BCl_3 and AIX_3 (X = Cl, Br, I) complexes of 4-amino-benzophenone

IDA M. VEZZOSI, ALINE F. ZANOLI and GIORGIO PEYRONEL

Istituto di Chimica Generale e Inorganica, Università di Modena, 41100 Modena, Italy

(Received 9 December 1980).

Abstract—The 4-amino-benzophenone (L) complexes: $2BCl_3 \cdot 3L$, yellow, $3AlCl_3 \cdot L \cdot 6H_2O$, yellow, $2AlCl_3 \cdot L \cdot 6H_2O$, red, $4AlCl_3 \cdot L$, yellow, $AlBr_3 \cdot 3L$, yellow and red, $3AlBr_3 \cdot 4L$, yellow and red, $AlI_3 \cdot 4L$, deep green, and $AlI_3 \cdot L$, black, have been prepared and investigated by i.r. spectroscopy. The ligand is H_2N -coordinated in the BCl_3 , $AlCl_3$ and $AlBr_3$ complexes for which a CO-coordination is excluded. A $\nu(CO)$ frequency decrease indicates a CO interaction in the aluminium iodide complexes for which a H_2N -coordination is excluded.

INTRODUCTION

In previous works we have shown that 4-aminobenzophenone is principally N-bonded in the zinc halide and O-bonded in the cadmium and mercury (II) halide complexes [1], is N-bonded in the yellow and red tin (IV) chloride and bromide complexes and presumably CO-bonded in the red tin (IV) iodide complex [2]. While in the antimony (III) halide complexes it is never O-coordinated and only for some complexes N-coordinated [3] in the vellow or orange BiX_3 (X = Cl, Br) complexes the NH₂ group is involved into the coordination but not in the red BiX_3 (X = Cl, Br, I) complexes while the CO group is never involved in the coordination [4]. Owing to this variable coordinating behaviour of 4-amino-benzophenone we have extended this study to its boron and aluminium halide complexes.

EXPERIMENTAL

The compounds were prepared as follows.

$2BCl_3 \cdot 3L$ (yellow)

By reaction at 0° C of liquid BCl₃ with solid L for some days; the product was washed with petroleum ether.

3AlCl₃·L·6H₂O (yellow)

By adding hexane to a saturated ethanolic solution of the components and abundantly washing with hexane the yellow pitch formed, a yellow powder was obtained.

2AlCl₃·L·6H₂O (red)

By reaction at 65°C of the solid components in a small volume of ethanol and repeatedly washing with hexane the red pitch formed, a red microcrystalline product was obtained.

4AlCl₃·L (yellow)

By adding small quantities of L to a saturated solution of $AlCl_3$ in cyclohexane and washing with petroleum ether the precipitate which is hydroscopic.

AlBr₃·3L (yellow and red)

By reaction of the solid components in cyclohexane; by heating in vacuo at 70°C the yellow compound became red.

3AlBr₃·4L (yellow and red)

By adding solid AlBr₃ to a saturated solution of L in cyclohexane and washing the crystalline product with petroleum ether; the yellow product heated *in vacuo* at 70° C became deep red.

$All_3 \cdot 4L$ (deep green)

By adding a solution of AlI_3 in cyclohexane to a saturated solution of L in cyclohexane and washing with petroleum ether the crystalline precipitate which is stable in air.

$AII_3 \cdot L$ (black)

By adding hexane to an ethanolic solution of the components in a 1:1 ratio and repeatedly washing with hexane the brown pitch formed, a black microcrystalline powder was obtained which was dried on P_2O_5 and is stable in air.

The compounds were analysed by standard methods (Table 1). Molar conductivities were determined at 25°C

Table 1. Analytical data, found % (calcd %), colour, molar conductivity $\Lambda_{M}(\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{2})$ in 10^{-3} M MeOH solution, Λ_{M}/n (n = number of MX₃ units in the formula) and charge-transfer bands (nm) of the 4-H₂N-Ph₂CO (L) complexes

• •	Colour	С	н	N	x	Λ_{M}	C.T. nm
2BCl ₃ ·3L	yellow	56.55 (56.65)	4.12 (3.99)	4.97 (5.08)	(a)	546	440 m
3AlCl ₃ ·L·6H ₂ O	yellow	21.73 (22.12)	3.52 (3.26)	1.88 (1.98)	(b)	278	430 m
2AlCl ₃ ·L·6H ₂ O	red	27.41 (27.27)	4.38 (4.02)	2.37 (2.44)		162	450 s, 500 sh
4AlCl ₃ ·L	yellow	20.92 (21.35)	1.66 (1.50)	1.74 (1.91)		407	440 m
AlBr ₃ ·3L	yellow	54.76 (54.52)	4.18 (3.84)	5.07 (4.89)		143	450 m
AlBr ₃ ·3L	red	54.62 (54.52)	4.15 (3.84)	5.11 (4.89)		144	440 s, 510 sh
3AlBr ₃ ·4L	yellow	39.45 (39.27)	3.12 (2.76)	3.55 (3.52)	(c)	450	440 m
3AlBr ₃ ·4L	red	39.56 (39.27)	3.18 (2.76)	3.51 (3.52)		433	446 s, 505 sh
All ₃ ·4L	deep green	52.12 (52.15)	3.88 (3.67)	4.72 (4.68)		24	460 m, 660 m
All ₃ ·L	black	26.02 (25.78)	2.04 (1.82)	2.28 (2.31)	(d)	ins.	

X = (a) 25.63 (25.75); (b) 45.36 (45.32); (c) 44.86 (45.26) and (d) 62.78 (62.92).

Table 2. Principal i.r. bands (cm⁻¹) of 4-H₂N-Ph₂CO (L) and its boron and aluminium complexes. Yellow (Y), red (R), green (G) and black (B) colours of the complexes are indicated

	L	2BCl ₃ 3L (Y)	$\begin{array}{c} 3AlCl_3\\ L\cdot 6H_2O\\ (Y) \end{array}$	$\begin{array}{c} 2AlCl_3\\ L\cdot 6H_2O\\ (R) \end{array}$	4AlCl ₃ L (Y)	AlBr ₃ 3L (Y)	AlBr ₃ 3L (R)	3AlBr ₃ 4L (Y)	3AlBr ₃ 4L (R)	All ₃ 4L (G)	AlI ₃ L (B)
ν(NH)	3418 ms	3410 sh	3400	3460 vs	3400	3420 s	3415 m	3400	3400	3425 sm	3420 s
	3335 s 3220 m	3330 sh 3210 vs	VSD 3070	3200 vs 3100 vs	100 vsb	3345 vs 3230 m	3335 s 3220 mw	1 vsb	vsb 3100	3340 vs 3225 s	3325 vs 3200 sm
v(CO)	1635 vs	1645 vs	1646 vs	1648 vs	1644 vs	1650 vs	1646 vs	1649 vs	1646 vs	5225 5	5200 SH
$\delta(NH_2)$	1625 vs		1630 sh		1626 sm	1630 s	1626 sm	1630 sh	1630 sh	1627 vs	1620 vs
		1603 m	1604 ms	1605 s	1602 sm	1610 w	1600 vw	1606 s	1604 sm		

with a WTW conductometer in MeOH solution. Electronic spectra of the solids on filter paper were recorded with a Shimadzu MPS 50L spectrophotometer. Infrared spectra (Table 2) were recorded on the solids in KBr disks ($4000-250 \text{ cm}^{-1}$) and as nujol mulls on polyethylene ($600-60 \text{ cm}^{-1}$) with a Perkin-Elmer 180 spectrophotometer. It was impossible to record the Raman spectra on the solids because the compounds are coloured and are decomposed by the laser beam.

RESULTS AND DISCUSSION

The molar conductivities (Table 1) were determined on MeOH solutions, the only solvent in which the complexes are sufficiently soluble, by using the most pure and anhydrous available methanol for spectroscopic uses, without any further dehydration. Owing to the high MeOH coordinating power toward boron and aluminium ions the molar conductivities measured in this solvent cannot be very significant for an interpretation of the complexes in the solid state. The molar conductivities of the three aluminium halides in the same solvent increase linearly with the electronegativities (EN) of the halogens [5]

	AlCl ₃	AlBr ₃	All ₃
EN	2.83	2.74	2.21
Λ_{M}	206	174	60

Molar conductivities in MeOH are 80-115 for 1:1, 160-220 for 1:2, 290-350 for 1:3 electrolytes [6]. In the MeOH and at the concentration used the aluminium chloride and bromide approximately behave as 1:2 electrolytes and the iodide does not reach the conductivity of a 1:1 electrolyte.

The 'unitary' molar conductivities of the complexes (Λ_M/n) referred to one MX₃ unit in the stoichiometric formula indicate an almost 1:3 electrolyte behaviour for BCl₃ in its complex while for all the aluminium complexes they are significantly lower than those of the corresponding free halides, in agreement with the fact that very often the conductance of aluminium halides diminishes by adding complexing agents stronger than the solvent [7, 8] at least in certain ratios. In fact the 'unitary' conductivities of the AlCl₃ complexes linearly increase in the order $2AlCl_3 \cdot L < 3AlCl_3 \cdot L < 4AlCl_3 \cdot L$. These preliminary experiments may therefore indicate that $H_2N \cdot Ph_2CO$ is a coordinating agent stronger than MeOH.

The $\nu(NH)$, $\nu(CO)$ and $\delta(NH_2)$ bands (Table 2) were identified by deuteriation of the ligand in a previous work [2]. In the BCl₃, AlCl₃ and AlBr₃ complexes a $\nu(CO)$ frequency increase indicates that the CO group is not coordinated. In the 3AlCl₃·L·6H₂O, 2AlCl₃·L·6H₂O, 4AlCl₃·L, 3AlBr₃·4L, yellow and red, complexes a broad unresolved band substitutes the three very distinct and sharp $\nu(NH)$ bands of the ligand, indicating a H₂N-coordination to the metal. In these complexes the $\delta(NH_2)$ band shifts from 1625 cm⁻¹ to 1602– 1606 cm⁻¹ being accompanied in some case by a much weaker band or shoulder at 1626–1630 cm⁻¹.

For the yellow $3AlCl_3 \cdot L \cdot 6H_2O$ and red $2AlCl_3 \cdot L \cdot 6H_2O$ complexes the bulky maximum is particularly intense in the $3400-3500 \text{ cm}^{-1}$ region with a distinct peak at 3460 cm^{-1} for the red complex corresponding to the water molecules contained in these complexes. The rocking and wagging motion bands observed at 835 and 595 cm⁻¹ for the coordinated water molecules in $Al(H_2O)_6^{+3}$ [9] cannot be identified in these complexes because all the complexes of this series show two rather strong bands in these positions and no other new bands appear in these regions for the two complexes containing the $6H_2O$ molecules.

In the 2BCl₃·3L complex only one very strong band is observed at 3210 cm^{-1} with two weak shoulders at 3410 and 3330 cm^{-1} and also the $\delta(\text{NH}_2)$ band is shifted to 1603 cm^{-1} indicating a H₂N-coordination.

The AlBr₃·3L, yellow and red, complexes show three distinct ν (NH) bands on a bulky maximum and two δ (NH₂) bands at 1626–1630 and 1600– 1610 cm⁻¹ indicating that some of the ligand molecules are not coordinated.

The AlI₃·4L and AlI₃·L complexes show three distinct ν (NH) bands with the same frequencies as in the ligand, indicating that the ligand is not H₂N-coordinated even in the 1:1 complex in which the presence of ν (NH) due to free molecules may be excluded. Only one band appears at 1627–1620 cm⁻¹ very likely due to the superimposition of

the $\nu(CO)$ and $\delta(NH_2)$ bands. A decrease of 8-15 cm⁻¹ in this frequency is of the order of that observed by us [2] for the $2SnI_4 \cdot 3(4-H_2N-Ph_2CO)$ complex, which also shows a unique band at 1620 cm⁻¹. This bathochromic shift of the ν (CO) band and the unaltered frequencies of the $\nu(NH)$ bands allows to conclude that in the aluminium iodide complexes, as in the tin (IV) iodide complex, the ligand is not H₂N-coordinated and that at least a weak (considering the low value of the $-\Delta\nu$ (CO) shift) $C = O \rightarrow aluminium$ iodide interaction may occur. This C=O interaction is ulteriorly supported by the fact that both the aluminium iodide complexes show only four bands attributable to ring vibrations and corresponding to the ligand bands at 1582 vs, 1550 s, 1510 m and 1440 s cm⁻¹ while the having H_2N -coordinated ligand complexes molecules show a greater multiplicity of bands in this spectral region due to the greater dissymmetry of the ligand molecule introduced by the H₂Ncoordination.

The far i.r. spectra of the compounds do not give valuable informations regarding the coordination geometry of these complexes. The great similarity of the spectra of the BCl₃ and AlCl₃ complexes notwithstanding their very different stoichiometries and the different acceptors suggests that many of the new bands observed in the complexes have a high, and for some of them predominant, ligand contribution.

A new band at 470–480 cm⁻¹ generally strong in the BCl₃, AlCl₃, AlBr₃ complexes having H₂Ncoordinated ligand molecules and present as a weak-broad band only in the black aluminium iodide complex may be considered as having a high ν (MN) contribution. ν (AlN) frequencies were reported at 509 cm⁻¹ for the Al(MeCN)₆⁺³ complex [10] and as a 30% contribution for the band at 560–570 cm⁻¹ for the AlX₃·NMe₃ complexes [11]. Few assignments of the MX vibrations modes may be tentatively done on the basis of their presence only in some groups of complexes and/or on their greater intensity with respect to a corresponding band eventually present in the ligand: ν (AlCl) at 413-409 and 312 cm⁻¹ and ν (AlBr) at 399-393 cm⁻¹ for the aluminium chloride and bromide complexes, respectively.

One charge transfer band at about 430-450 nm is observed for the solid yellow complexes independently from the halide ion present in the complex. A second CT band appears as a shoulder at about 500-510 nm for the red complexes. The very intense and dark colours and the bathochromic shift of the CT bands of the aluminium iodide complexes may confirm that they have a quite different type of coordination and of ligand-metal halide interaction but the presence of a strong band at 370 nm with a shoulder at 490 nm in the free AlI₃ solid may be at least in part responsible of the electronic spectra of the aluminium iodide complexes.

Acknowledgement—The i.r. spectra were recorded in the Centro Strumenti of the University of Modena.

REFERENCES

- [1] I. M. VEZZOSI, A. F. ZANOLI and G. PEYRONEL, Spectrochim. Acta, 36A, 1065 (1980).
- [2] I. M. VEZZOSI, A. F. ZANOLI and G. PEYRONEL, Spectrochim. Acta 36A, 219 (1980).
- [3] I. M. VEZZOSI, G. PEYRONEL and A. F. ZANOLI, Spectrochim. Acta 32A, 679 (1976).
 [4] I. M. VEZZOSI, A. F. ZANOLI and G. PEYRONEL,
- [4] I. M. VEZZOSI, A. F. ZANOLI and G. PEYRONEL, Spectrochim. Acta 35A, 105 (1979).
 [5] F. A. COTTON and G. WILKINSON, Advanced Inor-
- [5] F. A. COTTON and G. WILKINSON, Advanced Inorganic Chemistry, II Ed, Interscience, New York, 1972.
- [6] W. J. GEARY, Coord. Chem. Rev. 7, 81 (1971).
- 7] R. E. VAN DYKE, J. Am. Chem. Soc. 73, 398 (1951).
- [8] R. E. VAN DYKE and F. S. HARRISON, J. Am. Chem. Soc. 73, 402 (1951).
- [9] J. R. FERRARO, Low-Frequency Vibrations of Inorganic and Coordination Compounds. Plenum Press, New York (1971).
- [10] D. E. JONES and J. L. WOOD, J. Chem. Soc. (A) 3135 (1975).
- [11] I. R. BEATTHE and G. A. OZIN, J. Chem. Soc. (A) 2273 (1968).