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Purine N(1)-Oxide Complexes with 3d Metal Perchlorates*

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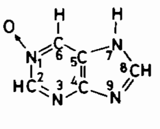
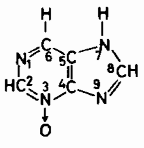
A series of purine N(1)-oxide (LH) complexes with 3d metal perchlorates were synthesized by refluxing mixtures of ligand and salt in ethanol–triethyl orthoformate. In one case (M = Cr^{3+}), an apparently hexacoordinated monomeric complex of the $[Cr(LH)_2(C_2H_5OH)_2(OClO_3)_2](ClO_4)$ type, with terminal imidazole nitrogen-bonded LH was isolated (N(7) and N(9) are considered as equally likely binding sites for terminal unidentate LH). A number of pentacoordinated M^{2+} complexes of the $M(LH)_2(C_2H_5OH)(ClO_4)_2$ type (M = Mn, Fe, Ni, Cu, Zn) seem to contain exclusively bidentate bridging LH, coordinated through the O(1) oxygen and one of the imidazole nitrogens (most probably N(7)); whereas, $Co(LH)_2(C_2H_5OH)_2(ClO_4)_2$ (pentacoordinated) and $Fe(LH)_3(ClO_4)_3$ (hexacoordinated) involve both bidentate bridging ligands of the preceding type and terminal unidentate imidazole nitrogen-bonded LH groups. Since all of the new polymeric complexes show normal ambient temperature magnetic moments, structural types involving single –M–LH–M–LH– bridges were considered as most probable. Simple linear chain-like structures with –M–LH–M–LH– sequences were proposed for the Co^{2+} and Fe^{3+} complexes (the latter compound also contains a bidentate $=O_2ClO_2$ ligand per Fe^{3+} ion), whilst for the Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} compounds, a more complicated structural type, involving cross-linking of linear chains of the preceding type, seems to be most likely.

Introduction

Studies of metal complexes with biologically important substituted purines have been the subject of numerous publications in recent years [2, 3]. Analogous reports on the metal complexes of the corresponding N-oxides are much more scarce and limited to a number of complexes with the N(1)-oxides of adenine [4–7], adenosine and inosine [4, 8–11]. Regarding the parent heterocycle (purine), there was until recently a relative dearth of information on its metal complexes (with only a number of Cu^{2+} [12], Hg^{2+} [13] and heavy transition metal, such as W, Rh, Ir [14], complexes having been adequately characterized), and a complete lack of studies dealing with metal complexes of the known purine N-oxides, *i.e.*, purine N(1)-oxide (I) and purine N(3)-oxide (II) [15]. These laboratories have recently reported on the syntheses and characterization of 3d metal chloride [16] and perchlorate [17] complexes with purine, and it was felt that extension of our work to include the corresponding metal complexes with purine N-oxides was in order. In addition to their interest from a purely inorganic chemical standpoint, these metal complexes would be also of bioinorganic interest, in view of the oncogenic activity [18] of the N-oxides of purine derivatives. Accordingly, research in this direction was undertaken, and a series of metal complexes with the commercially available (Aldrich, Alfred Bader rare chemicals) purine N(1)-oxide (I; puH-NO or LH) were prepared and are being characterized. The present paper deals with our synthetic and characterization studies of puH-NO complexes with 3d metal perchlorates.



(I)



(II)

Experimental

Synthetic Procedure

Reagent grade puH-NO, hydrated metal perchlorates and organic chemicals were generally used. 0.65 mmol of the metal salt is dissolved in a mixture of 15 ml triethyl orthoformate (teof) and 35 ml absolute

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*See Ref. 1.

TABLE I. Analytical Data for New Purine N(1)-Oxide (LH) Complexes with Metal Perchlorates.

Complex	Color	Analysis, Found (Calcd.) %				
		C	H	N	M	Cl
$Cr(LH)_2(ClO_4)_3 \cdot 2C_2H_5OH$	Dark green	23.86	2.80	15.53	7.60	15.26
		(23.53)	(2.82)	(15.68)	(7.28)	(14.88)
$Mn(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	Yellow green	25.22	2.71	19.18	9.50	12.52
		(25.19)	(2.47)	(19.59)	(9.60)	(12.39)
$Fe(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	Maroon	24.87	2.40	19.78	9.88	12.08
		(25.15)	(2.46)	(19.56)	(9.75)	(12.37)
$Fe(LH)_3(ClO_4)_3$	Reddish purple	23.81	1.70	21.66	7.21	14.42
		(23.63)	(1.59)	(22.04)	(7.32)	(14.64)
$Co(LH)_2(ClO_4)_2 \cdot 2C_2H_5OH$	Light brown	26.40	2.95	18.53	9.95	11.22
		(27.02)	(3.24)	(18.01)	(9.47)	(11.40)
$Ni(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	Light green	24.66	2.58	19.77	10.62	12.49
		(25.03)	(2.45)	(19.46)	(10.20)	(12.31)
$Cu(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	Light blue green	25.16	2.61	19.05	11.32	11.83
		(24.82)	(2.61)	(19.30)	(10.94)	(12.21)
$Zn(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	Pale yellow green	25.04	2.25	18.93	11.71	12.18
		(24.74)	(2.42)	(19.24)	(11.22)	(12.17)

ethanol. Then, 1.2 mmol PuH-NO are added and the resulting mixture is refluxed for 2–5 days (depending on the amount of precipitate formed). Precipitates start forming after a few hours of refluxing, and their amounts gradually increase. After the 2–5 days of refluxing, the volume of the supernatant is reduced to about one-half its original volume, by heating under reduced pressure. Then, the solid new complexes are separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. Analytical data (C, H, N, Cl by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.; metals by atomic absorption spectroscopy) are given in Table I. Yields (% of theoretical) of the new complexes: M = Cr^{3+} 20; Mn^{2+} 69; Fe^{2+} 33; Fe^{3+} 21; Co^{2+} 48; Ni^{2+} 47; Cu^{2+} 47; Zn^{2+} 43. With the exception of the Cr^{3+} complex, which is somewhat soluble in a few organic solvents, such as N,N-dimethylformamide, the new complexes are insoluble in organic media. All of the complexes reported are stable in the atmosphere.

Spectral and Magnetic Studies

Infrared spectra of the ligand and its 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 room temperature (298 K) magnetic susceptibility measurements (Table III) were obtained by methods previously described [19].

Discussion

Stoichiometries of the New Metal Complexes

Unlike adenine [20] and adenine N(1)-oxide [7], which, under the synthetic conditions employed in this work, produced 3d metal perchlorate complexes, involving either neutral or anionic (monodeprotonated) ligands or even mixed neutral-anionic ligand complexes, the new complexes with purine N(1)-oxide contain exclusively neutral ligand groups (Table I). With $Fe(ClO_4)_3$, a 3:1 puH-NO to Fe^{3+} complex, not involving any additional ligands, was obtained. In all other cases investigated, 2:1 puH-NO to metal ion complexes, also comprising ethanol ligands (2 for M = Cr^{3+}, Co^{2+} and 1 for M = Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), were isolated. It is noteworthy that no special precautions of operating under inert conditions and using previously deoxygenated solvents were necessary for the preparation of any of the new complexes; this is of especial interest for the Fe^{2+} compound, since precautions of this type are quite often required, in order to prevent possible oxidation of this metal ion during the preparation of ferrous complexes with purine bases and derivatives [7, 21].

Infrared Spectra of puH-NO and its Metal Complexes

As it appears that no IR data have been published for puH-NO, its main IR absorption maxima at 4000–1700 cm^{-1} are given below, while Table II shows the IR spectra of the free ligand and its metal perchlorate complexes at 1700–200 cm^{-1} (along with a number of pertinent IR bands occurring at higher wavenumbers). IR spectrum of puH-NO at

TABLE II. Infrared Spectra of Purine N(1)-Oxide and its 3d Metal Perchlorate Complexes (cm^{-1}).

puH-NO	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^{a}
	3390m,b	3400m,b	3375m,b		3340m	3365m	3380m	3350m,b	ν_{OH} (EtOH)
2725m	2680m,b	2695m,b	2700m,vb	2705m,b	2705m,b	2685m,b	2695m,b	2700m,b	A′ im ν_{NH}
1660ms, 1639ms	1680s,vb	1677s, 1648s	1650s,vb	1686s, 1630s	1680s, 1642s,sh	1670s, 1646s,sh	1660s,vb	1675s, 1650s,sh	^{b} + δ_{OH} (EtOH)
1611ms	1610ms	1613s,sh	1610s,sh	1612ms	1610ms	1611ms	1612ms	1609ms	A′ pym 8a
1569ms	1565m	1575m	1574m	1576m	1567m	1567m	1564m	1572m	A′ pym 8b
1508w	1519w	1514w	1516w	1520w,b	1519w,b	1516w	1520w,b	1518w,b	A′ im R_1
1487w, 1441w	1470w,b	1475w, 1450w	1469w, 1448w	1481w, 1442w	1473w, 1444w	1469m, 1446w	1470w, 1449w	1487w, 1450w	A′ pym 19b + A′ im R_2
1409m	1417m, 1402m	1412w, 1402w	1416w, 1397w	1419m	1415w, 1399w	1415w, 1398w	1420w, 1396w	1419w, 1403w	A′ im R_3 + δ_{CH} (EtOH)
1370w	1378m	1381m	1387m	1374m	1385m	1389m	1377w,b	1390mw	A′ pym 19a
1320w	1330w	1337w	1335w,sh	1329w	1324w,sh	1334w	1335w,b	1330w	A′ im R_4
1300w,b	1308w	1315w,b	1307w	1299m	1294w	1298mw	1300w,b	1307w	
1262w	1267w	1269w	1270w	1270w,sh	1266w,sh	1269w,sh	1270w,sh	1269w	A′ im δ_{NH}
1234m	1231m	1200m	1196m	1231m, 1192m	1230m, 1189m	1242w, 1197m	1200m	1216m, 1200m	ν_{N-O}^{c}
1140m, 1080m	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	A′, R
1022w									
	1141s, 1110vs, 1060s	1080vs,vb	1090vs,vb	1133m, 1095vs, 1077vs, 1050s,sh	1090vs,vb	1085vs,vb	1087vs,b	1078vs,b	ν_3 (ClO$_4$)
964m	960w,b	970w	971w	980w, 955w	968w	972w	969w	977w	A′ R
928m	^{d}	932w	934w	^{d}	931w	933w	933w	936w	A″ CH
	918mw			924m					ν_1 (ClO$_4$)
	880w,b	882w	887w,sh		890w	880w	882w	887w	δ_{CH} (EtOH)
870ms,b	^{d}	903w, 878w	898w, 883w	885w,b	905w, 875w	900w, 875w	908w, 872w	895w, 877w	A′ R + A″ im γ_{NH}
843m	836w,sh	839w,b	830w,b	827w	847w,sh	840w,b	834w,sh	839w,sh	δ_{N-O}
790w, 740w,b	780w,vb	800w, 762w	796w, 750w	775w,vb	799w, 750w	795w, 757w	802w, 751w	803w, 758w	A′ R + A″ γ_{CH}
700m	698w	702w	707w	702w	707w	708w	711w	704w	N–O mode
660w,sh	^{d}	657vw	660vw	^{d}	658vw	660vw	661vw	664vw	A′ R
632w	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	A′ R
612w	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	^{d}	A″ R
	650w, 624ms, 617ms	617ms	622ms	648w, 628ms, 619ms,b	620ms	620ms	619ms	621ms	ν_4 (ClO$_4$)
545m,sh	570m,b	555w,b	560w,b	570w, 554w	575w, 539w	550w, vb	545w	560w,b	A″ R
513m	527mw	520w,b	519w,b	525w	515w,sh	517w,sh	520w,sh	528w,b	
	490mw,sh			488w					ν_2 (ClO$_4$)
475m	480w,sh	475w,sh	470w,vb	475w	480w	480w,b	475w,sh	470w,sh	A″ R
		402m	410m	451m, 420m	418m,sh	423m,b	437m	398m,b	ν_{M-O} (N–O)
	442m	340w	351w		386m	388m	393m,sh	341m,sh	ν_{M-O} (EtOH)
	337w			329w					ν_{M-O} (ClO$_4$)
368w, 350w, 310vw,b, 290vw, 265m	370w, 345w, 305vw,^{e} 266m	360w, 347w, 310vw, 290vw, 266m,b	365w, 340w, 309w, 290w, sh, 263m	370w,sh, 348w,sh, 312m ^{e} ^{e}	373w, 341w, 306w,b, 293w,b, 265m,sh	375w, 343w, 311w,^{e} 265m,sh	370w,b, 339w, 313w^{e}, 264m,sh	376w, 342w, sh, 309vw, 292vw^{e}	A″ R
	288mw	272m,sh	277m,sh	295m, 257m,b	282w, 247m	285w, 250m	291m, 254m	268m,vb	ν_{M-N}

[a] Purine band assignments after Lautié and Novak [13, 22] (pym = pyrimidine; im = imidazole; R = ring skeletal vibration); main bands attributable to the N–O function assigned on the basis of IR spectral band assignments for a variety of aromatic amine N-oxides [29–31]. Among the various δ_{CH} modes of ethanol at 1500–1000 cm^{-1} [38, 39], only a band at ~1400 cm^{-1} could be identified in the spectra of the ethanol-containing complexes. The rest of these absorptions are masked by puH–NO or ClO$_4$ bands. [b] For the possible origin of these bands in free puH–NO see text. [c] ν_{N-O} completely masks several A′ δ_{CH} absorptions, present in the spectrum of the parent base (*i.e.*, 1241, 1212, 1199 cm^{-1}) [13, 16, 17, 22]; these bands are also masked, in all but one (M = Ni^{2+}) of the cases under study, by the shifted ν_{N-O} absorptions in the spectra of the new metal complexes. [d] Masked by perchlorate IR bands. [e] masked by M–N bands.

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Ambient Temperature (298 K) Magnetic Properties of Purine N(1)-Oxide (LH) Complexes with 3d Metal Perchlorates.

Compound	λ_{max}, nm[b]	$10^6 \chi_M^{cor}$, cgsu	μ_{eff}, μB
LH[a]	222vs, 246vs, 272vs, 308vs, (965w,b, 1350w)		
$Cr(LH)_2(ClO_4)_3 \cdot 2C_2H_5OH$	222vs, 248vs,sh, 269vs,sh, 303s,sh, 447s,sh, 562m,b, 655mw,sh, (955w, 1000w,sh, 1360w)	6013	3.80
$Mn(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	218vvs, 240vvs, 270vs,sh, 302vs,sh, 370ms,sh, 555w,b, 622w,b, (955w, 1000w,b, 1350w,b)	15,803	6.16
$Fe(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	229vvs, 255vvs, 268vvs, 307vs,sh, 517m,vb, 560m,sh, 902w,vb, (960w,b, 1000w,b, 1350w,b)	12,361	5.45
$Fe(LH)_3(ClO_4)_3$	228vvs, 252vvs,sh, 266vvs, 305vs,sh, 475m,vb, (960w, 1004w,b, 1350w,vb)	14,467	5.90
$Co(LH)_2(ClO_4)_2 \cdot 2C_2H_5OH$	208vvs, 236vvs,sh, 250vs,sh, 277vs,b, 298vs,sh, 397s,sh, 480m,sh, 555m,sh, 760w,b, 847w,sh, (960w, 995w,b, 1360w,b), 1860vw,b	10,317	4.98
$Ni(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	203vvs, 230vs,sh, 250vs,sh, 278vs,b, 302vs, 367s,sh, 450m,sh, 545m,sh, 698w,sh, 760w,sh, 895w,b, (950w), 1020w, 1215w,b, (1350w,b)	4721	3.37
$Cu(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	201vs, 225vvs, 241vvs, 273vvs,b, 297vvs,b, 545m,b, 597m,sh, 655w,sh, (960w, 988w,b, 1360w,b)	2012	2.20
$Zn(LH)_2(ClO_4)_2 \cdot C_2H_5OH$	223vs,sh, 244vs, 273vs, 304s,sh, (955w, 1005w,b, 1375w)	Diamagnetic	

[a] Reported solution spectrum of the free ligand (nm): at pH 1.2 230, 262, 318; at pH 6 230, 260, 316 [50] (the corresponding spectra of purine N(3)-oxide are: at pH 3 224, 295; at pH 14 225, 300 [15]). [b] Near-IR bands, common in the spectra of the free ligand and all of the metal complexes, and apparently due to vibrational overtones and combination modes originating from purine N(1)-oxide [42], are shown in parentheses.

4000–1700 cm^{-1}, with some band assignments [13, 22–28] given in parentheses: 3260w, 3155ms, 3130ms, 3070s, 3025s, (all five A′ pym ν_{CH} + A′ im ν_{CH}), 2725m (A′ im ν_{NH}), 2330m, 1870w, 1825w,sh, 1775vw (last four bands correspond to overtones and combination modes). The preceding bands are generally very similar to those observed in the IR spectrum of the parent base (purine) [13, 22, 23]. However, below 1700 cm^{-1} (Table II) differences are observed between the IR spectra of purine [13, 16, 17, 22, 23] and its N(1)-oxide in certain spectral regions. In addition to the bands corresponding to the N–O function (ν_{N-O}, δ_{N-O}) [4, 29–31], intensification and/or IR-activation of certain vibrational modes of the parent base seem to occur upon N-oxidation. Among the latter bands, most notable is the medium-to-strong intensity doublet at 1660, 1639 cm^{-1}. Purine shows a very weak maximum at 1669 cm^{-1}, with a possible shoulder at 1643 cm^{-1}; whereas pyrimidine shows a weak combination band (A′ 6b + 12) at 1666 cm^{-1} [25] and imidazole exhibits weak absorption at 1630–1625 cm^{-1} (overtone or combination bands) [26–28]. The appearance of medium-to-strong absorption in the above region, upon N-oxidation of purine, may be due to either intensification of the corresponding bands of the parent base [32] or shifts of fundamental ν_{CC} + ν_{CN} ring vibrations to higher wavenumbers, arising by increased localization of the double bonds in C=C and C=N vibrations [33]. The latter effect would be due to the appreciably larger contributions of conjugated systems to the resonance hybrid of the N-oxide relative to that of the parent base [34, 35]. It is also worth noticing at this point that oxidation of purine at N(1) would result in significant alteration of the electron density around the N(3) pyrimidine nitrogen, as well as the N(7) and N(9) imidazole nitrogen atoms [4, 36].

The spectra of the new metal complexes are generally characterized by the presence of A′ im

ν_{NH} absorption at 2705–2680 cm^{-1}, as would be expected for complexes with neutral puH-NO ligands [13, 16, 17]. Regarding the possibility of coordination of this ligand through the N(1)–O oxygen, the IR evidence is quite clearcut. Thus, in five cases (M = Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), ν_{N-O} is shifted to lower wavenumbers upon complex formation (the very weak band at 1242 cm^{-1} in the spectrum of the Ni^{2+} complex is presumably due to A′ δ_{CH} of purine; on the other hand, the shifted ν_{N-O} absorption is split in the spectrum of the Zn^{2+} complex). The negative ν_{N-O} frequency shifts observed in the spectra of the preceding complexes demonstrate that all the puH-NO ligands present are coordinated through the N(1)–O oxygen [29, 30]. For M = Cr^{3+}, no ν_{N-O} shift is observed, and so the ligands in this complex are obviously not coordinated through oxygen; whereas, for M = Fe^{3+}, Co^{2+}, the ν_{N-O} doublet (at *ca.* 1230 and 1190 cm^{-1}) suggests that some of the ligands are coordinated through the N(1)–O oxygen and some are not. As far as coordination of puH-NO through one of the imidazole ring nitrogens (N(7) or N(9)) is concerned, shifts of IR bands attributable to the imidazole fragment of the ligand (*e.g.*, A′ im R_1 and R_4), occurring upon complex formation, favor the presence of N-bonded puH-NO [13, 28]. Among the other potential ligands present, ethanol seems to be exclusively coordinated; in addition to the ν_{OH} band at 3400–3340 cm^{-1}, which is indicative of coordinated ethanol [37], some of the δ_{CH} bands of this ligand (at *ca.* 1400 and 880 cm^{-1}) [38, 39] were detected in the spectra of the ethanol-containing complexes. The new M^{2+} complexes seem to contain exclusively ionic perchlorate, as indicated by the single nature of the ν_3 and ν_4 (ClO_4) bands, but the two M^{3+} (M = Cr, Fe) compounds obviously involve both ionic and coordinated perchlorate (split ν_3 and ν_4 (ClO_4) and IR-active ν_1 and ν_2 (ClO_4) bands) [40, 41]. In the spectrum of the Cr^{3+} complex, each of the ν_3 and ν_4 (ClO_4) modes is triply split; this is suggestive of the presence of both ionic ClO_4^- (T_d symmetry) and unidentate coordinated $-OClO_3$ (C_{3v} symmetry) ligands. However, in the spectrum of the Fe^{3+} compound, ν_3 (ClO_4) is split into four components, whilst one of the bands of the seemingly triply split ν_4 (ClO_4) mode is broad; these features may be taken as indicative of the presence of both ionic ClO_4^- and bidentate coordinated $=O_2ClO_2$ (C_{2v} symmetry) groups [40, 41].

Tentative metal–ligand band assignments at 500–240 cm^{-1} (Table II) were based on previous far-IR studies of 3d metal complexes with purines [16, 17, 20, 21, 42] and diazines [43, 44], aromatic amine N-oxides [45–47], alcohols [48] and perchlorato ligands [49]. These assignments favor coordination number six for M = Cr^{3+}, Fe^{3+} and five for M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} [16, 17, 20, 21, 42–49]. The validity of our assignments is supported by the fact that, in the M^{2+} complexes, all the metal-sensitive bands (ν_{M-O} (N–O and C_2H_5OH) and ν_{M-N}) show the anticipated trends of frequency increase with metal ion variation (Irving-Williams series: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$).

Electronic Spectra and Magnetic Properties

The $\pi \rightarrow \pi^*$ (222–272 nm) and $n \rightarrow \pi^*$ (308 nm) UV transitions of the free ligand [50, 51] undergo small shifts in either direction, as well as occasional splittings, upon metal complex formation (Table III). Of course, the bands observed below 250 nm may involve contribution from ethanol absorption [52]. Near-IR bands, present in the spectrum of uncomplexed purine N(1)-oxide, and apparently due to vibrational overtones and combination bands of the ligand [42], appear also in the spectra of all the new complexes and are shown in parentheses in Table III. The new paramagnetic metal ion complexes are generally characterized by the presence of strong charge-transfer bands, originating in the UV and trailing off well into the visible region. Metal-to-ligand charge-transfer absorption of this type is quite common in the spectra of 3d metal complexes with diazines [53], including purine [16, 17], and with aromatic amine N-oxides [54].

The d–d transition spectrum of the Cr^{3+} complex is compatible with a low-symmetry hexacoordinated configuration [55], *i.e.*, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 447; $\rightarrow {}^4T_{2g}(F)$ 562, 655 nm; Dq = 1659 cm^{-1}. The calculated approximate Dq value for this complex is consistent for a CrN_2O_4 absorbing species (the four oxygens corresponding to two $-OClO_3$ and two ethanol ligands; *vide infra*) [56]. The spectra of the Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes are in apparent agreement with the far-IR evidence, *i.e.*, suggestive of pentacoordinated configurations. Thus, the presence of d–d transition maxima at 760–847 and at 1860 nm in the spectrum of the Co^{2+} complex is heavily in favor of coordination number five [55, 57], while the rich in d–d bands spectrum of the Ni^{2+} complex at 350–1220 nm [58] and the two maxima at 597, 655 nm in the Cu^{2+} compound spectrum [16, 20, 42, 59] can be also considered as indicative of the same coordination number. Finally, pentacoordinated Fe^{2+} complexes, exhibiting a single d–d transition band at 900–1020 nm, have been also previously reported [60].

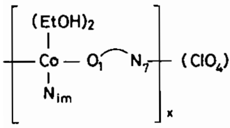
The ambient temperature magnetic moments of the new metal complexes are generally normal for high-spin $3d^3$ and $3d^5$–$3d^8$ compounds or the $3d^9$ configuration [61] (Table III). With the exception of the apparently monomeric Cr^{3+} complex, the new complexes seem to be bi- or poly-nuclear, in view of their insolubility in organic media and the obvious presence of bidentate bridging puH-NO ligands. The normal room temperature magnetic moments observed do not necessarily rule out polymeric configurations. In fact, we have recently demonstrated that the polymeric $[M(puH)_2(OH_2)_3](ClO_4)_2$ (M = Co, Ni, Cu; puH = purine) complexes, which most probably involve linear, chain-like, single-bridged polymeric complex cations (*i.e.*, –M–puH–M–puH– sequences), but exhibit normal room temperature magnetic moments, show clear-cut evidence of magnetic exchange interactions (significant μ_{eff} decreases with decreasing temperature, negative θ values, deviation from Curie-Weiss behavior at low temperatures) when studied at 300–80 K [17]. Studies of the temperature dependence of the paramagnetism of the new metal complexes herein reported are planned for the near future.

Ligand Binding Sites and Likely Structures of the Complexes

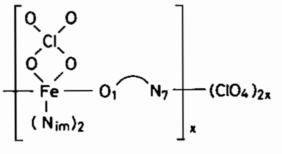
The IR evidence presented was clearcut as far as whether coordination of puH-NO through O(1) occurs or not is concerned (*vide supra*). Thus, in some cases (M = Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), all the ligands present are coordinated through O(1), whilst in the and Co^{2+} compounds some ligands are O(1) oxygen-bonded and some are not; the Cr^{3+} complex does not contain any O(1) oxygen-bonded puH-NO ligands. As regards the three potential ring nitrogen binding sites of the ligand, the imidazole N(7) and N(9) sites are much more likely candidates for coordination to metal ions, relative to the pyrimidine N(3) nitrogen [2, 13, 62]. Among the two imidazole ring nitrogens, the most likely binding site of a purine ligand appears to be the nitrogen atom, which is protonated in the free ligand [2]. This does not always refer to the site of protonation in the solid state or the most stable protonated isomer. For instance, 8-azahypoxanthine (ahxH) is protonated at N(8) in the solid [63a], but theoretical calculations suggest that for the isolated molecule the order of stabilities is N(9)–H > N(7)–H > N(8)–H [63b]; nevertheless, contrary to any predictions based on the general trends discussed above, $[Cd(ahx)_2(OH_2)_4]$ was found to comprise N(7) nitrogen-bonded ahx ligands [64]. The site of protonation of puH-NO is unknown, but even if it is protonated at N(7) (see (I)), as is the case with the parent base in the solid state [65], the prediction of the most likely ligand site among the imidazole ring nitrogens would not be easy. In fact, although the reported crystal structure of purine places the labile proton at N(7) [65], it is equally well established from carbon-13 NMR studies that the N(7)–H and N(9)–H tautomers of this compound are of comparable energies [66]. In previous studies we had considered the N(9) nitrogen as the most probable imidazole nitrogen coordinating site for either unidentate terminal or bidentate bridging purine ligands [16, 17]; nevertheless, in light of the preceding discussion, we now realize that the N(7) and N(9) nitrogens of puH are equally likely to function as ligand sites. With puH-NO, the likelihood of coordination through N(7) is greater when this ligand acts as bidentate bridging, being at the same time coordinated through the N(1)–O oxygen. In fact, in the crystal structures of complexes involving bidentate bridging purines, coordinated through one imidazole and one pyrimidine nitrogen, the N(7), N(1) [67, 68] or N(9), N(3) [69–71] pairs of ligand sites seem to be quite common; the N(7), N(3) or N(9), N(1) combinations have not as yet been established, but can not be completely ruled out, while the N(1), N(3) combination is highly unlikely [2]. As regards the probable binding site of unidentate, imidazole nitrogen-bonded puH-NO (N(3) nitrogen-bonding is again highly unlikely [2]), the N(7) and N(9) sites are equally likely. Hence, in the probable structure types discussed below, bidentate bridging puH-NO is designated as O_1N_7, and the unidentate N-bonded ligands as N_{im} (im being either 7 or 9).

The Cr^{3+} complex is the only obviously monomeric species of the series, since it shows some solubility in DMF and seems to contain exclusively unidentate, N-bonded, puH-NO ligands. This complex may be formulated as $[Cr(N_{im})_2(C_2H_5OH)_2(OClO_3)_2](ClO_4)$. The rest of the new complexes are insoluble in organic media and seem to involve bridging puH-NO ligands; their consideration as bi- or poly-nuclear is, therefore, justified, on the basis of this evidence and the pronounced tendency of purine-type ligands to function as bidentate bridging [2]. The fact that all these complexes, including the Cu^{2+} compound, show normal ambient temperature magnetic moments, is considered as favoring linear, chain-like, single-bridged polymeric structures over double- or multiple-bridged structural types [16, 17]. In fact, structures of the latter types would certainly favor subnormal room temperature magnetic moments, especially for Cu^{2+} [2, 7, 20, 72–74]. Whereas, single-bridged, chain-like polymeric metal complexes with large bridging ligands (purines, aromatic diazines, naphthyridines and their N-oxides; metal–metal separations in the chain exceeding 6.5 Å) are quite often characterized by normal room temperature μ_{eff} values, even in the case of Cu^{2+}, and show evidence favoring magnetic exchange only at lower temperatures [16, 17, 75–80].

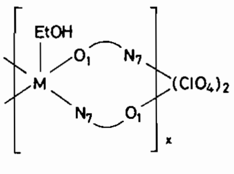
In light of the preceding discussion, the simplest linear polymeric structure for the Co^{2+} complex would be (III), with one bidentate bridging O,N-bonded and one unidentate terminal N-bonded puH-NO per Co^{2+} ion. For the Fe^{3+} complex, a structure such as (IV), with both unidentate terminal N-bonded and bidentate bridging O,N-bonded puH-NO ligands and bidentate coordinated perchlorato groups is consistent with the overall evidence. As far as the remaining M^{2+} complexes ($M = Mn, Fe, Ni, Cu, Zn$) are concerned, structure (V) would be the simplest, but would require double puH-NO bridges, which would certainly result in subnormal room temperature paramagnetism, at least for $M = Cu$. The most likely alternative is a more complicated structure, such as (VI), which is derived by cross-linking of linear –M–LH–M–LH– chains. The fact that structural types like (VI) have been proposed for several 1:2 3d M^{2+} (including Cu^{2+}) complexes with bridging diazines, characterized by normal ambient temperature magnetic moments [43], is in support of this formulation for the new Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes.



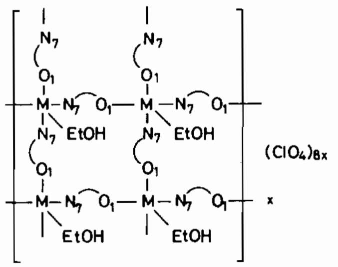
(III)



(IV)



(V)



(VI)

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