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Platinum metal thioether macrocyclic complexes: synthesis and single crystal X-ray structure of *cis*-$[IrCl_2(L)]BPh_4$ (L = 1,4,8,11-tetrathiacyclotetradecane)

Alexander J. Blake, Robert O. Gould, Gillian Reid and Martin Schröder *

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ (Great Britain)

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Abstract

Reaction of $IrCl_3$ with 1,4,8,11-tetrathiacyclotetradecane (L) in refluxing $EtOH/H_2O$ gives the complex cation $[IrCl_2(L)]^+$. Crystals of $[IrCl_2(L)]BPh_4$ are monoclinic, space group $P2_1$, with a 12.6927(14), b 12.1361(20), c 14.4912(18) Å, β 111.813(13)°, V 2072.4 Å^3, D_c 1.363 g cm^{-3}, $Z = 2$. The single crystal X-ray structure of $[IrCl_2(L)]BPh_4$ shows a distorted octahedral stereochemistry around Ir^{III}, with mutually *cis* Cl^- ligands, Ir–Cl(1) 2.389(5), Ir–Cl(2) 2.385(5) Å, angle Cl(1)IrCl(2) 91.02(16)°. The tetrathia macrocycle is coordinated to the metal centre via all four S-donors (Ir–S(1) 2.277(4), Ir–S(4) 2.287(5), Ir–S(8) 2.268(4), Ir–S(11) 2.343(5) Å) with S(1), S(4), and S(8) *trans* to Cl(2), S(11), and Cl(1) respectively.

Introduction

We have been investigating the synthesis, structure and redox properties of platinum metal complexes of polydentate thioether macrocycles [1,2]. The fourteen-membered ring, tetrathia ligand 1,4,8,11-tetrathiacyclotetradecane (L), the sulphur-donor analogue of cyclam, has been found to bind effectively to a range of second and third row transition metal centres including Hg^{II} [3,4], Nb^{V} [5], Ru^{II} [6], Rh^{I} [7,8], Rh^{III} [8], Pd^{II} [1], while ligands of larger hole size have been found to complex with Mo^{0}, Mo^{II} [9] and Mo^{IV} [10]. This contrasts with the poor binding properties of non-cyclic thioether ligands to transition metal ions [11]. Very few non-porphyrin macrocyclic complexes of Ir have been reported previously [1,12], and no examples of Ir complexation by L have been described. We report here the synthesis and crystal structure of the Ir^{III} species *cis*-$[IrCl_2(L)]BPh_4$.

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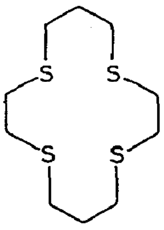

(L)

Results and discussion

$IrCl_3 \cdot 3H_2O$ was treated with one molar equivalent of L in refluxing $EtOH/H_2O$ under N_2 for 14 h in the presence of an excess of $NaBPh_4$. On cooling, the yellow/brown precipitate was collected and recrystallised from CH_3NO_2 to afford a cream-coloured product. The IR spectrum of this complex showed, in addition to bands due to coordinated L and BPh_4^-, two bands at 310 and 305 cm^{-1} assigned to Ir–Cl stretching vibrations, ν(Ir–Cl), suggesting the formation of a *cis*-dichloro complex. The electronic spectrum of the complex showed absorptions at 348 and 297 nm tentatively assigned to *d–d* transitions. The magnitudes of the extinction coefficients, 113 and 1,400 M^{-1} cm^{-1} respectively, for these absorptions are indicative of a *cis* configuration at the metal centre; *d–d* transitions in d^6 metal complexes have been shown previously to have larger extinction coefficients for *cis* than for *trans*-configurations owing to the lower symmetry of *cis*-isomers, e.g. *cis*- and *trans*-$[Rh(X)_2(cyclam)]^+$ [13–15]. The fast-atom bombardment mass spectrum of the complex shows the main molecular ion peak at $M^+ = 531$ corresponding to $[^{193}Ir^{35}Cl_2(L)]^+$, with the correct isotopic distribution. Daughter peaks at $M^+ = 496$ and 461 correspond to $[^{193}Ir^{35}Cl(L)]^+$ and $[^{193}Ir(L)]^+$ respectively, formed by successive loss of Cl. These data together with analytical data suggest that the complex isolated was *cis*-$[IrCl_2(L)]^+BPh_4^-$.

In order to confirm the structure of the complex and the connectivity and conformation of the macrocyclic ligand, a single crystal X-ray structural determination was undertaken. Crystals of *cis*-$[IrCl_2(L)]BPh_4$ were grown from CH_3NO_2/Et_2O. Figure 1 gives views of the complex cation. The structure analysis confirms the *cis* configuration of the Cl^- ligands, with Ir–Cl(1) 2.389(5), Ir–Cl(2) 2.385(5) Å. The macrocycle is coordinated to the Ir^{III} centre as a tetradentate ligand, Ir–S(1) 2.277(4), Ir–S(4) 2.287(5), Ir–S(8) 2.268(4), Ir–S(11) 2.343(5) Å, and adopts a folded conformation with Cl(1) and Cl(2) lying *trans* to S(8) and S(1) respectively. The conformation of the coordinated ligand in this complex is similar to that in *cis*-$[RuCl_2(L)]$ [6] and indicates a general tendency of L to bind to larger metal ions to give *cis* octahedral complexes. In contrast, cyclam binds to Rh^{III} to give both *cis*- and *trans*-dichloro complexes [12,15], while only a *trans* isomer has been isolated for the cation $[RhCl_2(tmc)]^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [16]. The ^{13}C NMR spectrum of *cis*-$[IrCl_2(L)]^+$ in CD_3NO_2 shows five resonances at δ 37.99, 29.52, 28.96, 28.39, 23.90 ppm for the secondary carbon centres of the coordinated macrocycle (L), confirming the presence of only one isomer and retention of the *cis* configuration in solution. The metal–sulphur

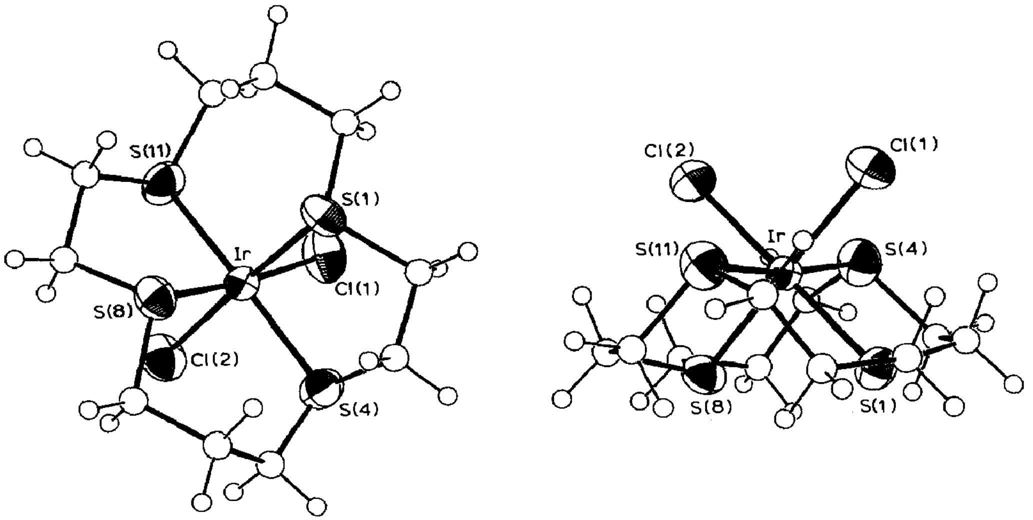

Fig. 1. Two views of the single crystal X-ray structure of *cis*-$[IrCl_2(L)]BPh_4$ with numbering scheme used.

bond lengths in *cis*-$[IrCl_2(L)]^+$ follow the same pattern as found for *cis*-$[RuCl_2(L)]^+$ [6]. For the Ru^{II} complex, it was noted that the metal–sulphur bond distances *trans* to Cl^- (2.262(1) Å) were shorter than those *trans* to S (2.333(1) Å). This is attributed to greater Ru → S(π) back-donation to the thioether donors *trans* to Cl^- [6]. For *cis*-$[IrCl_2(L)]^+$, the same general pattern in bond lengths is observed, with Ir–S 2.277(4), 2.268(4) Å (*trans* to Cl^-) and 2.287(5) 2.343(5) Å (*trans* to S).

Cyclic voltammetry of *cis*-$[IrCl_2(L)]PF_6$ in CH_3CN (0.1 *M* $^nBu_4NPF_6$) at platinum electrodes shows no oxidation in the range $0 \rightarrow +2.0$ V vs. Fc/Fc^+. The complex undergoes an irreversible reduction at $E_p = -1.82$ V vs. Fc/Fc^+ at a scan rate of 200 mV s^{-1}, presumably corresponding to the formation of an Ir^I species of type $[Ir(L)]^+$ via loss of Cl^-. This occurs at a considerably more cathodic potential than that for the analogous tetra-aza complex *trans*-$[RhCl_2(tmc)]^+$ which shows a quasi-reversible $Rh^{III/II}$ couple at $E_{1/2}$ -0.99 V vs. Fc/Fc^+ in CH_3CN [16]. Larger thioether ring systems may be more likely to give *trans*-dichloro complexes, and to stabilise lower valent, electron-rich Ir centres [7].

Experimental

Infrared spectra were recorded as Nujol mulls or as KBr or CsI discs on a Perkin–Elmer 598 spectrometer over the range 200–4000 cm^{-1}. UV-visible spectra were recorded for solutions in quartz cells using a Pye Unicam SP8-400 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. Electron impact mass spectra were obtained on a Kratos MS 902 and fast atom bombardment mass spectra on a Kratos MS 50TC spectrometer. Electrochemical measurements were performed with a Bruker E310 Universal Modular Polarograph; for all readings a three-electrode potentiostatic system in acetonitrile containing 0.1 *M* $^nBu_4NPF_6$ as supporting electrolyte was used. Cyclic voltammetric measurements were carried out with a double platinum electrode and a Ag/AgCl reference electrode. Potentials are quoted versus ferrocene/ferrocinium, Fc/Fc$^+$. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on Bruker a WP200 spectrometer.

1,4,8,11-Tetrathiacyclotetradecane was purchased from Aldrich Chemicals.

Synthesis of [IrCl$_2$(L)]BPh$_4$

To a solution of 1,4,8,11-tetrathiacyclotetradecane (0.04 g, 1.49×10^{-4} mol) in refluxing EtOH (50 cm^3) containing an excess of NaBPh$_4$ (0.075 g, 2.19×10^{-4} mol) was added a solution of $IrCl_3 \cdot 3H_2O$ (0.052 g, 1.47×10^{-4} mol) in water (5 cm^3). The mixture was refluxed under N_2 for 14 h then allowed to cool, and the yellow/brown precipitate collected. The product was dissolved in hot MeNO$_2$ and filtered to remove insoluble chloro-bridged polymers. The filtrate was cooled to afford a cream precipitate of [IrCl$_2$(L)]BPh$_4$, which was collected and dried in vacuo. Yield 0.042 g, 33%. Elemental analysis: found C, 47.4; H, 4.8% calculated for [IrCl$_2$(L)]BPh$_4$ C, 48.0; H, 4.7%. Infrared spectrum (CsI disc): (L): 2910(m), 1430(vs), 1270(m) cm^{-1}, BPh$_4^-$: 3060, 2980, 1580, 1480, 1430, 860, 840, 810, 610, 530 cm^{-1}, (Ir–Cl): 310, 305 cm^{-1}. Mass spectrum (FAB) in dmf/glycerol matrix: M^+ (found) = 531, 496, 461; M^+ (calculated) = 531 for [^{193}Ir^{35}Cl$_2$(L)]$^+$, 496 for [^{193}Ir^{35}Cl(L)]$^+$, 461 for [^{193}Ir(L)]$^+$. UV-VIS (MeCN): λ_{max} 348 (113), 297 (1, 400), 275 (2, 760), 267 (3, 370), 216 nm (ϵ_{max} 29,400 M^{-1} cm^{-1}).

Synthesis of [IrCl$_2$(L)]PF$_6$

The PF$_6^-$ salt was prepared by using NH$_4$PF$_6$ in place of NaBPh$_4$ in the above preparation. Elemental analysis: Found C, 18.1; H, 3.0; S, 18.8. [IrCl$_2$(L)]PF$_6$ calcd.: C, 17.8; H, 3.0; S, 18.9%. ^{1}H NMR (CD$_3$NO$_2$, 293 K, 200 MHz): δ 2.5–3.5 ppm (m, CH_2). ^{13}C NMR (CD$_3$NO$_2$, 293 K, 50.32 MHz): δ 37.99, 29.52, 28.96, 28.39, 23.90 ppm.

X-Ray structure determination of [IrCl$_2$(L)]BPh$_4$

A colourless crystal ($0.46 \times 0.15 \times 0.15$ mm) suitable for an X-ray diffraction study was obtained by diffusion of Et$_2$O vapour into a solution of the complex in CH$_3$NO$_2$.

Crystal data. $C_{34}H_{40}BCl_2IrS_4$, $M = 850.85$, monoclinic, space group $P2_1$, with *a* 12.6927(14), *b* 12.1361(20), *c* 14.4912(18) Å, β 111.813(13)°, *V* 2072.4 Å^3 (From θ values of 20 reflections measured at $\pm\omega$, $19 < 2\theta < 30$°, λ 0.71073 Å), $Z = 2$, D_c 1.363 g cm^{-3}, μ 35.18 cm^{-1}, $F(000) = 848$.

Table 1

Bond lengths (Å) with standard deviations

Ir(1)–S(1)	2.277(4)	S(8)–C(7)	1.772(21)
Ir(1)–S(4)	2.287(5)	S(8)–C(9)	1.775(20)
Ir(1)–S(8)	2.268(4)	S(11)–C(10)	1.851(23)
Ir(1)–S(11)	2.343(5)	S(11)–C(12)	1.811(21)
Ir(1)–Cl(1)	2.389(5)	C(2)–C(3)	1.55(3)
Ir(1)–Cl(2)	2.385(5)	C(5)–C(6)	1.46(3)
S(1)–C(2)	1.855(21)	C(6)–C(7)	1.58(3)
S(1)–C(14)	1.809(17)	C(9)–C(10)	1.59(3)
S(4)–C(3)	1.781(20)	C(12)–C(13)	1.48(3)
S(4)–C(5)	1.755(24)	C(13)–C(14)	1.57(3)

Table 2

Angles (degrees) with standard deviations

S(1)-Ir(1)-S(4)	88.10(15)	Ir(1)-S(4)-C(5)	111.3(8)
S(1)-Ir(1)-S(8)	86.42(15)	C(3)-S(4)-C(5)	102.1(10)
S(1)-Ir(1)-S(11)	97.65(15)	Ir(1)-S(8)-C(7)	110.1(7)
S(1)-Ir(1)-Cl(1)	91.29(16)	Ir(1)-S(8)-C(9)	103.5(6)
S(1)-Ir(1)-Cl(2)	176.15(15)	C(7)-S(8)-C(9)	103.7(9)
S(4)-Ir(1)-S(8)	98.93(16)	Ir(1)-S(11)-C(10)	103.1(7)
S(4)-Ir(1)-S(11)	172.26(16)	Ir(1)-S(11)-C(12)	111.0(7)
S(4)-Ir(1)-Cl(1)	86.72(16)	C(10)-S(11)-C(12)	100.2(10)
S(4)-Ir(1)-Cl(2)	88.96(16)	S(1)-C(2)-C(3)	103.5(13)
S(8)-Ir(1)-S(11)	86.64(16)	S(4)-C(3)-C(2)	109.0(14)
S(8)-Ir(1)-Cl(1)	173.81(16)	S(4)-C(5)-C(6)	118.5(18)
S(8)-Ir(1)-Cl(2)	91.58(15)	C(5)-C(6)-C(7)	118.7(20)
S(11)-Ir(1)-Cl(1)	87.97(16)	S(8)-C(7)-C(6)	108.0(15)
S(11)-Ir(1)-Cl(2)	85.51(16)	S(8)-C(9)-C(10)	105.0(13)
Cl(1)-Ir(1)-Cl(2)	91.02(16)	S(11)-C(10)-C(9)	107.4(14)
Ir(1)-S(1)-C(2)	99.9(7)	S(11)-C(12)-C(13)	120.4(15)
Ir(1)-S(1)-C(14)	110.0(6)	C(12)-C(13)-C(14)	116.3(17)
C(2)-S(1)-C(14)	104.8(9)	S(1)-C(14)-C(13)	106.5(12)
Ir(1)-S(4)-C(3)	103.4(7)		

Table 3

Torsion angles (degrees) with standard deviations

S(4)-Ir(1)-S(1)-C(2)	25.7(7)	S(1)-Ir(1)-S(11)-C(12)	23.7(7)
S(4)-Ir(1)-S(1)-C(14)	135.5(6)	S(4)-Ir(1)-S(11)-C(10)	139.5(13)
S(8)-Ir(1)-S(1)-C(2)	124.8(7)	S(4)-Ir(1)-S(11)-C(12)	-114.0(13)
S(8)-Ir(1)-S(1)-C(14)	-125.4(6)	S(8)-Ir(1)-S(11)-C(10)	3.1(7)
S(11)-Ir(1)-S(1)-C(2)	-149.1(7)	S(8)-Ir(1)-S(11)-C(12)	109.6(7)
S(11)-Ir(1)-S(1)-C(14)	-39.3(6)	Cl(1)-Ir(1)-S(11)-C(10)	-173.8(7)
Cl(1)-Ir(1)-S(1)-C(2)	-61.0(7)	Cl(1)-Ir(1)-S(11)-C(12)	-67.3(7)
Cl(1)-Ir(1)-S(1)-C(14)	48.8(6)	Cl(2)-Ir(1)-S(11)-C(10)	95.0(7)
Cl(2)-Ir(1)-S(1)-C(2)	66.0(24)	Cl(2)-Ir(1)-S(11)-C(12)	-158.5(7)
Cl(2)-Ir(1)-S(1)-C(14)	175.8(22)	Ir(1)-S(1)-C(2)-C(3)	-55.6(13)
S(1)-Ir(1)-S(4)-C(3)	3.7(7)	C(14)-S(1)-C(2)-C(3)	-169.5(12)
S(1)-Ir(1)-S(4)-C(5)	112.6(9)	Ir(1)-S(1)-C(14)-C(13)	67.0(12)
S(8)—Ir(1)-S(4)-C(3)	-82.4(7)	C(2)-S(1)-C(14)-C(13)	173.6(12)
S(8)-Ir(1)-S(4)-C(5)	26.5(9)	Ir(1)-S(4)-C(3)-C(2)	-40.6(14)
S(11)-Ir(1)-S(4)-C(3)	141.9(13)	C(5)-S(4)-C(3)-C(2)	-156.3(14)
S(11)-Ir(1)-S(4)-C(5)	-109.3(14)	Ir(1)-S(4)-C(5)-C(6)	-41.8(20)
Cl(1)-Ir(1)-S(4)-C(3)	95.1(7)	C(3)-S(4)-C(5)-C(6)	67.9(20)
Cl(1)-Ir(1)-S(4)-C(5)	-156.0(9)	Ir(1)-S(8)-C(7)-C(6)	60.6(15)
Cl(2)-Ir(1)-S(4)-C(3)	-173.8(7)	C(9)-S(8)-C(7)-C(6)	170.7(14)
Cl(2)-Ir(1)-S(4)-C(5)	-64.9(9)	Ir(1)-S(8)-C(9)-C(10)	-56.7(13)
S(1)-Ir(1)-S(8)-C(7)	-125.0(7)	C(7)-S(8)-C(9)-C(10)	-171.7(13)
S(1)-Ir(1)-S(8)-C(9)	124.7(7)	Ir(1)-S(11)-C(10)-C(9)	-37.2(14)
S(4)-Ir(1)-S(8)-C(7)	-37.5(7)	C(12)-S(11)-C(10)-C(9)	-151.8(14)
S(4)-Ir(1)-S(8)-C(9)	-147.8(7)	Ir(1)-S(11)-C(12)-C(13)	-37.5(18)
S(11)-Ir(1)-S(8)-C(7)	137.1(7)	C(10)-S(11)-C(12)-C(13)	70.9(18)
S(11)-Ir(1)-S(8)-C(9)	26.8(7)	S(1)-C(2)-C(3)-S(4)	64.7(14)
Cl(1)-Ir(1)-S(8)-C(7)	166.5(16)	S(4)-C(5)-C(6)-C(7)	72.1(25)
Cl(1)-Ir(1)-S(8)-C(9)	56.3(17)	C(5)-C(6)-C(7)-C(8)	-81.6(22)
Cl(2)-Ir(1)-S(8)-C(7)	51.7(7)	S(8)-C(9)-C(10)-S(11)	62.1(15)
Cl(2)-Ir(1)-S(8)-C(9)	-58.6(7)	S(11)-C(12)-C(13)-C(14)	70.0(22)
S(1)-Ir(1)-S(11)-C(10)	-82.8(7)	C(12)-C(13)-C(14)-S(1)	-84.5(18)

Table 4

Atomic coordinates with esds

	x	y	z	U_{iso}
Ir(1)	−0.13020(4)	0.0000	−0.16511(3)	0.0389(3)
S(1)	−0.3025(3)	−0.0714(4)	−0.2598(3)	0.0541(24)
S(4)	−0.0928(4)	−0.1606(4)	−0.0762(3)	0.062(3)
S(8)	−0.0728(4)	−0.0509(4)	−0.2896(3)	0.0557(25)
S(11)	−0.1573(4)	0.1766(4)	−0.2355(3)	0.068(3)
Cl(1)	−0.2034(4)	0.0680(4)	−0.0461(3)	0.078(3)
Cl(2)	0.0556(3)	0.0628(4)	−0.0661(3)	0.069(3)
C(2)	−0.3221(16)	−0.1701(16)	−0.1698(15)	0.083(13)
C(3)	−0.2142(15)	−0.2433(15)	−0.1396(15)	0.074(12)
C(5)	0.0160(18)	−0.2353(18)	−0.0949(18)	0.096(7)
C(6)	0.0163(20)	−0.2421(17)	−0.1955(19)	0.106(18)
C(7)	0.0491(16)	−0.1359(16)	−0.2423(16)	0.083(14)
C(9)	−0.0203(15)	0.0734(15)	−0.3208(13)	0.075(13)
C(10)	−0.1231(16)	0.1579(19)	−0.3481(16)	0.094(16)
C(12)	−0.3068(17)	0.2095(16)	−0.2922(14)	0.084(14)
C(13)	−0.3900(15)	0.1239(19)	−0.3451(14)	0.084(14)
C(14)	−0.4121(12)	0.0311(13)	−0.2789(13)	0.071(13)
B(1)	−0.7682(12)	0.0237(13)	−0.5127(10)	0.044(4)
C(1′)	−0.6589(5)	0.0257(10)	−0.6377(5)	0.054(4)
C(2′)	−0.6517(5)	0.0128(10)	−0.7309(5)	0.064(4)
C(3′)	−0.7481(5)	−0.0152(10)	−0.8130(5)	0.076(5)
C(4′)	−0.8517(5)	−0.0304(10)	−0.8019(5)	0.055(4)
C(5′)	−0.8589(5)	−0.0175(10)	−0.7087(5)	0.054(4)
C(6′)	−0.7625(5)	0.0105(10)	−0.6267(5)	0.043(3)
C(7′)	−0.9666(6)	−0.0705(5)	−0.5299(7)	0.042(3)
C(8′)	−1.0838(6)	−0.0678(5)	−0.5545(7)	0.058(4)
C(9′)	−1.1419(6)	0.0322(5)	−0.5778(7)	0.057(4)
C(10′)	−1.0828(6)	0.1295(5)	−0.5765(7)	0.056(4)
C(11′)	−0.9657(6)	0.1268(5)	−0.5519(7)	0.045(3)
C(12′)	−0.9076(6)	0.0268(5)	−0.5286(7)	0.043(3)
C(13′)	−0.6310(9)	−0.1535(9)	−0.4643(6)	0.059(4)
C(14′)	−0.5816(9)	−0.2434(9)	−0.4038(6)	0.064(4)
C(15′)	−0.6062(9)	−0.2644(9)	−0.3193(6)	0.063(4)
C(16′)	−0.6802(9)	−0.1954(9)	−0.2953(6)	0.072(5)
C(17′)	−0.7296(9)	−0.1054(9)	−0.3559(6)	0.060(4)
C(18′)	−0.7050(9)	−0.0845(9)	−0.4404(6)	0.046(3)
C(19′)	−0.6820(9)	0.1565(7)	−0.3568(6)	0.064(4)
C(20′)	−0.6334(9)	0.2549(7)	−0.3108(6)	0.069(5)
C(21′)	−0.6144(9)	0.3405(7)	−0.3669(6)	0.067(4)
C(22′)	−0.6439(9)	0.3277(7)	−0.4692(6)	0.072(5)
C(23′)	−0.6925(9)	0.2293(7)	−0.5152(6)	0.059(4)
C(24′)	−0.7116(9)	0.1437(7)	−0.4590(6)	0.045(3)

Data collection and processing. Stoe-Siemens AED2 four-circle diffractometer, graphite-monochromated Mo-K_α X-radiation, ω–θ scans with ω scan width $(1.4 + 0.35 \tan\theta)°$, 2882 reflections measured ($2\theta_{\max}$ 45°, h $-13 \to 12$, k $0 \to 13$, l $0 \to 14$), giving 2508 with $F \geqslant 6\sigma(F)$ for use in subsequent calculations. No significant crystal decay was observed.

Structure analysis and refinement. The Ir position was located from a Patterson synthesis and input to DIRDIF [17], which located the Cl and S atoms. Iterative least-squares refinements and difference Fourier syntheses [18] located all other non-H atoms. At isotropic convergence, final correction for absorption was made using DIFABS [19]. (An initial absorption correction was made using 48 Ψ scans (max. transmission factor = 0.2382, min. = 0.2022)). Anisotropic thermal parameters were refined for Ir, S, Cl, and C atoms of the cation. H atoms were included at calculated positions [18]. Phenyl groups of the BPh_4^- counter-ions were refined as rigid groups. The absolute configuration of the structure was not easy to establish with certainty as both hands refined well to essentially the same *R*-factors. The 20 reflections were selected with the greatest discrimination factor, defined as $D = |F_1F_2|\sin^2(\phi_1 - \phi_2)/|F_o|$ where subscripts 1 and 2 refer to structure factors calculated for the Ir atoms and for the other atoms respectively. For the fully refined data sets, these 20 data gave $R = 0.032$ for the hand chosen, and 0.049 for the opposite hand. More strikingly, bond lengths to Ir are much less consistent in the less favoured hand, the Ir–S lengths being more divergent, and the Ir–Cl lengths being much shorter. The weighting scheme $w^{-1} = \sigma^2(F) + 0.002572F^2$ gave satisfactory analyses. At convergence, $R, R_w = 0.0363$ and 0.0509 respectively for 205 parameters, $S = 1.137$. The maximum and minimum residues in the final ΔF syntheses were $+0.67$ and -0.64 eÅ^{-3} respectively. Illustrations were prepared by use of ORTEP [20] and molecular geometry calculations by use of CALC [21], scattering factor data were taken from ref. 22. Bond lengths, angles, torsion angles and fractional coordinates are given in Tables 1–4.

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