

Preparation, characterization and crystal structures of three salts of the quaterpyridine ligand

Artur Ciesielski^{a,b}, Artur R. Stefankiewicz^{a,b}, Violetta Patroniak^{a,*}, Maciej Kubicki^{a,*}

^a Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

^b ISIS/CNRS UMR 7006, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France

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ABSTRACT

As a result of a reaction between 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine $C_{22}H_{18}N_4$ and lanthanide(III) salts, compounds, $[C_{22}H_{20}N_4]^{2+} \cdot 2(CF_3SO_3)^-$ (**1**) and $[C_{22}H_{20}N_4]^{2+} \cdot 2(ClO_4)^-$ (**2**), have been obtained. They were characterized by spectroscopic techniques (ESI-MS, NMR, IR), elemental analysis, and their formulae were confirmed on the basis of X-ray crystallography. It turned out that the perchlorate crystallizes as two solvates: with acetonitrile and disordered water molecules. These are the first structural characterization of a 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridinium dication. Due to the intramolecular hydrogen bond it adopts the previously unobserved *cis/trans/cis* conformation. In all three crystals the dications have C_i symmetry, they occupy the special positions in their respective space groups. In the crystal structures the π - π stacking and weak hydrogen bonds add directionality to the dominating electrostatic interactions between cations and anions.

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1. Introduction

The synthesis of ligands containing pyridine units is of great interest in organic and supramolecular chemistry due to their interesting metal binding properties [1]. Multitopic ligands with N-donor sets may be employed in the metal ion directed assembly of coordination architectures [2–5].

In the previous studies, we have found that bis(tridentate) ligands with N,N,O donor atoms are good substrates for obtaining grids with metal ions which prefer tetrahedral and octahedral coordination geometry [6] and dinuclear complexes with lanthanides [7]. Looking for better complexing agents for lanthanides, we have designed new ligands that include bis(tetradentate) subunits [8]. Coordination is provided by the nitrogen atoms from the bipyridine and pyrimidine rings, while the fourth coordination site is the oxygen atom from the carbonyl donor group [9]. During the synthesis of one of the precursors of N,N,N,O donor ligands we obtained the N_4 -donor ligand, 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine (Scheme 1) [5], which we used in the reaction with lanthanide salts: $Eu(CF_3SO_3)_3$, $Eu(ClO_4)_3 \cdot 5H_2O$ and $Pr(ClO_4)_3 \cdot xH_2O$. Our aim was to generate the complexes of Eu(III) with coordination number 8. Such a coordination number is not favored by lanthanides, but some examples are reported in the literature [10–14]. Unexpectedly, we obtained crystals of a new ditriflate and two solvates of a perchlorate. New compounds were characterized by

ESI-MS, IR, microanalysis and their structures were unequivocally determined by X-ray crystallography.

2. Experimental

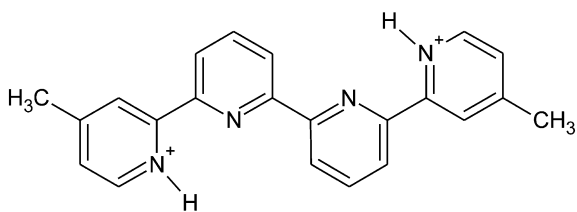
2.1. Material and physical measurements

6,6''-Dimethyl-2,2':6',2'':6'',2'''-quaterpyridine $C_{22}H_{18}N_4$ was prepared in our laboratory [5]. Solvents were freshly distilled under argon from CaH_2 . The lanthanide salts were used as received from Aldrich without further purification. 1H NMR spectra were recorded on a Varian Gemini 300 spectrometer using TMS as an internal reference. Microanalyses were conducted using a Perkin Elmer 2400 CHN microanalyzer. The IR spectra were recorded on a Perkin Elmer 580 spectrophotometer and are reported in cm^{-1} . Mass spectra were determined by ESI-MS using a Waters Micro-mass ZQ spectrometer in acetonitrile. The samples were run in the positive-ion mode. The concentrations of the compounds were about 10^{-4} mol dm^{-3} . Sample solutions were introduced into the mass spectrometer source with a syringe pump with a flow rate of $40 \mu L \min^{-1}$ with a capillary voltage of +3 kV and a desolvation temperature of $300^\circ C$. The source temperature was $120^\circ C$. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ to 1000 for 6 s, and 10 scans were summed up to obtain the final spectrum.

1: A solution of 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine (20.1 mg, 60 μmol) and $Eu(CF_3SO_3)_3$ (17.8 mg, 30 μmol) in 2:1

* Corresponding authors. Tel.: +48 618291256; fax: +48 618291505.

E-mail address: mkubicki@amu.edu.pl (M. Kubicki).



Scheme 1. The ligand $[\text{C}_{22}\text{H}_{18}\text{N}_4\cdot\text{H}]^{2+}$.

$\text{CH}_3\text{CN}-\text{CHCl}_3$ mixture (15 mL) was stirred at room temperature for 48 h under argon. The reaction volume was reduced under vacuum until crystallization commenced and the mixture was then allowed to equilibrate. The product was obtained as a pale yellow powder and was washed on the filter with CH_3CN (73%). ^1H NMR (300 MHz, CDCl_3): $\delta = 9.11$ (d, 2H, $J = 7.3$ Hz), 8.52 (t, 2H, $J = 7.2$ Hz), 8.44 (t, 2H, $J = 7.6$ Hz), 8.41 (d, 2H, $J = 7.4$ Hz), 7.52 (d, 2H, $J = 7.8$ Hz), 7.18 (d, 2H, $J = 7.4$ Hz), 1.91 (s, 6H, CH_3). IR (KBr): $\nu = 3245, 3177, 3086, 1625, 1619, 1586, 1567, 1524, 1442, 1390, 1285, 1255, 1227, 1141$ (CF_3SO_3^-), 1067, 1033 (CF_3SO_3^-), 876, 799, 757 (CF_3SO_3^-), 724, 648, 637 (CF_3SO_3^-), 572 (CF_3SO_3^-), 517, 422 cm^{-1} . ESI-MS: $m/z = 489$ (15% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2][\text{CF}_3\text{SO}_3^-]^+$), 339 (55% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}]^+$), 171 (100% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2]^{2+}$). $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2](\text{CF}_3\text{SO}_3)_2$ (638.56): calcd. C = 45.14%, H = 3.16%, N = 8.71%, S = 10.04%; found C = 44.985, H = 3.22%, N = 8.81%, S = 10.02%.

2a: A solution of 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine, $\text{C}_{22}\text{H}_{18}\text{N}_4$ (10.0 mg, 29 μmol) and $\text{Eu}(\text{ClO}_4)_3\cdot 5\text{H}_2\text{O}$ (12.0 mg, 29 μmol) in 2:1 $\text{CH}_3\text{CN}-\text{CHCl}_3$ mixture (15 mL) was stirred at room temperature for 48 h under argon. The volume was reduced under vacuum until crystallization commenced and the mixture was then allowed stand to equilibrate. The product was obtained as a pale pink powder and was washed on the filter with CH_3CN (82%). ^1H NMR (300 MHz, CDCl_3): $\delta = 9.1$ (d, 2H, $J = 7.6$ Hz), 8.50 (t, 2H, $J = 6.2$ Hz), 8.45 (t, 2H, $J = 7.6$ Hz), 8.40 (d, 2H, $J = 8.4$ Hz), 7.50 (d, 2H, $J = 7.8$ Hz), 7.18 (d, 2H, $J = 7.4$ Hz), 1.90 (s, 6H, CH_3). IR (KBr): $\nu = 3244, 3179, 3086, 1624, 1619, 1588, 1567, 1526, 1444, 1390, 1285, 1255, 1228, 1100$ (ClO_4^-), 1070, 877, 799, 721, 648, 624 (ClO_4^-), 576, 515, 423 cm^{-1} . ESI-MS: = 380 (60% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}]^+\cdot\text{CH}_3\text{CN}$), 339 (100% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}]^+$), 171 (30% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2]^{2+}$). $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2](\text{ClO}_4)_2\cdot\text{CH}_3\text{CN}$ (580.37): calcd. C = 49.37%, H = 3.99%, N = 12.07%; found C = 49.40%, H = 4.05%, N = 12.04%.

2b: A mixture of 40% $\text{Pr}(\text{ClO}_4)_3\cdot x\text{H}_2\text{O}$ (3.3 μL , 29 μmol) and 6,6''-dimethyl-2,2':6',2'':6'',2'''-quaterpyridine ($\text{C}_{22}\text{H}_{18}\text{N}_4$) (10 mg, 29 μmol) in 2:1 $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}$ (15 mL) was stirred at room temperature for 48 h under argon. The volume was reduced under vacuum until crystallization commenced and the mixture was then allowed stand to equilibrate. The product was obtained as a pale pink powder and was washed on the filter with CH_3CN (89%). ^1H NMR (300 MHz, CDCl_3): $\delta = 9.05$ (d, 2H, $J = 7.2$ Hz), 8.56 (t, 2H, $J = 6.0$ Hz), 8.42 (t, 2H, $J = 7.6$ Hz), 8.36 (d, 2H, $J = 8.5$ Hz), 7.41 (d, 2H, $J = 7.6$ Hz), 7.22 (d, 2H, $J = 7.5$ Hz), 1.94 (s, 6H, CH_3). IR (KBr): $\nu = 3244, 3178, 3088, 1624, 1616, 1586, 1567, 1524, 1445, 1391, 1285, 1259, 1229, 1102$ (ClO_4^-), 1067, 877, 799, 725, 648, 625 (ClO_4^-), 571, 517, 424 cm^{-1} . ESI-MS: = 339 (100% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}]^+$), 171 (50% $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2]^{2+}$). $[\text{C}_{22}\text{H}_{18}\text{N}_4\text{H}_2](\text{ClO}_4)_2\cdot 0.5\text{H}_2\text{O}$ (548.33): calcd. C = 48.19%, H = 3.86%, N = 10.22%; found C = 48.30%, H = 3.91%, N = 10.18%.

2.2. X-ray crystal structural analysis

Diffraction data were collected at room temperature by the ω -scan technique on a KUMA-KM4CCD diffractometer [15] with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). Data

were corrected for Lorentz-polarization and absorption effects [15] Accurate unit-cell parameters were determined by the least-squares fit of 3857 (**1**), 2724 (**2a**) and 3896 (**2b**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR-92 [16] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [17] Scattering factors incorporated in SHELXL97 were used. Function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + A \cdot P^2 + B \cdot P]$, where P is $[\text{Max}(F_o^2, 0) + 2F_c^2]/3$. All non-hydrogen atoms were refined anisotropically, N–H hydrogen atoms were located in subsequent difference Fourier maps and their positional and isotropic displacement parameters were refined, the other hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups; U_{iso} 's of these hydrogen atoms were set as 1.2 (1.3 for methyl groups) times U_{eq} 's of the appropriate carrier atoms. In both structures of **2** the perchlorate anions are disordered, the site occupation factors refined at 0.676(8)/0.324(8) in **2a** and 0.708(10)/0.292(10) in **2b**. The geometry of the anions were subjected to soft restraints in **2a** and the thermal parameters of the oxygen atoms were restrained in both cases, to prevent the ellipsoids to become too eccentric. In the case of **2b** the large electron density in the difference Fourier map was interpreted as the disordered water molecule; its occupancy was fixed at 0.25 in order to get the rational displacement parameters. Relevant crystal data are listed in Table 1, together with refinement details.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-292975 (**1**), CCDC-720513 (**2a**), and CCDC-720514 (**2b**). Copies

Table 1
Crystal data, data collection and structure refinement details.

	1	2a	2b
Formula	$\text{C}_{22}\text{H}_{20}\text{N}_4\cdot 2(\text{CF}_3\text{O}_3\text{S})$	$\text{C}_{22}\text{H}_{20}\text{N}_4\cdot 2(\text{ClO}_4)\cdot \text{CH}_3\text{CN}$	$\text{C}_{22}\text{H}_{20}\text{N}_4\cdot 2(\text{ClO}_4)\cdot 1/2(\text{H}_2\text{O})$
Formula weight	638.56	580.37	548.33
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	C2/c	P-1
<i>a</i> (Å)	7.367(1)	19.6191(16)	7.3463(8)
<i>b</i> (Å)	9.104(1)	11.3290(9)	7.6103(10)
<i>c</i> (Å)	10.336(1)	12.0457(9)	11.2758(13)
α (°)	82.25(1)	90	80.121(10)
β (°)	76.68(1)	102.706(8)	78.339(10)
γ (°)	83.13(1)	90	84.804(10)
<i>V</i> (Å ³)	665.5(2)	2611.8(4)	607.22(13)
<i>Z</i>	1	4	1
<i>D_x</i> (g cm ⁻³)	1.59	1.48	1.50
<i>F</i> (0 0 0)	326	1200	283
μ (mm ⁻¹)	0.29	0.31	0.33
Crystal size (mm)	0.4 × 0.3 × 0.1	0.45 × 0.2 × 0.1	0.4 × 0.23 × 0.2
2 θ range (°)	3.48–29.57	2.09–25.00	2.72–25.00
<i>hkl</i> range	−9 ≤ <i>h</i> ≤ 6 −12 ≤ <i>k</i> ≤ 12 −13 ≤ <i>l</i> ≤ 13	−23 ≤ <i>h</i> ≤ 23 −13 ≤ <i>k</i> ≤ 13 −14 ≤ <i>l</i> ≤ 13	−8 ≤ <i>h</i> ≤ 8 −9 ≤ <i>k</i> ≤ 8 −13 ≤ <i>l</i> ≤ 13
Reflections			
Collected	6529	12273	6471
Unique (<i>R</i> _{int})	3334 (0.018)	2318 (0.029)	2134 (0.020)
With <i>I</i> > 2 σ (<i>I</i>)	2559	1502	2134
<i>w</i> -Parameters			
<i>A</i>	0.03	0.05	0.097
<i>B</i>	0.46	1.9	0.1743
No. of parameters	219	247	213
<i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.047	0.043	0.049
<i>wR</i> (<i>F</i> ²) [<i>I</i> > 2 σ (<i>I</i>)]	0.142	0.102	0.144
<i>R</i> (<i>F</i>) [all data]	0.060	0.075	0.062
<i>wR</i> (<i>F</i> ²) [all data]	0.152	0.118	0.155
Goodness of fit	1.15	1.05	1.07
Max/min $\Delta\rho$ (e Å ⁻³)	0.32/−0.31	0.24/−0.22	0.37/−0.36

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