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Interaction of Divalent Metal Ions with Uracil.
I. Oxygen Coordinating Uracil Complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

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An increasing interest in divalent metal complexes with the constituents of nucleic acids has led many workers to study these complexes [1, 2]. The biological relevance of metal binding to RNA constituents indicates the importance of these complexes in biological systems. Very few studies [3] have been made on the divalent metal complexes of uracil which is present in RNA. Uracil exists in the dilactam form both in the solid state and in neutral aqueous solution which permits nitrogen atoms to coordinate to the metal ions only under basic conditions. Hence uracil in its anionic form can coordinate to the metal ion through the nitrogen atom and in its neutral form through the oxygen. Hence by changing the pH of the reaction medium, a variety of complexes of uracil having different donor atoms is expected. Here we report the isolation and characterisation of some new complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with uracil coordinating through its oxygen.

Experimental

Uracil used was from BDH, England. All the other chemicals used were of analytical grade. The electronic spectra were recorded in the solid state by a Carl-Zeiss DMR-21 spectrophotometer and the infrared spectra were recorded in KBr pellets by means of a Perkin-Elmer 257 i.r. spectrophotometer. Thermogravimetric analyses were carried out with a Derivatograph (System: F. Paulik, J. Paulik, L. Erdey, MOM, Budapest). About 100 mg of the finely powdered substances were heated at a rate of 2° per minute. All the complexes were prepared as follows. A calculated amount of uracil was first dissolved in the minimum quantity of boiling methanol. Then to this solution the respective metal salt solution in methanol was added, the ratio of methanol: uracil being 1:2. The solutions were refluxed for eight hours. The volume of the solution was reduced to one fourth of its original volume by evaporation. The complexes were precipitated on cooling and scratching. Metals in the complexes were estimated by standard methods after decomposing the uracil at high temperature (800 °C) and then digesting with HNO_3 and finally with H_2SO_4.

TABLE I. Analytical Data and Colour of the Complexes.[a]

Compound	Colour	Found				Calcd.			
		%M	%N	%C	%H	%M	%N	%C	%H
$[MnL_4(H_2O)_2]Cl_2$	Pale pink	9.01	18.68	31.39	3.34	9.00	18.36	31.47	3.28
$[FeL_4(H_2O)_2]SO_4$	Yellowish brown	8.92	17.70	30.86	2.97	8.80	17.61	30.20	3.14
$[CoL_4(H_2O)_2]Cl_2$	Pink	9.84	18.56	31.38	3.12	9.61	18.23	31.30	3.26
$[CoL_4(H_2O)_2](NO_3)_2$	Pink	8.88	17.93	28.91	2.88	8.85	18.00	28.78	3.00
$[NiL_4(H_2O)_2]Cl_2$	Pale Green	9.73	18.38	31.42	3.18	9.61	18.23	31.30	3.26
$[NiL_4(H_2O)_2](NO_3)_2$	Pale Green	8.92	18.18	28.87	2.89	8.85	18.00	28.78	3.00
$[CuL_4(H_2O)_2]SO_4$	Greenish blue	9.92	17.61	30.01	2.98	9.87	17.40	29.84	3.11
$[CuL_4(H_2O)_2]Cl_2$	Light blue	10.34	18.52	31.23	3.18	10.26	18.10	31.04	3.23
$[MnL_2Cl_2]$	White	15.52	16.21	–	–	15.71	16.00	–	–
$[CoL_2Cl_2]$	Pink	16.42	15.97	–	–	16.67	15.82	–	–
$[NiL_2Cl_2]$	Light Green	16.73	16.04	–	–	16.59	15.83	–	–
$[CuL_2Cl_2]$	Light blue	17.88	15.73	–	–	17.71	15.62	–	–

[a] L = Uracil.

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TABLE II. Tentative Assignments of the Infrared Spectral Bands in KBr.

Complexes	νNH	νCH	νC(2)=O	νC(4)=O + C=C	δNH(1)	δNH(3)
Uracil	3160m	3100s 3080s	1716s	1675s	1508m	1417s
$[MnL_4(H_2O)_2]Cl_2$	3200s 3145m	3115s 3085s	1710s	1640s,br	1515s 1510m	1420s
$[FeL_4(H_2O)_2]Cl_2$	3215s 3155m	3120s 3085s	1715s	1640s,br	1515s 1510m	1420s
$[CoL_4(H_2O)_2]Cl_2$	3210s 3155m	3105s 3080s	1715s	1635s,br	1515s 1510m	1415s
$[CoL_4(H_2O)_2](NO_3)_2$	3210s 3155m	3105s 3080s	1715s	1635s,br	1515s 1510m	1415s
$[NiL_4(H_2O)_2]Cl_2$	3205s 3155m	3100s 3080s	1715s	1640s,br	1515s 1510m	1415s
$[NiL_4(H_2O)_2](NO_3)_2$	3205s 3155m	3100s 3080s	1715s	1640s,br	1515s 1510m	1415s
$[CuL_4(H_2O)_2]SO_4$	3215s 3160m	3100s 3080s	1715s	1640s,br	1515s 1510m	1415s
$[CuL_4(H_2O)_2]Cl_2$	3205s 3145m	3115s 3085s	1715s	1640s,br	1515s 1510m	1415s
$[MnL_2Cl_2]$	3200s 3145m	3115s 3085s	1715s	1635s,br	1515s 1510m	1415s
$[CoL_2Cl_2]$	3210s 3155m	3105s 3080s	1715s	1635s,br	1515s 1510m	1415s
$[NiL_2Cl_2]$	3205s 3155m	3100s 3080s	1715s	1640s,br	1515s 1510m	1415s
$[CuL_2Cl_2]$	3215s 3155m	3100s 3080m	1715s	1640s,br	1515s 1510m	1415s

Carbon, hydrogen and nitrogen were analysed by Dr. Alfred Bernhardt's Mikroanalytisches Laboratorium, West Germany.

Results and Discussion

All the complexes are coloured (Table I), insoluble in non-polar solvents but decomposed by polar ones with the separation of uracil. On the basis of their analytical data (Table I) the complexes have been formulated as $[ML_4(H_2O)_2]X_2$ where M = Mn, Fe, Co, Ni, Cu; X = NO_3, Cl or ½$[SO_4]$, L = uracil.

Electronic Spectra

The iron complex is typically hexacoordinated in showing a doublet weak absorption band at 7950 cm^{-1} and at 10200 cm^{-1} [4]. For the cobalt complexes the weak bands around 7450 cm^{-1}, 14650 cm^{-1} and the strong band at 18700 cm^{-1} may be assigned to the transitions $^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1), $^4A_{2g} \leftarrow {}^4T_{1g}$ (ν_2) and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (ν_3) respectively [4]. The medium broad band around 7725 cm^{-1}, medium band around 12970 cm^{-1} and the strong sharp band around 24025 cm^{-1} of the nickel complexes may be assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1), $^3T_{1g} \leftarrow {}^3A_{2g}$ (ν_2) and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (ν_3) transitions respectively. The medium broad band at 14280 cm^{-1} may be assigned to the spin forbidden transition $^1E_g \leftarrow {}^3A_{2g}$ [4]. The value of Δ in the cobalt complexes is 7200 cm^{-1} and that in the nickel complexes is 7725 cm^{-1}, indicating the octahedral stereochemistry of the complexes. The copper complexes show a strong absorption band at around 12175 cm^{-1} indicating the hexacoordination of the metal ion.

Infrared Spectra

The infrared spectrum of uracil is given in the literature [5]. The tentative assignment of the bands is given in Table II. The complexes exhibit an appreciable lowering in the carbonyl frequency of the 4-keto group with respect to free uracil while the other frequencies remain almost unchanged. Hence, it can be concluded that the coordination of the uracil to the metal atoms takes place through C(4)=O of uracil.

Thermogravimetric Analysis

The TGA curve of the chloride salts of the manganese, cobalt, nickel and copper complexes shows that they start decomposing steadily at 120 °C and gave horizontals extending between 260–300 °C with a loss of around 42.5% in weight which corresponds to the loss of two mol of water and uracil each. The complexes [MnL_2Cl_2], [CoL_2Cl_2], [NiL_2Cl_2] and [CuL_2Cl_2] have actually been isolated (Table I) by heating the salts at 260 °C to constant weight. The electronic spectra of [CoL_2Cl_2], [NiL_2Cl_2] and [CuL_2Cl_2] resemble their parent complexes except in the cobalt complex where all the assigned band positions are shifted to a lower frequency compared with their parent complexes. This suggests that the thermally isolated complexes also possess octahedral stereochemistry. Their infrared spectra also show similar absorptions indicating appreciable change in the C(4)=O + C=C stretching frequency (Table II) with respect to free uracil indicating the coordination of uracil to the metal atom through the oxygen at C(4) of the uracil.

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