Synthesis and Chemical Characterization of the Chalcogenide Capped Iridium Carbonyl Anions: [Ir₃(μ₃-X)₂(CO)₆]⁻ (X = S or Se). Crystal and Molecular Structures of [NMe₃(CH₂Ph)][Ir₃(μ₃-S)₂(CO)₆] and [NMe₄][Ir₃(μ₃-Se)₂(CO)₆] *

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Reaction of [Ir₄(CO)₁₂] or [Ir₆(CO)₁₆] in tetrahydrofuran with SCN⁻, SeCN⁻, or polysulphides in MeOH gives the trinuclear anions [Ir₃(μ₃-X)₂(CO)₆]⁻ (X = S or Se) which have been isolated and investigated by X-ray analysis. The salt [NMe₃(CH₂Ph)][Ir₃(μ₃-S)₂(CO)₆] (1) crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with a = 9.303(2), b = 17.295(3), c = 28.274(4) Å, β = 94.19(2)°, Z = 8, R = 0.027 for 3 676 significant independent reflections having $I > 3\sigma(I)$. The salt [NMe₄][Ir₃(μ₃-Se)₂(CO)₆] (2) crystallizes in the monoclinic space group $C2/c$ (no. 15) with a = 15.930(3), b = 7.877(2), c = 15.040(2) Å, β = 108.22(2)°, Z = 4, R = 0.025 for 1 045 significant independent reflections having $I > 3\sigma(I)$. Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares methods. The anions consist of an Ir₃ triangle bicapped by triply bridging chalcogenide atoms. Each iridium atom, bearing two terminal CO groups, displays an almost square-planar geometry with respect to the ligands. In both compounds the Ir–Ir distances are long [mean values 3.086(1) and 3.170(1) Å for compounds (1) and (2) respectively] and suggest a very weak (if any) metal–metal interaction. The two anions can be considered therefore as trinuclear Ir¹ metal aggregates rather than triangular clusters.

There has been recent interest in complexes containing S or SR groups. This interest stems partially from the potential use of these complexes as models for biological systems[1] and more recently from their relevance to metal sulphide hydro-desulphurization catalysts.[2]

There are several examples of mononuclear[3] and dinuclear[4] iridium complexes containing organic sulphur but to our knowledge there are only a few examples of iridium complexes containing a 'naked sulphur'[5] and very few examples of trinuclear iridium derivatives containing sulphur atoms.[6]

In previous work on the reactions of [Rh₄(CO)₁₂] and [Rh₆(CO)₁₆] with anionic ligands we found that the SCN⁻ or SeCN⁻ ligands afford different types of complexes. At different molar ratios of metal carbonyls to SCN⁻ or SeCN⁻ it was possible to isolate [Rh₁₀X(CO)₂₂]²⁻ (X = S or Se),[7] [Rh₃(μ₃-X)₂(CO)₆]⁻ (X = S or Se),[8] and [Rh₆(CO)₁₄(CN)₂-Rh(CO)₂]₂²⁻.[9]

Since we are interested in iridium carbonyl cluster chemistry, and in pointing out the frequently observed differences with the rhodium analogues in the ligand stereochemistry around the same metal core,[10–14] we undertook a study of the reactivity of [Ir₄(CO)₁₂] or [Ir₆(CO)₁₆] towards SCN⁻ or SeCN⁻ and we report here the first products isolated from this type of reaction: the complexes [Ir₃(μ₃-X)₂(CO)₆]⁻ (X = S or Se)

which were found by X-ray analyses to be isostructural with the rhodium analogues.

Results and Discussion

Preparation of the [Ir₃(μ₃-X)₂(CO)₆]⁻ *Anions* [X = S (1) *or* Se (2)].—Anion (1) can be obtained by reacting neutral or anionic carbonyl clusters as well as some Ir¹ derivatives with sulphur or with thiocyanato, sulphido, or polysulphido anions.

Starting from neutral carbonyls we have found that treatment of [Ir₄(CO)₁₂] or [Ir₆(CO)₁₆] with K(SCN) (molar ratios in the range 1:6 to 1:8), in refluxing tetrahydrofuran (thf) leads to cluster fragmentation, giving a solution from which, after filtration of insoluble uncharacterized by-products, the [Ir₃(μ₃-S)₂(CO)₆]⁻ anion can be isolated in up to 50% yield as the salt of bulky cations such as [N(PPh₃)₂]⁺, [NMe₃(CH₂Ph)]⁺, [NMe₄]⁺, and [PPh₄]⁺. Infrared monitoring indicates that, in the early stage of the reaction, substitution of the neutral carbonyls takes place to give the corresponding monoanionic derivatives [Ir₄(CO)₁₁(SCN)]⁻ (3)[15] and [Ir₆(CO)₁₄(SCN)]⁻ (4),[13] respectively. These anions, which react at room temperature only slowly with excess of SCN⁻ ions, are rapidly degraded in hot solution to the trinuclear species.

The [Ir₃(μ₃-S)₂(CO)₆]⁻ anion can also be obtained by treating [Ir₄(CO)₁₂] or [Ir₆(CO)₁₆] with an excess of potassium polysulphides (K₂Sₓ, x = 1—8) in MeOH at room temperature with yields of 60—70%. Compound (1) can also be obtained by reacting [Ir₆(CO)₁₅]²⁻ with the stoicheiometric amount of sulphur as shown in equation (1). A more
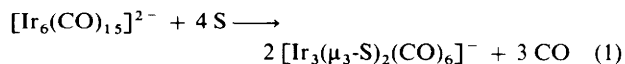
$$[Ir_6(CO)_{15}]^{2-} + 4 S \longrightarrow$$
$$2 [Ir_3(\mu_3\text{-}S)_2(CO)_6]^- + 3 CO \quad (1)$$

Figure 1. ORTEP drawing and numbering scheme for the $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion

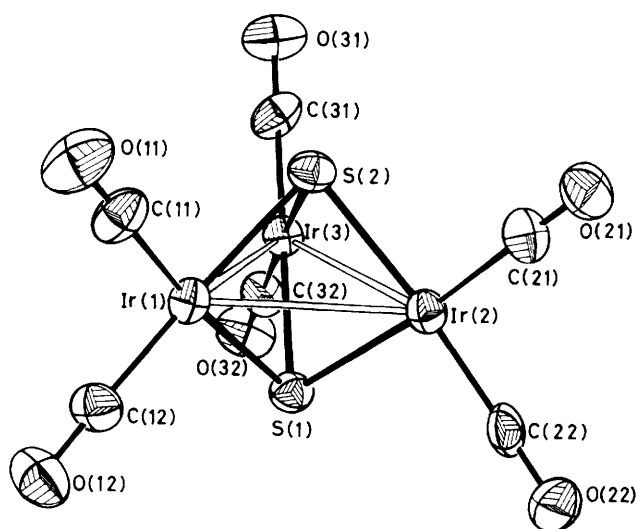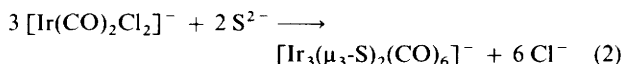**Figure 2.** ORTEP drawing and numbering scheme for the $[Ir_3(\mu_3\text{-}Se)_2(CO)_6]^-$ anion

straightforward synthesis starts from Ir^I derivatives, such as $[Ir(CO)_2Cl_2]^-$ with sulphido anions. In this case, halide-ligand displacement gives compound (1) as shown in equation (2).

$$3\,[Ir(CO)_2Cl_2]^- + 2\,S^{2-} \longrightarrow$$
$$[Ir_3(\mu_3\text{-}S)_2(CO)_6]^- + 6\,Cl^- \quad (2)$$

The selenium-containing compounds are obtained similarly to the sulphur derivatives, together with some uncharacterized anionic carbonyl species, by reacting $[Ir_4(CO)_{12}]$ or $[Ir_6(CO)_{16}]$ with $SeCN^-$ at molar ratios of metal carbonyls to $SeCN^-$ ranging from 1:6 to 1:10. Also in this case the inter-mediate formation of the monosubstituted anions $[Ir_4(CO)_{11}\text{-}(SeCN)]^-$ or $[Ir_6(CO)_{14}(SeCN)]^-$ has been detected by i.r. spectroscopy. These monosubstituted anions, not previously reported, are best prepared from the corresponding neutral carbonyls by reaction with a slight excess of $K(SeCN)$ (molar ratio 1:1.1) in thf at room temperature, and similarly to the sulphur analogues, are decomposed to the trinuclear species by excess of $SeCN^-$ in hot solution.

Chemical Characterization of the $[Ir_3(\mu_3\text{-}X)_2(CO)_6]^-$ *Anions* (X = S *or* Se).—In the above reported syntheses the molar ratio of neutral carbonyl to XCN^- (X = S or Se) was kept in the range 1:6 to 1:10 in order to optimize the yields of the tri-nuclear species. Thus with lower molar ratios the formation of mixtures containing, in addition to the trinuclear species, an amount of intermediate tetra- and hexa-nuclear mono-substituted anions occurs. At higher molar ratios increasing amounts of insoluble by-products are observed which are practically the only product obtained when the molar ratio of metal carbonyl to XCN^- (X = S or Se) is greater than 1:15. This last observation indicates that the trinuclear derivatives are also decomposed by a large excess of XCN^- ions.

Anions (1) and (2) are diamagnetic and air stable in the solid state for a few days; no decomposition results upon refluxing in thf, under nitrogen, for several hours. Compound (1) is not affected by an excess of chloride ions and it does not react with a stoicheiometric amount of acid, whereas, with a large excess of HCl in dichloromethane, evolution of H_2S is observed, with formation of the $[Ir(CO)_2Cl_2]^-$ anion. Compounds (1) and (2) do not react either with carbon monoxide or hydrogen over a long period of time.
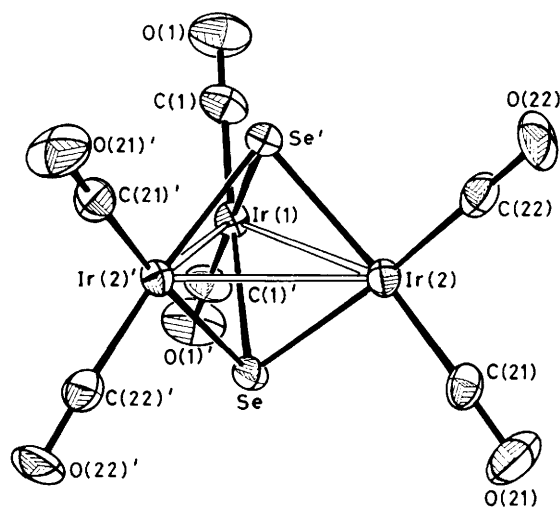
Spectroscopic Measurements.—Anions (1) and (2), in thf solution, show $v(CO)$ bands at 2 010vs, 1 965vs and at 2 005vs, 1 955vs cm^{-1}, respectively. These spectra are similar to those of the $[Ir(CO)_2Cl_2]^-$ complex [$v(CO)$ bands at 2 040vs, 1 955vs cm^{-1}] and are in keeping with the presence of two *cis* CO ligands around an Ir^I atom with square-planar co-ordination.

For both complexes the ^{13}C n.m.r. data are entirely consistent with the solid-state structure, in the range -95 to $+27\,°C$. The compound $[N(PPh_3)_2][Ir_3(\mu_3\text{-}S)_2(CO)_6]$ shows, in $[^2H_6]$ace-tone solution, a singlet at δ 174.3 p.p.m. (25 °C; downfield to the internal standard $SiMe_4$), which is shifted to δ 173.7 p.p.m. at $-90\,°C$. Similarly, $[N(PPh_3)_2][Ir_3(\mu_3\text{-}Se)_2(CO)_6]$ shows a singlet at δ 174.5 p.p.m. (27 °C) or at δ 173.9 p.p.m. ($-90\,°C$). The values of these resonances are comparable with the values of δ 170.3 p.p.m. (30 °C) or δ 169.8 p.p.m. ($-93\,°C$) found for $[N(PPh_3)_2][Ir(CO)_2Cl_2]$.

Description of the Structures.—Crystals of $[NMe_3(CH_2Ph)]$-$[Ir_3(\mu_3\text{-}S)_2(CO)_6]$ and $[NMe_4][Ir_3(\mu_3\text{-}Se)_2(CO)_6]$ suitable for *X*-ray structural investigation were obtained by slow diffusion of n-heptane into a thf solution of the salt.

Perspective views of the $[Ir_3(\mu_3\text{-}X)_2(CO)_6]^-$ anion (X = S or Se) are shown in Figures 1 and 2 respectively; bond distances and angles are reported in Tables 1 and 2 respectively. The anions (1) and (2) can be described as triangular arrangements of iridium atoms capped on each side by two triply bridging X atoms, with each metal atom bonded to two terminal carbonyls. For the sulphur derivative two different anions are present in the asymmetric unit: one anion with idealized D_{3h} symmetry and the other in which the symmetry is lowered to C_{2v}, due to the shortening of two Ir–Ir bonds and the lengthening of the remaining one. For the Se derivative the idealized symmetry is C_{2v}. As already observed in the case of the analogous derivatives of rhodium,[8] the metal–metal distances are exceptionally long if compared with the range of distances observed in tetra- and hexa-nuclear iridium carbonyl clusters (2.65—2.80 Å),[11,12,16-18] and are indicative of a weak metal–metal interaction. As a consequence, these distances are strongly influenced by inter-molecular factors such as packing forces, and the wide range of Ir–Ir separations observed is not surprising. The co-ordination geometry observed around the Ir atoms (see Table 3) is essentially square planar with only minor deviations from planarity.

Table 1. Interatomic distances (Å) and angles (°) within the anion $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ (1), with estimated deviations (e.s.d.s) in parentheses

Distances	Molecule A	Molecule B	Distances	Molecule A	Molecule B
Ir(1)–Ir(2)	3.065(1)	3.086(1)	Ir(2)–C(21)	1.86(2)	1.87(2)
Ir(1)–Ir(3)	3.064(1)	3.088(1)	Ir(2)–C(22)	1.86(2)	1.85(2)
Ir(2)–Ir(3)	3.127(1)	3.084(1)	Ir(3)–C(31)	1.81(2)	1.85(2)
Ir(1)–S(1)	2.361(4)	2.359(4)	Ir(3)–C(32)	1.83(2)	1.84(2)
Ir(1)–S(2)	2.361(4)	2.370(4)	C(11)–O(11)	1.15(2)	1.12(2)
Ir(2)–S(1)	2.375(4)	2.369(4)	C(12)–O(12)	1.16(2)	1.14(2)
Ir(2)–S(2)	2.357(4)	2.361(4)	C(21)–O(21)	1.11(2)	1.14(2)
Ir(3)–S(1)	2.366(4)	2.358(4)	C(22)–O(22)	1.16(2)	1.14(3)
Ir(3)–S(2)	2.361(4)	2.363(4)	C(31)–O(31)	1.18(2)	1.12(2)
Ir(1)–C(11)	1.83(2)	1.88(2)	C(32)–O(32)	1.16(2)	1.15(3)
Ir(1)–C(12)	1.83(2)	1.86(2)			

Angles	Molecule A	Molecule B	Angles	Molecule A	Molecule B
Ir(2)–Ir(1)–Ir(3)	61.36(2)	59.92(2)	S(1)–Ir(2)–C(21)	173.8(6)	174.0(5)
Ir(1)–Ir(2)–Ir(3)	59.30(2)	60.06(2)	S(2)–Ir(2)–C(22)	174.4(5)	174.7(6)
Ir(1)–Ir(3)–Ir(2)	59.34(2)	60.02(2)	S(1)–Ir(3)–C(31)	175.0(5)	175.3(5)
Ir(1)–S(1)–Ir(2)	80.6(1)	81.5(1)	S(2)–Ir(3)–C(32)	175.3(5)	174.6(5)
Ir(1)–S(1)–Ir(3)	80.8(1)	81.8(1)	S(1)–Ir(1)–C(12)	94.3(5)	94.9(5)
Ir(2)–S(1)–Ir(3)	82.5(1)	81.4(1)	S(2)–Ir(1)–C(11)	91.4(6)	92.3(4)
Ir(1)–S(2)–Ir(2)	81.0(1)	81.4(1)	S(1)–Ir(2)–C(22)	92.5(5)	92.8(5)
Ir(1)–S(2)–Ir(3)	80.9(1)	81.4(1)	S(2)–Ir(2)–C(21)	92.1(6)	92.5(5)
Ir(2)–S(2)–Ir(3)	83.0(1)	81.5(1)	S(1)–Ir(3)–C(32)	93.1(5)	92.6(6)
C(11)–Ir(1)–C(12)	92.0(8)	90.6(7)	S(2)–Ir(3)–C(31)	93.0(5)	93.4(5)
C(21)–Ir(2)–C(22)	93.2(8)	92.5(7)	Ir(1)–C(11)–O(11)	178.5(19)	175.0(19)
C(31)–Ir(3)–C(32)	91.6(7)	91.8(7)	Ir(1)–C(12)–O(12)	176.3(17)	178.7(16)
S(1)–Ir(1)–S(2)	82.3(1)	82.1(1)	Ir(2)–C(21)–O(21)	178.3(18)	179.0(17)
S(1)–Ir(2)–S(2)	82.1(1)	82.1(1)	Ir(2)–C(22)–O(22)	179.7(19)	177.1(17)
S(1)–Ir(3)–S(2)	82.2(1)	82.3(1)	Ir(3)–C(31)–O(31)	178.8(16)	178.7(18)
S(1)–Ir(1)–C(11)	173.6(6)	174.4(6)	Ir(3)–C(32)–O(32)	177.2(15)	179.0(19)
S(2)–Ir(1)–C(12)	176.5(6)	175.0(5)			

Table 2. Distances (Å) and angles (°) within the anion $[Ir_3(\mu_3\text{-}Se)_2(CO)_6]^-$ (2), with e.s.d.s in parentheses *

Distances

Ir(1)–Ir(2)	3.205(1)	Ir(2)–C(21)	1.82(1)
Ir(1)–Ir(2)'	3.099(1)	Ir(2)–C(22)	1.84(1)
Ir(1)–Se	2.482(1)	C(1)–O(1)	1.14(1)
Ir(2)–Se	2.477(1)	C(21)–O(21)	1.15(1)
Ir(2)'–Se	2.484(1)	C(22)–O(22)	1.16(2)
Ir(1)–C(1)	1.85(1)		

Angles

Ir(2)–Ir(1)–Ir(2)'	57.84(2)	Se–Ir(2)–Se'	84.92(4)
Ir(1)–Ir(2)–Ir(2)'	61.08(1)	Se–Ir(2)–C(21)	91.6(4)
Ir(1)–Se–Ir(2)	80.53(3)	Se'–Ir(2)–C(22)	89.9(4)
Ir(2)–Se–Ir(2)'	77.34(3)	C(21)–Ir(2)–C(22)	93.5(5)
Ir(1)–Se–Ir(2)'	80.38(3)	Se–Ir(2)–C(22)	174.8(4)
Se–Ir(1)–Se'	84.84(5)	Se'–Ir(2)–C(21)	175.2(4)
Se–Ir(1)–C(1)'	91.3(4)	Ir(1)–C(1)–O(1)	179.4(14)
C(1)–Ir(1)–C(1)'	92.6(8)	Ir(2)–C(21)–O(21)	174.4(13)
Se–Ir(1)–C(1)	176.0(4)	Ir(2)–C(22)–O(22)	176.6(14)

* The primed atoms are those generated by the crystallographic C_2 axis: $-x, y, \frac{1}{2} - z$.

Although a 48 valence-electron count (considering a sulphur atom as a four-electron donor) would also be in keeping with the presence of a saturated triangular metal cluster,[19] the anions (1) and (2) must be thought as derived from three square-planar Ir^I moieties sharing the two cis X atoms, in which each iridium atom achieves the 16-electron configuration usually found in d^8 square-planar complexes.

Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen atmosphere using the Schlenk-tube technique. $[Ir_4(CO)_{12}]$ was prepared by the carbonylation of $K_2[IrCl_6]$,[20] while $[Ir_6(CO)_{16}]$,[21] $[Ir_6(CO)_{15}]^{2-}$,[16,21] and $[Ir(CO)_2Cl_2]^-$ [22] were prepared as described in the literature. The compounds K(SCN), K(SeCN), and potassium polysulphide (K_2S_x, $x = 1—8$) were Fluka analytical grade products. $[N(PPh_3)_2]_2S$ was prepared by metathesis in water from $[N(PPh_3)_2]Cl$ and Na_2S.

Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer and on a Nicolet MX-1FT IR instrument, using calcium fluoride cells previously purged with N_2. Carbon-13 n.m.r. measurements were carried out on a Bruker WP 80 spectrometer. Carbon-13 carbonyl enrichments (*ca.* 30%) were carried out by direct exchange with ^{13}CO using standard vacuum-line techniques.

Preparation of Sulphur Derivatives.—(*a*) *From* $[Ir_4(CO)_{12}]$ *and* K(SCN). To a suspension of $[Ir_4(CO)_{12}]$ (0.52 g, 0.47 mmol) in thf (30 cm^3) under nitrogen was added K(SCN) (0.364 g, 3.76 mmol). The suspension was refluxed for 12 h to give a solution of the potassium salt of the trinuclear anion together with an insoluble by-product. The reaction mixture was filtered and the volume of the filtered solution was reduced, in vacuum, to 10 cm^3 and then added dropwise to an aqueous solution (75 cm^3) of $[NMe_3(CH_2Ph)]Cl$ (1.0 g). The resulting pale yellow precipitate was filtered off, washed with water (3 × 10 cm^3), and dried *in vacuo*. $[NMe_3(CH_2Ph)][Ir_3(\mu_3\text{-}S)_2(CO)_6]$: yield 0.292 g (48%) (Found: C, 20.4; H, 1.8; Ir, 62.2; N, 1.6. $C_{16}H_{16}Ir_3NO_6S_2$ requires C, 20.0; H, 1.7; Ir, 60.1; N, 1.5%). The compound is soluble in thf, CH_2Cl_2, $CHCl_3$, MeCN, and Me_2CO, and insoluble in aliphatic and aromatic hydrocarbons.

Using the same technique the anion (1) can be isolated as a salt of bulky cations such as $[NMe_4]^+$, $[NEt_4]^+$, $[PPh_4]^+$, and $[N(PPh_3)_2]^+$.

Table 3. Least-squares planes in the form $Ax + By + Cz + D = 0$

(*i*) Equations of planes through selected groups of atoms

Plane	Atoms	A	B	C	D
1[a]	Ir(1), S(1), S(2), C(11), C(12)	−0.5403	0.8365	−0.0912	−1.1591
2[a]	Ir(2), S(1), S(2), C(21), C(22)	0.4735	0.8209	−0.3191	−1.3441
3[a]	Ir(3), S(1), S(2), C(31), C(32)	0.9748	0.0301	−0.2211	−0.0802
4[b]	Ir(1), S(1), S(2), C(11), C(12)	−0.5799	0.8113	−0.0740	9.0079
5[b]	Ir(2), S(1), S(2), C(21), C(22)	0.3920	0.8699	−0.2994	4.3778
6[b]	Ir(3), S(1), S(2), C(31), C(32)	0.9751	0.0848	−0.2047	−3.9968
7	Ir(2), Se, Se′, C(21), C(22)	−0.4092	−0.8689	−0.2784	−0.4887

(*ii*) Distances (10^{-3} Å) of selected atoms from planes, with e.s.d.s in parentheses

Plane										
1[a]	Ir(1)	8(1),	S(1)	−13(4),	S(2)	10(4),	C(11)	−16(16),	C(12)	11(16)
2[a]	Ir(2)	25(1),	S(1)	−12(4),	S(2)	2(4),	C(21)	−15(16),	C(22)	1(16)
3[a]	Ir(3)	9(1),	S(1)	−12(4),	S(2)	8(4),	C(31)	−15(16),	C(32)	9(15)
4[b]	Ir(1)	−35(1),	S(1)	−19(4),	S(2)	34(4),	C(11)	−21(16),	C(12)	41(15)
5[b]	Ir(2)	30(1),	S(1)	−15(4),	S(2)	3(4),	C(21)	−19(15),	C(22)	2(15)
6[b]	Ir(3)	2(1),	S(1)	−25(4),	S(2)	24(4),	C(31)	−29(16),	C(32)	28(16)
7	Ir(2)	30(1),	Se	15(1),	Se′	−27(1),	C(21)	−35(12),	C(22)	18(15)

[a] Molecule A. [b] Molecule B.

Table 4. Summary of crystal data and intensity collection parameters

Formula	$C_{16}H_{16}Ir_3NO_6S_2$	$C_{10}H_{12}Ir_3NO_6Se_2$
M	1 918.07	976.79
System	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
a/Å	9.303(2)	15.930(3)
b/Å	17.295(3)	7.877(2)
c/Å	28.274(4)	15.040(2)
β/°	94.19(2)	108.22(2)
U/Å³	4 537(2)	1 793(1)
Z	8	4
D_c/g cm⁻³	2.808	3.619
$\mu(Mo\text{-}K_\alpha)$/cm⁻¹	176.99	261.81
Scan mode	ω	ω
θ range (°)	3—25	3—27
ω-scan width (°)	1 + 0.35 tan θ	1.1 + 0.35 tan θ
Scan rate (° min⁻¹)	3—10	2—10
Octants in the reciprocal space explored	+h, +k, ±l	+h, +k, ±l
Measured reflections	10 376	1 762
Unique observed reflections $[I \geqslant 3\sigma(I)]$	3 676	1 045
R, R'	0.027, 0.032	0.025, 0.032
Transmission factors	0.99—0.64	0.98—0.54

(*b*) *From* $[Ir_6(CO)_{16}]$ *and* K(SCN). $[Ir_6(CO)_{16}]$ (0.33 g, 0.2 mmol) and K(SCN) (0.12 g, 1.23 mmol) were refluxed in thf (50 cm³) for 6 h and the resulting mixture worked-up as described in (*a*); yield 0.249 g (65%) as $[NMe_3(CH_2Ph)]^+$ salt.

(*c*) *From* $[Ir_4(CO)_{12}]$ *and potassium polysulphide.* $[Ir_4(CO)_{12}]$ (0.65 g, 0.59 mmol) and potassium polysulphide (0.55 g) in MeOH (20 cm³) were stirred at room temperature for 20 h and the product was separated as described in (*a*); yield 0.436 g (58%) as $[NMe_3(CH_2Ph)]^+$ salt.

(*d*) *From* $[Ir_6(CO)_{16}]$ *and potassium polysulphide.* $[Ir_6(CO)_{16}]$ (0.22 g, 0.14 mmol) and potassium polysulphide (0.65 g) in MeOH (40 cm³) were stirred at room temperature for 14 h and the product was isolated as described in (*a*); yield 0.189 g (70%) as $[NMe_3(CH_2Ph)]^+$ salt.

(*e*) *Reaction of* $[N(PPh_3)_2][Ir_4(CO)_{11}(SCN)]$ *or* $[N(PPh_3)_2][Ir_6(CO)_{14}(SCN)]$ *with* K(SCN). A solution of $[N(PPh_3)_2][Ir_4(CO)_{11}(SCN)]$ (0.43 g, 0.26 mmol) in thf (30

cm³) was refluxed for 3 h with K(SCN) (0.126 g, 1.3 mmol) and the compound was separated as described in (*a*). $[N(PPh_3)_2][Ir_3(\mu_3\text{-}S)_2(CO)_6]$: yield 0.336 g (72%).

Compound (**1**) was prepared *via* similar reaction starting from $[N(PPh_3)_2][Ir_6(CO)_{14}(SCN)]$ (0.315 g, 0.15 mmol) and K(SCN) (0.073 g, 0.75 mmol); yield 0.283 g (70%).

(*f*) *Reaction of* $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ *with sulphur.* A solution of $[N(PPh_3)_2]_2[Ir_6(CO)_{15}]$ (0.81 g, 0.30 mmol) in thf (25 cm³) was stirred at room temperature for 2 h with sulphur (0.048 g, 1.5 mmol). The i.r. spectrum of the solution indicated the formation of the trinuclear species only.

(*g*) *Reaction of* $[N(PPh_3)_2][Ir(CO)_2Cl_2]$ *with* $[N(PPh_3)_2]_2S$. This reaction was accomplished as reported in (*f*) using $[N(PPh_3)_2][Ir(CO)_2Cl_2]$ (0.685 g, 0.8 mmol) and $[N(PPh_3)_2]_2S$ (1.5 g, 1.35 mmol); yield 0.8 g (75%).

(*h*) *Reaction of* $[N(PPh_3)_2][Ir_3(\mu_3\text{-}S)_2(CO)_6]$ *with* HCl. $[N(PPh_3)_2][Ir_3(\mu_3\text{-}S)_2(CO)_6]$ (0.415 g, 0.31 mmol) in dichloromethane (25 cm³) was stirred with aqueous concentrated HCl solution (12 mol dm⁻³, 1.0 cm³). A slow evolution of H₂S took place while the i.r. spectrum of the CH₂Cl₂ phase showed that the $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ anion was transformed into $[Ir(CO)_2Cl_2]^-$.

Preparation of the Selenium Derivatives.—Synthesis of $[Ir_3(\mu_3\text{-}Se)_2(CO)_6]^-$. This compound was obtained similarly to the analogous sulphur derivative by reacting $[Ir_4(CO)_{12}]$ or $[Ir_6(CO)_{16}]$ with K(SeCN) in refluxing thf and treating the resulting solution containing the potassium salt as reported in the corresponding section (*a*). In a typical experiment, reaction of $[Ir_4(CO)_{12}]$ (0.964 g, 0.87 mmol) in refluxing thf (75 cm³) with K(SeCN) (1.2 g, 8.3 mmol) for 3 h yielded $[NMe_3(CH_2Ph)][Ir_3(\mu_3\text{-}Se)_2(CO)_6]$; yield 0.85 g (70%).

Similarly, refluxing a thf (50 cm³) suspension of $[Ir_6(CO)_{16}]$ (0.35 g, 0.22 mmol) for 3 h with K(SeCN) (0.2 g, 1.38 mmol) gave 0.296 g (69% yield) of $[NMe_4][Ir_3(\mu_3\text{-}Se)_2(CO)_6]$ (Found: C, 12.0; H, 1.3; Ir, 56.9; N, 1.6. $C_{10}H_{12}Ir_3NO_6Se_2$ requires C, 12.3; H, 1.2; Ir, 59.0; N, 1.4%).

The anion has been also isolated as salts of $[NEt_4]^+$, $[PPh_4]^+$, $[AsPh_4]^+$, $[NEt_3(CH_2Ph)]^+$, $[N(PPh_3)_2]^+$ and $[PPh_3(CH_2Ph)]^+$. These salts are soluble in thf, acetone, and CH₂Cl₂, and insoluble in aliphatic and aromatic hydrocarbons.

Table 5. Fractional atomic co-ordinates for complex (1) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Ir(1A)	0.395 58(6)	0.122 51(3)	0.642 02(2)	C(22B)	0.223(2)	0.5726(9)	0.5456(6)
Ir(2A)	0.712 26(6)	0.120 94(3)	0.618 81(2)	O(22B)	0.271(1)	0.5416(8)	0.5149(4)
Ir(3A)	0.529 07(6)	0.272 25(3)	0.607 37(2)	C(31B)	-0.051(2)	0.857(1)	0.6183(5)
Ir(1B)	-0.179 35(6)	0.609 60(3)	0.617 02(2)	O(31B)	-0.046(1)	0.9129(7)	0.6386(4)
Ir(2B)	0.138 19(6)	0.624 52(3)	0.593 42(2)	C(32B)	-0.116(2)	0.8185(9)	0.5286(6)
Ir(3B)	-0.062 97(6)	0.766 24(3)	0.583 94(2)	O(32B)	-0.151(2)	0.8508(8)	0.4939(4)
S(1A)	0.5000(4)	0.1501(2)	0.5703(1)	N(1)	0.433(1)	-0.1548(6)	0.5791(4)
S(2A)	0.5943(4)	0.1949(2)	0.6743(1)	C(M1)	0.535(2)	-0.0887(9)	0.5689(6)
S(1B)	-0.0789(4)	0.6449(2)	0.5459(1)	C(M2)	0.298(2)	-0.150(1)	0.5467(6)
S(2B)	0.0091(4)	0.6891(2)	0.6505(1)	C(M3)	0.513(2)	-0.230(1)	0.5691(6)
C(11A)	0.333(2)	0.1051(9)	0.7010(6)	C(B1)	0.391(2)	-0.1548(8)	0.6307(5)
O(11A)	0.297(2)	0.0937(8)	0.7384(4)	C(B2)	0.515(1)	-0.1533(8)	0.6659(5)
C(12A)	0.245(2)	0.0674(9)	0.6133(6)	C(B3)	0.570(2)	-0.081(1)	0.6843(6)
O(12A)	0.150(1)	0.0348(8)	0.5930(5)	C(B4)	0.690(2)	-0.082(1)	0.7184(7)
C(21A)	0.867(2)	0.1006(9)	0.6623(6)	C(B5)	0.749(2)	-0.154(1)	0.7341(7)
O(21A)	0.958(1)	0.0867(8)	0.6882(4)	C(B6)	0.697(2)	-0.221(1)	0.7170(7)
C(22A)	0.788(2)	0.0625(9)	0.5716(7)	C(B7)	0.580(2)	-0.223(1)	0.6846(6)
O(22A)	0.835(1)	0.0258(7)	0.5418(5)	N(2)	0.481(1)	-0.1516(6)	0.8921(4)
C(31A)	0.552(2)	0.3615(8)	0.6407(5)	C(M4)	0.358(2)	-0.0988(9)	0.9071(6)
O(31A)	0.569(1)	0.4196(6)	0.6620(4)	C(M5)	0.607(2)	-0.137(1)	0.9255(6)
C(32A)	0.476(2)	0.3249(8)	0.5527(6)	C(M6)	0.427(2)	-0.235(1)	0.8981(6)
O(32A)	0.438(1)	0.3563(7)	0.5179(4)	C(B8)	0.518(2)	-0.1336(9)	0.8427(5)
C(11B)	-0.247(2)	0.5885(9)	0.6766(6)	C(B9)	0.398(2)	-0.1391(8)	0.8057(5)
O(11B)	-0.277(1)	0.5743(6)	0.7133(4)	C(B10)	0.365(2)	-0.212(1)	0.7829(6)
C(12B)	-0.332(2)	0.5545(8)	0.5875(5)	C(B11)	0.247(2)	-0.218(1)	0.7499(7)
O(12B)	-0.426(1)	0.5203(6)	0.5701(4)	C(B12)	0.163(2)	-0.155(1)	0.7379(7)
C(21B)	0.298(2)	0.6090(8)	0.6364(6)	C(B13)	0.191(2)	-0.083(1)	0.7579(7)
O(21B)	0.395(1)	0.5984(7)	0.6625(4)	C(B14)	0.313(2)	-0.076(1)	0.7940(6)

Table 6. Fractional atomic co-ordinates for complex (2) with e.s.d.s in parentheses

Atom	x	y	z
Ir(1)	0.000	-0.262 63(8)	0.250
Ir(2)	-0.093 92(3)	0.093 51(6)	0.177 79(3)
Se	0.043 78(7)	-0.0300(2)	0.162 25(7)
C(1)	-0.0375(8)	-0.425(2)	0.3184(9)
O(1)	-0.0610(8)	-0.524(1)	0.3602(7)
C(21)	-0.1212(8)	0.190(2)	0.0621(8)
O(21)	-0.1353(9)	0.263(2)	-0.0074(7)
C(22)	-0.1927(9)	0.179(2)	0.2006(8)
O(22)	-0.2524(6)	0.239(2)	0.2183(7)
N	0.220(2)	0.214(3)	-0.025(2)
C(M1)	0.169(2)	0.312(5)	0.025(2)
C(M2)	0.265(3)	0.121(5)	0.079(3)
C(MX)	0.208(4)	0.208(7)	0.059(4)
C(MY)	0.199(4)	0.363(8)	-0.031(4)

X-*Ray Analyses.—Intensity data collection.* Well formed prismatic crystals of [NMe₃(CH₂Ph)][Ir₃(μ₃-S)₂(CO)₆] (pale yellow, dimensions $0.14 \times 0.20 \times 0.22$ mm) and [NMe₄][Ir₃(μ₃-Se)₂(CO)₆] (yellow, dimensions $0.12 \times 0.14 \times 0.28$ mm) were used for data collection. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo-K_α radiation ($\bar{\lambda} = 0.710\ 73$ Å) with a graphite-crystal monochromator in the incident beam. Crystal data and collection details are summarized in Table 4. Standard CAD-4 setting, indexing, and data-collection programs were used. A periodic remeasurement of three standard reflections revealed a crystal decay which was evaluated on F_o at ca. 6% and 20% for species (1) and (2) respectively at the end of data collection. Lorentz, polarization, decay, and absorption corrections were applied, the latter performed with the empirical method described in ref. 23. For both compounds the structure solution was carried out by Patterson and Fourier methods and the refinement was by full-matrix least-squares methods; the mini-

mized function was $\Sigma w(F_o - K|F_c|)^2$. Individual weights were given as $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (iI)^2]^{\frac{1}{2}}/Lp$, and i (the 'ignorance factor') = 0.03 and 0.04 for compounds (1) and (2) respectively. Scattering factors and anomalous dispersion corrections were taken from ref. 24.

All computations were done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants tabulated therein.[25]

The positional parameters for compounds (1) and (2) are reported in Tables 5 and 6 respectively. Final difference Fourier maps showed only peaks not exceeding 0.3 e Å⁻³ near to the metal atoms.

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