

## Synthesis and Structure of Complexes of Acyl N-Aminides with Zinc(II) Salts

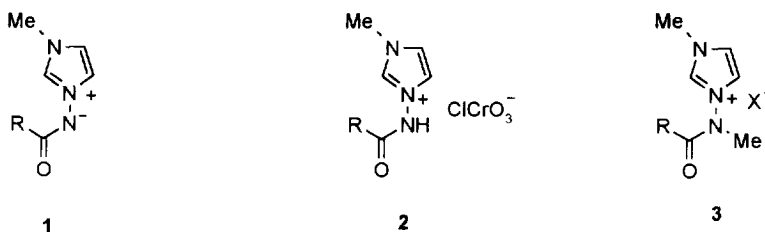
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**Abstract:** The structures of complexes obtained by reacting acyl N-aminides and ZnCl<sub>2</sub> were ascertained by X-ray analysis and were shown to incorporate one Zn atom and two molecules of the N-aminide in a distorted tetrahedral geometry. Bis-aminides act as bidentate ligands forming ZnLCl<sub>2</sub> complexes.

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We recently reported on the synthetic utility of N-aminides **1**<sup>1</sup> which, upon reaction with CrO<sub>3</sub> can be converted into selective oxidising reagents **2**<sup>2</sup> or when alkylated afford selective acylating reagents **3** which react with organometallics and DIBALH producing ketones and aldehydes in good to excellent yields.<sup>3-5</sup>



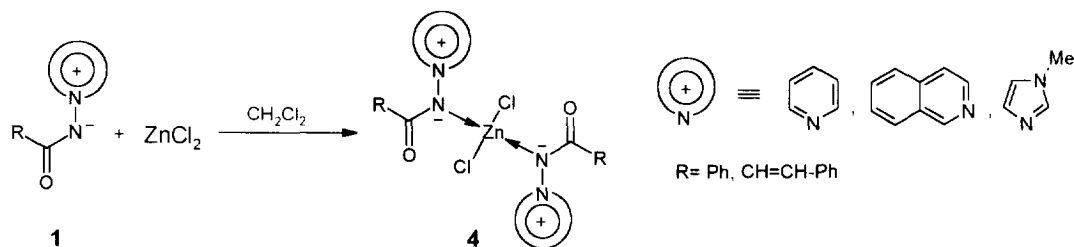
**Scheme 1**

Our interest in the chemical properties of these heterobetaines<sup>1c</sup> led us to explore the application of some acyl N-aminides as potential dienes in the Diels-Alder reaction. Although our efforts were all unsuccessful we observed that in one of the attempted reactions, the zinc chloride used as catalyst reacted with the N-cinnamoyl amidine forming a very stable complex with a stoichiometry ZnL<sub>2</sub>Cl<sub>2</sub>. Although the result was not unexpected since salts of Cobalt(II), Copper(II), Palladium(II), Platinum(II), Rhodium(III) and Iridium(III) have been reported to react with benzoyl N-aminides to afford products containing betaines metallated on the *ortho* position of aryl moiety,<sup>6,7</sup> in this case the *o*-metallation seemed to be less probable as such co-ordination would imply a seven membered ring.

When the benzoyl N-aminide was tested as ligand instead of cinnamoyl N-aminide, no evidence that the phenyl ring had been metallated in a position *ortho* to the carbonyl group was observed, and so we decide to unambiguously

establish the structure of these complexes by X-ray analysis. The results of this study are reported herein along with the structure of complexes obtained from the reaction of bis-aminides (bidentate ligands) with Zn(II) salts.

Complexes **4** were cleanly and rapidly obtained in good yields by reacting of aminides **1** with ZnCl<sub>2</sub> in dichloromethane. The complexes can also be formed in other solvents such as ethanol, although in some cases the reaction seems to be slower. All complexes are of a white colour and are stable in aqueous solution. As expected, the free betaine can be easily regenerated by treatment of the complex with common bases.



**Scheme 2**

The infrared spectra of these complexes show characteristic changes due to co-ordination of Zn with the nitrogen atoms, in particular the band corresponding to the carbonyl group, which in the complexes appears in the range 1642-1684 cm<sup>-1</sup> while in the precursor it shows up at a lower frequency ranged of 1566-1653 cm<sup>-1</sup> as a result of the contribution of the imidate resonance form. The localization of the negative charge on the nitrogen as a consequence of co-ordination to the metal enhances the double bond character of the carbonyl group, leading to a considerable shift to higher absorption frequencies with values closely approaching those found for N-methyl-N-cycloiminium amides (1652-1701 cm<sup>-1</sup>) which are obtained by N-methylation of the corresponding aminides.<sup>3</sup> On comparing the <sup>1</sup>H NMR spectra of the aminides with those of the complexes, the protons of the azinium moieties usually appeared deshielded in complexes bearing the benzoyl moiety (**4b** and **4d**) whereas in those containing the cinnamoyl substituent (**4a** and **4c**) the protons of the azinium rings appear at very similar chemical shifts in both the free aminide and the complex. On the other hand, in the imidazolium complexes **4e** and **4f** the C-2 protons of the imidazolium ring appear shielded, with the effect being most pronounced in **4e** (0.65 ppm) than in **4f** (0.02 ppm). The deshielding of the heteroaromatic protons in the complexes are consistent with co-ordination to the nitrogen atom which restricts delocalization of the negative charge over the pyridinium moiety. The apparent anomalous shielding observed for protons in **4e** and **4f** is likely the result of the stronger influence of the acyl substituent in these complexes which shifts them to highfield relative to the aminides

The structure of these complexes was established by X-ray analysis of the complex **4a**, which showed the best crystalline properties. In the asymmetric unit of the unit cell two crystallographic independent but chemically equivalent molecules appear. The two molecules are related by a pseudo-center of symmetry, and the differences between them are small. As expected, the metal appears co-ordinated to two organic ligands through the ylidic nitrogen atoms and surrounded by the two chloro atoms, adopting a distorted tetrahedral geometry. The largest angular deviation from a tetrahedral is 100.9(1)° for Cl1-Zn1-N2. The Zn-Cl bond distances range from 2.246(2) to 2.262(2) Å and the Zn-N distances range from 2.022(4) to 2.047(5) Å. The two betaine ligands bonded to the same Zn atom are similar except for the angle between the main plane of the pyridinium ring and the cinnamoyl moieties which are 79.8(2)° for the system with N1 and N2 and 58.9(2)° for the system with N3 and N4 ((79.12(2)° and 47.03(2)° are the values for the second molecule). The bond distances between the oxygen and the carbon atoms

of the carbonyl groups range from 1.208(7) Å to 1.249(7) Å, confirming the double bond character of these bonds. Figure 1 shows the structure of **4a** and Figure 2 its unit cell packing.

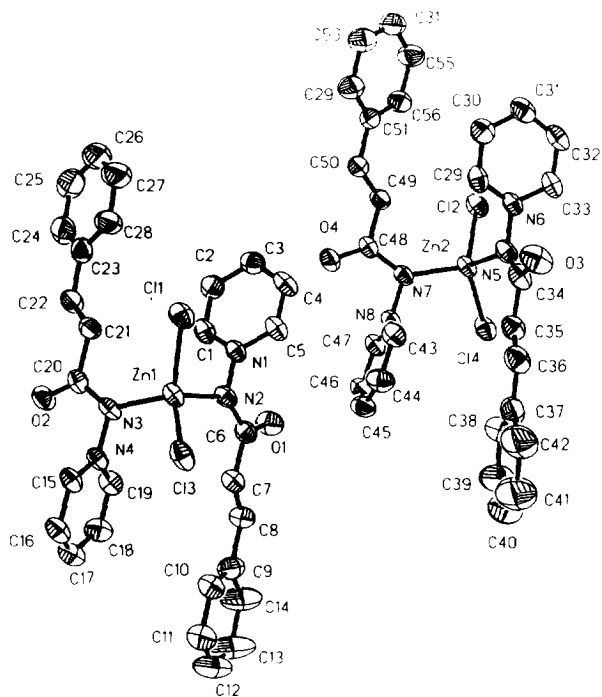


Figure 1. ORTEP drawing of compound **4a** with atomic numbering scheme.

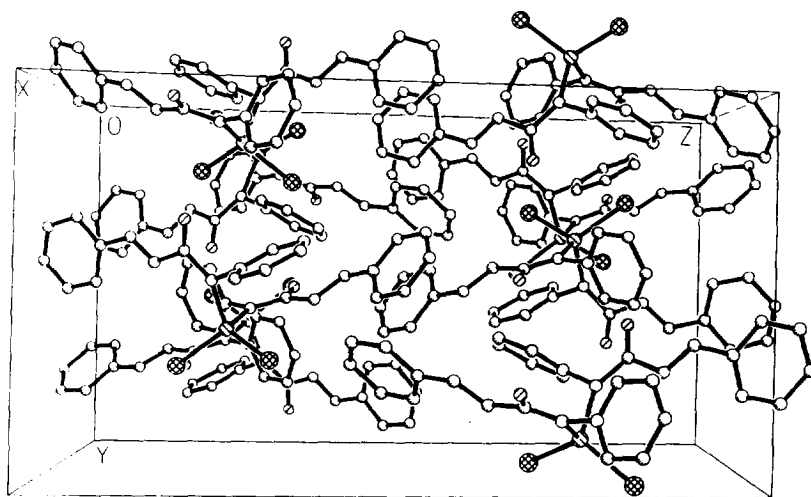
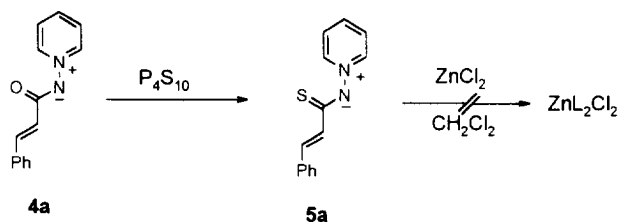


Figure 2. Unit cell packing of complex **4a**.

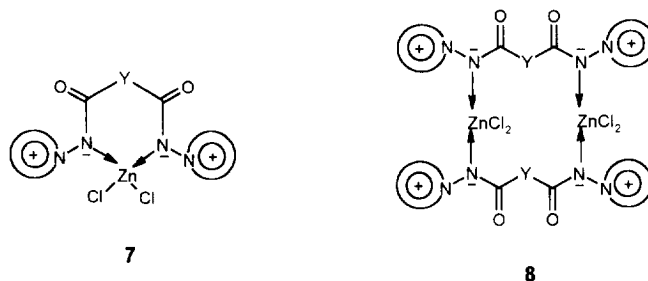
**Table.** Crystal data and structure refinement of **4a**.

<i>Empirical formula</i>	$C_{28}H_{24}N_4O_2Cl_2Zn_2$	<i>Absorption coefficient</i>	$11.36 \text{ cm}^{-1}$
<i>Formula weight</i>	584.8	<i>F(000)</i>	2400
<i>Temperature</i>	293(2) K	<i>Crystal size</i>	0.25x0.35x0.30
<i>Wavelength</i>	0.71069	<i><math>\theta</math> range for data collection</i>	$-21 < H < 21, 0 < K < 15,$ $0 < L < 28$
<i>Crystal system</i>	Monoclinic	<i>Reflections collected</i>	8044
<i>Space group</i>	P21/c	<i>Independent/observed</i>	7602(2 $\sigma$ I criterion)
<i>Unit cell dimensions</i>	a=18.175(4) Å b=12.874(5) Å c=23.821(4) Å $\beta=98.06(3)$	<i>Refinement method</i>	Full-matrix least-squares on F
<i>Volume</i>	5519(4) Å <sup>3</sup>	<i>Data/restraints/parameters</i>	7602/0/448
<i>Z</i>	8	<i>Final R indices [I <math>\geq</math> 2(I)]</i>	R1=0.072, Rw=0.098
<i>Density (calculated)</i>	1.408 g/cm <sup>3</sup>	<i>Largest diff. peak and hole</i>	0.851 and -1.109 eÅ <sup>-3</sup>

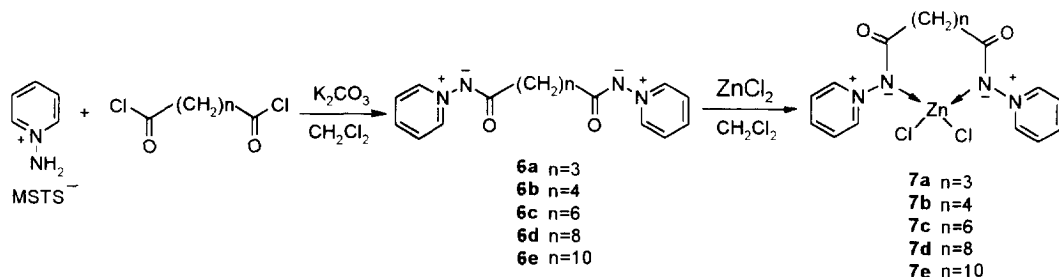
As with aminides **4**, we also tested the ability of some thio analogs **5** to act as ligands. For example, we prepared the thioaminide **5a** by reacting **4a** with  $P_4S_{10}$  in the presence of triethylamine.<sup>8</sup> However, after treatment of **5a** with  $ZnCl_2$  **4a** was invariably recovered unaltered even on heating at reflux.

**Scheme 3**

Once the structures of complexes **4** was established we reasoned that bis-aminides **6**<sup>4,9</sup> could behave as bidentate ligands to possibly give either the 1:1 complexes **7** or complexes **8** which involve the more unusual 2:2 mode of co-ordination.<sup>10,11</sup>

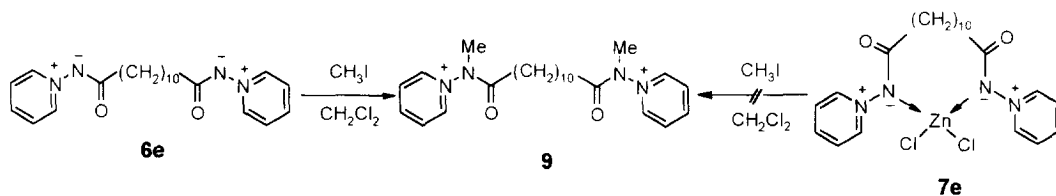
**Scheme 4**

The bis-aminides were prepared as previously described either from the reaction of dicarboxylic acids or diacyl dihalides with *N*-aminopyridinium mesitylene sulfonate.<sup>4</sup> When the bis-aminides **6**, in which the two aminide moieties were linked by a flexible polymethylene chain, were reacted with ZnCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> the complexes obtained showed physical and spectroscopic characteristics similar to those found for **4**. However, in this case we were unable to obtain suitable crystals for X-ray analysis and the structure **7** assigned to these complexes was established on the basis of analytical and spectroscopic data, in particular mass spectrometry (FAB-MS). In the infrared spectra of these complexes the carbonyl groups also appeared at higher wavelengths than in the corresponding bis-aminides although the shifts in frequencies were less significant than in complexes **4** since the carbonyls of these bis-aminides appeared in the range 1615-1620 cm<sup>-1</sup>.



Scheme 5

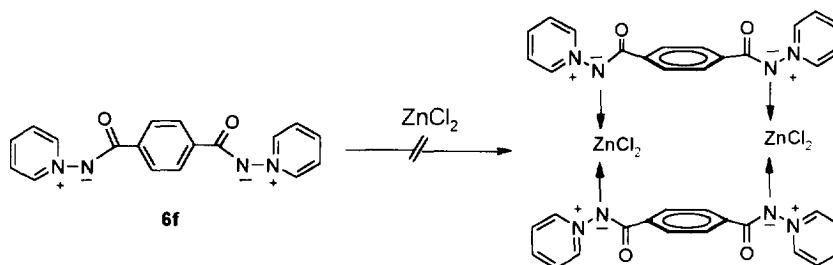
In the <sup>1</sup>H NMR of these complexes the chemical shifts of the pyridinium protons when compared to those of the corresponding protons in the bis-aminides show a similar pattern to that found for complexes **4**. Further evidence for nitrogen co-ordination was obtained when it was unsuccessfully attempted to double *N*-methylate complex **7e** while the corresponding aminide **6e** could easily be transformed into the bis-salt **9** by reacting with methyl iodide at room temperature.



Scheme 6

When compound **7e**, taken as representative of this series was subjected to FAB-MS in positive-ion spectrum the higher mass peak in the spectrum appeared at  $m/z=519$  (2%) with two significant peaks at  $m/z=483$  (36%) and  $m/z=383$  (78%) and were assigned as corresponding to  $(C_{22}H_{30}Cl_2N_4O_2Zn)H^+$ , to the loss of chloride ( $MH^+-Cl$ ) and to the loss of  $ZnCl_2$  ( $MH^+-Cl_2Zn$ ) respectively. This result seems to lend support to structure **7** for these complexes assuming that a similar fragmentation pattern for the 2:2 complex would afford a distribution of peaks clearly showing evidence for the structure **8**. The positive-ion FAB-MS of compounds **7b** and **7c** also showed a similar fragmentation pattern with the common fragments peaks for **7b** observed at  $m/z=435$  ( $C_{16}H_{18}Cl_2N_4O_2ZnH^+$ , 1%), 399 (12%) and 299 (100%) and for **7c** at  $m/z=463$  ( $C_{18}H_{22}Cl_2N_4O_2ZnH^+$ , 9%), 427 (67%) and 327 (100%).

In an attempt to form the complexes with the 2:2 stoichiometry we were able to prepare the bis-aminide **6f** in which the two nitrogen atoms are joined by a rigid linker, which would prevent the formation of complexes with the 1:1 stoichiometry. This bis-aminide was unaltered in the presence of  $\text{ZnCl}_2$  under similar or stronger conditions than those employed for the preparation of **7**. The result can be assumed as a further support for the structure assigned to complexes **7**.



Scheme 7

In conclusion, this work has shown that the reaction of acyl *N*-aminides and  $\text{Zn(II)}$  easily affords  $\text{ZnL}_2\text{Cl}_2$  complexes, the structures of which were established by X-ray analysis. Attempts to form complexes with the 2:2 stoichiometry by using flexible bis-aminides as bidentate ligands were unsuccessful, as these ligands tended to give the 1:1 complexes. Moreover, at this point in time the evidence suggests that a rigid bis-aminide unable to give the 1:1 complex is also incapable of forming 2:2 type complexes.

### Experimental

*General Procedures.* Melting points were determined on a Buchi SMP-20 apparatus and are uncorrected.  $^1\text{H}$  NMR were recorded on a Varian Unity 300 spectrometer and were referenced to TMS. IR spectra were obtained on a Perkin-Elmer 1310 spectrophotometer. Microanalyses were performed on a Heraeus CHN Rapid analyzer and MS were obtained on a Hewlett-Packard 5988 A spectrometer. Positive FAB-MS mass spectra were recorded using 3-nitrobenzyl alcohol matrix on a VG AutoSpec mass spectrometer. Chromatography was performed on silica gel 60 (230–400 meshes). All reagents were obtained from commercial sources and were used as acquired. Solvents were dried before using. Acyl *N*-aminides **1** were prepared as previously described.<sup>1</sup>

*Synthesis of Complexes 4. General Procedure.* To a solution of the aminide **1** (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) under argon a 1 M solution of  $\text{ZnCl}_2$  (1 mL) in  $\text{Et}_2\text{O}$  was added. The white precipitate formed was filtered off, washed with  $\text{Et}_2\text{O}$  and recrystallized to afford pure complexes **4**.

*Dichlorobis(1-cinnamoylamino-1-pyridinium) Zinc(II) (4a).* Yield: 65%. Mp 248–250°C (EtOH); IR (KBr)  $\nu_{\text{max}}$  3108, 3032, 1648, 1603, 1473  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ )  $\delta$  8.79 (dd, 2H,  $J=6.2$  and  $J=1.2$  Hz), 8.15–8.21 (m, 1H), 7.8–7.9 (m, 2H), 7.5–7.6 (m, 2H), 7.3–7.4 (m, 4H), 6.78 (d, 1H,  $J=15.8$  Hz) ppm; MS (70 eV)  $m/z$  (rel. int.): 224 (57), 223 (100), 121 (34), 102 (29), 79 (51), 77 (25). Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_3\text{Zn}$ : C, 57.51; H, 4.24; N, 9.58. Found: C, 57.46; H, 4.13; N, 9.62.

*Dichlorobis(1-benzoylamino-1-pyridinium) Zinc(II) (4b).* Yield: 85%. Mp 195–196°C (EtOH); IR (KBr)  $\nu_{\text{max}}$  3076, 2923, 1682, 1594, 1563  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ )  $\delta$  8.84 (dd, 2H,  $J=5.6$  and  $J=1.0$  Hz), 8.1–8.2

(m, 1H), 7.9-8.0 (m, 2H), 7.3-7.4 (m, 3H) ppm; MS (70 eV) *m/z* (rel. int.) 198 (40), 197 (92), 121 (100), 79 (79), 77 (78), 51 (43). Anal. Calcd for C<sub>24</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn: C, 54.11; H, 3.78; N, 10.52. Found: C, 54.02; H, 3.53; N, 10.30

*Dichlorobis(2-cinnamoylamino-2-isoquinolinium) Zinc(II) (4c)*. Yield: 95%. Mp 268-270 °C (CH<sub>2</sub>CN) IR(KBr)  $\nu_{\max}$  3028, 1646, 1603, 1469, 1380 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.91 (s, 1H), 8.44 (dd, 1H, J=7.0 and J=2.4 Hz), 8.35 (d, 1H, J=8.3 Hz), 8.31 (d, 1H, J=7.0 Hz), 8.21 (d, 1H, J=8.1 Hz), 8.0-8.1 (m, 1H), 7.8-7.9 (m, 1H), 7.5-7.6 (m, 2H), 7.2-7.4 (m, 3H), 7.43 (d, 1H, J=15.9 Hz) ppm; MS (70 eV) *m/z* (rel. int.): 274 (54), 273 (86), 130 (21), 129 (100), 102 (34). Anal. Calcd for C<sub>36</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn: C, 63.13; H, 4.12; N, 8.18. Found: C, 62.52; H, 4.36; N, 8.24.

*Dichlorobis(2-benzoylamino-2-isoquinolinium) Zinc(II) (4d)*. Yield: 70%. Mp 219-220 °C (EtOH). IR (KBr)  $\nu_{\max}$  3046, 1684, 1669, 1599, 1503 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 10.27 (s, 1H), 8.84 (d, 1H, J=6.9 Hz), 8.66 (d, 1H, J=6.9 Hz), 8.53 (d, 1H, J=8.4 Hz), 8.40 (d, 1H, J=8.4 Hz), 8.2-8.3 (m, 1H), 8.0-8.1 (m, 3H), 7.5-7.7 (m, 3H) ppm. MS (70 eV) *m/z* (rel. int.): 247 (56), 129 (35), 105 (45), 77 (100), 51 (51). Anal. Calcd for C<sub>31</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn: C, 63.73; H, 3.82; N, 8.85. Found: C, 63.68; H, 3.54; N, 8.87.

*Dichlorobis(1-cinnamoylamino-3-methyl-3H-1-imidazolium) Zinc(II) (4e)*. Yield: 70%. Mp 245-246 °C (EtOH); IR (KBr)  $\nu_{\max}$  3143, 1642, 1616, 1576, 1449 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.25 (s, 1H), 7.4-7.5 (m, 4H), 7.2-7.3 (m, 4H), 7.03 (d, 1H, J=16.14 Hz), 3.80 (s, 3H). MS (70 eV) *m/z* (rel. int.): 227 (22), 226 (92), 195 (56), 149 (72), 91 (38), 77 (58), 57 (100). Anal. Calcd for C<sub>26</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>Zn: C, 52.28; H, 4.43; N, 14.22. Found: C, 52.55; H, 4.50; N, 14.15

*Dichlorobis(1-benzoylamino-3-methyl-3H-1-imidazolium) Zinc(II) (4f)*. Yield: 92%. Mp >290 °C (dec.); IR (KBr)  $\nu_{\max}$  3146, 1692, 1591, 1554, 1552, 1484 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.65 (s, 1H), 7.9-8.0 (m, 2H), 7.64 (s, 1H), 7.48 (s, 1H), 7.2-7.3 (m, 3H), 3.8 (s, 3H) ppm; MS (70 eV) *m/z* (rel. int.): 201 (100), 200 (88), 124 (99), 105 (60), 103 (44), 82 (55), 77 (89), 51 (43). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>Zn: C, 49.05; H, 4.12; N, 15.60. Found: C, 48.84; H, 4.17; N, 15.45

*1-Thiocinnamoylpyridinium N-aminide (5a)*. To a suspension of *N*-cinnamoylpyridinium iodide (0.35 g, 1 mmol) in MeCN (15 mL) 0 °C cooled was added P<sub>4</sub>S<sub>10</sub> (0.44 g 1 mmol) and Et<sub>3</sub>N (0.56 mL, 4 mmol). The mixture was stirred at room temperature for 24 and then water (20 mL) was added. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4x35 mL) and the organic phase was separated and dried over MgSO<sub>4</sub>. After elimination of the solvent under reduced pressure the residue obtained was chromatographed on silica gel. Elution with EtOH afforded the title compound (95 mg, 39%) as a dark yellow solid. Mp. 115-117 °C (EtOAc); IR (KBr)  $\nu_{\max}$  3031, 1628, 1612, 1572, 1470, 1381, 1175 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) 8.63 (dd, 2H, J=6.8 and J=1.2 Hz), 8.30 (t, 1H, J=7.8 Hz), 7.9-8.0 (m, 2H), 7.75 (d, 1H, J=15.5 Hz), 7.6-7.7 (m, 2H), 7.3-7.4 (m, 3H), 7.10 (d, 1H, J=15.5 Hz) ppm. MS (70 eV) *m/z* (rel. int) 160 (24), 129 (100), 128 (25), 102 (38), 79 (42). Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S: C, 69.97; H, 5.03; N, 11.66; S, 13.34. Found: C, 69.62; H, 4.95; N, 11.43; S, 13.15

*Synthesis of Bis-aminides 6. General Procedure*. To a mixture of 0.44 g (2 mmol) of *N*-aminopyridinium iodide, 1.1 g (8 mmol) of K<sub>2</sub>CO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was slowly added 1 mmol of the corresponding diacyl chloride in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The reaction mixture was stirred at room temperature for 24 h. The inorganic precipitate was separated by filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> (2x5mL). The filtrate and washes were concentrated under reduced pressure and the oily residue was triturated with EtOAc. The solid thus obtained was isolated by filtration and purified by recrystallization to afford pure bis-aminides **6**.

*N,N'-(1,7-Diaza-2,6-dioxohepta-1,7-diyl)bis-1-pyridinium Diaminide (6a)*. Yield: 70%. Mp 176-178 °C (Acetone/CH<sub>3</sub>CN, white powder); IR (KBr)  $\nu_{\max}$  3112, 1616, 1554, 1337, 1049 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.63 (d, 4H, J=6.2 Hz), 8.06 (t, 2H, J=7.5 Hz), 7.79 (dd, 4H, J=7.5 and J=6.2 Hz), 2.08 (t, 4H, J=6.6 Hz), 1.86 (t, 2H, J=6.6 Hz) ppm; Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.23; H, 5.73; N, 19.92.

*N,N'-(1,8-Diaza-2,7-dioxoocta-1,8-diyl)bis-1-pyridinium Diaminide (6b)*. Yield: 81%. Mp 174-176 °C (Acetone/CH<sub>3</sub>CN, white powder); IR (KBr)  $\nu_{\max}$  3058, 2944, 1620, 1577, 1554, 1381, 1080 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.64 (d, 4H, J=6.6 Hz), 8.05 (t, 2H, J=7.0 Hz), 7.78 (dd, 4H, J=7.0 and J=6.6 Hz), 2.0-2.1 (m, 4H), 1.5-1.6 (m, 4H) ppm; MS (70 eV) *m/z* (rel. int.) 298 (1), 177 (22), 163 (12), 135 (18), 121 (100), 79 (93). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 60.75; H, 6.37; N, 17.71. Found: C, 60.68; H, 5.88; N, 17.66.

*N,N'-(1,10-Diaza-2,9-dioxodeca-1,10-diyl)bis-1-pyridinium Diaminide (6c)*. Yield: 94%. Mp 163-165 °C (CH<sub>3</sub>CN, brown powder); IR (KBr)  $\nu_{\max}$  3106, 2933, 1618, 1574, 1560, 1373, 1091 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.62 (dd, 4H, J=6.3 and J=1.2 Hz), 8.06 (m, 2H), 7.78 (dd, 4H, J=8.2 and J=6.3 Hz), 2.06 (t, 4H, J=7.5 Hz), 1.5-1.6 (m, 4H), 1.3-1.4 (m, 4H) ppm; MS (70 eV) *m/z* (rel. int.) 163 (3), 149 (10), 135 (32), 121(84), 93 (3), 79 (100). Anal. Calcd for C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>: C, 66.24; H, 6.79; N, 17.17. Found: C, 65.85; H, 6.85; N, 16.77.

*N,N'-(1,12-diaza-2,11-dioxododeca-1,12-diyl)bis-1-pyridinium Diaminide (6d)*. Yield: 70%. Mp 105-110 °C (AcOEt/Acetone, pale yellow powder); IR (KBr)  $\nu_{\max}$  3116, 2923, 1667, 1618, 1544, 1098 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.62 (d, 4H, J=6.7 Hz), 8.05 (t, 2H, J=7.5 Hz), 7.78 (dd, 4H, J=7.5 and J=6.7 Hz), 2.07 (t, 4H, J=7.0 Hz), 1.5-1.6 (m, 4H), 1.2-1.3 (m, 8H) ppm; MS (70 eV) *m/z* (rel. int.) 177 (4), 121 (69), 93 (10), 79 (100), 56 (29). Anal. Calcd for C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>: C, 67.77; H, 7.39; N, 15.81. Found: C, 67.89; H, 7.46; N, 15.93.

*N,N'-(1,14-diaza-2,13-dioxotetradeca-1,14-diyl)bis-1-pyridinium Diamide (6e)*. Yield: 89%. Mp 92-94 °C (EtOAc, white powder); IR (KBr)  $\nu_{\max}$  3116, 2922, 1668, 1618, 1548, 1374, 1096 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.62 (dd, 4H, J=6.8 and J=1.3 Hz), 8.07 (t, 2H, J=7.7Hz), 7.80 (dd, 4H, J=7.4 and J=6.8 Hz), 2.05 (t, 4H, J=7.1 Hz), 1.5-1.6 (m, 4H), 1.2-1.3 (m, 12H) ppm. Anal. Calcd for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.08; H, 7.91; N, 14.65. Found: C, 68.95; H, 8.02; N, 14.60.

*1,1-Terphthaloilimino-bis-1-pyridinium Diaminide (6f)*. Yield: 22%. Mp 275-277 °C (EtOH, white powder); IR (KBr)  $\nu_{\max}$  3064, 2944, 1549, 1466, 1335, 1301, 1250, 1179 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 300 MHz):  $\delta$  8.7-8.8 (m, 4H), 8.2-8.3 (m, 2H), 8.10 (s, 4H), 7.9-8.0 (m, 4H) ppm. Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 67.92; H, 4.43; N, 17.60. Found: C, 67.89; H, 4.39; N, 17.43.

*Synthesis of complexes 7. General procedure.* To a solution of **6** (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) a 1M solution of ZnCl<sub>2</sub> (1 mL) in Et<sub>2</sub>O was added at room temperature. The white precipitate which immediately formed was isolated by filtration and recrystallized to give pure complexes **7**.

*Dichloro[N,N'-(1,7-diaza-2,6-dioxohepta-1,7-diyl)bis-1-pyridinium] Zinc(II) (7a)*. Yield: 85%. Mp 313-314 °C (MeOH); IR (KBr)  $\nu_{\max}$  3114, 2944, 1622, 1584, 1390 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.65 (d, 4H, J=6.0 Hz), 8.34 (t, 2H, J=7.5 Hz), 7.98 (dd, 4H, J=7.5 and J=6.0 Hz), 2.41 (t, 4H, J=6.7 Hz), 1.86 (q, 2H, J=7.5 Hz) ppm. Anal. Calcd for C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn·H<sub>2</sub>O: C, 41.08; H, 4.14; N, 12.77. Found: C, 41.23; H, 4.03; N, 12.65.

*Dichloro[N,N'-(1,8-diaza-2,7-dioxoocta-1,8-diyl)bis-1-pyridinium] Zinc(II) (7b)*. Yield: 80%. Mp 309-311 °C (MeOH). IR (KBr)  $\nu_{\max}$  3113, 2925, 1621, 1609, 1560, 1374 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.63 (d, 4H, J=6.7 Hz), 8.09 (t, 2H, J=7.5 Hz), 7.81 (dd, 4H, J=7.5 and J=6.7 Hz), 2.1-2.2 (m, 4H), 1.60-1.65 (m, 4H) ppm.



Positive FAB-MS  $m/z$  (rel. int.) 435 (1), 399 (12), 299 (100), 95 (33). Anal. Calcd for  $C_{16}H_{18}Cl_2N_4O_2Zn \cdot H_2O$ : C, 42.46; H, 4.45; N, 12.38. Found: C, 42.23; H, 4.62; N, 11.95.

*Dichloro[N,N'-(1,10-diaza-2,9-dioxodeca-1,10-diyl)bis-1-pyridinium] Zinc(II) (7c)*. Yield: 89%. Mp 303-305 °C (MeOH); IR (KBr)  $\nu_{max}$  3114, 2936, 1622, 1586, 1554, 1398  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.60 (d, 4H,  $J=6.7$  Hz), 8.13 (t, 2H,  $J=7.3$  Hz), 7.82 (dd, 4H,  $J=7.3$  and  $J=6.7$  Hz), 2.14 (t, 4H,  $J=7.5$  Hz), 1.5-1.6 (m, 4H), 1.2-1.3 (m, 4H) ppm. Positive FAB-MS  $m/z$  (rel. int.) 463 (9), 427 (67), 327 (100), 95 (59). Anal. Calcd for  $C_{18}H_{22}Cl_2N_4O_2Zn \cdot H_2O$ : C, 44.98; H, 5.03; N, 11.06. Found: C, 45.11; H, 4.83; N, 11.25.

*Dichloro[N,N'-(1,12-diaza-2,11-dioxododeca-1,12-diyl)bis-1-pyridinium] Zinc(II) (7d)*. Yield: 90%. Mp 300-301 °C (MeOH); IR (KBr)  $\nu_{max}$  3117, 2923, 1624, 1591, 1554  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.59 (d, 4H,  $J=6.3$  Hz), 8.14 (t, 2H,  $J=7.4$  Hz), 7.84 (dd, 4H,  $J=7.4$  and  $J=6.3$  Hz), 2.14 (t, 4H,  $J=7.5$  Hz), 1.5-1.6 (m, 4H), 1.2-1.3 (m, 8H) ppm. Anal. Calcd for  $C_{20}H_{26}Cl_2N_4O_2Zn \cdot H_2O$ : C, 47.22; H, 5.55; N, 11.01. Found: C, 7.35; H, 5.31; N, 10.87.

*Dichloro[N,N'-(1,14-diaza-2,13-dioxotetradeca-1,14-diyl)bis-1-pyridinium] Zinc(II) (7e)*. Yield: 95%. Mp 140-142 °C (EtOH); IR (KBr)  $\nu_{max}$  3111, 2922, 3848, 1620, 1586, 1556, 1398, 1080  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.58 (d, 4H,  $J=6.0$  Hz), 8.17 (t, 2H,  $J=7.5$  Hz), 7.85 (dd, 4H,  $J=7.5$  and  $J=6.0$  Hz), 2.15 (t, 4H,  $J=7.3$  Hz), 1.5-1.6 (m, 4H), 1.2-1.3 (m, 12H) ppm. Positive FAB-MS  $m/z$  (rel. int.) 519 (2), 483 (36), 383 (78), 95 (100). Anal. Calcd for  $C_{22}H_{30}Cl_2N_4O_2Zn \cdot H_2O$ : C, 49.22; H, 6.01; N, 10.44. Found: C, 49.45; H, 6.28; N, 10.29.

*N,N'-(2,15-Diaza-3,14-dioxohexadeca-2,15-diyl)bis-1-pyridinium Diiodide (9)*. A mixture of **6e** (0.38 g, 1 mmol) and methyl iodide (0.56 g, 4 mmol) in acetone (10 mL) was refluxed for 18 h. The precipitate formed was isolated by filtration and recrystallized from acetone/EtOH to yield 0.62 g (95%) of a yellow powder. Mp 187-188 °C. IR (KBr)  $\nu_{max}$  3111, 3009, 2921, 1671, 1549, 1467, 1377, 1288  $cm^{-1}$ ;  $^1H$ -NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 9.23 (dd, 2H,  $J=6.9$  and  $J=1.2$  Hz), 8.80 (t, 2H,  $J=7.7$  Hz), 8.34 (m, 4H), 2.07 (m, 4H), 1.55-1.59 (m, 4H), 1.24-1.33 (m, 12H) ppm. Anal. Calcd for  $C_{24}H_{36}I_2N_4O_2$ : C, 42.98; H, 5.56; N, 8.67. Found: C, 43.26; H, 5.45; N, 8.41.

*Single-Crystal X-Ray Structure Determination of Complex 4a*. Intensity data were collected using a CAD4 diffractometer with graphite-monochromated  $MoK\alpha$  radiation (0.71069 Å). Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made.

The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full matrix least-squares calculations. All the non hydrogen atoms were anisotropically refined. In the last cycle of refinement hydrogen atoms were introduced from geometrical positions and fixed with thermal parameters equivalent to those of the carbons to which they were attached. Final values of  $R=0.072$  and  $R_w=0.098$  with  $R_w = [\sum [w(F_o - F_c)]^2 / \sum w(F_o)^2]^{1/2}$  and  $w = 4F_o^2 / [\sigma(F_o)]^2$  obtained.

Anomalous dispersion corrections and atomic scattering factors were taken from International Tables.<sup>12</sup> Calculations were performed with the SDP package on a Microvax II computer.<sup>13</sup>

**Acknowledgment.** The authors acknowledge the Comisió Interdepartamental de Recerca i Innovació Tecnològica (CIRIT, project QFN94-4619) for financial support and the Ministerio de Educación y Ciencia for a studentship (M.A.H.).

**References**

1. For reviews of N-aminides, see: (a) Timpe, H. J. *Adv. Heterocycl. Chem.*, **1974**, *17*, 213. (b) Y. Tamura, Y.; Ikeda, M. *Adv. Heterocycl. Chem*, **1981**, *29*, 71. (c) Ollis, W. D.; Stanforth, S. P. *Tetrahedron*, **1993**, *41*, 714.
2. Martinez, Y.; Heras, M. A.; Vaquero, J. J.; García Navio, J. L.; Alvarez-Builla, J. *Tetrahedron Lett.* **1995**, *36*, 8513.
3. Heras, M. A.; Molina, A.; Vaquero, J. J.; García Navio, J. L.; Alvarez-Builla, J. *J. Org. Chem.* **1993**, *58*, 5862.
4. Heras, M. A.; Vaquero, J. J.; García Navio, J. L.; Alvarez-Builla, J. *Tetrahedron*, **1996**, *45*, 14297.
5. Heras, M. A.; Vaquero, J. J.; García Navio, J. L.; Alvarez-Builla, J. *J. Org. Chem.* **1996**, *61*, 9009.
6. Dias, S. A.; Downs, A. W.; McWhinnie, W. R. *J. Chem. Soc.*, **1974**, 162.
7. Chia, L. Y.; Dias, S. A.; McWhinnie, W. R. *J. Inorg. Nucl. Chem.* **1975**, *38*, 1263.
8. Bhakagrahi, D. *Heterocycles*, **1982**, *19*, 11.
9. Heras, M. A.; Vaquero, J. J.; García Navio, J. L.; Alvarez-Builla, J. *Tetrahedron Lett.* **1995**, *36*, 455.
10. Rebek, J.; Trend, J. E.; Wattley, R. V.; Chakravorty, S. *J. Am. Chem. Soc.* **1979**, *101*, 4333.
11. Cuevas, J.-C.; Mendoza, J.; Prados, P.; Hernández-Cano, F.; Foces-Foces, C. *J. Chem. Soc. Chem. Comm.* **1986**, 1641.
12. *International Tables for X-Ray Crystallography*, vol IV, Kynoch, Birmighan, **1974**.
13. B. A. Frenz and Associates, Inc. SDP. Texas A&M and Enraf-Nonius. College Station Tx77840 and Delft, **1985**.

(Received in UK 30 January 1997; revised 18 March 1997; accepted 20 March 1997)