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Coordination of bis(2-pyridyl)phosphinic acid as a tridentate ligand. Crystal structure of the {bis(2-pyridyl)phosphinato}{tris(2-pyridyl)-phosphine oxide}ruthenium(II) cation, $[Ru\{py_2P(O)O\}\{py_3PO\}]BF_4 \cdot 2H_2O$

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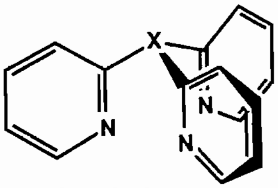
Abstract

In the synthesis of the bis{tris(2-pyridyl)phosphine oxide}ruthenium(II) cation, $[Ru(py_3P{=}O)_2]^{2+}$, the species {bis(2-pyridyl)phosphinato}{tris(2-pyridyl)phosphine oxide}ruthenium(II), $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$, was also isolated. The latter cation has been characterized by a structural determination and is the first example of a tridentate phosphinate anion. The electrochemical and spectral properties of both cations are reported. Crystals of $[Ru\{py_2P(O)O\}\{py_3PO\}]BF_4 \cdot 2H_2O$ crystallize in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 16.128(7)$, $b = 11.493(6)$, $c = 17.576(11)$ Å, $\beta = 102.64(4)°$, $V = 3178.9$ Å^3, $Z = 4$. The structure was refined by a full-matrix least-squares procedure, and converged with $R = 0.107$ and $R_w = 0.108$ for 1172 reflections.

Introduction

As part of a study of the synthesis and properties of transition metal complexes containing the tripodal ligands $(py)_3X$,



py = 2-pyridyl
X = N, CH, COH, P, P=O

we recently published details of the ruthenium(II) complexes of tris(2-pyridyl)amine, tris(2-pyridyl)-methane, tris(2-pyridyl)methanol and tris(2-pyridyl)-phosphine [1–3]. We had also undertaken the synthesis of the analogous compounds involving tris(2-pyridyl)phosphine oxide $\{py_3P{=}O\}$, a ligand reported previously [4, 5]. In the course of the work, we have indeed isolated $[Ru(py_3P{=}O)_2]^{2+}$, as well as the species $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ which we have characterized by a structural determination. Details of this structure are now presented, together with electrochemical characteristics of both the isolated products.

Results and discussion

Synthesis aspects

The synthetic route to the $[Ru(py_3P{=}O)_2]^{2+}$ cation was identical to that established in our earlier studies of the analogous $[RuL_2]^{2+}$ species containing the ligands py_3N, py_3CH and py_3P [2], which involved ligand substitution of the labile precursor $[Ru(DMF)_6]^{2+}$ (DMF = *N*,*N*-dimethylformamide) developed by Bernhard and Sargeson [6]. In addition to the desired (major) orange product, a minor amount of a sparingly soluble red product was also obtained, subsequently identified as containing $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$. The origin of the ligand bis(2-pyridyl)phosphinic acid in the reaction mixture is uncertain, but must arise either from a hydrolysis reaction during the synthesis of tris(2-pyridyl)-phosphine oxide, or alternatively because of the presence of small amounts of hydroxybis(2-pyridyl)-

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phosphine in the tris(2-pyridyl)phosphine precursor*. We regard the latter explanation as the more likely, and clearly the low solubility of the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ salts has allowed their ready isolation in this case.

Description of structure of the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ cation

The molecular structure of the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ cation is shown in Fig. 1 and selected interatomic parameters are given in the caption. While the structure is not of high precision owing to the poor quality of the crystals obtained, the analysis unambiguously establishes the stoichiometry of the compound and the molecular connectivity. The asymmetric unit comprises the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ cation, a BF_4^- anion and two water molecules of solvation associated with the ions via the expected hydrogen bonding contacts.

The Ru atom in the cation exists in a slightly distorted octahedral geometry comprised of an N_3 donor set derived from a $py_3P{=}O$ tripod ligand and an N_2O donor set derived from a hydrolyzed $py_3P{=}O$ ligand, i.e. $py_2P({=}O)O^-$ anion. The oxidation state of the Ru atom is +II owing to the presence of a BF_4^- anion in the lattice. The Ru–N bond distances lie in the narrow range 2.04(3)–2.11(3) Å with the shorter Ru–N bond distance being *trans* to the Ru–O bond of 2.11(2) Å reflecting the *trans* influence of the O(1) atom. The maximum deviation from the ideal octahedral geometry is manifested in the O(1)–Ru–N(1) bond angle of 82.9(9)°. The Ru–P(1) separation of 2.87(1) Å is not indicative of a significant interaction between these atoms. As expected the P(1)–O(1) bond distance of 1.56(2) Å is longer than the P(1)=O(2) distance of 1.44(3) owing to the coordination of the O(1) atom to the Ru atom; the P(2)=O(3) distance is 1.48(3) Å.

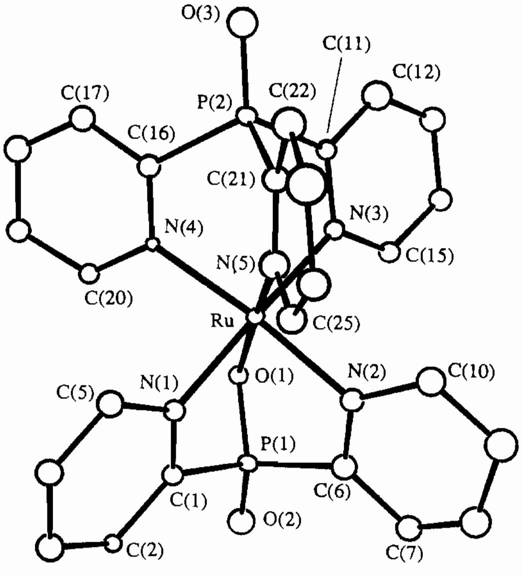

Fig. 1. The molecular structure of the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ cation showing the crystallographic numbering scheme employed. Selected interatomic parameters: Ru–O(1) 2.11(2), Ru–N(1) 2.06(3), Ru–N(2) 2.06(3), Ru–N(3) 2.11(3), Ru–N(4) 2.05(2), Ru–N(5) 2.04(3) Å; N(1)–Ru–N(3) 175(1), N(2)–Ru–N(4) 174(1) and O(1)–Ru–N(5) 176(1)°.

Ligating properties of bis(2-pyridyl)phosphinic acid

There are a limited number of examples of phosphinic acids (or their anions) acting as ligands for transition metal centers [7–11]. The bidentate coordination mode of the phosphinic acid in the species {bis(4,5-di-isopropylimidazol-2-yl)phosphinic acid}-dichlorozinc monohydrate [11] is noted, but the tridentate coordination mode observed in the title compound appears unique.

The π-backbonding characteristics of ligands coordinated to ruthenium are reflected in their ability to stabilize the Ru(II) oxidation state [12, 13]. In the present instance, the $E_{1/2}$ value of the $[Ru(py_3P{=}O)]^{3+/2+}$ redox couple ($E_{1/2}=1.26$ V; $\Delta E_p=60$ mV) in acetonitrile/0.1 M $(C_2H_5)_4NPF_6$ solution is not dissimilar to that for other $[Ru(py_3X)]^{3+/2+}$ species [14] (or indeed for $[Ru(bpy)_3]^{3+/2+}$) under the same conditions (i.e. $[Ru(py_3N)_2]^{3+/2+}$ (1.32 V; 80 mV); $[Ru(py_3CH)_2]^{3+/2+}$ (1.26 V; 60 mV); $[Ru(py_3P)_2]^{3+/2+}$ (1.37 V; 60 mV); $[Ru(bpy)_3]^{3+/2+}$ (1.29 V; 60 mV)).

For the $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^+$ species, the most valid comparison is with the ruthenium(II) complex containing the ligand tris(2-pyridyl)methanol [1], where $[Ru(py_3COH\text{-}N,N',N'')(py_3CO^-\text{-}N,N',O)]^+$ has the same charge type and the same immediate ligand environment (N_5O) as the present complex. In this case, from the $E_{1/2}$ values for the $[Ru(py_3X)]^{3+/2+}$ species, the contribution of the $py_3P{=}O$ and $py_3COH\text{-}N,N',N''$ ligands to the stabilization of Ru(II) is assumed to be similar. Accordingly, the difference between the $E_{1/2}$ values for $[Ru\{py_3P{=}O\}\{py_2P(O)O\}]^{2+/+}$ (0.65 V) and $[Ru(py_3COH)(py_3CO^-)]^{2+/+}$ (0.25 V) (both measured in aqueous solution) reflects a significantly greater degree of backbonding by the phosphinate ligand compared with the $py_3CO^-\text{-}N,N',O$ ligand.

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*The synthetic method for py_3P involves nucleophilic substitution of PCl_3 by a 3-molar ratio of the 2-pyridyl anion, with subsequent workup in aqueous solution. Clearly, incomplete substitution would lead to hydroxybis(2-pyridyl)phosphine which would give rise to bis(2-pyridyl)phosphinic acid in the subsequent oxidation.

Experimental

Measurements

Electrochemical measurements were obtained using a glassy carbon working electrode and are reported versus a saturated sodium chloride calomel (SSCE) reference electrode. Analyses were carried out by the Canadian Microanalytical Service (Delta, BC).

Materials

Tris(2-pyridyl)phosphine [5] and $[Ru(DMF)_6](tos)_2$ [6] (DMF = *N*,*N*-dimethylformamide; tos = 4-toluenesulfonate anion) were prepared as described previously.

Syntheses

Tris(2-pyridyl)phosphine oxide, $py_3P{=}O$

Tris(2-pyridyl)phosphine (200 mg; 0.75 mmol) dissolved in a minimum volume of ethanol was treated with H_2O_2 (1 ml of 30%), and the solution stirred for 2 h before drying over anhydrous Na_2SO_4. After filtering, the volume was reduced by rotary evaporation and solid tris(2-pyridyl)phosphine oxide ($py_3P{=}O$) crystallized on standing overnight in the refrigerator. The crystals were washed with diethyl ether and dried *in vacuo*. Yield 170 mg (80%); m.p. 210–211 °C (lit. 209 °C [15]).

$[Ru(py_3P{=}O)_2](PF_6)_2$ and
$[Ru(py_3P{=}O)\{py_2P(O)O\}]PF_6$

Tris(2-pyridyl)phosphine (145 mg) was dissolved in dry propan-1-ol (80 ml) under an argon atmosphere. After deaeration for 1 h, $[Ru(DMF)_6](tos)_2$ (104 mg) was added and the mixture refluxed overnight under argon. After cooling, the solvent was removed under vacuum, the residue extracted with methanol (5 ml), and the resulting orange solution was applied to a column of Sephadex LH20 and eluted with methanol. The front of the band was collected (λ_{max} = 429 nm), the eluant evaporated to dryness, the residue dissolved in water (20 ml) and converted to the PF_6^- salt by passage down a column of anion-exchange resin (Dowex 1×8–400). The water was removed by rotary evaporation and the residue recrystallized from acetone/diethyl ether. Yield 65 mg, 55%. Visible spectrum: λ_{max} (H_2O) = 429 nm. *Anal.* Calc. for $[Ru(py_3P{=}O)_2](PF_6)_2$, $C_{30}F_{12}H_{24}N_6O_2P_4Ru$: C, 37.8; H, 2.54; N, 8.8. Found: C, 38.3; H, 2.80; N, 9.1%.

The red residue remaining from the methanol extraction was collected and air dried. It was converted to the PF_6^- salt by anion exchange methods and the eluant evaporated to dryness. Yield 18 mg, 17%. Visible spectrum: λ_{max} (H_2O) = 452 nm. *Anal.* Calc. for $[Ru(py_3P{=}O)\{py_2P(O)O\}]PF_6$, $C_{25}F_6H_{20}N_5O_3P_3Ru$: C, 40.2; H, 2.70; N, 9.4. Found: C, 40.3; H, 2.94; N, 8.9%.

X-ray crystallography

$[Ru(py_3P{=}O)\{py_2P(O)O\}](tos)$ was converted to the BF_4^- salt by anion exchange methods. Crystals of $[Ru(py_3P{=}O)\{py_2P(O)O\}]BF_4 \cdot 2H_2O$ for the X-ray structural analysis were grown by liquid diffusion (ethanol/diethyl ether). Intensity data for 3844 reflections were measured at room temperature on a weakly diffracting crystal such that θ_{max} was 17°. The 3391 unique data were corrected for Lorentz and polarization effects and for absorption [16]; max. and min. transmission factors were 0.877 and 0.837.

Crystal data: $C_{25}H_{24}BF_4N_5O_5P_2Ru$, $M = 724.3$, monoclinic, space group $P2_1/n$, $a = 16.128(7)$, $b = 11.493(6)$, $c = 17.576(11)$ Å, $\beta = 102.64(4)°$, $V = 3178.9$ Å^3, $Z = 4$, $D_c = 1.513$ g cm^{-3}, $F(000) = 1456$, $\mu = 6.09$ cm^{-1}. The structure was solved by the Patterson method and refined by a full-matrix least-squares procedure using 1172 reflections which satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability. Owing to severe disorder in the structure and the lack of observed data, the BF_4^- anion was refined as a regular tetrahedron and only the Ru and P atoms were refined anisotropically; H atoms were not included in the model. The refinement converged with $R = 0.107$ and $R_w = 0.108$ for $w = 1.73/[\sigma^2(F) + 0.009|F|^2]$.

Supplementary material

Listings of fractional atomic coordinates and thermal parameters, interatomic bond distances and bond angles, and tables of F and $\sigma(F)$ are available from the authors on request (Tables S1–S4; 7 pages).

Acknowledgement

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