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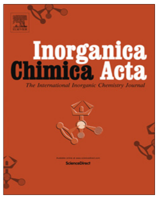

Research paper

Dinuclear fused salen complexes of group-10 metals: Peculiarity of the crystal structure and near-infrared luminescence of a bis(Pt-salen) complex

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ABSTRACT

Dinuclear fused salen complexes with Ni, Pd, and Pt nuclei were synthesized, and their crystal structures were determined. In the crystal structure of the Pt complexes, the molecules were virtually planar and formed a closely stacked dimer every two molecules, whose Pt—Pt interatomic distance was 3.43 Å. The absorption spectra of the dinuclear salen complexes were similar to each other both in solution and in the solid state. The dinuclear Pt complex exhibited photoluminescence, presumably related to the π-conjugated system of the naphthalene ring, both in solution and in the solid state. The low-energy emission, corresponding to a longer wavelength compared to that of analogous mononuclear complexes, ranged to the near-infrared region, suggesting that the naphthalene ring is perturbed by the adjoining chelate rings as if these moieties formed a fused aromatic ring system.

1. Introduction

Metal complexes of salen (*N*,*N*-bis[salicylidene]ethylenediamine) and salphen (*N*,*N*-bis[salicylidene]-1,2-phenylenediamine) ligands have attracted considerable attention owing to their photophysical properties, such as luminescence [1–3], and nonlinear optical properties [4–6]. Recently, there have been many reports of discrete molecules [7–17] and copolymers [18–21] bearing these complexes embedded in π-conjugated systems including benzene, naphthalene, biphenyl, phenylene vinylene, phenylene ethynylene, and oligothiophene. These materials are expected to exhibit uncommon photophysical properties originating from the electronic communication between the metal complex moieties through the π-system [22]. During the past years, we investigated a series of transition metal complexes with fused oligosalphen ligands containing 2,6-dihydroxynaphthalene-dicarbaldimine moieties [23–27]. Recently, we reported that the electronic state of the naphthalene moiety in the fused salphens is relatively similar to that of polycyclic aromatic hydrocarbons like chrysene or tetracene, depending on the connection topology of the adjoining chelate rings [28]. Thus, it is of interest to determine to which extent the virtually expanded π-conjugated system influences the photoluminescence of a fused salen/salphen complex as compared to its mononuclear analogues.

In this paper, we describe a set of fused salen complexes of group-10 metals, with a focus on the peculiarities of a platinum complex. Platinum(II) complexes with oligopyridines [29–31], Schiff bases [32–36], and other planar π-conjugated ligands [37–40] are of considerable interest in view of their photoluminescent properties. According to these studies, such compounds emit phosphorescence due to the intraligand charge transfer $^3(\pi \rightarrow \pi^*)$ and metal-to-ligand charge transfer (MLCT) $^3(\mathrm{Pt(5d)} \rightarrow \mathrm{ligand}(\pi^*))$ states, giving rise to a characteristic spectral band with a progression in the 1300–1400 $\mathrm{cm^{-1}}$ interval, in the absence of remarkable intermolecular interactions. When two molecular units of a Pt complex are placed in proximity, a slightly red-shifted featureless emission band originating from an excimer state is obtained. In special cases, the Pt—Pt interatomic distance is reduced to ~3.5 Å or less, resulting in an emission due to the metal-metal-to-ligand charge transfer (MMLCT) $(\mathrm{Pt(5d\sigma^*)} \rightarrow \mathrm{ligand}(\pi^*))$ state [31]. Among the above mentioned examples, the

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Abbreviations: MLCT, metal-to-ligand charge transfer; MMLCT, metalmetal-to-ligand charge transfer; DCB, *o*-dichlorobenzene; Na-TFPB, sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

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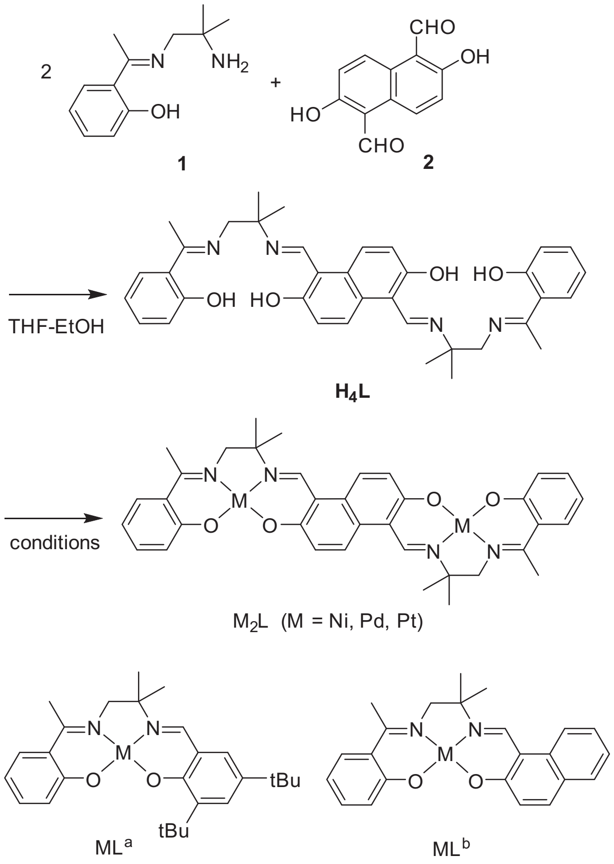

Fig. 1. Synthesis of dinuclear complexes M_2L, and structures of their mononuclear analogues ML^a and ML^b.

^{3}MMLCT emission band normally appears in the longest wavelength region, and red-shifts or exhibits sharp bands upon cooling. In some cases, the luminescence color is modulated by external stimuli that influence the intermolecular interactions even in a condensed phase.

In view of the peculiarities of Pt complexes mentioned above, the crystal structure and photophysical properties of a fused Pt-salen complex (Pt_2L, Fig. 1) are worth studying by comparison with other group-10 metal complexes (Ni_2L, Pd_2L) and analogous mononuclear complexes (ML^a, ML^b). In addition, it should be noted that mechanochromic photoluminescence properties were recently observed for a bis(Pt-salen) complex containing a semi-flexible linker [41]. Herein, we demonstrate that the fused bis(Pt-salen) complex investigated in the present study can serve as a good counterexample since it does not exhibit chromic response to mechanical stimuli.

2. Experimental

2.1. Measurements

The ultraviolet–visible (UV–Vis) absorption and emission spectra of the solid samples were acquired using a conventional optical microscope equipped with an optical fiber connected to a spectrometer (Ocean Optics USB4000). The incident light was guided from a high-pressure Hg lamp via a 330–380 nm bandpass filter and the transmitted light was guided from a Xe light source (Asahi Spectra LAX-103) through a custom-made adaptor. For these solid-state spectroscopy experiments, the samples were prepared as finely crashed microcrystals, and then amorphous thin films were smeared on a glass slide using the back of a stainless spatula. The solution-state UV–Vis absorption spectra of the complexes were measured in 1,2-dichlorobenzene (DCB) (2×10^{-5} M) with a JASCO V-630 spectrophotometer. The emission and excitation fluorescence spectra of the solutions were measured with a JASCO FP-6600 spectrofluorometer. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 spectrometer (400 MHz for ^{1}H) for samples in either chloroform-d or pyridine-d_5.

2.2. Synthesis

2.2.1. Bis(H_2-salen) ligand (H_4L)

An amine-imine (**1**) was prepared from 2′-hydroxyacetophenone and 2-amino-2-methylpropylamine [42]. Dialdehyde (**2**) was prepared according to Ref. [43]. Compound **2** of 138 mg (0.64 mmol) was dissolved in THF (15 mL), to which ethanol solution (1.3 mL) of **1** (265 mg, 1.28 mmol) was added. The mixture was left without stirring for 12 h at 25 °C, and then the solvent was removed by evaporation. Orange microcrystalline solid was collected by filtration, washed with ethanol, and dried under reduced pressure. Yield: 355 mg (94%). m.p. 204–205 °C. Elemental Analysis for $C_{36}H_{40}N_4O_4{\cdot}0.5H_2O$ (601.31): Calc. C, 71.86; H, 6.87; N, 9.31. Found: C, 71.94; H, 6.97; N, 9.12. FAB MS(+) *m*/*z* 593.6 (Calc. 593.3 for $M + H^+$). IR(KBr): 1616 cm^{-1} ($\nu_{C{=}N}$). ^{1}H NMR ($CDCl_3$): δ 1.60 (12H, s, $-CH_3$), 2.32 (6H, s, $-CH_3$), 3.74 (4H, s, $-CH_2-$), 6.75 (2H, dt, $J = 1.0$ Hz, 7.5 Hz, ArH), 6.92 (2H, dd, $J = 8.5$ Hz, 1.0 Hz, ArH), 7.01 (2H, d, $J = 9.5$ Hz, ArH), 7.27 (2H, dt, $J = 1.7$ Hz, 7.6 Hz, ArH), 7.47 (2H, dd, $J = 1.3$ Hz, 8.1 Hz, ArH), 7.97 (2H, d, $J = 9.5$ Hz, ArH), 9.04 (2H, s, CH=N), 15.30 (2H, brs, OH), 16.00 (2H, brs, OH), ^{13}C NMR ($CDCl_3$): $\delta = 15.04$, 25.80, 59.53, 60.81, 109.41, 117.65, 118.60, 119.49, 123.10, 125.85, 126.69, 128.30, 132.85, 156.71, 163.29, 167.00, 173.28.

2.2.2. Bis(Ni-salen) complex (Ni_2L)

H_4L (59 mg, 0.10 mmol) was dissolved in chloroform (5 mL). To this solution, methanol solution (9 mL) of nickel(II)acetate tetrahydrate (50 mg, 0.20 mmol) was added and stirred at 60 °C for 12 h, to afford reddish-brown suspension and some single crystals deposited on the glass wall. The solid was collected by filtration. A part of the sample was further recrystallized with *o*-dichlorobenzene (DCB)-methanol system for the purpose of X-ray diffraction and solid-state spectroscopy. Yield: 69 mg (98%), m.p.>300 °C (decomp.). Elemental Analysis for $C_{36}H_{36}N_4Ni_2O_4{\cdot}0.4CHCl_3$ (763.10): Calc. C, 58.00; H, 4.87; N, 7.43. Found C, 57.91; H, 4.92; N, 7.37; FAB MS(+) *m*/*z* 706.2 (Calc. 705.1 for $M + H^+$), IR (KBr): 1601(m), 1443(s), 1374(s), 1184(m), 1077(m), 753(m) cm^{-1}, ^{1}H NMR(C_5D_5N): $\delta = 1.51$ (6H, s, $-CH_3$), 2.07 (3H, s, $-CH_3$), 3.33 (2H, s, $-CH_2-$), 6.62 (1H, dt, $J = 1.4$ Hz, 7.1 Hz, ArH), 7.26 (1H, dt, $J = 1.6$ Hz, 6.9 Hz ArH), 7.34 (2H, d, $J = 8.9$ Hz, ArH), 7.51 (1H, d, $J = 8.1$ Hz, ArH), 7.97 (1H, d, $J = 9.0$ Hz, ArH), 8.45 (1H, s, CH=N), ^{13}C NMR spectrum could not be obtained due to a low solubility in the common NMR solvent.

2.2.3. Bis(Pd-salen) complex (Pd_2L)

H_2L (59 mg, 0.10 mmol) was dissolved in chloroform (5 mL). To this solution, toluene solution (1.2 ml) of palladium(II) acetate (45 mg, 0.2 mmol) was added and stirred for 24 h at 60 °C, to afford green microcrystalline precipitate. The solid was collected by filtration, washed by methanol. A part of the sample was further recrystallized from DCB for the purpose of X-ray diffraction and solid-state spectroscopy. Yield: 75 mg (94%), m.p. >300 °C (decomp.). Elemental analysis for $C_{36}H_{36}N_4O_4Pd_2$ (763.10):Calc. C, 53.95; H, 4.53; N, 6.99. Found: C, 53.71; H, 4.66; N, 6.86; FAB MS (+) *m*/*z* 801.3 (Calc. 801.1 for $M + H^+$), IR (KBr): 1597(s), 1436(s), 1365(s), 1179(m), 1075(s), 751(w) cm^{-1}, ^{1}H NMR (C_5D_5N) δ 1.54 (12H, s, $-CH_3$), 2.33 (6H, s, $-CH_3$), 3.71 (4H, s, $-CH_2-$), 6.65 (2H,