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 $M(LH)_2(C_2H_5)$ $OH/(ClO_4)_2$ 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 Fe³⁺ complexes (the latter compound also contains a bidentate = $O_2 ClO_2$ 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 crosslinking 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 Cu²⁺ [12], Hg²⁺ [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.



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

^{*}See Ref. 1.

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Complex	Color	Analysis, F	ound (Calcd.))%		
		C	н	N	М	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)
$Mn(LH)_2(CIO_4)_2 \cdot C_2H_5OH$	Yellow green	25.22	2.71	19.18	9.50	12.52
	2	(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
	Ũ	(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
	Light Brook	(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 vellow green	25.04	2.25	18.93	11.71	12.18
	, , ,	(24.74)	(2.42)	(19.24)	(11.22)	(12.17)

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

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 2-5days 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 CaCl₂. 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 Cr³⁺ 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 ($4000-500 \text{ cm}^{-1}$) and on Nujol mulls between highdensity polyethylene windows ($700-200 \text{ cm}^{-1}$), 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 perchloratc complexes, involving either neutral or anionic (monodeprotonated) ligands or even mixed neutralanionic ligand complexes, the new complexes with purine N(1)-oxide contain exclusively neutral ligand groups (Table I). With Fe(ClO₄)₃, a 3:1 puH-NO to Fe³⁺ 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 Fe²⁺ 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 $4000-1700 \text{ cm}^{-1}$ are given below, while Table II shows the IR spectra of the free ligand and its metal perchlorate complexes at $1700-200 \text{ cm}^{-1}$ (along with a number of pertinent IR bands occurring at higher wavenumbers). IR spectrum of puH-NO at

275 3300m,b 3400m,b 335m,b 3365m,b 535m,b 535m,b 536m,b	2705m,b 1686s, 1686s, 1686s, 1680s 1612ms 1612ms 1612ms 1576m 1576m 1570w,b 1329m 1329m 1329m 1329m 1329m 1329m 1330m, 1955s, 1133m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 224m 224m 224m 224m 225w 224m 225w	3340m 2705m,b 1680s, 16425,sh 1610ms 1519w,b 1385m 1385m 1328w,sh 1324w,sh 1224w 1224w,sh 1224w,sh 1230m, 1189m 1230m, 1189m 1230m, 1189m 1230m, 1189m 1230m, 1189m 1230m, 1189m	3365m,b 2885m,b 1670s, 1646s,sh 1611ms 15167m 15167w 1469m, 1446w 1415w, 1398w 1415w, 1398w 1415w, 1398w 1289mw 1298mw 1298wv 1298wv 1297m 1285vs,vb 972w 933w	3380m 2655m,b 1660s,vb 1612ms 1564m 1570w,b 1377w,b 1335w,b 1330w,sh 1330w,sh 1270w,sh 1200m 1270w,sh 1200m 1200m 200m	3350m,b 2700m,b 1675s, 1675s, 1659ms 1669ms 1518w,b 1487w,1450w 1419w,1403w 1300w 1300w 1300w 1300w 1300w 1307w 1266w 1206m 1078vs,b 977w	^v OH (EtOH) ^{A'} im ^w NH ^b + 5 OH (EtOH) A' pym 8a A' pym 19b + A' im R ₂ A' im R ₃ + 5 CH (EtOH) A' im R ₄ A' im 8 MH A' i
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1508w1514w1516w1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1519w,b1538m,1399w,b1338m,b1338m,1300w,b1348m,100,00,00,00,00,00,00,00,00,00,00,00,00	1520w,b 148w 1481w, 1442w 1314m 1314m 1329w 1229m 1229m 1231m, 1192m 1231m, 1192m 1231m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 924m 883w 885w,b 833w 885w,b	1519w,b 1473w, 1444w 1415w, 1399w 1385m 1324w,sh 1224w,sh 1224w,sh 1230m, 1189m 1230m, 1189m 1230m, 1189m 1968w 958w	1516w 1469m, 1446w 1415w, 1398w 1334w 1334w 1269w,sh 1269w,sh 1269w,sh 1285vs,vb 972w 933w	1520w,b 1470w, 149w 1420w, 1396w 1337w,b 1337w,b 1377w,b 1377w,b 1200m 1200m 1200m 1200m 1087vs,b	1518w,b 1487w,1450w 1390mw 1390mw 1330w 1307w 1307w 1266m,1200m d 216m,1200m d 216m,1200m d 217w	A' im R ₁ A' pym 19b + A' im R ₂ A' pym 19a A' pym 19a A' im 8 ₄ A' im 8 ₀ H Pyn-O ^C A' R Pyn-O ^C A' R
1457w, 1441w 1470w, 160w 1475w, 1460w 1466w, 1397w 1441w 1473w, 1444w 1466m, 1413w, 1402w 1400m 1417m, 1402m 1415w, 1402m 1415w, 1399w 1344w 1456m, 1438w 1300w 1378m 1315w 1335w, 1330w 1335m 1336m 1336m 1336m 1300w 1378m 1315wb 1315wb 1315wb 1315wb 1335w, 1410m 1386m 1336m 1300w 1330w 1330w 1315wb 1315wb 1315wb 1336m 1336m 1336m 1300w 1350w 1350w 1317w 1200w 1260w 1236w, 1100w 1336m 1236w, 1100w 1336m 1236w, 1100w 1286w, 1100w 1286w, 1100w	148w 1481w, 1442w 1419m 1412w 1329w 1329w 1229m 1270w, sh 1231m, 1192m 1133m, 1095vs, 1077vs, 1050s, sh 980w, 955w 924m 883w 885w, b 883w 825w 75w vh	1473w, 1444w 1415w, 1399w 1385m 1294w 1294w 1230m, 1189m 1230m, 1189m 1230w, vb 968w 931w	1469m, 1446w 1415w, 1398w 1334w 1334w 1269w,sh 1269w,sh 1285vs,vb 1085vs,vb 972w 933w	1470w, 1449w 1470w, 1396w 1377w,b 1300w,b 1200m 1200m 1200m 1087vs,b 1087vs,b	1487 w, 1450 w 1419 w, 1403 w 1390 m 1307 w 1307 w 1269 w 1216 m, 1200 m d 1078 vs, b 977 w	A' pym 19b + A' im R ₂ A' im R ₃ + 6 _{CH} (E:10H) A' pym 19a A' im R ₄ A' im 6 _{NH} P _N -O ^C A' R P ₃ (CIO ₄) A' R
1400m1417m, 1402m1412w, 1402m1416w, 1397w1419m1415w, 1399w1415w, 1309m1370w1378m1378m1378m1378m1378m1385m1338m1370w1378w1378w1378w1378m1336m1386m1370w1370w1378w1378w1378w1339w1415w1370w1370w1378w1378w1378w1399w1415w1370w1370w1378w1378w1269w1296w1336w1224w1231m1200m1120w1220wsh1242w1242w1231m1231m1200m1131m1095vs, 1090vs, vb1285w, vb937w1224m231m1133m, 1095vs, 1090vs, vb1085vs, vb933w933w1022w1040m960w, b970w970w970w972w928m960w, b970w974w980w, 955w972w972w928m887w, b970w978w880w972w972w928m880w, b932w887w, b972w972w972w928m880w, b930w, b887w, b972w972w972w928m880w, b930w, b887w, b978w880w972w928m880w, b930w, b887w, b972w972w972w928m880w, b930w, b887w, b972w972w972w928w880w, b930w, b887w, b972w972w972w930w, 750w700w	997w 1419m 1374m 1329w 1299m 1270w,sh 1270w,sh 1231m,1192m 1133m,1095vs, 1077vs,1050s,sh 980w, 955w 924m 924m 885w,b 885w,b	1415w, 1399w 1385m 1324w,sh 1266w,sh 1266w,sh 1230m, 1189m 1230m, 1189m 1230w,vb 1090vs,vb 931w	1415w, 1398w 1389m 1384w 1298mw 1298mw 1269w, 1197m 1242w, 1197m 1085vs,vb 972w 933w	1420w, 1396w 1337w,b 1335w,b 1330w,b 1270w,sh 1200m 1087vs,b 1087vs,b	1419w, 1403w 1390mw 1307w 1307w 1269w 1266m, 1200m d 1078vs,b 977w	A' im R ₃ + δ _{CH} (EtOH) A' pym 19a A' im R ₄ A' im δ _N H A' im δ _N H P _N -O ^C A' R P ₃ (ClO ₄) A' R
1370w1376m1381m1387m1374m1385m1398w1320w1315w1315w1315w1315w1315w1334w.fh1385m1394w.fh130wb130w1315wb1315wb1315wb1315wb1304w.fh1368m.fh1386m.ft1302w130w1315wb1315wb1315wb1315wb1304w.ft1386m.ft1386m.ft124m1261w1269w1270w1270w.ft1206m.ft1269w.ft1286m.ft124m1200m1200m1196m1270w.ft1206w.ft1269w.ft1240m.1080m1201m1200m1270w.ft1296m.ft1269w.ft1240m1260m1270w1270w.ft1296m1286w.ft1240m1240m1090vs,vb1090vs,vb1085s.ft928m964m960w.ft970w974w980w,ft970w970m960w.ft932w934w980w,ft930w980w.ft930w.ft870w,ft930w,ft970w930w980w.ft880w.ft882w.ft955w.ft970w970w918mw880w.ft882w.ft956w,ft795w,ft970w918mw880w.ft882w.ft882w.ft970w970w918ms880w.ft882w.ft950w,ft705w705w924m880w.ft880w.ft970w775w,ft707w918ms680w.ft700w775w,ft707w705w924m880w.ft880w.ft775w,ft7	1374m 1329w 1299w 1270w,sh 1270w,sh 1231m, 1192m 1231m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 924m 885w,b 885w,b 875w vb	1385m 1324w,sh 1294w 1266w,sh 1230m, 1189m 1230m, 1189m 1230w, b 1090vs,vb 968w 931 w	1389m 11334w 1298mw 1269w,sh 1242w, 1197m d242w, 1197m 972w 972w 933w	1377w,b 1335w,b 1300w,b 1200m d 1200m d 1087vs,b 969w	1390mw 1309w 1307w 1306w 1369w 1216m, 1200m 1078vs,b 977w	A' pym 19 A' im R4 PN-O ^C A' R P3 (ClO4) A' R
1320w 1330w 1337w 1335w.sh 1329w 1324w.sh 1334w.sh 1300w.b 1308w 1315w.b 1307w 1329w 1324w.sh 1334w.sh 1200w.b 1306w 1307w 1300w 1270w 1270w 1266w.sh 1200w 124m 1231m 1200w 1270w 1270w 1266w.sh 1269w.sh 1269w.sh 124m 1231m 1200m 1192m 1260w.sh 1260w.sh 1269w.sh 1269w.sh 1269w.sh 1022w 1140m.1080m 1231m 1192m 1260w.sh 1260w.sh 1269w.sh 1269	1329w 1299m 1270w.sh 1231m,1192m 1133m,1095vs, 1077vs,1050s,sh 980w,955w 924m 924m 885w,b 833w 885w,b 877 wb	1324 w,sh 1294 w 1266 w,sh 1230 m, 1189 m 1290 vs, vb 968 w 931 w	1334w 1298mw 1269w,sh 1242w,1197m 1285vs,vb 972w 933w	1335 w,b 1300 w,b 1200 m,sh 1200 m 1200 m 1087 vs,b 969 w	1330w 1307w 1269w 126m, 1200m 1078vs,b 977w	A' im R4 A' im 6NH b'N-O ^C A' R A' R
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1299m 1270w.sh 1270w.sh 1231m, 1192m 1133m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 924m 883w 885w,b 833w 885w,b	1294w 1266w,sh 1230m, 1189m 1090vs,vb 968w 931w	1298mw 1269w,sh 1242w, 1197m 1085vs,vb 972w 933w	1300w,b 1270w,sh 1200m 1087vs,b 969w	1307 w 1269 w 1216 m, 1200 m 1078 vs, b 977 w	A' im é _{NH} ^v N-O ^C A', R v ₃ (ClO ₄) A' R
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1270w.sh 1231m, 1192m d 1133m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 924m 883w 885w,b 883w 825w 775w vh	1266w,sh 1230m, 1189m 1090vs,vb 968w 931w	1269w,sh 1242w, 1197m 1085vs,vb 972w 933w	1270w,sh 1200m 1087vs,b 969w	1269w 1216m, 1200m 1078vs,b 977w	A' im 6 _{NH} ^b N-O ^C A', R ^b 3 (ClO4) A' R
124 124 124 124 124 124 124 124 124 124 124 124 124 124 123 113 113 113 113 113 113 124 124 113 124 125 113 124 124 120 124 120 124 120 124 120 124 120 123 123 123 123 123 123 123 123 123 123 123 123 125 126 123 126 123 126 123 126 123 126 126 126 126 126 126 126 126 126 126 126 126 126 126 126 126 126 126	1231m, 1192m 123m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 924m 827w 827w vh	1230m, 1189m 1090vs,vb 968w 931w	1242w, 1197m 1085vs,vb 972w 933w	1200m 1087vs,b 969w	1216m, 1200m 1078vs,b 977w	PN-O ^C A, R P3 (CIO4) A' R
	1133m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 827w 827w 50w 775w vb	1090vs,vb 968w 931 w	1085vs,vb 972w 933w	1087vs,b 969w	1078vs,b {	ν ₃ (CiO4) A' R
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1133m, 1095vs, 1077vs, 1050s,sh 980w, 955w 924m 883w 885w,b 823w 825w,b 875w vh	1090vs,vb 968w 931 w	1085vs,vb 972w 933w	1087vs,b 969w	1078vs,b {	ν ₃ (ClO4) A' R
964m 970w 971w 980w, 955w 968w 972w 973w 972w 972w 972w 972w 972w 973w 972w 973w 972w 976w, 150w 775w/th 799w, 750w 795w, 15 795w, 15 795w, 75 795w, 75 <t< td=""><td>980w, 955w 980w, 955w 924m 827w 827w 0w 775w vh</td><td>968w 931w</td><td>972w 933w</td><td>969w</td><td>977w</td><td>A' R</td></t<>	980w, 955w 980w, 955w 924m 827w 827w 0w 775w vh	968w 931w	972w 933w	969w	977w	A' R
928m 700w, 510w	d 900w, 955w 924m 883w 885w,b 823w 925w b	931 w	912W 933w	909W	W/16	AK
y_{20m} y_{31w} <	924m 883w b 827w b 175w vh	W164	935W			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	924m 883w,b 827w, 10w 775w vh			935W	936W	A CH
B80w,b B82w B87w,sh B96w, B17w,sh B90w B82w B80w, B83w, B85w, b B90w, 870w B83w, b B90w, 870w B83w, b B90w, 870w B90w, 830w, B30w, B30w, B30w, b	883w 885w,b 827w 50w 775w vh					v1 (CIO4)
870ms,b 903w, 878w 888w,b 905w, 875w 900w, 87 843m 836w,sh 839w,b 839w,b 833w 885w,b 905w, 875w 900w, 87 790w, 740w,b 780w, 762w 796w, 750w 775w,b 799w, 750w 795w, 75 700m 698w 702w 707w 707w 707w 707w 708w 660w,sh 698w 660vw d 57vw 660vw d 660vw 6 612w d d d d d d d d d d d d d d d d 517w, 538vw 660vw 652ms 619ms,b 620ms 650ms, 620ms 620ms 620ms 617ms 520w,b 519w,b 520w, 519w,b 525w 515w,sh 517w,sh 717m 490mv,sh 470w,vb 475w, 480w, 480w,b 755w, 539w 550w,vt 700m, 480w,sh 475w,b 715w, 715w, 515w,sh 5117w,sh	883w 885w,b 827w 50w 775w.vh	890w	880w	882w	887w	6CH (EtOH)
843m 836w.sh 839w.b 830w.b 830w.sh 830w.sh 830w.sh 847w.sh 799w, 750w 708w 660vw 60vw 610w 60vw 610w 60vw 610w	827w 50w 775w.vh	905w, 875w	900w, 875w	908w, 872w	895w, 877w	A'R+A″icorγ _{NH}
790w, 740w, b 780w, 750w 75w, b 799w, 750w 75w, 75 700m 698w 702w 707w 799w, 750w 795w, 75 700m 698w 702w 707w 707w 707w 708w 700m 698w 702w 707w 707w 707w 708w 600w, sh d 650w d 650w 660vw d 660vw 670w 670w 670w 670ms 620ms 620ms 670w, vt 575w, 539w 550w, vt 515w, 5	50w 77.5w vh	847w,sh	840w,b	834w,sh	839w,sh	0-N.º
700m 698w 702w 707w 707w 707w 708w 660vw 660vw 657vw 660vw 658vw 658vw 660vw 708w	2.6	799w, 750w	795w, 757w	802w, 751w	803w, 758w	$A' R + A'' \gamma_{CH}$
660w.sh d 657vw 660vw 660vw 660vw 660vw 660vw 660vw 660vw 612w d 60vw 612w 651w 652w 650w, 620ms 612w 617ms 622ms 648w, 628ms, 620ms 620ms 617ms 617ms 622ms 648w, 628ms, 620ms 620ms 617ms 617ms 622ms 648w, 628ms, 620ms 617ms 617ms 619ms, 619ms, 617w, 515w, 519w, 517w, 515w, 517w, 5170w, 517w, 517w, 517w, 517w, 517w, 517w, 517w, 517w, 5170w,	_702w	707w	708w	711w	704 w	N-O mode
632w d d d d d d d d d d d d d d d d d d d	5 7	558vw	660vw	<u>6</u> 61 vw	664vw	A' R
612w a a a a a 612w 650w, 624ms, 617ms 617ms 622ms 648w, 628ms, 620ms 620ms 650w, 624ms, 617ms 619ms, b 619ms, b 620ms 620ms 620ms 645m, 570m, b 555w, b 560w, b 519w, b 570w, 554w 575w, 539w 550w, vb 513m 527mw 520w, b 519w, b 525w 515w, sh 517w, sh 517w, sh 475m 480w, sh 475w, sh 470w, vb 475w, sh 480w, sh 515w, sh 517w, sh	в.	-				A' R
650w, 624ms, 617ms 622ms 648w, 628ms, 620ms 620ms 617ms 617ms 622ms 619ms,b 620ms 620ms 617ms 555w,b 560w,b 570w, 554w 575w, 539w 550w, vb 545m,sh 570m,b 555w,b 560w,b 570w, 554w 513w, sh 517w, sh 513m 527mw 525w,b 519w,b 525w 517w, sh 517w, sh 475m 480w,sh 475w,sh 470w,vb 475w 480w,b	U	-		Ð	P	A'' R
617ms 617ms 619ms,b 617ms 619ms,b 555w,b 560w,b 570w,534w 575w,539w 550w, vb 513m 527mw 520w,b 525w 515w,sh 517w,sh 517w,sh 475m 480w,sh 475w,sh 475w,sh 470w,vb 475w 480w 480w,b 500w,b	648w, 628ms,	6 20ms	620ms	619ms	621ms	ν4 (CIO4)
545m,sh 570m,b 555w,b 560w,b 570w,554w 575w,539w 550w, vb 513m 527mw 520w,b 519w,b 525w 515w,sh 517w,sh 490mw,sh 475w,sh 470w,vb 475w 480w 275m 480w,sh 475w,sh 200w,b 475w 280w,b 280w,b	619ms,b					
513m 527mv 520w,b 519w,b 525w 515w,sh 517w,sh 490mv,sh 475w,sh 470w,vb 475w 480w 480w,b 500w,b 500w,b 500w,500,500,500,500,500,500,500,500,500	570w, 554w	575w, 539w	550w, vb	545w	560w,b	A″ R
475m 490mv.sh 475w.sh 470v.vb 475w 480w 480w.b	525w	515w,sh	517w,sh	520w,sh	528w,b	
475m 480w.sh 475w,sh 470w,vb 475w 480w 480w,b	488w					v2 (Cl04)
	475w	480w	480w,b	475w,sh	470w,sh	A″ R
402m 410m 421m,420m 418m,5n 423m,0	451m, 420m	418m,sh	423m,b	437m	398m,b	$^{N-0}(N-0)$
442m 340w 351w 386m 388m		386m	388m	393m,sh	341m,sh	^p M-O (EtOH)
337w 329w	329w					^p M-0 (Cl0 ₄)
368w, 350w, 370w, 345w, 360w, 347w, 365w, 340w, 370w, sh, 373w, 341w, 375w, 34	40w, 370w,sh,	373w, 341w,	375w, 343w,	370w,b, 339w,	376w, 342w,	:
310vw.b. 305vw. 310vw, 290vw, 309w, 290w, 348w.sh, 312m 306w,b, 293w,b, 311w, ^e	90w, 348w,sh, 312m	306w,b, 293w,b,	311w, ^e	313w ^e ,	sh, 309vw, }	A R
290vw, 265m 266m 266m,b sh, 263m e e 265m,sh 265m,sh	9 9 1	265m,sh	265m,sh	264m,sh	292vw ^e	
288mw 272m,sh 277m,sh 295m, 257m,b 282w, 247m 285w, 2 ²	295m, 257m,b	282w, 247m	285w, 250m	291m, 254m	268m,vb	N-M4

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

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 ClO₄ bands. ^bFor the possible origin of these bands in free puH–NO see text. ${}^{\nu}N-O$ 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 = Ni²⁺) of the cases under study, by the shifted ν_{N-O} absorptions in the spectra of the new metal complexes. ^dMasked by perchlorate IR bands. ^emasked by M–N bands. 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

Purine N(1)-Oxide Metal Complexes

Compound	λ _{max} , nm ^b	$10^6 \chi_{\rm M}^{\rm cor}$, cgsu	μ _{eff} , μΒ
LH ^a	222vs, 246vs, 272vs, 308vs, (965w,b, 1350w)		
Cr(LH) ₂ (ClO ₄) ₃ ·2C ₂ H ₅ OH	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
ŀe(LH)₂(ClO₄)₂•C₂H₅OH	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 • 2C ₂ H ₅ OH	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 ·C ₂ H ₅ OH	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 •C ₂ H ₅ OH	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	

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.

^aReported 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]). ^bNear-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 v_{CC} + v_{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

 $\nu_{\rm NH}$ 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 guite 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 Ni²⁺ 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 v_{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 v_{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 v_{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 M2+ complexes seem to contain exclusively ionic perchlorate, as indicated by the single nature of the v_3 and v_4 (ClO₄) bands, but the two M³⁺ (M = Cr, Fe) compounds obviously involve both ionic and coordinated perchlorate (split v_3 and v_4 (ClO₄) and IRactive v_1 and v_2 (ClO₄) bands) [40, 41]. In the spectrum of the Cr³⁺ 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 Fe³⁺ compound, ν_3 (ClO₄) is split into four components, whilst one of the bands of the seemingly triply split v_4 (ClO₄) 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 C₂H₅OH) 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 guite 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 Cr³⁺ complex is compatible with a low-symmetry hexacoordinated configuration [55], *i.e.*, ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ 447; $\rightarrow {}^{4}T_{2g}(F)$ 562, 655 nm; Dq = 1659 cm⁻¹. The calculated approximate Dq value for this complex is consistent for a CrN₂O₄ absorbing species (the four oxygens corresponding to two -OClO3 and two ethanol ligands; vide infra) [56]. The spectra of the Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺ 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 Co²⁺ complex is heavily in favor of coordination number five [55, 57], while the rich in d-d bands spectrum of the Ni²⁺ complex at 350-1220 nm [58] and the two maxima at 597, 655 nm in the Cu²⁺ compound spectrum [16, 20, 42, 59] can be also considered as indicative of the same coordination number. Finally, pentacoordinated Fe²⁺ 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 -M-puH-M-puHcations (i.e., 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+} , Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺), all the ligands present are coordinated through O(1), whilst in the and Co²⁺ compounds some ligands are O(1) oxygen-bonded and some are not; the Cr³⁺ 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) nitrogenbonded 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 O₁N₇, and the unidentate N-bonded ligands as N_{im} (im being either 7 or 9).

The Cr³⁺ 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(C₂H₅OH)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 bior 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 Cu2+ 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 favor subnormal room temperature certainly magnetic moments, especially for Cu²⁺ [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 A) are quite often characterized by normal room temperature μ_{eff} values, even in the case of Cu²⁺, 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 Fe³⁺ 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 crosslinking of linear -M-LH-M-LH- chains. The fact that structural types like (VI) have been proposed for several 1:2 3d M²⁺ (including Cu²⁺) complexes with bridging diazines, characterized by normal ambient temperature magnetic moments [43], is in support of this formulation for the new Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺ and Zn²⁺ complexes.





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