Note

Platinum(II) imidazo[4,5-f]-1,10-phenanthroline chloride and thiolate complexes: Synthesis and crystal structures

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Abstract

The planar aromatic imidazo[4,5-f]-1,10-phenanthroline ligands have been used to prepare platinum(II) chloride and thiolate complexes. The X-ray structures of two thiolate compounds are reported, which show column-like packing in the solid state due to intermolecular aromatic π–π interactions. The compounds absorb moderately in the visible region, owing to {charge-transfer-to-diimine} electronic transition.

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1. Introduction

Platinum complexes with the diimine ligands are widely used as optical materials [1], DNA intercalators [2] and solar cell dyes [3]. We would like to introduce imidazo[4,5-f]-1,10-phenanthroline ligands (imP) to Pt(II) coordination chemistry, and illustrate it by synthesis of Pt(imP) chloride and thiolate complexes. The imP ligands are easy to prepare and modify and therefore have recently gained a lot of interest with respect to synthesis of novel metal compounds [4–11], amenable to the various applications stated above. In particular, the potential of flat extended aromatic system of imP ligands as a DNA intercalating unit has been exploited [4–6]. In order to increase solubility, and demonstrate synthetic versatility of the imP ligands, four new representatives of this class of diimines have also been prepared.

2. Results and discussion

The imidazo[4,5-f]-1,10-phenanthrolines were prepared by a reaction of 1,10-phenanthroline-5,6-dione with aldehyde in the presence of ammonium acetate in acetic acid [12] (Scheme 1). Four new ligands have been prepared, which contained either alkyl groups (imP-LtBu, L-tBu) to improve solubility, or extended aromatic chromophore groups (L-Ph, L-Nap) to potentially modify spectroscopic properties (Scheme 2).

The ligands were refluxed with Pt(DMSO)2Cl2 [13] in alcohols to give Pt(imP)Cl2 complexes that were then used as precursors to other Pt(imP) compounds.

Reaction of Pt(imP)Cl2 with thiophenols in methanol in the presence of a base gave thiolates Pt(imP)(S-R2S)2 as coloured precipitates that were purified by column chromatography (Schemes 1 and 2). Sonication was used to increase the rate of this reaction and drive it to completion because both the precursor and the product Pt(II) complexes were only sparingly soluble in methanol.

All new compounds were identified by CHN data and 1H NMR. In the 1H NMR spectra, the NH proton of imP ligand was observed as either a broad or a sharp singlet, indicating respectively fast or slow exchange of a proton between the two nitrogens of the imidazole ring. The fast exchange of a proton resulted in the apparent C2-symmetric structure of some ligands and complexes in the 1H NMR spectra in solutions.
The thiolate complexes Pt(imP)(S-RS)₂ were obtained as red or brown solids. Their colour was determined by the broad and structureless absorption band in the visible region, centred at 503–526 nm, with the values of extinction coefficients of $(2.7–4.3) \times 10^{3} \text{M}^{-1} \text{cm}^{-1}$ (Table 1), typical for a charge-transfer transition. The negative solvatochromic behaviour (e.g., a shift of the absorption maximum from 498 nm in CH₃CN to 519 nm in CH₂Cl₂ for Pt(imP–tBu)(S-Ph–tBu)₂), typical for Pt(diimine)(thiolate)₂ complexes [1], also indicates the charge-transfer nature of the corresponding electronic transition. The energy of the lowest absorption band was red-shifted with the increase of the electron donating ability of thiophenols in the order S-MeᵗBu > S-ᵗBu > S-CO₂Me, suggesting that the HOMO is largely localised on the thiolate part of the molecule. This assignment is in agreement with the absence of absorption bands at wavelengths >450 nm in the Pt(imP)Cl₂ precursors. At the same time, the energy of the lowest absorption band of Pt(imP)(S-RS)₂ was not very sensitive to the R₅ group of imP ligand, and remains similar to that of Pt(1,10-phenanthroline)(S-RS)₂ [1c]. These observations tentatively suggest that the corresponding electronic transition is mainly localised on the [phenanthroline–Pt–S-RS] core with a rather limited R₅ group participation. The lowest absorption band has therefore been assigned to a mainly thiolate-to-diimine charge-transfer transition.

The compounds were non-luminescent in degassed CH₂Cl₂ solutions at rt.

Crystal structures of Pt(L-NMe₂)(S-tBu)₂ and Pt(L-NO₂)(S-Me₅Bu)₂ complexes are shown in Figs. 1 and 2. The structural features are similar for both complexes. The Pt(II) is in a distorted square planar coordination environment. A particular distortion towards a tetrahedral coordination is observed for Pt(L-NO₂)(S-Me₅Bu)₂ with a dihedral angle of 7.32° between the planes defined by N(1) Pt(1) N(2) and S(1) Pt(1) S(2) atoms (Fig. 2).

The imP ligands are planar in both structures. The two thiol ligands are situated above the imP plane resulting in an overall L-shaped molecule. The ө-hydrogen atoms of thiol ligands are located above the coordination plane of Pt(II). In the Pt(L-NO₂)(S-Me₅Bu)₂ structure such

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_max/nm (10⁻³/M⁻¹/cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(imP–tBu)(S-CO₂Me)₂</td>
<td>503 (2.9), 364 (11), 295 (38), 257 (68)</td>
</tr>
<tr>
<td>Pt(imP–tBu)(S-tBu)₂</td>
<td>519 (2.7), 402 (5.7), 386 (6.2), 288 (43), 258 (81)</td>
</tr>
<tr>
<td>Pt(L-H)(S-Me₅Bu)₂</td>
<td>523 (3.4), 394 (6.4), 279 (72)</td>
</tr>
<tr>
<td>Pt(L-tBu)(S-tBu)₂</td>
<td>510 (2.9), 394 (6.4), 283 (75)</td>
</tr>
<tr>
<td>Pt(L-tBu)(S-CO₂Me)₂</td>
<td>510 (3.7), 285 (62)</td>
</tr>
<tr>
<td>Pt(L-OMe)(S-Me₅Bu)₂</td>
<td>526 (2.8), 285 (62)</td>
</tr>
<tr>
<td>Pt(L-NMe₂)(S-tBu)₂</td>
<td>507 (3.4), 439 (42), 287 (53), 257 (43)</td>
</tr>
<tr>
<td>Pt(L-NMe₂)(S-CO₂Me)₂</td>
<td>505 (4.3), 353 (46), 290 (48)</td>
</tr>
<tr>
<td>Pt(L-NO₂)(S-Me₅Bu)₂</td>
<td>520 (3.5), 358 (30), 288 (42), 260 (55)</td>
</tr>
<tr>
<td>Pt(L-Ph)(S-tBu)₂</td>
<td>515 (2.9), 287 (67)</td>
</tr>
<tr>
<td>Pt(L-Nap)(S-tBu)₂</td>
<td>512 (3.1), 390 (7.8, sh), 274 (85)</td>
</tr>
</tbody>
</table>

In CH₂Cl₂ or CH₂Cl₂ + 0.5% CH₃OH.
arrangement results in a short intramolecular Pt–H–C contact (<2.9 Å) [14] with the Pt1–H(C21) and Pt1–H(C36) distances of 2.772 Å and 2.838 Å respectively and with the Pt1–C angles of ca. 122°.

The intermolecular aromatic π–π interactions of imP ligands result in the packing of their Pt(II) complexes into dimers (Figs. 1 and 2). The thiol ligands are pointing outwards from the centre of the dimer, thus allowing a closer approach and a better overlap between aromatic rings of imP ligands. The dimers are further packed into columns running along the a-axis. Each molecule within the column is related to the next one by a centre of inversion. The intra- and inter-dimer distances between imP ligands within the column are 3.364 Å and 3.453 Å for Pt(L-NMe2)(S′tBu)2 and 3.360 Å and 3.374 Å for Pt(L-NO2)(S-Me′tBu)2 (the distances were measured between the planes defined by all non-hydrogen atoms of imP ligand except the NO2 or N(CH3)2 group).

The shortest Pt–Pt distances are 8.035 Å for Pt(L-NMe2)(S′tBu)2 and 8.923 Å for Pt(L-NO2)(S-Me′tBu)2 indicating absence of metal–metal interaction.

The co-crystallised molecule of DMSO in the structure of Pt(L-NO2)(S-Me′tBu)2 forms a hydrogen bond through sulfoxide oxygen with NH proton of imidazole ring with O–H distance 1.895 Å and O–H/N angle 165.28°.

In conclusion, this contribution has exploited synthetically versatile imidazo[4,5-f][1,10-phenanthroline, imP, ligands to form a new series of stable Pt(II) chloride and thiolate complexes. The compounds absorb moderately in the visible region, owing to {charge-transfer-to-diimine} electronic transition. The X-ray crystallography has shown column-like packing in the solid state due to the intermolecular aromatic π–π interactions between the neighbouring imP ligands.
The extended planar aromatic system of the imP ligands renders their Pt(II) complexes potential intercalators into DNA. The notable lack of influence of the R₅ substituent on the imP ligand on the electronic absorption spectra of these chromophores opens up future possibilities for altering their molecular properties, such as, for example, solubility, charge, or functionalisation required for incorporation into polynuclear assemblies and in solar cells, without altering absorption characteristics. These compounds thus offer a valuable alternative to the 2,2'-bipyridyl or 1,10-phenanthroline ligands that are widely used in Pt(II) chemistry.

3. Experimental

All reactions were carried out in the dark under N₂ using general grade solvents that were degassed by bubbling N₂ for 10 min. Purification, crystal growth and handling of all compounds were carried out under air with a minimum exposure to light. All products were air- and moisture-stable solids which were stored in the dark when not used.

3.1. Synthesis of imP ligands

1,10-Phenanthroline-5,6-dione, the corresponding aldehyde (small excess) and ammonium acetate (excess) were refluxed in degassed acetic acid (10 ml) under N₂ for 3 h. The reaction mixture was diluted with water (20 ml) and neutralized with NH₄OH to give a precipitate of the product which was filtered, washed with dilute NH₄OH (pH 8), water and ether and dried in vacuum. The products were often obtained as solvates with water and acetic acid. The ligands were soluble in alcohols, DMSO and mixtures of CH₂Cl₂ with alcohols but were insoluble in ether, hexane and CHCl₃. The ligands L-H, L-NO₂, L-OMe and L-NMe₂ were known from previous studies [4]. The ligands imP-tBu, L-tBu, L-tPh and L-Nap are new.

3.2. Synthesis of complexes Pt(imP)Cl₂

PtCl₂(DMSO)₂ [13] and imP in 1:1 molar ratio (0.3–0.6 mmol scale) were refluxed in degassed ethanol (30 ml) under N₂ for 24 h to give a precipitate of the product that was filtered, washed with methanol and ether and dried in a vacuum. The yields were in the range 80–90%. The products were yellow except for the deep red coloured Pt(L-NMe₂)Cl₂. The complexes Pt(L-tBu)Cl₂ and Pt(L-NMe₂)Cl₂ were soluble in DMSO. Other complexes were insoluble in all common solvents.

3.3. Synthesis of complexes Pt(imP)(thiolate)₂

tBuOK or triethylamine (0.31 mmol) and thiol (0.31 mmol) were stirred at rt for 5 min in degassed CH₃OH (15 ml) under N₂. Pt(imP)Cl₂ (0.15 mmol) was added to the resulting solution and the reaction mixture was sonicated for 8 h at rt and stirred overnight to give a red, green or brown suspension of the product. The solid was filtered and washed with CH₃OH (10 ml). Purification by column chromatography (SiO₂, CH₃OH:CH₂Cl₂, 1:99–3:97) gave main coloured fraction that was reduced to 5 ml. Addition of hexane precipitated the product that was filtered, washed with hexane or a mixture of hexane and ether (50:50) and dried in vacuum. The yields were in the range 30–70%. The complexes were obtained as dark red or brown solids that were insoluble in alkanes and alcohols, soluble to various extents in CH₂Cl₂, and highly soluble in DMF, DMSO and in the mixtures of CH₂Cl₂ with alcohols.

3.4. X-ray crystallography

Single crystals were obtained by vapour diffusion of diethyl ether to DMF [Pt(L-NMe₂)(S-C₂H₅)], or DMSO [Pt(L-NO₂)(S-Me₂C₆H₄)] solutions of the complexes.

Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3° in omega. All reflections were corrected for Lorentz and polarization effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods and refined by full matrix least squares methods on F². Complex scattering factors were taken from the program package SHELXTL (An integrated system for solving and refining crystal structures from diffraction data, Revision 5.1, Bruker AXS LTD) as implemented on the IBM PC. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with Uiso constrained to be 1.2 (1.5 for methyl groups) times Ueq of the carrier atom. Data in common: T = 150(2) K, λ = 0.71073 Å.

Pt(L-NMe₂)(S-C₂H₅)₂. CCDC Ref. 607251; C₄₁H₄₁N₅PtS₂; Mw = 865.01; red plates; size (mm): 0.32 × 0.12 × 0.10; monoclinic; space group P2₁/c (C₁₇₆ h, No. 14); a/b/c (Å) = 8.0354(6)/23.8089(16)/21.3169(14); α/β/γ (°) = 90/95.276(3)/90; V = 4060.9(5) Å³; Z = 4; ρcalc = 1.415 g cm⁻³; μ = 3.591 mm⁻¹; F(000) = 1736; θ range (°) = 1.29–29.05; reflections collected/Rint/data/restraints/parameters = 52304/0.0726/323/10698; goodness-of-fit on F² = 1.05; R(I > 2σ(I)) = 0.0487, wR₂ = 0.1199; R (all data) = 0.0746, wR₂ = 0.1288; Δρcalc = −1.629 ± 1.807 Å.

Pt(L-NO₂)(S-Me₂C₆H₄)₂. CCDC Ref. 607252; C₄₁H₄₁N₅O₃PtS₂·(C₂H₅OH); Mw = 973.14; red blocks; size (mm): 0.32 × 0.16 × 0.12; monoclinic; space group P2₁/n (a non-standard setting of P2₁/c C₁₇₆ h, No. 14); a/b/c (Å) = 12.4893(18)/20.476(3)/17.300(2); α/β/γ (°) = 90/105.269(2)/90; V = 4268.010(1) Å³; Z = 4; ρcalc = 1.514 g cm⁻³; μ = 3.478 mm⁻¹; F(000) = 1900; θ range (°) = 1.57–27.55; reflections collected/Rint/data/restraints/parameters = 48169/0.1059/9689/6/514; goodness-of-fit on F² = 0.920; R(I > 2σ(I)) = 0.0425, wR₂ = 0.0861; R
(all data): $R_1 = 0.0874$, $wR_2 = 0.0999$; $\Delta\rho_{\text{min/max}} (\text{e} \text{Å}^{-3}) = -0.997/2.209$.

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Appendix A. Supporting information

Additional experimental details are available as Supporting Information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.08.007.

References


