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Metal Complexes of 2,4-(1H, 3H)-Pteridinedione

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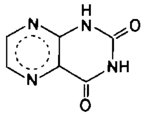
The preparations are described of a series of complexes of 2,4-(1H, 3H)-pteridinedione (DHP) with divalent metal ions. Those obtained from organic solvents contain DHP as a neutral ligand, while those from aqueous media at pH 6.5 contain anionic DHP. Electronic, infrared and e.s.r. spectra of the complexes are described, and the differences between the two groups of complexes are discussed.

Introduction

The study of riboflavin as a ligand for metal ions has been confined, for reasons of solubility, to aqueous solution, even though in enzyme systems the flavin is thought to be in a much less polar environment [1]. We have therefore studied a number of riboflavin analogues with increased solubility in less polar solvents, to determine the effect of solvent polarity on the coordination characteristics of flavin-type ligands. We report here a study of the metal complexes of 2:4-(1H, 3H)-pteridinedione (DHP) (I).



(I)

Results

The complexes formed from aqueous solution at neutral pH contained deprotonated DHP, and had

TABLE I. Analytical Results for the Complexes.

Compound	Colour *	% Found				Calculated			
		C	H	N	Br	C	N	N	Br
$Mn(DHP)_2Cl_2 \cdot 1.5H_2O$	Orange-yellow	30.08	2.46	23.08		29.95	2.28	23.29	
$Mn(DHP)_2Br_2 \cdot H_2O$	Orange-yellow	25.78	1.89	19.69		25.67	1.78	19.96	
$Mn(DHP)_2I_2 \cdot 2H_2O$	Orange	21.04	1.85	16.79		21.40	1.78	16.64	
$Co(DHP)_2Cl_2 \cdot H_2O$	Dark pink	30.98	2.31	23.24		30.26	2.10	23.54	
$Co(DHP)_2Cl_2 \cdot 3H_2O$	Pink	28.20	2.82	22.70		28.13	2.73	21.88	
$Co(DHP)Cl_2 \cdot 2H_2O$	Pink-grey	21.87	1.61	16.44		21.83	2.42	16.98	
$Co(DHP)Br_2$	Grey-green	18.40	1.94	15.15		18.80	1.04	14.62	
$Co_2(DHP)_3I_4 \cdot 3H_2O$	Brown-red	18.43	1.82	13.99		18.43	1.53	14.33	
$Co(DHP)_2 \cdot 2H_2O$	Orange-yellow	34.17	2.55	26.60		34.21	2.37	26.60	
$Ni(DHP)_2Cl_2 \cdot H_2O$	Green-yellow	30.34	2.26	23.31		30.28	2.10	23.55	
$Ni_2(DHP)_3Br_4 \cdot 3H_2O$	Yellow-orange	22.44	2.09	16.89		21.96	1.83	17.08	
$Ni(DHP)_2 \cdot 2H_2O$	Light-green	33.88	3.05	26.40		34.06	2.84	26.49	
$Cu(DHP)_2Cl_2$	Green	31.34	2.02	24.44		31.16	1.73	24.25	
$Cu(DHP)_2Br_2$	Intense green	26.95	1.90	20.64		26.11	1.45	20.31	
$Cu(DHP)_3Br_2 \cdot 4H_2O$	Leaf green	27.14	2.06	21.60		27.42	2.53	21.33	
$Cu_2(DHP)_3Br_4$	Olive green	22.64	1.11	17.45	33.90	23.00	1.27	17.88	34.07
$Cu(DHP)_2 \cdot 2H_2O$	Light brown-green	33.70	2.49	26.18		33.83	2.35	26.32	
$Zn(DHP)_2 \cdot 5H_2O$	Light-yellow	29.23	2.47	22.91		29.91	2.90	23.26	

TABLE II. Reflectance Spectra of the Complexes (cm^{-1}).

Compound	Absorption Maxima (shoulders in parentheses)					
DHP	28200	(26700)	24000	20800	18800		
$Co(DHP)_2Cl_2 \cdot 3H_2O$	27250	26000	19600	17850	14800	12050	6700
$Co(DHP)Cl_2 \cdot 2H_2O$	26700	(24700)	18000	16000	14600	7700	
$Co(DHP)Br_2$	(27400)	26300	(25000)	(19800)	18350	(15300, 14100) 5100	
$Co_2(DHP)_3I_4 \cdot 3H_2O$	(28600)	24400	16650	12500	6300		
$Co(DHP)_2 \cdot 2H_2O$	26600	24300	20400	9100			
$Ni_2(DHP)_3Br_4 \cdot 3H_2O$	26700	23000	12900	7900			
$Ni(DHP)_2 \cdot 2H_2O$	26800	23500	20750	16500	10400	8200	
$Cu(DHP)_2Cl_2$	26500	24000	23000	18000	16300	13900	
$Cu(DHP)_2Br_2$	24700	(21650)	14300				
$Cu(DHP)_3Br_2 \cdot 4H_2O$	(26700)	24700	(22600)	(16300)	13900		
$Cu_2(DHP)_3Br_4$	(28000)	25400	22700	17200	(12900, 10250, 8300)		
$Cu(DHP)_2 \cdot 2H_2O$	(27200)	25600	20800	13900			

the general formula $M(DHP)_2 \cdot nH_2O$. In less polar media, however, the DHP acted as a neutral ligand (Table I).

Manganese Complexes

These were all of stoichiometry $Mn(DHP)_2X_2 \cdot nH_2O$. Intense ligand bands masked the d–d spectra, and structural information was obtained from e.p.r. measurements. They all gave spectra with the main intensity at $g_{eff} = 2$, but with shoulders or weak bands to higher and lower field. These spectra indicate that the complexes do not contain bridging halide ions, and that the distortions from cubic symmetry are rather small. With such small distortions, accurate values of the zero-field splitting parameters could not be obtained. However, it was found that the shape of the spectra could be reproduced [2] with values of D of about 0.03 to 0.04 cm^{-1}, and λ of about 0.3. Such high values of λ are normally indicative of either pseudo-tetrahedral (C_{2v}) symmetry with a ligand field of the MnL_2X_2 type, or of rhombic distortion of an octahedron [3]. Since the cobalt complex of the same stoichiometry has octahedral geometry (see below), a tetrahedron for manganese, which usually prefers 6-coordination, seems unlikely, and chelating DHP is probably present.

If this is the case, the low D values would suggest very weak donation from N(5), making it almost equivalent, in a spectrochemical sense, to a halide ion. This is discussed further below.

The spectrum of the chloro-complex showed an additional broad band at $g_{eff} = 2$, not present in the other spectra. This band is typical of polymeric species, and may arise either from an isomeric form, or from a small amount of impurity not detectable by analysis.

Cobalt Complexes

The complex $Co(DHP)_2Cl_2 \cdot 3H_2O$ has an electronic spectrum typical of an octahedral complex with a very low Δ value (Table II). The $^4T_{1g} \rightarrow {}^4T_{2g}$ transition occurs at 6700 cm^{-1} and the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition, which is clearly split by spin–orbit coupling, at 17850 and 19600 cm^{-1}. A much weaker band at 14,800 cm^{-1} is assignable as the 2-electron $^4T_{1g} \rightarrow {}^4A_{2g}$ transition, which is usually seen only in weak ligand fields. All three bands are in excellent agreement with the calculated values [4] for a Δ value of 7000 cm^{-1}. This is exceptionally low if the ligand field is of the $N_2O_2Cl_2$ type, and confirms the observation for the manganese compounds that if N(5) acts as a donor, then the ligand field produced is unusually weak. There is certainly no indication that the ligand acts as a strong π-acceptor at this position, since this would increase the ligand field.

An alternative possibility is that in this compound the DHP donated through the oxygen only, since the spectral properties are very similar to those of L_2CoBr_2, where L = uracil or thymine, which are thought [5] to be polymeric with ligand fields of the O_2Br_4 type. Since DHP is a substituted uracil, a similar arrangement could be envisaged here, if N_5 takes no part in the bonding.

The compounds $Co(DHP)Cl_2 \cdot 2H_2O$, and $Co(DHP)Br_2$ give near infrared and visible spectra which indicate the presence of $CoCl_4^{2-}$ and $CoBr_4^{2-}$ respectively. Both also show the presence of octahedral species, with bands, in the chloride, at 7700 and 18,000 cm^{-1} which may be assigned as ν_2 and ν_3 respectively. These are consistent with a somewhat stronger ligand field than that in $Co(DHP)_2Cl_2$, and it seems likely that some at least of the water molecules are attached to the metal. However, if some nitrogen coordination is present, this must still be

TABLE III. E.s.r. Spectra of the Copper Complexes.

Compound	$g_{\|}$	$g_{\perp}$
$Cu(DHP)_2Cl_2$	2.24	2.06
$Cu(DHP)_2Br_2$	2.19	2.05
$Cu(DHP)_3Br_2 \cdot 4H_2O$	2.19	2.06
$Cu_2(DHP)_3Br_4$	2.18	2.04
$Cu(DHP)_2 \cdot 2H_2O$	2.31	2.07

TABLE IV. ν(C=O) Absorptions of the Complexes (cm^{-1}).

Compound	ν(C=O)		
DHP		1715	1690
$Mn(DHP)_2Cl_2 \cdot 1.5H_2O$		1732	1662
$Mn(DHP)_2Br_2 \cdot H_2O$		1730	1670
$Mn(DHP)_2I_2 \cdot 2H_2O$		1712	1658
$Co(DHP)_2Cl_2 \cdot H_2O$		1716	1672
$Co(DHP)_2Cl_2 \cdot 3H_2O$		1710	1670
$Co(DHP)Cl_2 \cdot 2H_2O$		1725	1670
$Co(DHP)Br_2$		1726	1670
$Co_2(DHP)_3I_4 \cdot 3H_2O$	1736	1710	1665
$Co(DHP)_2 \cdot 2H_2O$		1653	1620
$Ni(DHP)_2Cl_2 \cdot H_2O$		1725	1670
$Ni_2(DHP)_3Br_4 \cdot 3H_2O$		1726	1655
$Ni(DHP)_2 \cdot 2H_2O$		1653	1620
$Cu(DHP)_2Cl_2$		1725	1675
$Cu(DHP)_2Br_2$		1728	1675
$Cu(DHP)_3Br_2 \cdot 4H_2O$		1725	1668
$Cu_2(DHP)_3Br_4$		1730	1680
$Cu(DHP)_2 \cdot 2H_2O$		1645	1600
$Zn(DHP)_2 \cdot 5H_2O$		1653	1620

weak. In the bromide, which is anhydrous, the octahedral species appears to be very much like that in $Co(DHP)_2Cl_2$.

Cobalt iodide forms a complex of stoichiometry $Co_2(DHP)_3I_4 \cdot 3H_2O$. This, however, shows no bands indicative of a tetrahedral species. Similar stoichiometries were found with nickel bromide and copper bromide. In view of the remarks made above concerning the possible similarity to uracil complexes, it is interesting that uracil and thymine were found to give complexes of this type. They were considered to contain chains of MX_2 units, with uracil molecules occupying some of the remaining positions, and water molecules completing the coordination spheres.

Nickel Complexes

These again have very weak, essentially octahedral ligand fields. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is centred near 8000 cm^{-1} and is probably unsplit, the shoulders observed on the low energy side being due to vibrational overtones. This position may be compared with 8,500 cm^{-1} for the hexaquo ion. The $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition occurs near 13,000 cm^{-1}, the ν_3 transition being masked by ligand absorption.

Copper Complexes

The e.p.r. spectra (Table III) indicate that these have tetragonally distorted octahedral stereochemistry, and the electronic spectra are consistent with this.

Inner Complexes $M(DHP)_2 \cdot nH_2O$

These have much stronger ligand fields than the compounds described above, with Δ values of about 10,000 cm^{-1}, and a band splitting, for the nickel complex, which suggests coordination by two strong and four weaker donors.

Infrared Spectra

The free ligand shows strong absorption in the carbonyl stretching region, which appears to consist of two components at about 1715 and 1690 cm^{-1}. Uracil and related compounds generally give two strong bands in this region, the higher of which is assigned to $\nu(C_2{=}O)$ and the lower to $\nu(C_4{=}O)$ coupled with $\nu(C{=}C)$ [6, 7]. In uracil complexes, with donation through $C_4{=}O$, $\nu(C_2{=}O)$ is shifted very slightly to higher frequency [5], while $\nu(C_4{=}O)$ is lowered by about 14–25 cm^{-1}. In the neutral complexes of DHP a very similar pattern is observed (Table IV), and it is likely that the bands should be assigned in the same way, and that donation to the metal ion occurs through O_4.

At lower energy there is little change in the spectrum on coordination, apart from the disappearance of ligand bands at 745 and 712 cm^{-1}.

In the inner complexes, both ν(C=O) bands are shifted markedly to lower frequencies (Table IV), and also a group of three strong bands appears at 1500–1600 cm^{-1}, in place of the one band found for the ligand and the other complexes. Presumably these differences are a consequence of anion formation, but in the absence of band assignments more detailed speculation concerning their origin is unwarranted.

Discussion

These results show clearly that DHP will complex with a variety of metal ions, both as an anion and as a neutral ligand. In the latter case, donation occurs through O_4, and probably also through N_5, though this is a much weaker donor than is usual for nitrogen. It seems likely that the stereochemistry is dominated by the preferred angle at O_4, which would be 120° assuming full double-bond character for the

C=O bond, and, for one complex of 1,3-dimethyluracil [8], is as high as 133.5°. The attainment of angles as large as these would necessitate unusually long metal–nitrogen bonds as indeed have been found in some flavin complexes [9].

In anionic DHP, either N_1 or N_3 becomes available for donation, and the strength of the ligand field suggests that one of these pyrimidine nitrogens acts as a main donor.

Experimental

Preparation of Compounds

2,4-(1H, 3H)-pteridinedione was prepared by the method of Dallacker and Stein [10], and was recrystallised twice from ethanol. *Anal.* Found C, 43.68; H, 2.69; N, 33.42. Calc. for $C_6H_4N_4O_2$: C, 43.90; H, 2.43; N, 34.14%.

The general method used for the preparation of complexes was as follows: A boiling solution of the metal salt in a mixture of methanol and dimethoxypropane was added dropwise to a boiling solution of ligand in the same solvent. The combined solutions were evaporated to half volume, and an equal volume of ethyl acetate was added. On further evaporation the complex precipitated out, and was filtered off, washed, and dried at 120 °C.

The complexes $Cu(DHP)_2Cl_2$, $Cu_2(DHP)_3Br_4$ and $Cu(DHP)_3Br_2\cdot 4H_2O$ were prepared from ethanol solutions. The two bromides were obtained from the same preparation, $Cu_2(DHP)_3Br_4$ precipitating immediately, and $Cu(DHP)_3Br_2\cdot 4H_2O$ after a few days standing.

The inner complexes were made using a solution of ligand in water with the pH adjusted with NaOH to 6.5. To this solution, warmed to 60 °C, was added very slowly an aqueous solution of the metal nitrate, the pH being kept at 6.5. The precipitate was stirred for 15 min then collected and dried at 120 °C.

Physical Measurements

These were made as described previously [5].

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