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# Metal Complexes of Cytosine

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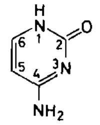
*The preparation is described of complexes of cytosine (= L) with the divalent metal ions manganese to zinc. The chloro- and bromo-complexes generally have the stoichiometry $ML_2X_2$, whereas iodides, nitrates and perchlorates commonly form $ML_4X_2 \cdot O$ or $2H_2O$. In the 4-coordinate complexes, the cytosine normally binds to the metal through N(3), with weak interaction through O(2), but, in the complexes of higher coordination number, hydrogen bonding of cytosine to coordinated water seems more likely. In $CoL_4I_2$, O-bonded cytosine may be present.*

## Introduction

There have been numerous reports of the interaction of RNA and DNA, their constituent nucleotides and nucleosides, and their purine bases, with a variety of metal ions [1]. Studies of the pyrimidine bases, however, are less common. Following our report of complexes of uracil and thymine [2], we describe here a number of complexes of the other major pyrimidine base, cytosine (I) (= L).

TABLE I. Analytical Results.

| Compound | Colour | % Found | | | % Calculated | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | C | H | N |
| $MnL_2Cl_2$ | pale pink | 27.78 | 3.21 | 23.63 | 27.61 | 2.90 | 24.15 |
| $MnL_2Br_2$ | pale pink | 22.52 | 2.35 | 19.56 | 21.99 | 2.31 | 19.23 |
| $MnL_4I_2 \cdot 2H_2O$ | pale pink | 24.34 | 3.63 | 21.08 | 24.35 | 3.06 | 21.30 |
| $MnL_4(ClO_4)_2 \cdot 2H_2O$ | pale pink | 26.95 | 3.31 | 23.08 | 26.17 | 3.29 | 22.89 |
| $MnL_4(NO_3)_2$ | pale pink | 30.78 | 3.61 | 31.82 | 30.82 | 3.23 | 31.46 |
| $FeL_2Cl_2$ | cream | 27.61 | 2.94 | 24.42 | 27.54 | 2.89 | 24.08 |
| $FeL_2Br_2$ | yellow | 21.64 | 2.19 | 19.12 | 21.94 | 2.30 | 19.19 |
| $CoL_2Cl_2$ | blue | 27.39 | 2.77 | 24.34 | 27.29 | 2.86 | 23.87 |
| $CoL_2Br_2$ | blue | 21.86 | 2.25 | 18.70 | 21.79 | 2.29 | 19.06 |
| $CoL_4I_2$ | blue | 26.34 | 2.74 | 22.85 | 25.38 | 2.66 | 22.20 |
| $CoL_4(ClO_4)_2 \cdot 2H_2O$ | lilac | 26.35 | 3.53 | 22.45 | 26.03 | 3.28 | 22.77 |
| $CoL_5(ClO_4)_2$ | purple | 29.49 | 3.04 | 25.92 | 29.53 | 3.10 | 25.83 |
| $CoL_2(NO_3)_2$ | cerise | 24.06 | 2.41 | 28.50 | 23.72 | 2.49 | 27.66 |
| $CoL_4(NO_3)_2 \cdot 2H_2O$ | lilac | 28.37 | 3.28 | 29.70 | 28.97 | 3.65 | 29.56 |
| $NiL_2Cl_2 \cdot 3H_2O$ | yellow | 23.98 | 3.46 | 20.52 | 23.67 | 3.97 | 20.71 |
| $NiL_2Br_2 \cdot 6H_2O$ | yellow | 17.44 | 3.00 | 15.03 | 17.51 | 4.05 | 15.31 |
| $NiL_4I_2 \cdot 2H_2O$ | yellow | 24.38 | 2.82 | 19.80 | 24.24 | 3.05 | 21.20 |
| $NiL_6(NO_3)_2 \cdot 2H_2O$ | green | 32.59 | 3.87 | 33.70 | 32.56 | 3.87 | 31.64 |
| $CuL_2Cl_2$ | blue | 27.19 | 2.75 | 23.74 | 26.94 | 2.83 | 23.56 |
| $CuL_2Br_2$ | green | 21.81 | 2.30 | 19.06 | 21.57 | 2.26 | 18.86 |
| $CuL_4(ClO_4)_2 \cdot CH_3OH$ | violet | 27.58 | 2.91 | 22.75 | 27.63 | 2.91 | 22.75 |
| $CuL_4(ClO_4)_2 \cdot C_2H_5OH$ | violet | 28.47 | 3.25 | 19.09 | 28.71 | 3.48 | 22.32 |
| $CuL_4(ClO_4)_2 \cdot 2H_2O$ | blue | 25.95 | 3.15 | 22.68 | 25.87 | 3.26 | 22.62 |
| $CuL_4(NO_3)_2 \cdot CH_3OH$ | lilac | 30.28 | 2.96 | 31.01 | 30.75 | 3.64 | 29.53 |
| $CuL_4(NO_3)_2 \cdot C_2H_5OH$ | lilac | 31.59 | 4.04 | 27.60 | 31.89 | 4.05 | 28.92 |
| $ZnL_2Cl_2$ | white | 27.02 | 2.78 | 23.48 | 26.80 | 2.81 | 23.44 |
| $ZnL_2Br_2$ | white | 21.50 | 2.36 | 18.75 | 21.48 | 2.25 | 18.78 |
| $ZnL_2I_2$ | white | 18.24 | 2.15 | 15.21 | 17.75 | 1.86 | 15.52 |
| $ZnL_4(ClO_4)_2$ | white | 27.71 | 2.90 | 23.93 | 27.12 | 2.84 | 23.71 |
| $ZnL_4(NO_3)_2$ | white | 30.68 | 3.01 | 28.97 | 30.32 | 3.18 | 30.94 |



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Weiss and Venner [3, 4] prepared the complexes $CuL_4(ClO_4)_2 \cdot 2H_2O$, $CoL_2(NCS)_2$, $NiL_3(NCS)_2 \cdot 3H_2O$ and $NiL_4(NCS)_2 \cdot 3H_2O$. The structure of $CuL_2Cl_2$ has been determined by X-ray crystallography [5] and, more recently, $CdL_2Cl_2 \cdot 1.5H_2O$ and $ZnL_2Cl_2 \cdot 0.5H_2O$ have been synthesised [6]. However, there appears to have been no systematic survey of the types of complex formed by this ligand. The complexes we have prepared, using the metal ions manganese to zinc are listed in Table I.

## Experimental

### *Preparation of Complexes*

The following general method was used. A warm solution of the metal salt in ethanol was added to a warm suspension of an equimolar amount of cytosine also in ethanol. After a few minutes heating and stirring, a clear solution was formed. The complexes precipitated either spontaneously after about ten minutes, or on evaporation of the solution to small bulk. In a few cases it was necessary to add ether to induce precipitation.

The iron(II) complexes were prepared under nitrogen, and a 2:1 mole ratio of cytosine to metal salt was used for these and for $CoL_2(NO_3)_2$. For $CoL_5(ClO_4)_2$ a 4:1 ratio was used.

The zinc complexes, the cobalt chloro- and bromo-complexes, and $CuL_4(ClO_4)_2 \cdot MeOH$ were prepared by a similar method from methanol, $CuL_4(ClO_4)_2 \cdot 2H_2O$ from water and $NiL_4I_2 \cdot 2H_2O$ from ethyl acetate.

Physical measurements were made as described previously [2].

## Results

### *Complexes of Stoichiometry $ML_2X_2$*

Most of the metal halides formed complexes of this type. The geometry of $CuL_2Cl_2$ is known [5] to be essentially planar with a *trans*-$CuN_2Cl_2$ chromo-

TABLE II. Far Infrared Spectra.

| Compound | $\nu$(M–X) | $\nu$(M–L) | Ligand | Unassigned |
|---|---|---|---|---|
| Cytosine | | | 442vs, 420vs, 233m, 199m, 112s, 93s | |
| $MnL_2Cl_2$† | 268vs | 230vs | 440vs, 432vs, 396vs, 204m | |
| $MnL_2Br_2$ | 208vs, 191sh | 257m, 243mw | 442vs, 431s, 388vs, 222sh, 122sh, 91m | 157w |
| $MnL_4I_2 \cdot 2H_2O$ | | 237ms, 209s | 431vs, 370w, 191ms, 129w | 170vs |
| $MnL_4(ClO_4)_2 \cdot 2H_2O$† | | 309*w, 216w | 432vs, 405sh, 393vs, 234w | |
| $MnL_4(NO_3)_2$† | | 222sh | 424vs, 409sh, 398vs | |
| $FeL_2Cl_2$† | 272vs, br | | 438vs, 429vs, 397vs, 227m | |
| $FeL_2Br_2$ | 223vs, 205vs | 269m, 247w | 442vs, 433vs, 399vs, 122m | 161w, 148w |
| $CoL_2Cl_2$† | 282vs | 265sh, 252sh | 444s, 435s, 401s, 232w | |
| $CoL_2Br_2$† | 219vs | 272ms, 252ms | 444vs, 435vs, 402vs | |
| $CoL_4I_2$ | | 287vs, 265sh, 253w | 443s, 434s, 403s, 231w, 127m | 161w |
| $CoL_4(ClO_4)_2 \cdot 2H_2O$† | | 306*sh, 222w | 431vs, 422vs, 405w, 395vs | |
| $CoL_5(ClO_4)_2$† | | 278m, 252ms | 421vs, 234w | |
| $CoL_2(NO_3)_2$† | 306sh, 289m, | 253sh, 216w | 438sh, 414vs, 235w | |
| $CoL_2(NO_3)_2 \cdot 2H_2O$† | | 210w | 414vs, br | |
| $NiL_2Cl_2 \cdot 3H_2O$† | 250vs, br | 300*sh | 425vs, 393vs | |
| $NiL_2Br_2 \cdot 6H_2O$ | 191sh, 180s | 300*m, 273sh | 427vs, 390sh, 235m | |
| $NiL_4I_2 \cdot 2H_2O$ | | 299*m, 264m | 427vs, 409sh, 130w, 93m | 173ms, 148w |
| $NiL_6(NO_3)_2 \cdot 2H_2O$† | | 300*w, 228sh | 423vs, 415s, 390s | |
| $CuL_2Cl_2$† | 296vs | 257s, 243w | 447vs, 433vs, 225w | |
| $CuL_2Br_2$† | 232vs | 292s, 276w, 256s | 445vs, 425vs | |
| $CuL_4(ClO_4)_2 \cdot CH_3OH$† | | 285vs | 438vs, 404vs, 221w | |
| $CuL_4(ClO_4)_2 \cdot 2H_2O$† | | 283s, 270s, 216vs | 434vs, 400vs | |
| $CuL_4(NO_3)_2 \cdot CH_3OH$† | | 287s | 438vs, 411s, 397sh, 212m | |
| $ZnL_2Cl_2$† | 270vs | | 443vs, 434vs, 415vs, 227w, 202m | |
| $ZnL_2Br_2$ | 205vs, 194sh | 268ms, 253ms | 442vs, 437vs, 407vs, 126m | 166w, 142m |
| $ZnL_2I_2$ | 176vs | 272ms, 220s | 427vs, 411vs, 196sh | 138w |
| $ZnL_4(ClO_4)_2$† | | 277w, 253s | 445vs, 421vs, 230w | |
| $ZnL_4(NO_3)_2$† | | 277w, 251s | 420vs, 230w | |

†450–200 $cm^{-1}$ region only. *Probably $\nu(M{-}OH_2)$ mode.

phore, and the oxygen atoms of the cytosine weakly coordinated above and below the plane. The infrared and electronic spectra of the corresponding bromide are so similar to those of the chloride as to suggest virtually identical structures for the two complexes. The very strong absorption at 296 and 232 $cm^{-1}$ (Table II) may be identified as due to $\nu(Cu–Cl)$ and $\nu(Cu–Br)$ respectively, with strong bands at 256 $cm^{-1}$ (chloride) and 257 and 292 $cm^{-1}$ (bromide) being due to vibrations with considerable $\nu(M–N)$ character. Any $\nu(M–N)$ at 280–310 $cm^{-1}$ in the chloride would be hidden by $\nu(Cu–Cl)$.

The chloro- and bromo-complexes of both iron(II) and cobalt(II) are shown by their electronic spectra (Table III) to have essentially tetrahedral structures, probably with $MN_2X_2$ chromophores. For cobalt, the $\nu_2(^4A_2 \rightarrow {}^4T_1(F))$ transition does not show the splitting usually seen for compounds of this type. However, this splitting is normally decreased when the nitrogen donor is α-substituted, probably for steric reasons. Since cytosine is effectively α-substituted, a rather small splitting might be expected. For manganese(II), the e.s.r. spectrum of the bromo-complex gives a strong band near $g_{eff}$ = 3.6, with many weaker lines up to about 1160 mT. This suggests that the complex is monomeric, with either a tetrahedral or distorted octahedral $(MnN_2O_2Br_2)$ structure. For these complexes, and also for $ZnL_2X_2$, the similarity of the far-infrared spectra to those of the iron and cobalt complexes is evident (Table II), and essentially tetrahedral structures are proposed for them all.

However, the values of $\nu(M–X)$ are towards the low end of the ranges normally observed in tetrahedral complexes, and there may perhaps be weak interaction of the metal ions with the C=O groups of the cytosine. The effect is much less marked, though, than in the complexes of pyrimidine-2-thione [7], where the exocyclic sulphur interacts more strongly with the metal ion.

### *Anhydrous Complexes of Metal Nitrates and Perchlorates*

The complex $CoL_2(NO_3)_2$ appears from its electronic spectrum (Table III) and magnetic moment of 4.38 to be analogous to the many complexes of this stoichiometry having chelating nitrate groups and distorted octahedral geometry.

The anhydrous complex obtained with cobalt perchlorate has the stoichiometry $CoL_5(ClO_4)_2$. The same stoichiometry was found in the case of pyrimidine-2-one [8], and the two complexes appear to be very similar. The electronic spectrum, and magnetic moment of 4.41, suggest a tetrahedral $CoN_4$ unit, with a Δ value of about 5100 $cm^{-1}$, analogous to that found, for example, in Co(benzimidazole)$_4$-$(ClO_4)_2$. The role of the fifth molecule of cytosine is not clear, but X-ray powder patterns showed no trace of unreacted cytosine.

The far infrared spectrum of this compound showed two medium to strong bands at 278 and 252 $cm^{-1}$, assigned as essentially Co–N stretches. For both $ZnL_4(ClO_4)_2$ and $ZnL_4(NO_3)_2$ a similar pair of bands was observed, though with considerably less intensity in the higher energy band. Moreover, these two complexes gave very similar spectra to $CoL_5$-$(ClO_4)_2$ in the $\nu(C=O)$ region (Table IV). It seems probable that these also contain tetrahedral $ZnL_4$

TABLE III. Electronic Spectra of the Complexes.

| Compound | Band Maxima ($cm^{-1}$) |
|---|---|
| $FeL_2Cl_2$ | 4760vs, 5710vs |
| $FeL_2Br_2$ | 4690vs, 5620vs |
| $CoL_2Cl_2$ | 7410vs, 16860vs, 20000sh, 23700sh |
| $CoL_2Br_2$ | 7140vs, 16130vs, 17240sh, 23250sh |
| $CoL_4I_2$ | 7140vs, 16000vs, 17150sh |
| $CoL_4(ClO_4)_2 \cdot 2H_2O$ | 8000w, br, 18420m, br |
| $CoL_5(ClO_4)_2$ | 8770s, 17540vs, 19610s |
| $CoL_2(NO_3)_2$ | 8680s, 18180vs, 19230sh |
| $CoL_4(NO_3)_2 \cdot 2H_2O$ | 8330w, br, 18180m, br |
| $NiL_2Cl_2 \cdot 3H_2O$ | 8000w, br, 13990w, 24100m, br |
| $NiL_2Br_2 \cdot 6H_2O$ | 7690w, br, 13330w, 23250m, br |
| $NiL_4I_2 \cdot 2H_2O$ | 8000w, br, 13800w, 24100sh |
| $NiL_6(NO_3)_2 \cdot 2H_2O$ | 8160vw, br, 14290vw, 24690w |
| $CuL_2Cl_2$ | 15870vs |
| $CuL_2Br_2$ | 15870vs |
| $CuL_4(ClO_4)_2 \cdot CH_3OH$ | 18350s, 15150sh |
| $CuL_4(ClO_4)_2 \cdot C_2H_5OH$ | 18520s, 14600sh |
| $CuL_4(ClO_4)_2 \cdot 2H_2O$ | 16260s, br |
| $CuL_4(NO_3)_2 \cdot CH_3OH$ | 17240s, 14390sh |
| $CuL_4(NO_3)_2 \cdot C_2H_5OH$ | 17860s, 14710sh |

TABLE IV. Spectra in the ν(C=O) Region ($cm^{-1}$).

| | |
|---|---|
| Cytosine (L) | 1703, 1662, 1615 |
| $MnL_2Cl_2$ | 1676, 1658, 1601 |
| $MnL_2Br_2$ | 1676, 1656, ~1621, 1593 |
| $MnL_4I_2 \cdot 2H_2O$ | 1682, 1645, 1620, 1597 |
| $MnL_4(ClO_4)_2 \cdot 2H_2O$ | 1730, 1683, 1646, 1610, 1575 |
| $MnL_4(NO_3)_2$ | 1712, 1660, 1601 |
| $FeL_2Cl_2$ | 1670, 1635, 1605 |
| $FeL_2Br_2$ | 1665, 1630, 1600 |
| $CoL_2Cl_2$ | 1668, 1633, 1605 |
| $CoL_2Br_2$ | 1663, 1630, 1603 |
| $CoL_4I_2$ | 1668, 1632, 1607 |
| $CoL_5(ClO_4)_2$ | 1650, 1627, 1610, 1572 |
| $CoL_4(ClO_4)_2 \cdot 2H_2O$ | 1725, 1705, 1655, 1610 |
| $CoL_2(NO_3)_2$ | 1670, 1635, 1610 |
| $CoL_4(NO_3)_2 \cdot 2H_2O$ | 1718, ~1651, ~1611 |
| $NiL_2Cl_2 \cdot 3H_2O$ | 1730, 1665, ~1620 (br), 1563 |
| $NiL_2Br_2 \cdot 6H_2O$ | 1730, 1660, ~1620 (br), 1560 |
| $NiL_4I_2 \cdot 2H_2O$ | 1724, ~1650, ~1601, 1560 |
| $NiL_6(NO_3)_2 \cdot 2H_2O$ | 1734, 1666, 1642, 1617 |
| $CuL_2Cl_2$ | 1676, ~1656, ~1621 |
| $CuL_2Br_2$ | 1683, 1660, 1630 |
| $CuL_4(ClO_4)_2 \cdot CH_3OH$ | ~1660br, 1615 |
| $CuL_4(ClO_4)_2 \cdot 2H_2O$ | ~1660br, ~1620br |
| $CuL_4(NO_3)_2 \cdot CH_3OH$ | ~1640v, br |
| $ZnL_2Cl_2$ | 1675, 1649, 1612 |
| $ZnL_2Br_2$ | 1675, 1637, 1610 |
| $ZnL_2I_2$ | 1675, 1637, 1625 |
| $ZnL_4(ClO_4)_2$ | 1657, 1630, 1610, 1580 |
| $ZnL_4(NO_3)_2$ | 1652, 1628, 1610sh, 1580 |

groupings, with N-bonded cytosines. The decreased intensity of the band at 277 $cm^{-1}$ suggests that the tetrahedron may be more nearly regular in the zinc complexes, the appearance of two bands being due to distortion. All of these complexes show, in fact, a weak band at 230 to 234 $cm^{-1}$, which may be the symmetric M–N stretch, but which may also be a ligand band.

Copper perchlorate and copper nitrate yield complexes of the type $CuL_4X_2 \cdot S$ where S is methanol or ethanol. These compounds have very similar electronic spectra. The X-ray crystal structure of $CuL_4(ClO_4)_2 \cdot CH_3OH$ has been determined in this Department [9]. It shows the copper to be surrounded by four nitrogen atoms, with cytosine oxygen atoms above and below the plane (two at 2.70 Å and two at 2.82 Å). The metal–ligand stretch occurs as a strong band near 285 $cm^{-1}$.

### *Hydrated Complexes*

The compound $CuL_4(ClO_4)_2 \cdot 2H_2O$ appears to be similar to the alcohol solvates described above, but with the water molecules probably weakly coordinated in place of the cytosine oxygens. The ligand field deviates more from the rigorously planar (Table III).

The other hydrated complexes with the exception of $MnL_4I_2 \cdot 2H_2O$, differ in several respects from the compounds described above. Firstly, in the majority of cases there are no medium to strong bands at 230–290 $cm^{-1}$ assignable as metal–ligand stretches. Secondly, the ligand fields in the cobalt and nickel complexes are much weaker than would be expected with nitrogen donors, and, thirdly, they have medium to strong absorption at 1700–1750 $cm^{-1}$ (Table IV).

This last observation would be consistent with the presence of an $LH^+$ cation, but we could find no evidence for this in the analyses and moreover, the remainder of the infrared spectrum resembled that of cytosine more closely than that of its hydrochloride. All of the observations could be explained if the cytosines were hydrogen bonded to water molecules, which were in turn coordinated to the metal ion. All of these complexes show weak, broad, absorption near 300 $cm^{-1}$, as expected for aquo-complexes.

Alone amongst this group of compounds, $NiL_4I_2 \cdot 2H_2O$ shows a medium intensity band at 264 $cm^{-1}$. Perhaps in this case the ligand field is of the $NiN_2O_2I_2$ type, with only two of the cytosines hydrogen bonded. The band at 1724 $cm^{-1}$ is weaker than in most of the other hydrates.

The complex $MnL_4I_2 \cdot 2H_2O$ has no absorption at 1700–1750 $cm^{-1}$, and has at least one band assignable as an Mn–N stretch. The e.s.r. spectrum shows only a broad $g_{eff} = 2$ signal, as is commonly found when extensive hydrogen bonding is present.

### *The Compound $CoL_4I_2$*

This is the only anhydrous iodide obtained with a 4:1 ratio of cytosine to metal ion. The electronic spectrum is entirely consistent with a tetrahedral chromophore, but the ligand field is much weaker than in $CoL_5(ClO_4)_2$, with Δ about 4100 $cm^{-1}$. The complex is bright blue, and the electronic spectrum shows no trace of a low-energy charge-transfer band such as is normally seen when iodide ions are coordinated to cobalt(II). Moreover, there is no band in the far infrared assignable as ν(Co–I). The low-energy spectrum is dominated by a rather broad, very intense band at 278 $cm^{-1}$, fairly close in energy to that assigned in other complexes a ν(M–N) (Fig. 1). We suggest that, in this complex, either two of the cytosines are N-bonded as usual, and the other two O-bonded, or, less probably, two of the cytosines are chelating, and the other two are hydrogen bonded. The spectrum of this compound in the C=O stretching region shows no significant difference from those of the N-bonded complexes.

## Discussion

It is clear cytosine readily forms complexes with a variety of metal ions. With metal halides, four-coordinate $MN_2X_2$ complexes appear to be preferred, probably with additional weak bonding by the exo-

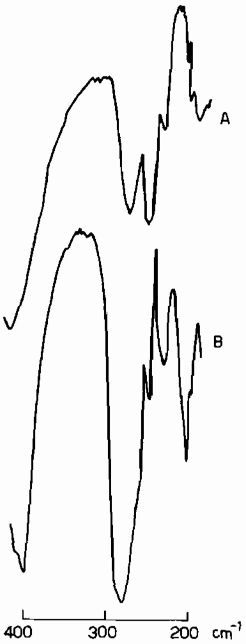

Fig. 1. Infrared spectra (200–400 $cm^{-1}$) of A, $CoL_5(ClO_4)_2$; B, $CoL_4I_2$.

cyclic oxygen in most cases. This type of bonding seems unfavourable, though, in complexes with higher coordination number. In these compounds the presence of water molecules, to which the cytosines are probably hydrogen bonded, seems to be necessary for the formation of complexes.

There is also evidence that, at least in $CoL_4I_2$, the cytosine may bond through the C=O group. Weak interaction of such groups with metal ions has frequently been suggested, and has excited considerable interest. However, it has only recently been shown that uracils may bond strongly to metal ions through C=O groups [10]. Even so, it is surprising that this bond should form in preference to the M–N. A Co–$L_4$ tetrahedron must be sterically rather constrained when N-bonding is present, but the existence of $CoL_5(ClO_4)_2$ shows that it is not impossible.

What seems quite clear is that, if O-bonded cytosines are present in $CoL_4I_2$, then this mode of bonding will not easily be detected by infrared studies above 600 $cm^{-1}$.

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