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^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR spectra and negative-ion electrospray mass spectra of the 2:1 aluminium(III) complexes of azo dyes derived from anthranilic acid

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Abstract

The ^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR spectra in DMSO and mass spectra of 2:1 aluminium(III) complexes (**1b**–**4b**) derived from anthranilic acid azo coupling products with 4-tert.butylphenol (**1a**), 2-naphthol (**2a**) acetoacetanilide (**3a**) 3-methyl-1-phenylpyrazol-5-one (**4a**) were measured and analysed. It was found that the aluminium atom was six-coordinated, being bound to two oxygens and the nitrogen originating from anthranilic acid. © 2001 Published by Elsevier Science Ltd.

Keywords: Aluminium(III)–azo dye complexes, ^{27}Al NMR; ^{15}N NMR; ^{13}C NMR; ^{1}H NMR; Negative-ion electrospray mass spectra

1. Introduction

Metal–dye complexes play a very important role in dyestuff technology [1–5]; chromium, cobalt, copper, nickel and aluminium derivatives are used most frequently for these purposes [1–6].

We have shown in previous papers [7–10] that NMR spectroscopy is a very sensitive probe to study such compounds. The aim of this paper was to characterise 2:1 aluminium(III) complexes of azo dyes **1b**–**4b** (Scheme 1) derived from anthranilic acid azo coupling products with 4-*tert*. butylphenol (**1a**), 2-naphthol (**2a**), acetoacetanilide (**3a**) and 3-methyl-1-phenylpyrazol-5-one (**4a**) (Scheme 2) by means of ^{27}Al, ^{15}N, ^{13}C and ^{1}H NMR and to study the structure from the viewpoint of coordination at the aluminium atom and to compare the data with those published for analogous complexes in which substituted 2-hydroxyanilines were used in preparation of starting azo dyes [9] (i.e. with compounds in which –COO group was substituted by –O group).

2. Experimental

2.1. Synthesis

Ammonium salts of compounds **1b**–**3b** (Scheme 1) were prepared from appropriate precursors **1a**–**3a**

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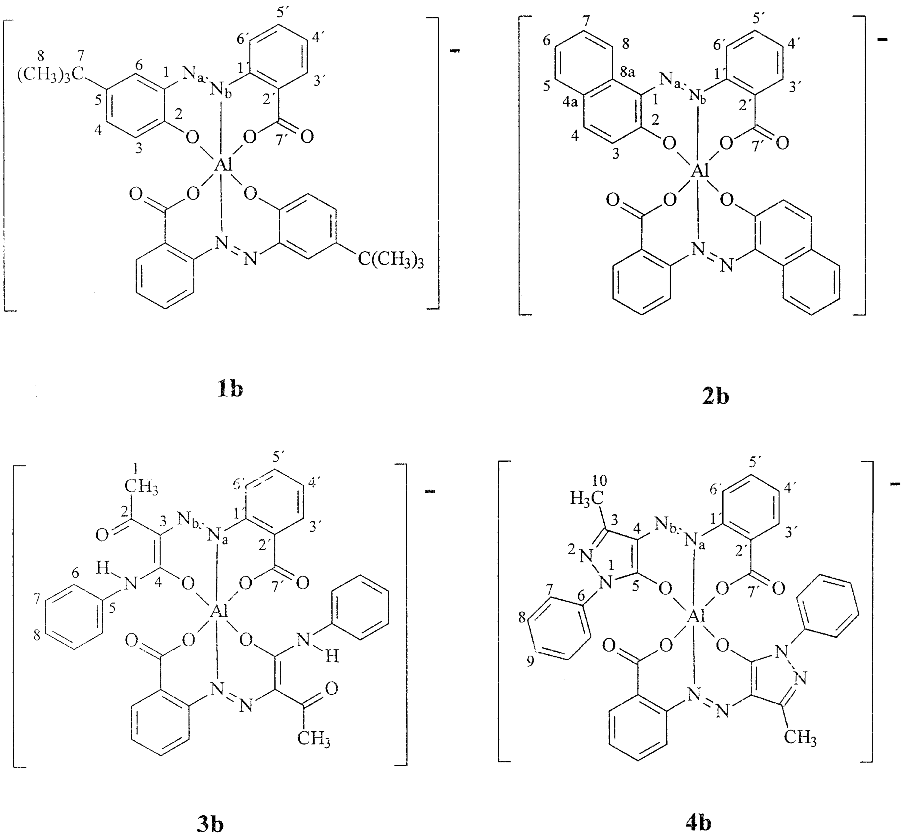


1b

2b

3b

4b

Scheme 1.

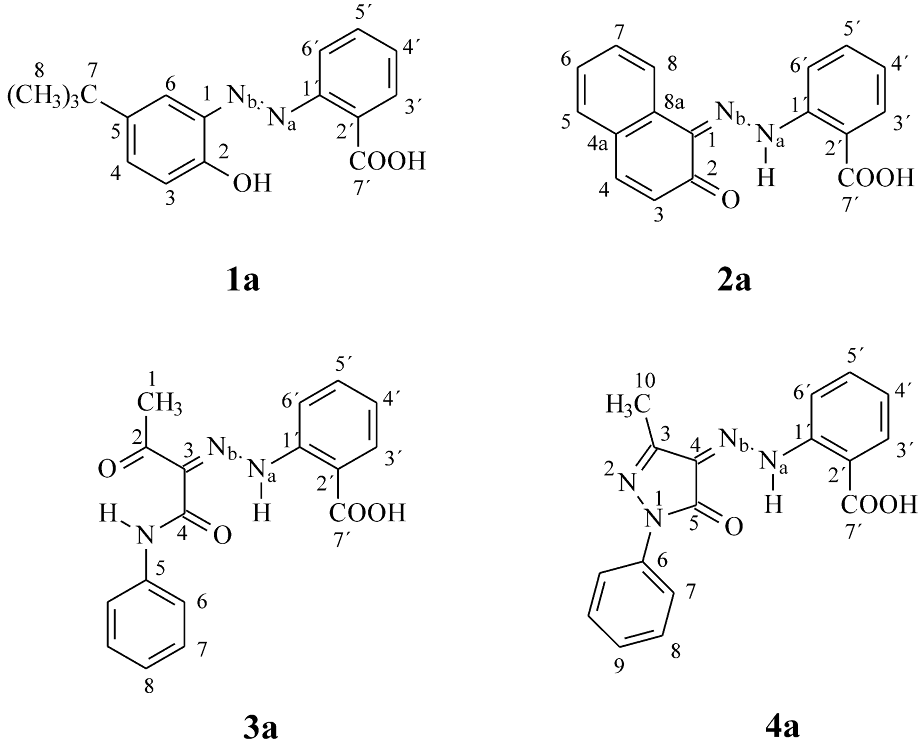
(Scheme 2) and $Al_2(SO_4)_3 * 18H_2O$ and ammonium analogously to cobalt derivatives in formamide solution [5]. Compound **4b** was prepared in the following way: 1.28 g of **4a** was dissolved in 20 ml of formamide and barium hydroxide dissolved in 10 ml of formamide was added. The mixture was heated 20 min at 70 °C and solid barium salt of **4a** was formed. Then 1.59 g of $Al_2(SO_4)_3 * 18H_2O$ in 20 ml of formamide was added and the mixture was stirred overnight at 90 °C. The reaction mixture was poured into 30 ml of water and the raw product was dried over P_2O_5.

All aluminium complexes were purified using column chromatography (Al_2O_3, methanol). Methanol was evaporated in vacuo at 25 °C.

At N_b ^{15}N labelled compounds were prepared analogously in formamide solution using Na $^{15}NO_2$ (95% ^{15}N) in preparation of compounds **1a–4a.**

2.2. NMR spectroscopy

The ^{27}Al (93.84 MHz), ^{15}N (36.50 MHz), ^{13}C (90.56 MHz) and ^{1}H (360.13 MHz) NMR spectra of compounds **1b–4b** were measured on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and 5 mm broadband inverse probe and a Silicon Graphic Indy computer in hexadeuteriodimethyl sulfoxide at ambient temperature. The ^{27}Al chemical shifts are referred to external $Al(OH)_6^{3+}$ in water [$\delta(^{27}Al) = 0.0$], ^{15}N chemical shifts to external neat nitromethane [$\delta(^{15}N) = 0.0$] and ^{13}C and ^{1}H chemical shifts were referred to the central peak of DMSO-d_6



Scheme 2.

[$\delta(^{13}C) = 39.60$, $\delta(^{1}H) = 2.55$]. Positive values of chemical shifts denote high frequency shifts with respect to standards.

Two-dimensional H,H-COSY, NOESY, gs (gradient selected)-HMQC and gs-HMBC [11,12] techniques were measured using standard microprograms provided by Bruker.

2.3. *Mass spectrometry*

Mass spectra were measured on the ion trap analyser Esquire3000 (Bruker Daltonics, Bremen, Germany). The samples were dissolved in 50% aqueous acetonitrile and analysed by direct infusion at the flow rate 1–3 μl/min. Mass spectra were recorded in the range m/z 15–1000 using electrospray ionization (ESI) in the negative-ion mode. The isolation width of the precursor ion for MS/MS and MS^n measurements was $m/z = 4$ and the collision energy was in the range 0.6–1 V depending on the stability of individual ions.

3. Results and discussion

3.1. *NMR spectra*

The ^{27}Al, ^{15}N, ^{13}C and ^{1}H chemical shifts of complexes **1b**–**4b** as well as starting azo dyes **1a**–**4a** measured in DMSO-D_6 are collected in Tables 1–4.

The ^{1}H and ^{13}C chemical shifts were assigned using H,H-COSY, gs (gradient selected)-HMQC and gs-HMBC [11,12] [optimised for $^{1}J(^{13}C, H)$ ca 150 Hz and $^{3}J(^{13}C, H)$ ca 8 Hz]. A correlation of proton H(3′) with carbon of COO group in HMBC spectra was a key information for the assignment of proton and carbon resonances C(1′)–C(7′).

Only one set of appropriate NMR signals was obtained for each of compounds **1b**–**4b** which means that both ligands in a molecule of complexes are equivalent, at least on the NMR time scale. On the contrary, Schetty and Kuster [13] observed three components having considerably different shade in cobalt analogue of compound **2b**.

Table 1
^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts of compounds **1a,b** in DMSO-d_6

	1a		**1b**	
	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$
1	–	137.62	–	140.46
2	–	150.15	–	157.28
3	6.99	118.34	6.18	122.12
4	7.51	131.03	7.30	135.46
5	–	142.03	–	138.73
6	7.89	127.29	7.69	109.97
7	–	33.88	–	33.58
8	1.36	31.17	1.34	30.99
1′	–	148.45	–	149.32
2′	–	133.52	–	128.65
3′	7.98	130.77	8.12	131.22
4′	7.59	130.63	7.56	129.01
5′	7.63	130.89	7.69	131.90
6′	7.84	115.21	7.81	120.32
7′	–	167.83	–	164.76
N_a	–	80. 9[a]	–	−34.0[a]
N_b	–	129.5[a,b]	–	99.5[a,b]
Al	–	–	–	0.5[c]

[a] $\delta(^{15}\mathrm{N})$.
[b] ^{15}N labelled compound.
[c] $\delta(^{27}\mathrm{Al})$.

Table 2
^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts of compounds **2a,b** in DMSO-d_6

	2a		**2b**	
	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$
1	–	130.59	–	128.78
2	–	179.16	–	160.40
3	6.67	126.87	6.42	124.51
4	7.88	142.71	7.80	139.90
4a	–	128.37	–	127.06
5	7.68	129.32	7.80	128.13
6	7.46	127.18	7.47	124.43
7	7.59	129.36	7.69	128.32
8	8.41	122.22	8.56	121.28
8a	–	133.37	–	133.90
1′	–	144.09	–	150.25
2′	–	117.08	–	134.33
3′	8.06	131.56	8.13	131.97
4′	7.33	124.50	7.54	128.78
5′	7.77	134.51	7.74	132.22
6′	8.34	116.32	7.87	120.90
7′	–	167.60	–	165.21
N_a	16.42	−195.7[a]	–	−59.7[a]
N_b	–	−21.4[a,b]	–	75.0[a,b]
Al	–	–	–	1.6[c]

[a] $\delta(^{15}\mathrm{N})$.
[b] ^{15}N labelled compound.
[c] $\delta(^{27}\mathrm{Al})$.

The coordination number of aluminium atom in compounds **1b–4b** can be determined by the measurement of NMR spectra of two nuclei directly involved in this process: nitrogen and aluminium.

^{27}Al NMR spectroscopy is a powerful tool for coordination studies [14–17]. The ^{27}Al chemical shifts are determined by two main factors: coordination number and the nature of ligands. The ^{27}Al chemical shifts move generally downfield passing from six- to five- and four-coordinated aluminium atoms, respectively. The ^{27}Al chemical shifts in compounds **1b–4b** were found to resonate in a very narrow range from 0.5 to 2.3 ppm and they give the evidence for the aluminium central atom to be six-coordinated, because the ^{27}Al chemical shifts practically coincide with the signal of standard. Hence, two measurements had to be performed for each sample, one with the standard in a coaxial capillary, in which the absolute resonance frequency of standard was determined, and the second one, in which relatively broad ^{27}Al NMR signal of a complex was detected.

To decide if the sixfold coordination is due to solvent interaction (because DMSO is known to be a strong coordinating solvent) or to interaction with one nitrogen of each azo/hydrazone bond, additional indications come from ^{15}N NMR spectra. In previous papers [7,9] we reported on the application of ^{15}N NMR as a very sensitive technique for the detection of the existence of coordination as well for the determination of coordination position of nitrogens in –N=N– and –NH–N= groups, respectively. To assign ^{15}N resonances undoubtedly and because of low solubility of compounds studied, it was necessary to prepare ^{15}N selectively enriched compounds for the measurement of ^{15}N chemical shifts.

Upfield ^{15}N chemical shifts of about 100 ppm were observed on protonation of various heterocyclic derivatives, e.g. pyridine, purine, indolizine, etc. [18,19], where the nitrogen atom lone pairs are engaged in a bonding. The similar effect [$\Delta\delta(^{15}\mathrm{N}) = 102$–$146$ ppm] [20] is also typical of the coordination of a nitrogen atom of azo dyes

Table 3
^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts of compounds **3a,b** in DMSO-d_6

	3a		**3b**	
	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$
1	2.54	26.20	2.61	26.30
2	–	198.97	–	198.61
3	–	129.27	–	125.48
4	–	160.69	–	160.06
5	–	137.53	–	135.87
6	7.67	120.28	7.17	120.71
7	7.39	129.15	7.07	128.83
8	7.17	124.53	7.07	125.10
1′	–	143.56	–	150.31
2′	–	116.41	–	125.88
3′	7.99	131.50	8.08	131.75
4′	7.22	123.69	7.34	125.20
5′	7.66	134.46	7.66	132.07
6′	7.92	115.28	7.73	120.13
7′	–	168.07	–	165.77
N_a	14.99	−211.3[a,b]	–	−107.9[a]
N_b	–	−12.5[a,c]	–	62.2[a,c]
N_c	11.10	−246.5[a,d]	12.48	−251.0[a,e]
Al	–	–	–	1.0[f]

[a] $\delta(^{15}\mathrm{N})$.
[b] $^{1}J(^{15}\mathrm{N}, \mathrm{H}) = 99.7$ Hz.
[c] ^{15}N labelled compound.
[d] $^{1}J(^{15}\mathrm{N}, \mathrm{H}) = 88.7$ Hz.
[e] $^{1}J(^{15}\mathrm{N}, \mathrm{H}) = 88.7$ Hz.
[f] $\delta(^{27}\mathrm{Al})$.

Table 4
^{1}H, ^{13}C, ^{15}N and ^{27}Al NMR chemical shifts of compounds **4a,b** in DMSO-d_6

	4a		**4b**	
	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$	$\delta(^{1}\mathrm{H})$	$\delta(^{13}\mathrm{C})$
1	–	−194.2[a]	–	
2	–	−74.3[a]	–	−96.2[a]
3	–	148.60	–	150.24
4	–	129.79	–	127.82
5	–	155.81	–	151.33
6	–	137.99	–	137.16
7	7.90	117.70	7.31	119.18
8	7.44	128.95	7.20	128.88
9	7.21	124.72	7.17	125.90
10	2.29	11.71	2.46	11.80
1′	–	143.15	–	149.38
2′	–	116.19	–	127.32
3′	7.99	131.42	8.04	131.88
4′	7.23	124.27	7.46	127.27
5′	7.66	134.40	7.54	128.78
6′	7.92	115.02	7.85	120.21
7′	–	167.95	–	165.45
N_a	14.61	−209.3[a,b]	–	−68.9[a]
N_b	–	−24.7[a,c]	–	58.1[a,c]
Al	–	–	–	2.3[d]

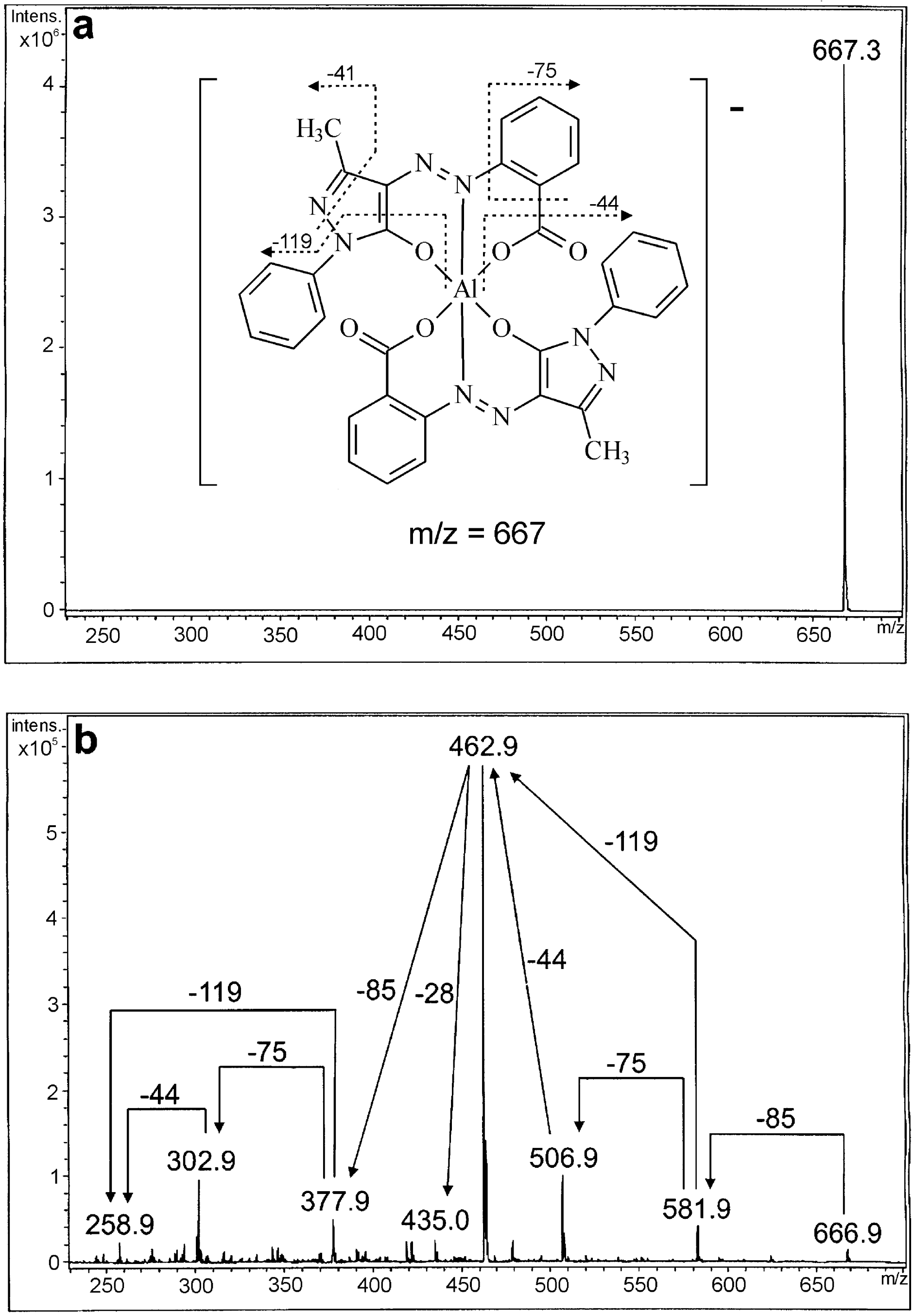
[a] $\delta(^{15}\mathrm{N})$.
[b] $^{1}J(^{15}\mathrm{N}, \mathrm{H}) = 100.3$ Hz.
[c] ^{15}N labelled compound.
[d] $\delta(^{27}\mathrm{Al})$.

provided the dyes exist in azo form. This is the case of compound **1b**. On the other hand, a coordination can cause a relatively large downfield shift in case a ligand exists in the hydrazone form (compounds **2b–4b**) and changes in $\delta(^{15}\mathrm{N})$ are due to a combination of two effects: the coordination (responsible for an upfield shift) and the change of the hydrazone tautomeric form to the azo form (responsible for even greater downfield shift). For details see Refs. [7,9].

We measured the ^{15}N chemical shifts of compound **1b–4b,** using in $^{15}\mathrm{N}_b$ enriched (95% ^{15}N) compounds using standard 1D spectra and both resonances at the natural abundance level using gs-^{1}H–^{15}N correlation spectra. Having compared the data with cobalt(III) compounds [7] it is clear that very similar ^{15}N chemical shifts were measured in compound **1b–4b** giving the evidence of N_a nitrogen coordination [7,9] with aluminium atom.

The conclusion is supported by Jagi's observation [21] who performed an X-ray study of cobalt complex of a dye, its ligand being derived from anthranilic acid, and also found the cordination of cobalt atom with nitrogen N_a.

The mutual differences in ^{1}H, ^{13}C and ^{15}N chemical shifts in compounds **1b–4b** are slightly greater then those in analogous hydroxy derivatives [9]. The reason might be that coordination procedure provides two new six-membered rings (see Scheme 1) while in analogous compounds in which –COO-group is substituted by –O-group [9] new six-membered and five-membered rings exist as a consequence of coordination. Due to a greater flexibility of six membered rings, small changes in bond lengths and bond angles can be expected.


a
Intens.
x10^6
667.3
-41
-75
-44
-119
H3C
CH3
Al
m/z = 667
250 300 350 400 450 500 550 600 650
m/z
b
intens.
x10^5
462.9
-119
-85
-28
-44
-75
-44
-75
-119
-85
258.9
302.9
377.9
435.0
506.9
581.9
666.9
250 300 350 400 450 500 550 600 650
m/z

Scheme 3.

3.2. Mass spectra

The complexes of three-valent metals with azo compounds carry a negative charge themselves, which is ideally suited for the negative-ion electrospray ionization (ESI) [22]. Similarly to the complexes of Al(III), Co(III) and Fe(III) with *o,o′*-dihydroxyazodyes, the molecular anionic species [M-cation]$^-$ are the only ions in the mass spectra of Al(III) complexes with *o,o′*-hydroxycarboxyazodyes (see Scheme 3a), which enables an easy molecular weight determination of all studied compounds. The character of cation does not influence ESI mass spectra in the negative-ion mode. The background noise in the spectra is very low, therefore ESI mass spectra can be used for monitoring of purity of synthesised complexes. The MS/MS analysis with the ion trap analyser is suitable for confirmation of expected structures, as demonstrated recently [23]. Scheme 3b shows an MS/MS spectrum of precursor ion at *m/z* 667, which confirms the structure assignment of compound **4b,** as shown on inset fragmentation scheme. The main observed losses are CO_2 (*m/z* 44), C_6H_3 (*m/z* 75), CO_2 and CH_3CN (*m/z* 85), phenylisocyanate (*m/z* 119) and N_2 (*m/z* 28). The typical feature of MS/MS spectra is the subsequent loss of the same fragments for both organic ligands, e.g. 85 (667–582 and 463–378), 75 (582–507 and 378–303) and 44 (507–463 and 303–259). This approach was applied for the structure verification of all studied complexes.

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