

**Fourier Transform Infrared Study
of Dichlorodioxochromium(VI),
Dichlorodioxomolybdenum(VI)
and Dichlorodioxotungsten(VI) Complexes
with 2,2'-Bipyridine***

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The Fourier transform infrared spectra of the 2,2'-bipyridine complexes of dichlorodioxochromium(VI), dichlorodioxomolybdenum(VI) and dichlorodioxotungsten(VI) were studied in the 4000 to 400 cm^{-1} region. The assignment of the bands originating from vibrations mainly localized in the bipyridine ligand is relatively straightforward. The essentially pure MO_2 stretching vibrations give rise to very strong bands, the separation of which increases in the order $\text{Cr} < \text{Mo} < \text{W}$ as a consequence of the greater sensitivity of the antisymmetric stretching O–M–O vibration to the changes in the mass of the M atoms. For this to be true, the symmetric stretching vibration should have a higher frequency than the antisymmetric one. The results of the preliminary *ab initio* HF SCF calculations on simple model structures are in line (at least qualitatively) with such a conclusion.

Key words: FTIR spectra, *ab initio* HF SCF, (2,2'-bipyridine)dichlorodioxochromium(VI), (2,2'-bipyridine)dichlorodioxomolybdenum(VI), (2,2'-bipyridine)dichlorodioxotungsten(VI).

* Dedicated, with utmost pleasure, to our dear friend and colleague Professor Boris Kamenar on the occasion of his 70th birthday and in recognition of his remarkable contributions to the structural chemistry (including that of molybdenum).

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INTRODUCTION

Continuing our work on the vibrational spectra of various 2,2'-bipyridine and 4,4'-bipyridine derivatives,¹⁻⁴ we now report the FTIR spectra (recorded at both room and liquid-nitrogen temperature) of the three title compounds. A very brief account of this work is given in Ref. 5.

All three compounds have been known for some time.⁶⁻⁸ To the best of our knowledge, the crystal structure has been determined only for the tungsten compound,⁹ although that of the 2,2'-bipyridine complex of dibromodioxomolybdenum(VI) has been known for quite some time.¹⁰ Apart from the spectroscopic data in our own work,⁴ some other infrared data for these compounds are available.^{8,9,11-14} However, as a rule, they are incomplete and (more often than not) only the bands due to the OMO stretching modes are mentioned (in some cases, a few additional frequencies are given, with or without assignment). The most comprehensive (but still far from complete) is the work of Butcher *et al.*¹² on several dihalodioxomolybdenum(VI) complexes including the bipyridine one. However, only the MoO₂Cl₂ fragment is treated, the ligand bands being omitted (in the case of the dimethylformamide complex, the assignment of the bands believed to originate from modes localized mainly in the studied fragment is supported by a normal coordinate analysis). In all mentioned papers, two very strong bands appearing in the 1000–900 cm⁻¹ region are assigned to the two stretches of the MO₂ fragment, from which the logical conclusion is drawn that the fragment is non-linear. It should be mentioned that a very long time ago we concluded on similar grounds that the WO₂ and MoO₂ groups must be bent,^{15,16} this being later shown directly, including here the work of Professor Kamenar and his co-workers on some dioxomolybdenum(VI) complexes.^{17,18} The analysis of the vibrational spectra and determination of the crystal structures indicated that the MO₂ fragments are nonlinear not only in complexes (*e.g.* Refs. 19–21) but also in the uncomplexed MO₂X₂ compounds (M = Cr, Mo, W; X = F, Cl or Br).^{22,23} As a rule, in the 1000–900 cm⁻¹ region, the band at higher frequency is assigned (if at all) to the antisymmetric MO₂ stretching and that at lower frequency to the symmetric MO₂ stretching, an assignment apparently based on the situation usually encountered in small triatomic molecules such as water. On the other hand, Kamenar and Penavić²⁴ state that the symmetric MoO₂ stretching vibration appears around 930 cm⁻¹ and the antisymmetric one near 890 cm⁻¹, and identical assignment is made in our work.⁴

The existence of assignments for various bipyridine complexes based on a normal coordinate analysis,²⁵ our experience with such compounds² (and with MO₂ complexes), the availability of equipment superior to that previously used and, especially, the fact that all three title compounds could be

studied simultaneously motivated us to reinvestigate, by Fourier transform infrared (FTIR) methods, the 2,2'-bipyridine complexes of dichlorodioxochromium(VI), dichlorodioxomolybdenum(VI) and dichlorodioxotungsten(VI). One of the main aims of this work was to settle (if possible) the question of correct assignments of the MO_2 stretching bands.

In order to support our experimental study, preliminary quantum mechanical calculations were carried out for hypothetical complexes consisting of MO_2Cl_2 molecules ($M = \text{Cr}, \text{Mo}$ or W), to which either an $\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2$ ligand (Figure 5b) or two NH_3 ligands (Fig. 5c) were assumed to be coordinated and which had to play the role of the actual 2,2'-bipyridine one (the details are described below). This was done in the belief that vibrations of the MO_2Cl_2 part of the three title molecules would be satisfactorily reproduced and the empirical assignments would be put on a safer ground (the results obtained for the actual MO_2Cl_2 molecules which are, apparently, polymeric are not exactly comparable to our case where the molecules composed of the corresponding MO_2Cl_2 fragments bonded to a 2,2'-bipyridine ligand are monomeric).

EXPERIMENTAL

The investigated complexes were prepared by methods which had been already described. The dioxochromium(VI) compound was synthesized following the procedure given by Majumder and Saha⁸ and the dioxomolybdenum(VI) and dioxotungsten(VI) ones by a method which is described in detail in Ref. 4 and consists of adding freshly synthesized MoO_2Cl_2 or WO_2Cl_2 to a tetrachloromethane solution of 2,2'-bipyridine. The two MO_2Cl_2 compounds themselves were prepared by passing (at 450 °C) a stream of chlorine gas over a 4:1 mixture of MO_3 and activated charcoal. The complexes were obtained as microcrystalline solids which could not be recrystallized owing to their poor solubility in the majority of solvents available to us. As it turned out, this resulted in the presence of impurities, which complicated the infrared spectra.

The Fourier transform infrared (FTIR) spectra were recorded, from pressed KBr disks, at room and at liquid nitrogen temperature (RT and LNT, respectively) using the Perkin Elmer System 2000 FT-IR instrument equipped with a variable temperature cell P/N 21525 (Graseby Specac) with KBr windows. The resolution was 4 cm^{-1} .

In order to get a theoretical basis for some of the assignments, an *ab initio* HF SCF study of the two model systems representing the coordination around the tungsten atom was performed. Full geometry optimizations were performed in redundant internal coordinates, the energy derivatives being computed analytically using Berny's optimization algorithm.²⁶ Numerical harmonic vibrational analysis was then done for the optimized geometries, the absence of negative frequencies and negative eigenvalues of the Hessian matrices for the stationary points found at the molecular potential energy hypersurfaces confirming that both structures correspond to real minima. All calculations were done within the standard LanL2DZ basis set (D95V²⁷

on the first row elements, and Los Alamos ECP plus DZ²⁸⁻³⁰ on the others), using the Gaussian94³¹ series of programs. The SymApps computer package was used to produce Figure 5 (see below).³²

RESULTS AND DISCUSSION

The FTIR spectra of the three studied complexes are shown in Figures 1–3. As seen, despite the above-mentioned microcrystallinity of the studied compounds, the spectral bands are, generally speaking, sharp. However, the

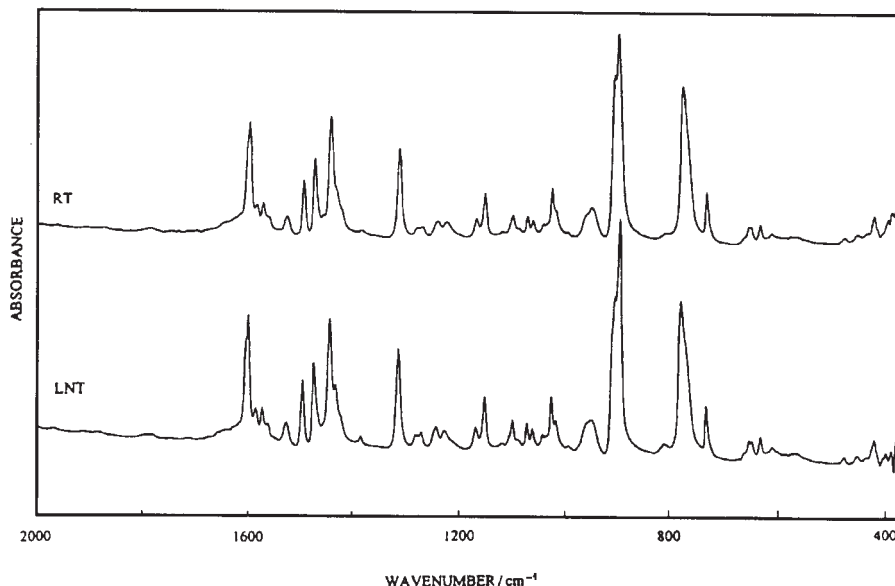


Figure 1. Fourier-transform infrared spectra of $\text{CrO}_2(\text{bpy})\text{Cl}_2$ recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT).

presence of broader bands (apparently due to oxide impurities) is an indication that the purity of our samples was not as it would have been desired (see above).

The bands, which are, beyond doubt, due to the vibrations in the coordinated 2,2'-bipyridine molecules, similar (in both shape and appearance) in the spectra of all three studied compounds and it is not difficult to assign them. The assignments of the 2,2'-bipyridine bands in the 2000–400 cm^{-1} region (based on the work by Strukl and Walter)²⁵ are summarized in Table I.

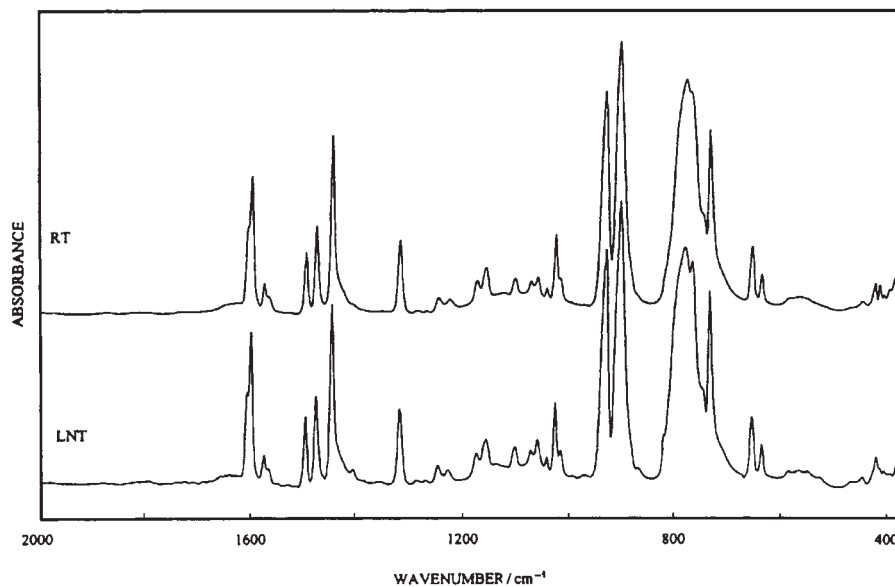


Figure 2. Fourier-transform infrared spectra of $\text{MoO}_2(\text{bpy})\text{Cl}_2$ recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT).

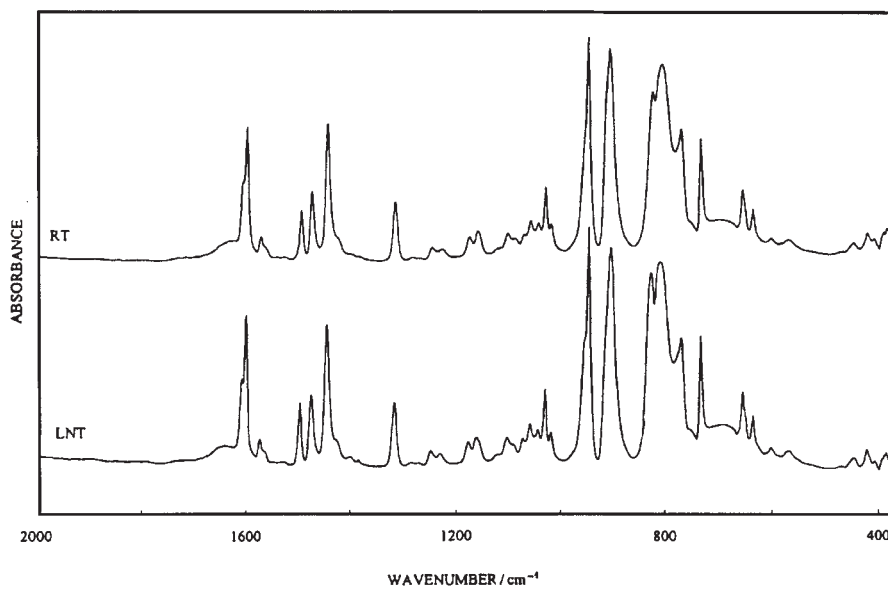


Figure 3. Fourier-transform infrared spectra of $\text{WO}_2(\text{bpy})\text{Cl}_2$ recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT).

TABLE I
Frequencies and assignments of the 2,2'-bipyridine bands in the
2000–400 cm⁻¹ region^a

| CrO ₂ (bpy)Cl ₂ | | MoO ₂ (bpy)Cl ₂ | | WO ₂ (bpy)Cl ₂ | | Assignment |
|---------------------------------------|----|---------------------------------------|----|--------------------------------------|----|---------------------------|
| 1605 | | 1605 | | 1608 | | ω |
| 1601 | s | 1602 | s | 1604 | s | |
| 1574 | | 1579 | | 1576 | | ω |
| 1564 | w | 1567 | w | 1568 | w | |
| 1496 | m | 1497 | m | 1498 | m | ω |
| 1475 | m | 1476 | m | 1477 | m | ω |
| 1443 | s | 1446 | s | 1448 | s | ω |
| 1432 | m | | | | | |
| 1315 | s | 1318 | s | 1319 | s | ω |
| 1283 | w | 1287 | vw | 1289 | vw | ring + inter-ring stretch |
| 1274 | w | 1274 | vw | 1272 | vw | |
| 1245 | w | 1248 | w | 1249 | vw | ω + δ |
| 1229 | w | 1231 | vw | 1232 | vw | |
| 1170 | w | 1177 | w | 1179 | w | δ |
| 1153 | m | 1158 | w | 1164 | w | δ |
| 1122 | vw | | | 1123 | vw | δ |
| 1101 | w | 1104 | vw | 1106 | vw | δ |
| 1072 | w | 1075 | vw | 1078 | vw | δ |
| 1064 | w | 1062 | vw | 1062 | vw | δ |
| 1027 | m | 1028 | m | 1032 | m | ring breathing |
| 1019 | m | 1018 | m | 1020 | m | |
| 779 | s | | | 771 | m | γ |
| 732 | w | 733 | m | 735 | m | γ |
| 655 | vw | 655 | w | 658 | w | Δ |
| 650 | vw | | | | | |
| 634 | w | 636 | w | 637 | w | Δ |
| 478 | vw | 468 | vw | 471 | vw | Γ |
| 453 | vw | 448 | vw | 448 | vw | Γ |
| 422 | w | 422 | w | 423 | w | Γ |

^a The meaning of the abbreviations is: ω – ring stretching; Δ – ring in-plane bending; Γ – ring out-of-plane bending; δ – C–H in-plane bending; γ – C–H out-of-plane bending; v – very; w –

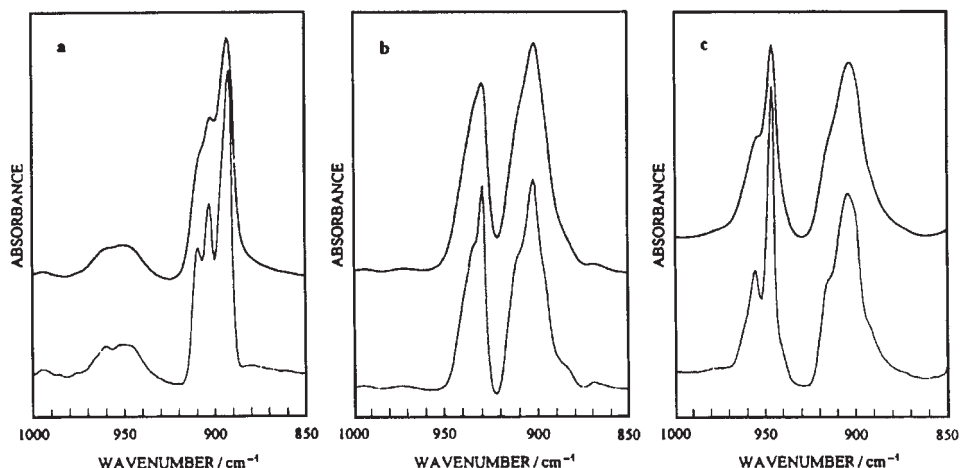


Figure 4. The region of the OMO stretching vibrations in the FTIR spectra of $\text{CrO}_2(\text{bpy})\text{Cl}_2$ (a), $\text{MoO}_2(\text{bpy})\text{Cl}_2$ (b) and $\text{WO}_2(\text{bpy})\text{Cl}_2$ (c); upper curves are the LNT traces and the lower ones are the result of self deconvolution.

The C–H stretching bands (as expected, they are found above 3000 cm^{-1}) are not reported.

The most interesting difference between the spectra of the three title compounds is found in the region where the stretching bands of the MO_2 groups ($M = \text{Cr}, \text{Mo}$ or W) are expected to appear (Figure 4). As seen, two very strong bands (or, rather, two groups of bands exhibiting, especially at low temperatures, observable splitting) appear in this region, the separation between them increasing in the order $\text{CrO}_2 < \text{MoO}_2 < \text{WO}_2$. Such behaviour was believed⁴ to be a consequence of the expected greater sensitivity of the antisymmetric stretching O–M–O vibration to the changes in the mass of the M atoms. In order for such an explanation to be true, the symmetric OMO stretchings must have higher frequencies than the antisymmetric ones.

To check this point, our *ab initio* analysis was carried out. As seen in Table II,* the main features of the optimized geometries for both models (referred to as structures in Figures 5b and 5c) are in satisfactory agreement with the X-ray crystallographic data, the minima on the molecular potential

* Since in the real structure the two oxygen and the two chlorine atoms are non-equivalent, two sets of data are given in Table II for the experimental structural parameters involving these atoms.

TABLE II

Comparison of the structural parameters (distances/pm, angles/deg) of $\text{WO}_2(\text{bpy})\text{Cl}_2^{\text{a}}$ and of the two model structures

| Parameter | $\text{WO}_2(\text{bpy})\text{Cl}_2$ | Structure in Fig. 5b | Structure in Fig. 5c |
|-----------|--------------------------------------|----------------------|----------------------|
| W–Cl | 236.72 and 235.54 | 247.00 | 246.39 |
| W–O | 174.47 and 179.18 | 169.51 | 169.68 |
| W–N | 226.36 and 228.73 | 235.09 | 236.19 |
| O–W–O | 106.65 | 107.08 | 105.31 |
| Cl–W–Cl | 159.50 | 152.12 | 150.95 |
| Cl–W–N | 82.11 and 81.00 | 77.97 | 77.91 |
| Cl–W–O | 96.70 and 95.52 | 98.22 | 98.74 |

^a Calculated on the basis of the data in Ref. 9.

energy hypersurfaces corresponding to *cis*-arrangement of the oxygen and *trans*-arrangement of the chlorine atoms, with a Cl–W–Cl angle which differs significantly from 180° (Figure 5). What is more important, the computed symmetric WO_2 stretching frequencies for both model structures (Table III) are indeed higher than the antisymmetric ones. The disagreement between the experimental and computed frequencies is not important for our present purposes since the latter are unscaled HF/LanL2DZ values and, moreover, the structures to which they pertain are only a rough approximation of the real one.

Taken all together, our present experimental data seem to indicate that the frequencies of the symmetric OMO stretching modes are higher than those of the antisymmetric ones and our *ab initio* analysis seems to prove

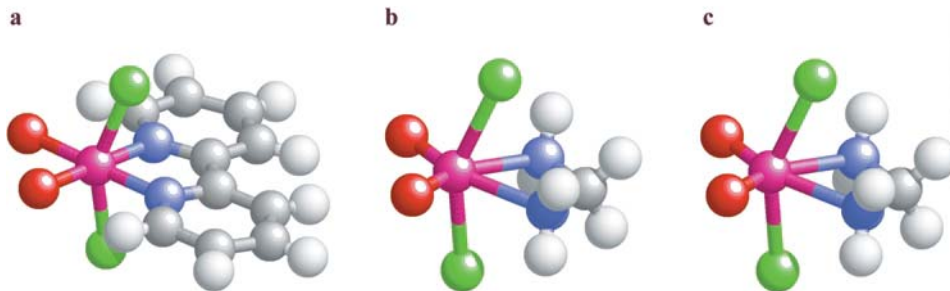


Figure 5. Representations of the experimental molecular structure of $\text{WO}_2(\text{bpy})\text{Cl}_2$ (a) and optimized structures of the hypothetical complexes of WO_2Cl_2 with one $\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2$ ligand (b) and with two NH_3 ligands (c).

TABLE III

Comparison of the frequencies/ cm^{-1} of the symmetric and antisymmetric OWO stretching modes in $\text{WO}_2(\text{bpy})\text{Cl}_2$ and in the two model structures^a

| Mode | $\text{WO}_2(\text{bpy})\text{Cl}_2$ | Structure in Fig. 5b | Structure in Fig. 5c |
|------------------------|--------------------------------------|----------------------|----------------------|
| $\nu_s(\text{OWO})$ | 956 sh, 946 vs | 1110.3 | 1102.9 |
| $\nu_{as}(\text{OWO})$ | 914 sh, 903 vs | 1026.9 | 1031.1 |

this for the case of the OWO stretching vibrations. Further theoretical work is in progress, aimed to reproduce the smaller separation for the two MoO_2 and, especially, two CrO_2 stretching modes as found experimentally.

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SAŽETAK

Studij diklorodioksokromovog(VI), diklorodioksomolibdenovog(VI) i diklorodioksovolframovog(VI) kompleksa s 2,2'-bipiridinom FT infracrvenom spektroskopijom

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Objašnjene su vrpce FT infracrvenih spektara diklorodioksokromova(VI), diklorodioksomolibdenova(VI) i diklorodioksovolframova(VI) kompleksa s 2,2'-bipiridinom snimljenih u području 4000 do 400 cm^{-1} . Opis vrpce koje se pojavljuju u spektru kao posljedica vibracija u području bipiridinskog liganda razmjerno je jednostavan. Međusobni razmak vrpce vrlo visokog intenziteta koje predstavljaju čiste istezne vibracije MO_2 povećava se u nizu $\text{Cr} < \text{Mo} < \text{W}$ kao posljedica veće osjetljivosti antisimetričnih isteznih vibracija O–M–O na povećanje mase atoma metala. Da bi to bilo točno, simetrične istezne vibracije trebaju imati višu frekvenciju od antisimetričnih. Rezultati prethodnih *ab initio* HF SCF proračuna jednostavnih strukturnih modela u skladu su, makar kvalitativno, s takvim zaključkom.