Inorganica Chimica Acta, *165* (1989) 249–253

Reaction of Dichloroaluminium Acetylacetonate with Lewis Bases IV*. Structural Properties of Octahedral Aluminium Diacetylacetonate Cation Complexes Derived from their Infrared Spectra

J. LEWIŃSKI**, S. PASYNKIEWICZ

Faculty of Chemistry, Warsaw Technical University (Politechnika) 00-661 Warszawa, Koszykowa 75 (Poland)

and D. J. STUFKENS

Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

(Received April 3, 1989; revised July 24, 1989)

Abstract

Infrared spectra (1750–350 cm^{-1}) are reported for the complexes $[(acac)_2Al\cdot nB][AlCl_4]$ and $[(acac)_2Al\cdot nB][AlBr_4]$ ($n = 2$, B = Et_2O, THF, Py, DMF; $n = 1$, B = DME) all containing an octahedral aluminium diacetylacetonate cation. Changes in the structure of the cation and in the strength of the complexed base mainly affect the vibrational bands in the 650–350 cm^{-1} region. From the number of these bands, their frequencies and intensities, the *cis* and *trans* geometric isomers of the cations could be distinguished. The relative amounts of these isomers in the reaction products could be determined approximately from the relative intensities of the Al–O stretching modes.

Introduction

The series of ionic complexes containing an aluminium diacetylacetonate cation stabilized by a Lewis base $[(acac)_2Al\cdot 2B]^+[AlCl_4]^-$ (B = Et_2O, THF, Py, DMF) and $[(acac)_2Al\cdot B]^+[AlCl_4]^-$ (B = DME) were studied by ^{27}Al, ^{13}C and ^1H NMR spectroscopy [1–3]. These spectra showed that the aluminium diacetylacetonate cation stabilized by THF or Py is present in solution mainly as a *trans* isomer. In the case of DMF the *cis* form is prevailing and the DME complex only occurs as the *cis* isomer. NMR results of the Et_2O complex indicated the presence of the *trans* isomer only. In several instances NMR data were not sufficient to determine unambiguously the structure of the metal acetylacetonate complexes [3, 4]. Infrared spectroscopy may then be a simple alternative method for the structural analysis.

Infrared data of acetylacetonate complexes have been investigated both theoretically and experimentally. Considerable difficulties were encountered in assigning individual bands to specific vibrations and this problem is still under study. Normal coordinate analyses on 1/1 [5, 6], 1/2 and 1/3 [7] (metal/acetonate) model systems have shown that several vibrations in the low frequency region are to a varying degree of M–O stretching character because of vibrational coupling. A number of investigators [8–10] have measured the infrared spectra of acetylacetonate complexes to confirm these theoretical assignments. Many reassignments were made by using deuterated [11, 12], ^{13}C [12] and ^{18}O [13, 14] derivatives of metal acetylacetonates and by studying metal isotope effects on metal–ligand vibrations [15]. The influence of substitution of the acac ring and of a change of metal on the M–O and acac vibrations has also been studied [14, 16–19].

Complexes of the $(acac)_2MX_2$ type can have a *cis* or *trans* structure. There are no simple correlations allowing us to distinguish such geometrical isomers on the basis of their infrared spectra. Since the *trans* isomer has a centre of symmetry, less vibrations are IR allowed than for the *cis* isomer. This rule must, however, be applied with caution in the case of the spectra of the solid compounds [20]. Only for $VO(acac)_2\cdot L$, where L is a substituted pyridine, could the *cis* and *trans* isomers be distinguished from each other by infrared spectra [21]. In other cases even for separated isomers, the structure determination on the basis of infrared studies was impossible or at least ambiguous [19, 22, 23].

Throughout the series of the octahedral complexes $[(acac)_2Al\cdot nB]^+$ studied by us, the infrared spectra are mainly determined by the configuration of the complex and by the electron donating power of the complexing Lewis base. It will be shown that the geometric isomers can be distinguished from each other by their frequencies and number of IR bands.

---

*Part III is ref. 3.

**Author to whom correspondence should be addressed.

0020-1693/89/$3.50

An accurate infrared spectral analysis of $[(acac)_2Al{\cdot}nB]^+[AlCl_4]^-$ complexes was prevented by the presence of a very intense $[AlCl_4]^-$ band in the low frequency region. We therefore also synthesized the corresponding $[AlBr_4]^-$ complexes by using dibromoaluminium acetylacetonate as a substrate. A comparison of the spectra of both groups of compounds enabled us to observe all absorption bands in the low frequency region of the spectrum.

Experimental

All operations were carried out under dry nitrogen. Commercially available CH_2Cl_2, Et_2O, THF, DME, Py and DMF were purified, and $[(acac)_2Al{\cdot}nB][AlCl_4]$ complexes were obtained by the method described earlier [1–3]. Dibromoaluminium acetylacetonate was synthesized from $MeAlBr_2$ and acacH by the procedure used for dichloroaluminium acetylacetonate [24]. The $[(acac)_2Al{\cdot}nB][AlBr_4]$ complexes were obtained in the same way as the $[(acac)_2Al{\cdot}nB][AlCl_4]$ complexes.

Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer. The measurements were carried out in nujol, in polyethylene film and in CH_2Cl_2 solution in a 0.1 mm thick cell made of KBr plates. The average error in frequency reading was ± 1 cm^{-1}.

Results and Discussion

The $[(acac)_2Al{\cdot}nB][AlCl_4]$ complexes were obtained according to the earlier described reactions of dichloroaluminium acetylacetonate with Lewis bases or by the exchange of bases in the complexes [1–3]. $[(acac)_2Al{\cdot}nB][AlBr_4]$ complexes were obtained in the same way as illustrated by the following equations

$$2Br_2Alacac + nB \longrightarrow [(acac)_2Al{\cdot}nB]^+[AlBr_4]^-$$

$$[(acac)_2Al{\cdot}nB]^+[AlBr_4]^- + nB' \longrightarrow [(acac)_2Al{\cdot}nB']^+[AlBr_4]^- + nB$$

$n = 1$ for B = DME, $n = 2$ for the remaining Lewis bases

Infrared spectra of $[(acac)_2Al{\cdot}nB]^+[AlCl_4]^-$ and $[(acac)_2Al{\cdot}nB]^+[AlBr_4]^-$ complexes were measured within the 1750–350 cm^{-1} region. A comparison of the infrared spectra of the complexes showed their great similarity. First of all, the $[AlCl_4]^-$ anion containing complexes are characterized by an intense band at 495 cm^{-1} which shifts to 405 cm^{-1} for the corresponding $[AlBr_4]^-$ compounds. These frequencies agree with the literature data for the antisymmetric stretching modes of these anions [25]. Table 1 presents the frequencies of the skeletal

TABLE 1. Observed frequencies and band assignments for octahedral aluminum diacetylacetonate cationic complexes solid in nujol

Bands (cm^{-1}) of $[(acac)_2Al{\cdot}nB]^+$					Assignment
B = Et_2O	THF	DME	Py	DMF[a]	
362	378	380, 396	387	400	Al–O(B) or Al–N(B) stretching
405	412	417, 422	442	420	Al–O(B) or Al–N(B) stretching
448	448	440, 448 (442)	450	440	ring deformation
468	479	487	478	474	ring deformation
532	529	536	524	517	(*cis*) Al–O stretching + ring deformation
559	552		548	537	(*trans*) Al–O stretching + ring deformation
623	620	587, 598, 613	609	585, 600	Al–O stretching
661	661	659	661	660	out of plane deformation
703	702	702	700		CCH_3 bend + ring deformation + Al–O stretching
807	808	806	808		C–H out-of-plane
894	875	873	878	870, 893	
950	953	946, 956	952	940	C–CH stretching + C=O stretching
1034	1032	1028	1033	1029	CH_3 rocking
1190	1198	1189, 1196	1194	1192	C–H in-plane bending
1297	1295	1297	1297	1292	C=C str. + C–CH_3 stretching
1338	1360	1360	1359	1368	CH_3 symmetrical bending
1402	1397	1390	1398	1400	CH_3 symmetrical bending
1430	1425	1428	1420	1427	CH_3 symmetrical bending
1531	1531	1532	1532	1530	C=C stretching
1570	1571	1570	1573	1587	C=O stretching

[a] In CH_2Cl_2.

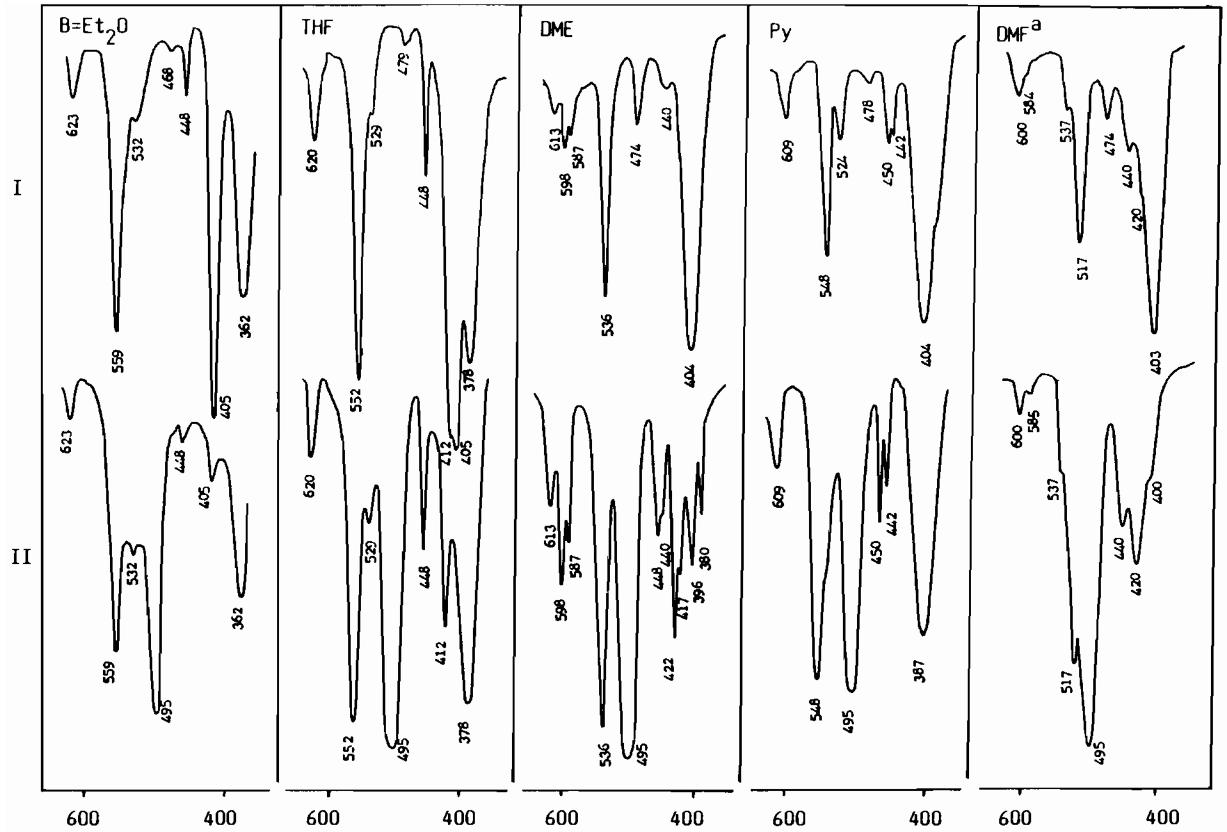

Fig. 1. Infrared spectra of solid (nujol mull) ionic complexes $[acac_2Al{\cdot}nB]^+[X]^-$, where B = Et_2O, THF, DME, Py and DMF; X = $AlBr_4$ (I) and $AlCl_4$ (II). ^{a}In CH_2Cl_2.

vibrations of the cations and of the acetylacetonate vibrations. The bands belonging to the Lewis bases are not included.

As can be seen from Table 1, two frequency regions can be distinguished in the spectra of the complexes: 1750–650 and 650–350 cm^{-1}. The first region comprises the bands belonging to acetylacetonate vibrations and their frequencies and intensities hardly differ for all complexes studied. The frequencies of these bands are very similar to those described in the literature for other metal acetylacetonates and their assignments agree with the results of Mikami *et al.* [7] and Nakamoto *et al.* [15]. Thus a change of structure of the diacetylacetonate cation and replacement of one complexing Lewis base by another has no effect on the acetylacetonate skeleton vibrations. The C=O and C=C stretching vibrations are even not sensitive to the strength of the Lewis base and to the structure of the cation. The only exception is the diacetylacetonate complex stabilized by DMF molecules which has its C=O vibration clearly shifted towards higher frequency. This can be explained by the fact that DMF is the strongest Lewis base used [3] and that the $[(acac)_2Al{\cdot}2DMF]^+$ cation occurs mainly as the *cis* isomer [2], in which the DMF molecules exert a strong *σ-trans* effect on the coordinating O atoms of the acac rings.

In the second region, 650–350 cm^{-1} (Fig. 1), the bands depend both on the structure of the aluminium diacetylacetonate cation and on the strength of the Lewis base stabilizing it. It should be noted that in metal acetylacetonates the metal–ligand vibrations are generally coupled with the vibrations of the acetylacetonate ligand. Therefore, the assignment of the bands in Table 1 on the basis of experimental data should be treated with caution. More detailed and reliable band assignments could be made by performing a normal coordinate analysis.

Especially interesting changes occur for the bands in the 515–560 cm^{-1} region. The cation $[(acac)_2Al{\cdot}DME]^+$, which occurs exclusively in a *cis* conformation, only shows a single intense band at 536 cm^{-1}. The other complexes, present in both isomeric forms, show two bands, the intensities of which depend on the relative amounts of the isomers. Complexes appearing mainly as the *trans* isomer, $[(acac)_2Al{\cdot}2THF]^+$ [1] and $[(acac)_2Al{\cdot}2Py]^+$ [3], have a dominating band at higher frequency and a weak band at lower frequencies. For complexes with an excess of the *cis* form, $[(acac)_2Al{\cdot}2DMF]^+$ [2], the intensity ratio of this pair of bands is reversed. These bands therefore provide direct information about the number of geometrical isomers in the complexes under study and about their relative ratio. On the basis of these observations we conclude that the $[(acac)_2Al \cdot 2Et_2O]^+$ cation occurs in both isomeric forms. Its IR spectrum shows two bands in the above-mentioned frequency region, and a comparison of their intensities shows that the *trans* isomer is in greater abundance. This result does not agree with previous ^1H NMR data [3], which showed the presence of the *trans* form only. The present result for this complex is, however, in agreement with the ^1H NMR data for the other complexes [1–3], which indicate that the aluminium diacetylacetonates stabilized by monodentate bases always occur in the form of both isomers. Describing further the bands in this 515–560 cm^{-1} region it should be noted that they are sensitive to the strength of the complexed Lewis base since their frequencies decrease with increasing electron donating power of the base according to the previously established order [3] $Et_2O < THF < DME < Py < DMF$. Apparently, these bands belong to coupled vibrations involving the Al–O stretching modes. The observed shifts are much larger for the bands belonging to the *cis* isomer (Table 1). Thus, substitution of the weakest base (Et_2O) by the strongest one (DMF) causes a shift of the *cis* and *trans* isomer bands by 18 and 8 cm^{-1}, respectively.

Another group of bands appearing at about 600 cm^{-1} is also sensitive to the strength of the complexed Lewis base and to the cation structure. They show a somewhat larger shift towards lower frequencies with an increase of the base strength than the above-mentioned bands between 515 and 560 cm^{-1}. Because of this these bands are assigned to relatively pure Al–O stretching modes. The DME complex having exclusively the *cis* structure, and the DMF complex occurring mainly in this isomeric conformation, show three or two Al–O stretching vibrations. However, for complexes with pyridine, tetrahydrofurane or diethyl ether, which occur mainly in the *trans* form, a broad single band of low intensity is observed. The broadening of this band at its base probably results from overlap with the bands of the *cis* isomer, present in small amounts.

The appearance of only one band in the case of the *trans* isomer is in accordance with the presence of a centre of symmetry in the $Al(acac)_2$ plane. Only the antisymmetric Al–O stretching mode is then IR allowed.

The bands at *c.* 440 and 480 cm^{-1} do not depend on the strength of the Lewis base. They are therefore assigned to deformation modes of the acac ring. Their relative intensities strongly depend on the isomeric composition of the complexes.

The bands between 360 and 430 cm^{-1} depend, however, on both the structure of the complex and the strength of the Lewis base. They are therefore assigned to Al–O(B) and Al–N(B) (B = Lewis base) stretching modes and this assignment is supported by the observation that $Al(acac)_3$ has no IR bands in this frequency region [26]. Those complexes, which mainly occur in the *trans* form, show an intense band varying from 362 ($B = Et_2O$) to 387 (B = Py) cm^{-1} which is attributed to the anti-symmetric Al–O(B) and Al–N(B) stretching mode, respectively. It may be that the 400 cm^{-1} band of the DMF complex also belongs to this vibration (see, however, hereafter). The bands at 405 and 412 cm^{-1} of the Et_2O and THF complexes, respectively, do not belong to the *trans* isomer since only the above-mentioned anti-symmetric Al–O(B) stretching mode of this isomer is IR allowed. These bands are therefore assigned to a stretching mode of the *cis* isomer. This assignment is supported by the data of the *cis* structured DME and DMF complexes, which indeed have their most intense band at *c.* 420 cm^{-1}. The corresponding symmetric Al–O(DME) and Al–O(DMF) vibrations are IR allowed and occur at *c.* 400 cm^{-1}. The frequencies, collected in Table 1, have been measured for the solid complexes in nujol, but similar results were obtained for the compounds dissolved in CH_2Cl_2. The intensities and the number of bands did not change. These results indicate that the structures of the complexes studied are identical in solution and in the solid state. Bands at about 870 and 890 cm^{-1} are an exception. In the case of the cationic complexes with Et_2O and DME only a single band of the same frequency is observed, both in nujol and in solution; 894 (Et_2O) and 873 (DME) cm^{-1}, respectively. Both bands are observed for the complexes with DMF and THF in solution, whereas the nujol spectrum of the THF complex only shows the band at 875 cm^{-1}. For the pyridine complex in nujol only the band at 878 cm^{-1} is present, and in solution only the band at 892 cm^{-1}.

Conclusions

Essential spectral differences occur for the various octahedral aluminium diacetylacetonate cations $[(acac)_2Al \cdot nB]^+$ below 650 cm^{-1}, which result from the changing strength of the Lewis base coordinated to the aluminium atom and from a difference in isomeric composition. The relationships which appeared to exist between the number, frequencies and intensities of the IR bands, enabled us to determine the isomeric composition and to assign the specific vibrations of these isomers.

References

1 J. Lewiński and S. Pasynkiewicz, *Inorg. Chim. Acta, 130* (1987) 23.

2 J. Lewiński and S. Pasynkiewicz, *Inorg. Chim. Acta, 122* (1986) 225.
3 J. Lewiński and S. Pasynkiewicz, *Inorg. Chim. Acta, 143* (1988) 39.
4 N. Serpone and K. A. Hersh, *Inorg. Chem., 13* (1974) 2901.
5 K. Nakamoto and A. E. Martell, *J. Chem. Phys., 32* (1960) 588.
6 K. Nakamoto, P. J. McCarthy and A. E. Martell, *J. Am. Chem. Soc., 83* (1961) 1272.
7 M. Mikami, J. Nakawaga and T. Shimanouchi, *Spectrochim. Acta, Part A, 23* (1967) 1037.
8 E. K. Lawson, *Spectrochim. Acta, 17* (1961) 248.
9 J. P. Dismukes, J. H. Jones and J. C. Bailar Jr, *J. Phys. Chem., 65* (1961) 729.
10 R. D. Gillard, H. G. Silver and J. L. Wood, *Spectrochim. Acta, 20* (1964) 63.
11 G. T. Behnke and K. Nakamoto, *Inorg. Chem., 6* (1967) 433.
12 H. Jung and H. Musso, *Spectrochim. Acta, Part A, 24* (1968) 513.
13 S. Pinchas, B. L. Silver and I. Laulicht, *J. Chem. Phys., 46* (1967) 1506.
14 K. W. Kradenow, B. A. Kolesow and J. K. Igumienow, *Koord. Chim., 9* (1987) 1179.
15 K. Nakamoto, C. Udovich and J. Takemoto, *J. Am. Chem. Soc., 92* (1970) 3973.
16 R. D. Mancock and D. A. Thornton, *J. Mol. Struct., 4* (1969) 377.
17 K. Nakamoto, Y. Morinoto and A. E. Martell, *J. Phys. Chem., 66* (1962) 366.
18 I. M. Oglezniewa and I. K. Igumienow, *Koord. Chim., 10* (1984) 313.
19 Y. Kawasaki, T. Tanaka and R. Okawara, *Spectrochim. Acta, Part A, 22* (1966) 1571.
20 K. Nakamoto and P. J. McCarthy, *Spectroscopy and Structure of Metal Chelate Compounds,* Wiley, New York, 1968.
21 M. R. Caira, J. M. Haigh and L. R. Nassimbeni, *J. Inorg. Nucl. Chem., 34* (1972) 3171.
22 R. C. Fay and R. N. Lowry, *Inorg. Nucl. Chem. Lett., 3* (1967) 117.
23 W. D. Courrier, C. J. L. Lock and G. Turner, *Can. J. Chem., 50* (1972) 1797.
24 W. R. Kroll, I. Kuntz and E. Birnbaum, *J. Organomet. Chem., 26* (1971) 313.
25 J. Derouault and M. T. Forel, *Inorg. Chem., 16* (1977) 3207.
26 K. Nakamoto, P. J. McCarthy, A. Ruby and A. E. Martell, *J. Am. Chem. Soc., 83* (1961) 1066.