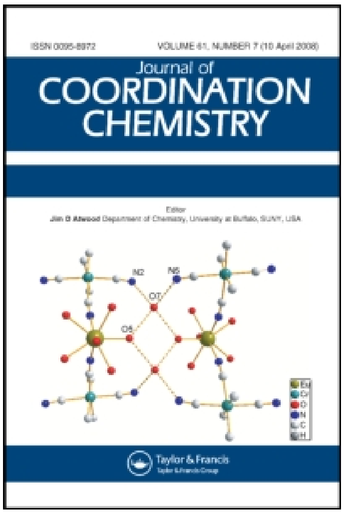

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Hypoxanthine and Xanthine Complexes with Some Mercury(II) and Lead(II) Halides

Chester M. Mikulski[a]; Donna L. Staley[a]; Nicholas M. Karayannis[b]
[a] Department of Chemistry and Physics, Beaver College, Glenside, PA, USA [b] Amoco Chemical Company, Napenille, IL, USA

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NOTE
HYPOXANTHINE AND XANTHINE COMPLEXES WITH SOME MERCURY(II) AND LEAD(II) HALIDES

CHESTER M. MIKULSKI, DONNA L. STALEY

Department of Chemistry and Physics, Beaver College, Glenside, PA 19038, USA

and NICHOLAS M. KARAYANNIS*

Amoco Chemical Company, P.O. Box 3011, Naperville, IL 60566-7011, USA

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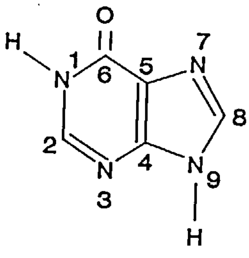
Complexes of the type Hg(LH)LX.H_2O (X = Br, I) and Pb(LH)LBr.H_2O were synthesized by refluxing 2:1 molar mixtures of hypoxanthine or xanthine (LH) and $HgBr_2$, HgI_2 or $PbBr_2$ in triethyl orthoformate-ethyl acetate. Characterization suggests that the new complexes are linear polymers, involving a $-(M-L)_x-$ backbone (M = Hg, Pb) and three terminal ligands (one halo, one LH and one aqua) per metal ion.

Keywords: Hypoxanthine, xanthine, mercury(II), lead(II), complexes, synthesis

Recent work in these laboratories has dealt with the syntheses and characterization of a variety of metal chloride, bromide and iodide complexes with hypoxanthine (hxH; I) and xanthine (xnH; II).[1,2] Thus far, complexes with various 3d metal {Co(II), Ni(II), Fe(III), V(III), Mn(II), Fe(II), Cu(I), Cu(II) and Zn(II)} halides were reported. More recent research is directed toward the preparation and characterization of the corresponding complexes with heavier transition metal, lanthanide, actinide and main group metal halides. The present communication deals with complexes produced by reaction of Hg(II) bromide and iodide and Pb(II) bromide with these ligands.



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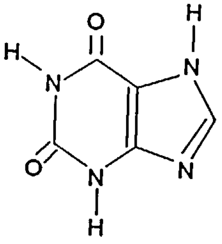

II

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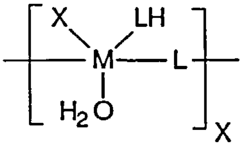
* Author for correspondence.

RESULTS AND DISCUSSION

Reaction of the ligand with the metal halides in a 7:3 (v/v) mixture of MeCOOEt-HC(OEt)$_3$ resulted in the isolation of solid metal complexes of general formula M(LH)LX.H$_2$O (M = Hg, Pb; LH = hxH, xnH; X = Br, I), produced by substitution of one monoanionic hypoxanthine or xanthine for one halo ligand. The new complexes are generally insoluble in common organic solvents and are most probably polymeric species.[1,2] Relevant i.r. spectral data (cm^{-1}) are as follows: ν(OH) and δ(H–O–H) modes of coordinated water appear at 3490–3430 and 1630–1620, respectively,[3] in the spectra of the complexes. The ν(CH) + ν(NH) modes of free hxH (3140, 3050, 2960, 2920, 2870) and xnH (3132, 3006, 2881, 2828) undergo minor shifts upon complex formation. The ν(C=O) bands of the ligands (hxH 1665; xnH 1702, 1660)[1,4,5] appear at 1682–1670 in the new hxH and at 1713–1707 and 1659–1652 in the new xnH complexes. With respect to the ligand absorptions in the ν(C=C) + ν(C=N) region (hxH: 1605, 1579; xnH: 1569, 1539, 1530),[1,4,5] mercury or lead halide complex formation results in more significant shifts and occasional splittings, *i.e.*, LH = hxH: 1618–1611, 1585–1580, 1560–1550; LH = xnH: 1600–1590, 1580–1570, *ca* 1565, 1543–1534. The preceding features suggest that the purine ligands bind through ring nitrogens, while C=O oxygens are not involved in coordination.[1,2,4–6] Bands attributable to ν(M–O, aqua) modes[3,7,8] are observed at 300–280 in the Hg(II) and 290–270 in the Pb(II) complexes. The ν(M–X) and ν(M–N) bands were tentatively assigned to maxima at 200–100, as follows: ν(Hg–Br) 187–181, ν(Pb–Br) 179–175, ν(Hg–I) ca 140, ν(M–N) (M = Hg, Pb) 160–145[9,10] The metal-ligand band assignments are compatible with pentacoordinated configurations.

The simultaneous presence of neutral LH and monoanionic L$^-$ ligands in the new metal complexes is clearly manifested by their electronic spectra.[1] In fact, the neutral free ligands show the following $\pi \rightarrow \pi^*$ transitions in aqueous solution (pH 5–7): hxH 249, xnH 225, 266–267; corresponding maxima for the monoanions are (pH 10–11): hx$^-$ 258; xn$^-$ 240–241, 276–277 nm.[11,12] The spectra of the complexes exhibit the following bands in the preceding regions, nm: 253–257 (hxH), 262–268 (hx$^-$), 231–235 and 280–284 (xnH), 257–262 and 290–296 (xn$^-$):[1] The n$\rightarrow\pi^*$ transitions of the ligands appear as shoulders at 305–313 nm in the spectra of the complexes,[1] which also exhibit maxima at 200–204 and 325–335 nm.

The general insolubility of the new complexes in organic media, combined with their pentacoordinated configurations as suggested by the i.r. evidence, and the pronounced tendency of purine to act as a bidentate bridging ligand,[1,13] favours a linear, chainlike, polymeric structural type, involving a $-\!(\text{M}-\text{L})\!-_x$ backbone and terminal LH, X and aqua ligands, as shown in III (M = Hg, Pb; X = Br, I). Terminal hxH would most likely bind *via* the N(7) imidazole nitrogen, since this is the preferred binding site of this ligand,[14,15] while for terminal xnH no adequate structural information is available to distinguish between N(7) and N(9) as the primary binding site.[1] As regards the binding sites of the bridging bidentate anionic L$^-$ ligands, N(3), N(7) are favoured in the case of hx$^-$, since the proposed structure (III) involves single purine bridges between adjacent Hg or Pb ions.[14] Bridging bidentate hypoxanthine binding *via* N(3), N(9) is observed only in several binuclear metal complexes with double or quadruple hxH bridges between the two metal ions.[16] In the case of bridging xn$^-$, binding *via* N(7), N(9) is most likely.[1,17] Binding of this ligand *via* N(3), N(7) or N(3), N(9) is considered as less favourable in view of the steric hindrance exerted by the C(2)=O group on the N(3) position.[18] Finally, it should be mentioned that several Hg(II) complexes with purine derivatives have been reported. These include a polymeric $HgCl_2$ complex with adenine-*N*(1)-oxide (in which the bridging ligand is O(1), N(7)-bound),[19] and numerous methylmercury(II) complexes (*e.g.*, complexes involving N(3), N(7), N(9)- and N(1), N(3), N(7), N(9)-bound xanthine dianion and trianion, respectively, with each nitrogen site coordinating to a different MeHg ion[5]). Studies of Pb(II) complexes with purines are rather scarce; an example is found in an electroanalytical study of Pb(II) interaction with 6-mercaptopurine.[20]



III

EXPERIMENTAL

Synthetic procedure: the hydrated metal salt (1.2 mmol) was dissolved in a mixture of 35 cm^3 MeCOOEt and 15 cm^3 $HC(OEt)_3$ with stirring for 1 h, and then the ligand (2.4 mmol) was added. The resultant mixture was boiled under reflux until a significant amount of solid precipitate was formed (1–2 days). The new metal complexes obtained analyzed as follows (complex formulae: $C_{10}H_9N_8O_3XM$ for LH = hxH; $C_{10}H_9N_8O_5XM$ for LH = xnH; X = Br, I; M = Hg, Pb): hypoxanthine complexes: X = Br, M = Hg: found C, 20.6; H, 1.4; N, 20.0; Br, 13.5; Hg, 35.8%; calcd.: C, 21.1; H, 1.6; N, 19.7; Br, 14.0; Hg, 35.2%. X = I, M = Hg: found C, 19.1; H, 1.5; N, 17.6; I, 21.2; Hg, 32.9%; calcd.: C, 19.5; H, 1.5; N, 18.2; I, 20.6; Hg, 32.5%. X = Br, M = Pb: found C, 20.3; H, 1.4; N, 19.9; Br, 14.6; Pb, 36.7; calcd.: C, 20.8; H, 1.6; N, 19.4; Br, 13.9; Pb, 36.0%. Xanthine complexes: X = Br, M = Hg: found C, 20.4; H, 1.6; N, 19.1; Br, 13.5; Hg, 32.7%; calcd.: C, 20.0; H, 1.5; N, 18.6; Br, 13.3; Hg 33.3%. X = I, M = Hg: found C, 18.2; H, 1.2; N, 17.6; I, 20.2; Hg 31.3%; calcd.: C, 18.5; H, 1.4; N, 17.3; I, 19.6; Hg, 30.9%. X = Br, M = Pb: found C, 19.3; H, 1.4; N, 18.8; Br, 12.7; Pb, 34.3; calcd.: C, 19.7; H, 1.5; N, 18.4; Br, 13.1; Pb, 34.1%. The $HgBr_2$ complexes are off-white in colour, those with HgI_2 off-white with a reddish tint, and the $PbBr_2$ compounds grey. I.r. spectra of the complexes were recorded in KBr discs and Nujol mulls, using a Perkin-Elmer 621 and a 181 spectrophotometer, while solid-state (Nujol mull) electronic spectra were obtained as described elsewhere.[21]

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