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Complexes of 9-Methyladenine with Some Divalent Metal Halides

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The preparations and spectral properties are reported of a range of complexes of 9-methyladenine (= 9-Mead) with halides of the series Mn–Zn, and also Cd and Hg(II). In most cases complexes of stoichiometry $M(9\text{-}Mead)X_2$ *are formed which have tetrahedral coordination geometry when M = Co, Zn, or Hg, but polymeric octahedral geometry in the case of the cadmium compounds and the chlorides of manganese(II) and iron(II). Distorted octahedral coordination is also present in the compounds* $Ni(9\text{-}Mead)_2Cl_2$, $Cu(9\text{-}Mead)_2X_2$ *(X = Cl or Br) and* $[M(9\text{-}Mead)_2(NO_3)_2(OH_2)_2]$ *(M = Co or Cu).*

Introduction

The interaction of heavy metal ions with nucleic acids and their components is a subject of current interest [1, 2]. During the course of our work on the coordination behaviour of nucleotides [3] we have found it helpful to carry out parallel studies with some simpler pyrimidine and purine derivatives related to those found in nucleic acids. We report here some results for 9-methyladenine (= 9-Mead), in which the methyl substituent occupies the same position as the ribose or deoxyribose moiety in nucleic acids.

A preliminary account of part of this work – the synthesis of $Co(9\text{-}Mead)Cl_2$ and its polymeric structure involving metal coordination to N1 and N7, has been given previously [4]. Since then the structures of several copper(II), zinc, platinum(II), and silver(I) complexes of 9-Mead have been reported [1, 5, 6]. In the copper compounds and in $[Pt(9\text{-}MeadH)Cl_3]$ coordination is at N7, but in $(9\text{-}MeadH)[Zn(9\text{-}Mead)Cl_3]\cdot H_2O$ zinc binds to N1. The remaining complexes ($Zn(9\text{-}Mead)Cl_2$, $[Ag(9\text{-}Mead)]NO_3\cdot H_2O$ and $Pt_2(9\text{-}Mead)(i\text{-}Pr_2SO)_2Cl_4$) contain 9-methyladenine bridging metal atoms via N1 and N7.

Experimental

Preparations

Except where otherwise stated the complexes were prepared from equimolar proportions of 9-Mead and the appropriate metal salt in hot ethanol. The complex usually precipitated immediately or within a short time after mixing the reactants. The products were washed with ethanol and dried *in vacuo*. Analyses (Table I) were by the Microanalytical Laboratory, Imperial College.

$MnLCl_2\cdot 2H_2O$

Equimolar amounts of the reactants were mixed in hot water. The solution was allowed to evaporate to dryness at room temperature, and the solid residue was boiled with ethanol to remove any unreacted 9-Mead or manganese(II) chloride. The complex was filtered, washed thoroughly with ethanol and dried over silica gel.

$FeLCl_2$

A nitrogen atmosphere and de-oxygenated solvents (ethanol/2,2-dimethoxypropane) were used in the preparation of this compound. The complex was dried *in vacuo* at 120 °C.

Nickel complexes

For both nickel chloride and bromide the initial precipitates were yellow, but they were hygroscopic and on standing as suspensions in ethanol, or on filtration and exposure to the air, formed blue-green hexahydrates. The anhydrous compounds were obtained by heating the hydrates at 140 °C.

CuL_2X_2 *(X = Cl or Br)*

9-Mead and the appropriate copper(II) halide were mixed in 2:1 molar ratio in hot ethanol and the solution was boiled for *ca.* 10 min. On cooling the initial precipitate was the $CuLX_2$ complex. This was filtered off and the filtrate was concentrated until the required CuL_2X_2 compound began to form. When precipitation was complete the product was collected, washed thoroughly with hot ethanol and dried *in vacuo* at 90 °C.

$ML_2(NO_3)_2\cdot 2H_2O$ *(M = Co and Cu)*

The hydrated metal nitrate in a small volume of ethanol was added dropwise, with stirring, to a concentrated ethanolic solution of 9-Mead (equimolar quantities). The solution was concentrated until a solid complex formed on cooling.

TABLE I. Analytical Data and Room Temperature Magnetic Moments of Some Complexes of 9-Methyladenine (= L).

		Analytical Results						Magnetic Moment[a]
		Found %			Calculated %			
		C	H	N	C	H	N	
$MnLCl_2$	White	26.40	2.78	25.20	26.20	2.56	25.47	5.93
$MnLCl_2 \cdot 2H_2O$	Pale Pink	23.17	3.56	22.51	23.08	3.03	22.06	–
$FeLCl_2$	Pale Yellow	26.15	2.58	25.09	26.11	2.55	25.38	5.55
$CoLCl_2$	Blue	25.97	2.71	25.28	25.83	2.53	25.10	4.52
$CoLBr_2$	Blue	19.94	1.93	18.89	19.58	1.91	19.03	4.55
$NiL_2Cl_2 \cdot 6H_2O$	Blue Green	26.98	4.94	26.20	26.88	4.88	26.13	–
$NiL_2Br_2 \cdot 6H_2O$	Blue Green	23.19	4.17	22.32	23.06	4.16	22.43	–
NiL_2Cl_2	Yellow	33.49	3.33	32.44	33.68	3.29	32.73	–
NiL_2Br_2	Dark Green	27.73	2.72	26.72	27.88	2.73	27.10	–
CuL_2Cl_2	Yellow Green	33.16	3.11	32.16	33.30	3.26	32.37	–
CuL_2Br_2	Green	27.57	2.66	26.43	27.62	2.70	26.85	–
$CuLCl_2$	Dark Green	25.39	2.75	24.72	25.41	2.49	24.70	1.95
$CuLBr_2$	Brown	19.48	2.26	18.78	19.35	1.89	18.80	1.85
$ZnLCl_2$	White	25.56	2.53	24.09	25.24	2.47	24.53	–
$ZnLBr_2$	White	19.40	2.00	18.62	19.25	1.88	18.71	–
$CdLCl_2$	White	21.64	2.13	21.14	21.67	2.12	21.06	–
$CdLBr_2$	White	17.20	1.74	16.70	17.01	1.66	16.60	–
$HgLCl_2$	White	17.32	1.85	16.84	17.14	1.70	16.70	–
$HgLBr_2$	White	14.37	1.41	13.93	14.14	1.37	13.70	–
$CoL_2(NO_3)_2 \cdot 2H_2O$	Pink	28.65	3.55	32.54	27.86	3.50	32.48	4.77
$CuL_2(NO_3)_2 \cdot 2H_2O$	Green	27.79	3.59	32.49	27.62	3.48	32.21	1.90

[a] At 297 °K.

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

$CoLCl_2$	16,100[a]	8,900	7,020	6,060
$CoLBr_2$	15,650[a]	8,400	6,750	6,000
$FeLCl_2$	8,900	6,100		
$NiL_2Cl_2 \cdot 6H_2O$	~25,300br	15,750	10,200	
$NiL_2Br_2 \cdot 6H_2O$	~25,300br	15,750	10,200	
NiL_2Cl_2	22,700br	12,900br	7,700	~6,500sh
NiL_2Br_2	16,100	9,520	~6,900br	
$CuLCl_2$	13,300			
$CuLBr_2$	12,200			
CuL_2Cl_2	14,300			
CuL_2Br_2	~17,600sh[b]	14,900sh[b]		
$CoL_2(NO_3)_2(H_2O)_2$	~21,300sh	19,300	8,200br	

[a] Centre of gravity of strong multicomponent peak (weak spin-forbidden bands at higher energy omitted). [b] On edge of intense 23,300 cm^{-1} charge transfer band.

Physical Measurements

Raman spectra were taken with a Laser Raman Cary 81 instrument using a krypton plasma tube. The other physical measurements were carried out as described previously [7].

Results and Discussion

The complexes we have isolated are listed in Table I. Most of the metal halides studied formed anhydrous 1:1 complexes in ethanol irrespective of

TABLE III. Infrared (IR) (400–180 cm^{-1}) and Raman (R) (450–100 cm^{-1}) Spectra of some 9-Methyladenine (= L) Complexes.

		ν(M–X)		ν(M–N)[a]
$CoLCl_2$	IR	343	312	221
	R	b	309	218
$CoLBr_2$	IR	272[c]	248	219
	R	272w	245	222
$ZnLCl_2$	IR	327	300	201
	R	328vw	298	200w
$ZnLBr_2$	IR	250	225	198
	R	247w	222	195
$HgLCl_2$	IR	305	280	b
	R	305w	280	b
$HgLBr_2$	IR	218	185	b
	R	217	186	b
$MnLCl_2$	IR	238		b
$FeLCl_2$	IR	246		b
$CdLCl_2$	IR	208		190[d]
	R	216		b
$CdLBr_2$	IR	b		192
	R	137		b
NiL_2Br_2	IR	262	243	215
CuL_2Cl_2	IR	320	217	b
CuL_2Br_2	IR	240		b
$CuLCl_2$	IR	310		200
$CuLBr_2$	IR	250	238	b
$NiL_2Cl_2 \cdot 6H_2O$	IR	e		218
$NiL_2Br_2 \cdot 6H_2O$	IR	f		217

[a] See text for designation of ν(M–N). [b] Not observed. [c] Overlapping ligand band. [d] Overlapping ν(Cd–Cl). [e] ν(Ni–OH$_2$) at 375 cm^{-1}. [f] ν(Ni–OH$_2$) at 372 cm^{-1}.

whether the metal salt used was hydrated or not. Both 2:1 and 1:1 complexes were obtained with the copper(II) halides, but, under the conditions employed here, nickel chloride and bromide formed only 2:1 compounds.

X-ray powder photographs show that the compounds M(9-Mead)Br$_2$ (M = Co and Zn) are isomorphous with their corresponding chlorides and, therefore, have structures of the type reported previously [4, 8] for these latter compounds. The electronic spectra and magnetic moments (Tables I and II) of the cobalt complexes are as expected for a distorted tetrahedral coordination geometry.

The metal–halogen stretching bands are readily assigned in the low frequency vibrational spectra of the cobalt and zinc complexes (Table III). The asymmetric ν(M–X) bands were very weak in the Raman spectra and that for CoLCl$_2$ was not resolved from the spectral base line noise.

As the metal ions in these compounds are each bound to two different purine nitrogen atoms (N1 and N7) it was of interest to identify any vibrational bands with significant ν(M–N) character (hereafter referred to simply as 'ν(M–N)'). Each of the complexes had a strong i.r. band, and a corresponding weak Raman band, in the region 272–276 cm^{-1} (overlapping ν_{as}(Co–Br) in the case of the cobalt bromide complex) which was absent from the spectra of 9-methyladenine. However its insensitivity to the replacement of Co by Zn suggests that it is probably an activated ligand mode and not a 'ν(M–N)' band. An alternative assignment for 'ν(M–N)' is the band at *ca.* 220 cm^{-1} for the cobalt complexes, which shifts to 195–200 cm^{-1} in the zinc analogues (Table III). Any other 'ν(M–N)' band is either of very low intensity or below 180 cm^{-1}. However, it may be noted that the two ν(M–N) bands expected for a C_{2v} ML_2X_2 species are by no means always observed [9].

The X-ray powder patterns of M(9-Mead)Cl$_2$ (M = Mn and Fe) differ from those of the analogous zinc and cobalt complexes, and also from each other. The electronic spectrum of the iron complex consists of a pair of low intensity bands at energies (8900 and 6100 cm^{-1}) indicative [10] of a polymeric halide-bridged six coordinate structure. Further support for this is provided by the Mössbauer spectrum, which, at room temperature, consists of a quadrupole split doublet (Δ = 1.53 mm s^{-1}) with an isomer shift, δ, of 1.12 mm s^{-1} relative to iron metal. This isomer shift value is within the usual range for six-coordinate, high spin FeL$_2$X$_2$ complexes containing halide bridges [11] and well above the range expected (*ca.* 0.78–0.87 mm s^{-1}) for tetrahedral FeL$_2$X$_2$ compounds involving N-donor ligands [12].

The e.p.r. spectra of the manganese complexes were obtained, but in each case there was simply a strong, broad band in the g_{eff} = 2 region with no evidence of fine structure. These results merely indicate strong dipolar coupling between the paramagnetic ions, as expected for a polymeric structure, but provide no information about the coordination geometry. However the low frequency i.r. spectrum of Mn(9-Mead)Cl$_2$ had a ν(Mn–Cl) band at 238 cm^{-1}, in the region expected [9] for a bridging halide, so this complex resembles the iron(II) analogue in having a six-coordinate polymeric structure.

The mercury compounds Hg(9-Mead)X$_2$ (X = Cl or Br) form an isomorphous pair. Their powder patterns are similar to those of the zinc and cobalt complexes but not closely enough reliably to establish isomorphism. However their low frequency vibrational spectra clearly point to their having a similar tetrahedral coordination geometry. There are two strong ν(Hg–X) i.r. bands at 305 and 280 cm^{-1} (chloride) and 218 and 185 cm^{-1} (bromide) with a corresponding pair of Raman bands in each case (in the Raman spectra the higher energy band, B_1 ν_{as}(Hg–X), is weak and the lower energy band, A_1 ν_s(Hg–X), is intense, as expected [13]).

The cadmium compounds Cd(9-Mead)X_2 (X = Cl or Br) have quite different powder patterns from those of their mercury analogues and their low frequency vibrational spectra (Table III) suggest that they contain halide bridges [14].

The nickel halides formed 2:1 complexes even when equimolar proportions of the nickel salt and 9-Mead were used. These nickel compounds were hygroscopic and various hydrates could be isolated depending upon the extent of exposure to the atmosphere. Because of the variability in the extent of hydration we report here only the limiting hexahydrates and the anhydrous compounds obtained by heating these.

The electronic spectra of the hexahydrates (Table II) are typical of octahedrally coordinated nickel(II) and have band energies which remain unchanged on replacing Cl by Br. Their far i.r. spectra showed no halogen dependent bands above 180 cm^{-1}, but in each case there was a strong band assignable as ν(Ni–OH_2) [at 375 cm^{-1} when X = Cl, and at 372 cm^{-1} when X = Br]. We conclude, therefore, that the hexahydrates contain non-coordinated halide ions and are $[Ni(9\text{-}Mead)_2(OH_2)_4]X_2 \cdot 2H_2O$.

On heating in a thermogravimetric balance both complexes start to lose water at 90–100 °C and conversion to the anhydrous compounds is complete for the chloride by 140 °C (wt. loss found 20.29%, calcd. 20.15%) or, for the bromide, by 150 °C (wt. loss found 17.26%, calcd. 17.29%).

The electronic spectrum of the yellow, anhydrous nickel chloride complex, $Ni(9\text{-}Mead)_2Cl_2$, shows that it is six coordinate with bridging chlorides, whereas that of the dark green bromide, $Ni(9\text{-}Mead)_2Br_2$ is typical of an essentially tetrahedral geometry.

Assignment of the coordination geometries of the compounds $Cu(9\text{-}Mead)_2X_2$ (X = Cl or Br) is relatively straightforward. Their electronic spectra are very similar to those of $Cupy_2X_2$ in which planar CuN_2X_2 units are interlinked by longer Cu–X bonds to give a distorted octahedral geometry [15]. We list in Table III the halogen-dependent i.r. bands observed above 200 cm^{-1} for all the copper(II) halide complexes. Although the diagnostic value of such information is limited because of appreciable overlap between frequency ranges given in the literature for the various coordination geometries, we note that the results for the $Cu(9\text{-}Mead)_2X_2$ complexes are at least in accord with the geometries indicated by their electronic spectra [16, 17].

The dark brown 1:1 copper bromide complex has a very intense electronic spectral band at significantly lower energy (12,200 cm^{-1}) than in its 2:1 analogue. These observations suggest the presence of a very distorted tetrahedral geometry about the copper ion, as in the adenine complex $[Cu(adenineH)Br_2]Br_2$ [18], but involving purine bridges, probably via N1 and N7.

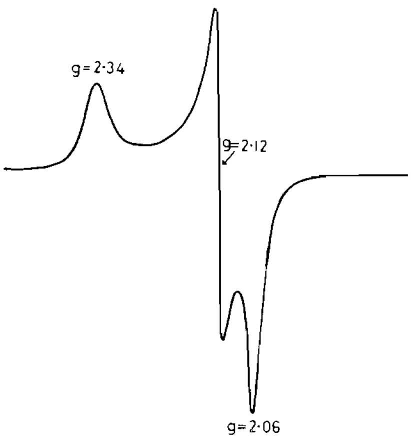

Figure 1. X-Band e.p.r. spectrum of a polycrystalline sample of $[Cu(9\text{-}Mead)_2(NO_3)_2(OH_2)_2]$.

In the case of the corresponding chloride, Cu(9-Mead)Cl_2, the spectral evidence is less clear-cut; the electronic band was at higher energy (13,300 cm^{-1}) than in the bromide and its intensity was much lower – similar to those found for the halide-bridged 2:1 complexes. Unfortunately the X-band e.p.r. spectrum was of no help in assigning a structure as the dipolar interactions between the copper atoms in this compound, indeed for all four copper(II) halide complexes, were strong enough to yield only a single, broad band at $g \approx 2.1$.

On reacting equimolar amounts of 9-Mead with hydrated cobalt(II) nitrate or copper(II) nitrate in ethanol, 2:1 complexes of stoichiometry $M(9\text{-}Mead)_2(NO_3)_2 \cdot 2H_2O$ (M = Co or Cu) were obtained. Their i.r. spectra show the presence of coordinated water (ν(Co–OH_2) 369 cm^{-1}, ν(Cu–OH_2) 378 cm^{-1}) and coordinated nitrate (Co, 818, 1025, 1290, and 1440 cm^{-1}; Cu, 822, 1043, 1310, and 1380 cm^{-1}). The purines are therefore bonded via only one ring nitrogen. The electronic spectrum of the cobalt nitrate complex is typical of slightly distorted octahedral geometry. However, the X-band e.p.r. spectrum of the copper analogue (Figure 1) clearly shows the rhombic nature of the ligand field expected for the proposed coordination geometry.

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