THE INFRA-RED SPECTRA OF METAL ACETYLACETONATES IN THE SODIUM CHLORIDE REGION

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Abstract—The infra-red spectra of eighteen metal derivatives of acetylacetone have been studied in the sodium chloride region. The spectra of all the compounds, including those of the alkali metals, are markedly similar in this region, indicating that the arrangement of acetylacetone groups around the metal atom is similar for all of the compounds studied. Structural implications of differences in infra-red absorption frequencies among acetylacetonates are discussed.

THE nature of the metal-oxygen bonding in metallic derivatives of enols has been the subject of much speculation since the cyclic, chelated structure for these complexes became generally accepted.⁽¹⁾ In recent years several investigators have examined the infra-red spectra of metal derivatives of acetylacetone and other $enols^{(2-7)}$ in the hope of providing some information about the problem of bonding. The most complete and thorough of these infra-red structural studies are those of DUVAL, FREYMANN and LECOMTE⁽²⁾ who were able to make vibrational assignments for most of the absorption bands of metal acetylacetonates by considering the spectra to be derived from the inphase and out-of-phase coupled vibrations of two joined acetone molecules. These workers stated that the spectra required a cyclic chelated form for the acetylacetone complexes, but they recognized that their studies did not give conclusive information about the nature of the bonds to the metal atoms.

Since numerous discrepancies are found in published data on the infra-red absorption of metal acetylacetonates, we thought it important to repeat determinations of the spectra in the sodium chloride region for a number of these compounds, using previously analysed samples (Table 1). None of the previous investigators has reported analyses for acetylacetonates used for spectral studies. The absorption bands for the 18 compounds studied are given in Table 2, and some illustrative spectra are shown in detail in Fig, 1.

No infra-red studies on acetylacetonates of univalent metals have been published previously. Six such compounds are included in the present study. Their spectra are of special interest because co-ordinate covalent bonding to the metal should be considerably less important than in the acetylacetonates of polyvalent metals. The

⁽⁵⁾ R. L. BELFORD, A. E. MARTELL and M. CALVIN J. inorg. nucl. Chem. 2, 11 (1956).

⁽¹⁾ H. DIEHL Chem. Rev. 21, 39 (1937).

⁽²⁾ J. LECOMTE Disc. Faraday Soc. 9, 125 (1950); C. DUVAL, R. FREYMANN and J. LECOMTE Bull. soc. chim. 19, 106 (1952).

⁽³⁾ L. J. BELLAMY and R. F. BRANCH J. Chem. Soc. 1954, 4491; L. J. BELLAMY, G. S. SPICER and J. D. H. STRICKLAND J. chem. Soc. 1952, 4653.

⁽⁴⁾ D. M. SHIGORIN Izv. Akad. Nauk S.S.S.R. Ser. Fiz. 17, 196 (1953); Zh. Fiz. Khim. 27, 554 (1953).

 ⁽⁶⁾ H. W. MORGAN U.S. Atomic Energy Commission Report AECD 2659 (1949).
 ⁽⁷⁾ D. JOHNSON Thesis, University of Wisconsin.

large and weakly polarizing ions of the heavy alkali metals are known for their reluctance to act as electron pair acceptors.⁽⁸⁾ If chelation implies covalent bonding to the metal atom, then it should be a minimum in the acetylacetonates of these elements.

Unlike acetylacetonates of most divalent and trivalent metals, alkali metal derivatives of beta-diketones are "saltlike" in their physical properties and highly dissociated in dilute solution in ethanol.^(9a) The lithium and sodium compounds of this type become more "covalent" in their properties (lower melting and more soluble in hydrocarbons) when the alkali metal ion is complexed by two or more additional donor groups, e.g. water molecules or a molecule of diketone.^(9b) Thallium acetylacetonate, however, has "covalent" properties in the absence of additional complexing.⁽¹⁰⁾

EXPERIMENTAL*

Infra-red spectra. Baird Model S and Perkin-Elmer Model 21 automatic recording double-beam spectrophotometers were used. The infra-red spectrum in the region $625-5000 \text{ cm}^{-1}$ of each compound was determined both as a pressed disc in KBr, and as a mull in white petroleum oil. No significant differences were found.

The frequencies given in Table 2 are believed to be correct to $\pm 8 \text{ cm}^{-1}$ in the region 1100–1700 cm⁻¹ and to ± 5 cm⁻¹ in the region 625–1100 cm⁻¹. Between 1700 and 5000 cm^{-1} the compounds showed no absorbtion except for weak bands at about 2900 cm⁻¹ due to C—H stretching. These did not seem to show significant variations, and were not carefully examined in our study.

Analyses. As earlier workers have reported⁽¹¹⁾ it is difficult to obtain good combustion analyses of alkali metal acetylacetonates. We analysed these compounds volumetrically as follows: a weighed sample was dissolved in water and immediately titrated with HCl to an end point at pH 4.5⁽¹²⁾ using a glass electrode pH meter. Accuracy is estimated to be better than +1 per cent.

Sodium acetylacetonate. Sodium (0.7 g, 0.03 mole) was dissolved in absolute ethanol (30 ml). To the resulting sodium ethoxide solution was added 3 g (0.03 mole) of acetylacetone (Eastman Kodak white label). Anhydrous ether (50 ml) was added and the mixture was stored at 5°C overnight. The fine white crystals of product which formed were filtered with suction, washed with anhydrous ether, and dried in vacuo. Yield 2.5 g (80 per cent).

Lithium acetylacetonate, potassium acetylacetonate, and calcium acetylacetonate were prepared in the same manner as the sodium compound. The lithium compound is highly soluble in ethanol, and in this case the amount of ethanol was reduced to 20 ml and no ether was added.

Caesium acetylacetonate. Caesium amalgam was prepared in low yield by the electrolysis of a concentrated solution of CsCl with a mercury cathode, using a method described for the preparation of barium amalgam.⁽¹³⁾ The amalgam was separated and washed twice with small portions of absolute ethanol to remove water, and then shaken

^{*} The symbol A will be used to represent the acetylacetonate group in this and subsequent sections of this paper.

⁽⁸⁾ K. FAJANS and G. ZOOS Z. Physik 23, 1 (1924); K. FAJANS Naturwiss. 11, 165 (1923); Z. Kristallogr. 61, 18 (1924).

⁽⁹⁾ (a) E. WHITE J. chem. Soc. 1929, 1413; (b) N. V. SIDGWICK and F. M. BREWER Ibid. 127, 2379 (1925); F. M. BREWER Ibid. 1931, 361.

⁽¹⁰⁾ R. C. MENZIES and A. R. P. WALKER J. chem. Soc. 1936, 1678

 ⁽¹¹⁾ L. F. HATCH and G. SUTHERLAND J. org. Chem. 13, 249 (1948).
 (12) L. G. VAN UITERT, C. G. HAAS, W. C. FERNELIUS and B. E. DOUGLAS J. Amer. chem. Soc. 75, 455 (1953).

⁽¹³⁾ B. C. MARKLEIN, D. H. WEST and L. F. AUDRIETH Inorg. Synth. 1, 12 (1939).

vigorously with a third portion of ethanol to give a solution of caesium ethoxide. Acetylacetone was then added dropwise to the solution until a test drop gave a neutral reaction in water. White crystals of the caesium compound⁽¹⁴⁾ were precipitated.

Thallium acetylacetonate. Finely-divided thallium metal (2.0 g, 0.01 mole) was dissolved in warm ethanol with the aid of oxygen. Acetylacetone (1.0 g, 0.01 mole) was added to the warm solution, which was then chilled. The white crystals of TIA which formed were filtered off, washed with ethanol and recrystallized from chloroform. Yield 2.0 g (65 per cent); m.p. 158-159°, lit. 160.5°.⁽¹⁰⁾

Silver acetylacetonate. This compound was prepared by mixing equimolar quantities of approximately one M solutions of AgNO₃ and $C_5H_7O_3Na$ dissolved in oxygenfree water. The creamy-white silver compound precipitated immediately. It was filtered rapidly onto a porous sintered glass plate and quickly washed with a little oxgen-free water, then dried under high vacuum. The yield is nearly quantitative. The compound was analysed by treating with excess standard NaCl solution, followed by titration of excess chloride with AgNO₃.

Silver acetylacetonate, first prepared in 1893,⁽¹⁵⁾ has not been well characterized. The pure compound can be kept for a few days with only moderate darkening.

Compound	Method		Calculate	d	Found					
	of prep.	С	Н	Equiv. wt.	С	Н	Equiv. wt			
CsA	†			232			234			
KA	Ť ĺ		ſ	138			139			
NaA	+			122			121			
LiA	+			106			106			
TIA	+*	19.8	2.32		20.0	2.34				
AgA	†			207			207			
CaA ₂	t			119			119			
MgA ₂	(16)	54·0	6.3		54.4	6.4				
BeA ₂	(16)*	58·0	6.8		58.3	6.9				
CoA ₂	(17)	46.7	5.5		46.3	5.3				
CuA ₂	(18)*	45.9	5.4		45.7	5.6				
ZnA ₂	(16)*	45.6	5.4		45.6	5-3				
PdA ₂	(‡)*	39.4	4.6		39.1	4.9	1			
LaA ₃	(19)	40.4	4.7	145	39.9	4.6	146			
AlA ₃	(17a)*	55.7	6.5		56.1	6.4	1			
FeA ₃	(19)	51·0	6.0		51.3	6.1				
CrA ₃	(20)	51.6	6.1		51.8	5.8				
CoA ₃	(20)	50.6	5.9		50.6	5-9				

* Purified by sublimation in vacuo.

[‡] Prepared by the reaction of acetylacetone with a solution of PdCl₂. ⁽¹⁴⁾ G. T. MORGAN and H. W. Moss J. chem. Soc. 105, 189 (1914).

⁽¹⁵⁾ J. U. NEF Ann. Chem. 277, 68 (1893).

- (18) A. ARCH and R. C. YOUNG Inorg. Synth. 2, 17 (1945).
 (17) F. GACH Monatsh. Chem. 21, 100 (1900).
 (17a) R. C. YOUNG Inorg. Synth. 2, 25 (1946).

A. COMBES C.R. Acad. Sci., Paris. 119, 1122 (1894).
 A. HANTZSCH and C. H. DESCH Ann. Chem. 323, 1 (1902).
 B. E. BRYANT and W. C. FERNELIUS Inorg. Synth. 5, in press.

[†] See experimental section.



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Decomposition with the liberation of silver is more rapid when the compound is exposed to water, organic solvents, or oxygen, or when it is heated. AgA is insoluble in and not wetted by water, slightly soluble in ethanol, and insoluble in benzene, ether and chloroform.

Other acetylacetonates were prepared by standard methods referred to in Table 1. The compounds were purified by recrystallization, followed by drying or sublimation *in vacuo*.

RESULTS

The frequencies found for BeA_2 , ZnA_2 , CoA_2 , AlA_3 , FeA_3 , CrA_3 and CoA_3 are in fairly good general agreement with those reported by LECOMTE,⁽²⁾ while those for CuA_2 agree well with those found by CALVIN.⁽⁵⁾

From an examination of the frequencies listed in Table 2, or the spectra shown in Fig. 1, it is apparent that the general appearance of the spectrum and position of absorption bands is strikingly similar for all of the acetylacetonates. The physical



properties of the compounds cannot be correlated with their infra-red spectra. For instance, the highly saltlike compound CsA has a spectrum virtually identical with that of the "covalent" TlA. Likewise, the inner orbital⁽²¹⁾ complex $CoA_3^{(22)}$ has a spectrum closely similar to that of the outer orbital complex $FeA_3^{(23)}$. The differences between the spectra among the compounds studied appear to be differences of degree rather than of kind. LECOMTE noticed the similarity among spectra of covalent acety-lacetonates and stated that "the main regions of absorption for all of the acety-lacetonates are found in the same position, whatever the metal."⁽²⁰⁾ We confirm this generalization and find that it holds true even for the highly ionic alkali metal compounds.

The close similarity of the spectra of the alkali metal acetylacetonates to those of the polyvalent acetylacetonates is evidence that the geometrical arrangement of acetylacetonate groups around the metal atoms must be much the same for both types of compounds. Both the infra-red spectra and the other properties of the alkali metal compounds are consistent with an essentially ionic structure, with the oxygen atoms of the symmetrical enolate anions taking up positions near to the metal ions in the crystals (Fig. 2a and b). The number of oxygens which are "nearest neighbours" equidistant from each alkali metal ion is probably greater than two, accounting for the high melting point and "ionic" solubility behaviour of these compounds.

In considering differences between positions of absorption bands among acetylacetonates, most attention has been paid to the prominent band at 1560-1620 cm⁻¹.

⁽²²⁾ L. CAMBI and L. SZEGO Ber. dtsch. chem. Ges. 64, 2591 (1931).

⁽²¹⁾ H. TAUBE Chem. Rev. 50, 69 (1952).

⁽²³⁾ R. O. WHIPPLE, R. WEST and K. EMERSON J. chem. Soc. 1953, 3715.

	CoA ₃	1565	1520	(1429)	1385	(1365)	1279	(1216)	(0611)	1022	932	(262)	752	688	663
	CrA ₈	1568	1522	1424	1383	(1364)	1279		0611	1019	928	(263)	770	683	656
	FeA ₃	1570	1525	(1428)	1368	-	1272		1188	1015	923	(800)	769	(722)	663
	AIA ₃	1586	1527	(1466)	1389	(1364)	1285		1188	1026	931	(06L)	763	682	657
	LaA ₃	1610	1514	(1439)	1385	(1360)	1252		(0611)	1010	917	(262)	762		647
	PdA2	1561 1543	1520		1393	(1357)	1267		(5611)	1018	930	784	778	676 674	658
	ZnA ₂	1588	1524	(1454)	1404	(1371)	1261		((11)	1017	922	804	786		645
	CuA ²	1572 1553	1527	(1455)	1408	(1360)	1274		(0611)	1018	933	-	781	680	650
	CoA ₂	1592	1517	1464	1402	(1368)	1258		(9611)	1016	919	(789)	766		649
	BeA ₂	1572	1529	1444	1393		1300		((171)	1040 (1013) (957)	921	822	753		099
	MgA ₂	1608	1520	1474	1409	(1367)	1262	(0011)	(1193)	1018 (937)	920	(783)	768		656
	CaA2	1607	1508	(1462)	1395	(1362)	1244	(0001)	(1700)	1013	915		778	(120)	651
	AgA	1612	1508	1464	1414	(1366)	1232			1008	905		764		
	TIA	1610	1507	1464	1412	(1385)	1230	(0011)	(9611)	1008	905		765		646
	LiA	1595	1512	143	1404	(1346)	1258	(1106)		1014	915	800	763		654
	NaA	1604	1508	1462	1408	(1360)	1228	(1103)	(6411)	1008	906	-	763		650
	KA	1608	1508	1456	1408	(1383)	1232	(E011)	(1411)	1009	905		760		652
	CsA	1613	1506	1464	1408		1230	100117	(6611)	1009	606		763		658

TABLE 2.---INFRA-RED ABSORPTION FREQUENCIES IN CM⁻¹

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This band is one of two which LECOMTE assigns to the C=O stretching vibration.⁽²⁾ Among acetylacetonates of six divalent metals, BELLAMY found little difference in the position of this carbonyl peak.⁽³⁾ We find slight but apparently real differences in the position of the first carbonyl band among such complexes. The carbonyl band is shifted to lower frequency in spectra of the acetylacetonates of the more electronegative metals. A shift in this direction implies a loosening of the C-O bond, probably as a result of increased covalent metal-oxygen bonding in the compounds containing the more negative metals.* Among the acetylacetonates of divalent metals, there is a roughly linear relationship between carbonyl frequency and second ionization potential of the metal (Fig. 3),[†] and hence also between frequency and stability of the complex.(24)



In so far as we can judge from the few examples which were studied, a similar relationship also holds for the trivalent metals, but not for the univalent metals. Among the latter, more ionic complexes, there is no correlation between first ionization potential and frequency of the first carbonyl band. There is a small shift toward lower frequency for NaA and especially LiA, perhaps a result of polarization effects due to the small size of the lithium and sodium ions.

The second carbonyl band, at 1360-1415 cm⁻¹, shows a somewhat more irregular variation with ionization potential. However, in general, this band shifts in the opposite direction to the first carbonyl band; that is, to higher frequency with increasing ionization potential. Other absorption bands also show irregular frequency shifts, but, in general, for bands other than the carbonyl bands, mass (or ion size) effects seem to be more important than ionization potential; the largest shifts are usually found for LiA and BeA₂.

LECOMTE⁽²⁾ found bands in the 600-700 cm⁻¹ region which varied depending on the nature of the metal, and which he tentatively ascribed to metal-oxygen vibration. We find slight variations in the positions of absorption bands in the 650 cm^{-1} region, but far less variation, and also lower intensity, than would be expected for bands due to

^{*} A similar relationship between carbonyl frequencies and ionization potential was noted by BELLAMY⁽³⁾ among metal derivatives of salicyladehyde.

[†] The point for the highly ionic CaA, appears on the plot, but was not used in determining the position of the line.

⁽²⁴⁾ L. G. VAN UITERT, W. C. FERNELIUS and B. E. DOUGLAS J. Amer. chem. Soc. 75, 2736 (1953).

metal-oxygen vibration. In our opinion, for most acetylacetonates, bands due to metal-oxygen vibration should be found out of the sodium chloride region, at less than 600 cm^{-1} . The first-row metals may be exceptions to this generalization, because their very low mass should lead to a high vibrational frequency. An example is beryllium, which shows a very strong band at 822 cm^{-1} , in a region where none of the other compounds show marked absorption. A similarly intense band at nearly the same frequency is also found in the infra-red spectrum of beryllium basic acetate, $Be_4O(CH_3COO)_6$. Tentatively we assign this band to the Be-O stretching vibration.



Finally, we should like to put forth some speculations regarding bonding in metal acetylacetonates. The metal acetylacetonates are commonly supposed to have symmetrical, resonance-stabilized structures. The most important evidence leading to this belief is the work of CALVIN and WILSON⁽²⁵⁾ who have shown convincingly that resonance in the enol ligand is much more important for the stability constant of the Cu(II) complex than it is for the acid dissociation constant of the enol, i.e. that enol resonance is much more important for the copper than for the hydrogen compound. To explain this, CALVIN proposed two structures, both involving resonance in a chelate ring covalently bonded to copper (Figs. 4 and 5). However, both of CALVIN's models require that the copper be symmetrical with respect to the two oxygens of the ring in order for resonance to take place. Recent X-ray structure determinations for CuA₂ show that the C—O and O—Cu distances for each oxygen of the acetylacetonate ligand are slightly but significantly different.^(26,27,28)*

It is our suggestion that CALVIN's results can be explained on the basis of a model involving resonance between the ionic and covalent forms, with an appreciable contribution of the ionic form to the resonance hybrid. This ionic-covalent resonance model (Fig. 2) does not require symmetrical placement of the copper atom, and is

^{*} Cf. bond distances in the closely related copper(II) tropolonate.⁽²⁸⁾

⁽²⁵⁾ M. CALVIN and K. W. WILSON J. Amer. chem. Soc. 67, 2003 (1947).

⁽²⁶⁾ E. A. SHUGAM Dokl. Akad. Nauk. S.S.S.R. 81, 853 (1951). Cu-O 1.94 and 1.88 Å; C-O 1.25 and 1·30 Å.

 ⁽²⁷⁾ H. KOYAMA, Y. SAITO and H. KUROYA J. Inst. Polytech. Osaka City Univ., Ser. C 4, 43 (1953). C-O 1.94 and 1.95 Å; C-O 1.24 and 1.29 Å.
 (28) J. M. ROBERTSON J. chem. Soc. 1951, 1222.

therefore more consistent with the known structure of CuA2.* CALVIN's stability data⁽²⁵⁾ is explained by our model, if we assume that the ionic form makes a significantly greater contribution to the resonance hybrid in CuA₂ than in HA. With metals more electropositive than copper, the relative importance of the ionic form should be still greater, $^{(32)}$ and the structure should become more nearly symmetrical. $^{(33)}$

(Note added in proof) HOLTZCLAW and COLLMAN⁽³⁴⁾ have recently published a paper on infra-red absorption of metal chelates of various beta-diketones. These authors, studying acetylacetonates of seven divalent metals and of sodium, find a relationship between the frequency of the carbonyl absorption and the stability constant for the complex. This finding is confirmed by our work.

‡ Significant differences in C-O and Fe-O distances were not found in FeA3.(33)

(34) H. F. HOLTZCLAW, JR. and JAMES P. COLLMAN J. Amer. chem. Soc. 79, 3318 (1957).

^{*} According to Pauling's postulate of 3d4s4p² bonding in planar Cu(II) complexes,⁽²⁹⁾ one might not at first sight expect an important contribution from the ionic form, because the Cu⁺⁺ ion could only be present as an excited state with a 3d electron "promoted" to the 4p level. Actually, our model is not inconsistent with $3d_{4s}4p^2$ hybridization about copper, since the ionic excited state should be strongly stabilized by crystal field forces.⁽³⁰⁾ In addition, our structure is thoroughly consistent with HUGGINS' suggestion of $4s4p^24d$ bonding to Cu(II) in planar copper complexes.⁽³¹⁾

[†] While there is no direct evidence to this point, it is known that the influence of the acid dissociation constants of diketones on the stability of their metal complexes decreases in the order Cu Ni Ba. (32)

⁽²⁹⁾ L. PAULING, The Nature of the Chemical Bond, p.104, Second Edition, Cornell Univ. Press, Ithaca, New York, 1945.

⁽³⁰⁾ L. E. ORGEL J. chem. Soc. 1952, 4756.

⁽³¹⁾ M. HUGGINS J. chem. Phys. 5, 527 (1937); cf. D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL and L. E. SUTTON J. chem. Soc. 1954, 332. (32) L. G. VAN UITERT, W. C. FERNELIUS and B. E. DOUGLAS J. Amer. chem. Soc. 75, 457 (1953).

⁽³³⁾ R. B. ROOF, JR. Acta. Cryst. 9, 781 (1956).