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Adenosine Adducts with First Row Transition Metal Perchlorates*

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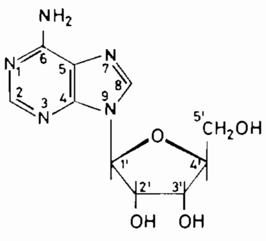
Abstract

Adducts of adenosine (ado) with 3d metal perchlorates were synthesized by refluxing mixtures of ligand and salt in ethanol–triethyl orthoformate. Metal(III) perchlorates formed adducts involving 2:3 metal to ado molar ratio (M = Cr, Fe), *i.e.*, $M_2(ado)_3(ClO_4)_6\cdot4H_2O$, whereas 1:1 adducts were produced by metal(II) perchlorates, as follows: $M(ado)(ClO_4)_2\cdot2H_2O$ (M = Mn, Co, Ni, Cu); and $M(ado)(ClO_4)_2$ (M = Fe, Zn). All the new complexes seem to be polymeric, involving a linear chainlike backbone with single ado bridges between adjacent metal ions in most cases, *i.e.*, $-(-M-ado-)-_n$. The coordination sphere of each metal ion is completed by terminal aqua, ado and, with the exception of the Cu^{2+} complex, $-OClO_3$ ligands, in the case of the hydrated new complexes. Ado would be binding through the N(1) and N(7) ring nitrogens, when functioning as bridging, bidentate. As regards the two water-free M(II) complexes (M = Fe, Zn), which are apparently distorted tetrahedral, the evidence available is interpreted in terms of the presence of tridentate bridging ado, binding through N(1), N(7) in the same fashion as above, and through one of the ribose hydroxyl oxygens, which form weaker bonds to M^{2+} ions located in a neighboring linear polymeric $-(-M-ado-)-_n$ unit; the coordination sphere in these complexes is completed by one $-OClO_3$ ligand.

Intrduction

Adenosine (ado; **I**) metal complexes have been the subject of numerous publications [2, 3]. Most intensively studied were complexes with Pt^{2+} and Pd^{2+}, ranging from simple adducts of the metal halides to complex species involving additional ligands (e.g., aminoacids, NH_3, ethylenediamine) or metal ions (e.g., K^+) [4–14]. Reported complexes of ado with other 4d and 5d metal ions include several MCl_3 (M = Ru, Rh, Ir) [15], MCl_2 (M = Cd, Hg) [16], Rh^{2+} acetate [13, 17] and low-valent W and Rh carbonyl [18–20] adducts, complexes with methylmercury(II) [21] and oxomolybdenum(VI) [22] and the bis(pyridine)osmate(VI) ester of ado [23]. Among compounds of the main group elements, $SnCl_2$ [24] and organotin(IV) chloride [25] adducts, as well as diorganotin(IV) complexes with anionic adenosine [26] were reported. Regarding complexes of 3d metal ions with ado, there is relatively little information, especially as far as solid complexes synthesized are concerned. Thus, adducts with M^{2+} chlorides (M = Co, Ni, Cu, Zn) have been prepared [16], while these laboratories presented the preparations and some characterization data of 3d metal perchlorate (M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) adducts with ado in preliminary communications [1, 27]. Now our studies have been completed and are the subject of the present paper. Some additional solid 3d metal complexes with ado, including Co^{3+} [28, 29], Cu^{2+} [30] and Mn carbonyl [18] complexes, were previously reported, while numerous spectral and magnetic studies of the interaction of ado with 3d metal salts and complexes, as, for instance, with $CuCl_2$ [31] and Cu^{2+}–glycylglycine [32], have also appeared.



I

Ado has four potential nitrogen binding sites, *i.e.*, the pyrimidine N(1) and N(3) and the imidazole

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N(7) ring nitrogens, and the N(6) nitrogen of the exocyclic NH_2 group. Since N(9), which is the preferred binding site of adenine (adH) [33], is blocked by the ribose substituent in ado, N(7) becomes the primary binding site of the latter ligand when it is acting as terminal unidentate, with N(1) and N(7) being the most common binding sites of bridging bidentate ado [7, 13, 34–36]. This is substantiated by several crystal structures available for complexes with ligands analogous to ado, *i.e.*: 2′-deoxyadenosine (dado) is unidentate N(7)-bonded in $[Co(dado)(acac)_2(NO_2)]\cdot 2H_2O$ (acac = acetylacetonato ligand) [37] (the corresponding ado complex has been also prepared [29]); 9-methyladenine (mad) acts as bridging N(1), N(7)-bonded in its 1:1 adducts with $CoCl_2$ [38] and $ZnCl_2$ [39], while adenine N(1)-oxide is bridging O(1), N(7)-bonded in $[(adH-NO)HgCl_2]_2$ [40]. Binding of ado through N(3) would be unlikely, owing to the steric hindrance introduced by the ribose substituent at N(9) [41]. On the other hand, use of the exocyclic N(6) nitrogen as binding site is rather uncommon for ado, but is apparently facilitated upon N(1)-oxidation of this compound [4]. In fact, whereas ado seems to be N(7)-bonded in its PtX_2 (X = Cl, Br) complexes, the corresponding adenosine N(1)-oxide complexes clearly involve ligand binding through N(6), probably due to chelation via O(1), N(6) [4]. It should be noted, in this connexion, that a recent crystal structure determination of a Cu^{2+} complex with doubly deprotonated adenine N(1)-oxide revealed chelation of the ligand through O(1), N(6) [42]. As regards the hydroxyl oxygens of the ribose fragment of ado (O(2′), O(3′) and O(5′)), they may enter in competition with nucleobase binding sites, especially in the absence of water [3]. Alkali or alkaline earth metal ions will often coordinate to the O(2′), O(3′) chelating site of ribose, and several crystal structures reported established coordination of both or at least one of these oxygens in nucleotide complexes with Na^+ [43], Rb^+ [44], Ba^{2+} [45] or Cd^{2+} [46]. Cu^{2+} or Co^{3+} coordination to ribose oxygens of nucleosides or nucleotides has been observed in non-aqueous media [47] or at high pH (>10 or >8, respectively) [48, 49]. In several other studies, binding of ribose nucleoside oxygens either exclusively or concurrently with purine or pyrimidine binding sites was postulated as most compatible with the spectral and magnetic properties of Cu^{2+} [50, 51], Mn^{2+} [52], Fe^{2+} [53, 54] and Sn^{2+} [24] complexes. The O(2′), O(3′) oxygens of ado are chelated to Os^{6+} in the bis-(pyridine)osmate(IV)–ado ester [23], while similar type of chelation appears to occur in several organotin(IV) complexes with nucleosides [26, 55]. Finally, the crystal structure determination of a polymeric Cu^{2+} complex with guanosine 2′-monophosphate revealed that each Cu^{2+} ion has a distorted [4 + 2]-octahedral symmetry, and is coordinated to three different ligand molecules via two mutually *trans*-equatorial Cu–N(7) bonds and one axial Cu–O(5′) longer bond; the coordination sphere is completed by three aqua ligands [56].

For adducts of the type herein reported, the adenine ring nitrogens of ado would be expected to function as primary binding sites, *i.e.*, N(1), N(7) for bridging bidentate and N(7) for terminal unidentate ado. Participation of ribose oxygens in coordination could arise by cross-linking between linear $-(-M-ado-)-_n$ polymeric units, involving single bridges of N(1), N(7)-bonded ado between adjacent metal ions. In our preliminary studies, we proposed that ado is exclusively coordinated through adenine ring nitrogens in all its hydrated metal perchlorate adducts isolated (M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}), but may also involve participation of ribose oxygens in coordination in the two water-free adducts prepared (M = Fe^{2+}, Zn^{2+}) [1, 27]. Our completed studies tend to support these conclusions.

Experimental

The new metal complexes were prepared by refluxing 2:1 (for M^{2+}) or 3:1 (for M^{3+}) molar mixtures of ado and hydrated metal perchlorate in a 7:3 (v/v) mixture of ethanol–triethyl orthoformate

TABLE I. Analyses of ado Adducts with Metal Perchlorates

Complex	Color	Yield %	C%		H%		N%		Metal%		Cl%	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Cr_2(ado)_3(ClO_4)_6\cdot 4H_2O$	ash gray	43.7	22.89	23.12	3.01	2.88	13.34	13.21	6.60	6.72	13.51	13.49
$Mn(ado)(ClO_4)_2\cdot 2H_2O$	beige	16.8	21.56	21.77	3.08	3.15	12.57	12.69	9.86	10.14	12.73	12.60
$Fe(ado)(ClO_4)_2$	mustard yellow	49.1	23.01	22.79	2.51	2.50	13.42	13.76	10.51	10.44	13.58	13.28
$Fe_2(ado)_3(ClO_4)_6\cdot 4H_2O$	yellow green	50.0	22.77	22.87	2.99	2.75	13.28	12.97	7.06	7.29	13.44	13.79
$Co(ado)(ClO_4)_2\cdot 2H_2O$	brick red	43.0	21.41	21.84	3.05	2.87	12.48	12.70	10.50	10.88	12.64	12.93
$Ni(ado)(ClO_4)_2\cdot 2H_2O$	green	51.4	21.41	21.65	3.05	3.16	12.49	12.24	10.47	10.31	12.64	12.38
$Cu(ado)(ClO_4)_2\cdot 2H_2O$	dark green	69.7	21.23	21.45	3.03	2.76	12.38	12.30	11.23	11.42	12.53	12.21
$Zn(ado)(ClO_4)_2$	off white	77.6	22.60	22.99	2.47	2.33	13.18	13.34	12.30	12.27	13.34	13.58

TABLE II. Relevant Infrared Spectral Data for ado and its Metal Perchlorate Adducts (cm^{-1})

ado[a]	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Cu^{2+}	M = Zn^{2+}	Band assignment
	3390s,vb	3440s,b		3440s,b	3430s,b	3420s	3420s,b		$\nu_{\mathrm{OH}}(\mathrm{H_2O})$
3460m, 3400ms	b	b	3460m, 3440ms, 3400ms, 3380s,sh	b	b	b	b	3460m, 3440m, 3400ms, 3375s	ν_{OH}(ribose)
3335s, 3160s	3160s,sh	3350s, 3160ms	3340s, 3160s	3345s, 3160s	3340ms, 3150m	3340s, 3175s	3350ms, 3155m	3340s, 3155s	$\nu_{\mathrm{NH_2}}$
2920m, 2840mw	2925ms, 2850m	2940m, 2840w	2930m 2840w	2950mw, 2860w	2935m, 2850mw	2925mw, 2845w	2920m, 2835mw	2920m, 2840w	ν_{CH}
1670vs	1689vs	1697m, 1660s	1687m, 1672s	1680s	1707m, 1658s	1705m, 1668s	1702m, 1660s	1675s,b	$\delta_{\mathrm{NH_2}}$
1652ms,sh, 1605ms, 1572m, 1537m, 1470m, 1450m,sh, 1411m, 1387w, 1338ms, 1299s	1645s, 1630s, vb, 1592s, 1577ms, 1540w, 1510w, 1470w, 1417mw, 1390m, 1365w, 1305mw	1642s, 1625s, 1590s, 1570s, 1523m, 1509mw, 1465w, 1441ms, 1405m, 1353ms, 1330ms, 1295mw	1654s, 1646ms, 1611s, 1579m, 1540w, 1510w, 1472m, 1450w, 1411m, 1390w, 1370w, 1330m, 1299ms	1650s, 1630s, 1580m, 1540w, 1508w, 1469w, 1420m, 1390m, 1360w, 1302mw	1640s, 1600s, 1578m, 1529s, 1510m, 1465w, 1445s, 1408m, 1340s, 1302m	1649s, 1608s, 1573m, 1529s, 1510m, 1470mw, 1448s, 1413s, 1400s, 1345s, 1330s, 1303m	1646s, 1612s, 1580s, 1530s, 1444s, 1412s, 1385m, 1335s, 1300m,sh	1652s, 1643m, 1610s, 1579m, 1540w, 1512w, 1475m, 1450m, 1412m, 1390w, 1370w, 1332m, 1301ms	$\nu_{\mathrm{C=C}} + \nu_{\mathrm{C=N}} + \delta_{\mathrm{HOH}}$ + ring vibration
1244m, 1225m, 1203m, 1170w, 1132w, 1119w, 1098mw, 1080w, 1061m, 1048m, 1028m, 998mw	1240w, 1218w, 1209m, 1180w, 1135s,sh[b], 1025vs,sh, 1002s,sh	1250w,b, 1220w, 1208mw, 1170vw, 1135s, sh[b], 1030s, sh, 1000mw,b	1240w, 1218w, 1209mw, 1170w, 1135s,sh[b], 1030vs, 1005ms	1240vw, 1225w, 1212w, 1180vw, 1132s,sh[b], 1030s,sh, 999mw	1255w, 1220m, 1208m, 1180mw, 1150m,sh[b] 1033s,sh, 1010m	1245w, 1217w, 1202m, 1170w, 1132s,sh[b], 1030s,sh, 1002m,sh	1207m,b, 1180w[b], 1050vs,sh, 1030s,sh, 1007m,b	1240w, 1220w 1210m, 1168w, 1133s,sh[b] 1028vs, 1006ms	$\nu_{\mathrm{C-NH_2}}$ + ring + $\nu_{\mathrm{C-N}}$ + $\rho_{\mathrm{NH_2}}$ + $\nu_{\mathrm{C-O}}$(ribose)
	1110vs, 1085 vvs,b, 1050vs	1122vs, 1095 vs,b, 1060vs	1118vs, 1100 vs,b, 1065vs	1113vs, 1090 vvs,b, 1050vs	1115vs, 1085 vs,b, 1057vs	1119vs, 1095 vs,b, 1067vs	1090vs,vb	1120vs, 1100 vs,b, 1060vs	$\nu_3(\mathrm{ClO_4})$
968mw, 952w, 900w, 890mw, 840w, 820m, 790w, 765w, 720mw, 700w, 660m,b, 635ms	972mw, 955mw, 933w, 900vw, 838vw, 815mw, 792vw, 760mw, 712w, 685w, 650mw,b	966m, 947m, 925w, 900vw, 845vw, 817w, 790vw, 755w, 711w, 697w,b, 650mw,b	970mw, 950mw, 930w, 898mw, 840vw, 813mw, 790vw, 757mw, 710mw, 695w,b, 650mw,b	967mw, 952mw, 930w, 900vw, 842vw, 815w, 792vw, 758w, 712w, 688w, 650mw,b	962m, 951mw, 934w, 897vw, 841vw, 816w, 793vw, 761w, 708vw, 686vw, 645mw,b	965m, 950mw, 928w, 899vw, 840vw, 812w, 785vw, 758w, 710vw, 688vw, 647mw,b	970m, 950m, 902vw, 840vw, 810w, 790vw, 760w, 710vw, 685vw, 645mw	971vw, 950mw 925w, 897mw, 840vw, 815mw 790vw, 755mw, 712mw, 690w, 650mw,b	$\nu_{\mathrm{C-O}}$(ribose) + $\rho_{\mathrm{NH_2}}$ + $\gamma_{\mathrm{NH_2}}$ + $\nu_1(\mathrm{ClO_4})$ + ring vibration
	642ms, 629ms, 621ms	636ms, 626ms, 617ms	637m,sh, 626ms, 618ms	640ms, 627ms, 620ms	634ms, 625ms, 616ms	632m,sh, 627ms, 614ms	618ms	633ms, 624ms, 617ms	$\nu_4(\mathrm{ClO_4})$
598m, 570m, 550m,b, 530w, 520w, 450w,sh, $\underline{415}$w, $\underline{390}$w, $\underline{350}$w, 335w, $\underline{320}$w, $\underline{290}$w, 267w, $\underline{250}$w, 225mw,b	600m, 580m, 550m, 530m, 465mw, 450mw, $\underline{415}$w, $\underline{387}$w, $\underline{355}$w, $\underline{317}$w, 265w,sh, $\underline{247}$mw	595m, 580mw, 520w, 470w,b, 450w, $\underline{395}$w, $\underline{355}$w,b, 335w, $\underline{298}$w, 270w, 223m,b	595m, 578mw, 560mw, 528w, 510w, 470w, $\underline{405}$w, $\underline{360}$w,b, 265w, $\underline{246}$mw, 228m,b	597m, 580m, 550m, 460mw, 450mw, $\underline{412}$w, $\underline{390}$w, $\underline{352}$w, $\underline{320}$w, 267w, $\underline{245}$mw, 228m,b	598m, 580m, 560m, 520mw, 475w, 450w,b, $\underline{411}$w, $\underline{396}$w, $\underline{355}$w, $\underline{317}$w, $\underline{290}$w, $\underline{250}$mw, 232m,b	596m, 577m, 553m, 530mw, 520mw, 475w, 450w, $\underline{410}$w, $\underline{385}$w,b, $\underline{315}$w, $\underline{290}$w, $\underline{245}$mw, 227m,b	601m, 580m, 550m, 530m, 447mw, $\underline{415}$w, $\underline{390}$w, $\underline{352}$w, 337w, 265w, $\underline{250}$mw, 230m,b	595m, 580m 555mw, 530w, 513w, 470w,b $\underline{406}$w, $\underline{356}$w,b, 266w, $\underline{250}$mw, 225m,b	ν_{ado} (600–200 cm^{-1})[c] + $\nu_2(\mathrm{ClO_4})$
	500m	426w		490m	434w	438w	475m		$\nu_{\mathrm{M-O}}(\mathrm{H_2O})$
	338w	319w	344w,b	334w,b	342w	344w		338w	$\nu_{\mathrm{M-O}}(\mathrm{OClO_3})$
	294w,b	251mw, 246mw	303w, 295w	285w,b	278w, 262w	280w, 265w	314w, 299w	285w, 271w	$\nu_{\mathrm{M-N}}$

[a] For references used in making band assignments see text. [b] Masked by stronger bands. [c] Bands at 420–240 cm^{-1} which are underlined, present in the spectrum of ado but absent from that of adenine (which shows maxima at 546, 450, 330, 267 and 225 cm^{-1} [62]), are probably associated with the ribofuranose residue [53, 66].

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of ado Adducts with 3d Metal Perchlorates

M^{n+}	λ_{max} (nm)[a]	$10^6 \chi_M^{cor}$ (cgsu)	μ_{eff}, (μB)
Cr^{3+}	<200vvs, 242vs 267vs,b, 310s,sh, 355s, 422s, 447s, 491m,sh, 540mw,sh, 571w,b, 629w,b, 690w,b	5951	3.78
Mn^{2+}	<200 vvs 245vs 268vs,b, 309s,sh, 355s, 424s, 490w,b	14,112	5.82
Fe^{2+}	231vs, 245vs,b, 270vs,b 307s,sh, 360s,vb, 503m, 588mw, 601mw, 702m, 750m,b, 977w,b	11,421	5.24
Fe^{3+}	217vs 246vs,b, 272vs,b, 312s, 353s, 411s, 525w,sh	14,529	5.91
Co^{2+}	<200vvs 244vs, 266vs,b, 311s,sh, 355s,b, 472s,sh, 496s, 522s,sh, 620w,b, 715w,vb, 833w,b, 917w,b, 1050w,vb, 1260w,b, 1850vw,b	8804	4.60
Ni^{2+}	210vs,b, 240vs, 271vs b, 308s, 360s, 385s, 421ms, 445ms,sh, 497m,sh, 590mw,b, 671mw,b 740mw,b, 975mw,b, 1260w,b	3727	2.99
Cu^{2+}	<200vvs 243vs 272vs,b, 307s,sh, 355s, 415s sh, 572w,sh, 618mw,b, 770s,b	1452	1.87
Zn^{2+}	210vs,b 236vs, 269vs,b, 308s,sh, 355s,b	Diamagnetic	

[a] Nujol mull spectrum of ado, nm: 210vvs, 230vs,vb, 260vs,vb. Reported aqueous solution spectrum at pH 6.0, nm (ϵ): 228(2000), 260(14100) (81).

for 5–10 days, as previously described in detail [27]. Adducts of the following stoicheiometries were isolated (Table I): $M_2(ado)_3(ClO_4)_6 \cdot 4H_2O$ (M = Cr, Fe), $M(ado)(ClO_4)_2 \cdot 2H_2O$ (M = Mn, Co, Ni, Cu) and $M(ado)(ClO_4)_2$ (M = Fe, Zn) [27]. With the exception of the Mn^{2+} complex, which was obtained in relatively low yield (16.8%), the synthetic method employed produced adducts in satisfactory yields (43–78%). The complexes are either insoluble or very sparingly soluble in organic solvents. Infrared spectra (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 magnetic susceptibility measurements at 298 K (Table III) were obtained by methods described elsewhere [57].

Discussion

Infrared Evidence

The IR spectrum of ado obtained during this work (Table II) agrees with published complete or partial spectral data [16, 22, 24, 26, 51, 58]. Band assignments were based on analogous IR studies of adenine [59–62], adenosine 5′-monophosphate [63] and various nucleosides [64–66], as well as partial assignments made for ado [16, 22, 24, 26]. The ν_{OH} of the ribose fragment appears as a doublet at 3460, 3400 cm^{-1} in free ado [64, 65], while in the spectra of the two anhydrous complexes (Fe^{2+}, Zn^{2+}) four bands appear in the same region at 3460, 3440, 3400 and 3380–3375 cm^{-1}; these ν_{OH} splittings, which involve appearance of one component of each of the split bands at 20–25 cm^{-1} lower frequency, could be due to weak coordinative interaction between one of the ribose hydroxyl oxygens and the metal ion, as well as to other reasons (H-bonding interactions, etc.). Possible additional ν_{OH} shifts beyond 3350 cm^{-1} can not be detected, owing to the strong ν_{NH_2} absorptions at 3335 and 3160 cm^{-1}. Other regions of significant absorption due to the ribofuranose residue are at 1200–800 cm^{-1} (ν_{C-O} bands) [24, 26, 51, 63–65, 67, 68]. Most notable ν_{C-O} modes in these regions correspond to maxima at 1130–1090 and 900–870 cm^{-1} [26, 51, 63–65]. In the spectra of the new complexes, the former of these regions is completely masked by the strong $\nu_3(ClO_4)$ bands [69, 70], but in the latter it may be significant that the absorption at *ca.* 900 cm^{-1} is considerably more intense for the Fe^{2+} and Zn^{2+} adducts, relative to the hydrated new complexes. Several bands of ado at 450–200 cm^{-1} do not have counterparts in the corresponding adenine spectrum [61, 62] and may be associated with the ribofuranose ring [66]. It was previously suggested that the stronger perturbation observed for some of the ribose bands in this region in the spectra of anhydrous rather than hydrated nucleoside metal complexes might be due to binding of ribose oxygens to the metal ion in the water-free complexes [53]. The spectra of the new Fe^{2+} and Zn^{2+} complexes, unlike the spectra of the remaining adducts, are absorption-free at around 390 and 320 cm^{-1}, where two of the bands probably due to ribose occur in ado. It is, therefore, not unlikely that the two anhydrous new complexes involve weak bond formation between the M^{2+} ion and the O(2′) or O(3′) ribose oxygen, in addition to the stronger bonds of the metal ion with the N(1) and N(7) nitrogens (*vide infra*). No evidence of the presence of ν_{M-O} (ribose) bands was found. These bands should occur at 430–320 cm^{-1} in divalent 3d metal complexes [26, 71–73], and, if present in the spectra under discussion, they would be probably weaker than and masked by the ligand and $\nu_{M-O}(OClO_3)$ absorptions in this region. It is also noteworthy that the ado ribose band at 415 cm^{-1} undergoes larger shifts in the spectra of the anhydrous new complexes.

The δ_{NH_2} band of ado at 1670 cm^{-1} does in no case exhibit substantial shifts toward lower wavenumbers upon formation of the new adducts, so that it may be concluded that no coordination occurs at the exocyclic N(6) nitrogen [59–63]. In most cases this band is split into two components (1707–1687 and 1672–1658 cm^{-1}), while in other cases it undergoes small positive frequency shifts (1689–1675 cm^{-1}). Occurrence of this δ_{NH_2} band at higher frequencies relative to the uncomplexed nucleoside has been observed upon protonation of adenine ring nitrogens [74, 75] and upon H-bond formation between the NH_2 hydrogens and ligands present in the coordination sphere of a metal ion complexed to the nucleoside (e.g., chloro ligands) [59]. Since ado remains neutral in the new complexes, the most likely cause of the δ_{NH_2} positive frequency shifts is H-bonding between NH_2 and perchlorato or aqua ligands. Several $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of ado at 1650–1300 cm^{-1} undergo significant shifts and splittings in the spectra of the adducts. For example, the 1470 cm^{-1} ligand band appears weakened or even disappears in the spectra of some of the M^{2+} complexes (Mn, Co, Ni, Cu) and is replaced by a doublet of strong bands at 1530–1523 and 1448–1441 cm^{-1}; the spectra of the remaining complexes show also shifts and splittings of ado bands in the region, but in a less dramatic fashion. The preceding features are consistent with participation of adenine ring nitrogens in coordination [59–63]. The tentatively assigned ν_{M-N} bands favor coordination number six for M = Cr^{3+}, Fe^{3+} [61, 75], five for M = Mn^{2+}, Co^{2+}, Ni^{2+} [62, 76] and four for M = Fe^{2+}, Cu^{2+}, Zn^{2+} [76, 77].

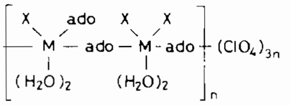
The hydrated complexes generally exhibit a strong $\nu_{OH}(H_2O)$ band at 3440–3390 cm^{-1} [78], which masks the ν_{OH}(ribose) absorptions completely and the 3335 cm^{-1} ν_{NH_2} band partially. The δ_{H-O-H} mode of coordinated water appears at *ca.* 1630 cm^{-1} [78], overlapping with the $\nu_{C=C} + \nu_{C=N}$ absorptions in this region. The Cu^{2+} complex exhibits clearly single ν_3 and ν_4 (ClO_4) bands at 1090 and 618 cm^{-1}, respectively, and contains, therefore, exclusively ionic ClO_4^- [69, 70]. The rest of the new complexes show triply split ν_3 and $\nu_4(ClO_4)$ bands and IR-active ν_1 and $\nu_2(ClO_4)$ absorptions (at 934–925 and 475–460 cm^{-1}, respectively). In all these cases both ionic ClO_4^- and unidentate coordinated $-OClO_3$ ligands are present [69, 70]. It should be noted that the presence of ionic ClO_4^- in the latter complexes is established beyond any doubt, by the characteristic very strong and broad ν_3 band at 1100–1085 cm^{-1}, so that that the possibility that the ν_3 and $\nu_4(ClO_4)$ splittings into three components arise from the exclusive presence of bidentate $=O_2ClO_2$ ligands can be ruled out [69, 70]. Tentative ν_{M-O}(aqua) and ν_{M-O}(perchlorato) band assignments are in support of the coordination numbers suggested by the location of the ν_{M-N} bands [61, 62, 75–80].

Electronic Spectra and Magnetic Moments

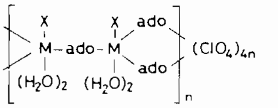
The solid-state (Nujol mull) UV spectrum of ado (Table III) is in agreement with the published aqueous solution spectrum [81]. The main $\pi \rightarrow \pi^*$ transition bands of the ligand at 230 and 260 nm undergo shifts toward lower energies upon metal complex formation. The band appearing at 307–312 nm in the spectra of the new complexes is due to the $n \rightarrow \pi^*$ transition of the ligand [82]. The new paramagnetic metal complexes are generally characterized by strong metal-to-ligand charge-transfer bands [83], originating in the UV and trailing off well into the visible. The d–d transition spectrum of the Cr^{3+} complex is compatible with a low symmetry hexacoordinated configuration [75, 84]: $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 422, 447, 491; $\rightarrow {}^4T_{2g}(F)$ 540, 571, 629, 690 nm (approximate Dq = 1646 cm^{-1}). The Co^{2+} and Ni^{2+} complexes exhibit multiple d–d band maxima at 472–1850 and 385–1260 nm, respectively, as would be expected for pentacoordinated compounds of these metal ions [84–87]. The occurrence of the main d–d transition maximum at 770 nm in the spectrum of the Cu^{2+} complex is consistent with a distorted tetrahedral symmetry [16, 77, 88–90], as is also the extensive splitting of the d–d transition in the spectrum of the Fe^{2+} complex [91, 92]. The ambient temperature magnetic moments of the new complexes are generally normal for high-spin $3d^3$–$3d^8$ compounds or the $3d^9$ configuration [93]. This is not incompatible with linear polymeric structures, involving single ado bridges between adjacent metal ions. In fact, Co^{2+}, Ni^{2+} and Cu^{2+} purine complexes of this type were found magnetically normal at room temperature, showing evidence of magnetic exchange at lower temperatures (below 110 K) [94]; whereas in the case of [Fe(uridine)-$Cl_2]_x$, for which a cross-linked polymeric structure, involving a linear double-bridged $-(-Fe-Cl_2-)-_x$ backbone and axial bridging uridine ligands, coordinated through the uracil oxygen at C(4) and one ribose hydroxyl oxygen and connecting adjacent linear polymeric units, was proposed, a μ_{eff} value of 5.24 μB at 298 K, which decreases to 1.55 μB at 1.73 K, was reported [54].

Likely Structures

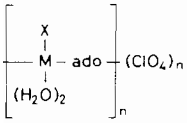
The new complexes are most probably linear polymeric species, involving single bridges of N(1), N(7)-bonded ado between adjacent metal ions, in view of their poor solubility in organic media and the pronounced tendency of purines to act as bridging ligands [33, 38–40, 75–77, 94]. The most likely structural types for the Cr^{3+} and Fe^{3+} complexes are **II** and **III** (X = $-OClO_3$ ligand); the former of these types seems more probable, since it does not involve any double ado bridges between metal ions, which would lead to increased magnetic exchange interactions. The terminal ado ligand in structure **II** would be expected to bind through N(7) [37]. It should be also noted that the stoicheiometry of the M^{3+} complexes (3:2 ado to M^{3+}) further supports a polymeric over a monomeric structural type. As regards the hydrated M^{2+} complexes, structure **IV** would be most likely for the Mn^{2+}, Co^{2+} and Ni^{2+} adducts, and an analogous structure (**V**) without coordinated perchlorate for the Cu^{2+} complex. Both these structures involve the familiar linear chainlike polymeric $-(-M-ado-)-_n$ backbone [75–77, 94, 95], as is also structural type **II**. With respect to the anhydrous Fe^{2+} and Zn^{2+} complexes, coordination number four can be attained only if the ado acts as tridentate bridging or if the perchlorate groups are either exclusively unidentate coordinated or one is ionic and the other is bidentate chelating or bridging. Since the IR spectra of these complexes ($\nu_3(ClO_4)$ bands; *vide supra*) are not in favor of the latter two possibilities and provide some indications that in these complexes coordination of ado through ribose hydroxyl oxygens may be occurring, structural type **VI** can be considered as most consistent with the overall evidence available (L–OH: tridentate ado, bonding through N(1), N(7) and the O(2′) or O(3′) ribose oxygen) [53, 54]. A cross-linked structure of type **VI** would not be expected to result in a subnormal room temperature magnetic moment for the Fe^{2+} complex [54].



II

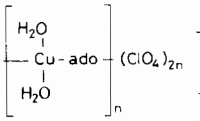


III



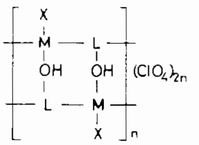
$$\left[\overset{X}{\underset{(H_2O)_2}{-M}}-ado-\right](ClO_4)_n$$

IV



$$\left[\overset{H_2O}{\underset{H_2O}{-Cu}}-ado-\right](ClO_4)_{2n}$$

V



VI

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