Inorganica Chimica Acta, 158 (1989) 201–204

Crystal Structure and X-ray Photoelectron Spectroscopy of Bis(*o*-amidothiophenolato)platinate(II)

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(Received August 10, 1988)

Abstract

The deep blue [Pt(S(NH)C_6H_4)$_2$] has been synthesized and characterized by X-ray structure analysis and X-ray photoelectron spectroscopy. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.691(7)$, $b = 5.916(2)$, $c = 8.125(4)$ Å, $\beta = 96.10(4)°$ and $Z = 2$. The Pt atom has a *trans*-planar coordination by 2S and 2N atoms. The Pt–S and Pt–N bond lengths are 2.278(2) and 1.938(5) Å, respectively. The *o*-amidothiophenolato ligand assumes *o*-thionequinoneimine structure as indicated from short S–C(1) [1.713(7) Å], N–C(2) [1.344(8) Å], C(3)–C(4) [1.369(10) Å] and C(5)–C(6) [1.368(12) Å] bond lengths. The Pt $4f_{7/2}$ binding energy (73.9 eV) for the complex is slightly higher than those for usual Pt(II) compounds, but lies within the highest limit for Pt(II) $4f_{7/2}$ binding energies.

Introduction

A deep blue nickel compound of *o*-aminothiophenol was originally prepared by Hieber and Bruck [1]. The compound was claimed to have the composition [NiO(S(NH$_2$)C_6H_4)$_2$] with the dimeric μ,μ-dioxo-bridged structure, and had been thought to be an example of Ni(IV) complex. The compound was subsequently formulated as [Ni(S(NH)C_6H_4)$_2$] and ESR study disclosed that [Ni(S(NH)C_6H_4)$_2$] is assigned as a Ni(II)–radical–ligand complex [2]. However, no X-ray structure of the complex has been reported, because of difficulty in obtaining a good crystal.

As we have prepared the platinum analogue [Pt(S(NH)C_6H_4)$_2$], the complex has been characterized by X-ray structure analysis and X-ray photoelectron spectroscopy.

Experimental

Preparation of [Pt(S(NH)C_6H_4)$_2$]

K_2PtCl_4 (1 mmol) was added to a methanol–water (1:1) solution (100 cm^3) of *o*-aminothiophenol (2 mmol). The mixture was stirred and adjusted to pH 10–11 by KOH aqueous solution. The solution soon turned blue and then a blue precipitate appeared. The mixture was further stirred for 3 h. The product was collected by filtration, washed with water and methanol, and air dried. Purification was accomplished by Sephadex LH-20 column chromatography (4.5 cm diameter and 40 cm in length). Concentrated dimethylsulfoxide (DMSO) solution (2 cm^3) of the complex was put on the top of the column and was eluted with methanol–acetone (1:1). The elution was repeated two times. Black thin parallelograms were obtained from the final eluate kept standing for 2 weeks in air. *Anal.* Found: C, 32.88; H, 2.29; N, 6.14. Calc. for [Pt(S(NH)C_6H_4)$_2$]: C, 32.65; H, 2.27; N, 6.35%. The mass spectrum shows three peaks at $m/e = 440$, 441 and 442 with intensities expected on the basis of relative isotopic abundance of platinum (^{194}Pt 32.9, ^{195}Pt 33.8 and ^{196}Pt 25.3%). These peaks correspond to the parent ion of formula $C_{12}H_{10}N_2S_2Pt^+$. The molar conductivity (0.27 S cm^2 mol^{-1}) of the complex in DMSO is much smaller than those of usual 1:1 electrolytes, indicating a non-electrolyte. The complex is diamagnetic at ambient temperature.

X-ray Data Collection

Crystal data: $C_{12}H_{10}N_2S_2Pt$, molecular weight = 441.4 a.m.u., monoclinic, space group $P2_1/c$, $a = 12.691(7)$, $b = 5.916(2)$, $c = 8.125(4)$ Å, $\beta = 96.10(4)°$, $U = 606.6(4)$ Å^3, $Z = 2$, $D_c = 2.42$ g cm^{-3}, $F(000) = 412$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 124.6 cm^{-1}.

Preliminary X-ray photographic data indicated that the space group is $P2_1/c$. The unit-cell dimensions were derived by the least-squares fit from the scattering angles of 20 centered reflections. Intensity data with $4° \leqslant 2\theta \leqslant 40°$ were measured on a Philips

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PW1100 diffractometer at ambient temperature. The crystal used for data collection had dimensions of 0.03 × 0.40 × 0.57 mm. The ω-scan method was employed with scan range of $(1.2 + 0.4 \tan \theta)^\circ$. Three standard reflections monitored every 3 h showed no significant variation. The intensity data were corrected for Lorentz-polarization [3] and absorption effects [4]. Maximum and minimum correction coefficients were 1.38 and 11.49. A total of 1005 reflections with $F_o^2 \geqslant 2\sigma(F_o^2)$ was used in the structure refinement.

Structure Solution and Refinement

The structure was solved by conventional Patterson-Fourier procedure and refined by least-squares method using anisotropic thermal parameters. The R factor is 0.025 ($R_w = 0.034$). Hydrogen atoms were fixed at idealized positions (N–H, C–H = 1.0 Å) with a common isotropic temperature factor of $B = 5.0$ Å^2. The function minimized was $\Sigma w(F_o - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.0006F_o^2]^{-1}$ was used. The final difference Fourier map had a peak of 1.1 e Å^{-3} near the Pt atom but was featureless. The atomic coordinates are given in Table 1. The computer programs used in the calculations were a local version of UNICS (HBLS-IV, RSSFR-5, and DAPH) [5]. Figure 1 was drawn by use of ORTEP [6]. Calculations were performed on FACOM M280II AD and HITAC M-660K computers at Osaka City University.

TABLE 1. Atomic Coordinates and Temperature Factors

Atom	x	y	z	U [a]
Pt	0.0	0.5	0.5	0.0317
S	0.13719(13)	0.75016(26)	0.52227(20)	0.0417
N	0.0950(4)	0.3152(7)	0.6461(6)	0.037
C(1)	0.2280(6)	0.5958(11)	0.6465(7)	0.039
C(2)	0.1942(5)	0.3806(9)	0.7001(7)	0.035
C(3)	0.2656(5)	0.2452(11)	0.8044(8)	0.043
C(4)	0.3657(6)	0.3224(12)	0.8529(8)	0.053
C(5)	0.3993(7)	0.5353(12)	0.7970(11)	0.057
C(6)	0.3313(6)	0.6666(11)	0.6959(8)	0.047

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

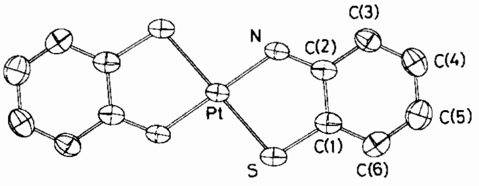

Fig. 1. Molecular structure of $[Pt(S(NH)C_6H_4)_2]$ with atomic numbering scheme. H atoms are omitted. The Pt atom lies on a crystallographic inversion center.

Measurements

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. Mg Kα (1253.6 eV) radiation was used as the excitation source. The samples were ground to powder and dusted on to a double-backed adhesive tape. The measurement was conducted at ambient temperature under a vacuum of about 10^{-7} Torr. All binding energies were corrected relative to the symmetric C 1S peak at 285.0 eV. The binding energies were reproducible to within ±0.1 eV. No appreciable X-ray damage was observed.

Magnetic susceptibility was measured by Shimadzu MB-2 Faraday balance. Conductivity was determined by use of a Yanaco MY-8 conductivity bridge. Mass spectrum was recorded on a Jeol D-300 spectrometer using 30 eV ionizing electrons. Cyclic voltammograms were recorded at 23 °C with a Yanaco P-1100 system equipped with a Rika Denki RW-201K X-Y recorder. A glassy carbon working electrode and an Ag/AgCl reference electrode were used. The absorption spectrum was recorded on a Hitachi 330 spectrophotometer at ambient temperature.

Results and Discussion

Reaction of K_2PtCl_4 with o-aminothiophenol in methanol–water at pH 10–11 in the presence of air gives a deep blue compound, which is soluble in DMSO, dimethylformamide, acetone and methanol. Recrystallization did not afford crystals. Purification by use of column chromatography gave thin black crystals of $[Pt(S(NH)C_6H_4)_2]$ for X-ray diffraction study.

Figure 1 gives a perspective view of $[Pt(S(NH)C_6H_4)_2]$ with atomic numbering scheme. The complex has a crystallographically imposed center of symmetry. Deviations of atoms from the PtN_2S_2 coordination plane are as follows: C(1) 0.050, C(2) 0.029, C(3) 0.057, C(4) 0.100, C(5) 0.140, and C(6) 0.120 Å. Bond lengths and angles are given in Table 2. The S–C(1) bond length of 1.713(7) Å is equal to the S=C double bond length of 1.714(2) Å [7] and is shorter than the S–C bond length (1.764(4) Å) in $[Coen_2(S(H_2N)C_6H_4)]^{2+}$ [8]. The N–C(2) bond (1.344(8) Å) has a considerable double bond character (N=C 1.287 Å) [9] and is also short compared with the N–C bond (1.458(4) Å) in $[Coen_2(S(H_2N)C_6H_4)]^{2+}$ [8]. Moreover, the C(3)–C(4) (1.369(10) Å) and C(5)–C(6) (1.368(12) Å) bond lengths in the benzene ring are 0.03–0.06 Å shorter than the other four C–C bond lengths. The overall structure of the complex may be described as the o-thionequinoneimine structure (Fig. 2). The Pt–S bond length [2.278(2) Å] is short compared with that in $[Pt(C_4H_6N_2S)_4]Cl_2 \cdot 2H_2O$ [2.3214(5) Å] [7] but is comparable to that in $(C_3H_3S_2)_2Pt-C_{12}H_4N_4$ [2.280(1) Å] [10]. The Pt–N bond length

TABLE 2. Bond Lengths (Å) and Bond Angles (°)

Pt–S	2.278(2)
Pt–N	1.938(5)
S–C(1)	1.713(7)
N–C(2)	1.344(8)
C(1)–C(2)	1.427(9)
C(1)–C(6)	1.394(10)
C(2)–C(3)	1.420(9)
C(3)–C(4)	1.369(10)
C(4)–C(5)	1.420(12)
C(5)–C(6)	1.368(12)
S–Pt–N	84.1(2)
Pt–S–C(1)	99.3(3)
Pt–N–C(2)	122.5(4)
S–C(1)–C(2)	116.8(5)
S–C(1)–C(6)	124.2(5)
C(2)–C(1)–C(6)	119.0(6)
N–C(2)–C(1)	117.3(6)
N–C(2)–C(3)	123.2(6)
C(1)–C(2)–C(3)	119.5(6)
C(2)–C(3)–C(4)	119.8(6)
C(3)–C(4)–C(5)	120.3(7)
C(4)–C(5)–C(6)	120.3(8)
C(1)–C(6)–C(5)	121.0(7)
N–Pt–S^{I}	95.9(2)

Symmetry code: none, (x, y, z); I, $(-x, 1-y, 1-z)$.

[1.938(5) Å] is slightly shorter than those previously reported.

The Pt 4f binding energies have been shown to be diagnostic of the Pt oxidation state [11]. Pt(II) compounds have Pt $4f_{7/2}$ binding energies between 72.4 and 74.3 eV [11, 12], while those for Pt(III) lie between Pt(II) and Pt(IV) at about 75.0 eV [11]. The binding energies for $[Pt(S(NH)C_6H_4)_2]$ (1), $[Pt_2(SC_5H_4N)_4]$ (2) [13] and $[Pt_2Cl_2(SC_5H_4N)_4]$ (3) [13] are shown in Table 3. **1** has a Pt $4f_{7/2}$ binding energy of 73.9 eV, which is very close to 74.1 eV of **3**. The binding energy for **2** (72.6 eV) is a typical value of Pt(II), while that (74.1 eV) for **3** is much less than those for Pt(III) complexes [12]. The Pt $4f_{7/2}$ binding energy for **1** has the same value as those for K_2PtCl_4 and $Pt(NH_3)_2(NO_2)_2$ [11, 12], but is 0.4 eV less than that (74.3 eV) for $K_2Pt(NO_2)_4$ [12]. The binding energy for **1** would be, however, comparable to that for $K_2Pt(NO_2)_4$, taking account of the ionic lattice effect which may contribute a variation of about 0.5 eV in Pt(II) complexes [14]. Though **1** has the high Pt $4f_{7/2}$ binding energy compared with other Pt(II) complexes, the oxidation number of II can be assigned to Pt in **1**.

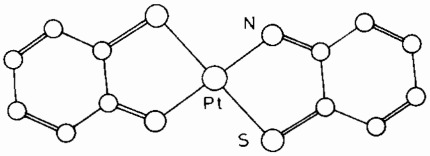

Fig. 2. *o*-Thionequinoneimine structure.

TABLE 3. Pt $4f_{7/2}$ Binding Energies (eV)

Compounds	Pt $4f_{7/2}$ (eV)
$[Pt(S(NH)C_6H_4)_2]$ (1)	73.9
$[Pt_2^{II}(SC_5H_4N)_4]$ (2)	72.6
$[Pt_2^{III}Cl_2(SC_5H_4N)_4]$ (3)	74.1

The electronic spectrum of **1** in methanol–acetone (1:1) shows a very intense absorption at 720 nm ($\epsilon = 7.4 \times 10^4$ cm^{-1} dm^3 mol^{-1}). A cyclic voltammetric study of **1** (0.25 mM, scan rate 100 mV/s) in acetone solution containing $n\text{-}Bu_4NClO_4$ (0.05 M) as supporting electrolyte displays two quasi-reversible one-electron reduction processes at −0.421 V ($\Delta E_p = 58$ mV) and −1.202 V ($\Delta E_p = 57$ mV) and one quasi-reversible oxidation process at 0.763 V ($\Delta E_p = 69$ mV) *versus* ferrocenium–ferrocene (+0.400 V). The electrode reaction is, therefore, represented by

$$[Pt(S(NH)C_6H_4)_2]^{1+} \underset{0.763\text{ V}}{\rightleftharpoons} [Pt(S(NH)C_6H_4)_2]^{0} \underset{-0.421\text{ V}}{\rightleftharpoons} [Pt(S(NH)C_6H_4)_2]^{1-} \underset{-1.202\text{ V}}{\rightleftharpoons} [Pt(S(NH)C_6H_4)_2]^{2-}$$

The electrochemical behavior of **1** is similar to that of $[Ni(S(NH)C_6H_4)_2]$ [2, 15].

Supplementary Material

Tables of observed and calculated structure factors for $[Pt(S(NH)C_6H_4)_2]$, hydrogen atom coordinates, and anisotropic temperature factors are available from the author on request.

Acknowledgements

The authors wish to thank Drs Seiichiro Eguchi, Tsutomu Morikawa, and Tooru Yoshida of Osaka Prefectural Industrial Research Institute for measurement of the X-ray photoelectron spectra. The authors also thank Mr Jyunichi Gohda for elemental analyses and Mr Tetsuya Shimada for measurement of the mass spectrum.

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