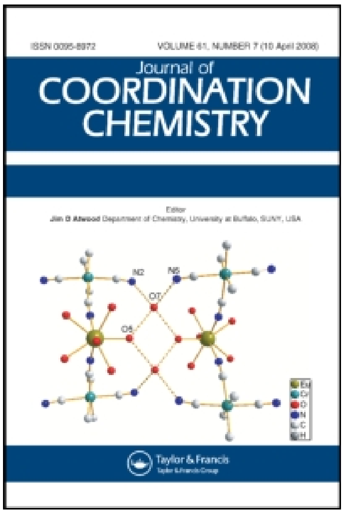

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5'-DEOXYADENOSINE COMPLEXES WITH DIVALENT 3d METAL PERCHLORATES

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5′-DEOXYADENOSINE COMPLEXES WITH DIVALENT 3d METAL PERCHLORATES*

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5′-deoxyadenosine (LH) complexes with divalent 3d metal perchlorates were prepared by refluxing mixtures of LH and salt in triethylorthoformate-ethylacetate. With one exception (M = Co), adducts of the types $M(LH)_2(ClO_4)_2.3EtOH$ (M = Mn, Fe, Ni, Zn) and $Cu(LH)_3(ClO_4)_2.2EtOH$ were obtained. Ethanol is introduced to the system by hydrolysis of triethylorthoformate during the dehydration of the metal salts. Co(II) perchlorate yielded a complex involving both neutral LH and monoanionic L^- ligands, i.e., $Co_2(LH)L_2(ClO_4)_2.4EtOH$. An analogous Cu(II) complex, $Cu_2(LH)L_2(ClO_4)_2.EtOH.3H_2O$, was also obtained by refluxing substantially more dilute suspensions of LH and Cu salt, relative to the standard preparative method employed. The new complexes were characrerized as dimers or linear polymers, involving bridging bidentate N1,N7-bound LH ligands between adjacent metal ions and coordination number six. The new adducts also involve terminal N7-bound LH and EtOH ligands and ionic perchlorate, and the Co and Cu complexes a chelating N6,N7-bound L^- (monodeprotonation of the exocyclic NH_2 group) per metal ion and terminal $-OClO_3$ and ROH (R = Et or H) ligands.

KEY WORDS: 5′-deoxyadenosine, first row complexes, perchlorates, synthesis.

INTRODUCTION

Previous work in these laboratories has dealt with 3d metal complexes of adenosine (ado)[2] and 2′-deoxyadenosine (2′-dado).[3–5] Both these ligands produce exclusively molecular adducts with 3d metal perchlorates[2,3] or halides.[4–6] Our studies in this direction were recently extended to include 3d metal perchlorate complexes with 5′-deoxyadenosine (dado; LH; I). Complexes formed by interaction of neutral LH with metal salts have not been previously reported. 5′-Deoxyadenosylcobaloximes have been prepared by reaction of the 5′-bromo- or 5′-tosyl-derivative of LH with bis(dimethylglyoximato)cobalt(II).[7–9] The present paper deals with the complexes formed by interaction of LH with divalent 3d metal perchlorates (M = Mn, Fe, Co, Ni, Cu, Zn) in triethylorthoformate (teof)-ethylacetate (ea).

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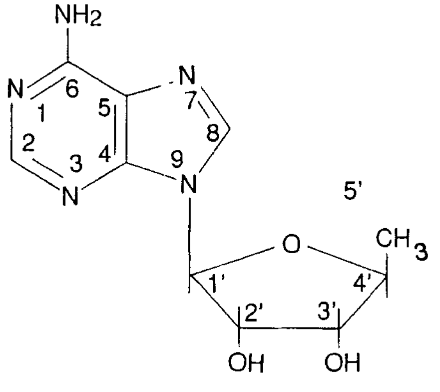


dado I

EXPERIMENTAL

The synthetic procedure employed was as follows: 1mmol hydrated metal perchlorate was dissolved in 50cm^3 of a 1:1 (v/v) mixture of teof-ea and the resulting solution stirred at 50°C for 2h. Then, 2mmol LH were added and the mixture boiled under reflux for 4–5 days. The mixture was allowed to cool and the solid complex formed collected by gravity filtration, washed with anhydrous diethylether and stored *in vacuo* over anhydrous calcium chloride. Analytical data for these products, given in Table 1, show that, with one exception (M = Co), adducts of LH with the metal salt were obtained. In the case of Co, the compound isolated is a complex involving both neutral LH and monodeprotonated L$^-$ ligands. We subsequently attempted the preparation of analogues of the Co complex and were successful in isolating a similar Cu complex by refluxing a mixture of 0.2mmol Cu salt and 0.4mmol LH in 50cm^3 teof-ea. The new complexes are generally insoluble in organic media. Infrared spectra (Table 2) were recorded in KBr discs (4000-500cm^{-1}) and Nujol mulls between high density polyethylene windows (700-200cm^{-1}) using a Perkin Elmer 621 spectrophotometer. Solid-state (nujol mull) electronic spectra and ambient temperature (300°K) magnetic susceptibility measurements (Table 3) were obtained by methods previously described.[10]

RESULTS AND DISCUSSION

Unlike adenosine and 2′-deoxyadenosine, which produce exclusively molecular adducts with 3d metal salts,[2-6] 5′-deoxyadenosine was found to form in certain cases complexes involving partial substitution of perchlorate groups with monoanionic L$^-$ ligands. Monodeprotonation of the exocyclic NH_2 group of nucleobases (e.g., adenine, cytosine) and their nucleosides is not generally facile,[11] but has been observed in some metal complexes as, for instance, tris(methylmercury(II)) complexes of adenine, in which this ligand is terdentate bridging, binding *via* N6, N7 and N9.[12] More facile is the monodeprotonation at NH_2 of the N(1)-oxides of adenine or ado, which act as strong chelating agents binding through O1 and N6.[13,14] The ethanol ligands present in the new complexes are obviously produced by hydrolysis of teof to ethanol and ethylformate during the dehydration of the hydrated metal perchlorates.[15] Isolation of ethanol,[16] ethylformate or formato[17] complexes from teof solutions of metal salts, although rather uncommon, can occur.[16,17] The new adducts involve either 2:1 (Mn, Fe, Ni, Zn) or 3:1 (Cu) LH to metal ion molar ratios, while two complexes contain one L^- and one-half of an LH ligand per metal ion (Co, Cu; Table 1). Ethanol is present in all the new adducts and complexes, while the Cu complex also contains water.

The infrared spectrum of LH is fairly similar to those of ado and 2'-dado. IR band assignments for the free ligand were based on analogous previous studies of 2'-dado,[3,18,19] ado,[2,6,20,21] adenine,[12,22,23] adenosine 5'-monophosphate[24] and groups of nucleobases and nucleosides[25,26] (Table 2). Free LH exhibits the following maxima at 3500-3000cm^{-1}: 3420, 3375 (νOH, 5'-deoxyribose), 3270 and 3140 (νNH_2). The former two bands are masked in the spectra of the complexes by the broad νOH of coordinated ethanol and (Cu complex) water, occurring at 3460-3380;[27] νNH_2 bands are observed at 3200-3050.[2,3] The δNH_2 mode, which appears at 1664cm^{-1} in free LH, is split into two components in the spectra of the complexes: a week band at 1725-1700 and a very strong absorption at 1670-1655 (Table 2). The former band is indicative of H-bonding between NH_2 hydrogens and perchlorate groups,[3,12,14,22] while the latter appears near the location of the free LH δNH_2 and is not suggestive of participation of the N6 nitrogen of the neutral ligands in coordination.[2-6,12,14,22-24] The ρNH_2 mode of LH is observed at *ca* 1020cm^{-1} in the spectra of all the new compounds, while the δNH of the monodeprotonated L^- ligand appears at 1135-1128 only in the case of the Co and Cu complexes,[3,12,14] which also exhibit νM-N6 bands. Binding of the LH and L^-ligands through adenine ring nitrogens is suggested by the shifts and occasional splitings of the $\nu C=C$ and $\nu C=N$ ligand vibrational modes (1640-1500cm^{-1} region).[2-6,12,22-24] The sugar-puckering ligand mode at 825, diagnostic of conformation,[28] appears at 821-826cm^{-1} in the spectra of the complexes, which generally do not show any evidence favouring sugar binding *via* its hydroxyl oxygens.[2] The perchlorate groups are ionic in the adducts, showing single ν_3 and $\nu_4(ClO_4)$ bands, and act as unidentate $-OClO_3$ ligands in two complexes, in the

Table 1 Analytical data for the new metal complexes[a]

Complex	Colour	C%	H%	N%	M%	Cl%
$Mn(LH)_2(ClO_4)_2.3EtOH$	Brown	35.13 (34.92)	4.73 (4.96)	15.15 (15.66)	6.23 (6.14)	7.97 (7.93)
$Fe(LH)_2(ClO_4)_2.3EtOH$	Brown	35.42 (34.88)	4.55 (4.95)	16.11 (15.66)	6.53 (6.24)	8.21 (7.92)
$Co_2(LH)L_2(ClO_4)_2.4EtOH$	Mustard	38.67 (38.39)	4.88 (5.17)	17.87 (17.67)	9.82 (9.92)	6.35 (5.96)
$Ni(LH)_2(ClO_4)_2.3EtOH$	Yellow-green	35.19 (34.77)	4.67 (4.94)	15.85 (15.60)	6.13 (6.56)	7.52 (7.89)
$Cu(LH)_3(ClO_4)_2.2EtOH$	Avocado green	37.10 (36.85)	4.37 (4.64)	18.52 (18.96)	6.02 (5.73)	6.78 (6.40)
$Cu_2(LH)L_2(ClO_4)_2.EtOH.3H_2O$	Brown	34.21 (34.51)	4.04 (4.43)	18.53 (18.86)	11.82 (11.41)	6.39 (6.37)
$Zn(LH)_2(ClO_4)_2.3EtOH$	Beige	34.25 (34.52)	5.05 (4.90)	15.71 (15.48)	7.34 (7.22)	8.00 (7.84)

[a] Found% with calcd.% in parentheses; the complexes are obtained in yields ranging between 40-70% of the theoretical.

Table 2 Pertinent infrared data for the new metal complexes (cm^{-1})

LH[a]	M = Mn	M = Fe	M = Co	M = Ni	M = Cu[b]	M = Cu[c]	M = Zn	Band assignment
1664vs	1710w, 1669vs	1704w, 1657vs	1713w, 1655s	1708w, 1659vs	1722w, 1665s	1700w, 1656s	1717w, 1661vs	δNH_2
1609vs, 1569m	1617s, 1598vs	1620s, 1600s	1617s, 1597vs	1610s, 1595vs	1620vs, 1580vs	1637s, 1620s	1614s, 1593vs	$\nu C=C+\nu C=N+\delta HOH$
1517w,b	1574vs, 1567s	1571vs, b	1568vs, 1552s	1580vs, 1548m	1550m, 1512m,b	1595vs, 1570s	1566vs, 1547s	
	1515m,b	1520ms	1517vs	1510m,b		1550s, 1518m	1515m,b	
			1135s,sh			1128s,sh		δNH
	1090vvs,vb	1085vvs,vb	1112vvs	1080vvs,vb	1095vvs,vb	1111vvs	1080vvs,vb	$\nu_3(ClO_4)$
			1070vvs			1075vvs		
1025m	1022m,sh	1017m,sh	1024m,sh	1022m,sh	1023m,sh	1023m,sh	1021m,sh	ρNH_2
			928w			925w		$\nu_1(ClO_4)$
825m	821m	826m	824m	824m	822m	823m	822m	Sugar conformation
	622ms	625ms	637m, 620m	624ms	625ms	634m, 621m	621ms	$\nu_4(ClO_4)$
632m, 597m	598w, 575vw	600w, 571vw	601w, 574vw	600w, 577vw	597w, 572vw	602w, 575vw	596w, 572vw	νdado at 650-200cm^{-1}
562w, 535w	540w, 495w	539w, 500w	542w, 497w	537w, 499w	540w, 498w	540w, 500w	538w, 497w	
490w,b, 453w	450w,sh	455w,sh	423w,sh	450w,sh	455w,sh	432w,ah	452w,sh	
432vw, 410mw	425w,b, 405w	427w, 407w	397w,sh	430w,sh	428w,sh	400w,sh	431w,sh	
398w, 365w	370w, 350w	376w, 348w	375w, 348w	400w, 368w	402w, 370w	372w, 349w	404w, 371w	
349w, 321w	318w, 304w	320w, 307w	322w, 279w	350w, 324w	351w, 322w	324w, 280w	352w, 321w	
311w, 299w	283w, 260mw	280w, 262mw	261mw	303w, 280w	305w, 278w	260mw, 222w	304w, 279w	
262w, 240w				259mw	261mw		263mw, 242w	
225w,b				240w,sh	242w,sh			
			477w,sh			480w,sh		$\nu_2(ClO_4)$
			456m			463m		$\nu M\text{-}N6$
	395mw	398mw	404mw	413mw	411mw	418mw, 414mw	392mw	$\nu M\text{-}O(ROH)$; R = Et, H
			309mw			315mw		$\nu M\text{-}O(OClO_3)$
	240w, 223w	244w, 223w	249w, 228w	254w, 232w	253w, 232w	254w, 234w	237w, 219w	$\nu M\text{-}N$(ring nitrogen)

[a] For free LH assignments see text.
[b] Cu adduct.
[c] Cu complex.

spectra of which ν_3 and ν_4 are doubly split and ν_1 and ν_2 IR-active.[29,30] Tentative metal-ligand band assignments (Table 2), based on our previous studies of 3d metal perchlorate complexes with nucleosides and derivatives, aqua and ethanol ligands[2,3,14] are generally in favour of hexacoordinated configurations. The new adducts exhibit only νM-O(EtOH) and νM-N(ring) bands, while the Co and Cu complexes show, in addition to the preceding modes, νM-N6 and νM-O(-$OClO_3$) absorptions.

The ambient temperature magnetic moments of the complexes reported are generally normal for high-spin $3d^5$-$3d^8$ compounds or the $3d^9$ confiuration.[31] This does not preclude single-bridged linear bi- or polynuclear structures proposed later in the text. Several single-bridged polymeric 3d metal complexes (Cu, Ni, Co) wth diazine (including purine) bridges exhibit normal room temperature magnetic moments and show evidence favouring magnetic exchange interactions only at low temperatures.[32-34] The $\pi \rightarrow \pi^*$ transitions of LH[35] are shifted toward lower energies upon metal complex formation (200–280nm region), whil the $n \rightarrow \pi^*$ transition of the ligand appears at 304–312nm[3] in the UV spectra of the complexes. The new paramagnetic complexes exhibit strong metal-to-ligand charge-transfer absorption,[36] originating in the UV and trailing off into the visible region (Table 3). The d-d transition spectra of the new complexes are generally consistent with hexacoordinated configurations,[2,3,5,14,32] and in agreement with the lower frequency IR evidence, *viz* nm: M = Fe: ${}^5T_{2g} \rightarrow {}^5E_g$ 824, 1157 ($Dq = 1010cm^{-1}$); M = Co: ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 476; $\rightarrow {}^4A_{2g}(F)$ 504, 527; $\rightarrow {}^4T_{2g}(F)$ 1170; M = Ni: ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 427; $\rightarrow {}^3T_{1g}(F)$ 635, 732; $\rightarrow {}^3T_{2g}(F)$ 965, 1171 ($Dq = 936cm^{-1}$). The ${}^2E_g \rightarrow {}^2T_{2g}$ transition appears at 663nm in the new Cu adduct and at 670nm in the Cu complex. The preceding data are compatible with low symmetry, hexacoordinated structures involving MN_3O_3 (M = Fe, Co, Ni and Cu {complex}) and CuN_4O_2 (adduct) chromophores[2,3,5,14,32,37] (*vide infra*).

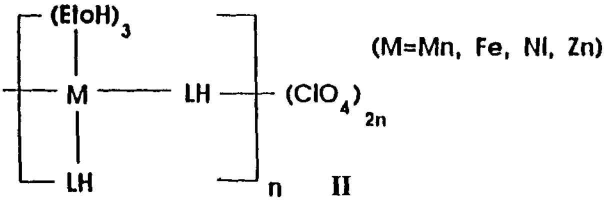
The evidence presented, combined with the insolubility of the new metal complexes in organic media and the pronounced tendency of purine derivatives to function as bidentate bridging ligands,[38] favours linear dimeric or polymeric structures with single bridges involving LH ligands between adjacent metal ions. Likely structural types for the new adducts are depicted in **II** for Mn, Fe, Ni, Zn and **III** for Cu. N7 is the primary binding site of terminal 9-substituted adenines, especially in octahedral metal complexes.[3-5,39-41] Bidentate bridging ligands of this type usually bind *via*

Table 3 Solid-state (nujol mull) electronic spectra and magnetic susceptibilities at 300°K of the new metal complexes

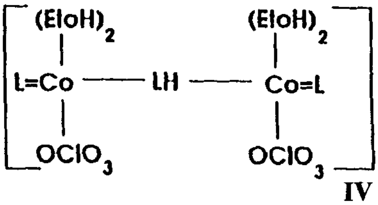
M	λ max, nm[a]	$10^6\chi_M^{cor}$, cgsu	μeff, μB
Mn	<200vvs, 218vvs, 243vs, 275vs, b, 310s, sh, 350s, 432s, 492w, b	14,761	5.98
Fe	<200vvs, 216vvs, 240vs, 278vs, b, 312s, sh, 353s, 824mw, b, 1157w, vb	10,466	5.03
Co	<200vvs, 213vvs, 239vs, 280vs, b, 307s, sh, 345s, 476s, sh, 504s, 527s, sh, 1170w, b	9726	4.85
Ni	<200vvs, 217vvs, 244vs, 275vs, b, 304s, sh, 352s, 427s, 635mw, 732mw, b, 965w, 1171w, b	3922	3.08
Cu[b]	<200vvs, 212vvs, 241vs, 272vs, b, 307s, sh, 355s, 575m, sh, 663ms, b	1528	1.92
Cu[c]	<200vvs, 212vvs, 244vs, 276vs, b, 311s, sh, 354s, 569m, sh, 670ms, b	1447	1.87
Zn	<200vs, 215vs, 241vs, 269vs, b, 309s, sh, 355s, b	Diamagnetic	

[a] Nujol mull spectrum of LH, nm: 206vvs, 223vs, sh, 261vs, b.
[b] Cu adduct.
[c] Cu complex.

N1, N7.[42] Coordination number six in the adducts is attained by the presence of two or three ethanol ligands, while the perchlorates are exclusively ionic. The two new complexes are most probably dimers of types IV and V, involving an N1,N7-bound bridging LH ligand, two terminal ROH (R = Et or H), one unidentate $-OClO_3$, and one bidentate chelating L^- ligand per metal ion. Binding of L^- presumably ocurs *via* N6,N7 rather than N1,N6 (formation of a five- *vs* four-membered chelate rings, respectively). This situation is quite different in the case of metal chelates of anionic adenine or adenosine N(1)-oxide ligands, which bind *via* O1,N6[13,43,44] (five-membered chelate ring).



II



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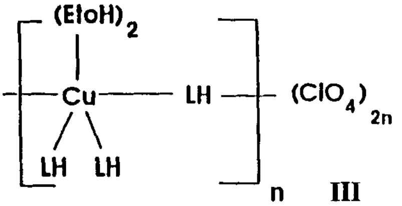

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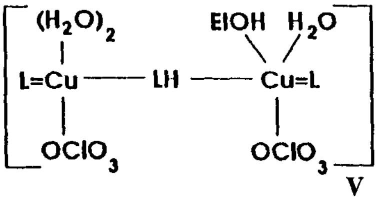

V

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