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Metal–Oxygen Binding by Uracils: Metal Complexes of 1,3-Dimethyluracil

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In spite of the recent surge of interest in the interaction of transition metal ions with components of nucleic acids, there have been relatively few reports of complexes of uracils [1]. Moreover, the only reported structural determination of a metal ion–uracil complex showed a very long, and presumably weak, metal–oxygen bond [2]. We recently showed [3] that under fairly non-polar conditions uracil forms a variety of complexes with first-row transition metals, but the ligand fields generated are weak, and there are only small changes in the infrared spectrum of the ligand.

The complex of 1,3-dimethyluracil (1,3-DMU) with copper(II) chloride, however, shows a short (1.985 Å) copper–oxygen bond, indicating strong interaction [4]. We report here a study of some other complexes of 1,3-dimethyluracil, which shows that this ligand is a good model for uracil itself in its metal complexes.

Stereochemistry of the Complexes

The compounds we obtained are reported in Table I. The chloro- and bromo- complexes all appear to have polymeric octahedral structures based on bridging halide ions, with the exception of the blue form of $Co(1,3\text{-}DMU)_2Br_2$. This is shown by the electronic spectra (Table II), by the fact that the manganese complexes give e.p.r. spectra with broad, unstructured signals at $g_{eff} = 2$, and by the isomorphism of $Mn(1,3\text{-}DMU)_2Br_2$ with $Fe(1,3\text{-}DMU)_2Br_2$. The nickel and cobalt bromides (lilac form) also give very similar X-ray powder patterns to those of the manganese and iron bromides and there is likewise strong similarity in the patterns of the four corresponding chlorides.

The nickel iodide complex, and the blue form of $Co(1,3\text{-}DMU)_2Br_2$, have electronic spectra indicating tetrahedral coordination.

Infrared Spectra

The bands arising from the stretching vibrations of the 2- and 4-keto groups of 1,3-dimethyluracil have been assigned by Angell [5] and by Lord and Thomas [6]. The band above 1700 cm^{-1} is attributed to $\nu(C_2{=}O)$ while the $\nu(C_4{=}O) + \nu(C{=}C)$ mode occurs as a broad absorption at 1660–1670 cm^{-1}. No assignments are available for lower energy bands.

On complex formation, three strong, sharp bands normally appear in the $\nu(C{=}O)$ region (Table III), the highest being shifted slightly to higher energy compared with $\nu(C_2{=}O)$ for the ligand, and with increased intensity. The band near 1650 cm^{-1} is probably $\nu(C_4{=}O)$ shifted to lower energy, and the lowest component is due to a mode which is normally inactive in the infrared. These changes are exactly parallel to those observed for uracil [3].

TABLE I. Analytical Results for Complexes of 1,3-Dimethyluracil.

Compound	Colour	% Found			% Calculated		
		C	H	N	C	H	N
MnL_2Cl_2	Pale Pink	35.84	3.80	14.27	35.49	3.97	13.79
MnL_2Br_2	Pale Pink	28.45	3.00	11.80	29.11	3.26	11.32
$MnL_4I_2\cdot 2H_2O$	Pale Pink	31.93	3.53	12.86	31.84	4.01	12.38
FeL_2Cl_2	Cream	35.30	4.00	13.96	35.41	3.96	13.76
FeL_2Br_2	Yellow	29.01	3.20	11.66	29.06	3.25	11.30
$CoL_2Cl_2\cdot 0.5H_2O$	Pale Lilac	34.27	3.84	13.15	34.39	4.09	13.37
CoL_2Br_2	Pale Lilac	29.30	3.33	11.28	28.88	3.23	11.23
CoL_2Br_2	Blue	28.23	3.59	10.93	28.88	3.23	11.23
NiL_2Cl_2	Yellow	36.05	4.16	13.60	35.16	3.93	13.67
$NiL_2Br_2\cdot 2.5H_2O$	Orange	26.56	3.40	10.12	26.50	3.89	10.30
$NiL_2I_2\cdot 2.5H_2O$	Red	22.32	2.53	8.80	22.60	3.32	8.78
CuL_2Cl_2	Pale Green	33.79	3.56	13.80	34.75	3.89	13.51
$CdLCl_2\cdot 2H_2O$	White	20.02	2.08	8.31	20.05	3.36	7.79
$CdLBr_2$	White	17.03	1.94	6.63	17.48	1.95	6.79
CdL_2I_2	White	21.90	2.28	8.84	22.29	2.49	8.67

TABLE II. Diffuse Reflectance Spectra of the 1,3-Dimethyluracil Complexes.

Compound	Band Maxima (cm^{-1})					
FeL_2Cl_2	*ca.* 5750w[a],	9100w				
FeL_2Br_2	*ca.* 5560w[a],	9170mw				
$CoL_2Cl_2 \cdot 0.5H_2O$	*ca.* 7270w[a],	12500sh,	16000m,	17950s,	19120s,	20000sh
CoL_2Br_2 (lilac)	*ca.* 7020w[a],	11630sh,	15150m,	17700s,	18420s,	19490sh
CoL_2Br_2 (blue)	6020sh,	6540vs,	14490vs,	15270sh,	18420sh,	21280sh
NiL_2Cl_2	6900mbr,	11560m,	13330sh,	20750sh,	22220s	
$NiL_2Br_2 \cdot 2.5H_2O$	6330mbr,	11170m,	12660sh,	17860sh,	21370s	
$NiL_2I_2 \cdot 2.5H_2O$	*ca.* 4540mbr[a],	7870s,	11760sh,	12270vs,	12820sh	
CuL_2Cl_2	12120s					

[a] Low energy band partially obscured by ligand vibrational bands.

TABLE III. Shifts of Infrared Bands (cm^{-1}) in the 1,3-Dimethyluracil Complexes.

Compound	ν(C=O) + ν(C=O)					δC=O
1,3-dimethyluracil	1708m,	1655vsbr				679w
MnL_2Cl_2	1711s,	1647vs,	1611s			688vw
MnL_2Br_2	1710s,	1645vs,	1606s			687vw
$MnL_4I_2 \cdot 2H_2O$	1712s,	1646vs,	1611s			687vw
FeL_2Cl_2	1718s,	1647vs,	1610s			689vw
FeL_2Br_2	1715s,	1644vs,	1604s			689vw
$CoL_2Cl_2 \cdot 0.5H_2O$	1714s,	1648vs,	1610s			689vw
CoL_2Br_2 (lilac)	1726s,	1649vs,	1609s			690vw
CoL_2Br_2 (blue)	1714sh,	1687s,	1638vs,	1585s		696vw
NiL_2Cl_2	1711ms,	1649vsbr,	1609s			688vw
$NiL_2Br_2 \cdot 2.5H_2O$	1714s,	1648vs,	1608vs			688vw
$NiL_2I_2 \cdot 2.5H_2O$	1707sh,	1679s,	1631vs,	1581vs		696vw
CuL_2Cl_2	1717vs,	1647vs,	1604vs			690vw
$CdLCl_2 \cdot 2H_2O$	1690s,	1647vs,	1609s			687vw
$CdLBr_2$	1689vs,	1650vs,	1630sh,	1610s		687vw
CdL_2I_2	1705s,	1690ms,	1650vs,	1630sh,	1610s	687vw

Several changes also occur in the 600–900 cm^{-1} region. A strong band at 815 cm^{-1} in the free ligand, which may be due [5] to an out-of-plane C–H deformation, appears to be split into two components of equal intensity. Also, a weak absorption at 681 cm^{-1}, which we tentatively assign to a carbonyl deformation mode, is reduced in intensity, and shifted to higher energy, in the complexes.

All these changes are consistent with donation through C_4=O, as found [4] for the copper complex. Indeed, the strong similarity between the infrared spectra of all the complexes suggests that very similar bonding is present in all of them.

Discussion

The complexes of 1,3-dimethyluracil show a strong resemblance to those of uracil itself, in their stereochemistry, in the weakness of the ligand field, and in the changes of infrared spectrum on complex formation. It seems likely, therefore, that the strength of metal–oxygen interaction shown for bis(1,3-dimethyluracil)dichlorocopper(II) is present in other transition-metal uracil complexes. Although the bonds are labile in highly polar solvents, it seems that under conditions of low polarity, binding to the exocyclic oxygen atoms of uracils may well be important in the interaction of heavy metals with nucleic acids. Metal binding of this type has been suggested [7] as a possible factor in nucleic acid recognition processes.

Experimental

1,3-Dimethyluracil was prepared by the method of Davidson and Baudisch [8]. The complexes were made by addition of a warm, concentrated solution of the metal salt in ethanol, to a hot solution of the ligand in ethyl acetate. After heating and stirring for a few minutes, the complexes were precipitated, or could be precipitated by evaporation to low bulk and addition of ether. For the cadmium complexes, one drop of the appropriate concentrated acid was added to the reaction mixture to prevent hydrolysis.

The blue form of $Co(1,3\text{-DMU})_2Br_2$ was prepared by exposing the pink form to the atmosphere overnight, and then drying it at 60 °C.

Physical measurements were made as described previously [3].

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