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Xanthine and Hypoxanthine Complexes with Cobalt(II) Halides*

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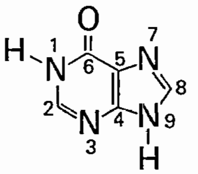
Abstract

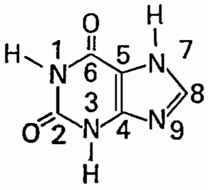
Complexes of the $Co(LH)_2LX$ and $Co(LH)_2$-$LI{\cdot}H_2O$ (LH = xanthine or hypoxanthine; X = Cl, Br) types were synthesized by refluxing 2:1 molar mixtures of LH and CoX_2 in triethyl orthoformate–ethyl acetate for one week. Characterization studies suggest that the new complexes are monomeric involving exclusively terminal neutral LH and monoanionic L^- ligands. The Co(II) chloride and bromide complexes are tetrahedral (CoN_3X chromophores), while the monohydrated Co(II) iodide complexes are pentacoordinated (CoN_3IO absorbing species). The hypoxanthine ligands are probably N7-bound to Co(II). In the case of the xanthine complexes, N7 and N9 were considered as about equally likely to function as the primary binding site of the terminal unidentate xanthine ligands.

Introduction

Hypoxanthine (hxH; 6-oxopurine; I) and xanthine (xnH; 2,6-dioxopurine; **II**) are constituents of RNA and form as intermediates in the reduction of nucleic acids to uric acid in man, catalyzed by the Fe- and Mo-containing enzyme xanthine oxidase. Mo complexes with xnH or hxH apparently contribute to the action mechanism of this enzyme [3]. Hence, the coordination chemistry of these bases is of significant medical importance in connection with diseases resulting from disturbances in purine metabolism, such as xanthinuria and gout [4]. Hypoxanthine is protonated at N1 and N9 (**I**) in the solid [5] or aqueous solution [6, 7], whereas xanthine in solution is protonated at N1, N3 and N7 (**II**) [6–8]. Crystal structure determinations of the metal complexes revealed that hxH binds via N7 when acting as a terminal unidentate [9–11] and via N3,N7 [9] or N3,N9 [12] when functioning as a bridging bidentate ligand. Structural information on metal complexes with xanthine is more scarce. The xn^- monoanion is protonated at N1,N3 and binds via N9 in bis(dimethylglyoximato)(xanthinato)(tri-n-butylphosphine)Co(III) [13], but in $Na(xn){\cdot}4H_2O$ it is protonated at N1,N9 [14]. The most acidic proton of xn^- is apparently involved in a tautomeric equilibrium, whereby N3,N7 or N9 could act as acceptors [15]. 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 [15].



I



II

Earlier work in these laboratories has dealt with the syntheses and characterization of xnH and hxH complexes with 3d metal perchlorates [16–18], Pd(II), Pt(IV) [19] and oxozirconium(IV) [20] chlorides. Studies of complexes of these ligands with various 3d metal halides (chlorides, bromides and iodides) were considered to be in order and recently undertaken [1, 2]. The present paper reports on the syntheses and characterization of Co(II) chloride, bromide and iodide complexes with xanthine and hypoxanthine.

Experimental

The general synthetic procedure employed was as follows. One mmol of hydrated Co salt was dissolved in 25 ml of a 7:3 (vol./vol.) mixture of triethyl

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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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orthoformate (teof)–ethyl acetate (ea), and the solution was stirred under reflux for 1 h. Two mmol of ligand (xnH or hxH) were mixed with 25 ml of 7:3 teof–ea, and the mixture was warmed to form a slurry, which was added to the stirring, refluxing Co(II) halide solution. The resultant mixture was refluxed for one week. Subsequently, the mixture was allowed to cool to room temperature, 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 complexes obtained are of the $Co(LH)_2LX{\cdot}nH_2O$ type (LH = xnH or hxH; $n = 0$ for X = Cl, Br; $n = 1$ for X = I), as shown by the analytical data given in Table 1. They are rather sparingly soluble in organic solvents, showing increased solubility in binary solvent mixtures, such as nitromethane–acetone. Infrared spectra (Tables 2 and 3) were recorded on KBr

TABLE 1. Analytical data for the new Co(II) complexes

Complex	Color	Yield (%)	Analysis: found (calc.) (%)				
			C	H	N	Co	X[a]
$Co(xnH)_2(xn)Cl$	blue–purple	73	32.60 (32.77)	2.11 (2.02)	30.36 (30.58)	10.53 (10.72)	6.41 (6.45)
$Co(hxH)_2(hx)Cl$	blue	83	35.66 (35.90)	2.40 (2.21)	33.33 (33.49)	11.98 (11.75)	6.89 (7.07)
$Co(xnH)_2(xn)Br$	blue	59	30.44 (30.32)	1.72 (1.87)	28.55 (28.29)	10.12 (9.92)	13.68 (13.45)
$Co(hxH)_2(hx)Br$	blue	75	33.21 (32.98)	2.12 (2.03)	30.49 (30.77)	11.04 (10.79)	14.51 (14.63)
$Co(xnH)_2(xn)I{\cdot}H_2O$	lavender	52	27.10 (27.33)	1.86 (1.99)	25.33 (25.50)	9.15 (8.94)	19.61 (19.25)
$Co(hxH)_2(xn)I{\cdot}H_2O$	lavender	60	29.66 (29.47)	2.27 (2.14)	27.31 (27.50)	9.37 (9.64)	21.08 (20.76)

[a] X = Cl, Br, I.

TABLE 2. Relevant IR data for the new xanthine Co(II) complexes (cm^{-1})

xnH[a]	X = Cl	X = Br	X = I	Band assignment
			3390w,b	νOH(aqua)
3132w, 3006s, 2881s, 2828m	3140ms, 3020s, 2920m, 2875ms, 2835ms	3135ms, 3020s, 2920m, 2875ms, 2830ms	3140ms, 3018s, 2915m, 2875ms, 2830ms	νCH + νNH
1702vs, 1660vs	1693vs, 1657vs	1694vs, 1660vs	1700vs, 1663vs	νC=O
			1635s, sh	δH–O–H
1569m, 1539m, 1530w, sh	1588m, 1580m, 1569w, 1537w	1595m, 1579m, 1564w, 1541w	1590m, 1573w, 1540w	νC=C + νC=N + δNH
1462ms, 1449ms, 1437m, 1415ms, 1390w, 1336m, 1328m, 1255w, 1234vw, 1206w, 1199m, 1161w, 1153w, 1112w 1120w	1490w, 1477w, 1458mw, 1420m, 1390w, 1340m, 1305w, 1262w, 1203mw, 1179mw, 1150mw, 1140mw, 1118w	1488m, 1469w, 1445mw, 1420mw, 1385w, 1340mw, 1312w, 1260w, 1231w, 1210mw, 1200mw, 1160mw, 1145mw, 1119w	1487w, 1462mw, 1440mw, 1421mw, 1370w, b, 1339m, 1329mw, 1307w, 1261w, 1230w, 1209mw, 1200mw, 1163mw, 1154mw	Ring vibrations + νC–N + δNH
520w, 507w, sh, 495w, 430w, 371w, 355w, 345w, sh, 320vw, 232w, 208vw	539ms, 499m, 435vw, 422w 373w, 231w 209w, b	540ms, 502ms, 433w, 420w 371w, 352mw, 330w, 211w	540ms, 500ms, 430w, 417vw, 370w, 351mw, 328w, 290vw, 231w, 210w	νxnH(600–200 cm^{-1})
			442w	νCo–O(aqua)
	350w, 326mw	260w, 235mw	190w	νCo–X
	294w, 281, 250w	290w, 278w, 247m	266w, 241w	νCo–N

[a] Free xnH band assignments based on refs. 15, 17, 19, 20, 25, 26 and 28.

TABLE 3. Relevant IR data for the new hypoxanthine Co(II) complexes (cm^{-1})

hxH^a	X = Cl	X = Br	X = I	Band assignment
			3400m, b	νOH(aqua)
3140m, 3050m, 2960s, 2920s, 2870s	3145ms, 3100ms, 3050s, 2950ms 2930ms, 2860m	3140ms, 3100ms, 3055s, 2959ms, 2925ms, 2865m	3140ms, 3095ms, 3055s, 2940ms, b, 2865m	νCH + νNH
1665vs	1672vs	1668vs	1670vs	νC=O
			1630s, sh	δH–O–H
1605mw, 1579m	1612w, 1582mw, 1555w	1613mw, 1580m 1560m	1615w, 1580ms, 1558m	νC=C + νC=N + δNH
1510w, 1455s, 1419m, 1377m, 1360m, 1341m, 1268m, 1205m, 1141m, 1123m	1525w, b, 1495w, 1462w, 1450w, 1420w, 1397mw, 1363w, 1342w, 1278w, 1219mw, 1158w, 1144w, 1100vw	1520w, b, 1490w, 1467w, 1450w, 1419mw,.1400mw, 1370w, 1351w, 1275w, 1250vw, 1215mw, 1200w, 1160w, 1142w, 1100vw	1516w, 1490w, 1469mw, 1449w, 1420mw, 1399mw, 1368mw, 1349mw, 1272w, 1246vw, 1212ms, 1195m, 1150m, 1137m 1100w	Ring vibrations + νC–N + δNH
580m, sh, 545m, 520m, 450mw, 387w, 362w, 345w, b, 241w, 231w, 211w	590vw, 561w, 545w, 522vw, 470vw, 439vw, 390w, 228w, 210w	566w, 548w, 520w, 5500w, 465w, 388w, 370w, 345w, 230w, 212w	568mw, 555w, 520w, 497w, 388w, 369w, 343w, 229w, 212w	νhxH(600–200 cm^{-1})
			447w	νCo–O(aqua)
	354w, 327mw	261w, 242mw	187w	νCo–X
	297w, 282w, 251w	294w, 280w, 248m	263w, 239w	νCo–N

^{a}Free hxH band assignments based on refs. 18–20, 27 and 28.

discs (4000–500 cm^{-1}) and Nujol mulls between high density polyethylene windows (700–100 cm^{-1}) using Perkin-Elmer 621 and (for the iodide complexes) 181 spectrophotometers. 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 (vol./vol.) nitromethane–acetone at 25 °C) measurements (Table 4) were obtained by methods described elsewhere [21].

Results and Discussion

The synthetic reactions performed invariably resulted in the precipitation of Co(II) complexes involving two neutral and one monodeprotonated xanthine or hypoxanthine ligand (the latter displacing one halo anionic ligand). Similar halogen substitution reactions by anionic purine ligands were previously observed during the syntheses of Co(II) chloride complexes with adenine (adH) [22] and guanine (guH) [23] from non-aqueous media. The teof present in the ligand–salt interaction mixture was effective in removing the water of the hydrated Co(II) chloride or bromide [24], but not in the case of Co(II) iodide, which yielded monohydrated complexes (Table 1).

IR spectra of the new xanthine complexes are given in Table 2, and those of the hypoxanthine complexes in Table 3. Free ligand band assignments were based on our previous studies [17–20] in combination with relevant IR work on xnH [15], methylxanthines [25], xanthosine 5′-monophosphate [26], inosine 5′-monophosphate [27] and guH [28]. The νC=O modes of the ligands are not appreciably sensitive to Co complex formation, while several νC=C, νC=N and ring vibrations of the free ligands appear significantly shifted and occasionally split in the spectra of the complexes. This rules out participation of the C=O oxygens of the ligands in coordinative bonding interactions with Co(II), and favors use of xanthine or hypoxanthine ring nitrogens in binding [15–20, 25–28]. The νCH + νNH bands of the ligands remain virtually unchanged upon complex formation. The νOH and δH–O–H modes of coordinated water appear at 3400–3390 and 1635–1630 cm^{-1}, respectively [29], in the spectra of the Co(II) iodide complexes. Co–ligand stretching modes were easily distinguishable from the ligand bands at 450–200 cm^{-1} [30], and tentatively assigned as νCo–O-

TABLE 4. Solid-state (nujol mull) electronic spectra, magnetic properties (300 K) and molar conductivities of the new complexes

Complex	λ_{max} (nm)	$10^6 \times \chi_M^{cor}$ (cgsu)	μ_{eff} (μB)	Λ_M (Ω^{-1} cm^2 mol^{-1})
L = xnH				
X = Cl	202vvs, 234vs, sh, 257vs, 279vs, 293vs, 311vs, sh, 325s, sh, 550ms, 621s, 658s, 702ms, 1400mw, 1630w, 1880w, 2100mw	8639	4.57	17
X = Br	200vvs, 233vvs, sh, 258vs, 282vs, 295vs, 309vs, sh, 330s, sh, 544ms, 617s, 653s, 726ms, 1375mw, 1647w, 1915w, 2160mw	8492	4.51	22
X = I	200vvs, 235vs, sh, 260vs, 280vs, 291vs, 309vs, sh, 328s, sh, 550m, 631m, 747mw, 872mw, 991w, 1865vw, b	8253	4.47	20
L = hxH				
X = Cl	204vvs, 235vs, sh, 254vs, 267vs, 308s, sh, 333s, 547ms, 616s, 660s, 708ms, 1400mw, 1644w, 1895w, 2110mw	8422	4.51	22
X = Br	201vvs, 234vs, sh, 256vs, 264vs, 307s, sh, 329s, 545ms, 612s, 667s, 729ms, 1370mw, 1651w, 1920w, 2180mw	8702	4.58	19
X = I	203vvs, 232vs, sh, 255vs, 265vs, 308s, sh, 331s, 555m, 643m, 755mw, 880mw, 997w, 1845vw, b	8840	4.62	21

[a] UV spectra of the free ligands: Nujol mulls, nm: xnH < 200vvs, 225vs, sh, 270vs, b; hxH: 200vvs, 247vs, 280vs, sh, 340s, sh [16–20]. Aqueous solution spectra [8, 39], λ_{max}, (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).

(aqua) at 447–442 [31], νCo–N at 297–248 for X = Cl, Br and 266–239 for X = I [22, 23], νCo–Cl at 354–326, νCo–Br at 261–235 and νCo–I at 190–187 (32–35) cm^{-1}. Comparisons of the spectra of the Co chloride and bromide complexes lend support to the νCo–N band assignments. The νCo–ligand assignments favor coordination number four for the Co chloride and bromide [23, 32–35] and five for the iodide [22, 31–35] complexes.

The molar conductivities of the new complexes (Table 4) correspond to non-electrolytes [36] and indicate that these compounds are neutral species. The room temperature magnetic moments of the complexes are normal for high-spin tetrahedral (X = Cl, Br) [37] or pentacoordinated (X = I) [38] Co(II) compounds. The UV spectra of the ligands [8, 39] undergo shifts of their $\pi \rightarrow \pi^*$ transitions (225–267 nm) toward lower energies upon Co(II) complex formation (Table 4). Bands corresponding to both the neutral and monoanionic purine ligands present in the new complexes were identified, i.e. xnH at 233–235 and 279–282; xn$^-$ at 257–260 and 291–295; hxH at 254–256; hx$^-$ at 264–267 nm [8, 17–20, 39]. The $n \rightarrow \pi^*$ transition of the ligands is observed at 307–311 nm in the spectra of the complexes [40], which are also characterized by strong Co-to-ligand charge-transfer absorption [41], originating in the UV and trailing off into the visible. The d–d transition spectra of the Co chloride and bromide complexes are consistent with pseudotetrahedral configurations [23, 32–34, 42], viz: $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) 544–550, 612–621, 653–667, 702–729; $\rightarrow {}^4T_{1g}$ (F) 1370–1400, 1630–1651, 1880–1920; $\rightarrow {}^4T_{2g}$ (F) 2100–2180 nm. The d–d spectra of the Co iodide complexes are characterized by six maxima (550–1865 nm), substantially weaker in intensity than the d–d bands of the tetrahedral complexes, and compatible with pentacoodinated configurations [31, 43].

The overall evidence presented suggests that the new complexes are generally monomeric species with terminal neutral and monoanionic purine and halo ligands, and in the case of the Co iodide complexes, an additional aqua ligand. The Co chloride and bromide complexes are distorted tetrahedral of the [Co(LH)$_2$LX] type (LH = xnH or hxH; X = Cl or Br; CoN$_3$X chromophores), whilst the Co iodide complexes attain coordination number five through the presence of the aqua ligand, and are of the [Co(LH)$_2$LI(OH$_2$)] type (CoN$_3$IO chromophores). The terminal unidentate hxH and hx$^-$ ligands would bind via the N7 imidazole nitrogen to Co(II), since this is apparently the preferred binding site of terminal hypoxanthine in complexes with 3d metal(II) ions (M = Co, Ni) [9, 10]. As regards the new xanthine complexes, terminal xnH or xn$^-$ are considered as about equally likely to bind via the N7 or the 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 xn$^-$ binds via N9 [13], as already mentioned. It has been pointed out, however, that binding of xn$^-$ via N9 in the latter complex may be promoted by H bonding between the xn$^-$ hydrogen at N3 and dimethylglyoxime oxygens [15]. On the other hand, neutral and monoanionic theophylline (1,3-dimethylxanthine) was established to preferentially bind via N7 in most of its metal complexes [44, 45], with the exception of a few complexes prepared under acidic conditions, in which it binds via N9 [46]. Neutral xnH [6–8] resembles theophylline [44–46] in that it is protonated at N7. In light of the preceding discussion and the relative paucity of structural information on 3d metal complexes with terminal xnH or xn$^-$, it is not possible to propose N7 over N9 or vice versa as the primary binding site of these ligands. A final point of interest is that, as was the case with the corresponding Co(II) perchlorate complexes [17, 18, 47–49], xnH and hxH produced Co(II) halide complexes with higher ligand to Co ratios than the complexes formed by interaction of $CoCl_2$ with purine [31], adH [22] or guH [23]. In fact the new complexes involve three xanthine or hypoxanthine ligands per Co^{2+} ion, while the $CoCl_2$ complexes with purine, adH or guH isolated from non-aqueous media involved 2:1 or 1:1 ligand to Co molar ratios [22, 23, 31].

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