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Complexes of Pyrimidine-2-one with Some First Transition Series Metal Ions

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The preparations and spectral properties are reported of complexes of pyrimidine-2-one (Hpymo) with metal ions of the series Mn–Zn, and also Cd. The results show that the exocyclic oxygen atom in Hpymo has much less tendency to bind to these metal ions than does the sulphur atom in pyrimidine-2-thione. With cobalt(II) Hpymo readily forms tetrahedral $[Co(Hpymo)_4]^{2+}$ *ions in which Hpymo binds through the non-protonated ring nitrogen. Such cations are present in:* $[Co(Hpymo)_4]X_2 \cdot Hpymo$ *(X = I or* ClO_4*),* $[Co(Hpymo)_4][CoCl_4]$*, and* $[Co(Hpymo)_4]X_2$ *(X = Cl or Br).*

Introduction

One of the interesting questions arising from recent studies of the binding of metal ions to nucleic acid components [1, 2] concerns the extent of coordination by exocyclic atoms or groups of the pyrimidine or purine bases. Although the exocyclic amine groups of adenine, guanine, or cytosine were at one time frequently cited as potential metal ion binding sites, there is now clear evidence [1–3] that the involvement of the 'lone pair' electrons on these groups in π-delocalization renders them unsuitable for strong metal binding.

Less is known about coordination by exocyclic oxygen or sulphur atoms, although the possible changes induced in nucleic acids by such bonding have occasioned suggestions as to their involvement in nucleic acid recognition processes [4]. Several structural studies on complexes with ligands containing the cytosine unit have shown that primary metal–N3 bonding is reinforced by a weaker M–O2 interaction [2, 5]. Uracil is known to coordinate to mercury(II) through O4 in dichlorobis(uracil)mercury(II) [6] and there is spectral evidence for coordination by carbonyl oxygen in a range of uracil and thymine complexes [7].

As we had found [8] that pyrimidine-2-thione (Hpymt) coordinates to some first row transition metal ions strongly by the unprotonated ring nitrogen and more weakly by the exocyclic sulphur atom, to give a four-membered chelate ring, we were interested to make a direct comparison with the behaviour of its oxygen analogue pyrimidine-2-one (Hpymo).

Results and Discussion

The compounds isolated using Hpymo (Table I) had a wider range of stoichiometries than was found for Hpymt. Those reported here for a given metal are not necessarily the only ones obtainable, as we were more interested in surveying the general coordination possibilities of Hpymo with these metal ions than in an extensive synthetic programme.

The results of physical measurements are given in Tables I and II. The electronic spectra of the complexes of composition $Co(Hpymo)_4X_2$ (X = Cl or Br) (Table II) showed intense multicomponent bands centred on ~9000–9500 cm^{-1} and on ~18,500 cm^{-1} with a weaker, broad band near ~5000 cm^{-1}. Such spectra are characteristic of cobalt(II) in an essentially tetrahedral environment of nitrogen donor atoms, suggesting that the correct formulation of these compounds is $[Co(Hpymo)_4]X_2$, with Hpymo coordinated to cobalt only by the non-protonated ring nitrogen.

To confirm this structural assignment and to examine more directly the extent of any secondary metal–oxygen bonding, a single crystal X-ray diffraction study of the bromide has been made by Dr. C. D. Reynolds of this Department. Full crystallographic details will be published elsewhere [9], but we note here the main features of the geometry of the cation relevant to the present discussion. The coordination about cobalt is a distorted tetrahedron of ring nitrogen atoms with N–Co–N angles ranging from ~102° to ~119° and Co–N bond lengths of 2.02 and 2.03 Å. The Co–O2 distances are 2.82 and 2.84 Å and there is no indication of any significant degree of cobalt–oxygen bonding, in agreement with the conclusions from the spectral studies.

We have examined the i.r. spectra of the compounds down to 200 cm^{-1} to identify any bands with significant M–N stretching character (hereafter denoted as ν(M–L), though we recognize that the

TABLE I. Analytical and Low Frequency I.R. Data for Complexes of Pyrimidine-2-one.

Complex	Colour	Analysis (%)[a]			I.R. bands (cm^{-1})	
		C	H	N	ν(M–X)	ν(M–L)
$Mn(Hpymo)_2Cl_2$	White	30.1 (30.2)	3.1 (2.5)	18.2 (17.6)	–	235br
$Mn(Hpymo)_2Br_2 \cdot 2H_2O$	Pink	21.5 (21.7)	2.4 (2.7)	12.8 (12.65)	d	249
$Fe(Hpymo)Cl_2$	Deep Orange	21.7 (21.6)	2.1 (1.8)	12.6 (12.6)	–	250br
$Co(Hpymo)_2Cl_2$	Royal Blue	30.0 (29.8)	2.55 (2.5)	17.6 (17.4)	310	255
$[Co(Hpymo)_4][CoCl_4]$	Purple	30.0 (29.8)	2.7 (2.5)	17.5 (17.4)	310 288	241
$[Co(Hpymo)_4]Cl_2$	Red	37.3 (37.4)	3.3 (3.1)	21.6 (21.8)	–	273sh 260 220
$Co(Hpymo)_2Br_2$	Royal blue	23.6 (23.4)	2.2 (2.0)	13.7 (13.6)	254 238	c
$[Co(Hpymo)_4]Br_2$	Red	32.0 (31.9)	2.7 (2.7)	18.8 (18.6)	–	273 260 237
$Co(Hpymo)_5I_2$[b]	Red	29.7 (30.3)	2.3 (2.5)	17.5 (17.7)	–	274sh 258 220
$Co(Hpymo)_5(ClO_4)_2$	Pink	32.6 (32.5)	3.1 (2.7)	19.1 (19.0)	–	260 220
$Co(pymo)_2$	Pink	38.6 (38.6)	2.65 (2.4)	22.7 (22.5)	–	274sh 261 219
$Ni(Hpymo)Cl_2$	Pale Yellow	21.3 (21.3)	1.9 (1.8)	12.5 (12.4)	234[e]	258 211
$Ni(Hpymo)_2Br_2 \cdot 2H_2O$	Emerald	21.7 (21.5)	2.8 (2.7)	12.6 (12.5)	f	263
$Ni(Hpymo)_4I_2$	Yellow Green	27.35 (27.6)	2.5 (2.3)	15.8 (16.1)	–	–
$Ni(pymo)_2$	Pale Green	38.7 (38.6)	2.7 (2.4)	22.6 (22.5)	–	–
$Cu(Hpymo)_2Cl_2$	Blue	29.6 (29.4)	2.6 (2.5)	17.3 (17.15)	306	273 261
$Cu(Hpymo)_2Br_2$	Dark Green	23.0 (23.1)	1.9 (1.9)	13.4 (13.5)	233	280 254
$Cu(Hpymo)_4(ClO_4)_2 \cdot EtOH$	Purple	31.3 (31.2)	3.35 (3.2)	16.2 (16.2)	–	281
$Cu(Hpymo)_4(ClO_4)_2 \cdot 1\text{-}PrOH$	Purple	32.0 (32.3)	3.2 (3.4)	15.8 (15.85)	–	279
$Zn(Hpymo)_2Cl_2$	White	29.55 (29.25)	2.6 (2.5)	17.3 (17.1)	306 296	241
$Zn(Hpymo)_2Br_2$	White	22.8 (23.0)	1.5 (1.9)	13.6 (13.4)	215	241
$Zn(Hpymo)_4(NO_3)_2$	White	33.8 (33.5)	2.9 (2.8)	24.6 (24.4)	–	240br
$Cd(Hpymo)Cl_2$	White	17.3 (17.2)	1.5 (1.4)	10.1 (10.0)	–	–
$Cd(Hpymo)_2Br_2$	White	20.5 (20.7)	1.7 (1.7)	12.2 (12.1)	–	–
$Cd(Hpymo)_2I_2$	White	17.1 (17.2)	1.5 (1.4)	10.0 (10.0)	–	–

[a] Calculated values are given in parentheses. [b] Iodide analysis: Found, 31.8; Calc. 32.0%. [c] Region obscured by strong ν(Co–Br) band. [d] ν(Mn–OH_2) at 370 cm^{-1}. [e] Tentative assignment (see text). [f] ν(Ni–OH_2) at 360 cm^{-1}.

modes responsible will not have pure ν(M–N) character). The free ligand Hpymo has a medium intensity band at 403 cm^{-1} (which on complexation has a variable position in the range 402–426 cm^{-1}) but no other bands between 400 and 200 cm^{-1}. The spectra of the compounds $[Co(Hpymo)_4]X_2$ show, in each

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

$Fe(Hpymo)Cl_2$	6,560,	9,520			
$[Co(Hpymo)_2Cl_2]$	6,900br,	16,450			
$[Co(Hpymo)_2Br_2]$	6,250sh	7,250,	9,090sh,	16,130	
$[Co(Hpymo)_4]Cl_2$	~5,200,^{b}	8,400sh,	9,760,	10,900sh,	18700
$[Co(Hpymo)_4]Br_2$	~4,500,^{b}	7,350sh,	8,930,	10,700sh,	18,350
$[Co(Hpymo)_4][CoCl_4]$	5,500,^{c,d}	9,900,^{e}	14,900,^{c,d}	18,700^e	
$Co(Hpymo)_5I_2$	~5,500sh,^{b}	9,600,^{c}	18,500		
$Co(Hpymo)_5(ClO_4)_2$	~5,000,^{b}	9,200br,	18,250		
$Co(pymo)_2$	4,700,	9,300,	18,500		
$Ni(Hpymo)Cl_2$	8,000,^{f}	12,400,	13,500,	20,400sh,	23,000
$Ni(Hpymo)_2Br_2 \cdot 2H_2O$	7,630,	9,900,	~12,900sh,	14,800,	^{g}
$Ni(Hpymo)_4I_2$	9,050,	15,380,	^{g}		
$Ni(pymo)_2$	8,550,	~13,000sh,	14,900,	25,250	
$Cu(Hpymo)_2Cl_2$	16,400				
$Cu(Hpymo)_2Br_2$	14,800				
$Cu(Hpymo)_4(ClO_4)_2 \cdot S^a$	18,700				

[a] S = EtOH or 1-PrOH (identical spectra). [b] Broad band, exact energy uncertain because of vibrational bands in same region. [c] Centre of multicomponent band. [d] Assigned to $CoCl_4^{2-}$. [e] Assigned to $Co(Hpymo)_4^{2+}$. [f] Asymmetric to lower energy. [g] Band expected at higher energy obscured by strong absorption from U.V. region.

case, a pair of bands at 260 and 273 cm^{-1} and a weaker band at lower energy (Table I). For a regular tetrahedral geometry only one ν(M–L) band would be expected (ν_3, F_2, in T_d). However, the distortion of the $[Co(Hpymo)_4]^{2+}$ ion, shown by the X-ray studies on the bromide, lowers the symmetry of the CoN_4 primary coordination sphere to C_{2v}, so a splitting of ν_3 and the appearance of a third band at lower energy (ν_1, i.r. forbidden in T_d) are expected.

The ν(Co–L) bands observed for $Co(Hpymo)_4^{2+}$ are at somewhat higher energy than that observed recently [10] for the more regularly tetrahedral ion CoL_4^{2+}, where L = 1-methylpyrimidine-2-thione.

Somewhat unexpectedly, cobalt iodide and perchlorate yielded 5:1 complexes with Hpymo. Their electronic spectra (Table II) are unlike those reported for five coordinate cobalt(II) complexes [11], but are very similar to those of the compounds $[Co(Hpymo)_4]X_2$, as are their low frequency i.r. spectra (Table I). We conclude that, despite their 5:1 stoichiometry, these compounds are of the type $[Co(Hpymo)_4]X_2 \cdot (Hpymo)$. There was, however, no evidence from their i.r. spectra for the presence of two different types of Hpymo, but this is not unexpected because the non-coordinated Hpymo is likely to be hydrogen-bonded to the $[Co(Hpymo)_4]^{2+}$ cations.

The strong tendency of Hpymo to react with cobalt(II) to form the tetrahedral $[Co(Hpymo)_4]^{2+}$ ion is also apparent from the products of its reaction with cobalt chloride in 2:1 ligand:metal ratio. Variations in reaction conditions (see Experimental Section) gave either blue (B) or purple (P) compounds of composition $Co(Hpymo)_2Cl_2$. The electronic spectrum of form B is characteristic of a distorted tetrahedral CoN_2Cl_2 coordination arrangement, as is the far i.r. spectrum (ν(Co–Cl) at 288 and 310 cm^{-1}).

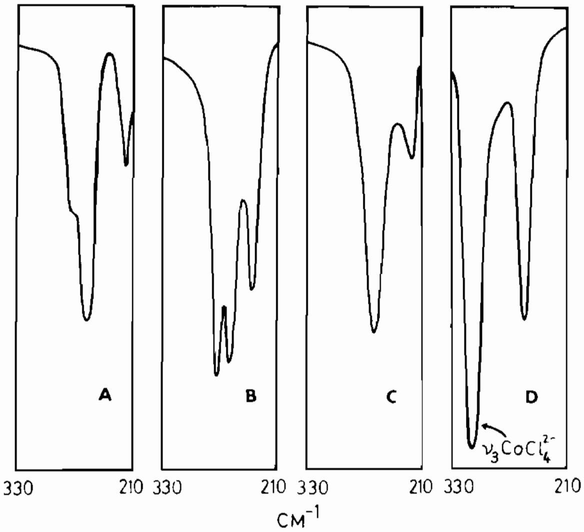

Figure 1. I.R. spectra (210–330 cm^{-1}) of: A, $[Co(Hpymo)_4]Cl_2$; B, $[Co(Hpymo)_4]Br_2$; C, $[Co(Hpymo)_4](ClO_4)_2 \cdot Hpymo$; D, $[Co(Hpymo)_4][CoCl_4]$.

The results for form P, however, show that it is $[Co(Hpymo)_4][CoCl_4]$. The electronic spectrum (Table II) is a composite of the spectra found for the complexes containing the $Co(Hpymo)_4^{2+}$ ion discussed above and of the spectrum of the $CoCl_4^{2-}$

ion [12]. Also its far infrared spectrum has a very strong band at 310 cm^{-1} due to the ν_3 mode of $CoCl_4^{2-}$ [13]. Between 200 and 300 cm^{-1} the complex has a single, medium–strong ν(Co–L) band at 255 cm^{-1} due to $Co(Hpymo)_4^{2+}$. It is interesting to compare this last observation with the analogous spectral results for $[Co(Hpymo)_4]X_2$ (X = Cl or Br) and $[Co(Hpymo)_4](ClO_4)_2 \cdot Hpymo$ (Figure 1). It can be seen that on replacing Br by Cl in the complexes $[Co(Hpymo)_4]X_2$ there is a significant change in the relative intensities of the ν(Co–L) bands, and that at lowest energy is shifted from 237 cm^{-1} to 220 cm^{-1}. There is a further change in the case of the perchlorate in which the highest energy component is no longer resolved and the 220 cm^{-1} band is somewhat weakened. In $[Co(Hpymo)_4]$ $[CoCl_4]$ the 220 cm^{-1} band is absent and the 255 cm^{-1} band is not even broadened.

It seems probable that these observations reflect changes in the extent of distortion of the $Co(Hpymo)_4^{2+}$ ion from T_d symmetry, with the distortion being greatest for the bromide (*vide* the X-ray results) and apparently very small for the $CoCl_4^{2-}$ compound (a regular geometry for a tetrahedral cation might reasonably be expected when its counter anion has the same charge and geometry). There is a corresponding decrease in the splitting of the ν_2 electronic band for this series of $Co(Hpymo)_4^{2+}$-containing complexes, but the changes in their low frequency i.r. spectra are more significant.

Blue and purple compounds of composition $Co(Hpymo)_2Br_2$ also exist but, in this case, the purple form tended to change to the blue form during the synthesis and pure samples could not be obtained. Blue $Co(Hpymo)_2Br_2$ resembles the analogous blue chloride in having tetrahedral CoN_2X_2 geometry. For neither of the $Co(Hpymo)_2X_2$ complexes is there any evidence from the electronic or the far i.r. spectra for any significant degree of Co–O bonding similar to the weak Co–S bonding observed [8] for the analogous $Co(Hpymt)_2X_2$ compounds.

From their far i.r. spectra (Table I), the compounds $Zn(Hpymo)_2X_2$ (X = Cl or Br) may also be assigned tetrahedral structures, but the 2:1 complexes of cadmium bromide and iodide had no ν(Cd–X) bands above 200 cm^{-1}. The X-band e.p.r. spectra of the manganese complexes $Mn(Hpymo)_2Cl_2$ and $Mn(Hpymo)_2Br_2 2H_2O$ each consisted of a broad band in the g = 2 region. The absence of fine structure indicates a polymeric, octahedral structure. This is probably achieved by means of halide bridges as no ν(Mn–X) bands were observed above 200 cm^{-1}.

Polymeric structures are also formed by the complexes $M(Hpymo)Cl_2$ (M = Fe and Ni). The electronic spectrum of the iron(II) complex consists of a pair of relatively low intensity bands in the near i.r. region, similar to those found for $Fepy_2Cl_2$ and related six coordinate polymers [15]. The band energies (6560 and 9520 cm^{-1}) suggest that both halide and pyrimidine bridges are present. However the electronic spectrum of $Ni(Hpymo)Cl_2$ resembled that of $NipyCl_2$ [16] much more closely than that of $Nipy_2Cl_2$ [17] which would suggest that, in this case, chloride bridges are formed in preference to pyrimidine bridges; the iron and nickel complexes have different X-ray powder patterns.

As expected [14] no ν(Fe–Cl) band was observed above 200 cm^{-1} for $Fe(Hpymo)Cl_2$, and the assignment recorded in Table I as ν(Ni–Cl) for the nickel analogue is very tentative as it seems rather high in comparison with other halide bridged nickel complexes [14].

From their electronic spectra, the other nickel complexes isolated ($Ni(Hpymo)_2Br_2 \cdot 2H_2O$, $Ni(Hpymo)_4I_2$, and $Ni(pymo)_2$) are all six coordinate. In the case of the bromide the water molecules appear to be coordinated as there was a band at 360 cm^{-1} assignable as $\nu(Ni–OH_2)$. The iodide does not show the pronounced splittings of the ν_1 and ν_2 electronic bands found for compounds such as $Nipy_4I_2$ [17]. The X-ray structural study [18] on the copper complex $Cu(Hpymo)_4(ClO_4)_2 \cdot EtOH$ (*vide infra*) shows that the coordination of four Hpymo molecules via nitrogen in a planar array about a metal ion can result in the exocyclic oxygen atoms lying in pairs above and below the MN_4 plane, thus blocking the close approach of iodide ions. Although the Cu–O interaction in the copper complex is not strong (Cu–O 2.78 and 2.90 Å) the greater propensity of nickel for octahedral coordination would be expected to favour a greater degree of Ni–O interaction leading to a pseudo-octahedral ligand field geometry.

The exocyclic oxygen atoms certainly seem to be bonded to nickel in the inner complex $Ni(pymo)_2$ as its electronic spectrum shows it to be six coordinate, in contrast to $Co(pymo)_2$ which has a spectrum typical of a tetrahedral CoN_4 chromophore. A tetrahedral ZnN_4 array is also likely to be present in $Zn(Hpymo)_4(NO_3)_2$ as the i.r. spectrum of the complex shows the presence of ionic nitrates.

The electronic spectra of the copper(II) halide complexes, $Cu(Hpymo)_2X_2$, are typical of distorted six coordinate copper(II). These results and the far infrared spectra are very similar to those of the analogous cytosine complexes [19], the chloride of which is known [20] to have a distorted (4 + 2) coordination with the O2 atoms of the cytosines binding weakly (2.74 and 2.88 Å) in axial positions.

The reaction of pyrimidine-2-one with copper(II) perchlorate in either ethanol or propan-1-ol gave purple compounds of stoichiometry $Cu(Hpymo)_4(ClO_4)_2 \cdot S$ (S = EtOH or n-PrOH). The electronic spectra of these complexes were indicative of a planar CuN_4 coordination geometry which was confirmed by an X-ray diffraction study on the ethanol solvate [18]. As discussed above, the structural study also showed that the exocyclic oxygen atoms formed weak Cu–O axial bonds similar to the Cu–O interactions observed in cytosine complexes.

Experimental

Pyrimidine-2-one was prepared by literature methods [21]. Except where otherwise stated the complexes were prepared by mixing the appropriate amounts of Hpymo and the metal salt in warm ethanol. The products, which usually precipitated immediately or within a short time after mixing the reactants, were washed with ethanol and dried *in vacuo* over P_2O_5. Analyses (Table I) were by the Microanalytical Laboratory, Imperial College.

$Mn(Hpymo)_2Br_2 \cdot 2H_2O$

Propan-1-ol was used as solvent and the product formed as pink crystals during 3 days at 0 °C.

$Fe(Hpymo)Cl_2$

This was prepared under nitrogen using de-oxygenated propan-1-ol as solvent.

$Co(Hpymo)_2Cl_2$ *(form B) and* $Co(Hpymo)_2Br_2$

A solution of Hpymo (4 mmol) in propan-1-ol (10 cm^3) was added quickly, with stirring, to one of the anhydrous cobalt halide (2 mmol) in propan-1-ol (10 cm^3). The royal blue solid that formed almost immediately was filtered, washed with propan-1-ol and dried *in vacuo* over P_2O_5.

$[Co(Hpymo)_4][CoCl_4]$ *(form P)*

A solution of Hpymo (0.384 g, 4 mmol) in ethanol (10 cm^3) was slowly added dropwise, with stirring to a warm solution of cobalt(II) chloride hexahydrate (0.476 g, 2 mmol) in ethanol (15 cm^3). After heating and stirring for 15 min the solution was allowed to stand for 2 hr at room temperature. The purple solid that precipitated was filtered, washed with ethanol, and dried as before.

$[Co(Hpymo)_4]Cl_2$

A solution of cobalt(II) chloride hexahydrate (0.238 g, 1 mmol) in ethanol (10 cm^3) was added dropwise, with stirring, to a warm solution of Hpymo (0.384 g, 4 mmol) in ethanol (15 cm^3). Refluxing for 30 min gave a red solid which was collected and dried as before.

$[Co(Hpymo)_4]Br_2$

A hot ethanolic solution of cobalt(II) bromide hexahydrate (0.327 g, 1 mmol) was added, with stirring, to one of Hpymo (0.384 g, 4 mmol) in hot ethanol (35 cm^3). After 10 min the solution was cooled quickly to room temperature and filtered to remove some purple solid (probably $[Co(Hpymo)_4][CoBr_4]$, but this could not be obtained free from blue $Co(Hpymo)_2Br_2$). Slow evaporation of the filtrate gave deep red crystals of the desired complex.

$Ni(Hpymo)_2Br_2 \cdot 2H_2O$

This was prepared as for its manganese(II) analogue but using butan-1-ol.

$Ni(Hpymo)_4I_2$

A nickel iodide solution, made metathetically from $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in propan-1-ol (5 cm^3) and sodium iodide (0.3 g, 2 mmol) in propan-1-ol (5 cm^3) was added to Hpymo (0.384 g, 4 mmol) in the same solvent (10 cm^3). After evaporation to half volume on a water bath and storage at 0 °C for 24 hr the yellow green complex was formed.

$Cu(Hpymo)_2Cl_2$

A green solid was immediately precipitated on adding an ethanolic (10 cm^3) solution of Hpymo (0.192 g, 2 mmol), with stirring to a hot solution of $CuCl_2 \cdot 2H_2O$ (0.241 g, 2 mmol) in ethanol (10 cm^3). After heating and stirring for a further 10 min, the green solid redissolved and a blue precipitate formed which was isolated as before.

$Zn(Hpymo)_2X_2$ *(X = Cl or Br)*

In the preparation of these complexes it was found advisable to add a drop of the corresponding concentrated acid to prevent partial solvolysis.

$M(pymo)_2$ *(M = Co or Ni)*

These were prepared as for the analogous inner complexes of pyrimidine-2-thione [8].

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