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Adenine N(1)-Oxide Complexes with First Row Transition Metal Perchlorates*

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A series of adenine N(1)-oxide (LH) complexes with 3d metal perchlorates were prepared by refluxing mixtures of ligand and salt in ethanol–triethyl orthoformate. Characterization studies revealed significant differences in ligand binding sites and probable complex structural types, with metal ion variation. Thus, $[Cr(LH)_2(OClO_3)_2(EtOH)_2](ClO_4)$ *and* $[M(LH)_2(OClO_3)(EtOH)_2](ClO_4)$ *(M = Mn, Zn) seem to be monomeric with unidentate, imidazole nitrogen-bonded (most probably N(7)) LH, while the* Co^{2+} *analogue of the latter two complexes is apparently a linear polymer, with single bridges of bidentate O(1), N(7)-bonded LH, as well as terminal unidentate imidazole nitrogen-bonded ligand groups. The rest of the complexes involve both neutral LH and anionic* L^- *ligands. The subnormal room temperature magnetic moment of the* Cu^{2+} *complex (1.68 μB) favours a triple ligand-bridged structure of the* $[(O_3ClO)Cu(LH)L_2Cu(OClO_3)]$ *type, with O(1), N(7)-bonded bridging ligands.* $Ni(LH)L(ClO_4)\cdot 2EtOH$ *and* $Fe(LH)_2L(ClO_4)_2$ *were considered as linear polymers, with single bridges of O(1), N(7)-bonded adenine N(1)-oxide ligands; the rest of the ligands present seem to be terminal, unidentate imidazole nitrogen-bonded for M =* Ni^{2+} *and bidentate chelating, O(1), N(6)-bonded for M =* Fe^{3+}*.*

Introduction

A number of studies of adenine N(1)-oxide (adH-NO or LH; *1*) metal complexes have been reported in the past [2, 3]. Studies of CuL_2 or LH complexes with various CuX_2 salts (X = Cl, ClO_4, ½SO_4) [2] and stability constant investigations of the corresponding complexes with first row transition M^{2+} ions (M = Mn through Zn) [3], led to the conclusion that neutral LH or the deprotonated anionic L^- ligand functions as bidentate, coordinating through the NH_2 (or =NH in the deprotonated form) and N(7) nitrogen atoms, without any involvement of the N(1)–O oxygen in coordination [2, 3]. However, the corresponding nucleoside, adenosine N(1)-oxide, was considered as having the tendency to chelate through the N(1)-O oxygen and the NH_2 nitrogen [3–6], but it was also independently concluded that the most favoured binding site of this ligand is the N(7) nitrogen [7, 8]. Following our recent studies of purine complexes with 3d metal chlorides [9] and perchlorates [10] and adenine complexes with 3d metal perchlorates [11], it was of interest to us to extend our work to the complexes of the corresponding N-oxide ligands [1]. Studies of the coordination chemistry of purine N-oxides would be of interest not only from the purely inorganic chemical standpoint, but also in view of the established oncogenic activity [12] of these ligands. In a preliminary communication we presented the results of our synthetic and characterization studies of well-defined, solid adenine N(1)-oxide complexes with Co^{2+}, Ni^{2+} and Cu^{2+} perchlorates [13]. All three of these complexes have been found to contain N(1)-O oxygen-bonded LH or L^- ligands [13]. Now our studies in this direction have been completed and are reported in the present paper, which deals with the preparation and characterization of several 3d metal perchlorate (M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) complexes with adenine N(1)-oxide.

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*Ref. 1.

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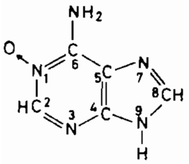
TABLE I. Analyses of Adenine N(1)-Oxide (LH) Complexes with 3d Metal Perchlorates.

Complex	Colour	Analysis, Found (Calcd.) %				
		C	H	N	M	Cl
$Cr(LH)_2(ClO_4)_3 \cdot 2EtOH$	Dark green[a]	22.8	3.3	19.05	6.8	14.2
		(22.6)	(3.0)	(18.8)	(7.0)	(14.3)
$Mn(LH)_2(ClO_4)_2 \cdot 2EtOH$	Beige	26.2	3.4	21.7	8.7	11.2
		(25.9)	(3.4)	(21.6)	(8.5)	(10.9)
$Fe(LH)_2L(ClO_4)_2$	Maroon	25.8	1.7	29.5	8.2	10.3
		(25.5)	(2.0)	(29.7)	(7.9)	(10.0)
$Co(LH)_2(ClO_4)_2 \cdot 2EtOH$	Brick red	25.4	3.65	21.55	8.9	11.2
		(25.8)	(3.4)	(21.5)	(9.0)	(10.9)
$Ni(LH)L(ClO_4) \cdot 2EtOH$	Light green	30.1	3.7	25.8	10.7	6.8
		(30.5)	(3.8)	(25.4)	(10.6)	(6.4)
$Cu_2(LH)L_2(ClO_4)_2$	Olive green	22.9	1.9	26.75	16.4	9.6
		(23.2)	(1.7)	(27.0)	(16.3)	(9.1)
$Zn(LH)_2(ClO_4)_2 \cdot 2EtOH$	Pale grey-green	25.9	3.1	20.9	9.5	10.5
		(25.5)	(3.4)	(21.3)	(9.9)	(10.8)

[a] Almost black.



(1)

Experimental

Synthetic Procedures

Reagent grade adH-NO (Aldrich), hydrated metal perchlorates and organic solvents were generally used. 1.4 mmol metal perchlorate is dissolved in a mixture of 15 cm^3 triethyl orthoformate (teof) and 35 cm^3 absolute ethanol. Then, 2.5 mmol adH-NO are added, and the mixture is refluxed for 48 hr. After 2–5 hr of refluxing, precipitates begin forming in all but one (M = Cr^{3+}) cases, and their quantities gradually increase as refluxing continues. As already mentioned [13], in two cases (M = Ni^{2+}, Cu^{2+}) precipitates differing in colours from those of the final products start forming at the early stages of refluxing; these precipitates are eventually dissolved in the mother liquor and replaced by the green-coloured final precipitates. After 48 hr of refluxing, the volume of the reaction mixture is reduced to about one-half the original volume. The solid new complexes (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) are then separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. With Cr^{3+}, a green oily precipitate is obtained after refluxing and reduction of the volume of the mother liquor (heating under reduced pressure). The supernatant is then decanted and the oily product is mixed with 10 cm^3 anhydrous diethyl ether, the mixture is stirred, the ether layer is then allowed to separate and is subsequently decanted; this type of treatment is repeated 4–5 times. Finally, the oily Cr^{3+} complex is stored *in vacuo* over anhydrous $CaCl_2$. This product gradually solidified after 1–2 months' storage in the desiccator. Elemental analyses (C, H, N, Cl by Schwarzkopf Microanalytical Laboratory, Woodside, New York: metals by atomic absorption spectroscopy) are given in Table I. The yields of the new complexes (% of the theoretical) obtained by the above synthetic method were: M = Cr^{3+} 20; Mn^{2+} 72; Fe^{3+} 39; Co^{2+} 72; Ni^{2+} 56; Cu^{2+} 55; Zn^{2+} 52.

Spectral and Magnetic Studies

Infrared spectra of the ligand and the new metal complexes (Table II) were recorded on Nujol and hexachloro-1,3-butadiene mulls between NaCl windows (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 ambient temperature (300 K) magnetic susceptibility measurements were obtained by methods described elsewhere [14] (Table III).

Results and Discussion

Type of Complexes Synthesized

Table I shows the stoichiometries of the new metal complexes, along with analytical data. In most of these compounds the adenine N(1)-oxide to metal molar ratio is 2:1 (Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}); all these complexes are also characterized by the presence of two ethanol ligands. On the other hand, the Fe^{3+} and Cu^{2+} complexes involve 3:1 or 3:2 ligand to metal ratios and are EtOH-free. The Cr^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+} complexes contain exclusively neutral LH ligands (*i.e.*, $Cr(LH)_2(ClO_4)_3 \cdot 2EtOH$ and $M(LH)_2(ClO_4)_2 \cdot 2EtOH$ (M = Mn, Co, Zn)). In contrast, $Fe(LH)_2L(ClO_4)_2$, $Ni(LH)L(ClO_4) \cdot 2EtOH$ and

TABLE II. Selected Regions of the Infrared Spectra of Adenine N(1)-Oxide (LH) and its Complexes with 3d Metal Perchlorates, cm^{-1}.

LH	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Cu^{2+}	M = Zn^{2+}	Band assignment[a]
	3400m,b	3370m,b		3330m,b	3360m,b		3345m,b	ν(OH) (EtOH)
2720w, 2670w	2705w,vb	2710w, 2680w	2770w,sh	2715w, 2675w	2720w, 2660w	2715w, 2655w	2710w,b	ν(NH)
1663s	1688s	1680s	1699s, 1631ms	1670s	1660ms	1656ms	1675s,b	NH_2 defomration[b]
1608m, 1593m	1633m, 1610m	1639w, 1610w	1611m	1635w, 1608m	1640w, 1611m	1614m	1642m, 1609m	A′ pym (8a) + δ(OH)
1560ms	1563m	1566m	1564m	1557m,b	1555m,b	1570m	1561m	A′ pym (8b)
1513w							1489m	A′ im (R_1) +
1487w	1488vw	1490w	1485vw	1483m	1490m	1486m	1471m,sh	A′ pym (19b) +
1442w	1450w,b	1447m	1451vw	1450m	1452m	1450w	1450bw	A′ im (R_2)
1411m			1413mw			1402mw		A′ im (R_3) +
	1387m,b	1390ms,b		1386ms,b	1382ms,b		1393ms,b	δ(CH)(EtOH) +
1371w			1370w			1367w		A′ pym (19a)
1345w	1353w	1345w	1339w	1350w	1340w	1343w	1338w	A′ pym (14) +
1321w	1300w,b	1302w,b	1299w,b	1297w,b	1303w,b	1309w	1304w,b	A′ im (R_4) +
1308w						1299w		NH_2 wag
1272m								NH_2 def,[b] + A′ im (NH)
1264m,sh	1270mw,b	1271m,b	1261w	1273ms	1270w	1248m	1270m,b	+ ν(N–O) + A′δ(CH)
1240m	1235m,b	1237m,b	1227m	1238ms	1236m		1236ms,b	
1210w			1191s	1195ms,b	1198s	1199s		
1155m, 1091w	c	c	c	c	c	c	c	NH_2 wag + twist
1020w,b	c	c	c	c	1010w	1010m	c	A′ (R)
	1153vs, 1085 vvs, 1051vs	1150vs, 1095 vvs, 1050vs	1075vs,b	1137vs, 1095 vvs, 1052vs,b	1100vs,b, 1045vs,sh	1092vvs, 1056vs	1150s, 1080 vs,b, 1047vs	$\nu_3(ClO_4)$
	c	1041vs,sh		1037vs,sh	1035s,sh		c	δ(CH)(EtOH)
971m, 940m	966m	960m	963m	969m	968m	970w, 949m	965m	NH_2 def.[b] + A′ (R) +
918m	931m,b	927m,b	914m,b	930m,b	931m,b	922m	928m,b	A″ γ(CH) + $\nu_1(ClO_4)$
721ms	717mw	720ms	724w, 699w	720ms	721ms	722ms	714m	NH_2 defomation[b]
648w, 629vw	c	c	648w,sh	c	c	c	c	A′ (R)
	653m, 632m, 624m	640m, 628m, 620m	621ms	641w, 628m, 621m,sh	619m, 611m	632m, 614m	639w, 626m, 618m	$\nu_4(ClO_4)$
d			446m,b	361w	377m	461s, 421m,sh		ν(M–O) (N-oxide)
	450m	368m		347w,b	355mw		345m	ν(M–O) (EtOH)
	341m	316m		307w,b	312w,b	372ms	310m,b	ν(M–O) ($-OClO_3$)
	282w	272w	270m,b	255w, 232w	258w, 234w	319m, 302m, 275m	264w	ν(M–N)

[a] Band assignments for free LH based on works dealing with ir spectra of purine, adenine, their metal complexes and various N-oxides [9–11, 13, 16–20]; purine band assignments after Lautié and Novak [16] (pym = pyrimidine; im = imidazole; R = ring skeletal vibration); NH_2 band assignments from refs. 17 and 18. [b] NH_2 deformation modes of LH: symmetric in-plane 1663; asymmetric out-of-plane 1272–1240 region; symmetric out-of-plane 940; asymmetric in-plane 721 cm^{-1} [17, 18]. [c] Masked by other absorption. [d] Main bands of LH at 550–200 cm^{-1}: 530m, 488m,b (masking $\nu_2(ClO_4)$ in the spectra of the complexes), 446w,sh, 422vw, 403vw,b, 382vw, 354vw, 330vw, 290vw, 281vw, 269vw, 247vw, 230 vw,vb.

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Ambient Temperature (300 K) Magnetic Properties of Adenine N(1)-Oxide (LH) Complexes with Metal Perchlorates.

Complex	λ_{max}, nm^{a,b}	$10^6\ \chi_M^{cor}$, cgsu	μ_{eff}, μB
$Cr(LH)_2(ClO_4)_3 \cdot 2EtOH$	242vs, 278vs, 292vs, 315vs, 337vs, 462s,sh, 550ms,vb, 602m,sh, 650w,sh, (935w,sh, 1350w,vb)	6191	3.86
$Mn(LH)_2(ClO_4)_2 \cdot 2EtOH$	208vvs,sh, 247vs,sh, 267vs, 303vvs,b, 375ms,b 455m,sh, 560w,sh, (940w,b, 1370w,b)	14,802	5.96
$Fe(LH)_2L(ClO_4)_2$	220vs, 245vs,sh, 266s,sh, 280s, 313vs,sh, 360ms,b, 475m,vb, (970w, 1345w)	15,022	6.01
$Co(LH)_2(ClO_4)_2 \cdot 2EtOH$	219vvs, 240vvs,sh, 257vvs,b, 283vvs,b, 320vs,sh, 375s,sh, 468m, 512m, 900w,sh, (965w,b), 1300w,b, (1350w,sh)	10,930	5.13
$Ni(LH)L(ClO_4) \cdot 2EtOH$	214vvs, 235vvs, 264vs,vb, 278vs,sh, 313s,sh, 395s, 625m, 747m, (950w), 1025w,b, 1265w,b, (1360w,sh)	4600	3.33
$Cu_2(LH)L_2(ClO_4)_2$	225vvs, 255vvs,b, 283vvs,b, 318vvs,b, 380s,sh, 617s,sh, 660s,b, (960w, 1350w,b)	1174	1.68
$Zn(LH)_2(ClO_4)_2 \cdot 2EtOH$	215vvs, 243s, 281s,sh, 308vs, 367m,sh, (950w,b, 1375w)	Diamagnetic	

[a] Reported spectrum of the free ligand at pH 7: 231, 262.5 nm [39]. [b] Near-ir bands, common in the spectra of all the metal complexes, and apparently due to vibrational overtones and combination bands originating from adenine N(1)-oxide [31] are shown in parentheses; near-ir bands of uncomplexed adH-NO, nm: 960vw, 1355vw.

$Cu_2(LH)L_2(ClO_4)_2$ are characterized by the presence of both neutral LH and monodeprotonated anionic L^- ligands. It was previously mentioned that, during the preparation of the Ni^{2+} and Cu^{2+} complexes, small amounts of precipitates, differing in colour from the finally isolated solids, were formed after 1–2 hr of refluxing (see Experimental; colours of early precipitates: golden orange for M = Ni; maroon for M = Cu). These precipitates were eventually dissolved in the mother liquor, upon continuation of refluxing, and were finally replaced by the green-coloured complexes shown in Table I [13]. The above early products are most probably analogues of the new Mn^{2+}, Co^{2+} and Zn^{2+} complexes, *i.e.*, of the $M(LH)_2(ClO_4)_2 \cdot xEtOH$ type (M = Ni, Cu). We have not managed as yet to isolate sufficient quantities of these two intermediates for characterization. During the preparation of the Fe^{3+} complex, no formation of any intermediate precipitate was observed. It should be also mentioned that, during attempts at the isolation of a Fe^{2+} complex with adenine N(1)-oxide, the Fe^{3+} complex of Table I was precipitated, even when we operated under inert conditions [15].

Among the complexes of Table I, those with Cr^{3+}, Mn^{2+} and Zn^{2+} show limited solubility in some organic solvents, such as N,N-dimethylformamide. The rest of the new complexes (M = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) are generally insoluble in all common organic solvents. Finally, all of the new complexes are stable in the atmosphere.

Infrared Spectra

Selected regions of the ir spectra of the ligand and its metal complexes are given in Table II. Band assignments for free adenine N(1)-oxide were based on analogous assignments for purine [16], adenine [17, 18] and the N-oxides of various pyrimidines and other diazines [19–21]. Regarding the ν(N–O) mode, it has been quite often found to occur as a doublet in the spectra of diazine N-oxides [19–21], and it is not unlikely that more than one of the bands at 1272–1240 cm^{-1} in the spectrum of free adH-NO have ν(N–O) character. The spectra of the new metal complexes in the same region (1272–1190 cm^{-1}) are of particular interest. Thus, in the spectra of the new Cr^{3+}, Mn^{2+} and Zn^{2+} complexes, the two main bands of the ligand (1272, 1240 cm^{-1}) appear virtually unshifted; this indicates that the ligand does not coordinate through either the N(1)-O oxygen [22] or the NH_2 nitrogen [17, 18] in these three compounds. The non-participation of the NH_2 group in coordination in these complexes is also suggested by the positive frequency shifts of the NH_2 symmetric in-plane deformation mode, occurring at 1663 cm^{-1} in free LH, and the relatively small shifts of the other two NH_2 deformation modes (940–918 and 721 cm^{-1}) [17]. The Co^{2+}, Ni^{2+} and Cu^{2+} complexes also do not appear to involve ligands coordinating through NH_2, as they show similar to the preceding behaviour of the NH_2 deformation bands in their spectra. However, these complexes obviously contain N(1)-O oxygen-bonded adenine N(1)-oxide ligands, as shown by the occurrence of a strong band at 1199–1195 cm^{-1}, attributable to a shift of ν(N–O) to lower wavenumbers [22], in their spectra. It is rather well established that in the ir spectra of adenine metal complexes, no strong absorption at 1200–1190 cm^{-1} is normally observed [17, 18, 23] (a single exception to this is $[Cu(adH)(ad)(phen)_2(OH)]_2 \cdot 2H_2O$, were adH = adenine and phen = 1,10-phenanthroline; this complex exhibits a strong band at 1196 cm^{-1} [18], but this absorption is certainly due to the phen [24] rather than the adenine ligands). Hence, the absorption at 1199–1195 cm^{-1} in the spectra of the Co^{2+}, Ni^{2+} and Cu^{2+} complexes can only arise by a shift of ν(N–O) to lower wavenumbers, owing to coordination of the ligand through the N–O oxygen [22]. The spectra of the Co^{2+} and Ni^{2+} complexes indicate that these compounds contain some N–O oxygen-bonded ligands and other adenine N(1)-oxide ligands, that are not O-bonded (three distinct maxima at 1273–1270, 1238–1236 and 1198–1195 cm^{-1}) [22]; on the other hand, the Cu^{2+} complex shows only two bands at 1248 and 1199 cm^{-1}, and apparently contains exclusively O-bonded ligands [13, 22]. Finally, in the Fe^{3+} complex, all the ligands are also O-bonded (maximum at 1191 cm^{-1}). The behaviour of the NH_2 deformation bands in the spectrum of this compound is of particular interest; thus, all of these bands (*i.e.*, at 1663, 1272–1240, 940–918 and 721 cm^{-1} in free LH) are split, with the low wavenumber components corresponding to substantial negative frequency shifts, relative to their location in the spectrum of the free ligand. These features favour coordination of a part of the ligands through the NH_2 nitrogen [7, 11, 17, 25]. With respect to the ring nitrogens of the ligand, the presence of the ν(NH) absorption in the spectra of all the new complexes (2720–2655 cm^{-1}) ascertains that, at least part of the ligands, are in the neutral, protonated form [9–11, 15]. On the other hand, all the complexes appear to also involve coordination of adenine N(1)-oxide through one of the imidazole nitrogens (*vide infra*), as suggested by characteristic shifts of the A′ im (R_1) and (R_3) bands [9, 10, 15].

As regards the rest of the ligands present in the new metal complexes, the i.r. evidence is as follows: the Fe^{3+} complex contains exclusively ionic perchlorate (single ν_3 and ν_4 (ClO_4) absorptions), but the rest of the complexes contain coordinated perchlorate, as shown by ν_3, $\nu_4(ClO_4)$ splittings [26, 27]. Each of these fundamental vibrational modes appears as triply split in the spectra of the Cr^{3+}, Mn^{2+}, Co^{2+} and Zn^{2+} complexes, which seem to contain both ionic ClO_4^- (T_d symmetry) and unidentate coordinated $-OClO_3$ ligands (C_{3v} symmetry); whereas in the spectra of the Ni^{2+} and Cu^{2+} complexes, ν_3 and $\nu_4(ClO_4)$ are split into only two components, presumably due to the exclusive presence of coordinated $-OClO_3$ [13, 26, 27]. The complexes involving coordinated EtOH (M = Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) show the characteristic ν(OH) and δ(OH) bands at 3400–3330 and 1642–1633 cm^{-1}, respectively [28, 29]. The various C–H bending vibrational bands of ethanol at 1500–1000 cm^{-1} [30] are, in most cases, masked by ligand and perchlorate absorptions. In some cases, EtOH bands are observed as shoulders of the split $\nu_3(ClO_4)$ absorptions (1041–1035 cm^{-1}), while in the 1420–1360 cm^{-1} region, the overlap of the EtOH band at *ca.* 1400 cm^{-1} [30] with the A′ im (R_3) and A′ pym (19a) modes results in a single broad maximum (M = Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}). This is not observed in the spectra of the EtOH-free Fe^{3+} and Cu^{2+} complexes, which exhibit two distinct maxima at 1415–1402 (A′ im (R_3)) and 1370–1367 (A′ pym (19a)) cm^{-1}.

Tentative metal–ligand band assignments at 500–200 cm^{-1} were based on previous far-ir studies of 3d metal complexes with purines [9–11, 14, 31] and diazines [32, 33], aromatic amine N-oxides [34–36], perchlorato [37] and ethanol [11, 38] ligands. These assignments (Table II) favour coordination number six for M = Cr^{3+}, Fe^{3+}, Co^{2+} and Ni^{2+}, five for M = Mn^{2+} and Zn^{2+} and four for M = Cu^{2+} [9–11, 13, 14, 31–38].

Electronic Spectral and Magnetic Data

These data are given in Table III. The main $\pi \rightarrow \pi^*$ transition bands of the ligand (231, 262.5 nm) [39] appear in most cases as split in the spectra of the metal complexes, showing an overall trend of being shifted to lower energies upon metal complex formation. A similar trend was observed during complex formation between adenine and Pt^{2+} [40]. The UV bands of the complexes in the region below 250 nm may also involve contribution from EtOH absorption [41]. An absorption band at 300–320 nm in the spectra of the new complexes is presumably due to the $n \rightarrow \pi^*$ transition of the ligand. The spectra of the paramagnetic metal complexes, exhibit also strong metal-to-ligand charge-transfer bands, originating in the UV and trailing off into the visible region. Charge-transfer absorption of this type is quite common in 3d metal complexes with diazines [42], purines [9, 10] and aromatic amine N-oxides [43]. The spectra of the ligand and its metal complexes are also generally characterized by the presence of near-i.r. bands at 935–970 and 1345–1375 nm, which are due to vibrational overtones and combination modes of LH [31].

The d–d transition spectra of the Cr^{3+}, Co^{2+} and Ni^{2+} complexes are compatible with low-symmetry hexacoordinated configurations [44]; band assignments, nm: M = Cr^{3+}: ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 462; $\rightarrow {}^4T_{2g}(F)$ 550, 602, 650 (Dq = 1665 cm^{-1}); M = Co^{2+}: ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, ${}^4A_{2g}(F)$ 468, 512; $\rightarrow {}^4T_{2g}(F)$ 1300; M = Ni^{2+}: ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 395; $\rightarrow {}^3T_{1g}(F)$ 625, 747; $\rightarrow {}^3T_{2g}(F)$ 1025, 1265 (Dq = 873 cm^{-1}). The approximate Dq of 873 cm^{-1}, calculated for the Ni^{2+} complex is consistent with a NiN_2O_4

absorbing species, with the four oxygens corresponding to one N-oxide, one $-OClO_3$ and two EtOH ligands [6, 13, 31] Likewise, the Dq of 1665 cm^{-1}, calculated for the Cr^{3+} complex, seems to agree with a CrN_2O_4 absorbing species, with two $-OClO_3$ and two EtOH ligands in this case (*vide infra*) [21, 45] Regarding the Cu^{2+} complex, the occurrence of the split d–d band maxima at 617 and 660 nm can be attributed to a square-planar configuration, with adenine N(1)-oxide functioning as a bidentate bridging O,N-ligand [6, 13, 31]

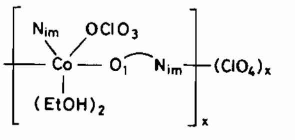
The ambient temperature magnetic moment of the Cu^{2+} complex (1 68 μB) is low for magnetically normal compounds of this metal ion Several binuclear Cu^{2+} complexes, involving quadruple adenine bridges, and exhibiting room temperature magnetic moments of 1 5–1 7 μB, have been reported [11, 31, 46–49], these complexes show deviation from Curie–Weiss behaviour, due to antiferromagnetic exchange, even at relatively high temperatures [46–48] Hence, the magnetic behaviour of the new Cu^{2+} complex is suggestive of a binuclear structure with multiple adenine N(1)-oxide bridges The ambient temperature magnetic moments of the rest of the new complexes are generally normal for high-spin $3d^3$, $3d^5$, $3d^7$ or $3d^8$ compounds Some of these complexes (M = Cr^{3+}, Mn^{2+}, Zn^{2+}) seem to be monomeric, but other complexes (M = Fe^{3+}, Co^{2+}, Ni^{2+}) are presumably bi- or poly-nuclear In the latter cases, the normal room temperature μ_{eff} values do not necessarily rule out polymeric configurations In fact, we have recently demonstrated that polymeric Co^{2+}, Ni^{2+} and Cu^{2+} purine complexes, most probably involving single-bridged, chainlike –M–(purine)–M–(purine)– sequences, exhibit normal room temperature magnetic moments, but show clearcut evidence in favour of magnetic exchange interactions (significant μ_{eff} decreases with decreasing temperature, negative θ values, deviation from Curie–Weiss behaviour at low temperatures) when studied at 300–80 K [10] Studies of the temperature dependence of the paramagnetism of the new metal complexes are to be undertaken in the near future

Ligand Binding Sites and Likely Structures of the Complexes

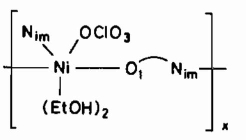
As discussed in the preceding sections, some of the new metal complexes (M = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) involve ligands binding through the O(1) oxygen, while in the Fe^{3+} complex part of the ligands appear to coordinate through the NH_2 nitrogen It is quite obvious that most common in the majority of the complexes investigated is binding of the ligand through a ring nitrogen, the imidazole N(7) and N(9) nitrogens are much more likely binding sites, relative to the pyrimidine N(3) nitrogen [16, 25, 50, 51] Regarding the two imidazole nitrogens, the most probable binding site of a purine ligand appears to be the ring nitrogen, which is protonated in the free ligand [50] Thus, in the case of free adenine the N(9) is protonated [50, 52], and the most common binding site of adenine is indeed N(9) [46–48] The protonation of free adH-NO at N(9) (*1*) is not unlikely, but this has not been established Hence, at this point, we have to go by the early evidence on this ligand, which seemed to tend to coordinate through N(7) rather than N(9) [2, 3]

The three new complexes that show some solubility in organic media and do not involve coordination of the ligand through either O(1) or the NH_2 nitrogen (M = Cr^{3+}, Mn^{2+}, Zn^{2+}), are most probably monomeric, with imidazole nitrogen-bonded adH-NO Most likely formulations are $[Cr(N_{im})_2(OClO_3)_2(EtOH)_2](ClO_4)$ and $[M(N_{im})_2(OClO_3)(EtOH)_2](ClO_4)$ (M = Mn, Zn, N_{im} indicates the imidazole nitrogen-bonded unidentate adH-NO, im = 7 or 9, with im = 7 being more likely [2, 3]), on the basis of the overall evidence presented For the Cu^{2+} complex, a binuclear structure of the $[(O_3ClO)Cu(adH\text{-}NO)(ad\text{-}NO)_2Cu(OClO_3)]$ type, with triple ligand bridges (involving two anionic monodeprotonated and one neutral ligand) was previously proposed [12] When functioning as bidentate bridging ligands, the purines most commonly coordinate through either the N(3), N(9)- [49, 50, 53] or the N(1), N(7)- [50, 54] sites However, examples of complexes with N(7), N(9)-bonded bidentate bridging purines are also known [25, 51, 55], and it is, therefore, not inconceivable that the N(1), N(9)-combination is possible Since one of the binding sites of the bridging N-oxide ligands in the Cu^{2+} complex is the O(1) oxygen, the preceding structural type can be written as $[(O_3ClO)Cu(\overset{\frown}{O_1N_{im}})_3Cu(OClO_3)]$, where $\overset{\frown}{O_1N_{im}}$ indicates the binding sites of the bridging ligand, and im = 7 is again more likely than im = 9

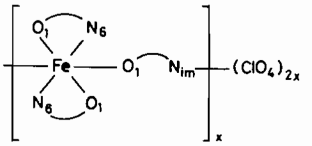
The remaining three complexes (M = Fe^{3+}, Co^{2+}, Ni^{2+}) are apparently bi- or poly-nuclear Since their ambient temperature magnetic moments are normal, it is considered as more probable that they involve single rather than multiple adenine N(1)-oxide bridges [9, 10], as the latter type of bridging would be expected to cause somewhat low magnetic moment values even at room temperature, at least for Fe^{3+} [56, 57] Whereas, in the case of single-bridged chainlike polymeric complexes, with large separations between adjacent metal ions, the effects of spin–spin coupling would not be obvious for M = Fe^{3+}, Co^{2+} or Ni^{2+}, and possibly even Cu^{2+} [9, 10, 56, 58, 59] At lower temperatures, these single-bridged complexes would be, of course, expected to show deviations from Curie–Weiss behaviour [10, 58, 59] On the basis of the preceding discussion, and the fact that only part of the adenine N(1)-oxide ligands are coordinated through O(1) in the Co^{2+} and Ni^{2+} complexes, these compounds may be formulated as linear polymers of types (*2*) and (*3*), with one unidentate, imidazole nitrogen-bonded and one bridging bidentate, N(1)-O oxygen- and imidazole nitrogen-bonded ligand per metal ion. As far as the Fe^{3+} complex is concerned, the i.r. evidence seems to favour a structure involving two types of bidentate coordinated adenine N(1)-oxide ligands, *viz.*, some chelating through the N(1)-O oxygen and the NH_2 nitrogen [3–6] and some bridging, N(1)-O oxygen and imidazole nitrogen-bonded, as shown in (*4*). The fact that in the Ni^{2+} and Fe^{3+} complexes, one ligand per metal ion is anionic and the rest (one for M = Ni^{2+}, two for M = Fe^{3+}) are neutral (Table I), might be taken as suggesting that the bridging ligand in structural types (*3*) and (*4*) is the anionic monodeprotonated species.



(2)



(3)



(4)

In conclusion, in a series of new complexes of adenine N(1)-oxide with 3d metal(II) and (III) perchlorates, striking differences, as far as the binding site or sites of the ligands and the likely structural types of the complexes are concerned, were observed with metal ion variation. Some of these differences may be due to the presence of anionic ad-NO^- and EtOH ligands in some new complexes, in addition to the neutral adH-NO ligands, which are present in all the complexes reported. However, differences were observed even between species with the same stoichiometries, *i.e.*, the monomeric Mn^{2+} and Zn^{2+} complexes *vs.* the polymeric Co^{2+} analogue. Hence, it appears that, as is the case with the parent base [11, 25, 31, 46–51, 53, 54], the binding sites of adenine N(1)-oxide with a given metal salt and the structural type of the resulting complex are not easily predictable. Regarding the various adenine N(1)-oxide sites used for binding in the complexes herein reported, our work seems to confirm previous conclusions from studies of metal complexes with adenine and adenosine N(1)-oxides [2–8]. The ligand under study seems to bind exclusively through an imidazole nitrogen (most probably N(7)), when functioning as unidentate, terminal. It may also act as bidentate, chelating, O(1), N(6)-bonded or bidentate, bridging, O(1), N(im)-bonded.

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