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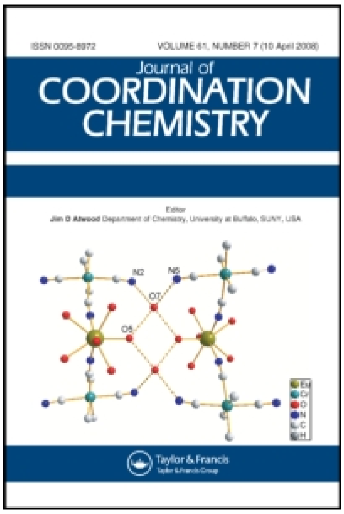

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mikulski, Chester M. , Minutella, Robert , De Franco, Nancy , Borges Jr., Guillermo , Renn, Amy and Karayannis, Nicholas M.(1989) 'Adenosine *N*(1)-Oxide Complexes with Divalent 3d Metal Perchlorates', Journal of Coordination Chemistry, 20: 1, 39 — 47

To link to this Article: DOI: 10.1080/00958978909408846

URL: http://dx.doi.org/10.1080/00958978909408846

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J. Coord. Chem. 1989, Vol. 20. pp. 39–47
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ADENOSINE *N*(1)-OXIDE COMPLEXES WITH DIVALENT 3d METAL PERCHLORATES*

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(Received August 23, 1988; in final form November 22, 1988)

Complexes of adenosine *N*(1)-oxide (LH), I, with divalent 3d metal perchlorates (M = Mn, Fe, Co, Ni, Cu, Zn) were synthesized by refluxing 2:1 molar mixtures of ligand and hydrated metal salt in triethyl orthoformate-ethanol. The new complexes isolated are of the $ML(LH)ClO_4$ (M = Mn, Cu), $ML(LH)ClO_4.EtOH$ (M = Fe, Co, Zn) and $NiL(LH)ClO_4.2EtOH$ types, containing one neutral LH and one anionic L^- ligand deprotonated at the exocyclic NH_2 group and replacing one ClO_4^- anion. Characterization studies suggest that LH acts as bridging bidentate (O1,N7-bound) and L^- as a bidentate chelator binding *via* O1,N6. The complexes appear to be linear chainlike polymers with a $-(-M-LH-)-_n$ single-bridged backbone and a chelating L^- ligand per metal ion. The alcohol-free Mn(II) and Cu(II) complexes are distorted tetrahedral with ionic perchlorate, while the remaining complexes are hexacoordinated with either two additional EtOH ligands and ionic perchlorate (M = Ni) or one EtOH and one $-OClO_3$ ligand (M = Fe, Co, Zn) in the inner coordination sphere of the metal ion.

Keywords: Adenosine *N*(1)-oxide, complexes, perchlorates, polymers

INTRODUCTION

Previous synthetic and characterization studies in these laboratories have dealt with metal complexes of purine *N*(1)-oxide (puH-NO),[2] adenine *N*(1)-oxide (adH-NO),[3,4] adenine (adH)[5,6] and adenosine (ado).[7] We recently extended our work to include the complexes formed by interaction of adenosine *N*(1)-oxide (adoNO; LH; I) with 3d metal perchlorates,[1] and have already reported on dimeric hydroxo-bridged M(III) complexes of the $[(H_2O)(LH)LM(OH)_2ML(LH)(OH_2)](ClO_4)_2$ type (M = Cr, Fe), which are magnetically subnormal (magnetic moments at 300 K: 3.41 μB for M = Cr, 2.94 μB for M = Fe) and were characterized as hexacoordinated with bidentate chelating O1,N6-bound anionic L^- and terminal O1-bound LH ligands.[8] The present paper deals with our synthetic and characterization studies of adoNO complexes with divalent 3d metal perchlorates (M = Mn, Fe, Co, Ni, Cu, Zn).

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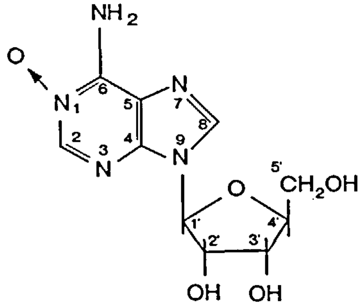
* Presented in part at the 194th Natl. Meetg., Am. Chem. Soc., see ref. 1. ** Author for correspondence.



I

The coordination chemistry of the *N*-oxides of nucleobases, nucleosides and nucleotides has attracted attention in view of their highly oncogenic nature[9,10] and their distinctly different coordination patterns from those of the biologically important parent bases.[11] Differences in the reactivities and coordinative affinities of ado and adoNO arise from the influence of the N–O group in labilizing a NH_2 proton within the adoNO molecule,[12] and are manifested in solution by the decrease of pK_a for NH_2 deprotonation from 16.7 in ado[13] to 12.86 in adoNO.[14,15] As a result of this, adoNO in its monodeprotonated form acts as a strong chelator toward metal ions binding *via* O1,N6,[16,17] while the coordinative tendencies of neutral adoNO[18] or the parent ado base[16] are rather weak. Chelation of adenosine 5′-monophosphate *N*(1)-oxide *via* O1,N6 was proposed for its complexes with a series of 3d metal ions.[19] This type of chelation was recently established by the crystal structure determination of a Cu(II) complex with doubly deprotonated adH–NO (deprotonated at an imidazole ring nitrogen and at NH_2).[20] On the other hand, neutral adH–NO was found to act as bidentate bridging O1,N7-bound ligand in its 1:1 adduct with $HgCl_2$.[21] Structures involving either or both these types of bidentate adH–NO binding were proposed by these laboratories for several complexes of this ligand with metal perchlorates[3] or chlorides.[4]

EXPERIMENTAL

The following synthetic procedure was employed: 0.26 mmol $M(ClO_4)_2.xH_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn) and 0.52 mmol adoNO was dissolved separately in 50 cm^3 of a 7:3 (v/v) mixture of triethyl orthoformate (teof)–EtOH. Both solutions were warmed to about 50°C, under gentle agitation, for about 1 h, and then combined. The resultant mixture was maintained at *ca* 50°C under stirring, until a precipitate was formed or a colour change occurred (0.5–1 h), and the mixture was subsequently cooled to room temperature. The precipitate formed was separated by filtration, washed with EtOH and stored *in vacuo* over anhydrous $CaCl_2$. The new complexes, which are free-flowing powders, are of the $ML(LH)ClO_4$ (M = Mn, Cu), $ML(LH)ClO_4.EtOH$ (M = Fe, Co, Zn) and $NiL(LH)ClO_4.2EtOH$ types, as shown by the analytical data of Table I. They are generally insoluble in organic media. Their characterization was based on infrared spectra, recorded in KBr discs (4000–500 cm^{-1}) and Nujol mulls between high-density polyethylene windows (700–200 cm^{-1}) using a Perkin-Elmer 621 spectrophotometer (Table II), and solid-state (Nujol mull) electronic spectra and ambient temperature (300 K) magnetic susceptibility measurements (Table III), obtained by methods described elsewhere.[22]

TABLE I
Analytical data for the new adoNO (LH) metal complexes[a]

Complex	Colour	Yield %	C %	H %	N %	M %	Cl %
$MnL(LH)ClO_4$[b]	Green	29	33.12 (33.37)	3.66 (3.50)	19.80 (19.46)	7.67 (7.63)	5.07 (4.92)
$FeL(LH)ClO_4 \cdot EtOH$	Brick red	66	34.77 (34.46)	3.91 (4.07)	18.04 (18.27)	7.40 (7.28)	4.75 (4.62)
$CoL(LH)ClO_4 \cdot EtOH$	Light brick red	43	34.16 (34.32)	4.19 (4.06)	18.12 (18.19)	7.92 (7.66)	4.43 (4.60)
$NiL(LH)ClO_4 \cdot 2EtOH$	Light green	60	35.88 (35.34)	4.61 (4.57)	17.30 (17.17)	6.99 (7.20)	4.18 (4.35)
$CuL(LH)ClO_4$	Light green	69	33.12 (32.97)	3.55 (3.46)	19.45 (19.23)	8.92 (8.72)	5.02 (4.87)
$ZnL(LH)ClO_4 \cdot EtOH$	Off-white	55	33.81 (34.04)	3.87 (4.02)	17.94 (18.04)	8.55 (8.42)	4.60 (4.57)

[a] Found % with Calc. % in parentheses. [b] Fluorescent solid.

RESULTS AND DISCUSSION

Unlike ado, which invariably yielded adducts with 3d metal perchlorates,[7] the interaction of adoNO with the same perchlorates generally leads to the formation of complexes involving substitution of one monodeprotonated L^- ligand for a perchlorate group. This is clear from the results of the present synthetic work (Table I), as well as the previously reported formation of dimeric Cr(III) and Fe(III) perchlorate complexes with adoNO, in which ClO_4^- groups were replaced not only by L^- ligands, but also by OH^- groups.[8] As discussed in the Introduction, adoNO has a greater tendency than ado to lose one NH_2 proton, and the resulting L^- ligand can act as a strong O1,N6-bound chelating agent.[12–19] Monodeprotonation of adoNO is probably preceded by adduct formation *via* coordination of the neutral ligand through O1,[2–4] which facilitates the subsequent loss of one *o*-NH_2 proton.[12,20] The deprotonation reaction may be occurring either in solution or in the solid state, depending on the solubility of the initially formed adduct in teof–EtOH.[2–4] It is assumed that this adduct involves a 2:1 adoNO to metal ion molar ratio, since the final complexes precipitated contain one L^- and one LH ligand.

IR band assignments for free adoNO were based on earlier assignments for ado,[7] adH[23] and adenosine 5′-monophosphate,[24] as well as various *N*-oxides,[25,26] including adoNO.[15] At 3500–3100 cm^{-1}, free LH exhibits four very strong maxima at 3440, 3380 (νOH, ribose) and 3280, 3130 (νNH_2) cm^{-1}.[7,23,24] In the spectra of the Mn and Cu complexes, which do not contain alcohol, medium intensity bands appear at *ca* 3450, 3400, 3290 and 3145 cm^{-1}. The remaining complexes show a strong to very strong νOH(EtOH)[27] maximum at 3400–3340 cm^{-1} with shoulders in both the higher and lower wavenumber directions and a weaker νNH_2 band at 3160–3130 cm^{-1}. Table II gives pertinent IR data for free LH and the new complexes at 1750–200 cm^{-1}. The δNH_2 mode of LH, appearing at 1670 in the spectrum of the free ligand, is split into a weak (1725–1710) and a stronger (1671–1657 cm^{-1}) component in the spectra of the complexes. The former band is suggestive of H-bonding between NH_2 and ClO_4^-,[23] whilst the occurrence of the stronger absorption

TABLE II
Pertinent infrared data for the new adoNO metal complexes at 1750-200 cm^{-1}.

adoNO[a]	M = Mn	M = Fe	M = Co	M = Ni	M = Cu	M = Zn	Band assignment
1670vvs	1720w, 1668vs	1722w, 1671vs	1718w, 1670vs	1712mw, 1666vs	1725mw, 1657vs	1710mw, 1663vs	δNH_2
1648m,sh, 1589mw	1652s,sh, 1632s	1645s,sh, 1599m	1633s, 1588m	1651s,sh, 1580m	1640vs, 1595m	1650vs, 1589m	νC=C +
1573mw, 1490m	1585m, 1490ms	1563m,sh, 1520mw	1561mw, 1493m	1555mw, 1488m	1560w, 1530w	1560m, 1490ms	$\nu_{C=N}$ +
1470m, 1412m	1462ms, 1409m	1500mw, 1440w,b	1412w, 1372m	1412w, 1367mw	1485m, 1457mw	1411m, 1370m	
1371m, 1337m	1365ms,b	1410m, 1371mw	1347mw	1341mw, 1310mw	1406w, 1361m	1342m, 1310m,b	
1320mw		1328w, 1300w			1300w,b		ring vibr.
1251w, 1212ms	1199ms	1201ms	1197ms	1194ms	1195ms	1188ms	νN-O region
1175w, 1117m	1170w[b]	1150m[b]	1175w[b]	1165m[b]	1160m[b]	1165w[b]	νC-O(ribose) +
1078s, 1045s							νC-N
	1124s,sh	[b]	[b]	1122s,sh	1126s,sh	[b]	$\rho NH (L^-)$
	1080vvs,b	1112vvs, 1085vvs	1110vvs, 1075vvs	1095vvs,b	1090vvs,b	1108vvs, 1075vvs	$\nu_3(ClO_4)$
1020m,sh	1020m,sh	1025m,sh	1022m,sh	1024m,sh	1017m,sh	1018m,sh	$\rho NH_2 (LH)$
	920vw	933mw	935mw	915vw	920vw	930mw	$\nu_1(ClO_4)$
	624s	633s, 621s	635s, 623s	622s	624s	637s, 626s	$\nu_4(ClO_4)$
598m, 573m, 550m	600m, 580m, 550m	595m, 575m, 550m	590m, 570m, 555m	600m, 575m, 559m	595m, 570m, 552m	595m, 565m, 553m	
510w, 480w, 460w	510w, 390w,sh	515w, 341w,sh	520w, 345w,sh	520w, 480w,sh	515w, 390w, 345w	520w, 420w,sh	ν Ligand at
420w, 387w, 340w	340w, 315w, 266w	320w,sh, 295w	322w,sh, 293w	325w,sh, 290w	325w,sh, 270w	390w,sh, 320w,sh	600-200 cm^{-1}
320w, 290w, 267w	250w, 220w,b	265w,sh, 220w,b	270w, 225w,b	270w,sh, 227w,b	250w, 224w,b	285w,sh, 267w,sh	
250w, 225w,b						215w,sh	
		475mw,b	470mw,b			470mw,b	$\nu_2(ClO_4)$
	477m	454m	457m	461m	484m	448m	νM-N6
	443mw, 408mw	413mw, 375mw	417mw, 378mw	420mw, 381mw	455mw, 414mw	408mw, 369mw	νM-O1
		357mw	362mw	367mw		353mw	νM-O(EtOH)
		308mw	312mw			302mw	$\nu M-O(OClO_3)$
	301mw, 287mw	252w, 233w	256w, 236w	259w, 241w	312mw, 293mw	250w, 229w	$\nu M-N7^-$

[a] free adoNO band assignments based on refs. 7, 15, 23–26, 28. [b] Masked by $\nu_3(ClO_4)$.

TABLE III

Solid-state (Nujol mull) electronic spectra and magnetic properties (300 K) of the new adoNO (LH) complexes

Complex	λ_{max}, nm[a]	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB
$MnL(LH)ClO_4$	223vvs, 244vvs, 280vs, 306vs, 361ms,b, 444mw, 471mw, 506w	14,722	5.97
$FeL(LH)ClO_4.EtOH$	221vvs, 243vvs, 277vs, 309vs, 364ms,b, 911m, 1115m	10,670	5.08
$CoL(LH)ClO_4.EtOH$	226vvs, 247vvs, 279vs, 311vs, 366ms,b, 462ms, 510m, 519m, 1160w,sh	9,832	4.88
$NiL(LH)ClO_4.2EtOH$	224vvs, 244vvs, 281vs, 309vs, 363ms,b, 442ms,b, 655m, 697m, 989m, 1145w,b	4,309	3.23
$CuL(LH)ClO_4$	222vvs, 245vvs, 278vs, 313vs, 360ms,b, 405ms, 777m,b, 990w,sh	1,561	1.94
$ZnL(LH)ClO_4.EtOH$	223vvs, 245vvs, 282vs, 312vs, 368ms,b	Diamagnetic	

[a] Reported spectrum of free adoNO at pH 5.3: 232, 272 nm.[12]

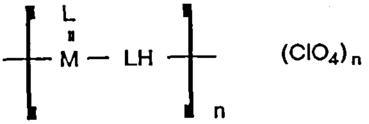
at 1671–1657 cm^{-1} rules out coordination of the neutral ligand *via* the amino group (N6) nitrogen.[3–8,23,24] The δNH mode of anionic L$^-$ is detected as a shoulder at 1126–1122 cm^{-1},[23] only in the spectra of the complexes with ionic ClO_4^- (M = Mn, Ni, Cu; *vide infra*), while the δNH_2 vibration of LH appears as a shoulder (1025–1017 cm^{-1}) of the strong $\nu_3(ClO_4)$ absorption, which also masks the νC–O (ribose) and νC–N ligand bands at 1117–1045 cm^{-1}.[23,24,28] The νN-O mode of the *N*-oxide group is shifted from 1212 in free LH[15] to 1201–1188 cm^{-1} in the spectra of the complexes, indicating use of the O1 oxygen in binding.[2–4,8,15,29] The perchlorate group is ionic in the Mn, Ni and Cu complexes (single ν_3, $\nu_4(ClO_4)$ bands) and coordinated as a unidentate ($-OClO_3$) in the Fe, Co and Zn compounds (ν_3, ν_4 split into doublets and Ir-active ν_1, ν_2 (ClO_4)).[30,31] Tentative metal–ligand band assignments were based on reported data for 3d metal complexes with ado,[7,32] adH–NO,[3] ethanol,[33] perchlorato[34] and aniline[35] ligands. The identification of νM–N6[8,35] and νM–N7[3,4,7] bands and M–O1 doublets[2–4,8,36,37] favours coordination of both L$^-$ and LH *via* the O1 oxygen as one binding site and use of N6 by L$^-$ (bidentate chelating)[8,12–20] and N7 by LH (bidentate bridging)[2–7,21] as the second binding site. Coordination of the ligands *via* O1 and N7 is also suggested by significant shifts and occasional splittings of νC=C, νC=N and ring vibrations of free LH (1650–1300 cm^{-1} region) upon metal complex formation.[2–8,23,24,32] The location of the νM-ligand bands is suggestive of coordination numbers four for M = Mn, Cu and six in the remaining cases.[2–7,23,24,32] Finally, several adoNO bands at 450–200 cm^{-1}, having counterparts in the spectrum of ado[7] but not in that of adH,[5,23] are probably associated with the ribofuranose ring.[38] These bands appear at 420, 387, 320, 290 and 250 cm^{-1} in the spectrum of adoNO. It should be noted that no indication of participation of the O2′ or O3′ hydroxyl oxygens of the ribose fragment of the ligand in coordination is provided by the IR spectra of the new complexes.[7]

The ambient temperature magnetic moments of the new complexes (Table III) are generally normal for high-spin $3d^5$–$3d^8$ compounds or the $3d^9$ configuration.[39] Linear polymeric 3d metal(II) complexes (Co, Ni, Cu) with single purine bridges between adjacent metal ions were found to exhibit normal room temperature magnetic moments and evidence favouring magnetic exchange interactions only at low temperatures (<110 K).[40] Similar trends were reported for various single-bridged polymeric Cu(II) complexes with diazine, diazole and *N*,*N*-dioxide bridging ligands (Cu–Cu separations >6.5 Å).[41,42] Hence, the normal ambient temperature magnetic moments of the complexes herein reported do not rule out the single-bridged polymeric structures proposed later in the text.

The main $\pi \rightarrow \pi^*$ transition bands (232, 272 nm at pH 5.3) in the UV spectrum of free adoNO[12] tend to occur at somewhat lower energies in the spectra of the complexes, with the high energy band split into two components. A band at 306–313 nm in the spectra of the complexes is due to the $n \rightarrow \pi^*$ ligand transition.[2–8,43] Strong metal-to-ligand charge-transfer absorption,[44] originating in the UV and trailing off into the visible region, is observed in the spectra of the paramagnetic complexes. The d–d transition spectrum of the Cu complex, showing the main maximum at 777 and a shoulder at 990 nm, is compatible with a distorted tetrahedral configuration.[32,45–47] The tetrahedral symmetry of the Mn complex is suggested by its fluorescent nature (Table I) and the appearance of distinct sharp maxima at 444–506 nm in its spectrum (Table III), due to the $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ (G) transitions.[48] The d–d spectra of the Fe, Co and Ni complexes are consistent with low symmetry hexacoordinated configurations,[49] *i.e.*, nm: M = Fe $^5T_{2g} \rightarrow {}^5E_g$ 911, 1115 (Dq = 987 cm^{-1}); Co $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 462; $\rightarrow {}^4A_{2g}(F)$ 510, 519; $\rightarrow {}^4T_{2g}(F)$

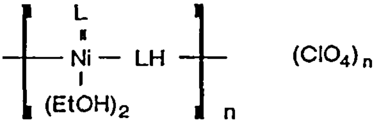
1160; Ni $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 442; $\rightarrow {}^3T_{1g}(F)$ 655, 697; $\rightarrow {}^3T_{2g}(F)$ 989, 1145 (Dq = 937 cm^{-1}). The approximate Dq values calculated for M = Fe, Ni are compatible with MN_2O_4 absorbing species.[50]

On the basis of the evidence discussed, the insolubility of the new complexes in organic media, and the established tendency of the *N*(1)-oxides of adH or ado to function as bridging O1,N7-bound ligands in the neutral form[21] and as chelating agents binding *via* O1,N6 when they are monodeprotonated at NH_2,[16–20] linear chainlike polymeric structures with bridging LH and chelating L^- ligands are considered as most probable for these compounds. The Mn and Cu complexes are presumably distorted tetrahedral of type II with L^- chelating *via* O1,N6 and LH bridging *via* O1,N7 (MN_2O_2 chromophores) and ionic ClO_4^-. The remaining complexes involve a similar arrangement of the L^- and LH ligands, and contain also two additional terminal ligands, *i.e.*, two EtOH (M = Ni; III) or one EtOH and one $-OClO_3$ ligand (M = Fe, Co, Zn; IV), attaining coordination number six.



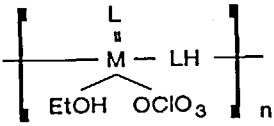
$$\left[-\overset{L}{\overset{\|}{M}}-LH-\right]_n (ClO_4)_n$$

II



$$\left[-\underset{\underset{(EtOH)_2}{|}}{\overset{L}{\overset{\|}{Ni}}}-LH-\right]_n (ClO_4)_n$$

III



$$\left[-\underset{EtOH\quad OClO_3}{\overset{L}{\overset{\|}{M}}}-LH-\right]_n$$

IV

A final point of interest is that teof apparently dehydrates effectively[51] the hydrated M(II) perchlorates used as starting materials. In contrast, reaction of adoNO with $M(ClO_4)_3.6H_2O$ (M = Cr, Fe) in teof–EtOH, under exactly the same conditions, led to precipitation of dimeric $ML(LH)(OH)ClO_4.H_2O$ complexes.[8] In this case, the water of crystallization of the metal salts did not react completely with teof (yielding EtOH and ethyl formate[51]) and this resulted in the formation of complexes containing aqua and hydroxo ligands.[8]

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