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Ambidentate Ligand Behaviour of 4,6-Dimethylpyrimidine-2-one

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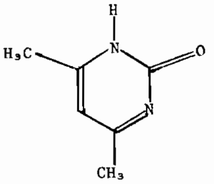
The preparation is reported of complexes of 4,6-dimethylpyrimidine-2-one with a series of divalent metal ions. Complexes with metal chlorides and bromides usually have the stoichiometry ML_2X_2, with the ligand bonded through nitrogen, plus probably in most cases a weak metal–oxygen interaction. With iodides, nitrates and perchlorates, however, the stoichiometry is usually ML_4X_2, and the ligand appears to be O–bonded. Physical studies of the compounds are reported, and differences in the infrared spectra of the N– and O–bonded ligands are described.

Introduction

A recent study [1] of the complexing ability of pyrimidine-2-one showed that in most compounds there is very little interaction between the metal ion and the exocyclic oxygen atom, in contrast to the situation for the corresponding thione, where N-S chelation, albeit with rather long metal–sulphur bonds, appeared to be common [2]. With cytosine (4-aminopyrimidine-2-one) the degree of metal–oxygen interaction is somewhat enhanced, though still fairly small [3], while with 1,4,6-trimethylpyrimidine-2-one chelation through N and O occurs in a number of complexes [4].

The question therefore arises as to the function of the substituents in increasing the donor ability of the oxygen, especially since the possibility of such metal–oxygen interactions in DNA has aroused appreciable interest. We report here a study of the complexes of 4,6-dimethylpyrimidine-2-one (I, = L) in an attempt to provide more information on this.



I

Experimental

Preparation of 4,6-Dimethylpyrimidine-2-one

Concentrated hydrochloric acid (25 cm^3) was added to a warm suspension of finely powdered urea (6 g, 0.1 mol) in 2,4-pentanedione (12 g, 0.12 mol) and absolute ethanol (250 cm^3), and the mixture boiled under reflux for two hours. After cooling, the colourless crystals of 4,6-dimethylpyrimidinone hydrochloride were collected. To the mother-liquor was added more powdered urea (6 g), 2,4-pentanedione (11 g), ethanol (10 cm^3), and concentrated hydrochloric acid (15 cm^3), and the mixture boiled as before. The crystals of the hydrochloride were again collected. After two such preparations, making use of the original mother-liquor, the final solution was discarded.

The combined yield of hydrochloride (37.3 g, 77.5%) was dissolved in the minimum of cold water, neutralised with sodium hydroxide solution and evaporated to one third of its original volume on a water bath. The solution was cooled overnight to give colourless crystals of 4,6-dimethyl-2-pyrimidinone dihydrate. This was recrystallised from water, and the anhydrous compound prepared by heating in vacuo at 80 °C. (16.8 g, 45%; M.P., 201–202 °C; Lit. M.P., 201–202 °C [5]).

Preparation of the Complexes

The following general method was used. A solution of the metal salt in ethanol was added with stirring to a suspension of the ligand in ethyl acetate. The ligand gradually dissolved on heating, and after a few minutes a precipitate of the complex was formed. This was filtered off, washed with ethyl acetate, and dried over silica gel. In a few cases 1-propanol was used in place of ethanol, and for some of the anhydrous complexes it was necessary to add 2,2-dimethoxypropane to the reaction mixture. Metal iodides were prepared metathetically from the chlorides.

All of the complexes had satisfactory analyses for C, H and N (microanalytical laboratory, Imperial College).

Results

Most of the complexes had the stoichiometry ML_2X_2 (including M = Mn, Fe, Co, Ni; X = Cl, Br; M = Zn, X = Cl; M = Cu, X = Br, NO_3; M = Cd, X = Br, I, NO_3) or ML_4X_2 (including M = Mn, X = I, NO_3; M = Co, X = ClO_4, NO_3; M = Ni, X = Br, I). A few hydrates were also formed, especially from the bromides, iodides and perchlorates.

The chloro- and bromo-complexes of cobalt(II) have been reported previously [6]. They were considered to contain essentially tetrahedral CoN_2X_2 chromophores, distorted by a weak metal–oxygen interaction. The corresponding iron complexes have intense bands in the near infrared region (Table I) as found for tetrahedral complexes, but the bands are at somewhat higher energy, and more widely separated, than in typical FeN_2X_2 tetrahedra such as Fe(quinoline)$_2$Cl$_2$. A similar spectrum, though with an even greater band separation, was found for Fe(pyrimidine-2-thione)$_2$Cl$_2$, for which an essentially 6-coordinate structure with chelating pyrimidinethiones was postulated [2]. We suggest that, like the cobalt complexes, the iron, and probably also the corresponding manganese and zinc complexes (*vide infra*) contain approximately tetrahedral MN_2X_2 groupings, with two additional, weak metal–oxygen bonds.

The manganese chloro- and bromo-complexes give e.p.r. spectra with the main band near $g_{eff} = 4$, and a number of weaker bands to higher field. This establishes that they are monomeric, but does not distinguish between the extremes of tetrahedral MnN_2X_2 and octahedral $MnN_2O_2X_2$.

The far infrared spectra of the complexes ML_2Cl_2 (M = Mn, Fe, Co, Zn) are similar to one another (Table II), with two very strong bands at 262–281 and 236–259 cm^{-1}. The corresponding bromides have a somewhat weaker band at 248–267 cm^{-1} and a very strong band at 219–234 cm^{-1}. It seems reasonable to assign these last as ν(M–Br) with the higher, weaker band as essentially ν(M–N). In the chlorides, then, considerable mixing of ν(M–N) with ν(M–Cl) would be expected, giving rise to the two very strong bands observed.

The range 248–267 cm^{-1} for ν(M–N) is very similar to that assigned [2] as ν(M–L) for pyrimidinethione complexes (231–265 cm^{-1}). The ν(M–X), however, are at slightly lower energy than is normally found for tetrahedral species, in accord with the proposed weak interaction with the pyrimidinone oxygen, though the effect is much less marked than in the thiones [2]. They are not consistent with the alternative possibility of MN_2O_2 tetrahedra plus weak M–X bonding.

The corresponding nickel complexes give electronic spectra similar to those of octahedral complexes with weak ligand fields, except that the bands are quite intense, especially that due to the $^3A_{2g} \rightarrow$

TABLE I. Reflectance Spectra of the Complexes.

Compound	Band Maxima (cm^{-1})
FeL_2Cl_2	5200s, 6600s
FeL_2Br_2	5000sh, 6250s
CoL_2Cl_2	6250sh, 6900m, 9600m, 17000vs
CoL_2Br_2	6500mbr, 9300m, 16550vs
$CoL_2Br_2 \cdot 3H_2O$	5000m, 5800m, 7140m, 14300sh, 15600s, 16400sh, 17540m, 23600s
CoL_2I_2	7300s, br, 15600vs, 17300vs
CoL_4I_2	6250sh, 7100m, 9500m, 16800vs
$CoL_4I_2 \cdot 3H_2O$	7000w, 13300sh, 16700sh, 17540m, 18600sh, 19400sh, 20100sh, 21500sh
$CoL_4(ClO_4)_2$	7690w, 10500sh, 18520m, 21140sh, 23600w, br
$CoL_4(NO_3)_2$	7690w, 15040w, sh, 19200m, 20400sh, 21050sh, 24570sh
NiL_2Cl_2	6060m, br, 11760s, 21280vs
NiL_2Br_2	6250m, br, 11760s, 20620vs
$NiL_2Br_2 \cdot 4H_2O$	6900w, br, 12200w, 19050sh, 22470m
NiL_4Br_2	7190mw, 12500mw, 19420sh, 22730s
$NiL_4Br_2 \cdot 2H_2O$	8160w, 14080w, 21280sh, 25000m
NiL_4I_2	7020mw, br, 12500mw, 19000sh, 21980[a]sh
$NiL_3(NO_3)_2 \cdot 3H_2O$	8330w, 13790w, 24690m
$CuLCl_2$	13790s
CuL_2Br_2	9520sh, 13740sh, 16530s
$CuL_4(ClO_4)_2 \cdot H_2O$	Obscured by charge-transfer band.
$CuL_2(NO_3)_2$	9800sh, 13330s

[a] Partially obscured by charge-transfer band.

TABLE II. Metal–Ligand and Metal–Anion Stretching Vibrations.

Complex	ν(M–L)	ν(M–X)
MnL_2Cl_2	262vs, 236vs[a]	
MnL_2Br_2	248s	219vs
MnL_4I_2	227s	141vs
$MnL_4(ClO_4)_2 \cdot H_2O$	239s	
$MnL_4(NO_3)_2$	243s, br	
FeL_2Cl_2	270vs, 252vs[a]	
FeL_2Br_2	255m	226vs
CoL_2Cl_2	281vs, 259vs[a]	
CoL_2Br_2	267ms	234vs
$CoL_2Br_2 \cdot 3H_2O$	275ms	236vs, 220vs
CoL_2I_2	279s	195vs, 179vs
CoL_4I_2	275vs, 261vs	
$CoL_4I_2 \cdot 3H_2O$	234s	150vs
$CoL_4(ClO_4)_2$	219s, br	
$CoL_4(NO_3)_2$		287vs, 275sh
NiL_2Cl_2	279s	263vs, 248vs
NiL_2Br_2	275m	236vs, (219s, 189s?)[b]
$NiL_2Br_2 \cdot 4H_2O$	233ms	190vs
NiL_4Br_2	234s	190s
$NiL_4Br_2 \cdot 2H_2O$	231vs, 219s	
NiL_4I_2	250ms, 231s	166vs
$NiL_3(NO_3)_2 \cdot 3H_2O$	250s, br	
$CuLCl_2$		310vs, 276vs[c]
CuL_2Br_2	261s	214vs
$CuL_4(ClO_4)_2 \cdot H_2O$	279ms	
$CuL_2(NO_3)_2$	269vs	315vs, br
ZnL_2Cl_2	270vs, 254vs[a]	
$ZnL_4Br_2 \cdot H_2O$	277s, (253vs, 220s?)[b]	
$ZnL_4(ClO_4)_2 \cdot H_2O$	278ms, 219m	
CdL_2Br_2	246m	184vs, 165vs
CdL_2I_2	261s	152vs, 131vs

[a] Contribution from both ν(M–L) and ν(M–Cl). See text.
[b] (?) indicates doubt over assignment, not presence, of band.
[c] Probably contains contribution from ν(M–L).

$^3T_{1g}$(P) transition. A similar spectrum was found for Ni(1,4,6-trimethylpyrimidine-2-one)$_2$Br$_2$, though there even greater band intensities were present [4]. We conclude that these compounds also have structures intermediate between octahedron and tetrahedron, but with a greater degree of metal–oxygen interaction than for the other metals, giving a structure realistically regarded as 6-coordinate. The far infrared spectra are reasonably in accord with this.

Three different complexes were obtained from cobalt iodide. Use of one mole of hydrated cobalt iodide to two moles of ligand gave a turquoise complex of stoichiometry CoL_2I_2. From its electronic (Table I) and far infrared (Table II) spectra it seems to contain a normal CoN_2I_2 tetrahedron, with very little Co–O bonding.

The use of strictly anhydrous reaction conditions, however, gave a royal blue complex CoL_4I_2, whose spectra both electronic and vibrational, are very similar to those of CoL_2Cl_2 (Fig. 1). There is no band assignable as ν(Co–I) and no low-energy charge-transfer band, such as is normally seen for iodo-complexes of cobalt(II). We suggest that the compound contains two 'semichelating' pyrimidinones, plus two further oxygen-bonded ligands, making a distorted tetrahedral chromophore similar to that of CoL_2Cl_2.

It is interesting that cytosine also forms a complex Co(cytosine)$_4$I$_2$ which appears to contain a tetrahedral CoN_2O_2 grouping [3], whereas in Co(1,4,6-trimethylpyrimidinone)$_2$I$_2$ there is no apparent involvement of the oxygen in binding to the metal [4]. Probably the bulk of the iodide ions precludes the formation of $CoN_2O_2I_2$, and forces a change to one of the two types observed.

The third complex prepared from cobalt iodide, $CoL_4I_2 \cdot 3H_2O$, is obtained from $CoI_2 \cdot 6H_2O$ using a 6:1 ratio of ligand to metal salt. It is lilac-coloured, and its electronic spectrum indicates an essentially octahedral, weak ligand field. This is typical of the other complexes of ML_4X_2 stoichiometry, such as $CoL_4(ClO_4)_2$, $CoL_4(NO_3)_2$ and NiL_4X_2 (X = Br or I).

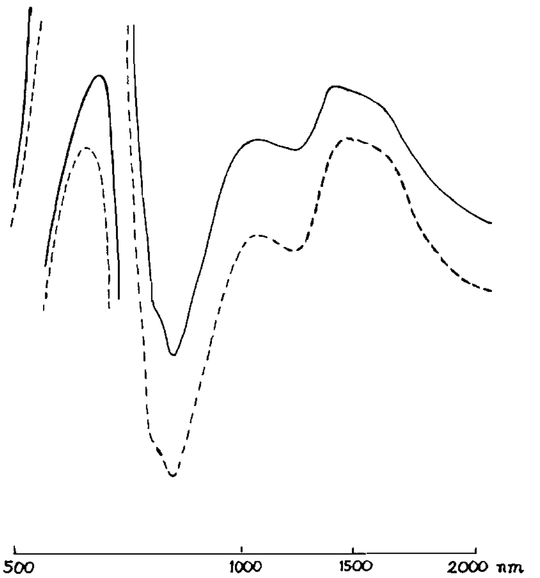


Fig. 1. Electronic Spectra of (-----) CoL_2Cl_2 and (——) CoL_4I_2.

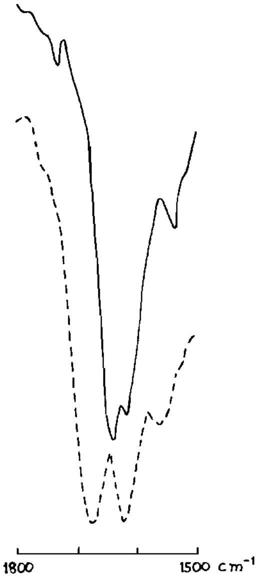


Fig. 2. Infrared Spectra (1500–1800 cm^{-1}) for the compounds (-----) CoL_2I_2 and (———) MnL_4I_2.

The low values of Δ show that either the pyrimidinones are producing an unusually weak ligand field, or else the structures involve bridging anions.

The last possibility, which seems unlikely in view of the stoichiometries, may be ruled out by the e.p.r. spectrum of MnL_4I_2, which is isomorphous with NiL_4I_2. The X-band spectrum has its main band near $g_{eff} = 5$, and numerous other bands to higher field. This indicates a monomeric structure, and it differs markedly from the spectra of other MnN_4I_2 complexes [7].

The weakness of the ligand field in these complexes must then be attributed either to the formation of very long metal–nitrogen bonds, or to donation through oxygen. Interpretation of the far infrared spectra is complicated by a weak ligand band near 230 cm^{-1}. However, these octahedral complexes have considerably enhanced absorption in the range 220–240 cm^{-1} which we believe may be assigned as ν(M–L). This would imply donation through oxygen, since ν(M–N) in an octahedral complex with weak bonds would be expected below 200 cm^{-1}.

The difference between O- and N-coordination would be expected to show in the infrared spectrum of the ligand, especially, perhaps, in the C = O stretching frequency. However, the 1600–1700 cm^{-1} region of the spectrum is complicated, and ν(C = O) is appreciably mixed with ring and NH vibrations. Moreover, there is probably a considerable amount of hydrogen bonding involving the C = O group, in both ligand and complexes. While some consistent differences can be seen between the complexes thought to be O- and N-bonded respectively, it is difficult to assign these with any certainty. The main differences are, firstly, a greater separation in the N-bonded complexes of the two strong bands at 1600–1700 cm^{-1} (Fig. 2). A similar observation was made for the N-bonded complexes of 1,4,6-trimethylpyrimidine-2-one [4] compared with those involving N,O chelation, and may well be due to a lower ν(C = O) when the oxygen is bonded to the metal. Bonding through nitrogen, on the other hand, would tend to increase the C–O bond order. It is interesting that NiL_2X_2 (X = Cl, Br) (*vide supra*) give an intermediate value for the band-separation in this region.

At 1200–625 cm^{-1}, the spectra of the O-bonded complexes are similar to that of the ligand, with the addition of a weak to medium intensity, rather broad band at about 900 cm^{-1}. In the N-bonded compounds, however, there is no band at 900 cm^{-1}, but considerable differences in intensity compared with the ligand. In particular, the band near 800 cm^{-1} (799 cm^{-1} in the ligand) is much enhanced, and is the dominant band in this region. Taken together, these differences provide a useful clue to the mode of coordination.

Some of the complexes are hygroscopic, forming hydrates either on exposure to the atmosphere, or directly if prepared from damp solvents. Attempts to prepare CoL_2Br_2 in the absence of 2,2-dimethoxypropane gave the green complex $CoL_2Br_2 \cdot 3H_2O$, which has a magnetic moment of 5.19 B.M., although its electronic spectrum is similar to that of a tetrahedral complex. The infrared spectrum suggests that the pyrimidinones are N-bonded to the metal.

In contrast, exposure of MnL_4I_2 to the atmosphere yields $MnL_4I_2 \cdot 6H_2O$, which may also be obtained as yellow crystals from1-propanol. Its infrared spectrum is quite different from that of MnL_4I_2, resembling more closely those of the N-bonded complexes, though with some intensity differences. There are no bands assignable as ν(M–L). Its e.p.r., spectrum has its main band at $g_{eff} = 2$, and there is apparently little distortion from octahedral symmetry. An X-ray crystal structure determination [8] showed it to contain $Mn(H_2O)_6^{2+}$ ions, hydrogen-bonded to the pyrimidinones.

Discussion

Throughout the series of compounds, there is more involvement of the oxygen in binding to the metal than was found for pyrimidine-2-one itself [1]. While this may well be due to the steric hindrance to N-bonding introduced by the 4-methyl group, it is interesting that the oxygen-bonding is even greater than in 1,4,6-trimethylpyrimidinone. It seems that the possibility of M–O bonds formed preferentially to M–N must be considered for ligands of this type, especially when steric constraints are present.

The metal–oxygen bonds, however, are readily attacked by water, and in polar conditions hydrogen-bonded pyrimidinones may be encountered more frequently. It would seem that the relatively non-polar, sterically constrained regions of natural systems may be most conducive to involvement of the exocyclic oxygen in metal binding.

Acknowledgements

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