[a] Water determinations by Karl Fischer titration.

solvents were generally used. 192 mg (1.6 mmol) puH was dissolved in 15 ml hot absolute ethanol, and the resultant solution was added to a stirred hot (*ca.* 60 °C) solution of 0.8 mmol of the metal chloride in 40 ml of a 1:1 (v/v) mixture of ethanol and triethyl orthoformate (teof). Precipitation was immediate in all cases. The new metal complexes were allowed to remain under the mother liquor overnight and then they were separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaSO_4$. These compounds are stable in moist air and can be generally prepared in the atmosphere; even in the case of the Fe^{2+} complex, which could conceivably be susceptible to oxidation [16], it was established that the same product is obtained either in the atmosphere or by operating in a dry N_2 atmosphere and using previously deoxygenated solvents. It was also established that variation of the puH to MCl_2 molar ratio from 1:1 to 4:1, under the preceding synthetic conditions, does not affect the stoichiometry of the complexes precipitated (1:1 complexes being generally obtained, regardless of the ligand to metal ratio employed).

Spectral and Magnetic Studies: Infrared spectra were obtained on KBr discs (4000–500 cm^{-1}) and Nujol mulls between high-density polyethylene windows (700–200 cm^{-1}) with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and magnetic susceptibility measurements at 294 K were obtained by using apparatus and techniques described elsewhere [17, 18].

Results

The new metal complexes involve 1:1 puH to metal ratios. The Mn^{2+} and Ni^{2+} complexes contain two molecules of coordinated water per metal ion, while the Fe^{2+}, Co^{2+} and Cu^{2+} compounds comprise one aqua ligand per metal ion, and the Zn^{2+} complex is anhydrous (its IR spectrum is devoid of any bands attributable to the presence of coordinated or lattice water). Analytical results (A. Bernhardt Mikroanalytisches Laboratorium, Elbach-über-Engelkirchen, West Germany) are given in Table I. The hydrated new metal complexes do not lose water even after prolonged desiccation *in vacuo*; attempts at their dehydration by heat-treatment at 100–150 °C, under reduced pressure, resulted in partial decomposition of the solid complexes. Some of the complexes (M = Mn, Fe, Co, Ni) are readily soluble in water, while the Cu^{2+} and Zn^{2+} compounds are, respectively, only sparingly soluble and almost insoluble in this medium. The Fe^{2+} and Cu^{2+} complexes are very sparingly soluble in N,N-dimethylformamide, but the rest of the new complexes are insoluble in this solvent. All of the new complexes were found to be generally insoluble in a wide variety of common

TABLE II. Infrared Data for puH Complexes with Metal Chlorides (cm^{-1}).[a]

puH	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn	Band assignment[b]
	3325vs,b	3410vs,vb	3385vs,vb	3320vs,vb	3420vs,vb		ν_{OH} (water)
2725s,b	2690m,b	2680m,b	2685m,b	2675m,b	2695m,b	2670m,b	A′ im (ν_{NH})
1613vs	1632m,sh 1613vs	1640m,sh, 1616vs	1642m,sh, 1616vs	1637ms,sh, 1615vs	1638m,sh, 1612vs	1617s	A′ pym (8a) + δ_{H-O-H}
1568s	1593vs	1596s	1595s	1597s	1592vs	1589s	A′ pym (8b)
1499w	1489s	1488m	1489mw	1488ms,sh	1490m	1481m,b	A′ im (R_1)
1462s	1464ms	1469m, 1464m	1468m, 1462m	1473s, 1469s,sh	1475m,sh, 1464ms	1459ms	A′ pym (19b) + A′ im (R_2)
1421s	1430vs,sh	1435vs,sh	1435s,sh	1439s,sh	1433s,sh	1439m,sh	A′ im (R_3)
1398vs	1410vs, 1382s	1412vs, 1385s,sh	1412vs, 1385s,sh	1411vvs, 1406vvs	1415vs, 1409vs, 1383s,sh	1419vs, 1410vs, 1383s,sh	A′ pym (19a)
1353w	1356w	1360w,sh	1360w,sh	1365w,sh	1360w,sh	1365w,sh	A′ pym (14)
1329s	1333vs	1332s	1333s	1333svs	1332vs	1330vs	A′ im (R_4)
1308w	1294m	1307m, 1301m	1307w, 1300w	1390w,sh, 1303w	1315m,sh	1312ms,sh	
1267vs	1261m	1261m	1262m	1261s	1260mw	1263m, 1260w	A′ im (δ_{NH})
1241sh	1229vs	1231s	1231s	1232svs	1232s	1228s	A′ (δ_{CH})
1212s	1213s	1220m,sh	1215m,sh	1213ms,sh	1205m,b	1215ms	A′ (δ_{CH})
1199sh	1181s	1190ms, 1183sh	1189ms	1191m,sh	1177m	1197m, 1192m	A′ (δ_{CH})
1139w	1129w	1132w	1130w	1140w,sh	1149w	1152w	
1093s	1100s	1109m, 1101m	1110m, 1097m,b	1109m,sh, 1105ms	1117m, 1100ms	1097s	A′ (R)
1037m,b	1041w	1035w,b	1037w,b	1043w,b	1045w,b	1058w,b	
963s	955s	961m	963m	962m	972m	969ms	A′ (R)
938m 922m	927s	919m	930m, 918m,	928ms, 919ms	931w, 911m	930m, 900mw	A″ (γ_{CH})
904s	882mw	880w,b	899w,sh	890w	897w,sh	880w,sh	A′ (R)
861w	867w,sh		875w,b	870w	862w	864w,sh	A″ im (γ_{NH})
800s	793ms	811w	809w,sh	812w, 800m	820w, 797mw	822w	A′ (R)
786m	789s	788m	794m, 788m	791s	783ms, 779m	793s, 785m	A″ (γ_{CH})
720w	722w		715w,b	722w,vb	725w, 705mw	715w,b	
651w	678ms, 663m	666w	669w	670w	674w	669ms, 658w	A′ (R)
635m		634m	633m	639s	628s	638s	A′ (R)
621w	622vvs			622w		620mw	A″ (R)
602vs	607m,sh	608m	606m	606ms	609m		A″ (R)
564m	579m	581mw	583mw	585m	590m	579m	A″ (R)
547mw,sh	562w,sh, 550w,b	560w,sh, 544w	567w, 550w,b	567mw, 539w	569w, 550w,b	555w, 540w,b	
510w,b	492vw	502vw,b	500vw,b	506vw	530w, 497w	510w	
447m	461s	470m,b	471m,b	476mw	477m	462m	A″ (R)
413w	412w	408w,sh	411w	409w,sh	416w,b	415w,b	A″ (R)
	402w,sh	437mw,b	448mw,b	418w	456mw		ν_{M-O} (aqua)
337vw	348vw,b	345vw,b	340vw	349vw,b	350vw,b	345vw,sh	
310vw,b	313vw,b	317vw,b	318vw	314vw	314vw,b		
	252m, 232ms	289m, 270m	219m, 277mw	258mw, 243w	298w, 284mw	312m, 304m	ν_{M-Cl}

(continued overleaf)

TABLE II. *(continued)*

puH	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn	Band assignment[b]
268m	281w, 270w	281m	280mw,sh	283w,	281mw	280m,sh	A″ (R)
	223m, 209ms	261m, 249mw	269m, 254mw	239w, 222w	275mw, 260w	277mw, 242w	ν_{M-N}
230w	238ms,sh	231w	233w	230m,sh	234w	231w	A″ (R)
212mw	215w,sh	211mw	211mw	212mw	210mw	214w, 209m	

[a] Abbreviations: pym, pyrimidine; im, imidazole; R, ring skeletal vibration; s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder. [b] puH band assignments after Lautié and Novak [6, 19].

TABLE III. Solid-state (Nujol Mull) Electronic Spectra and Magnetic Susceptibilities (294 K) of puH Complexes with Metal Chlorides.

Complex	λ_{max}, nm[a,b]	$10^6\ \chi_M^{cor}$, cgsu	μ_{eff}, μB
$Mn(puH)Cl_2 \cdot 2H_2O$	213vvs, 242vvs,sh, 250vvs, 260vvs,sh, 278vs,b, 345s,sh, (1120w,b), (1290w,vb)	14,736	5.91
$Fe(puH)Cl_2 \cdot H_2O$	215vs, 252vvs, 277vvs, 344s, 360s,b, 397s,sh, 770ms,sh, 888m,sh, 965m,b, (1130w,b), (1280w,b), 1360w,vb	11,948	5.32
$Co(puH)Cl_2 \cdot H_2O$	203vvs, 217vvs,sh, 252vs, 274vs, 343s,sh, 550m,b, 633m,sh, 750m,sh, 865w,b, 988w,sh, (1120w,b), (1300w,vb), 1840w,vb	10,279	4.91
$Ni(puH)Cl_2 \cdot 2H_2O$	214vvs, 227vvs, 251vvs,b, 279vvs,b, 341s,sh, 395s,sh, 424m,sh, 637m,b, 747m,sh, 820w,b, 1035w,vb, (1120w,b), 1255w,b,sh, (1295w,vb)	3879	3.03
$Cu(puH)Cl_2 \cdot H_2O$	211vvs, 223vs,sh, 246vs,sh, 252vs, 275vs,vb, 345s,sh, 655ms,vb 770ms,sh, 995w,sh, (1120w,b), (1290w,vb)	1811	2.07
$Zn(puH)Cl_2$	214vvs, 222vvs,sh, 253vvs, 280vvs,b, 344s,sh, (1130w,vb), (1305w,vvb)	Diamagnetic	

[a] UV spectrum of puH (Nujol mull), nm: 188vvs, 204vvs (both $A_{1g} \rightarrow E_{1u}$), 252vs ($A_{1g} \rightarrow B_{1u}$), 267vs ($A_{1g} \rightarrow B_{2u}$), 293s, sh ($n \rightarrow \pi^*$), 345m,sh; $\pi \rightarrow \pi^*$ (188–267 nm) and $n \rightarrow \pi^*$ transition assignments after Clark and Tinoco [35]. [b] Near-IR bands, common in the spectra of all the metal complexes, and apparently due to vibrational overtones and combination bands originating from puH [26] are shown in parentheses; near-IR bands of uncomplexed puH, nm: 1155vw, vvb, 1350vw,vvb.

organic solvents, including methanol, ethanol, acetone, teof, diethyl ether, nitromethane, nitrobenzene, acetonitrile and chloroform. X-ray powder diffraction patterns indicate that the Fe^{2+}, Co^{2+} and Ni^{2+} complexes are amorphous, whilst those with Mn^{2+}, Cu^{2+} and Zn^{2+} are characterized by a low degree of crystallinity. The patterns of the latter three complexes do not show any peaks attributable to the presence of uncomplexed puH.

Table II shows the complete IR spectrum of puH at 1620–200 cm^{-1} [6, 19, 20], with band assignments after Lautié and Novak [6, 19], along with the spectra of the metal complexes in the same region. In addition, the characteristic ν_{OH} absorptions of coordinated water [21] and the A′(ν_{NH}) band of the imidazole fragment of the ligand [6] are also shown. The presence of significant absorption attributable to the latter vibrational mode in the spectra of all the metal complexes ascertains that we are dealing with compounds containing the neutral puH ligand [6]. Table III shows the electronic spectra and the ambient temperature (294 K) magnetic properties of the new complexes. The insolubility of the complexes in organic media precluded the performance of any studies in solution (electronic spectra, molar conductivities, *etc.*).

Discussion

Infrared Evidence (Table II)

The possible participation of both pyrimidine (pym) and imidazole (im) nitrogens in coordination is suggested by shifts of several characteristic ring vibrational modes, attributable to these fragments of puH {*e.g.*, A′ pym (8b) and (19a) [22] and A′ im (R_1) and (R_3) [23]}, upon metal complex formation [6]. Tentative ν_{M-O}(aqua), ν_{M-Cl} and ν_{M-N} band assignments, in the lower frequency ir region, were based on previous studies of 3d metal(II) complexes with various diazine-type ligands [24, 25], including purines [16, 26], as well as chloro [16, 24–31] and aqua [21, 32] ligands. Among the preceding three types of metal-sensitive absorptions, those corresponding to the ν_{M-Cl} modes are the strongest and rather easily distinguishable. They generally consist of a broad absorption with two distinct maxima, and occur at three different spectral regions, as follows: 312–304 cm^{-1} for M = Zn, 298–270 cm^{-1} for M = Fe, Co, Cu and 258–232 cm^{-1} for M = Mn, Ni. These features are consistent with tetra-, penta- and hexa-coordinated configurations, respectively [16, 24–31] which would be also predicted from the stoichiometries of the new complexes [*i.e.*, $Zn(puH)Cl_2$, $M(puH)Cl_2 \cdot H_2O$ (M = Fe, Co, Cu) and $M(puH)Cl_2 \cdot 2H_2O$ (M = Mn, Ni)]. Likewise, the ν_{M-N} band assignments favor coordination number four for M = Zn, five for M = Fe, Co, Cu and six for M = Mn, Ni [16, 24–26]. Finally, regarding the ν_{M-O}(aqua) bands for the hydrated metal complexes, they occur at 456–437 cm^{-1} in the spectra of pentacoordinated Fe^{2+}, Co^{2+} and Cu^{2+} complexes and at 418–402 cm^{-1} in those of the hexacoordinated Mn^{2+} and Ni^{2+} compounds, as would be expected [21, 32, 33]. It is worth noticing that the metal-sensitive IR bands in the spectra of the penta- or hexa-coordinated new complexes generally follow the trends of the Irving–Williams series of wavenumber increase with metal ion variation, *i.e.*, $Fe^{2+} < Co^{2+} < Cu^{2+}$ and $Mn^{2+} < Ni^{2+}$. Far-IR spectra in the region below 200 cm^{-1} were also obtained by using a Perkin-Elmer 181 spectrophotometer, in order to establish whether any ν_{M-Cl} bands, attributable to bridging chloro ligands [26], were present in the spectra of any of the new complexes; in none of the compounds under investigation were metal-sensitive bands at 200–150 cm^{-1} observed.

Magnetic Properties and Electronic Spectra (Table III)

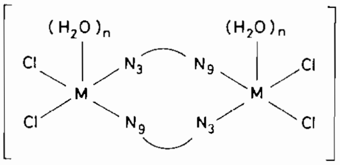
The ambient temperature magnetic moments of the new complexes are generally normal for high-spin $3d^5$–$3d^8$ compounds or the $3d^9$ configuration [34]. The UV bands of free puH [35, 36] show the following changes upon metal complex formation: The $\pi \rightarrow \pi^*$ transition bands at 188–204 and at 267 nm undergo sizeable shifts to lower energies, whereas the $\pi \rightarrow \pi^*$ absorption at 252 nm is practically insensitive to metal complex formation. The $n \rightarrow \pi^*$ transition band at 293 nm is generally masked by the shifted low energy $\pi \rightarrow \pi^*$ absorption, but the shoulder at 345 nm is observed in the spectra of all of the new complexes. Near-IR bands of puH, presumably due to vibrational overtones and combination modes [26], appear somewhat shifted in the spectra of the metal complexes and are shown in parentheses in Table III. Strong metal-to-ligand charge transfer absorption [37], originating in the UV and trailing off into the visible region is also observed in the spectra of the paramagnetic new complexes.

The d–d transition spectrum of the Ni^{2+} complex is compatible with a low symmetry hexacoordinated configuration [38]; band assignments, nm: $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 395, 424; $\rightarrow {}^3T_{1g}(F)$, $^1E_g(D)$ 637, 747, 820; $\rightarrow {}^3T_{2g}(F)$ 1035, 1255. An approximate *Dq* value of 873 cm^{-1}, calculated from this spectrum, seems reasonable for a $NiN_2O_2Cl_2$ absorbing species [26]. The d–d spectrum of the Co^{2+} complex shows at least six maxima at 550–1840 nm and is suggestive of coordination number five (the bands at 750–865 and 1840 nm are particularly in favor of a pentacoordinated configuration) [38, 39]. The presence of more than two d–d maxima at 770–1360 nm in the spectrum of the Fe^{2+} complex also favors a penta- [40] over a distorted hexa- [41] coordinated structure, while the occurrence of the main d–d transition maximum at 655 nm in the spectrum of the Cu^{2+} complex may be attributed to a square pyramidal CuN_2OCl_2 absorbing species [26, 42] (for instance, in binuclear, pentacoordinated, quadruple-bridged adenine (adH) complexes of the $[XCu(adH)_4CuX]^{n+}$ type, with a CuN_4X absorbing species, the main d–d transition maximum occurs at the following wavelengths as X is varied: X = Cl 629 nm, X = Br 602 nm, X = water oxygen 538–559 nm [26], X = $-OClO_3$ oxygen 540 nm [43]). On the basis of the overall evidence, the new Zn^{2+} complex appears to be pseudotetrahedral, the Fe^{2+}, Co^{2+} and Cu^{2+} compounds pentacoordinated (probably square pyramidal) and the Mn^{2+} and Ni^{2+} complexes low symmetry hexacoordinated.

Likely Structural Types

In order to satisfy the preceding coordination numbers, the new metal complexes should involve either bidentate puH and exclusively terminal chloro ligands or unidentate puH and both terminal and bridging chloro groups. Since the latter possibility was ruled out from the far-IR evidence (*vide supra*), it seems most likely that puH is coordinated as a bidentate ligand. Purines do not appear to have any pronounced tendency to function as bidentate chelating agents, but their coordination as bidentate, bridging groups is common [2, 3]. The poor solubility of the new complexes in organic media favors di- or oligo-meric over monomeric structures, whilst the function of puH as a bidentate ligand, coordinating through one pyrimidine and one imidazole nitrogen atom, is suggested by the IR evidence [6] (*vide supra*). The question that arises is which of the puH nitrogens are involved in coordination. Among various biologically important substituted purines, adenine, guanine and xanthine show a pronounced tendency to use the N(9) site in coordination [2, 44–48], but theophylline seems to prefer coordination through the N(7) site [49, 50]. During their function as bidentate bridging, N,N-bonded, these ligands appear to always coordinate through the N(9) site, involving either N(3), N(9)- (in complexes with either neutral or monodeprotonated purines) [2, 44–46] or N(7), N(9)- (in exclusively monodeprotonated purine complexes) [51, 52] bonding; on the other hand, N(1), N(7)-bonding is observed only in bi-or poly-nuclear metal complexes with 9-substituted purines (*e.g.*, 9-methyladenine) [53, 54]. As far as free puH is concerned, it exists in the N(7)-protonated form (I) in the crystal, with the 7H-purine planar molecules joined together in infinite chains by relatively short (2.85 Å) N(7)–H•••N(9) hydrogen bonds [55]. Regarding its coordinating ability, Lautié and Novak pointed out that the N(1), N(3) and N(9) nitrogen atoms are particularly susceptible to act as electron-pair donor sites, in donor–acceptor interactions between 7H-purine and Lewis acids [6].

In light of the preceding discussion, it would appear as most likely that neutral puH would have the tendency to coordinate through the N(9) site, while retaining the N(7)-protonated form; the second site of coordination of the bidentate bridging ligand would have to be either N(1) or N(3). Bridging of puH through the N(1) and N(9) sites is not inconceivable. However, the fact that no metal complexes with N(1), N(9)-bonded purine ligands have been established, combined with the frequent occurrence of N(3), N(9)-bonded, bridging purine ligands [44–46] is considered as being in favor of the latter type of bridging for the complexes herein reported. Hence, di- or oligo-meric structures of types (II) and (III), respectively ($N_3\frown N_9$-bonding sites of bridging 7H-purine; n = 0 for M = Zn; n = 1 for M = Fe, Co, Cu; n = 2 for M = Mn, Ni), are considered as most probable.



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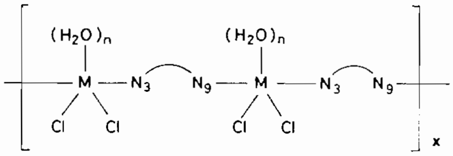

(III)

The linear, single-bridged, oligomeric structural type (III) is considered as more likely than the double-bridged binuclear type (II). In fact, all the paramagnetic new complexes, including the Cu^{2+} compound, are characterized by normal room temperature magnetic moments. Double- or multiple-bridged Cu^{2+} complexes, involving bridging aromatic N or O ligands, are usually magnetically subnormal even at ambient temperature [56–61]. Among complexes of this type, the previously mentioned compounds of the quadruple-bridged $[XCu(adH)_4CuX]^{n+}$ cationic species, as well as the neutral $[(H_2O)Cu(ad)_4\text{-}Cu(OH_2)]$ complex with monodeprotonated adenine, which generally display low room temperature magnetic moments (1.50–1.65 μB) [43, 59–61], are of especial interest as far as the complexes under study are concerned. On the other hand, it is rather well established that linear, single-bridged, polynuclear 3d metal complexes with bridging aromatic diazine or diazole ligands, are usually characterized by normal ambient temperature magnetic moments. Cu^{2+} complexes of the latter type show evidence favoring antiferromagnetic exchange interactions only at lower temperatures; spin–spin coupling between adjacent Cu^{2+} ions occurs in this case, despite the large separation (>6.5 Å) between the magnetic centers, via a π pathway mechanism, involving overlap of the π and π^* orbitals of the heterocyclic ligand with the symmetric and antisymmetric combinations of the metal orbitals [62, 63]. The magnetic evidence available is, therefore, in favor of structural type (III) for the new metal complexes. We intend to undertake studies of magnetic susceptibility variation with temperature in the future, in order to further substantiate this structural assignment. Prior to concluding, it should be mentioned that a series of 3d M^{2+} perchlorate complexes with puH, of the general type $[M(puH)_2(OH_2)_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn), were also recently characterized by these laboratories as involving hexacoordinated structures similar to (III), with one bridging, bidentate, N(3), N(9)-bonded and one terminal unidentate N(9)-bonded puH, as well as three aqua ligands per metal ion [1, 64].

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