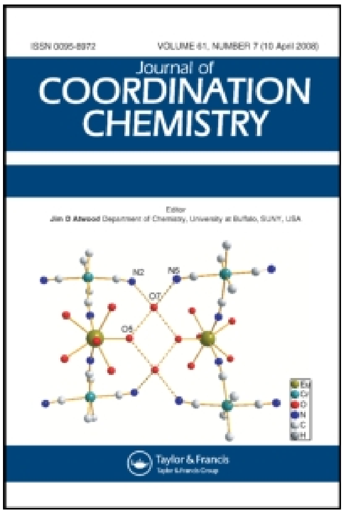

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FERRIC CHLORIDE AND BROMIDE COMPLEXES WITH XANTHINE AND HYPOXANTHINE*

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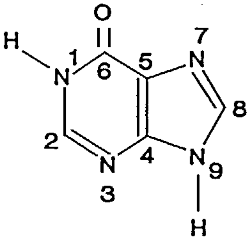
Complexes of the type $Fe(LH)_3LX_2$ (LH = xanthine or hypoxanthine; X = Cl or Br) were synthesized by refluxing 2:1 molar mixtures of LH and FeX_3, in triethyl orthoformate–ethyl acetate for one week. Characterization studies suggest that the new complexes are hexacoordinated and monomeric, involving a *cis*-FeN_4X_2 arrangement of the terminal ligands around the Fe^{3+} ion. The hypoxanthine ligands probably bind *via* the N7 imidazole nitrogen to Fe(III). In the case of the xanthine complexes, the N7 and N9 imidazole nitrogens are considered as about equally likely to function as the binding site of the terminal neutral and monoanionic xanthine ligands.

Keywords: Xanthine, hypoxanthine, iron(III), halide, complexes

INTRODUCTION

Synthetic and characterization studies of hypoxanthine (hxH; 6-oxopurine; **I**) and xanthine (xnH; 2,6-dioxopurine; **II**) complexes with 3d metal perchlorates,[3-5] Pd(II), Pt(IV)[6] and oxozirconium(IV)[7] chlorides were previously reported from these laboratories. The synthetic work in these studies was conducted in non-aqueous media.[3-7] More recently, we extended our research to include complexes of the same ligands with various 3d metal halides,[1,2] and the present paper deals with the complexes formed by the interaction of Fe(III) chloride or bromide with xnH or hxH in triethyl orthoformate (teof)–ethyl acetate (ea).



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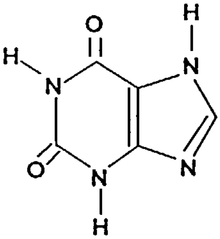

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* Presented in part at the 3rd Chem. Congress of North America (LH = xanthine) and the XXVI ICCC (LH = hypoxanthine), see refs. 1 and 2, respectively.

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Both xnH and hxH are constituents of RNA,[8] and their metal complexes are of significant biological and medical interest. The free bases form as intermediates in the reduction of nucleic acids to uric acid in man, catalyzed by the Mo- and Fe-containing enzyme xanthine oxidase. Mo complexes with xnH or hxH apparently contribute to the activity of this enzyme.[9] Hence, the coordination properties of xnH and hxH are important in connection with diseases such as xanthinuria and gout, resulting from disturbances in purine metabolism.[10] Hypoxanthine is protonated at N1 and N9 (I) in the solid[11] state or in aqueous solution,[12,13] whereas xanthine in solution is protonated at N1, N3 and N7 (II).[12–14] Crystal structure determinations of metal complexes revealed that terminal unidentate hxH binds *via* N7 in Co(II),[15] Ni(II)[16] and Ru(III)[17] complexes, while bridging bidentate hxH coordinates *via* N3,N7[15] or N3,N9[18] in Cu(II) complexes involving single or multiple hxH bridges, respectively, between adjacent Cu^{2+} ions. Structural information on xanthine metal complexes is relatively scarce. The xn$^-$ monoanion is protonated at N1 and N3 and binds *via* N9 in bis(dimethylglyoximato)(xanthinato)(tri-*n*-butylphosphine)Co(III),[19] but in Na(xn).4H$_2$O it is protonated at N1 and N9.[20] The most acidic proton of xn$^-$ is apparently involved in a tautomeric equilibrium, whereby N3, N7 or N9 could act as the acceptor.[21] The dianion (xn^{2-}, protonated at N1) and trianion (xn^{3-}) of xanthine function as tridentate N3,N7,N9-bound and quadridentate N1,N3,N7,N9-bound bridging ligands, respectively, in their methylmercury(II) complexes.[21]

EXPERIMENTAL

The general synthetic procedure employed was: 1 mmol hydrated Fe(III) salt was dissolved in 25 cm^3 of a 7:3 (v/v) mixture of teof–ea, and the resulting solution was stirred under reflux for 1 h. Then, 2 mmol LH were mixed with 25 cm^3 of 7:3 teof–ea, and the mixture was warmed to form a slurry, which was added to the stirring, refluxing Fe(III) halide solution. The resultant mixture was boiled under reflux for one week. Subsequently, the mixture was allowed to cool to room temperature, and the solid complex formed was collected by gravity filtration, washed thoroughly with anhydrous diethyl ether and stored *in vacuo* over anhydrous CaSO$_4$. The new

TABLE I

Analytical data for the Fe(LH)$_3$LX$_2$ complexes.*

LH	X	Colour	Yield%	C%	H%	N%	Fe%	X%
xnH	Cl	Pale yellow	55	32.50 (32.72)	1.95 (2.06)	30.78 (30.52)	7.92 (7.61)	9.39 (9.66)
xnH	Br	Light brown	59	28.85 (29.19)	1.70 (1.84)	27.47 (27.23)	6.88 (6.79)	19.12 (19.42)
hxH	Cl	Tan	40	36.11 (35.84)	2.36 (2.26)	33.67 (33.43)	8.07 (8.33)	10.31 (10.58)
hxH	Br	Light brown	79	31.28 (31.64)	2.13 (1.99)	29.97 (29.52)	7.46 (7.36)	20.65 (21.05)

* Found % with calc. % in parentheses; X = Cl or Br.

TABLE II
Pertinent IR data for the $Fe(xnH)_3(xn)X_2$ complexes (cm^{-1}).

xnH*	X = Cl	X = Br	Band assignment
3132w,3006s, 2881s,2828m	3145ms,3025s, 2920m,2840ms, 2830ms	3135ms,3020s, 2925m,2875ms, 2840ms	$\nu_{CH} + \nu_{NH}$
1702vs,1660vs	1704vs,1667vs	1700vs,1656vs	$\nu_{C=O}$
1569m,1539m, 1530w,sh	1592m,1579m, 1570w,1535w	1597m,1581m, 1566w,1532w	$\nu_{C=C} + \nu_{C=N} + \delta_{NH}$
1462ms,1449ms, 1437m,1415ms, 1390w,1336m, 1328m,1255w, 1234vw,1206w, 1199m,1161w, 1120w	1500w,1477w, 1452mw,1420m, 1400w,1385w, 1339m,1304w, 1267w,1255w, 1209mw,1180m, 1163mw,1140mw, 1135mw,1120w	1497w,1475w, 1450mw,1422m, 1396w,1388w, 1335m,1308w, 1265w,1250w, 1206mw,1185mw, 1160mw,1141mw, 1133mw,1118w	Ring vibrations + $\nu_{C-N} + \delta_{NH}$
520w,507w,sh, 495w,403w,371w, 355w,345w,sh, 320vw,232w,208vw	550ms,502ms,435w, 420w,370w,sh, 295w,232w,211w,b	545ms,498ms,433w, 419w,373w,354mw, 333mw,290vw,210w	ν_{xnH} at 600–200 cm^{-1}
	352m,336m	245mw,233mw	ν_{Fe-X}
	282w,269w	278w,268w	ν_{Fe-N}

* Free xnH band assignments based on refs. 4, 6, 7, 21, 33, 34 and 36. The spectra are devoid of absorptions attributable to the presence of water.

complexes are of the $Fe(LH)_3LX_2$ type (LH = xnH or hxH; X = Cl or Br), as indicated by the analytical data given in Table I. They are relatively sparingly soluble in organic solvents, showing increased solubility in binary solvent mixtures, such as, for instance, nitromethane–acetone. Infrared spectra (Tables II, III) were recorded in KBr discs (4000–500 cm^{-1}) and 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, ambient temperature (300°K) magnetic susceptibility and conductance (on 10^{-3} *M* solutions of the complexes in 1:1 (v/v) nitromethane–acetone, at 25°C) measurements, given in Table IV, were obtained by methods described elsewhere.[22]

RESULTS AND DISCUSSION

The syntheses performed resulted invariably in substitution of one monoanionic L for one chloro or bromo ligand. During the corresponding synthetic work involving

TABLE III

Pertinent IR data for the $Fe(hxH)_3(hx)X_2$ complexes (cm^{-1}).

hxH*	X = Cl	X = Br	Band assignment
3150m,3050m, 2960s,2920s 2870s	3145ms,3095ms, 3055s,2960s, 2930ms,2870m	3145ms,3100ms, 3050s,2955s, 2935ms,2870m	$\nu_{CH} + \nu_{NH}$
1665vs	1672vs	1667vs	$\nu_{C=O}$
1605w,1579m,	1615w,1583mw, 1555w	1612mw,1585m, 1550w	$\nu_{C=C} + \nu_{C=N} + \delta_{NH}$
1510w,1455s, 1419m,1377m, 1360m,1341m, 1268m,1205m, 1141m,1123m,	1525w,b,1498w, 1465w,1447w, 1420w,1397ms, 1361w,1338w, 1282w,1219w, 1167w,1142w, 1100vw	1518w,b,1492w, 1462w,1450w, 1419mw,1400mw, 1370w,1351w, 1285w,1250vw, 1162w,1140w, 1102vw	Ring vibrations + $\nu_{C-N} + \delta_{NH}$
580m,sh,545m, 520m,450mw,378w, 362w,345w,b,241w, 231w,211w,	595vw,560w,552w, 523w,480vw,440vw, 390w,370w,243w, 230w,207w	573w,548w,527w, 500w,475w,440vw, 387w,368w,344w, 210w	ν_{hxH} at 600–200 cm^{-1}
	351m,338m	246w,231w	ν_{Fe-X}
	284w,272w	277w,270w	ν_{Fe-N}

* Free hxH band assignments based on refs. 4–7, 35 and 36. No absorptions associated with water were detected in the spectra of the complexes.

TABLE IV

Solid state electronic spectra, magnetic properties (300°K) and molar conductivities of the $Fe(LH)_3LX_2$ complexes.

LH	X	λmax, nm*	$10^6\chi_m^{cor}$, cgsu	μeff,μB	Λ_M, $\Omega^{-1}\,cm^2\,mol^{-1}$
xnH	Cl	200vvs,234,vs,sh,259vs,281vs,289vs, 310vs,sh,335s,sh,421m,sh,540m,b	14,840	5.99	9
xnH	Br	201vvs,236vs,sh,258vs,278vs,291vs, 311s,sh,337s,sh,432m,555m,b	15,511	6.13	13
hxH	Cl	204vvs,231vs,sh,255vs,267vs, 309s,sh,329s,425m,535m,b	14,962	6.02	11
hxH	Br	204vvs,230vs,sh,257vs,266vs, 310s,sh,332s,437m,550m,b	15233	6.07	8

* UV spectra of the free ligands: Nujol mulls, nm: xnH < 200vvs, 255vs,sh, 270vs,b; hxH 200vvs, 247vs, 280vs,sh, 340s,sh.[3-7] Aqueous solution spectra,[14,44] λmax, nm (logε): xnH (pH 5–7): 225 (3.49), 266–267 (3.90–4.03); xn (pH 10–11): 240–241 (3.91–3.95), 276–277 (3.92–3.97); hxH (pH 5–7): 249 (4.02); hx (pH 10–11): 258 (4.05). Absorption coefficients in $M^{-1}\,cm^{-1}$.

$FeCl_3$ complexes with purine (puH), adenine (adH) and guanine (guH), using teof–EtOH as the interaction medium, adducts of the type $Fe(L'H)_2Cl_3$ were generally obtained,[23,24] but adenine *N*(1)-oxide produced both an adduct of the preceding type and a $Fe(L'H)L'Cl_2$ complex[25] (L'H = puH, adH, guH, adenine N(1)-oxide). Chloro ligand substitution by L' monoanionic ligands was also observed during the interaction of other metal trichlorides with puH, adH and guH (M = Al,[26] V,[27,28] Dy[29,30]), as well as that of $CrCl_3$ with puH and adH.[31] The teof present in the LH–salt interaction mixture proved effective in removing the water of the hydrated Fe(III) halides[32] used in the preparation of the new complexes.

Infrared spectra of the xanthine complexes are given in Table II, and those of the hypoxanthine complexes in Table III. Free ligand band assignments were based on our previous studies,[4–7] in combination with relevant IR work on xnH,[21] methylxanthines,[33] xanthosine 5'-monophosphate,[34] inosine 5'-monophosphate[35] and guH.[36] The $\nu_{C=O}$ bands of the ligands are not appreciably sensitive to Fe complex formation, while several $\nu_{C=C}$, $\nu_{C=N}$ and ring free ligand vibrations appear significantly shifted and occasionally split in the spectra of the complexes. This favours coordination of the ligands exclusively through ring nitrogens rather than C=O oxygens.[3–7,21,33–36] The $\nu_{CH} + \nu_{NH}$ bands of the ligands do not undergo significant changes upon Fe complex formation. Fe–ligand stretching modes were easily distinguishable from the ligand bands at 400–200 cm^{-1},[37] and tentatively assigned as ν_{Fe-N} at 284–268,[23–25] ν_{Fe-Cl} at 352–336 and ν_{Fe-Br} at 246–231 cm^{-1}.[23–25,38,39] These assignments are suggestive of *cis*- rather than *trans*-octahedral arrangements of the ligands around Fe^{3+} in the FeN_4X_2 chromophore (occurrence of more than one ν_{Fe-N} or ν_{Fe-X} absorption).[38,39]

The molar conductivities of the new complexes in nitromethane–acetone clearly indicate that these compounds are non-electrolytes[40] and therefore neutral species. The room temperature magnetic moments are normal for high-spin ferric compounds.[41] It should be noted at this point that a number of purine-bridged di- or polymeric Fe(III) complexes have been shown to exhibit subnormal paramagnetism.[42,43] The UV spectra of the free ligands[14,44] undergo shifts of their $\pi \to \pi^*$ transitions (225–267 nm) towards lower energies in the spectra of the complexes (Table IV). UV bands attributable to both the neutral LH and anionic L^- (LH = xnH or hxH) ligands present in the new complexes are observed, *i.e.*, xnH at 234–236 and 278–281; xn^- at 258–259 and 289–291; hxH at 255–257; and hx^- at 266–267 nm.[4–7,14,44] The $n \to \pi^*$ transition of the ligands occurs at 309–311 nm[45] in the spectra of the complexes. Strong Fe-to-ligand charge-transfer absorption bands,[46] originating in the UV and trailing off well into the visible region interfere with the weak d–d transition bands of the Fe^{3+} ion.[47]

On the basis of the overall evidence, and especially the solubility of the complexes in organic solvents, their normal paramagnetism, non-electrolyte nature and Ir spectra, these compounds are formulated as neutral *cis*-octahedral species of the $[Fe(LH)_3 LX_2]$ type. The first coordination sphere of the Fe^{3+} ion is occupied by three LH, one L^- and two X^- terminal ligands (LH = xnH or hxH; X = Cl or Br), with the latter two ligands in a *cis*-arrangement relative to each other. The terminal hxH and hx^- ligands would bind *via* the N7 imidazole nitrogen to Fe(III), since this is apparently the preferred binding site of unidentate hypoxanthine in its transition metal complexes (M = Co^{2+}, Ni^{2+}, Ru^{3+}).[15–17] Regarding the new xanthine complexes, terminal xnH or xn^- are considered as about equally likely to bind *via* the N7 or N9 imidazole nitrogen. The only crystal structure determination available of a complex with terminal xn^- is that of a mixed-ligand (dimethylglyoxime–xn^-–tri-

n-butylphosphine) Co(III) complex, in which this ligand binds *via* N9,[19] as already mentioned. It has been pointed out, however, that binding of xn^- *via* N9 in the latter compound may be promoted by H-bonding between the xn^- hydrogen at N3 and dimethylglyoxime oxygens.[21] On the other hand, neutral and monoanionic theophylline (1,3-dimethylxanthine) was established to preferentially bind *via* N7 in most of its metal complexes,[48,49] with the exception of a few compounds prepared under acidic conditions, in which it binds *via* N9.[50] Neutral xnH[12-14] resembles theophylline[48-50] in that it is protonated at N7. In the light of the preceding discussion and the relative paucity of structural information on metal complexes with unidentate xanthine, it is not possible to propose N7 over N9 or *vice versa* as the primary binding site of xnH or xn^-.

It should be mentioned that a general trend of xanthine and hypoxanthine to form complexes involving higher ligand to metal ratios than the corresponding complexes with puH, adH or guH is observed in the case under study. In fact, the new complexes involve 4:1 ligand to Fe molar ratios, while the corresponding $FeCl_3$ complexes with puH, adH and guH were 2:1.[23,24] In the case of ferric perchlorate complexes, xnH and hxH also produce 4:1 complexes,[4,5] while adH forms a 3:1[43] and guH a 2:1[51] complex.

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