Experiment 4S

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2nd Year Spring Term Synthesis Labs

Experiment 4S

Identification of Stereochemical (Geometrical) Isomers of $[Mo(CO)_4(L)_2]$ by Infrared Spectroscopy

20/01/2011-24/01/2011

Aims

The aim of this experiment is to perform two ligand exchanges to produce a $[Mo(CO)_4(PPh_3)_2]$ complex and use Infra-red spectroscopy to look at its geometrical isomerisation. This gives an idea of how infra-red is affected by cis and trans carbonyl stretches and also looks at the thermodynamic properties of cis and trans isomers. This information can also be used to look at the mechanism to which way ligand exchange can occur and how isomerisation can occur.

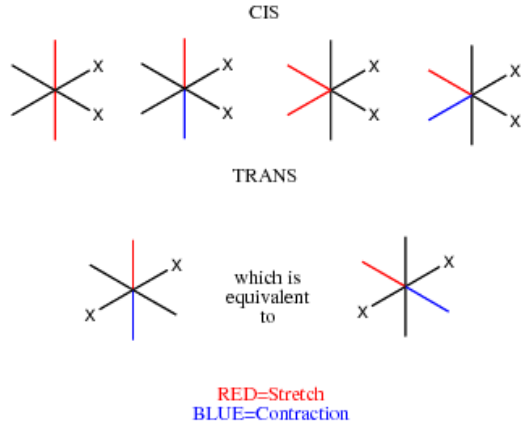
tick 1

IR Analysis

In a $[Mo(CO)_4(L)_2]$ the L ligand can either be cis or trans. This will effect the stretching in the C-O region of the IR spectra. This is due to the fact when the L ligands are cis to each other there are 4 different bond stretches/contractions that will cause a movement in the molecules dipole allowing it to be IR active. This is because the CO ligands are cis to each other being symmetrical movement will still cause a movement in the dipole. However when the CO ligands are cis to each them are opposite to ech other. This means when they both stretch symmetrically there is no overall change in the dipole and the stretch is not IR active. Only a stretch with the opposing ligand contracting will cause an absorption. This effect is increased due to each of the two stretches are completely in the same environment therefore making them appear as one absorption. Therefore the cis isomer will have four separate absorptions when the trans will have one[1]. The IR active stretches can be seen below.

tick 2

3



Part 1: $[Mo(CO)_4(pip)_2]$
C=O stretches are at 1890.2, 1839.4 and 1778.4 where the last is two separate peaks forming a broader peak. Therefore this is the *cis* isomer

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Part 2: $[Mo(CO)_4(PPh_3)_2]$
C=O stretches are at 1924.5, 1896.2, 1870.0 and the last is not very strong in signal just right of the last. Therefore this is the *cis* isomer

Part 3: $[Mo(CO)_4(PPh_3)_2]$
There is one C=O stretch at 1891.1
Therefore this is the *trans* isomer

N.B All values stated in cm^{-1}

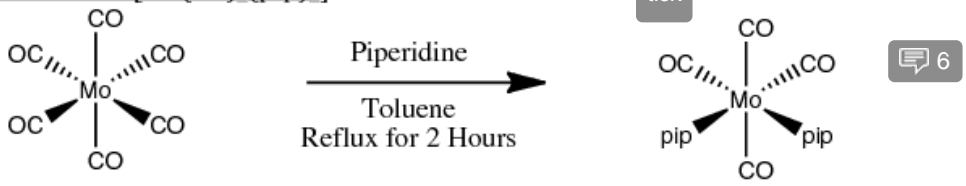
Another key feature to mention of the Infra-red spectrum of Product 1 is the collection of peaks between 1265.5-1340.4cm^{-1}. I believe these to be the C-N stretches present in the piperidine. This shows the reaction has gone to form the expected product

5

tick

Reaction Mechanisms

1.Preparation of $[Mo(CO)_4(pip)_2]$

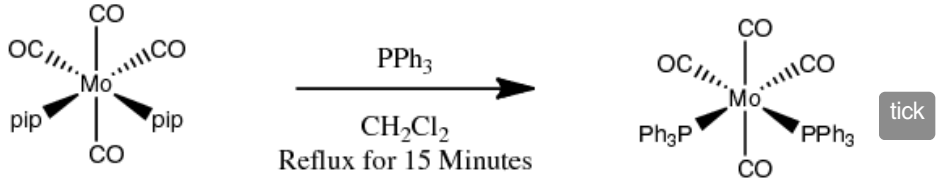


tick

6

1.248g (87%)
Mpt:100-120°C (lit.120°C[2])
Point Group:C_{2v}

2.Preparation of *cis* $[Mo(CO)_4(PPh_3)_2]$

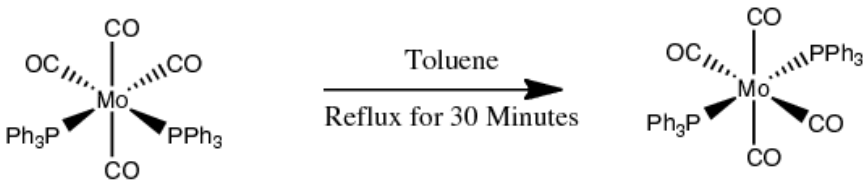


tick

0.785 (76%)
Mpt: 136-140°C (lit.148-150°C[2])
Point Group:C_{2v}

7

3.Preparation of *trans* $[Mo(CO)_4(PPh_3)_2]$



0.412 (82%)
Mpt:136-138°C (lit. 148-150°C[3])
Point Group:D_{4h}

8

Isomerisation

The isomerisation reaction can happen via a dissociative mechanism or a associative mechanism. Dissociative mechanism occurs in a similar way to a Sn1 mechanism where a ligand will break off lowering the oxidation state of the complex, and allowing another ligand or its self to bond back to the complex. This mechanism will happen when using bulky ligands. In this case PPh_3 due to the steric strain on the cis isomer, under reflux a phosphine group breaks away and bonds in a trans configuration. However for less bulky substituents a nucelophilic ligand attacks the metal centre kicking out a ligand, this is the associative mechanism similar to Sn2 mechanism. This would occur to a ligand such as P^nBu_3. This is because the cone angle of which metal centre is bonded to the ligand effects how easily a ligand can dissociate, for less bulky ligands the angle is small and the bond is harder to break meaning an associative mechanism occurs. Other factors that may be taken into account for which mechanism occurs is how easily the oxidation state can alter on the metal centre. The dissociative mechanism requires the oxidation state to lower when the associative mechanism will require the oxidation state to increase. This will mostly be affected by the electron withdrawing/donating properites of the ligands. If the ligands are electron withdrawing this means in the increased oxidation state can be stabilised by the electron density being pulled away meaning a associative mechanism is most likely when if the liagnds are electron donating the lower oxidation state can be stabilised therefore dissociative is preferred.

These arguments bring up the account for the thermodynamically unstable cis isomer. Under kinetic conditions the cis isomer is formed however when allowed to reach thermodynamically favoured conditions the cis isomer will convert to the trans isomer where the steric strain between the bulky ligands is minimised. This is shown with the IR evidence in the conversion from product 2 to 3. Therefore the trans isomer of $[Mo(CO)_4(PR_3)_2]$ is the more thermodynamically stable. tick 9

Conclusion

From this investigation it has been shown that Infra-red analysis is vital in the analysis of geometrical isomers of a octahedral complex. This could be applied to a lot more complexes, either other metal centres and ligands. From this it has also brought light upon the thermodynamic properties of geometrical isomers, which is also very important when synthesising specific molecules. This is also important because from all of this data we can modify reactions knowing the mechanism of which isomerisation and ligand exchange occurs. tick

References

1. M. Y. Darensbourg and D. J. Darensbourg, *J. Chem. Ed.* **1970**, *47*, 33.
http://jchemed.chem.wisc.edu/Journal/Issues/1970/Jan/jceSubscriber/JCE1970p0033.pdf
2. [1] Strohmeier, W.; Gerlach, K.; Hobe, D. Chemische Berichte 1961, 94, 164–168.
3. [1] A. D. Allen and P. F. Barrett, Phosphine-substituted carbonyl halide complexes of chromimum and molybdenum, Canadian Journal of Chemistry, Vol. 46, 1968, p. 1650

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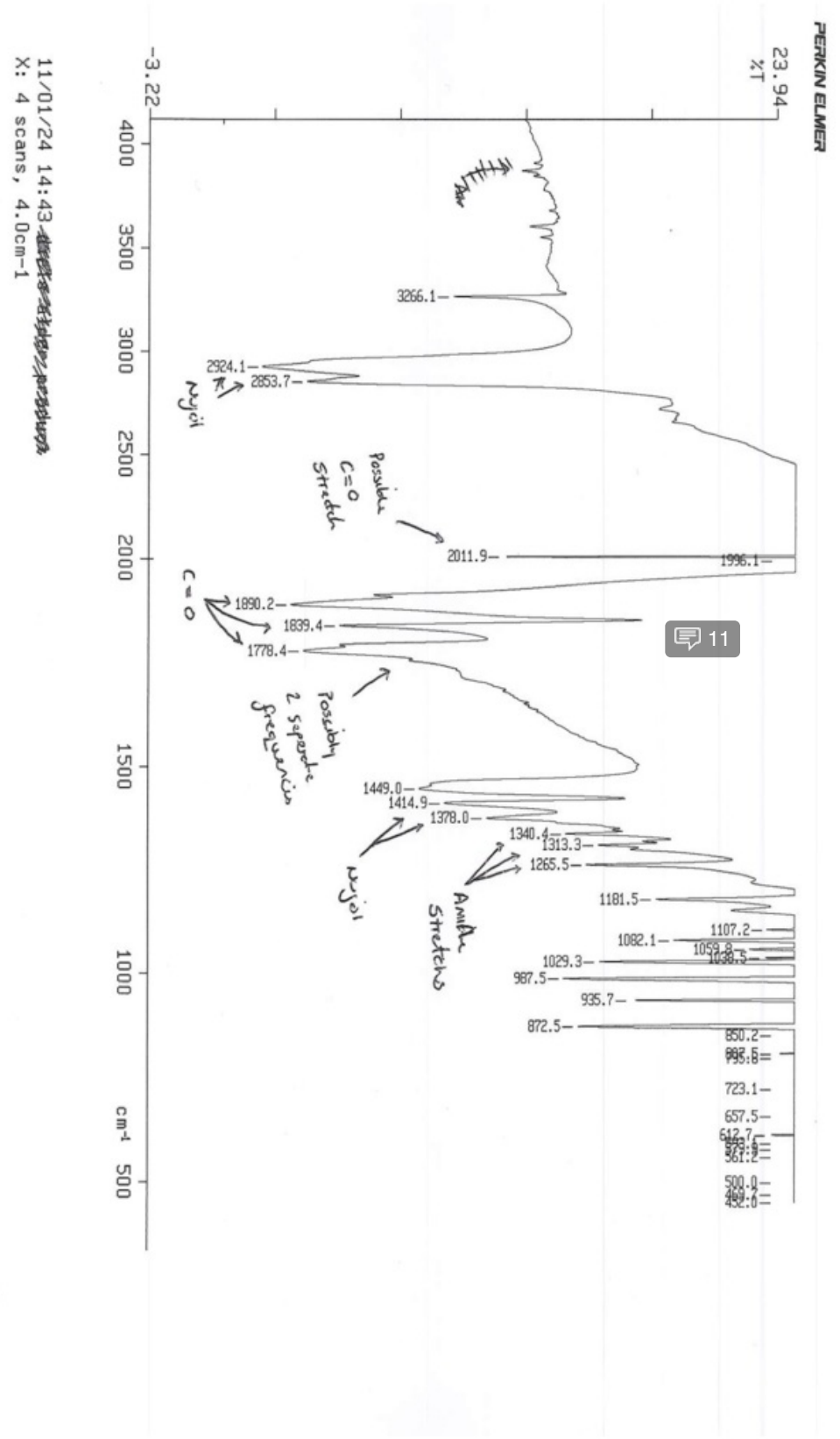
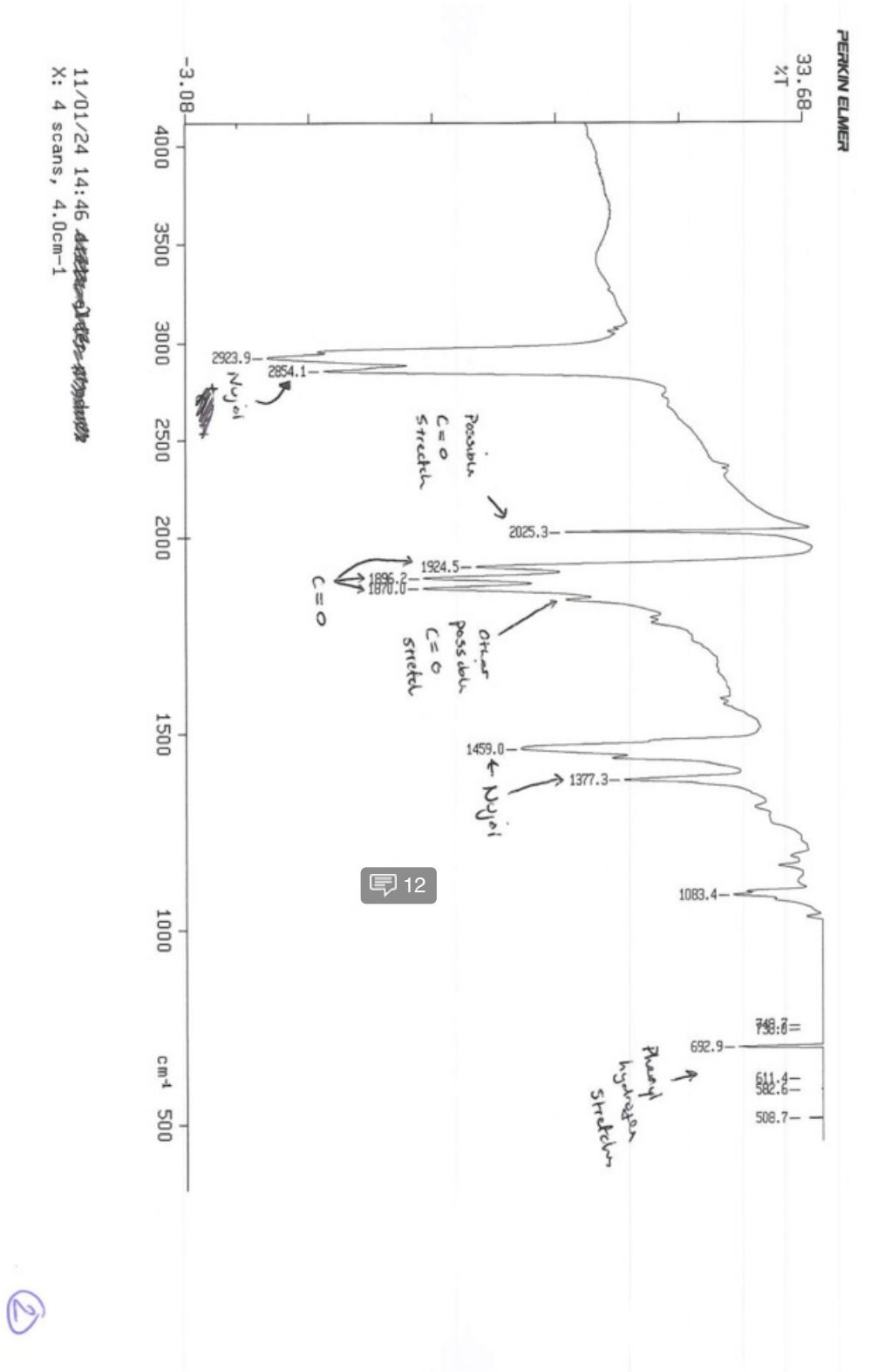
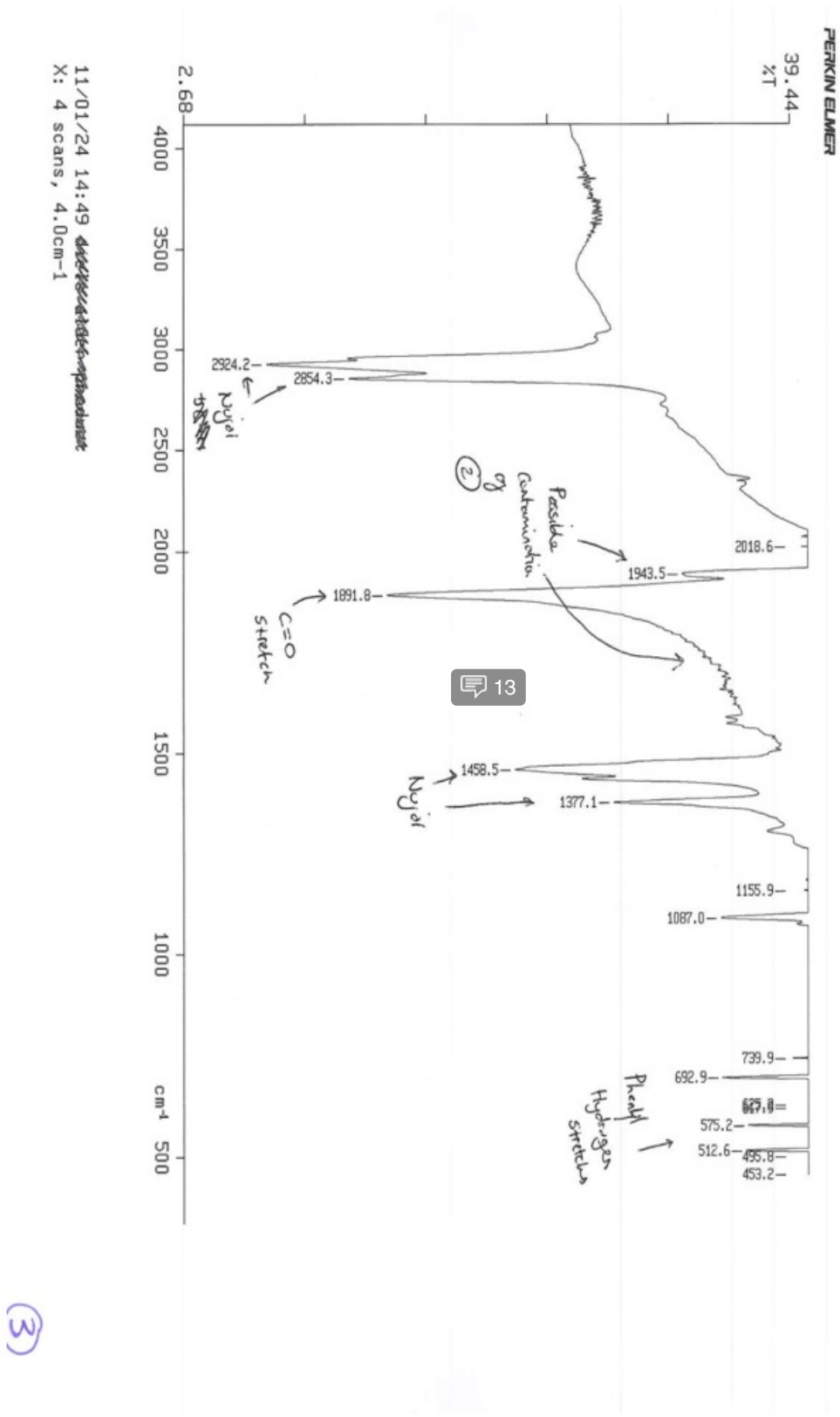
Additional Material

Page 04- Infra-red Spectrum of Product 1 : $[Mo(CO)_4(pip)_2]$ (0-4000cm^{-1})
Page 05- Infra-red Spectrum of Product 2 : *cis* $[Mo(CO)_4(PPh_3)_2]$ (0-4000cm^{-1})
Page 06- Infra-red Spectrum of Product 3 : *trans* $[Mo(CO)_4(PPh_3)_2]$ (0-4000cm^{-1})


PERKIN ELMER
23.94
%T
-3.22
11/01/24 14:43
X: 4 scans, 4.0cm-1
4000
3500
3000
2500
2000
1500
1000
500
cm-1
3266.1
2924.1
2853.7
Nujol
Possible C=O Stretch
2011.9
1996.1
C=O
1890.2
1839.4
1778.4
Possibly 2 Separate Frequencies
1449.0
1414.9
1378.0
Nujol
1340.4
1313.3
1265.5
Amide Stretch
1181.5
1107.2
1082.1
1059.8
1029.3
987.5
935.7
872.5
850.2
723.1
657.5
612.7
500.0
11


PERKIN ELMER
33.68
%T
-3.08
4000
3500
3000
2500
2000
1500
1000
500
cm-1
11/01/24 14:46
X: 4 scans, 4.0cm-1
2923.9
2854.1
Nujol
Possible C=O stretch
2025.3
1924.5
1896.2
1870.0
C=O
Other possible C=O stretch
1459.0
1377.3
Nujol
1083.4
748.7
730.0
692.9
Phenyl hydrogen stretching
611.4
582.6
508.7

12


PERKIN ELMER
%T
39.44
2.68
4000
3500
3000
2500
2000
1500
1000
500
cm-1
11/01/24 14:49
X: 4 scans, 4.0cm-1
2924.2
2854.3
2018.6
1943.5
1891.8
1458.5
1377.1
1155.9
1087.0
739.9
692.9
575.2
512.6
495.8
453.2
C=O stretch
Possible contamination
Phenyl Hydrogen stretches

GRADEMARK REPORT

FINAL GRADE
/ 0

GENERAL COMMENTS

A good report has been written. A nice introduction stating the aims of the experiment and a good discussion as to why different numbers of peaks are seen for each complex. The discussion of the questions is good but try to break it up with a separate paragraph for each question.

A

PAGE 1

√

1. Good aims section and a nice start to the report.

√

2. This should say trans rather than cis

3. This is a good discussion but remember to read through reports to make sure you have written the correct isomers.

4. The peak at 2011cm-1should be quoted as your final CO stretch for both part 1 and part 2 complexes

5. The first person shouldn't be used in lab reports.

√

PAGE 2

√

6. This is a good reaction scheme but draw the piperidine ligands out to show you know what their structure is and how they are coordinated.

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7. Melting point is a bit low compared to the literature value but the point group has been correctly assigned

8. Reaction schemes are well drawn and point groups have been correctly assigned.

PAGE 3

√

9. You have answered the questions correctly and the discussion is good however it is easier to read if there are breaks between each question being answered rather a large paragraph.

√

10. Internet sources for journal references do not need to be included in the reference list.

PAGE 4

11. Spectrum shows the CO peaks but do not let the spectrum go off the page as can be seen by the flat top.

PAGE 5

12. This is a good spectrum and clearly shows the CO stretches in this complex

PAGE 6

13. Good spectrum but make sure the top of the spectrum is not lost off the top of the page.