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The Crystal and Molecular Structure of Thiocyanato and Isothiocyanato Ir and Rh Complexes. I. Thiocyanatopenta-ammineiridium(III) Diperchlorate, $[Ir(SCN)(NH_3)_5](ClO_4)_2$

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$[Ir(SCN)(NH_3)_5](ClO_4)_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a=7{\cdot}506$, $b=15{\cdot}744$, $c=14{\cdot}108$ Å, $\beta=121{\cdot}75°$ and 4 formula units per unit cell. The crystals are pseudo-orthorhombic. The structure has been determined by Patterson and Fourier methods and refined to an R value of 0·058, using three-dimensional diffractometer data. The structure consists of octahedrally coordinated monomeric Ir units $[Ir(SCN)(NH_3)_5]^{2+}$ and tetrahedral $(ClO_4)^-$ ions. The SCN group is not quite linear with S–C–N = 174·20° and Ir–S–C = 109·0°. If there is any hydrogen bonding between NH_3 and $(ClO_4)^-$ it is exceedingly weak.

Introduction

The ultraviolet, visible and infrared spectra of a series of acidopenta-ammine-iridium(III) and -rhodium(III) complexes have been studied in detail by Schmidtke (1966). For the thiocyanato- and isothiocyanatopenta-ammineiridium(III) complexes, Schmidtke deduced that they were non-bridged, although binuclear iridium complexes with two SCN bridges would have given very similar spectra. It is thus interesting to verify Schmidtke's conclusions by crystal structure analysis and to attempt to see in what measure it is possible to explain the structural differences and similarities of the two thiocyanate isomers. This paper presents the first in a series of structures of thiocyanato and isothiocyanato complexes of Ir(III) and Rh(III), that of $[Ir(SCN)(NH_3)_5](ClO_4)_2$.

Experimental

The crystals were prepared by slow evaporation *in vacuo* from a warm 10% solution of perchloric acid (Schmidtke, 1966). A crystal of dimensions 80 × 60 × 60mμ was selected. The intensity data were collected on an automatic four-circle Philips diffractometer using Mo $K\alpha$ radiation, graphite monochromator and $\theta/2\theta$ scan. Intensities were measured for each observable independent reflexion with $\sin\theta/\lambda < 0{\cdot}5946$ Å^{-1}. 2180 reflexions were recorded of which 2128 were greater than 2σ in $|F|$. Lorentz and polarization corrections were applied as usual. No absorption correction was applied as $\mu R \simeq 0{\cdot}5$.

In the least-squares refinement only those 2128 reflexions with $|F| > 2\sigma_F$ were used. Atomic scattering factors for Ir,N,S,C,Cl, and O were taken from *Inter-*

Table 1. *Final values of the positional and vibrational parameters for* $[Ir(SCN)(NH_3)_5](ClO_4)_2$

Space group $P2_1/c$. All atoms in point positions 4(*e*).

E.s.d.'s are shown in parentheses. All values have been multiplied by 10^4.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ir	1701 (1)	8857 (1)	2584 (1)	118 (2)	17 (1)	42 (1)	0 (1)	31 (1)	1 (1)
N(1)	9775 (25)	7839 (9)	2509 (12)	234 (48)	35 (7)	31 (12)	−11 (16)	65 (21)	− 5 (8)
N(2)	9544 (24)	9740 (9)	2551 (13)	199 (47)	28 (7)	59 (14)	25 (14)	74 (22)	18 (8)
N(3)	3814 (24)	7955 (10)	2580 (14)	153 (46)	27 (7)	71 (15)	16 (14)	34 (22)	3 (8)
N(4)	41 (25)	8887 (10)	827 (14)	230 (48)	29 (7)	74 (14)	25 (16)	86 (22)	15 (9)
N(5)	3277 (23)	8821 (10)	4353 (11)	149 (40)	40 (8)	26 (10)	13 (16)	−12 (17)	0 (8)
S	4144 (9)	9891 (4)	2755 (7)	177 (15)	32 (3)	158 (8)	− 7 (5)	−80 (9)	21 (4)
C	2966 (36)	786 (14)	2315 (22)	325 (79)	26 (9)	144 (28)	15 (23)	160 (42)	13 (14)
N(6)	2172 (46)	1423 (17)	1934 (30)	508 (103)	49 (13)	301 (49)	51 (31)	232 (61)	26 (21)
Cl(1)	6217 (7)	1321 (3)	117 (4)	147 (11)	27 (2)	41 (3)	9 (4)	25 (5)	0 (2)
O(1)	7351 (22)	573 (9)	176 (11)	281 (47)	34 (7)	63 (12)	44 (14)	71 (21)	12 (7)
O(2)	7184 (27)	2038 (9)	9952 (14)	407 (60)	33 (8)	109 (17)	−12 (16)	125 (28)	13 (9)
O(3)	6281 (36)	1448 (12)	1114 (14)	844 (104)	61 (10)	76 (15)	− 4 (25)	213 (36)	−18 (10)
O(4)	4098 (23)	1251 (10)	9209 (15)	162 (42)	51 (9)	110 (16)	16 (15)	−56 (22)	−13 (10)
Cl(2)	1039 (7)	1378 (3)	4860 (4)	158 (11)	28 (2)	32 (3)	11 (4)	19 (5)	− 1 (2)
O(5)	1986 (24)	667 (11)	4691 (11)	315 (50)	60 (9)	31 (10)	60 (18)	6 (19)	−20 (8)
O(6)	2229 (27)	2107 (11)	4900 (12)	358 (57)	59 (10)	54 (13)	−56 (18)	25 (22)	5 (9)
O(7)	8908 (24)	1496 (12)	3917 (13)	207 (46)	78 (11)	72 (14)	26 (18)	− 7 (21)	3 (10)
O(8)	1116 (35)	1300 (11)	5870 (16)	758 (96)	55 (10)	140 (20)	43 (23)	283 (40)	12 (11)

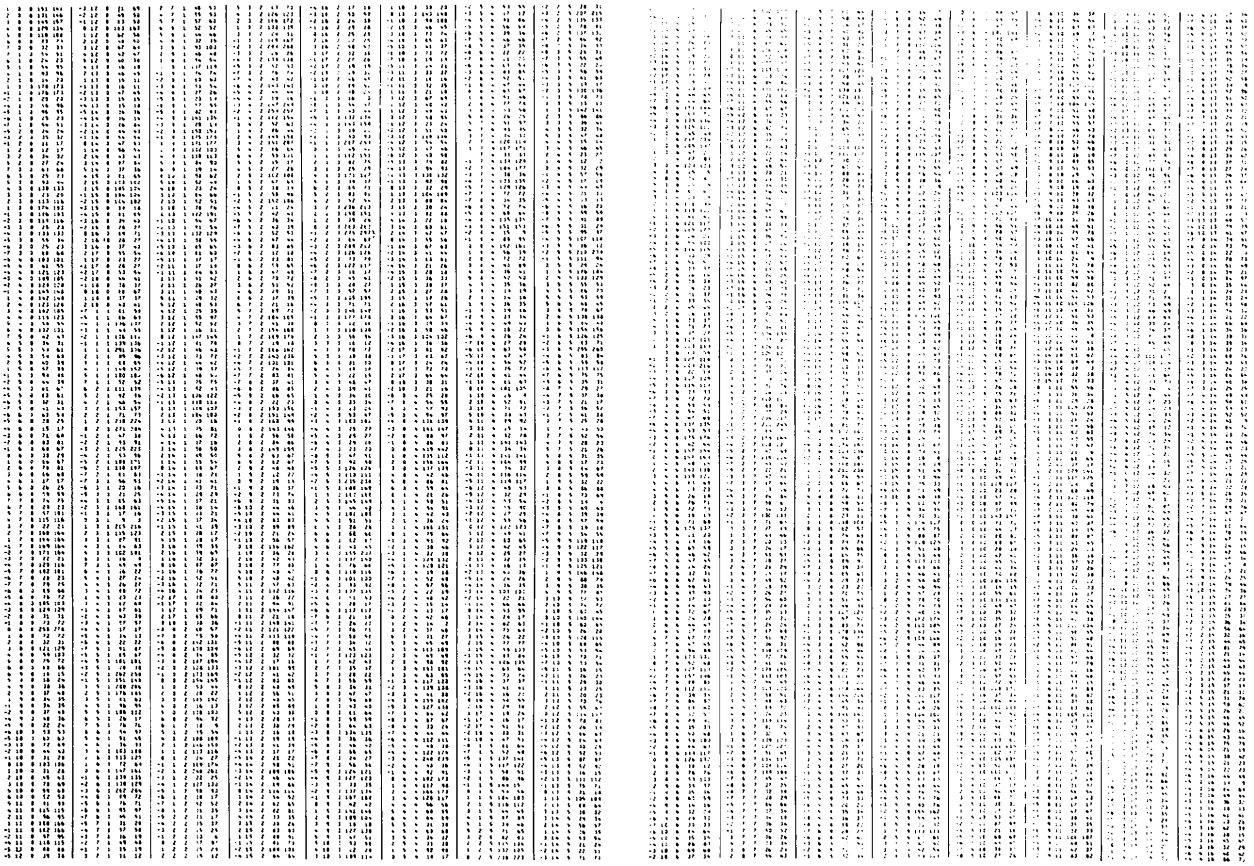
national Tables for X-ray Crystallography (1962). Allowance was made for the $\Delta f'$ and $\Delta f''$ terms for all atoms, but at no stage were contributions from the hydrogen atoms included.

Crystal and molecular data

Thiocyanatopenta-ammineiridium(III) diperchlorate, $[Ir(SCN)(NH_3)_5](ClO_4)_2$, F.W. 534·34. Monoclinic: $a=7{\cdot}506(2)$, $b=15{\cdot}744(4)$, $c=14{\cdot}108(4)$ Å, $\beta=121{\cdot}75(5)°$; $V=1418$ Å^3, calculated density 2·58 g cm^{-3} for $Z=4$, $F(000)=1016$, $\mu=108{\cdot}7$ cm^{-1} ($\lambda=0{\cdot}71069$ Å). Systematic absences: $h0l$ absent when $l\neq 2n$, $0k0$ absent when $k\neq 2n$; these absences are characteristic of the space group $P2_1/c$ (C_{2h}^5). The crystals are pseudo-orthorhombic, (001) being a pseudo-mirror plane and $(10\bar{1})$ being a pseudo-glide plane with a translation component parallel to **b**.

Table 2. *Observed and calculated structure factors for* $[Ir(SCN)(NH_3)_5](ClO_4)_2$

Reading from left to right the columns contain the values h, k, l, $|F_o|$ and $|F_c|$.



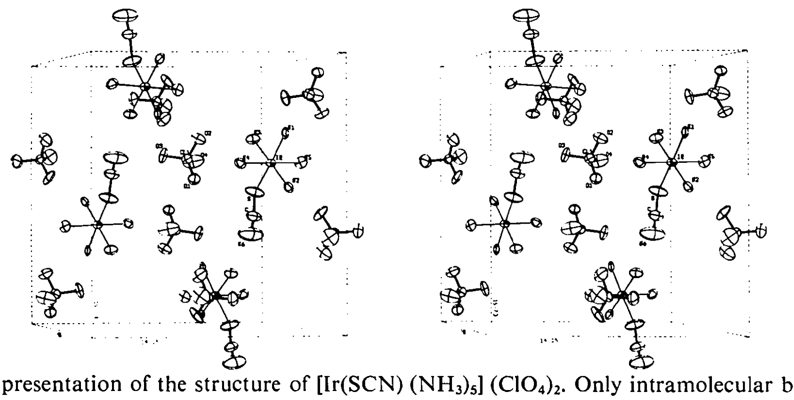


Fig. 1. Stereoscopic representation of the structure of $[Ir(SCN)(NH_3)_5](ClO_4)_2$. Only intramolecular bonds are shown.

Determination and refinement of the structure

From a three-dimensional Patterson synthesis the positions of the iridium atoms were found readily, and these were used as the starting point for a three-dimensional electron density synthesis which showed all the atoms except the C and N of the SCN group. A further electron density synthesis using the positions so obtained showed these two atoms. All the atoms are situated in general positions 4(*e*) of the space group $P2_1/c$.

The refinement was carried out with the full-matrix least-squares program *XFLS*3 (Busing *et al.*, 1971*a*). At first one scale factor and the positional parameters were refined. The isotropic temperature factors were then allowed to vary and subsequently anisotropic temperature factors for all atoms were refined. In the final cycle the weights were set at $1/\sigma^2$ where σ is the experimental standard deviation of the $|F_o|$. 172 parameters were allowed to vary in this cycle. The value of the index $R=\sum|\varDelta F|/\sum|F_o|$ was 5·8%. The form of the anisotropic temperature factors used was:

$$\exp\left[-\{b_{11}h^2+b_{22}k^2+b_{33}l^2+2hkb_{12}+2hlb_{13}+2klb_{23}\}\right].$$

The final values of the positional and vibrational parameters are listed in Table 1, together with their e.s.d.'s derived from the inverse least-squares matrix. The values of $|F_o|$ and $|F_c|$ are given in Table 2.

Discussion

Fig. 1 shows a stereoscopic representation of the structure drawn by the program *ORTEP* (Johnson, 1970). There is a symmetry centre at the centre of the drawing. It is clear that the unit cell comprises eight ClO_4 tetrahedra and four units each with an Ir atom octahedrally coordinated by one SCN and five NH_3 groups. Thus the structure consists of isolated $[Ir(SCN)(NH_3)_5]^{2+}$ and $(ClO_4)^-$ ions. There is no bridging between the Ir complex ions by the SCN groups, in agreement with the deductions of Schmidtke (1966). It is possible to recognize in the packing arrangement of the ions a highly distorted form of the fluorite structure. The relationship of ionic shape to the distortion of the fluorite structure in this and related compounds will form the subject matter of a forthcoming publication.

Intra- and interionic bond distances and angles given in Table 3 were calculated with the program *ORFFE*3 (Busing *et al.*, 1971*b*). This table shows that all interionic contacts are greater than 2·96 Å. Hydrogen-bond distances for N–H···O normally lie in the range 2·73–3·22 Å (*International Tables for X-ray Crystallography*, 1962) with an average distance of 2·88 Å. In

Table 3. *Bond lengths and angles*

(*a*) Bond lengths (Å) with standard deviations in parentheses

Ir–N(1)	2·124 (15)	Cl(1)–O(1)	1·429 (14)
Ir–N(2)	2·116 (14)	Cl(1)–O(2)	1·426 (15)
Ir–N(3)	2·131 (15)	Cl(1)–O(3)	1·396 (14)
Ir–N(4)	2·108 (16)	Cl(1)–O(4)	1·428 (14)
Ir–N(5)	2·128 (14)	Cl(2)–O(5)	1·413 (15)
Ir–S	2·367 (6)	Cl(2)–O(6)	1·437 (15)
S–C	1·604 (23)	Cl(2)–O(7)	1·457 (15)
C–N(6)	1·146 (30)	Cl(2)–O(8)	1·402 (16)

(*b*) Bond angles (°) with standard errors in parentheses

N(1)–Ir–N(2)	90·1 (6)	Ir——S——C	109·0 (9)
N(1)–Ir–N(3)	89·1 (6)	S——C——N(6)	174·2 (28)
N(1)–Ir–N(4)	89·6 (6)	O(1)–Cl(1)–O(2)	108·8 (9)
N(1)–Ir–N(5)	88·9 (6)	O(1)–Cl(1)–O(3)	110·8 (10)
N(1)–Ir–S	174·1 (5)	O(1)–Cl(1)–O(4)	109·7 (9)
N(2)–Ir–N(3)	178·6 (6)	O(2)–Cl(1)–O(3)	107·6 (11)
N(2)–Ir–N(4)	89·3 (6)	O(2)–Cl(1)–O(4)	109·7 (10)
N(2)–Ir–N(5)	89·4 (6)	O(3)–Cl(1)–O(4)	110·3 (13)
N(2)–Ir–S	95·3 (4)	O(5)–Cl(2)–O(6)	106·4 (11)
N(3)–Ir–N(4)	89·6 (6)	O(5)–Cl(2)–O(7)	110·8 (9)
N(3)–Ir–N(5)	91·7 (6)	O(5)–Cl(2)–O(8)	110·3 (10)
N(3)–Ir–S	85·5 (5)	O(6)–Cl(2)–O(7)	107·2 (10)
N(4)–Ir–N(5)	178·0 (6)	O(6)–Cl(2)–O(8)	109·8 (11)
N(4)–Ir–S	93·0 (5)	O(7)–Cl(2)–O(8)	112·2 (12)
N(5)–Ir–S	88·6 (5)		

(*c*) Interionic contacts (Å) less than 3·1 Å

N(1)–O(4)	2·994 (20)	N(3)–O(7)	3·061 (23)
N(1)–O(8)	3·020 (20)	N(4)–O(1)	3·079 (21)
N(2)–O(5)	2·963 (21)	N(4)–O(4)	3·087 (24)
N(2)–O(4)	2·988 (22)	N(5)–O(2)	3·053 (23)
N(2)–O(8)	3·008 (21)	N(6)–N(1)	2·988 (31)
N(3)–O(3)	3·028 (23)		

$[Ir(SCN)(NH_3)_5](ClO_4)_2$ the minimum N–H···O distance is 2·96 Å suggesting that the hydrogen bonds are relatively weak. This is to be expected in view of the acidic strength of $HClO_4$.

The arrangement surrounding the Ir atom is slightly distorted from a regular octahedron. Large distortions are not to be expected for low-spin d^6 complexes and it seems likely that this is caused by the difference in size of the N and S atoms. The Ir–S–C angle of 109·0° agrees well with the value found for Co–S–C in $[Co(SCN)(NH_3)_5]Cl_2.H_2O$ (Snow & Boomsma, 1972) and confirms that the compound is the thiocyanato and not the isothiocyanato isomer.

We would like to thank Professor C. K. Jørgensen for suggesting this problem and for helpful discussions, and A. Regnard who carried out some preliminary measurements for us.

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The Crystal Structures of Methyl 5-Thio-α-D-ribopyranoside and Methyl 5-Thio-β-D-ribopyranoside

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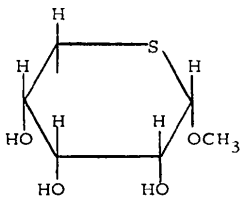
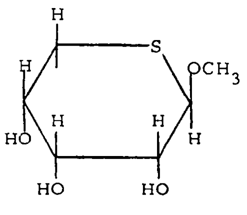
The crystal structures of methyl 5-thio-α-D-ribopyranoside and methyl 5-thio-β-D-ribopyranoside, $C_6H_{12}O_4S$, have been determined from Cu $K\alpha$ radiation data and refined to R values of 0·03 and 0·04 respectively. Both structures have space group $C2$ with four molecules in unit cells of $a=12·26$ (1), $b=4·942$ (6), $c=13·76$ (1) Å, $\beta=105·07$ (8)° and of $a=12·39$ (3), $b=4·786$ (9), $c=14·57$ (4) Å, $\beta=109·96$ (7)°, respectively. The molecules have the $^4C_1$ ring conformation. In the α configuration, this gives rise to a *synaxial* O···O interaction at 2·99 Å with no intramolecular hydrogen bond formation. In the β compound, one hydroxyl hydrogen [H(2)] has three oxygen nearest neighbour distances of 2·5, 2·6 and 2·7 Å, the shortest of which may correspond to a weak intramolecular hydrogen bond between vicinal hydroxyl groups. The bond lengths are normal with a mean C–S distance of 1·815 Å and a ring angle at the sulfur atom of 98°. In both structures, the molecules are hydrogen-bonded into layers, two molecules wide, with van der Waals interactions between the layers.

Introduction

This paper is the second of a series describing crystal structural studies on some thioribopyranosides supplied to us by Professor N. A. Hughes, of the University of Newcastle upon Tyne, U. K. The first was that on methyl 1-thio-α-D-ribopyranoside (Girling & Jeffrey, 1971, 1973); this work has determined the structure of two compounds with the sulfur atom in the pyranose ring, methyl 5-thio-α-D-ribopyranoside (I) and methyl 5-thio-β-D-ribopyranoside (II).



(I)



(II)

Experimental

The compounds I and II were recrystallized from three different solvents: ethanol, ethanol–benzene and

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