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Cyclometalated rhodium(III) and iridium(III) complexes containing amino acids as N,O-chelates

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ABSTRACT

The synthesis of bis-cyclometalated aminocarboxylato complexes [M(α-aminocarboxylato)(ptpy)$_2$] (M = Rh, **3**, **4**, **5**; M = Ir, **6**, **7**, **8**), ptpy = 2-(p-tolyl)pyridinato; aminocarboxylato = glycinato, L-alaninato, L-prolinato) from [{M(μ-Cl)(ptpy)$_2$}$_2$] (M = Rh, **1**; M = Ir, **2**) is described. The molecular structure of [Ir(L-alaninato)(ptpy)$_2$] (**7**) was confirmed by a single-crystal X-ray diffraction study. Compound **7** crystallized from methanol-*iso*-hexane in the space group $P2_1$. For **7** the two diastereoisomers Δ_{Ir}, S_C and Λ_{Ir}, S_C were found crystallizing twice per unit. Absorption and emission spectra were recorded. The rhodium compounds are weak yellow-green and the iridium species strong green emitters.

1. Introduction

Iridium(III) complexes with cyclometalated ligands of the 2-phenylpyridinato type have attracted considerable attention for a potential application in the domain of phosphorescent organic light-emitting devices (OLEDs), e.g. [1–4]. Currently also cyclometalated rhodium(III) complexes are investigated as luminescent biotinylation reagents beside the analogous iridium compounds which have been used yet longer in this field [5]. Recently we reported some contributions in the field of compounds for OLED applications [6]. Beck and co-workers have reported several complexes containing biologically important ligands, e.g. amino acids, with the cyclometalated Ir(ppy)$_2$ and Rh(ppy)$_2$ fragment, respectively, (Hppy = 2-phenylpyridine) [7]. The chlorido-bridged complexes [{M(μ-Cl)(C^N)$_2$}$_2$] (C^N = cyclometalated ligand) represent useful starting complexes in bridge-splitting reactions introducing numerous other co-ligands. Frequently phenylpyridinato ligands without other substituents were investigated. In the literature some complexes with the ptpy ligand (Hptpy = 2-(p-tolyl)pyridine) were described, e.g. with iridium [8] or rhodium [9]. Herein we describe new complexes using the metal ligand fragments M(ptpy)$_2$ (M = Rh, Ir) in the synthesis of compounds bearing amino acids as ligands.

2. Experimental

2.1. General considerations

All manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques. Solvents and reagents were used as received: Methanol, dichloromethane, isohexane, 2-(p-tolyl)pyridine, glycine, L-alanine (all from Aldrich), L-proline (from Agros) NMR spectra: Jeol ECX 400. Chemical shifts are referenced to the residual solvent signal (CD_3OD; $\delta(^{13}C)$ = 49.0 ppm; $\delta(^1H)$ = 3.30 ppm relative to TMS). ^{13}C NMR data of all compounds are collected in Table 1. Mass spectra were measured using a Jeol Mstation JMS 700. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

2.2. Synthesis of compounds **3**–**8**

Synthesis of bis-cyclometalated aminocarboxylato complexes [M(α-aminocarboxylato)(ptpy)$_2$] (M = Rh, Ir; ptpy = 2-(p-tolyl)-pyridinato; aminocarboxylato = glycinato, L-alaninato, L-prolinato, **3**–**8**): The α-amino acid (0.3 mmol) was dissolved in 4 mL of methanol and 0.30 mL of a 1 M solution of NaOMe in methanol was added. The solution was stirred for 30 min. To this solution 0.15 mmol of the complex [{M(μ-Cl)(ptpy)$_2$}$_2$] (M = Rh [9], Ir [8]) was added and stirred for 2 d at room temperature. The mixture was evaporated to dryness and the residue dissolved in 3 mL of dichloromethane. To dissolve the compound completely,

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Table 1
^{13}C NMR data of compounds **3**–**8**.

	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
3	166.7/ 167.8	120.1	139.0	123.1/123.2	149.9/150.9	142.4/143.1	124.1/124.4/124.6/124.8		139.9/140.0	135.0/135.1	166.8/169.4
6	170.0// 170.1	119.7/119.8	138.6/138.7	122.7/122.8	149.3/151.0	142.9/143.5	125.0/125.1	123.0/ 123.1	140.0/140.2	134.1/134.3	146.1/152.4
4	166.9/ 167.0/167.8	120.09/ 120.14/ 120.2/120.3	138.9/139.0	122.9/ 123.11/ 123.15/ 123.2	149.6/ 149.7/151.1	142.45/ 142.47/ 143.1/143.2	124.0/124.1/124.4/ 124.7/124.88/124.90		139.8/ 139.9	135.09/ 135.13/ 135.3	167.0/ 167.1/ 169.7/169.8
7	170.2/ 170.3/ 171.1/ 171.2	119.66/ 119.73/ 119.8/119.9	138.58/ 138.61/ 138.7	122.5/122.6/ 122.8	149.0/ 149.1/ 150.8/151.2	142.95/ 142.97/ 143.6	124.96/ 124.98/ 125.19/ 125.23	123.0/ 123.1	140.0/140.1	134.09/ 134.13/ 134.3/134.6	146.5/146.7
5	167.9/??	120.21/ 120.28/ 120.5/120.6	139.0/ 139.1/ 139.2/139.4	122.81/ 123.17/ 123.3	149.93/ 150.38/ 150.96	142.22/ 142.87/ 143.04	124.4/124.6/124.8/124.9		139.8/ 139.9/ 140.1/140.4	134.9/135.1/ 135.3/135.4	n.o.
8	170.0/??	119.8/119.9/ 120.2	138.8/ 138.9/ 139.0/139.3	122.6/122.8/ 122.9	149.3/ 149.5/ 150.3/151.1	142.3	124.0/125.1/ 125.2/125.3	123.1/ 123.3	139.9/ 140.1/ 140.4/140.5	134.1/134.2/ 134.3/134.5	146.4

	C13	COO	C_α	C_β
3	21.7/21.8	184.3	45.5	–
6	21.5/21.6	186.5	45.2	–
4	21.7/21.8	185.7/186.2	52.6	21.5/22.0
7	21.5/21.6	187.4/188.0	52.2/52.3	21.9
5	21.8	185.7/185.6	64.5/63.5	32.5/32.3
8	21.7/21.6	187.8/187.4	64.2/63.3/63.2	32.5/32.4

sometimes it was necessary to add a small amount of methanol. The formed NaCl was filtered off and the solution reduced to 1 mL. After addition of pentane (or *iso*-hexane) the product was precipitated, filtered off and dried in vacuo. All compounds seem to co-crystallize with NaCl.

*2.2.1. [Rh(glycinato)(ptpy)$_2$] (**3**)*

Yield: 78 mg (48.8%), M = 532.42. *Anal.* Calc. for $C_{26}H_{25}N_3O_2Rh \times H_2O$: C, 58.56; H, 5.11; N, 7.89. Found: C, 58.22; H, 4.90; N, 7.85%. MS (FAB$^+$): m/z = 515 [M$^+$]. IR (KBr, cm^{-1}): 3028 w, 2993 sh, 2915 ν(NH), 1600s (COO), 1586 versus, 1562 versus (C═C, C═N). ^{1}H NMR (400 MHz),: δ 8.77 and 8.63 (2 "d", 5.5/5.8 Hz, 2H, H6), 8.01–7.97 (m, 4H, H3, H4), 7.61–7.54 (m, 2H, H8), 7.37–7.31 (m, 2H, H5) 6.70 ("d", 7.7 Hz, 2H, H9), 6.09 and 5.87 (2s, 2H, H11), δ_A 3.53/δ_B 3.41 (AB-system,, $J_{AB} \approx 18$ Hz, 2H, C*H*), 1.97 and 1.94 (2s, 6H, ptpy-CH_3).

*2.2.2. [Ir(glycinato)(ptpy)$_2$] (**6**)*

Yield: 95 mg (40.0%), M = 720.61. *Anal.* Calc. for $C_{26}H_{25}N_3O_2Ir \times 2NaCl$: C, 43.34; H, 3.50; N, 5.83. Found: C, 43.62; H, 3.70; N, 5.83%. MS (FAB$^+$): m/z = 604 [M$^+$]. IR (KBr, cm^{-1}): 3032 w, 2916 ν(NH), 1629s, 1603s (COO), 1589 versus, 1560m (C═C, C═N). ^{1}H NMR (400 MHz): δ 8.85 and 8.66 (2 "d", 5.5/5.8 Hz, 2H, H6), 8.01–7.95 (m, 2H, H3,), 7.89–7.85 (m, 2H, H4), 7.51–7.48 (m, 2H, H8), 7.32–7.27 (m, 2H, H5), 6.61–6.60 (m, 2H, H9), 6.08 and 5.85 (2s, 2H, H11), 4.70–4.64 and 4.14–4.07 (2m, 2H, NH_2), 3.61–3.48 (m, 2H, CH_2) 1.98 and 1.95 (2s, 6H, ptpy-CH_3).

*2.2.3. [Rh(L-alaninato)(ptpy)$_2$] (**4**)*

Yield: 80 mg (40.5%), M = 644.31. *Anal.* Calc. for $C_{27}H_{26}N_3O_2Rh \times 2NaCl$: C, 50.33; H, 4.07; N, 6.52. Found: C, 49.97; H, 4.25; N, 6.50%. MS (FAB$^+$): m/z = 528 [M$^+$]. IR (KBr, cm^{-1}): 3028 w, 2913 ν(NH), 1602s (COO), 1587 versus, 1562 versus (C═C, C═N). ^{1}H NMR (400 MHz): δ 8.90, 8.80, 8.66, 8.58 (4d, $J \approx 5$ Hz, 2H, H6) 8.05–7.95 (m, 4H, H3, H4), 7.60–7.55 (m, 2 H, H8), 7.38–7.31 (m, 2H, H5) 6.70 and 6.69 (2s, br, 2H, H9), 6.12 and 5.8 (2s, br, 2H, H11), 3.63 ("q", J = 7.4 Hz, 1H, C*H*), 1.98 and 1.95 (2s, 6H, ptpy-CH_3), 1.47 and 1.34 (2d, J = 7.2 Hz, ala-CH_3).

*2.2.4. [Ir(L-alaninato)(ptpy)$_2$] (**7**)*

Yield: 90 mg (40.4%), M = 675.19. *Anal.* Calc. for $C_{27}H_{26}N_3O_2Ir \times NaCl$: C, 48.03; H, 3.88; N, 6.22. Found: C, 48.20; H, 3.82; N, 6.29%. MS (FAB$^+$): m/z = 617 [M$^+$]. IR (KBr, cm^{-1}): 3295 w, 3247 ν(NH), 1640s (COO), 1598 versus, 1550m (C═C, C═N). ^{1}H NMR (400 MHz,): δ 8.95, 8.88, 8.67, 8.61 (4d, $J \approx 7.3$ Hz, 2H, H6) 8.02–7.94 (m, 2H, H3), 7.90–7.82 (m, 2H, H4) 7.54–7.47 (m, H8), 7.33–7.24 (m, H5) 6.63–6.59 (m, 2H, H9), 6.12, 6.11 and 5.87 (3s, 2H, H11), 5.11, 4.40, 4.24, 3.52 (4m, 2H, NH_2), 3.69–3.60 and 3.40–3.30 (2m, 1H, α-C*H*), 1.998/1.993/1.963 (3s, 6H, ppy-CH_3), 1.45 and 1.33 (2d, $J \approx 7$ Hz, 3H, ala-CH_3).

*2.2.5. [Rh(L-prolinato)(ptpy)$_2$] (**5**)*

Yield: 80 mg (43.5%), M = 611.91. *Anal.* Calc. for $C_{29}H_{28}N_3O_2Rh \times NaCl$: C, 56.92; H, 4.61; N, 6.87. Found: C, 57.46; H, 4.79; N, 6.33%. MS (FAB$^+$): m/z = 554 [M$^+$]. IR (KBr, cm^{-1}): 3192 w, 2956 w, 2914 ν(NH), 1588 versus, 1562s (C═C, C═N). ^{1}H NMR (400 MHz): δ 8.77*, 8.66*, 8.62, 8.58 (4 "d", 5.5/5.8/5.5/5.2 Hz, 2H, H6), 8.07–7.94 (m, 4H, H3 + H4) 7.63–7.55 (m, 2H, H8), 7.41–7.34 (m, 2H, H5) 6.74–6.66 (m, 2 H, H9), 6.19*, 6.14, 5.83*, 5.77 (4s, 2H, H11), 4.06–4.02* and 3.81–3.76 (2m, 1H, α-C*H*), 3.50–3.43, 3.19–3.04, 2.84–2.77, 2.72–2.68, 2.43–2.21, 2.15–2.08, 1.86–1.78, 1.70–1.62, 1.52–1.43 (9m, 7H, N*H*+ β/γ/δ-CH_2), 2.01, 1.94, 1.93 (3s, 6H, ppy-CH_3). Asterix (∗) mark the signals of the dominant isomer.

*2.2.6. [Ir(L-prolinato)(ptpy)$_2$] (**8**)*

Yield: 110 mg (43.9%), M = 759.67. *Anal.* Calc. for $C_{29}H_{28}N_3O_2Ir \times 2NaCl$: C, 45.85; H, 3.72; N, 5.53. Found: C, 45.54; H, 3.88; N, 5.48%. MS (FAB$^+$): m/z = 643 [M$^+$]. IR (KBr, cm^{-1}): 3030 w, 2960 w, 2868 ν(NH), 1602 versus (COO), 1590 versus, 1560 sh (C═C, C═N). ^{1}H NMR (400 MHz): δ 8.86*, 8.69, 8.59 (3 "d", 5.5/5.8/5.8 Hz, 2H, H6), 8.05–7.95 (m, 2H, H3), 7.93–7.85 (m, 2H, H4), 7.56–7.46 (m, 2H, H8), 7.36–7.30 (m, 2H, H5) 6.65–6.59 (m, H9), 6.19*, 6.12, 5.82*, 5.80 (4s, 2 H, H11), 4.11–4.03*, 3.92–3.87 (2m, 1H, α-C*H*), 3.49–1.12 (14m, 7H, N*H*+ β/γ/δ-CH_2), 2.02*, 2.01, 1.95*, 1.94 (4s, 6H, ppy-CH_3). Asterix (∗) mark the signals of the dominant isomer.