

Infra-red spectra of dioxobis(acetylacetonato) tungsten (VI) and dioxobis(acetylacetonato) molybdenum (VI)

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Abstract—The infra-red spectra of dioxobis(acetylacetonato) tungsten (VI) and the corresponding molybdenum (VI) compound were investigated between 4000 and 300 cm^{-1} and an empirical assignment of the observed bands was made. The splitting of the bands in the low-frequency region was interpreted as a result of coupling of the vibrations of the two ligand rings connected through the metal atom. The WO_2^{2+} group was shown to be bent.

INTRODUCTION

THE study of the infra-red spectra of metal acetylacetonates has been the subject of numerous investigations (among these, cf. [1–16]). Some recent experimental [13] and theoretical [16] evidence indicated that some of the assignments made on the basis of the early normal co-ordinate calculations of NAKAMOTO and his co-workers [7–9] should be revised. This is particularly true for the assignment of some of the modes involving the oxygen atoms of the ligand rings where the interpretation is made much easier by having data on the spectra of ^{18}O -labeled acetylacetonates [13].

In the light of this new evidence and hoping to obtain some insight into the vibrations of the WO_2^{2+} and MoO_2^{2+} groups we investigated the infrared spectra of dioxobis(acetylacetonato) tungsten (VI), $\text{WO}_2(\text{acac})_2$ and of the corresponding molybdenum (VI) compound, $\text{MoO}_2(\text{acac})_2$. LARSON and MOORE [17] have listed the main absorption bands between 1600 and 650 cm^{-1} in the spectrum of the latter compound but without assignments, except for the $\text{Mo}=\text{O}$ stretching to which they

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assigned the band at 904 cm^{-1} suggesting that the MoO_2^{2+} group was linear. Some other data concerning the $\text{M}=\text{O}$ stretching frequencies of the MoO_2^{2+} and WO_2^{2+} groups became available quite recently [18–20], in most cases after this work was almost completed.

The crystallographic data concerning the geometry of the MO_2^{2+} ($\text{M} = \text{W}$ or Mo) groups are also very scarce and, to the best of our knowledge, only in $\text{K}_2[\text{MoO}_2\text{F}_4]\cdot\text{H}_2\text{O}$ the MoO_2^{2+} group was, quite recently, shown to be bent (OMO angle $\approx 95^\circ$) [20]. The space group and the parameters of the unit cell of $\text{MoO}_2(\text{acac})_2$ have been determined by GRDENIĆ and TKALČEC [21] and no crystallographic data are available for $\text{WO}_2(\text{acac})_2$.

EXPERIMENTAL

Dioxobis(acetylacetonato) tungsten (VI) has been first synthesized by one of us [22]. The corresponding molybdenum compound was prepared by the method of FERNELIUS *et al.* [23]. Elemental analysis was performed to ascertain the composition of the investigated compounds.

The infra-red spectra were recorded ($4000\text{--}300\text{ cm}^{-1}$) on a Perkin–Elmer Model 521 infra-red spectrophotometer. KBr pressed discs and Nujol and fluorolube mulls between CsBr plates were used. The spectra obtained by the two methods were essentially identical.

RESULTS AND DISCUSSION

The infra-red spectra of $\text{WO}_2(\text{acac})_2$ and $\text{MoO}_2(\text{acac})_2$ are shown in Fig. 1 and the frequencies of the observed bands, together with a qualitative estimation of their intensity and an empirical approximate description are listed in Table 1. A number of very weak bands were observed in the region $2650\text{--}1700\text{ cm}^{-1}$ but, since no fundamental frequency is expected in this region and since all these bands could easily be interpreted as binary combinations, they are not listed in Table 1.

$4000\text{--}800\text{ cm}^{-1}$ region

The assignment of the ligand bands above 800 cm^{-1} in the spectra of acetylacetonates has not been controversial, except for the two strongest bands—those in the $1600\text{--}1500\text{ cm}^{-1}$ region. The comparison of the spectra of normal and ^{18}O -labeled acetylacetonates [13] and the calculations of BEHNKE and NAKAMOTO [16] seem to have definitely established that the higher-frequency band belongs to a predominantly $\text{C}=\text{O}$ and the lower-frequency one to a predominantly $\text{C}=\text{C}$ vibration. The assignment of all other bands found in this region and attributable to vibrations located mainly in the ligand rings seems to be rather well-established and, therefore, straightforward.

Except for the ligand bands, in the spectrum of $\text{WO}_2(\text{acac})_2$ one can find two sharp and intense bands at 954 and 908 cm^{-1} which are undoubtedly due to the

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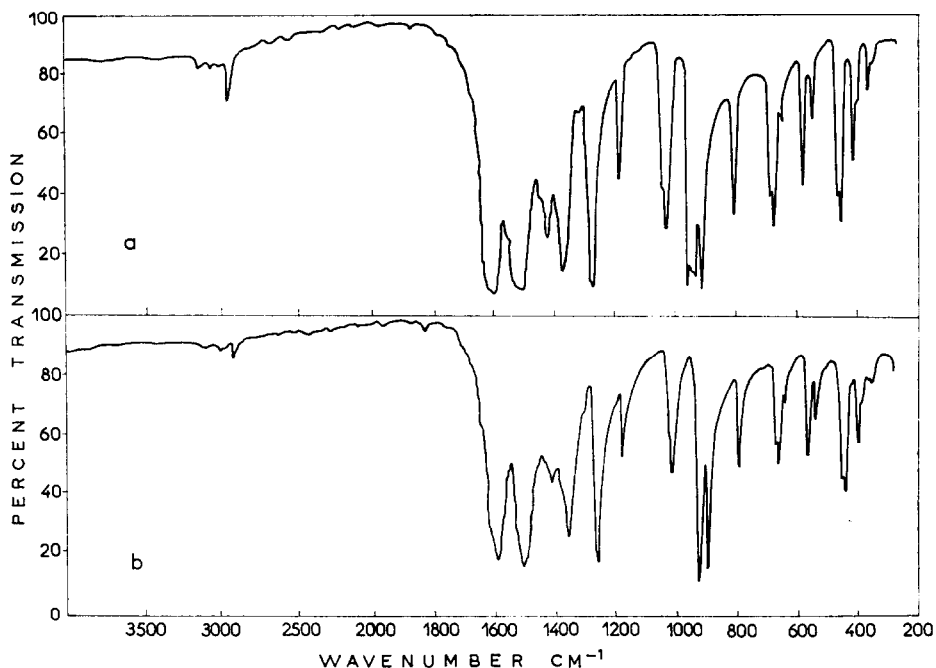


Fig. 1. Infra-red spectra of: (a) $\text{WO}_2(\text{acac})_2$ and (b) $\text{MoO}_2(\text{acac})_2$.

symmetric and asymmetric stretching vibrations of the WO_2^{2+} group. A similar pair of bands, attributed to $\text{W}=\text{O}$ vibrations was found, at almost the same frequency, in the spectra of $\text{WO}_2\text{BipyX}_2$ (Bipy = 2,2'-bipyridyl, X = Cl and Br) [18]. In the spectrum of $\text{MoO}_2(\text{acac})_2$ only one such band is clearly visible (at 904 cm^{-1}), although on the basis of the very close overall similarity between the spectra of the tungsten and molybdenum compounds one would expect to find a pair of bands in the case of $\text{MoO}_2(\text{acac})_2$ too. Further work is in progress to determine whether the second $\text{Mo}=\text{O}$ stretching band is actually absent or only hidden under the 933 cm^{-1} band, where it would be expected by analogy with $\text{MoO}_2\text{BipyX}_2$ [18].

The existence of two $\text{W}=\text{O}$ stretching bands strongly suggests that the WO_2^{2+} group in $\text{WO}_2(\text{acac})_2$ is not linear, whereas the MoO_2^{2+} group in the corresponding acetylacetonate may or may not have a geometry similar to that found in the case of $(\text{MoO}_2\text{F}_4)^{2-}$ [20]. To be sure, the appearance of the symmetric stretching vibration in the infra-red spectrum of a solid need not, in principle, indicate a significant physical departure from linearity of an XY_2 molecule, since the asymmetry of the force field around the molecule in the crystal lattice might be sufficient reason for this. However, the fact that the two $\text{M}=\text{O}$ stretching bands are almost equally intense indicates that here we do not merely have a relaxation of the selection rules but, rather, a genuine case of a non-linear atomic arrangement. Further results are reported elsewhere [24].

800–300 cm^{-1} region

If there is little ambiguity in the assignment of the bands above 800 cm^{-1} , this is not quite so for the bands in the region below the C—H out-of-plane bending

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Table 1. Infra-red spectra of $\text{WO}_2(\text{acac})_2$ and $\text{MoO}(\text{acac})_2^*$

$\text{WO}_2(\text{acac})_2$		$\text{MoO}_2(\text{acac})_2$		Approximate description
ν	I	ν	I	
3115	vw	3118	vw	C—H stretch
3005	vw	3006	vw	CH_3 deg. stretch (in-plane)
2965	vw	2968	vw	CH_3 sym. stretch
2915	w	2918	w	CH_3 deg. stretch (out-of-plane)
1584	vs	1584	vs	C===O stretch
1495	vs	1500	vs	C===C stretch
1430	sh	1431	sh	CH_3 deg. deform. (out-of-plane)
1412	m	1410	m	CH_3 deg. deform. (in-plane)
1358	vs	1355	vs	CH_3 sym. deform.
1302	vw	1300	vw	Combination
1270	vs	1260	vs	C===C stretch + C— CH_3 stretch
1264	vs	1253	vs	
1171	m	1179	m	C—H deform. (in-plane)
1036	sh	1032	sh	CH_3 deg. rock (out-of-plane)
1023	s	1023	s	CH_3 deg. rock (in-plane)
954	vs			M=O stretch
940	sh	933	vs	C— CH_3 stretch + C===O stretch
935	vs			
908	vs	904	vs	M=O stretch
805	s	799	s	C—H deform. (out-of-plane)
684	s	679	s	Ring. deform. + M—O stretch
674	s	670	s	
652	w	652	w	Out-of-plane deformation
578	m	576	s	M—O stretch
551	w	550	m	
464	s	459	s	C— CH_3 deform. + M—O stretch
455	s	451	s	
412	m	409	m	In-plane deformation
401	sh	400	sh	
363	m	375	vw	
351	sh	370	vw	?

* ν : frequency (in cm^{-1}); I: intensity; w: weak; m: medium; s: strong; v: very.

mode. Here too the isotopic-substitution study of PINCHAS *et al.* [13] showed that some of the previously accepted assignments should be interchanged. Thus, the band found in the spectra of acetylacetonates in the region $650\text{--}550\text{ cm}^{-1}$ [9] and theretofore assigned to an out-of-plane deformation mode, was shown to undergo the largest shift upon substitution of ^{16}O with ^{18}O and was, consequently, assigned to an almost pure M—O stretching. On the other hand, the band found in the region $670\text{--}650\text{ cm}^{-1}$ (and assigned by NAKAMOTO [9] to a C— CH_3 bending + M—O stretching mode) was found to exhibit the smallest shift and was assigned to an out-of-plane deformation mode. Almost all other bands in the low-frequency region were more or less affected by the isotopic substitution, the shift being presumably related to the degree of M—O character in the corresponding mode.

Our spectra seem to corroborate similar conclusions. It can be seen (cf. Fig. 1 and Table 1) that most bands in the low-frequency region are split, apparently as a result of coupling of the vibrations of the two ligand rings connected through the metal atom and it is reasonable to assume that the more M—O character a vibration has, the stronger the coupling would be. Consequently, the largest splitting

is expected to occur for the mode which is almost pure M—O stretching. In the spectra of both the W- and the Mo-chelate the largest splitting is found for the 578/551 cm^{-1} and the 576/550 cm^{-1} doublet respectively, thus supporting the assignment of PINCHAS *et al.* [13]. The fact that the coupling is, generally, rather strong indicates that the symmetry of the molecule is rather low, apparently as a result of its *cis*-configuration. Since the coupling seems to be of the same order of magnitude in both chelates, one is inclined to suspect that not only the WO_2^{2+} , but also the MoO_2^{2+} group is bent.

The origin of the weak band found in the 375–350 cm^{-1} region is not clear. It seems to be too high to belong to the O=M=O deformation and is, more likely, due to an out-of-plane deformation vibration or to a lattice mode.