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Complexes of 9-Methylhypoxanthine with some Divalent Metal Ions

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The preparations and spectral properties are reported of a range of complexes of 9-methylhypoxanthine (= 9Mehyp) with divalent metal ions of the series Mn–Zn, and also Cd and Hg(II). With the transition metal ions the compounds mostly contained a 2:1 9Mehyp: metal ratio, but the complexes $Cu(9Mehyp)_4(NO_3)_2 \cdot H_2O$ *and* $Cu(9Mehyp)_4(ClO_4)_2$ *were also isolated. With zinc, tetrahedral complexes* $[Zn(9Mehyp)(OH_2)X_2]$ *(X = Cl or Br) were obtained, but mercury(II) chloride and bromide gave the compounds* $[Hg(9Mehyp)X_2]$ *in which planar* $HgNX_2$ *units are interconnected by long, axial Hg–X bonds.*

Introduction

The results of X-ray structural and other studies on the bonding of metal ions to pyrimidines or purines have shown [1, 2] that the ring nitrogen atoms are generally the preferred coordination sites when these are freely available to the metal ions. There is, however, a growing interest in the possible coordination of exocyclic oxygen atoms. Examples of strong M–O bonding of this type are rare [3], but there are several compounds in which strong M–ring nitrogen bonding is reinforced by weaker, secondary interaction with exocyclic oxygen [1, 4].

Continuing our own work in this area [5] we have studied the compounds formed by 9-methylhypoxanthine (= 9Mehyp) with a range of metal ions.

In hypoxanthine and its derivatives the labile proton of the formal hydroxyl group on C6 gives rise to lactam–lactim tautomerism. Experimental evidence supports the lactam arrangement, with the proton on N1, as the major form [6, 7]. Unless the interaction with metal ions induces proton migration, this protonation position precludes coordination by N1 which, in contrast, is known to occur for the related ligand 9-methyladenine [1, 8–11].

Weiss and Venner have reported [12, 13] the preparations of some hydrated complexes of cobalt, nickel, and copper with hypoxanthine and 7- and 9-methylhypoxanthine, but no physical measurements were described. X-Ray structural information is available on $[Cu(9Mehyp)_2(OH_2)_2Cl_2] \cdot 3H_2O$ [14], $[Cu(9Mehyp)_2(OH_2)_4]SO_4$ [15] and, as part of this work, on $Hg(9Mehyp)Cl_2$ [16]. In all three compounds the purine ligand binds only through N7. In contrast, hypoxanthine itself has a strong tendency to coordinate via N3 and N9, as in the dimer $[Cu_2(hypoxanthine)_4Cl_2]Cl_2 \cdot 6H_2O$ [17].

Results and Discussion

The complexes we obtained with 9-methylpoxanthine are listed in Table I. The stoichiometries reported do not necessarily represent the only ones obtainable for a given metal salt with 9Mehyp as we were interested only in a general survey of the coordination of this purine ligand with these metal ions. The use of hydrated metal salts in methanol or ethanol generally afforded hydrated complexes, from which anhydrous compounds could be obtained by heating. Exceptions to this were the compounds $Cu(9Mehyp)_2X_2$ (X = Cl or Br) and $M(9Mehyp)X_2$ (M = Cd or Hg; X = Cl or Br) which were obtained directly as anhydrous compounds from the organic solvents.

Cobalt and Nickel Complexes

The electronic spectra of the solid, hydrated cobalt and nickel complexes are typical of these metal ions in octahedral coordination (Table II). The band energies of $M(9Mehyp)_2X_2 \cdot 4H_2O$ (M = Co or Ni; X = Cl or Br) are shifted slightly on replacing Cl by Br but these changes alone are too small to provide good evidence for the presence of coordinated anions. Their low frequency vibrational spectra are, however, more helpful in this respect.

The i.r. and Raman bands of 9-methylhypoxanthine in the 180–400 cm^{-1} region are listed in Table III. The 185 cm^{-1} band was generally shifted by *ca.* ±5 cm^{-1} in the complexes, that at 212 cm^{-1} was raised in frequency and the 360 cm^{-1} band shifted to *ca.* 373–400 cm^{-1}. Some of the complexes had a band of medium to weak intensity in the 270–285 cm^{-1} region. Except for the cobalt nitrate complex (discussed below) this band is probably an activated ligand band (or possibly a shifted 243 cm^{-1} ligand band) similar to that found previously for the 9-methyladenine complexes [10].

TABLE I. Analytical Data of Some Complexes of 9-Methylhypoxanthine (= L).

Complex	Colour	Analytical Results					
		Found %			Calculated %		
		C	H	N	C	H	N
$MnL_2Cl_2\cdot 2H_2O$	pink	31.67	3.32	23.67	31.18	3.49	24.24
$MnL_2Br_2\cdot 2H_2O$	pink	26.26	3.22	20.53	26.15	2.92	20.33
$CoL_2Cl_2\cdot 4H_2O$	pink	28.67	3.89	22.42	28.70	4.01	22.31
$CoL_2Br_2\cdot 4H_2O$	pink	24.63	3.52	18.94	24.38	3.41	18.98
CoL_2Cl_2	dark blue	33.23	3.13	25.75	33.51	2.81	26.00
CoL_2Br_2	dark blue	27.49	2.59	21.33	27.77	2.33	21.58
$NiL_2Cl_2\cdot 4H_2O$	pale blue	28.63	4.03	22.00	28.71	4.01	22.32
$NiL_2Br_2\cdot 4H_2O$	pale blue	24.36	3.40	19.01	24.39	3.41	18.96
NiL_2Cl_2	gray blue	33.45	2.81	25.94	33.52	2.81	26.00
NiL_2Br_2	green	27.94	2.63	21.59	27.78	2.33	21.59
CuL_2Cl_2	gray blue	33.32	2.70	26.07	33.16	2.78	25.78
CuL_2Br_2	dark green	27.64	2.53	21.34	27.52	2.31	21.39
$ZnLCl_2\cdot H_2O$	white	24.31	2.71	18.55	23.67	2.64	18.40
$ZnLBr_2\cdot H_2O$	white	18.85	2.01	13.95	18.32	2.05	14.24
$HgLCl_2$	white	17.15	1.35	12.79	17.11	1.43	13.30
$HgLBr_2$	white	14.38	1.27	11.27	14.11	1.18	10.97
$CdLCl_2$	white	21.45	2.18	16.97	21.61	1.81	16.80
$CdLBr_2$	white	17.06	1.63	12.85	17.06	1.43	13.26
$CoL_2(BF_4)_2\cdot 4H_2O$	pink	24.11	3.46	18.92	23.83	3.33	18.52
$NiL_2(BF_4)_2\cdot 6H_2O$	pale blue	22.47	3.44	16.99	22.49	3.77	17.48
$CoL_2(NO_3)_2\cdot 4H_2O$	pink	25.79	3.48	24.50	25.93	3.63	25.21
$CuL_4(NO_3)_2\cdot H_2O$	dark blue	35.49	3.16	30.82	35.75	3.25	31.26
$CuL_2(NO_3)_2\cdot 3H_2O$	pale blue	26.66	3.26	25.57	26.61	3.35	25.85
$CuL_4(ClO_4)_2$	dark blue	33.90	3.10	26.33	34.03	2.86	26.46

TABLE II. Reflectance Spectral Band Energies (cm^{-1}) of Some Complexes of 9-Methylhypoxanthine (= L).

$CoL_2Cl_2\cdot 4H_2O$	20,000 br	8700		
$CoL_2Br_2\cdot 4H_2O$	21,200 sh	20,000	8650	
$CoL_2(BF_4)_2\cdot 4H_2O$	20,800 br	8700		
$CoL_2(NO_3)_2\cdot 4H_2O$	21,300 br	8600		
$CoL_2(BF_4)_2\cdot 2H_2O$	17,550	7700 br		
CoL_2Cl_2	16,350	6900 br		
CoL_2Br_2	16,000	6900 br		
$NiL_2Cl_2\cdot 4H_2O$	25,700	15,750	14,000 wsh	9450
$NiL_2Br_2\cdot 4H_2O$	25,600	15,600	14,000 wsh	9050
$NiL_2(BF_4)_2\cdot 6H_2O$	25,100	15,150	9300	
NiL_2Cl_2	22,600	15,400	8500	
NiL_2Br_2	22,600[a]	14,800	8500[b]	
CuL_2Cl_2	18,350	15,750		
CuL_2Br_2	15,600[a]			
$CuL_2(NO_3)_2\cdot 3H_2O$	13,800	11,100		
$CuL_4(NO_3)_2\cdot H_2O$	16,350			
$CuL_4(ClO_4)_2$	16,150			

[a] On strong absorption edge from U.V. region. [b] Asymmetric to lower energy.

The low frequency i.r. spectra of $M(9Mehyp)_2Cl_2\cdot 4H_2O$ (M = Co or Ni) are very similar, and, in addition to $\nu(M-OH_2)$ bands (Table III), each contains a band assignable as $\nu(M-Cl)$ which is absent from the spectra of the corresponding bromides. The bromides had no $\nu(M-Br)$ bands above 180 cm^{-1} and this fact, together with the very small differences in the electronic spectral band energies on replacing Cl by Br, suggest that the chlorides may be formulated as $[M(9Mehyp)_2(OH_2)_2Cl_2]\cdot 2H_2O$, whereas the bromides resemble the hydrated complexes of 9-methyladenine [10] and are $[M(9Mehyp)_2(OH_2)_4]Br_2$.

TABLE III. Infrared (IR) and Raman (R) Spectra (180–400 cm^{-1}) of 9-Methylhypoxanthine (= L) and Some of Its Complexes.

Compound		ν(M–X)	ν(M–OH_2)	ν(M–N)	Ligand Bands	Unassigned
L	IR	–	–	–	361 s, 306 vw, 243 m, 212 s, 185 s	–
	R	–	–	–	366 m, 361 m, 244 m, 212 m	–
$CoL_2Cl_2 \cdot 4H_2O$	IR	252 m	348 m	239 m	400 s, 272 mw, 214 s, 181 s	205 m
$CoL_2Br_2 \cdot 4H_2O$	IR	–	380 sbr^{a}	222 sbr^{a}	276 m, 180 s	314 m
$CoL_2(BF_4)_2 \cdot 4H_2O$	IR	–	380 sbr^{a}	250 s, 228 s	313 w	340 mw, 283 vs
$CoL_2(NO_3)_2 \cdot 4H_2O$	IR	270 ms^{a,c}	380 sbr^{a}	240 ms^{a}	218 ms	250 w
CoL_2Cl_2	IR	312 vs, 298 vs	–	265 m, 220 m	380 m, 276 m, 244 m, 210 m, 184 s	252 w
CoL_2Br_2	IR	256 vs, 232 s	–	^{b}, 225 s	373 m, 313 w, 283 mw, 210 s	–
$NiL_2Cl_2 \cdot 4H_2O$	IR	260 m	361 s	250 m, 230 m	400 s, 312 vw, 276 mw, 216 s, 195 s	–
$NiL_2Br_2 \cdot 4H_2O$	IR	–	385 sbr^{a}	220 sbr^{a}	278 mw, 210 sh, 180 s	319 m
$NiL_2(BF_4)_2 \cdot 4H_2O$	IR	–	363 vsbr	246 s, 228 s	380 sh, 317 w, 282 w, 195 s	–
CuL_2Cl_2	IR	305 vs	–	294 s, sh	399 s, 228 ms, 180 ms	332 w
CuL_2Br_2	IR	250 mw^{d}	–	301 vs, br	395 m, 230 mw	–
$CuL_2(NO_3)_2 \cdot 3H_2O$	IR	–	378 m	288 s	400 s, 241 m, 218 w	260 w, 250 w
$CuL_4(NO_3)_2 \cdot H_2O$	IR	–	–	283 s	400 s	–
$MnL_2Cl_2 \cdot 2H_2O$	IR	182 sbr^{a,d}	354 br, sh	250 sh, 236 m	393 s, 212 s, 182 br^{e}	–
$MnL_2Br_2 \cdot 2H_2O$	IR	–	349 ms	259 mw, 230 ms	390 s, 258 w, 212 s, 192 s	–
$ZnLCl_2 \cdot H_2O$	IR	325 vs, 305 s	370 m	222 s^{a}	393 ms, 180 s	–
$ZnLBr_2 \cdot H_2O$	IR	244 vs	370 m	225 ms^{a}	385 mw	–
$HgLCl_2$	IR	325 s, 275 w	–	260 w	381 m, 227 m, 194 s	300 vw
	R	325 w, 276 s	–	254 w	382 m	298 vw
$HgLBr_2$	IR	230 s, 179 w	–	253 m	377 s	298 vw
	R	230 w, 179 s	–	–	382 w	–

[a] Overlapping ligand band in same region. [b] Region where ν(M–N) expected obscured by strong, broad ν(M–Br) band. [c] ν(M–ONO_2). [d] Assignment uncertain (see text). [e] Overlapping ν(M–X) (?).

TABLE IV. Thermogravimetric Results.

Initial Complex	% Weight Lost			Temperature Range (°C)
	For:	Calc.	Found	
$Ni(9Mehyp)_2Cl_2·4H_2O$	$4H_2O$	14.35	14.40	130–180
$Ni(9Mehyp)_2Br_2·4H_2O$	$4H_2O$	12.19	12.15	130–185
$Co(9Mehyp)_2Cl_2·4H_2O$	$4H_2O$	14.0	13.93	110–175
$Co(9Mehyp)_2Br_2·4H_2O$	$4H_2O$	12.19	12.07	110–160
$Co(9Mehyp)_2(BF_4)_2·4H_2O$	$2H_2O$	5.95	6.19	100–195
$Zn(9Mehyp)_2Cl_2·H_2O$	$1H_2O$	5.91	5.87	120–185
$Zn(9Mehyp)_2Br_2·H_2O$	$1H_2O$	4.98	4.30	120–190

X-Ray powder photographs show that the compounds $[M(9Mehyp)_2(OH_2)_4]Br_2$ (M = Co or Ni) form an isomorphous pair but this is not so for the chlorides or, indeed, for any of the other compounds listed in Table I.

Dehydration of the hydrated halide complexes of cobalt and nickel was carried out in a thermogravimetric balance. The nickel complexes began to lose water at *ca.* 130 °C and dehydration was complete by 180–185 °C. There was no evidence for the formation of compounds with intermediate degrees of hydration under these experimental conditions. Similar results were obtained for the cobalt complexes but at slightly lower temperatures (Table IV).

The dehydrated cobalt complexes were dark blue and remained anhydrous when exposed to air. They have electronic spectra characteristic of a tetrahedral CoN_2X_2 (X = Cl or Br) chromophore (Table II) and this geometry is confirmed by the positions of the strong ν(Co–X) bands in their low frequency i.r. spectra (Table III).

Assignment of the structures of the anhydrous complexes of nickel chloride or bromide, $Ni(9Mehyp)_2X_2$, is less straightforward. They are very hygroscopic, and reliable low frequency i.r. spectra were not obtained. Their electronic spectra (Table II, Fig. 1) show that they are not tetrahedral NiN_2X_2 species, but neither are the spectra in good accord with a polymeric octahedral structure involving halide bridges, as in $Nipy_2Cl_2$.

The bands are much more intense than those usually observed [18] for such a six coordinate geometry and the fact that the band at *ca.* 15,000 cm^{-1} is stronger than the others, particularly so in the case of the bromide, is also unexpected. The band intensities suggest the presence of a non-centrosymmetric nickel environment, possibly due to a *cis*-arrangement of two 9Mehyp molecules chelating via N7 and O6. Unfortunately single crystals could not be obtained for X-ray diffraction work.

The electronic spectra of $Co(9Mehyp)_2(NO_3)_2·4H_2O$ and the cobalt and nickel tetrafluoborate complexes show that they have octahedral stereochemistry. All three compounds had a strong, broad band in the 360–380 cm^{-1} region, assignable as $\nu(M–OH_2)$ of coordinated water. The cobalt nitrate complex had i.r. bands characteristic of monodentate coordinated nitrate groups (825, 1040, 1310 and 1410 cm^{-1}). Further support for nitrate coordination is provided by a band at 270 cm^{-1} which was significantly stronger than the ligand band in that region for the other complexes; this absorption probably comprises both $\nu(Co–ONO_2)$ [19] and the ligand mode. The compound may, therefore, be formulated as $[Co(9Mehyp)_2(OH_2)_2(ONO_2)_2]·2H_2O$.

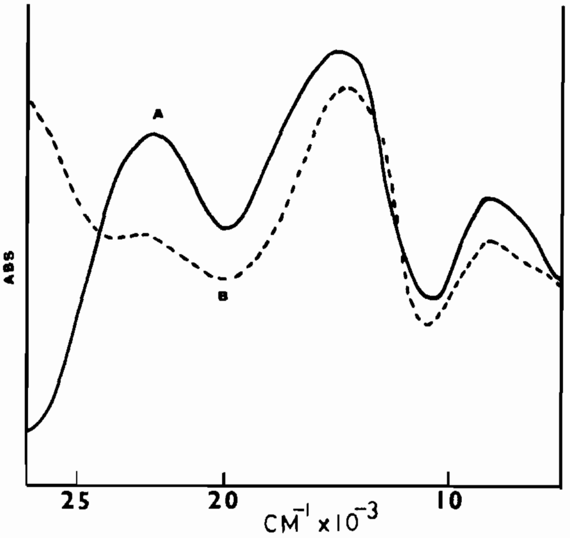

Fig. 1. Reflectance spectra of: A, $Ni(9Mehyp)_2Cl_2$; B, $Ni(9Mehyp)_2Br_2$.

On heating in a thermogravimetric balance the complex $Co(9Mehyp)_2(BF_4)_2·4H_2O$ lost two molecules of water between 100 and 195 °C and changed colour from pink to violet. The product had an electronic spectrum (Table II) typical of an essentially tetrahedral geometry. The ligand field was stronger than that in $Co(9Mehyp)_2Cl_2$ but weaker than those found for related tetrahedral CoN_4 chromophores [5, 20], pointing to a CoN_2O_2 donor set. However, it is

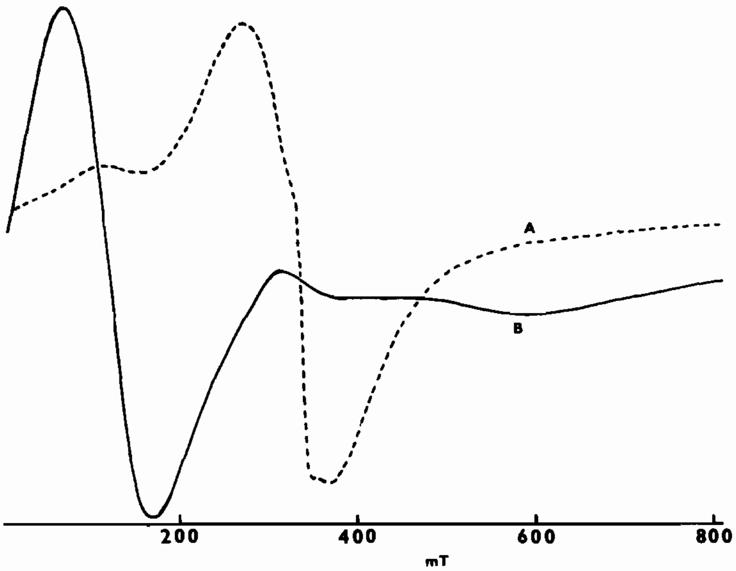

Fig. 2. X-band (9.528 GHz) epr spectra of: A, $Mn(9Mehyp)_2Cl_2 \cdot 2H_2O$; B, $Mn(9Mehyp)_2Br_2 \cdot 2H_2O$.

not known whether the oxygen donor atoms are from water or O6 of the purine. Attempts to dehydrate the complex completely by heating it above 195 °C resulted in decomposition.

Manganese Complexes

The X-band e.p.r. spectra of polycrystalline samples of both the compounds $Mn(9Mehyp)_2X_2 \cdot 2H_2O$ (X = Cl or Br) show the presence of zero field splitting (zfs) (Fig. 2). The breadths of the bands precluded accurate determination of the zfs parameters, though it is clear that D is greater for the bromide than for the chloride. However, several useful structural conclusions may be drawn from these spectra. The differences between the two spectra show that the halide ions are coordinated. The observations of the effects of zfs indicates that the compounds do not have polymeric structures [21]. The results are consistent with distorted octahedral [21] but not distorted tetrahedral (C_{2v}) [22] geometries.

In the low frequency i.r. spectra there were no bands clearly assignable as ν(Mn–X) within the range of our spectrometer. There was a band at 182 cm^{-1} for the chloride which was stronger and broader than the ligand band normally found in this region, and this may contain ν(Mn–Cl) as well as the ligand mode. There is a very wide range of ν(Mn–X) frequencies reported in the literature for octahedral manganese(II) complexes, but the work of Goldstein and Unsworth [23] has shown that terminal ν(Mn–Cl) modes in six-coordinate complexes can occur in the 180–210 cm^{-1} range, with the corresponding ν(Mn–Br) bands at 140–175 cm^{-1}. Both complexes had a band at *ca.* 350 cm^{-1} assignable as ν($Mn-OH_2$) so it appears that the compounds complete their octahedral coordination sphere with water molecules rather than with the O6 atoms of the purine.

Copper Complexes

The electronic spectrum of $Cu(9Mehyp)_2Cl_2$ exhibits a well-defined doublet band at 18,350 and 15,750 cm^{-1}, indicative of a somewhat elongated rhombic–octahedral geometry [24] as in $Cu(cytosine)_2Cl_2$ [25] and $Cu(NH_3)_2(CH_3CO_2)_2$ [26].

In the spectrum of $Cu(9Mehyp)_2Br_2$ only the lower energy component (15,600 cm^{-1}) was resolved from a strong absorption edge of an intense U.V. band. However, the X-band e.p.r. spectrum of the bromide (Fig. 3) is in accord with a distorted structure of this type, in which the weaker axial field component is provided by O6. Moreover the ν(Cu–X) bands (Table III) are as expected for terminal Cu–X bonds [the band at 250 cm^{-1}, assigned as ν(Cu–Br), is rather weaker than usually observed, so this assignment is only tentative].

With copper(II) nitrate both dark blue $Cu(9Mehyp)_4(NO_3)_2 \cdot H_2O$ and pale blue $Cu(9Mehyp)_2(NO_3)_2 \cdot 3H_2O$ were obtained. From their i.r. spectra, the former contains ionic nitrate groups whereas in the 2:1 complexes the nitrates are coordinated. The electronic reflectance spectra of $Cu(9Mehyp)_4(NO_3)_2 \cdot H_2O$ and dark blue $Cu(9Mehyp)_4(ClO_4)_2$ consist of a single band at 16,350 cm^{-1} and 16,150 cm^{-1} respectively. These energies are somewhat lower than those observed [5] for the related complex $Cu(pyrimidine\text{-}2\text{-}one)_4(ClO_4)_2 \cdot EtOH$ (18,700 cm^{-1}) in which the exocyclic oxygen atoms of the pyrimidine ligands lie in pairs above and below the CuN_4 plane

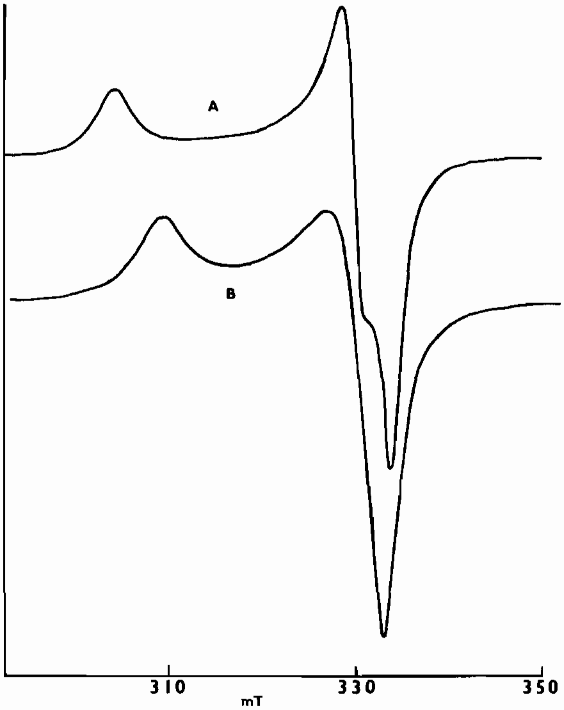

Fig. 3. X-band (9.525 GHz) epr spectra of: A, $Cu(9Mehyp)_2Cl_2$; B, $Cu(9Mehyp)_2Br_2$.

[27]. The bathochromic shift observed for the 9Mehyp complexes presumably reflects the changes in the axial ligand field produced by the O6 atoms in the purines as compared with the differently disposed O2 atoms of the pyrimidine ligand.

From its spectral properties (Tables II and III, and nitrate bands at 822, 1040, 1310, and 1410 cm^{-1}) we conclude that the 2:1 copper nitrate complex is *trans*-octahedral $[Cu(9Mehyp)_2(ONO_2)_2(OH_2)_2]\cdot H_2O$ like the corresponding complex formed by 9-methylguanine [28].

Zinc, Cadmium and Mercury Complexes

Use of 1:1 mixtures of acetone and water as solvent gave the anhydrous complexes $M(9Mehyp)X_2$ (M = Cd or Hg; X = Cl or Br), but in the case of zinc similar reactions using 1:1 ethanol/water afforded the monohydrates $Zn(9Mehyp)X_2\cdot H_2O$ (X = Cl or Br).

The metal–halogen stretching bands in the spectra of the zinc complexes (Table III) are in the region for those of tetrahedral ZnL_2X_2 compounds [29] and the presence of a $\nu(Zn-OH_2)$ band at 370 cm^{-1} suggests that the water molecule is coordinated to the metal ion. These compounds, therefore, appear to be quite analogous to $Zn(9\text{-ethylguanine})Cl_2\cdot H_2O$ in which the zinc ion is known [1] to be tetrahedrally coordinated to two chlorine atoms, one water molecule and N7 of the purine.

On heating the monohydrates in a thermogravimetric balance there was a weight loss equivalent to one molecule of water between 120 and 190 °C (Table IV), but the resultant compounds started to decompose at the temperatures required for complete removal of the water, and reproducible analyses could not be obtained for the anhydrous products.

We have already reported and discussed [16] the molecular structure of $Hg(9Mehyp)Cl_2$ obtained as part of this work, together with the relevant details from its vibrational spectra. The vibrational spectra of the corresponding bromide (Table III) are quite analogous to those of the chloride, allowing for the expected shifts in $\nu(Hg-X)$, so this compound very probably has the same type of structure in which planar $HgN(7)Br_2$ units are connected by two long Hg–Br axial intermolecular bonds.

The structures of the cadmium complexes are uncertain. They have quite different X-ray powder patterns from those of their mercury(II) analogues, and their i.r. spectra have no bands above 200 cm^{-1} that can be assigned to $\nu(Cd-X)$ modes.

In conclusion, it appears that, under the experimental conditions we have employed, the O6 atom of 9-methylhypoxanthine shows little tendency to coordinate to the metal ions in question. Sletten has drawn attention [30] to the fact that the formation of a chelate ring by coordination of both O6 and N7 would impose a significant contraction of the angle C5–N7–M from the normal value for simple unidentate coordination by N7. The spatial dispositions of the lone pair electrons on O6 are evidently insufficiently flexible to provide a strong enough M–O interaction to offset the angular distortion at N7.

Experimental

Preparations

9-methylhypoxanthine was prepared from 9-methyladenine by the method of Elion [31]. Except where stated otherwise the complexes were prepared by the following general method. The purine ligand (0.5 mmol) and the appropriate metal salt (0.5 mmol) were refluxed in methanol for *ca.* 24 hr and then allowed to stand at room temperature for 1 or 2 days. In some cases the desired product crystallized directly from these solutions, but in others concentration of solvent, after filtration to remove any unreacted 9Mehyp, was necessary before the solid complex separated. The precipitates thus obtained were air-dried.

Analyses (Table I) were by the Microanalytical Laboratory, Imperial College.

$M(9Mehyp)_2X_2$ (M = Co or Ni; X = Cl or Br)

These were obtained by heating the appropriate tetrahydrates in vacuo at 180 °C.

$Cu(9Mehyp)_4(NO_3)_2 \cdot H_2O$ and $Cu(9Mehyp)_2(NO_3)_2 \cdot 3H_2O$

Use of the general method outlined above gave an initial crop of deep blue crystals of the 4:1 complex. Storage of the mother liquor after filtration resulted in the formation of pale blue crystals of the 2:1 complex.

$M(9Mehyp)X_2$ (M = Cd or Hg; X = Cl or Br)

The solvent employed was a 1:1 mixture of acetone and water.

$Zn(9Mehyp)X_2 \cdot H_2O$ (X = Cl or Br)

A solution of the appropriate zinc halide (2 mmol) and 9Mehyp (0.5 mmol) in water (10 cm^3) was heated for 5 minutes and then stored at room temperature for 1 day. Addition of ethanol (10 cm^3) gave a white precipitate of the desired complex.

$Mn(9Mehyp)_2X_2 \cdot 2H_2O$ (X = Cl or Br)

These were prepared as for the zinc complexes except that a 1:1 ratio of 9-Mehyp to metal salt was used and the solutions were concentrated to small volume. The solid products were well washed with ethanol.

Physical Measurements

Thermogravimetric studies were carried out on a Stanton Redcroft TG-750 thermobalance. The other physical measurements were carried out as described previously [10].

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