

Short Communication

Crystal Structure of *cis*-C,C-[Carbonylchloro-(2-(2'-thienyl)-pyridinato-C, ³N')-platinum(II)], [Pt(tpy)(CO)Cl]

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Recently it was shown that when solutions of Bu₄N[Pt(ppy)Cl₂] and Bu₄N[Pt(tpy)Cl₂] in a mixture of dichloromethane and methanol are treated with carbon monoxide [Pt(ppy)(CO)Cl] and [Pt(tpy)(CO)Cl] will slowly precipitate;¹ (ppy and tpy represent cyclometalated 2-phenylpyridine and 2-(2'-thienylpyridine). The yields, as based upon purified products, were 86 and 70%, respectively. Owing to the limited solubility of the products in all the usual organic solvents it was not possible to determine their configuration with certainty from the poor NMR spectra. Watts *et al.*² have prepared the more soluble palladium compound from 2-phenylpyridine, [Pd(ppy)(CO)Cl], and have concluded that the carbonyl group is *cis* to the phenyl part of the *N,C*-chelate.

Owing to the solubility problems the configuration of this class of compounds can only be determined unequivocally by means of crystallographic studies. Unfortunately, uncharged metal complexes containing a carbonyl group rarely form crystals of satisfactory size and quality, and few accurate structural studies have appeared.^{3,4} We have, however, succeeded in obtaining a thin orange plate, 0.025 × 0.11 × 0.16 mm, of [Pt(tpy)(CO)Cl] when a saturated solution in acetone is allowed to evaporate during several months. In this work we report the results from a structural study of this compound.

Experimental

[Pt(tpy)(CO)Cl], C₁₀H₆ClNOPtS, mol. wt. 418.76, m.p. 227°C, crystallizes in the *P2₁/c* space group with the following unit-cell dimensions: *a* = 9.2515(11),

b = 16.9912(18), *c* = 6.9209(8) Å, α = γ = 90.00° and β = 97.00(1)°. *V* = 1079.8(2) Å³; *Z* = 4, *d*(calc) = 2.576 g cm⁻³, μ = 13.40 mm⁻¹ and *T* = 293(2) K.

Measurements of cell dimensions, based on 24 reflections, and intensity data were collected with an Enraf-Nonius CAD4 diffractometer using graphite monochromated MoK_α radiation (λ = 0.71073 Å). Of 2115 reflections, 1308 with *I* > 2σ were retained for the structure analysis. The structure was solved by direct methods using SHELXS86.⁵ The absorption correction was made using the DIFABS procedure,⁶ 0.28 < *T* < 1.00. This procedure was found to be the only one that led to acceptable results. 137 parameters were refined by SHELXL93⁷ using full-matrix least-squares on all reflections. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were treated isotropically with a common *U*_{iso} refined to 0.074(15) using a riding model with carbon–hydrogen bond lengths of 0.96 Å. The final *R*-value was 0.0346 (*wR* = 0.0777). Atomic scattering factors were taken from Ref. 8.

Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1. Lists of anisotropic temperature factors, least-squares planes and structure factors are available from the authors.

Results and discussion

Figure 1 shows a perspective view of the molecule with numbering of the atoms. Figure 2 shows the packing in the unit cell. The molecules in the adjacent layers form stacks along the *Z*-direction with a Pt–Pt distance of 3.507(4) Å; ∠Pt–Pt–Pt being 161.2(5)°. The molecules in each layer seem to be held together with fairly short

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (in $\text{\AA}^2 \times 10^3$)^a

| Atom | x | y | z | U(eq) |
|-------|----------|---------|----------|-------|
| Pt(1) | 4855(1) | 7332(1) | 1791(1) | 44(1) |
| Cl(1) | 6383(3) | 8461(2) | 2043(5) | 78(1) |
| S(1) | 803(3) | 5923(2) | 1111(3) | 48(1) |
| O(1) | 7366(9) | 6234(7) | 2254(13) | 99(3) |
| N(1) | 2948(8) | 7977(5) | 1453(9) | 40(2) |
| C(1) | 6411(12) | 6686(9) | 2062(16) | 71(4) |
| C(2) | 1699(9) | 7524(5) | 1243(12) | 36(2) |
| C(3) | 339(10) | 7872(7) | 1029(12) | 46(2) |
| C(4) | 250(11) | 8690(7) | 1047(13) | 54(3) |
| C(5) | 1487(13) | 9116(7) | 1263(14) | 57(3) |
| C(6) | 2792(13) | 8768(6) | 1412(13) | 53(3) |
| C(2') | 2002(9) | 6699(6) | 1284(11) | 37(2) |
| C(3') | 3433(10) | 6441(6) | 1544(12) | 41(2) |
| C(4') | 3519(11) | 5613(7) | 1579(13) | 52(2) |
| C(5') | 2222(12) | 5283(6) | 1362(13) | 52(2) |

^a U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

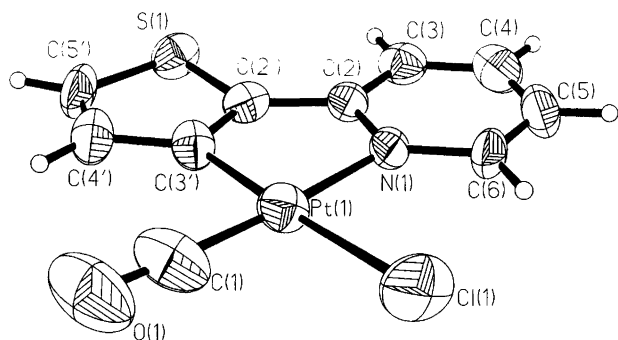


Fig. 1. A perspective view of [Pt(tpy)CO]Cl with numbering of the atoms. Thermal ellipsoids are given with 50% probability.

Cl...H(C5'') contacts, 2.73 \AA , with $\angle C5''-H-Cl = 136^\circ$. The compound is in principle quite similar to the red form of [Pt(2,2'-bpy)Cl₂].⁹ Bond angles and bond distances are listed in Table 2.

Table 2. Bond lengths (in \AA) above and bond angles (in $^\circ$) below with estimated standard deviation

| | | | |
|-------------------|-----------|-------------------|-----------|
| Pt(1)—C(1) | 1.801(12) | C(2)—C(3) | 1.382(12) |
| Pt(1)—C(3') | 1.998(10) | C(2)—C(2') | 1.429(12) |
| Pt(1)—N(1) | 2.066(8) | C(2)—C(4) | 1.39(2) |
| Pt(1)—Cl(1) | 2.377(3) | C(4)—C(5) | 1.35(2) |
| S(1)—C(5') | 1.698(11) | C(5)—C(6) | 1.34(2) |
| S(1)—C(2') | 1.718(9) | C(2')—C(3') | 1.385(12) |
| O(1)—C(1) | 1.166(14) | C(3')—C(4') | 1.409(14) |
| N(1)—C(6) | 1.352(13) | C(4')—C(5') | 1.316(14) |
| N(1)—C(2) | 1.382(11) | | |
| | | | |
| C(1)—Pt(1)—C(3') | 93.3(5) | C(3)—C(2)—C(2') | 126.6(8) |
| C(1)—Pt(1)—N(1) | 174.5(5) | C(2)—C(3)—C(4) | 118.7(9) |
| C(3')—Pt(1)—N(1) | 81.3(4) | C(5)—C(4)—C(3) | 119.2(10) |
| C(1)—Pt(1)—Cl(1) | 91.4(5) | C(6)—C(5)—C(4) | 121.2(11) |
| C(3')—Pt(1)—Cl(1) | 175.4(3) | C(5)—C(6)—N(1) | 122.3(10) |
| N(1)—Pt(1)—Cl(1) | 94.1(2) | C(3')—C(2')—C(2) | 119.7(8) |
| C(5')—S(1)—C(2') | 90.0(5) | C(3')—C(2')—S(1) | 111.4(8) |
| C(6)—N(1)—C(2) | 117.8(9) | C(2)—C(2')—S(1) | 128.9(7) |
| C(6)—N(1)—Pt(1) | 128.2(7) | C(2')—C(3')—C(4') | 111.7(9) |
| C(2)—N(1)—Pt(1) | 114.1(6) | C(2')—C(3')—Pt(1) | 112.3(7) |
| O(1)—C(1)—Pt(1) | 176.2(13) | C(4')—C(3')—Pt(1) | 136.0(7) |
| N(1)—C(2)—C(3) | 120.8(8) | C(5')—C(4')—C(3') | 112.0(9) |
| N(1)—C(2)—C(2') | 112.7(7) | C(4')—C(5')—S(1) | 114.9(8) |

The molecule is strictly planar as viewed by the sum of the bond angles around the metal atom, $360.1(8)^\circ$. The two aromatic rings are essentially coplanar with an angle between the two planes of only 3.0° . The bond lengths and bond angles in the aromatic ligand are as observed in similar compounds.^{10–14} One may mention the following features: (i) The Pt(1)—N(1) bond length, 2.066(8) \AA , is significantly longer than in the [Pt(tpy)Cl₂][−] anion, 2.032(3) \AA ,¹⁵ presumably due to the larger *trans* influence of the carbonyl ligand. (ii) The Pt(1)—Cl(1) bond length, 2.377(3) \AA , is slightly shorter than the Pt—Cl bond *trans* to the carbon atom in [Pt(tpy)Cl₂][−], 2.396(2).¹⁵ (iii) The Pt(1)—C(1)—O(1) bond angle, $176.2(13)^\circ$, is probably less than 180° ; a non-linear coordination of CO is quite common in metal carbonyl complexes.^{3,4,16} (iv) The C(2)—C(2') bond length, 1.43(1) \AA , is fairly short and indicates some conjugation between the aromatic rings. (v) The C(2')—S(1)—C(5') bond angle is only $90.0(5)^\circ$ as compared with $93.8(4)^\circ$ in the free ligand. This suggests an

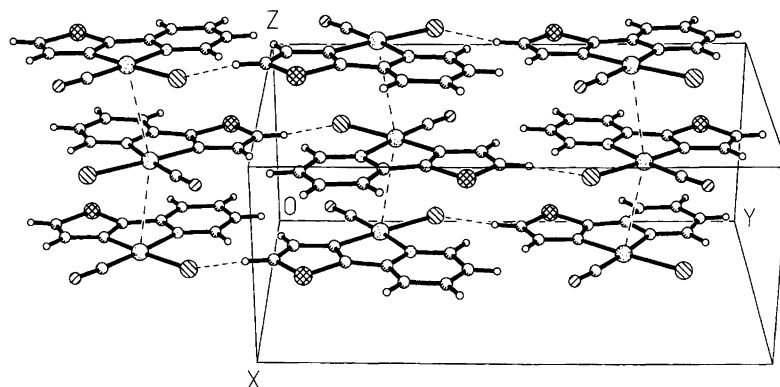


Fig. 2. The crystal structure of [Pt(tpy)(CO)Cl]. Dashed lines indicate close interatomic contacts.

increase in the s-character of the sulfur atom upon complexation.¹⁷

The main result of the present study is that the carbonyl group is *cis* to the carbon atom in the *N,C*-chelate. Based upon the difference in the *trans* influence¹⁸ of an aromatic carbanionic ligand and of pyridine, as exemplified by the Pt–Cl bond lengths in [Pt(tpy)Cl₂][−], 2.313(2) Å *trans* to N and 2.396(2) Å *trans* to C,¹⁵ the carbonyl group was expected to enter *trans* to the carbon atom. van Eldik *et al.*¹⁹ have recently shown that the Pt–C bond in a metallocycle can labilize an aqua ligand located in the *trans* position to an extent that the aqua ligand can act as a Brønsted acid. Nevertheless, several substitution reactions toward Pt(II) substrates in which the metal is part of an *N,C*-chelate lead only to products in which the entering ligand is *cis* to the carbon atom.¹ When *trans*- or *cis*-[Pt(SEt₂)₂Cl₂] is allowed to react with two equivalents of 2'-lithiated 2-phenylpyridine in diethyl ether only *cis*-bis(2-phenylpyridinato)platinum(II) is obtained.²⁰

The observed configuration of substitution products from cyclometalated Pt(II) complexes may lead one to conclude that the *trans* effect²¹ may not be valid for this class of compounds. By the expected associative mechanism, however, the first formed five-coordinated intermediate may have sufficient lifetime to isomerize forming directly the thermodynamic product, the *cis*-C complex. Alternatively, the expected *trans*-C product, the kinetic product, is formed but, owing to the presence of the *N,C*-chelate, will isomerize exceptionally rapidly to the thermodynamic product. This latter isomerization may be facilitated by the ability of the pyridine part of the *N,C*-chelate to act as a hemilabile ligand.²² The dissociative mechanism²³ has also to be considered since addition of methanol to the reaction mixture in dichloromethane greatly accelerates the substitution reaction.¹ By this mechanism the first formed T-shaped three-coordinated ion has to isomerize prior to addition of the reacting ligand. Hoffmann *et al.*²⁴ however, have suggested that the energy of the transition state for this kind of isomerization reactions is fairly high.

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