

[CONTRIBUTION FROM JEPSON LABORATORY OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Infrared Spectra of Metal Chelate Compounds. IV. Infrared Spectra of Addition Compounds of Metallic Acetylacetonates^{1a}

BY KAZUO NAKAMOTO,^{1b} YUKIYOSHI MORIMOTO^{1b} AND ARTHUR E. MARTELL^{1b}

RECEIVED MARCH 27, 1961

The infrared spectra of the addition compounds of bisacetylacetonato-Ni(II) and bisacetylacetonato-oxovanadium(IV) with pyridine and bisacetylacetonato-dioxouranium(VI) with pyridine and water have been measured in the range between 4000 and 400 cm^{-1} . Band assignments have been made by combining the previous normal coordinate treatments on metallic acetylacetonates with the spectra of the corresponding addition components. The effect of the coordinated adduct on the strength of the metal-oxygen bonds is discussed quantitatively in terms of the change of the metal-oxygen stretching force constants in these compounds. Remarkable changes of the frequencies and the force constants occurring in the formation of the addition compounds suggest that the bonds are formed directly between the central metal ion and the oxygen or nitrogen of the added ligand.

Introduction

It is well known² that some metallic acetylacetonates form addition compounds with water, pyridine and other weak bases. Bonding in these addition compounds may occur between the basic atom of the donor molecule and the central metal ion. Since the binding is weak, however, there is also a possibility that the donor molecules are associated with the ligand. In order to examine the structure of the addition compounds in metallic acetylacetonates, it was decided to compare the infrared spectra with those³ of metal acetylacetonates previously described in detail, on the basis of the normal coordinate treatment.

If the coordination occurs directly between the metal and donor molecule, marked frequency shifts of the metal-oxygen stretching bands would be expected. On the other hand, simple association of the metal acetylacetonates with the donor molecules produces only secondary effects on the metal-oxygen stretching bands. Typical examples of the latter type are seen in the interactions of the Fe(III), Cr(III) and Al(III) acetylacetonates with chloroform.⁴

This paper mainly concerns infrared investigations of complexes having fairly strong coordinate bonds between the metal of the metal chelate and the donor molecules.

Experimental

Preparation Compounds.—All of the compounds studied in this research were prepared according to the methods described in the literature.² The purity of each compound was checked by microanalysis, the results of which are given in Table I.

Spectral Measurements.—A Perkin-Elmer Model 21 infrared spectrophotometer equipped with NaCl and KBr optics was used to obtain the spectra in the range between 4000 and 400 cm^{-1} . The KBr disk method was employed for the preparation of the sample. Calibration of the frequency reading was made with Polystyrene film (NaCl region), with 1,2,4-trichlorobenzene (KBr region) and with water vapor for both regions.

(1a) This work was supported by the Office of Ordnance Research under Contract No. DA-19-020-ORD-5119. (b) Department of Chemistry Illinois Institute of Technology, Technology Center, Chicago 16, Illinois.

(2) For example, see N. V. Sidgwick, "Chemical Elements and their Compounds," Oxford University Press, London, 1950.

(3) (a) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960); (b) K. Nakamoto, A. Ruby, P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1066, 1272 (1961).

(4) J. F. Steinbach and J. H. Burns, *ibid.*, **80**, 1839 (1958).

TABLE I

	RESULTS OF MICROANALYSIS			
		C, %	H, %	N, %
Ni(acac) ₂ ·(pyridine) ₂	Calcd.	57.86	5.83	6.75
	Found	57.89	6.00	6.55
VO(acac) ₂	Calcd.	45.29	5.32	
	Found	45.37	5.31	
VO(acac) ₂ ·pyridine	Calcd.	52.32	5.57	4.08
	Found	52.74	5.47	3.84
UO ₂ (acac) ₂ ·H ₂ O	Calcd.	24.70	3.32	
	Found	24.77	3.16	
UO ₂ (acac) ₂ ·pyridine	Calcd.	32.91	3.49	2.56
	Found	32.85	3.08	2.35

Results and Discussion

I. Bisacetylacetonato-nickel(II).—Figure 1 indicates the comparison of the infrared spectra of bisacetylacetonato-nickel(II), of pyridine and of the addition compound. Since the general feature of the spectrum of the addition compound is an overlap of the spectra of the two components, it is possible to attribute the observed bands to either one of the components as is shown by the dotted lines.

While it is noted that most of the bands are shifted to higher or lower frequencies in the formation of the addition compound, the band shifts are somewhat ambiguous in the region where the band overlappings are serious. In this respect, the spectrum below 700 cm^{-1} is particularly suitable in examining the shifts caused by the addition of pyridine since pyridine has almost no absorption bands in this range.

As seen in Fig. 1, all the bands below 700 cm^{-1} are shifted to lower frequencies in the formation of the addition compound. This result is interesting when compared to the results of the previous normal coordinate treatment since all of these bands involve the Ni-O stretching vibration. As was shown previously,³ the band at 452 cm^{-1} in the nickel complex was proved to be an almost pure Ni-O stretching band. This band is now shifted to 439 cm^{-1} in the addition compound. The results of the perturbation calculations^{3b,5} listed in Tables II and III indicate that formation of the pyridine adduct decreases the Ni-O, as well as the C=O and C=C, stretching force constants. The most remarkable change is seen in the Ni-O stretch-

(5) E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955, p. 229.

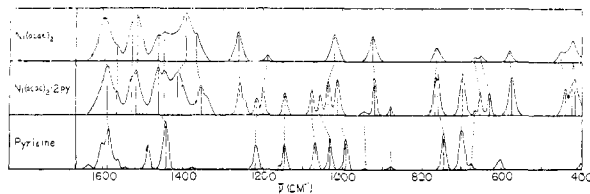


Fig. 1.—Infrared spectra of bisacetylacetononickel(II), pyridine and their addition compound.

ing force constant which becomes weaker by 0.27×10^5 dyne/cm. Such marked changes of the force constants provide good evidence for direct coordinate bonding between the metal and the nitrogen atom of pyridine. It is conceivable that in the addition compound the metal has octahedral configuration with the two pyridine molecules in the *trans* positions.

TABLE II

Compound	Mass of metal (atomic weight)	M—O distance (Å.)	Force constant (10^5 dyne/cm.) ^a		
			K (C=O)	K (C=C)	K (M—O)
Ni(acac) ₂	58.69	2.05	7.65	5.35	2.05
Ni(acac) ₂ ·(pyridine) ₂	58.69	2.05	7.50	5.27	1.78
VO(acac) ₂	50.95	1.95	6.94	5.16	2.88
VO(acac) ₂ ·pyridine	50.95	1.95	6.95	5.16	2.37
UO ₂ (acac) ₂	238.07	2.30	6.78	5.46	1.65
UO ₂ (acac) ₂ ·H ₂ O	238.07	2.30	6.78	5.42	1.48
UO ₂ (acac) ₂ ·pyridine	238.07	2.30	6.76	5.59	1.62

^a Other force constants are the same as before.³

Finally, it should be mentioned that the structure of bisacetylacetononickel(II) in the crystalline state has not yet been determined completely. Bullen⁶ has suggested that the compound is trimer, the three Ni atoms being nearly collinear. However, the positions of other atoms were not resolved in his Fourier analysis. Since this compound is somewhat volatile, it is reasonable to assume that the intermolecular interaction is fairly small. As to the configuration around the Ni atom, Shibata⁷ has found from X-ray and electron diffraction studies that it is tetrahedral in the crystalline state and planar in the gaseous state. In accordance with this observation, we have previously suggested from the infrared study^{3b} that the Ni complex is not square planar. In any event, further detailed interpretation of the band shifts and force constant changes reported in this paper should be made when more definite structural data become available.

II. Bisacetylacetonoxovanadium(IV).—According to recent X-ray measurements,⁸ the structure of bisacetylacetonoxovanadium(IV) is tetragonal pyramidal, the vanadium atom being slightly displaced from the square plane of the ligand oxygen atoms. The complex is mononuclear, since the distance between the nearest adjacent vanadium atom and the vanadyl oxygen atom is 6.27 Å. This relatively large distance indicates that polymerization through the O=V···O bonds

(6) G. J. Bullen, *Nature*, **177**, 537 (1956).

(7) S. Shibata, *Bull. Chem. Soc. Japan*, **30**, 753, 842 (1957).

(8) R. P. Dodge, U. S. Atomic Energy Comm., UCRL-8225, 1958, p. 27.

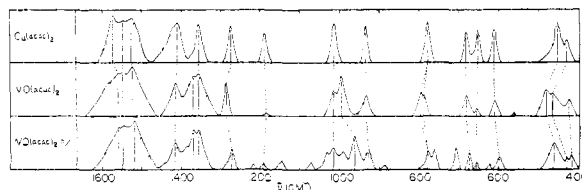


Fig. 2.—Infrared spectra of bisacetylacetonoxovanadium(IV) and its addition compound.

does not occur in the crystalline state. Jones⁹ has shown previously that the sixth coordinate site of the central metal ion is occupied only by bases such as quinoline and methylamine, but not by water, although Rosenheim and Mong¹⁰ reported a hydrate of vanadyl acetylacetonate. Jones' conclusion was also confirmed by analysis of this compound, as is indicated in Table I.

Figure 2 compares the infrared spectra of bisacetylacetonoxovanadium(IV) and of its addition compound with pyridine with that of bisacetylacetonocopper(II) for which a normal coordinate treatment was made previously.^{3a} A comparison of the simple complexes shows that the strong band at 995 cm.⁻¹ in the vanadyl complex is due to the V=O stretching mode of the oxo group. The same band appears at 980 cm.⁻¹ in vanadyl sulfate dihydrate. The coordinated V—O stretching band of vanadyl acetylacetonate is found at 480 cm.⁻¹. According to the results of the perturbation calculation shown in Tables II and III, the corresponding V—O stretching force constant was estimated as 2.88×10^6 dyne/cm. This value is the highest among many metal acetylacetonates calculated thus far.³ The V—O bonds in this compound are concluded, therefore, to be fairly strong. On the other hand, the V=O stretching force constant of the oxo group is estimated as 9.04×10^5 dyne/cm., assuming a simple harmonic oscillator, and is therefore very much stronger.

Fig. 2 indicates that the V=O stretching band at 995 cm.⁻¹ in the simple acetylacetonate is shifted to 964 cm.⁻¹ in the addition compound with pyridine. Since the 964 cm.⁻¹ band corresponds to the force constant of 8.49×10^5 dyne/cm., the effect of addition of a pyridine molecule on the V=O bond is estimated as a decrease of the force constant by 0.55×10^6 dyne/cm. It is also seen that in the simple acetylacetonate the V—O stretching band between vanadyl ion and the acetylacetonate ligand at 480 cm.⁻¹ is shifted to a considerably lower frequency in the addition compound. The pyridine compound shows this band at 463 cm.⁻¹. Perturbation calculations on the metal complex indicate that this change corresponds to a decrease of the force constant of 0.51×10^6 dyne/cm. The marked decrease in the force constant obtained above definitely indicates formation of a strong bond between the central metal and the donor nitrogen. It is noted, however, that almost no change in force constant is seen in the C=O as well as the C=C bonds in the chelate ring.

(9) M. M. Jones, *J. Am. Chem. Soc.*, **76**, 5995 (1954).

(10) A. Rosenheim and H. Y. Mong, *Z. anorg. allgem. chem.*, **148**, 25 (1925).

TABLE III

COMPARISON OF OBSERVED ^a AND CALCULATED FREQUENCIES IN METALLIC ACETYLACETONATES (CM. ⁻¹)														
Ni(acac) ₂		Ni(acac) ₂ ·py ₂		VO(acac) ₂		VO(acac) ₂ ·py		UO ₂ (acac) ₂		UO ₂ (acac) ₂ ·H ₂ O		UO ₂ (acac) ₂ ·py		Predominant modes ^a
Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	
1598	1599	1588	1586	1561	1562	1560	1562	1584	1583	1578	1578	1597	1596	$\nu_{(C-O)}$ ν_8
1598	1602	1588	1589	1547	1545	1548	1543	1561	1561	1562	1560	1563	1564	$\nu_{(C-O)}$ ν_1
1526	1518	1527	1511	1523	1493	1520	1491	1512	1480	1509	1480	1517	1480	$\nu_{(C-O)}$ + $\delta(C-H)$, ν_9
1515		1516												
1463	..	1462	1449	..	$\nu_{(C-O)}$ or pyridine
1448		1447												
1398	..	1412	..	1416	..	1416	..	1423	..	1420	..	1422	..	CH ₃ deg. def.
1367	..	1354	..	1371	..	1371	..	1367	..	1369	..	1360	..	CH ₃ sym. def.
				1358		1356		1342		1353				
1261	1268	1257	1263	1287	1258	1274	1256	1274	1267	1269	1265	1271	1271	$\nu_{(C-C)}$ + $\nu_{(C-CH_3)}$, ν_2
								1260						
1198	1235	1200	1231	1187	1228	1193	1226	1196	1223	1193	1223	..	1224	$\delta(C-H)$, ν_{10}
1020	..	1038	..	1017	..	1017	..	1022	..	1030	..	1023	..	CH ₃ rock.
								1014		1012		1014		
..	997	..	964	$\nu_{(V=O)}$
929	944	921	939	934	946	929	938	925	929	943	927	925	929	$\nu_{(C-CH_3)}$, ν_3 and ν_{11}
		904		901		907		901		897		896		898
..	915	..	916	..	909	..	$\nu_{(U=O)}$, antisym.
..	838	827	..	$\nu_{(U=O)}$, sym.
764	..	766	..	797	..	796	..	777	..	793	..	793	..	$\pi(C-H)$
				790		781				779				
666	658	654	648	683	702	675	681	652	603	662	601	650	603	Ring def. + $\nu_{(M-O)}$, ν_4
653	623	630	608	658	669	656	642	646	582	648	572	627	580	$\delta(C-CH_3)$ + $\nu_{(M-O)}$, ν_{12}
578	..	572	..	610	..	599	..	525	..	527	..	521	..	π
				562										
452	452	439	439	480	479	463	463	433	433	421	422	431	431	$\nu_{(M-O)}$, ν_5
422	..	419	..	462	..	429	..	410	..	404	..	404	..	π
				424		419		400						
..	374	..	374	366	373	360	373	..	374	..	373	..	374	Ring def., ν_{13}
..	290	..	276	..	327	..	311	..	276	..	242	..	251	$\nu_{(M-O)}$, ν_{14}
..	256	..	253	..	283	..	279	..	253	..	275	..	276	$\delta(C-CH_3)$, ν_6
..	183	..	182	..	203	..	203	..	159	..	158	..	160	Ring def., ν_7

^a All the pyridine bands are not listed in the table. ^b ν , δ , and π denote stretching, bending and out-of-plane bending modes, respectively. Numbers given by ν_N refer to the band assignments in the previous normal coordinate treatment.³

III. Bisacetylacetonato-dioxouranium(VI).—The infrared spectrum of uranyl acetylacetonate in the sodium chloride region has been studied by several investigators. Comyns, *et al.*,¹¹ have reported the infrared spectrum of the anhydrous complex to be quite similar to the results shown in Fig. 3. By comparing this spectrum with that of bisacetylacetonato-copper(II) for which a normal coordinate treatment has been reported previously,^{3a} the 926 cm.⁻¹ band is assigned to the C-CH₃ stretching vibration of acetylacetonate, and a shoulder at 915 cm.⁻¹ is assigned to the antisymmetric UO₂ stretching vibration of the oxo group. This assignment is supported by the fact that benzoyl and dibenzoyl derivatives exhibit a single band at 910 cm.⁻¹.¹² The U-O stretching band of the uranium-(VI)-oxygen band of the acetylacetonate group is found at 433 cm.⁻¹.

Comyns, *et al.*,¹¹ have found that anhydrous uranyl acetylacetonate is a dimer in benzene solution and is polymerized in the crystalline state. Therefore, these frequencies correspond to polynuclear forms in which the coordination number of uranium is greater than 6. A possible structure of the polymeric form may be square archimedean antiprisms sharing one edge with neighboring mole-

(11) A. E. Comyns, B. M. Gatehouse and E. Wait, *J. Chem. Soc.* 4655 (1958).

(12) L. Sacconi, G. Caroti and P. Paoletti, *ibid.*, 4257 (1958).

cules by forming U—O—U bonds. With these

considerations in mind it would be of interest to compare the oxouranium stretching frequencies of the polymeric species with those of the monomer having a coordination number of 6. Although such a monomeric form of the acetylacetonate may

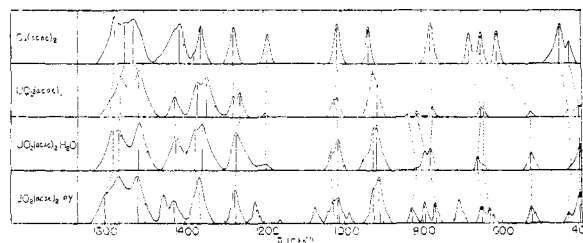


Fig. 3.—Infrared spectra of bisacetylacetonato-dioxouranium-(VI) and its addition compounds.

exist in dilute solution, the infrared spectrum of this species was not obtained because of the low concentration required. It should be pointed out, however, that uranyl nitrate hydrate and rubidium uranyl nitrate have antisymmetric UO₂ stretching

bands at $960 \sim 950 \text{ cm.}^{-1}$,¹³ which is much higher than the value observed in the present investigation. The fact that the frequencies in these salts are much higher than those of anhydrous uranyl acetylacetonate implies the possibility of association through the oxo groups of the latter. On the other hand, the greater basicity of the acetylacetonate ligand over that of the nitrate group may be sufficient to account for the difference. In any case, the possibility of association of uranyl ions in its complexes warrants further study.

As is shown in Tables II and III, a perturbation calculation on uranyl acetylacetonate indicates that the stretching force constant for the bond between uranium and the acetylacetonate oxygens is $1.65 \times 10^5 \text{ dyne/cm.}$ and, therefore, the coordinate U-O bonds are fairly weak. On the other hand, the oxouranium stretching force constant is estimated to be about $6.9 \times 10^5 \text{ dyne/cm.}$ on the basis of the results reported by Jones.¹⁴

The spectrum of the monohydrate of uranyl acetylacetonate is almost identical with that of "form I" obtained by Comyns, *et al.*¹¹ A broad OH stretching band between 3300 and 3150 cm.^{-1} indicates that water is not free in the crystalline state. The oxouranium stretching band is located at 915 cm.^{-1} , which is almost the same as that of the anhydrous compound. The coordinate U-O stretching band is shifted to a lower frequency by 9 cm.^{-1} as compared with the anhydride. The perturbation calculation indicates that this lower-

ing of the frequency corresponds to a decrease of the force constant by $0.17 \times 10^5 \text{ dyne/cm.}$ In accordance with the conclusions of Sacconi, *et al.*,¹² these results seem to suggest that water is coordinated to the metal by forming U-OH₂ bonds and that the water hydrogen probably is bonded to the oxygen of acetylacetonate, thus weakening the coordinate U-O bonds.

The spectrum of uranyl acetylacetonate-pyridine complex exhibits the oxouranium stretching band at 909 cm.^{-1} , which is lower than those of either of the previous two compounds. This result indicates that the oxouranium bond in the former is weaker than in the latter two compounds. Using the results of Jones,¹⁴ the corresponding stretching force constant is estimated to be about $6.8 \times 10^5 \text{ dyne/cm.}$ On the other hand, the coordinate U-O stretching frequency is about the same as that of anhydrous uranyl acetylacetonate.

From the studies of solution equilibria, Wendlandt, *et al.*,¹⁵ have concluded recently that nitrogen-containing solvates form stronger bonds with uranium than do oxygen-containing solvates. It is rather difficult, however, to compare the strength of the U-N bond of the pyridine complex with that of the U-OH₂ bond of the monohydrate from the present infrared study, since both the effects of coordination and hydrogen bonding are involved in the latter compound.

Acknowledgment.—The authors are indebted to the M.I.T. Computation Center for the use of the I.B.M. computer for our calculation.

(13) B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 802 (1958).

(14) L. H. Jones, *Spectrochim. Acta*, **6**, 409 (1959).

(15) W. W. Wendlandt, J. L. Bear and G. R. Horton, *J. Phys. Chem.*, **64**, 1289 (1960).