

# Iridium Complexes of Macrocyclic Tetraamine Ligands. Preparation, Characterization and Crystal Structure of a Macrocyclic Iridium(III) Complex Coordinated with the 4-Cycloocten-1-yl Anion

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The reaction between  $[\text{Ir}(\text{cod})\text{Cl}]_2$  and cyclam (cod = cycloocta-1,5-diene, cyclam = 1,4,8,11-tetraazacyclotetradecane) results in oxidation of iridium(I) to iridium(III) and reduction of cycloocta-1,5-diene to cyclooctene. The product of the reaction is a diastereomeric mixture of octahedral *cis*-tetraamine-iridium(III) complexes coordinated with a cyclam ligand and a 4-cycloocten-1-yl anion (coei), isolated as the perchlorate salt.

The molecular structure of the trifluoromethanesulfonate salt of the dominant diastereomer  $[\text{Ir}(\text{cyclam})(\text{coei})](\text{CF}_3\text{SO}_3)_2$  was determined by a single-crystal X-ray investigation. The compound crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 9.227(4)$ ,  $b = 24.838(6)$ ,  $c = 12.537(3)$  Å,  $\beta = 107.59(3)^\circ$  and  $Z = 4$ . The cyclam ligand adopts the *cis* configuration, while the coei ligand is coordinated via a  $\sigma$ -bond to the deprotonated carbon atom and by a  $\pi$ -bond to the double bond, giving a distorted octahedral coordination geometry around the iridium atom.

Addition of strong base to the complex causes further deprotonation of the cyclooctenylidene ligand. This process has been investigated in some detail by deuterium labelling experiments using  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

Coordination compounds of the macrocyclic tetraamine ligand, cyclam, have been investigated during the past decades and high yield synthetic procedures have been developed for the preparation of coordination compounds of most transition metals. Recently, synthetic procedures for the preparation of both (*R,R,R,R/S,S,S,S*)-*cis*- $[\text{Ir}(\text{cyclam})\text{Cl}_2]\text{Cl}$  and (*R,R,S,S*)-*trans*- $[\text{Ir}(\text{cyclam})\text{Cl}_2]\text{Cl}$  were presented starting from  $\text{IrCl}_3 \cdot \text{aq}$  and  $\text{Ir}(\text{thtp})_3\text{Cl}_3$ , respectively. The *trans* complex could be prepared in high yield while the procedure for the synthesis of the *cis* complex was less satisfactory, since significant amounts of both metallic iridium and unidentified polymeric material appeared as unavoidable by-products.<sup>1</sup>

The use of more reactive iridium(I) complexes for the synthesis of very robust iridium(III) compounds has

been demonstrated by the successful use of the dinuclear iridium(I) compound  $[\text{Ir}(\text{coe})_2\text{Cl}]_2$  for the preparation of iridium(III) complexes coordinated with 1,4,7-trithiacyclononane<sup>2</sup> and (2-aminoethyl)dimethylphosphine.<sup>3</sup> The present work describes the preparation of a macrocyclic iridium(III) complex using the readily available and air-stable  $[\text{Ir}(\text{cod})\text{Cl}]_2$  compound.

## Results and discussion

**Preparations.** Addition of solid cyclam to an aqueous suspension of  $[\text{Ir}(\text{cod})\text{Cl}]_2$  followed by heating gives a yellow solution which gradually becomes more basic. The solution was kept neutral by addition of 4 M HCl, and after refluxing for 2 h free cyclam ligand is not detectable in the reaction mixture. Purification of the resulting product mixture by column chromatography followed by precipitation with aqueous sodium perchlor-

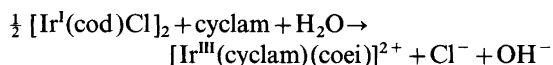
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Table 1. Ligand name abbreviations.

cyclam	1,4,8,11-tetraazacyclotetradecane
cod	cycloocta-1,5-diene
coe	cyclooctene
coei <sup>-</sup>	4-cycloocten-1-ide
coedi <sup>2-</sup>	4-cyclooctene-1,6-diide
dmso	dimethylsulfoxide
en	ethane-1,2-diamine (chelate ligand)
en*	ethane-1,2-diamine (monodentate ligand)
enH <sup>+</sup>	2-aminoethyl-1-ammonium
chxn	<i>trans</i> -cyclohexane-1,2-diamine
tacn	1,4,7-triazacyclononane
thtp	tetrahydrothiophene

ate gives yellow crystals with the stoichiometric composition  $[\text{Ir}(\text{cyclam})(\text{C}_8\text{H}_{13})](\text{ClO}_4)_2$  in high yield.

<sup>13</sup>C NMR of this product shows 36 resonances which, based upon their intensity differences, are interpreted as two sets, each of 18 resonances, suggesting the solid reaction product to be a mixture of two isomers. The two sets of resonances are very similar, and DEPT spectra<sup>4</sup> identify 2 CH-units at high  $\delta$ -values, 1 CH-unit at low  $\delta$ -values and 15 CH<sub>2</sub>-units at intermediate  $\delta$ -values in each set; cf. Fig. 1. This may be interpreted as due to a cyclam ligand with 10 CH<sub>2</sub> units and a deprotonated cyclooctene ligand, corresponding to the following stoichiometric scheme involving an intramolecular redox reaction:



The carbon atom of the cyclooctenide ligand coordinated to iridium is chiral. In combination with the chirality of a *cis* configuration of the coordinated cyclam ligand, this accounts for the presence of two diastereomers in the reaction product.

Reaction of the  $[\text{Ir}(\text{cyclam})(\text{coei})]^{2+}$  cation with aqueous NaOH results in further deprotonation of the cyclooctenide ligand and precipitation of white  $[\text{Ir}(\text{cyclam})(\text{C}_8\text{H}_{12})]\text{ClO}_4$ . The <sup>13</sup>C NMR spectrum of this compound shows 18 resonances and is very similar to that of a recently prepared iridium compound containing a  $\eta^1, \eta^3\text{-C}_8\text{H}_{12}$  ligand.<sup>5</sup> The deprotonation is con-

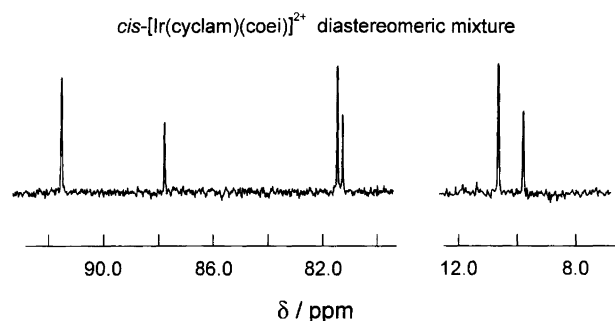
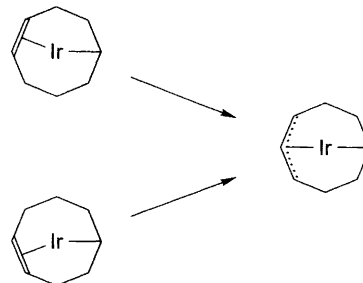


Fig. 1. <sup>13</sup>C NMR spectrum of the diastereomeric mixture of *cis*- $[\text{Ir}(\text{cyclam})(\text{coei})]^{2+}$  isomers in  $\text{dms0-d}_6$ . Only the parts of the spectrum with resonances due to coordinated carbon atoms are shown.

sequently accompanied by a change of the bond between iridium and the carbon-carbon double bond into a  $\pi$ -allylic-type bond. Further evidence in favour of this  $\pi$ -allylic-type bond is the production of the same isomer from both diastereomers of the original reaction product as indicated in Scheme 1.



Scheme 1.

The deprotonation reaction is only partially reversible, and the reaction of  $[\text{Ir}(\text{cyclam})(\text{coei})]^+$  with 1 M  $\text{HClO}_4$  results in an almost exclusive formation of the dominating  $[\text{Ir}(\text{cyclam})(\text{coei})]^{2+}$  diastereomer while only trace amounts of the less dominating diastereomer could be detected. Small amounts of uncoordinated cyclam and an unidentified iridium complex is also formed by this reaction. The dominating diastereomer could be isolated as the trifluoromethanesulfonate salt with crystals suitable for a single-crystal X-ray investigation.

**Description of the structure.** *cis*- $[\text{Ir}(\text{cyclam})(\text{coei})](\text{CF}_3\text{SO}_3)_2$  crystallizes in the monoclinic space group  $P2_1/c$ ; cf. Experimental. A view of the cation is shown in Fig. 2. A packing diagram of the unit cell is given in Fig. 3. Selected bond distances and angles are presented in Tables 2 and 3. The macrocyclic ligand is coordinated in the *cis* configuration to give *R,R,R,R* and *S,S,S,S* chiralities of the coordinated nitrogen atoms and *gauche* and *chair* conformations of the five- and six-membered chelate rings. This conformation of the macrocyclic amine is the one normally observed for *cis* complexes.

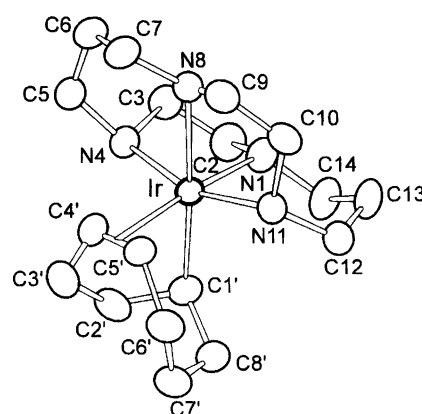


Fig. 2. Structure and numbering scheme of a *cis*- $[\text{Ir}(\text{cyclam})(\text{coei})]^{2+}$  enantiomer. The crystal structure is that of the racemic mixture. The thermal ellipsoids are drawn at the 50% probability level.

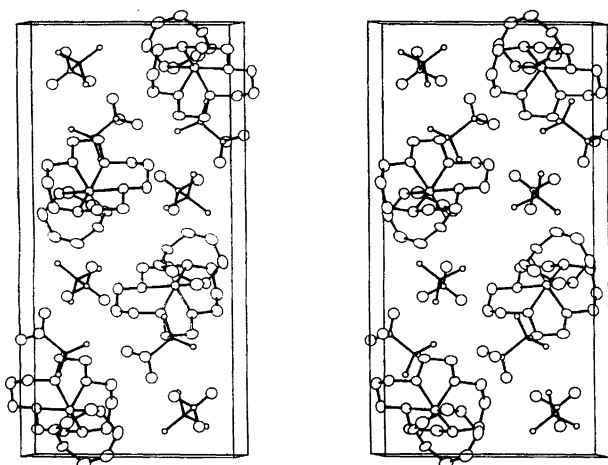


Fig. 3. Packing diagram of *cis*-[Ir(cyclam)(coei)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>.

Table 2. Summary of structural data for the *cis*-[Ir(cyclam)(coei)]<sup>2+</sup> cation.

Bond lengths/Å:	
Ir–N1	2.128(4)
Ir–N4	2.140(4)
Ir–N8	2.229(4)
Ir–N11	2.157(4)
Ir–C1'	2.120(5)
Ir–C4'	2.212(5)
Ir–C5'	2.247(5)
Ir–C <sub>M</sub> <sup>a</sup>	2.118(5)
C–C (cyclam ligand)	1.493–1.514(8) <sup>b</sup>
C–N (cyclam ligand)	1.483–1.505(8) <sup>b</sup>
C4' = C5' (coei <sup>-</sup> ligand)	1.394(7)
C'–C' (coei <sup>-</sup> ligand)	1.503–1.548(8) <sup>b</sup>
Angles/°:	
C4'–Ir–C <sub>M</sub> <sup>a</sup>	81.13(19)
N–Ir–N (NCCN-unit)	80.32–81.45(15) <sup>b</sup>
N–Ir–N (NCCCN-unit)	85.26–87.24(16) <sup>b</sup>

<sup>a</sup> C<sub>M</sub> is the midpoint between the C4' and C5' atoms.

<sup>b</sup> The standard deviations are almost constant for each bond and angle type.

Table 3. Summary of structural data for the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anions.

Bond lengths/Å:	
S–O	1.399–1.434(6) <sup>a</sup>
S–C	1.789–1.815(11) <sup>a</sup>
C–F	1.235–1.351(12) <sup>a</sup>
Angles/°:	
O–S–O	113.0–116.2(4) <sup>a</sup>
O–S–C	102.6–104.6(5) <sup>a</sup>
S–C–F	106.0–115.3(7) <sup>a</sup>
F–C–F	105.4–110.6(9) <sup>a</sup>

<sup>a</sup> The standard deviations are almost constant for each bond and angle type.

The compound is a racemic mixture with *R*- and *S*-cyclooctenide ligands coordinated to (*R,R,R,R*)- and (*S,S,S,S*)-*cis*-Ir(cyclam) units, respectively.

Bond lengths and bond angles in the coordination sphere and in the carbocyclic ligand support the formula-

tion of this ligand as a 4-cycloocten-1-ide ligand, coordinated with an iridium–carbon  $\sigma$ -bond to the C1' carbon atom and a  $\pi$ -bond to the C4'/C5' double bond; cf. the data in Table 2. The iridium–carbon bond lengths are similar to those found for the  $\eta^1, \eta^3$ -C<sub>8</sub>H<sub>12</sub>-iridium complex in Ref. 5, which has a  $\sigma$ -bond length of 2.115 Å and bond lengths of 2.189, 2.147 and 2.256 Å, respectively, to the three carbon atoms of the allylic unit.<sup>5</sup> The iridium–nitrogen bond lengths are longer than those seen for iridium(III) amine complexes, normally between 2.06 and 2.09 Å; cf. the data in Fig. 4.<sup>3,6–9</sup> This bond lengthening is most pronounced for the bond to the nitrogen atom in the *trans* position to the  $\sigma$ -bonded carbon atom for which an exceptionally long bond of 2.229(4) Å is found. The remaining three iridium–nitrogen bond lengths are similar to those seen in the presence of phosphine ligands in the coordination sphere, as exemplified by complexes containing the (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> ligands.<sup>3,10</sup> These latter complexes have iridium–nitrogen bond lengths from 2.09 Å, for a *trans* amine ligand, to 2.17 Å, for a *trans* phosphine ligand, corresponding to a charge delocalization which will effectively reduce the charge on the central iridium atom.

*Deuterium labelling experiments.* Further details of the protonation and deprotonation reactions were obtained by isolation of the reaction products formed in acidic and basic D<sub>2</sub>O solutions; cf. Scheme 2.

Addition of DClO<sub>4</sub> to the basic *cis*-[Ir(cyclam)(coedi)]<sup>+</sup> cation (II) gives an acidic form of the *cis*-[Ir(cyclam)(coei)]<sup>2+</sup> cation (III<sub>a</sub>) with an NMR DEPT spectrum characterized by the disappearance of a CH<sub>2</sub> resonance at 24.2 ppm, cf. Fig. 5. This is indicative of introduction of deuterium into the cyclooctenide ligand. Addition of OH<sup>-</sup> or OD<sup>-</sup> to this deuterated product generates a basic form (IV) in which the CH resonance at 51.2 ppm has disappeared, also indicative

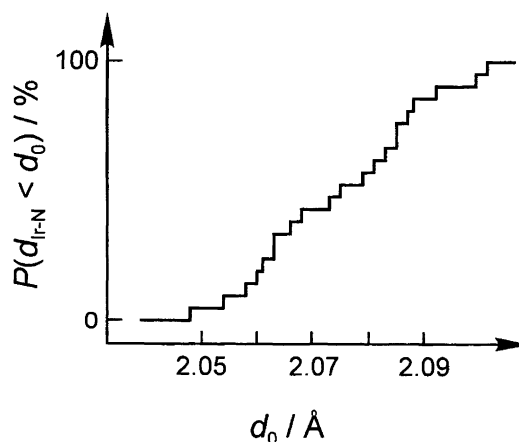
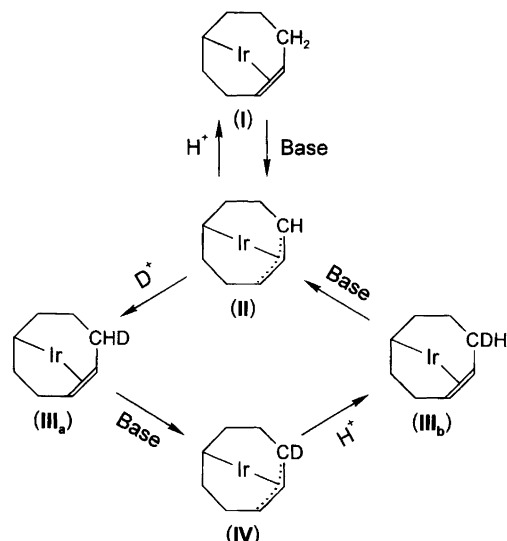


Fig. 4. Cumulative distribution function for iridium(III)-nitrogen bond lengths in [(en)<sub>2</sub>(H<sub>2</sub>O)Ir(OH)Ir(OH)(en)<sub>2</sub>]<sup>4+</sup>,<sup>6</sup> *mer*-[Ir(en)(en<sup>+</sup>)Cl<sub>3</sub>]<sup>7</sup>, *mer*-[Ir(en)(enH)Cl<sub>3</sub>]<sup>7</sup>, [Ir(tacn)Cl<sub>3</sub>]<sup>8</sup>, [Ir(tacn)<sub>2</sub>]<sup>3+</sup>,<sup>9</sup> and of two isomers of [Ir(chxn)<sub>3</sub>]<sup>3+</sup>.<sup>3</sup>



Scheme 2.

of deuterium being incorporated into the deprotonated cyclooctene ligand. Addition of  $\text{HClO}_4$  to this deuterated basic  $\text{cis-}[\text{Ir}(\text{cyclam})(\text{coedi})]^+$  cation (IV) gives an acidic form of the  $\text{cis-}[\text{Ir}(\text{cyclam})(\text{coei})]^{2+}$  cation (III<sub>b</sub>) with an NMR spectrum very similar to that of the product (III<sub>a</sub>) obtained by addition of  $\text{DClO}_4$  to the undeuterated basic form (II). The NMR spectroscopic data and the methods of formation indicate the presence of *one* deuterium atom in the cyclooctenide ligand in products (III<sub>a</sub>) and (III<sub>b</sub>). The reactivity of the two monodeuterated products is very different, however, as addition of  $\text{OH}^-$  or  $\text{OD}^-$  to the latter product, (III<sub>b</sub>), generates a basic form in which a stereospecific removal of the deuterium atom has taken place; cf. Scheme 2.

The  $\text{H}^+/\text{D}^+$  addition and abstraction reactions are not simple protonation and deprotonation reactions, as indicated by further NMR studies which indicate the

presence of short-lived intermediates for the reactions in acid and base. Further studies of the intermediates in these reactions is underway.

## Experimental

**Caution!** The described perchlorate salts are potentially explosive and should be handled accordingly.

**Materials.** 1,4,8,11-Tetraazacyclotetradecane and  $[\text{Ir}(\text{cod})\text{Cl}]_2$  were prepared according to the literature.<sup>11,12</sup> All other chemicals were of analytical or reagent grade and were used without further purification.

**Diastereomeric mixture of  $\text{cis-}[\text{Ir}(\text{cyclam})(\text{coei})](\text{ClO}_4)_2$ .** 3.00 g of  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (4.47 mmol) and 1.79 g of cyclam (8.94 mmol) were added to 25 ml of water and the suspension was refluxed for 15 min. The basic yellow reaction solution was acidified by addition of 2.3 ml of 4 M HCl and was further refluxed for 2 h. The resulting solution was filtered, diluted with water to a volume of 250 ml and was applied to a SP-Sephadex C-25 filled column, ca. 20 cm long and 2 cm in diameter. The column was washed with water and the iridium complex was eluted as a yellow band with 0.5 M NaCl. The eluate was evaporated to dryness and the iridium product was removed by extraction with 96% ethanol. The ethanolic extract was evaporated to dryness, and the resulting product dissolved in 35 ml of water. This solution was filtered and the product was precipitated by slow addition of 5 ml of a saturated  $\text{NaClO}_4$  solution. The mixture was cooled to 5 °C and left overnight. The crystals were filtered off, washed with 2 × 10 ml of ice-cold water and dried in air. Yield: 5.5 g (88%) of crude  $[\text{Ir}(\text{cyclam})(\text{coei})](\text{ClO}_4)_2$ .

The crude product was recrystallized by dissolution of 5.00 g in 50 ml of water at 100 °C followed by filtration. The filtrate was left to stay for crystallization, first at

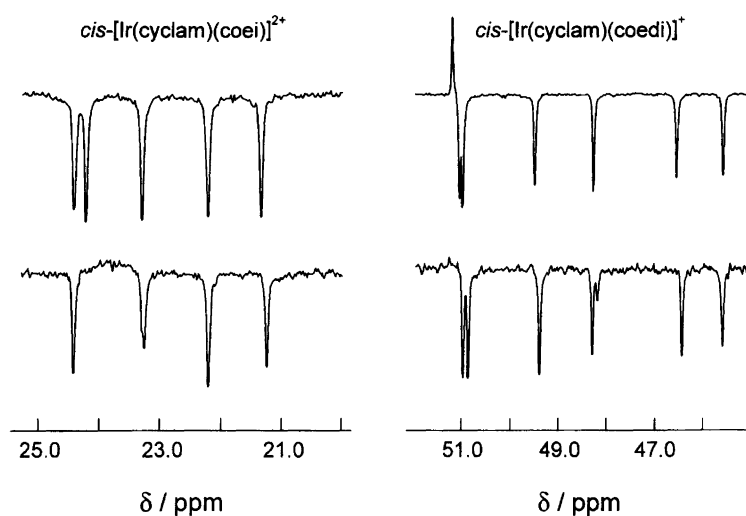


Fig. 5.  $^{13}\text{C}$  NMR DEPT spectra of iridium complexes of normal and deuterated deprotonated cyclooctene ligands in  $\text{dmsO-}d_6$ ; cf. Scheme 2. The splitting of some resonances in the lower two spectra is caused by partial deuteration of the nitrogen atoms of the cyclam ligand during preparation.

room temperature, and then at 5 °C overnight. The crystals were isolated as described above. Yield: 4.3 g (69%) of *cis*-[Ir(*cyclam*)(*coei*)](ClO<sub>4</sub>)<sub>2</sub>. Analyses: C, H, N and Cl.

*cis*-[Ir(*cyclam*)(*coedi*)]ClO<sub>4</sub>. 1.00 g of [Ir(*cyclam*)(*coei*)](ClO<sub>4</sub>)<sub>2</sub> (1.43 mmol) was dissolved in 10 ml boiling water. 10 ml boiling 2 M NaOH was added. The mixture was kept at 95 °C for 30 min, during which time a copious precipitate of white crystals was formed. The product was filtered from the solution while still hot. The crystals were washed with ice-cold water until the washings were neutral. Yield: 0.75 g (87%) of [Ir(*cyclam*)(*coedi*)]ClO<sub>4</sub>. Analyses: C, H, N and Cl.

*cis*-[Ir(*cyclam*)(*coei*)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>. 0.50 g of [Ir(*cyclam*)(*coedi*)]ClO<sub>4</sub> (0.83 mmol) was added to 10 ml of 1 M HClO<sub>4</sub> and the suspension was heated to boiling. A yellow solution was formed which was allowed to cool in ice for crystallization. The crystals were filtered off, washed with 5 ml of ice-cold water and dried in air. Yield: 0.50 g (86%) of the pure dominant diastereomer of *cis*-[Ir(*cyclam*)(*coei*)](ClO<sub>4</sub>)<sub>2</sub>. This perchlorate salt was converted into the chloride salt, by column chromatography as described earlier, and the trifluoromethanesulfonate salt was precipitated by addition of NaCF<sub>3</sub>SO<sub>3</sub>. Slow evaporation of water from a saturated aqueous solution of the trifluoromethanesulfonate salt containing a small excess of CF<sub>3</sub>SO<sub>3</sub>H gave crystals suitable for single-crystal X-ray diffraction investigation.

*Deuteration experiments.* The deuteration experiments were carried out as described above, except for the use of D<sub>2</sub>O, DClO<sub>4</sub> and NaOD whenever appropriate.

Table 4. Crystal data, data collection and reduction characteristics with standard deviations in parenthesis.

Formula	IrS <sub>2</sub> F <sub>6</sub> O <sub>8</sub> N <sub>4</sub> C <sub>20</sub> H <sub>33</sub>
Formula weight/g mol <sup>-1</sup>	795.8
Crystal system and space group	Monoclinic: <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
Unit cell parameters:	
<i>a</i> /Å	9.227(4)
<i>b</i> /Å	24.838(6)
<i>c</i> /Å	12.537(3)
$\beta$ /°	107.59(3)
<i>V</i> /Å <sup>3</sup>	2739(2)
<i>Z</i>	4
Crystal size/mm <sup>3</sup>	0.13 × 0.22 × 0.30
$\mu$ (MoK $\alpha$ )/cm <sup>-1</sup>	50.9
Transmission factor range	0.3171–0.4401
Number of reflections, $\theta_{\max} < 30^\circ$ :	
Total	8598
Independent reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	6326
Structure refinement:	
Number of refined parameters	353
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.035
$w^{-1}$	$\sigma^2(F_o) + 0.0002F_o^2$
$R_w = \sum w  F_o  -  F_c  ^2 / \sum wF_o^2$	0.038

<sup>13</sup>C NMR measurements. Proton-decoupled <sup>13</sup>C NMR spectra were recorded at 62.896 MHz with a Bruker AC 250 MHz Fourier-transform spectrometer. Data, usually about 3 × 10<sup>4</sup> transients, were recorded at 300 K using a pulse width of 2  $\mu$ s (45°), spectral width 14286 Hz and 32 K data points, giving a digitizer resolution of 0.872 Hz/point in the final spectrum. Under these conditions the acquisition time is 1.147 s per free induction decay. A relaxation delay between pulses was not found to be necessary. <sup>13</sup>C NMR DEPT spectra<sup>4</sup> with  $\tau = 3.8$  ms and  $\theta = 135^\circ$  were used to differentiate CH and CH<sub>2</sub> groups. Chemical shifts are reported on the  $\delta$ -scale with reference to the solvent, dms-*d*<sub>6</sub>, at  $\delta = 39.5$  ppm.

Table 5. Fractional coordinates and equivalent isotropic thermal parameters.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> /Å <sup>2</sup>
Cation				
Ir	0.06550(2)	0.10585(1)	0.22955(1)	0.0254(1)
N1	-0.0054(5)	0.17114(15)	0.3118(3)	0.0373(11)
N4	0.1499(5)	0.17068(14)	0.1528(3)	0.0351(11)
N8	-0.1479(4)	0.11062(14)	0.0867(3)	0.0341(11)
N11	-0.0817(4)	0.05748(16)	0.2955(3)	0.0352(11)
C2	0.0889(6)	0.21885(19)	0.3033(4)	0.0447(16)
C3	0.0926(6)	0.22303(18)	0.1851(4)	0.0429(16)
C5	0.1163(6)	0.1714(2)	0.0277(4)	0.0428(16)
C6	-0.0491(6)	0.1658(2)	-0.0407(4)	0.0462(16)
C7	-0.1290(6)	0.11427(19)	-0.0268(4)	0.0433(16)
C9	-0.2429(6)	0.06391(19)	0.0971(4)	0.0412(14)
C10	-0.2399(5)	0.0610(2)	0.2167(4)	0.0404(16)
C12	-0.0900(6)	0.0662(2)	0.4122(4)	0.0457(17)
C13	-0.1230(7)	0.1235(2)	0.4389(5)	0.0498(19)
C14	-0.0056(7)	0.1634(2)	0.4297(4)	0.0482(18)
C1'	0.2757(5)	0.10156(19)	0.3586(4)	0.0386(12)
C2'	0.4068(6)	0.1049(2)	0.3057(5)	0.0472(16)
C3'	0.3712(6)	0.0751(2)	0.1925(5)	0.0471(17)
C4'	0.2043(6)	0.06094(18)	0.1432(4)	0.0384(14)
C5'	0.1285(5)	0.02277(18)	0.1881(4)	0.0763(12)
C6'	0.1942(6)	-0.0157(2)	0.2833(5)	0.0477(16)
C7'	0.3260(6)	0.0004(2)	0.3820(5)	0.0504(17)
C8'	0.3025(6)	0.0526(2)	0.4359(4)	0.0481(16)
Anion 1				
S	0.17310(18)	0.09527(5)	0.76120(11)	0.0467(4)
F	0.4565(7)	0.0675(3)	0.8088(7)	0.173(4)
F	0.4192(8)	0.1434(3)	0.8736(6)	0.176(4)
F	0.3875(9)	0.1358(3)	0.6989(8)	0.194(5)
O	0.0985(7)	0.14587(19)	0.7382(4)	0.092(2)
O	0.1663(6)	0.06997(17)	0.8623(3)	0.0715(16)
O	0.1454(5)	0.05860(16)	0.6689(3)	0.0602(5)
C	0.3735(13)	0.1111(4)	0.7913(10)	0.108(4)
Anion 2				
S	0.59349(17)	0.23018(6)	0.17424(14)	0.0561(5)
F	0.5659(10)	0.3235(2)	0.0812(7)	0.189(5)
F	0.4860(10)	0.2622(4)	-0.0281(6)	0.202(5)
F	0.7212(8)	0.2756(3)	0.0416(6)	0.158(3)
O	0.6393(9)	0.1819(2)	0.1368(7)	0.150(4)
O	0.4440(5)	0.23047(18)	0.1792(5)	0.0804(19)
O	0.7040(9)	0.2519(4)	0.2672(5)	0.181(5)
C	0.5927(10)	0.2761(3)	0.0641(8)	0.089(3)

**Structure determination.** The single-crystal X-ray data were collected at room temperature on an Enraf-Nonius CAD-4F diffractometer. The unit-cell parameters were found by least-squares fitting of refined diffractometer setting angles for 25 reflections. Four standards for intensity and orientation control, measured every 4 h, showed no fading. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. The final map showed peaks of 3.38 and  $-1.37 \text{ e}/\text{\AA}^3$ , both of which were at a distance of 0.78 Å from the iridium atom. The maximum final parameter shift of  $0.57\sigma$  was seen for the  $x$ -coordinate of a fluorine atom in one of the  $\text{CF}_3\text{SO}_3^-$  anions. Further data for the crystal and the X-ray diffraction experiment are given in Table 4. SHELX76<sup>13</sup> was used for the calculations and ORTEP II<sup>14</sup> was used for the drawing of Figs. 2 and 3. The fractional coordinates and equivalent isotropic temperature parameters are given in Table 5.

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