Aggregation of *fac*-$[Ir(aet)_3]$ (aet = 2-aminoethanethiolate) around the $[Co^{II}{}_4O]^{6+}$ Core. Structures and Some Properties of Spontaneously Resolved S-Bridged Octanuclear Complexes $[\{Ir(aet)_3\}_4M_4O]Br_6$ (M_4 = $Co^{II}{}_4$, $Zn^{II}{}_4$ or $Zn^{II}{}_{2.8}Co^{II}{}_{1.2}$)†

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Novel S-bridged octanuclear complexes, $[\{Ir(aet)_3\}_4M_4O]Br_6$ [aet = 2-aminoethanethiolate; M = Co^{II} **1**, Zn^{II} **2** or M_4 = $Zn^{II}{}_{2.8}Co^{II}{}_{1.2}$ **3**], containing a tetrahedral M_4O core, have been prepared. In the octanuclear complexes, the cobalt(II) oxidation state is stabilized and the species are not oxidized to Co^{III} either in the crystalline state or in aqueous solution. The crystal structure and absolute configuration of the spontaneously resolved $(-)^{CD}_{300}$ isomer for each of **1** and **3** were determined by single-crystal X-ray diffraction. The four octahedral *fac*-$[Ir(aet)_3]$ sub-units aggregate around the tetrahedral $[M_4O]^{6+}$ core in a tetrahedral arrangement. The chiral configurations of the $(-)^{CD}_{300}$ isomer for each of **1** and **3** is Δ for all four *fac*-$[Ir(aet)_3]$ sub-units and *S* for all 12 bridging sulfur atoms. Cyclic voltammetric measurements for **1** in water exhibited a reversible redox couple at −0.97 V (*vs.* Ag–AgCl), which corresponds to the $[Co_4O]^{6+}$–$[Co_4O]^{5+}$ redox reaction. The electronic absorption, circular dichroism (CD), ^1H and ^{13}C NMR spectral behaviour of these complexes are discussed in relation to the geometry of the tetrahedral Co^{II}.

Recently, S- or Se-bridged polynuclear complexes such as $[\{M(NH_2CH_2CH_2E)_3\}_4Zn_4O]^{6+}$ (M = Co^{III} or Rh^{III}, E = S or Se) containing a tetrahedral M_4O core have been investigated by spectrochemical, stereochemical and electrochemical techniques.[1–5] In these complexes, four *fac*-$[M(NH_2CH_2CH_2E)_3]$ units aggregate around a $[Zn_4O]^{6+}$ core to give an octanuclear structure. The S-bridged complexes, in which each of the four Zn^{II} centres has a tetrahedral geometry, were selectively formed and spontaneously resolved as the ΔΔΔΔ or ΛΛΛΛ isomers, and are stable in solution.[1–3,5] The unique structure and properties of the S-bridged polynuclear complexes will depend mainly on whether the tetrahedral aggregation of four *fac*-$[M(aet)_3]$ (aet = 2-aminoethanethiolate) sub-units is a consequence of the specific stereochemical behaviour of Zn^{II} in forming the $[Zn_4O]$ core. In order to elucidate the selective formation and properties of these octanuclear complexes, we studied the reaction of *fac*-$[Ir(aet)_3]$ with Co^{II}, which can assume either octahedral or tetrahedral coordination geometries, and the reaction of the linear S-bridged trinuclear complex, $[Co^{III}\{Ir(aet)_3\}_2]^{3+}$, in which Co^{III} is octahedral, with Zn powder. When Co^{2+} is octahedrally coordinated by six sulfur atoms from two *fac*-$[Ir(aet)_3]$ moieties, it is readily oxidized to Co^{III}.[6–8] However, it is expected that the Co^{II} oxidation state would be stabilized, if it is incorporated in the tetrahedral cage-type structure in an enforced tetrahedral geometry. Furthermore, the synthesis of such complexes composed of *fac*-$[Ir(aet)_3]$ sub-units will prove helpful for clarifying the spectrochemical contribution of tetrahedral Co^{II}, especially in the visible region, since *fac*-$[Ir(aet)_3]$ shows no absorption bands in this region.[8] The present paper deals with the preparation, structure and some properties of the novel spontaneously resolved S-bridged polynuclear complexes, $[\{Ir(aet)_3\}_4M_4O]^{6+}$ (M = Co^{II} **1**, Zn^{II} **2** or M_4 = $Zn_{2.8}Co_{1.2}$ **3**).

Experimental

Materials.—Cobalt(II) oxide and zinc(II) bromide were purchased from Wako Pure Chemicals Ind. Ltd. All chemicals were of reagent grade and were used without further purification.

Syntheses.—$[\{Ir(aet)_3\}_4Co_4O]Br_6{\cdot}9.5H_2O$ **1**. To a suspension of *fac*-$[Ir(aet)_3]$[8] (0.30 g, 0.7 mmol) in water (35 cm^3) was added CoO (0.72 g, 9.6 mmol) under a nitrogen atmosphere. The mixture was stirred at 80 °C for 10 min, and then $CoBr_2$ (0.72 g, 3.3 mmol) was added. After stirring at 80 °C for 4 h under a nitrogen atmosphere, the reaction mixture was filtered to remove insoluble materials. The black-brown filtrate was allowed to stand at room temperature for 2 d. The resulting black crystals, which were spontaneously resolved, were collected by filtration. One of these crystals, which showed a negative CD spectrum at 300 nm, was used for X-ray crystal structure analysis. Yield: 0.30 g (66%) (Found: C, 11.35; H, 3.40; Co, 8.95; Ir, 29.10; N, 6.45. Calc. for $C_{24}H_{72}Br_6Co_4Ir_4N_{12}OS_{12}{\cdot}9.5H_2O$: C, 11.15; H, 3.55; Co, 9.10; Ir, 29.75, N, 6.50%).

$[\{Ir(aet)_3\}_4Zn_4O]Br_6{\cdot}9.5H_2O$ **2**. To a suspension of *fac*-$[Ir(aet)_3]$ (0.60 g, 1.4 mmol) in water (30 cm^3) was added ZnO (1.35 g, 16.6 mmol) and $ZnBr_2$ (1.16 g, 5.2 mmol). After stirring at room temperature for 1.5 h, the mixture was centrifuged and filtered to remove insoluble materials. To the pale yellow filtrate were added several drops of a saturated NaBr solution, followed by standing at room temperature for 3 d. The resulting white-yellow crystals, which were spontaneously resolved, were collected by filtration. Yield: 0.43 g (46%). This complex (0.11 g) was recrystallized from water (2.8 cm^3) at room temperature. Yield: 0.07 g (Found: C, 11.15; H, 3.55; Ir, 27.95; N, 6.35; Zn, 9.70. Calc. for $C_{24}H_{72}Br_6Ir_4N_{12}OS_{12}Zn_4{\cdot}9.5H_2O$: C, 11.05; H, 3.50; Ir, 29.45; N, 6.45; Zn, 10.00%).

$[\{Ir(aet)_3\}_4Zn_{2.8}Co_{1.2}O]Br_6{\cdot}9.5H_2O$ **3**. To a dark brown solution of $[Co\{Ir(aet)_3\}_2][NO_3]_3{\cdot}H_2O$[8] (0.3 g, 0.3 mmol) in water (30 cm^3) was added Zn powder (0.9 g, 13.8 mmol). Stirring the mixture at room temperature produced $[Co^{II}\{Ir(aet)_3\}_2][NO_3]_2$ as a purple precipitate in a few minutes, which

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

gradually dissolved to give a green solution after 1 h. To this green solution was added $ZnBr_2$ (1.0 g, 4.4 mmol), followed by stirring at room temperature for 1 h. After unreacted Zn powder was filtered off, the deep green filtrate was allowed to stand at room temperature for several days. The resulting dark green crystals, which were spontaneously resolved, were collected by filtration and recrystallized from water at room temperature. One of these crystals, which showed a negative CD sign at 300 nm, was used for X-ray crystal structure analysis. Yield: 0.3 g (Found: C, 11.20; H, 3.45; Co, 2.65; Ir, 28.85; N, 6.55; Zn, 6.85. Calc. for $C_{24}H_{72}Br_6Co_{1.2}Ir_4N_{12}OS_{12}Zn_{2.8}\cdot 9.5H_2O$: C, 11.05; H, 3.50; Co, 2.70; Ir, 29.55; N, 6.45; Zn, 7.05%).

Measurements.—The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer and CD spectra with a JASCO J-600 spectropolarimeter. All measurements were carried out in aqueous solutions at room temperature. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer in D_2O at the probe temperature. Sodium 4,4-dimethyl-4-silapentanesulfonate was employed as an internal reference. The concentrations of iridium, cobalt and zinc in the complexes were determined by plasma spectral analyses, on a Jarrel-Ash model 96–975 emission spectrophotometer. Electrochemical measurements were made with a CV-1B apparatus [Bioanalytical Systems, Inc., BAS)] using a glassy-carbon working electrode (BAS, GCE). An aqueous Ag–AgCl–NaCl (3 mol dm^{-3}) electrode (BAS, RE-1) and platinum wires were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22 °C in aqueous solutions containing 0.1 mol dm^{-3} $NaNO_3$ as supporting electrolyte and employing complex concentrations of 1.0 mmol dm^{-3}.

Crystallography.—*Data collection*. Unit-cell parameters and intensity data for the spontaneously resolved crystals $(-)^{\mathrm{CD}}_{300}$-**1** and $(-)^{\mathrm{CD}}_{300}$-**3** were measured on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell dimensions were determined by least-squares refinement of 25 reflections. The intensity data were collected by the ω–2θ scan technique and the scan rate was varied from 1 to 5° min^{-1} (in ω). Three intensity standards were monitored every 2 h of the X-ray exposure time and a linear decay correction was applied (correction factor on I: 1.000–1.007 for **1**, 1.000–1.005 for **3**). The orientation (for the same three reflections) was monitored after every 200th scan. The intensities were corrected for Lorentz and polarization factors. An empirical absorption correction based on a series of ψ scans was applied (transmission factor on I: 0.80–1.00 for **1**, 0.84–1.00 for **3**).

Crystal data. $[\{Ir(aet)_3\}_4Co_4O]Br_6\cdot 9.5H_2O$ **1**, $C_{24}H_{91}Br_6Co_4Ir_4N_{12}S_{12}O_{10.5}$, M = 2584.89, cubic, space group $P2_13$ (no. 198), a = 19.033(1) Å, U = 6895.1(4) Å^3, D_c = 2.49 g cm^{-3} (Z = 4), $F(000)$ = 4884, μ(Mo-Kα) = 124.5 cm^{-1}, black crystal 0.18 × 0.23 × 0.23 mm, N_o = 1960, R = 0.035, R' = 0.032 $\{w = 2.8787/[\sigma^2(F_o) + 0.000\,169|F_o|^2]\}$. Refinement assuming enantiomeric structure: R = 0.057, R' = 0.056 $\{w = 3.6910/[\sigma^2(F_o) + 0.000\,301|F_o|^2]\}$.

$[\{Ir(aet)_3\}_4Zn_{2.8}Co_{1.2}O]Br_6\cdot 9.5H_2O$ **3**, $C_{24}H_{91}Br_6Co_{1.2}Ir_4N_{12}S_{12}O_{10.5}Zn_{2.8}$, M = 2602.97, cubic, space group $P2_13$ (no. 198), a = 19.096(1) Å, U = 6963.3(4) Å^3, D_c = 2.48 g cm^{-3} (Z =4), $F(000)$ = 4918, μ(Mo-Kα) = 126.9 cm^{-1}, dark green crystal 0.15 × 0.15 × 0.18 mm, N_o = 1861, R = 0.050, R' = 0.049 $\{w = 1.9543/[\sigma^2(F_o) + 0.001\,075|F_o|^2]\}$. Refinement assuming enantiomeric structure: R = 0.067, R' = 0.067 $\{w = 2.7013/[\sigma^2(F_o) + 0.000\,955|F_o|^2]\}$.

Structure analysis and refinement. For both $(-)^{\mathrm{CD}}_{300}$ isomers of **1** and **3**, the systematic absences led to the choice of either the space group $P2_12_12_1$ (no. 19) or $P2_13$ (no. 198). Initially, the structure of **3** was solved by using the space group $P2_12_12_1$. The Ir and Zn atom positions were determined by direct methods and other non-hydrogen atom positions were determined by successive Fourier difference maps. All atoms of the complex cation exist almost on the positions expected for the site symmetry of the space group $P2_13$. Hence, this space group was assumed and this assignment was confirmed by the eventual structure refinement. The structure of **1** was almost isostructural with that of **3**. The Ir(B), Zn(B) or Co(B), and O atoms, four Br atoms [Br(2), Br(3A) and Br(3B) for **1** and **3**; Br(4A) for **1**, Br(4) for **3**], and one O atom of the water molecule [O(4W) for **1** and **3**] were constrained to special positions of symmetry element 3. Three [Br(1), Br(3) and Br(4) for **1**] or two [Br(1) and Br(3) for **3**] of four independent Br atoms exhibited positional disorder and were best modelled with two positions for each atom (Tables 1 and 2). The hydrogen atoms in **1** and **3** were not included in the calculation. The structures of $(-)^{\mathrm{CD}}_{300}$-**1** and $(-)^{\mathrm{CD}}_{300}$-**3** were refined by full-matrix least squares using anisotropic thermal parameters for all the non-hydrogen atoms. For both **1** and **3** the enantiomeric structure could be rejected at the 0.005 significance level by the Hamilton test.[9] All calculations were performed with SHELX 76[10] on the Facom M-1800/20 computer in the Computer Centre of the University of Tsukuba and the molecular illustration was drawn using PLUTO on a Vax computer using SDP/VAX.[11] Scattering factors were taken from ref. 12. The final atomic parameters are listed in Tables 1 and 2 for **1** and **3** respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

Results and Discussion

Crystal Structure of $(-)^{\mathrm{CD}}_{300}$-$[\{Ir(aet)_3\}_4M_4O]Br_6$ (M_4 = Co_4 *or* $Zn_{2.8}Co_{1.2}$).—Compounds **1** and **3**, which are spontaneously resolved and exhibit a negative CD spectrum at 300 nm, are isostructural with each other, and a perspective drawing of the entire complex cation for $(-)^{\mathrm{CD}}_{300}$-**1** is shown in

Table 1 Final atomic coordinates and occupancy factors (o.f.) for non-H atoms of $[\{Ir(aet)_3\}_4Co_4O]Br_6$

Atom	x	y	z	o.f.
Ir(A)	0.064 75(3)	0.143 91(3)	0.868 00(3)	
Ir(B)	0.188 72(3)	x	x	$\frac{1}{3}$
Co(A)	0.162 0(1)	0.067 4(1)	1.029 30(9)	
Co(B)	0.008 0(1)	x	x	$\frac{1}{3}$
O	0.066 4(4)	x	x	$\frac{1}{3}$
S(1A)	0.167 6(2)	0.145 2(2)	0.935 1(2)	
S(2A)	−0.009 1(2)	0.189 3(2)	0.955 2(2)	
S(3A)	0.038 6(2)	0.026 2(2)	0.891 0(2)	
S(1B)	0.237 4(2)	0.100 6(2)	1.118 6(2)	
N(1A)	0.130 9(7)	0.110 5(7)	0.785 6(6)	
N(2A)	0.083 5(7)	0.251 4(6)	0.843 8(7)	
N(3A)	−0.023 1(7)	0.140 4(7)	0.800 1(7)	
N(1B)	0.272 5(7)	0.250 1(6)	1.151 6(7)	
C(1A)	0.227(1)	0.101(1)	0.868(1)	
C(2A)	0.202(1)	0.103(2)	0.803(1)	
C(3A)	0.007 1(9)	0.285 6(8)	0.942 8(8)	
C(4A)	0.079(1)	0.294 6(8)	0.907(1)	
C(5A)	−0.046(1)	0.022(1)	0.842(1)	
C(6A)	−0.050(2)	0.069(2)	0.782(1)	
C(1B)	0.310 7(9)	0.150(1)	1.080(1)	
C(2B)	0.302(1)	0.224(1)	1.083(1)	
Br(1A)	0.693 5(2)	0.251 9(2)	0.574 1(2)	0.85
Br(1B)	0.671(1)	0.236 6(9)	0.516(2)	0.15
Br(2)	−0.076 2(1)	$\frac{1}{2} + x$	$-x$	$\frac{1}{3}$
Br(3A)	−0.296 3(3)	$\frac{1}{2} + x$	$-x$	$\frac{1}{6}$
Br(3B)	−0.266 8(4)	$\frac{1}{2} + x$	$-x$	$\frac{1}{6}$
Br(4A)	0.413(1)	x	x	$\frac{1}{9}$
Br(4B)	0.427(3)	0.422(2)	0.374(2)	$\frac{1}{9}$
O(1W)	0.611(1)	0.529(1)	0.277(1)	
O(2W)	0.553(1)	0.521(1)	0.409(1)	
O(3W)	0.821(1)	0.158 0(9)	0.445(1)	
O(4W)	0.317(2)	x	x	$\frac{1}{6}$

Table 2 Final atomic coordinates and occupancy factors (o.f.) for non-H atoms of $[\{Ir(aet)_3\}_4Zn_{2.8}Co_{1.2}O]Br_6$*

Atom	*x*	*y*	*z*	o.f.
Ir(A)	0.064 80(5)	0.143 27(5)	0.866 42(4)	
Ir(B)	0.188 73(4)	*x*	*x*	$\frac{1}{3}$
Zn(A)	0.162 1(1)	0.066 8(1)	1.028 8(1)	0.97
Zn(B)	0.007 0(1)	*x*	*x*	0.3233
O	0.066 3(7)	*x*	*x*	$\frac{1}{3}$
S(1A)	0.167 5(3)	0.143 7(3)	0.933 0(3)	
S(2A)	−0.008 9(3)	0.188 5(3)	0.953 1(3)	
S(3A)	0.038 5(4)	0.026 2(3)	0.889 2(3)	
S(1B)	0.237 7(3)	0.101 1(3)	1.118 9(3)	
N(1A)	0.130(1)	0.109(1)	0.784(1)	
N(2A)	0.084(1)	0.250(1)	0.844(1)	
N(3A)	−0.024(1)	0.142(1)	0.799(1)	
N(1B)	0.273 8(9)	0.250(1)	1.152(1)	
C(1A)	0.225(1)	0.099(2)	0.871(1)	
C(2A)	0.200(2)	0.101(3)	0.802(2)	
C(3A)	0.006(2)	0.285(1)	0.943(1)	
C(4A)	0.079(1)	0.293(1)	0.905(2)	
C(5A)	−0.047(2)	0.021(2)	0.843(2)	
C(6A)	−0.051(3)	0.066(3)	0.780(2)	
C(1B)	0.310(2)	0.149(2)	1.079(2)	
C(2B)	0.305(2)	0.222(2)	1.085(2)	
Br(1A)	0.695 6(4)	0.250 0(3)	0.574 1(3)	$\frac{4}{5}$
Br(1B)	0.670(2)	0.236(1)	0.513(2)	$\frac{1}{5}$
Br(2)	−0.076 6(2)	$\frac{1}{2}+x$	$-x$	$\frac{1}{3}$
Br(3A)	−0.292 0(4)	$\frac{1}{2}+x$	$-x$	$\frac{2}{9}$
Br(3B)	−0.262 9(7)	$\frac{1}{2}+x$	$-x$	$\frac{1}{9}$
Br(4)	0.413 6(6)	*x*	*x*	$\frac{1}{6}$
O(1W)	0.614(1)	0.534(2)	0.273(2)	
O(2W)	0.551(2)	0.526(3)	0.409(2)	
O(3W)	0.830(3)	0.154(2)	0.449(2)	$\frac{5}{6}$
O(4W)	0.316(2)	*x*	*x*	$\frac{1}{6}$

* Each atom of the mixed Zn/Co site (0.7 Zn, 0.3 Co) was refined as a Zn atom with a site occupancy factor of 0.97.

Fig. 1, together with its atomic numbering scheme. The entire complex cations of $(-)^{\mathrm{CD}}_{300}$-**1** and $(-)^{\mathrm{CD}}_{300}$-**3** have crystallographically imposed C_3 symmetry, and the Ir(B), O, and M(B) (M = Co and/or Zn) atoms lie on the 3-fold axis. Both of the complex cations consist of four approximately octahedral *fac*-$[Ir(aet)_3]$ sub-units, four M atoms, and one central μ_4-O atom (Fig. 1). This is consistent with the fact that the plasma emission spectral analysis of the complexes gives the values of Ir:Co = 4:4 for **1** and Ir:Zn:Co = 4:2.8:1.2 for **3**. The central O atom is bound to four M atoms which are located at the apices of the inner tetrahedron [M–O–M; 109.3(4) and 109.6(4)° for **1** and 109.3(7) and 109.7(7)° for **3**] (Fig. 1 and Tables 3 and 4). The three sulfur atoms in each *fac*-$[Ir(aet)_3]$ sub-unit are bound to three different M atoms of each trigonal plane of the central tetrahedron. The four iridium atoms in the four *fac*-$[Ir(aet)_3]$ sub-units form the outer tetrahedron. These crystal structures indicate the adoption of an S-bridged octanuclear structure in complex cations **1** and **3** with a central tetrahedral M_4O core.

Each Co atom in $(-)^{\mathrm{CD}}_{300}$-**1** is bound to the central O atom and three different S atoms and assumes tetrahedral geometry (Fig. 1). As a result, the bond distances and angles around the Co atoms are quite similar to those around the tetrahedral Zn atoms in $[\{Co(aet)_3\}_4Zn_4O]^{6+}$ (Table 2).[1] In addition to the geometry around the Co atom, it is suggested from the number of bromide anions and elemental analysis results that the entire complex cations in **1** and **3** have a 6+ charge. These facts indicate that the Co atoms in **1** and **3** are in the +2 oxidation state.

The optically active complex cations **1** and **3** contain two types of chiral centres, Δ or Λ for the *fac*-$[Ir(aet)_3]$ sub-units and *R* or *S* for the bridging sulfur atoms. Anomalous dispersion indicates that the $(-)^{\mathrm{CD}}_{300}$ isomer for each of **1** and **3** has ΔΔΔΔ configuration, in which all 12 bridging sulfur atoms are regulated to the *S* configuration, as shown in Fig. 1.

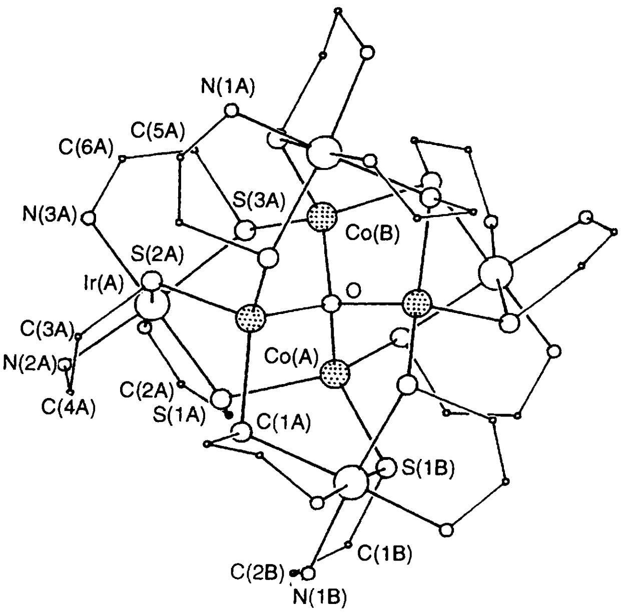

Fig. 1 Perspective view of $(-)^{\mathrm{CD}}_{300}$-ΔΔΔΔ-$[\{Ir(aet)_3\}_4Co_4O]^{6+}$ with the atom labelling scheme

Properties.—The reaction of *fac*-$[Ir(aet)_3]$, which is sparingly soluble in water, with CoO and $CoBr_2$ gave the spontaneously resolved S-bridged octanuclear complex, $[\{Ir(aet)_3\}_4Co_4O]^{6+}$ **1**, containing the $[Co^{II}_4O]^{6+}$ tetrahedral core. The reaction of the linear S-bridged trinuclear complex, $[Co^{III}\{Ir(aet)_3\}_2]^{3+}$, with Zn powder in water at room temperature, followed by the addition of $ZnBr_2$, produced successively $[Co^{II}\{Ir(aet)_3\}_2]^{2+}$ and then the octanuclear complex $[\{Ir(aet)_3\}_4Zn_{2.8}Co_{1.2}O]^{6+}$ **3**. The co-ordination geometry around the cobalt atom is octahedral in the trinuclear reagent but tetrahedral in the octanuclear product. The optically active isomers of **1** and **3** are fairly stable in aerated aqueous solution, and no significant electronic absorption or CD spectral changes with time were observed over several hours. This contrasts with the behaviour of trinuclear cobalt(II) complexes with octahedral geometry such as $[Co\{Ir(aet)_3\}_2]^{2+}$ which are readily oxidized to Co^{III}.[6–8] In **1** and **3**, therefore, it is suggested that the cobalt(II) state is stabilized, presumably owing to the tetrahedral geometry, which is enforced by the aggregation of the four *fac*-$[Ir(aet)_3]$ sub-units.

A similar reaction of *fac*-$[Ir(aet)_3]$ with ZnO and $ZnBr_2$ in water produced white-yellow crystals **2**, which are spontaneously resolved. Complex **2**, like **1**, is stable in aerated water. Furthermore, the absorption and CD spectral pattern for the optically active isomer of **2** are quite similar to those for the corresponding isomers of **1** and **3** above 25 000 cm^{-1} (see below) (Fig. 2). The plasma emission spectral analysis of **2** indicated a Ir:Zn ratio of 4:4. Accordingly, **2** is assigned as the S-bridged octanuclear complex $[\{Ir(aet)_3\}_4Zn_4O]^{6+}$. This is supported by ^1H and ^{13}C NMR spectral behaviour, suggesting a tetrahedral symmetrical structure.

The complex $[\{Ir(aet)_3\}_4Zn_4O]^{6+}$ **2** apparently exhibits two ^{13}C NMR resonances at δ 33.36 and 52.69 due to CH_2S and CH_2NH_2 for the 12 aet ligands, as in the case of $[\{Co(aet)_3\}_4Zn_4O]^{6+}$.[1] The 500 MHz ^1H NMR spectrum of **2** shows resonances at δ 2.37, 2.59 and 3.12 (ratio 1:2:1) due to the two types of methylene protons. These indicate that four *fac*-$[Ir(aet)_3]$ sub-units with the same absolute configurations aggregate to form only ΔΔΔΔ and ΛΛΛΛ isomers with a *T* symmetry element. If the absolute configurations of the four sub-units were not uniform, molecular-model examinations

Table 3 Selected bond distances (Å) and angles (°) for [{Ir(aet)$_3$}$_4$Co$_4$O]Br$_6$

Ir(A)–S(1A)	2.338(4)	Ir(B)–N(1B)	2.10(1)
Ir(A)–S(2A)	2.339(4)	Co(A)–S(1A)	2.328(4)
Ir(A)–S(3A)	2.337(4)	Co(A)–S(2A)	2.316(4)
Ir(B)–S(1B)	2.336(4)	Co(A)–S(1B)	2.311(4)
Ir(A)–N(1A)	2.11(1)	Co(B)–S(3A)	2.328(4)
Ir(A)–N(2A)	2.13(1)	Co(A)–O	1.953(5)
Ir(A)–N(3A)	2.11(1)	Co(B)–O	1.93(2)
S(1A)–Ir(A)–S(2A)	96.4(1)	S(2A)–Co(A)–S(1B)	110.2(2)
S(1A)–Ir(A)–S(3A)	95.0(1)	S(3A)–Co(B)–S(3A)	110.2(1)
S(2A)–Ir(A)–S(3A)	95.4(1)	O–Co(A)–S(1A)	109.1(1)
S(1B)–Ir(B)–S(1B)	95.8(1)	O–Co(A)–S(2A)	108.2(3)
S(1A)–Ir(A)–N(1A)	84.8(4)	O–Co(A)–S(1B)	108.4(4)
S(1A)–Ir(A)–N(3A)	175.3(4)	O–Co(B)–S(3A)	108.8(1)
S(2A)–Ir(A)–N(1A)	175.7(4)	Co(A)–O–Co(A)	109.3(4)
S(2A)–Ir(A)–N(2A)	84.2(4)	Co(A)–O–Co(B)	109.6(4)
S(3A)–Ir(A)–N(2A)	176.9(4)	Ir(A)–S(1A)–Co(A)	112.1(2)
S(3A)–Ir(A)–N(3A)	85.1(4)	Ir(A)–S(2A)–Co(A)	112.5(2)
S(1B)–Ir(B)–N(1B)	84.6(3)	Ir(A)–S(3A)–Co(B)	112.0(2)
S(1A)–Co(A)–S(2A)	109.5(1)	Ir(B)–S(1B)–Co(A)	111.8(2)
S(1A)–Co(A)–S(1B)	111.3(2)		

Table 4 Selected bond distances (Å) and angles (°) of [{Ir(aet)$_3$}$_4$Zn$_{2.8}$Co$_{1.2}$O]Br$_6$*

Ir(A)–S(1A)	2.337(6)	Ir(B)–N(1B)	2.12(2)
Ir(A)–S(2A)	2.338(5)	Zn(A)–S(1A)	2.348(6)
Ir(A)–S(3A)	2.333(7)	Zn(A)–S(2A)	2.343(6)
Ir(B)–S(1B)	2.335(6)	Zn(A)–S(1B)	2.340(6)
Ir(A)–N(1A)	2.11(2)	Zn(B)–S(3A)	2.356(6)
Ir(A)–N(2A)	2.12(2)	Zn(A)–O	1.964(8)
Ir(A)–N(3A)	2.13(2)	Zn(B)–O	1.96(2)
S(1A)–Ir(A)–S(2A)	96.8(2)	S(2A)–Zn(A)–S(1B)	110.6(2)
S(1A)–Ir(A)–S(3A)	94.8(2)	S(3A)–Zn(B)–S(3A)	110.6(2)
S(2A)–Ir(A)–S(3A)	95.3(2)	O–Zn(A)–S(1A)	109.2(2)
S(1B)–Ir(B)–S(1B)	96.1(2)	O–Zn(A)–S(2A)	107.9(4)
S(1A)–Ir(A)–N(1A)	84.8(6)	O–Zn(A)–S(1B)	107.9(6)
S(1A)–Ir(A)–N(3A)	175.6(6)	O–Zn(B)–S(3A)	108.3(2)
S(2A)–Ir(A)–N(1A)	176.1(6)	Zn(A)–O–Zn(A)	109.7(7)
S(2A)–Ir(A)–N(2A)	84.0(6)	Zn(A)–O–Zn(B)	109.3(7)
S(3A)–Ir(A)–N(2A)	177.5(6)	Ir(A)–S(1A)–Zn(A)	112.6(2)
S(3A)–Ir(A)–N(3A)	85.9(6)	Ir(A)–S(2A)–Zn(A)	113.1(2)
S(1B)–Ir(B)–N(1B)	84.2(6)	Ir(A)–S(3A)–Zn(B)	112.5(3)
S(1A)–Zn(A)–S(2A)	109.3(2)	Ir(B)–S(1B)–Zn(A)	111.9(2)
S(1A)–Zn(A)–S(1B)	111.8(2)		

* Each atom of the mixed Zn/Co site labelled as a Zn atom.

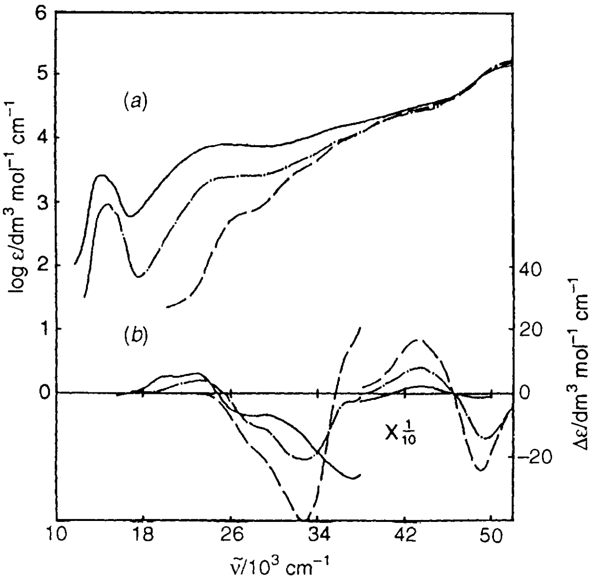

Fig. 2 Absorption (*a*) and CD spectra (*b*) of ΔΔΔΔ-[{Ir(aet)$_3$}$_4$Co$_4$O]$^{6+}$ (——), ΔΔΔΔ-[{Ir(aet)$_3$}$_4$Zn$_{2.8}$Co$_{1.2}$O]$^{6+}$ (– · – · –), and ΔΔΔΔ-[{Ir(aet)$_3$}$_4$Zn$_4$O]$^{6+}$ (– – – –)

reveal that significant non-bonding interactions would occur among the adjacent aet chelate rings. In contrast with **2**, **1** exhibits no ^{13}C NMR resonances and only two broadened ^{1}H NMR signals due to the two kinds of methylene protons. These are observed at remarkably low field (δ 13.62 and 27.60). This NMR spectral behaviour is probably a consequence of the presence of the paramagnetic Co^{II} in the complex cation.[13] On the other hand, **3** gives two ^{13}C NMR signals at δ 39.31 and 63.27, in addition to the two resonances in the same positions as found for **2**. Similarly **3** also exhibits the same ^{1}H NMR resonances as **2** but with some additional poorly resolved broad signals. It is presumed that the NMR spectral behaviour of **3** is due to the partial presence of paramagnetic Co^{II} (*ca.* 30%), which is isostructurally trapped in the place of Zn^{II}.

In the visible and near-UV region (25 000–52 000 cm^{-1}) complex **2** exhibits five absorption components (with corresponding CD bands) (Fig. 2). The absorption bands at *ca.* 27 900, 32 900 and 37 600 cm^{-1} correspond to d–d transitions and two bands at *ca.* 44 300 and > 52 000 cm^{-1} are sulfur-to-iridium charge transfer (c.t.) bands. Similar absorption spectral behaviour was observed for the cobalt(III) and rhodium(III) complexes, [{M(aet)$_3$}$_4$Zn$_4$O]$^{6+}$ (M = Co^{III} or Rh^{III}), although all absorption bands of **2** show shifts to higher energy relative to the complexes of Co^{III} and Rh^{III}.[1,4,5,7] Further, the absorption spectrum of [{Ir(aet)$_3$}$_4$Zn$_4$O]$^{6+}$ **2** is the same as that of 4 mol equivalents of *fac*-[Ir(L-cys-*N*,*S*)$_3$]$^{3-}$ (L-cys = L-cysteinate) which has the same donor-atom framework as aet. This indicates that the absorption spectrum of **2** is dominated by the contribution of the four *fac*-[Ir(aet)$_3$] sub-units,[8] and that the electronic state of *fac*-[Ir(aet)$_3$] is little affected by bridging with Zn^{II}.[1]

In the region 25 000–52 000 cm^{-1} the overall absorption and CD spectral patterns for the $(-)^{CD}_{300}$ isomer of **2** are similar to those for the $(-)^{CD}_{300}$ isomers of **1** and **3**, which are assigned to the ΔΔΔΔ configuration, although the positive CD band at *ca.* 37 000 cm^{-1} for **2** is of opposite sign to that of **1** containing a tetrahedral Co^{II} centre (Fig. 2). The σ component of the sulfur-to-metal c.t. bands has been observed at *ca.* 37 000 cm^{-1} for mononuclear tetrahedral cobalt(II) complexes with thiolate ligands.[14] Thus, it is assumed that the CD bands at *ca.* 37 000 cm^{-1} for **1** and **3** are affected by the σ component of the sulfur-to-metal c.t. band based on the tetrahedral Co^{II}. The CD intensities in the sulfur-to-iridium c.t. band region (38 000–52 000 cm^{-1}) decrease in the order Zn$_4$ < Zn$_{2.8}$Co$_{1.2}$ < Co$_4$ in the [M$_4$O]$^{6+}$ core, though the influence on the CD spectra due to the presence of Co^{II} is not clarified in the present work. Despite the CD contribution of the tetrahedral Co^{II}, the absolute configurations of these complexes can be confidently assigned from the CD spectral pattern in the d–d and c.t. band regions, because of the similarity of the CD spectral behaviour for the isostructural forms of the octanuclear complexes.[7,15] The $(-)^{CD}_{300}$ isomer of **2** is therefore assigned a ΔΔΔΔ configuration.

Complexes **1** and **3** exhibit additional absorption and CD bands in the region 13 000–25 000 cm^{-1}, with those of **1** being more intense than those of **3**, in accord with the amount of Co^{II} incorporated into the complex cation (Fig. 2). This suggests that the absorption bands at *ca.* 14 000 cm^{-1} arise from the spin-allowed d–d transition $^4A_2(F) \longrightarrow {}^4T_1(P)$. Similar absorption bands have been observed for tetrahedral cobalt(II) complexes with thiolato donor atoms.[14,16] Furthermore, cobalt(II) complexes with S-donor atoms exhibit a π component of the sulfur-to-metal c.t. band at *ca.* 26 000 cm^{-1}, in addition to the σ component of the same band (at *ca.* 38 000 cm^{-1}).[14] Therefore, the absorption bands for **1** and **3** at *ca.* 22 000 cm^{-1} seem to be due to the π component of the sulfur-to-cobalt c.t. bands (Fig. 2). It is noted that the Co^{II}-dependent CD bands lie in this region (18 000–25 000 cm^{-1}). The bands at *ca.* 14 000 cm^{-1} do not overlap with any absorption components of the Co^{III}, Rh^{III} or Ir^{III} sub-units. Hence, the appearance of these bands apparently indicates the presence of tetrahedral Co^{II} for the cage structure.

The cyclic voltammogram for $[\{Ir(aet)_3\}_4Co_4O]^{6+}$ **1** at a glassy-carbon electrode yields an electrochemically reversible redox couple (E_{pc} −1.00 V, E_{pa} −0.94).

No other redox couple was observed in the potential region of +0.9 to −1.2 V (*vs.* Ag–AgCl). On the other hand, cyclic voltammograms for **2** and **3** do not show any redox couple in the same potential region. The electrochemical behaviour of **1** differs significantly from that of $[\{Co(aet)_3\}_4Zn_4O]^{6+}$,[1] which exhibits four successive Co^{III}–Co^{II} couples, and the $E^{\circ\prime} = -0.97$ V value of **1** is more negative than those of these Co^{III}–Co^{II} couples ($E^{\circ\prime} = -0.40$ to -0.83 V). Therefore, the redox process observed in **1** is assigned to $[Co_4O]^{6+}$–$[Co_4O]^{5+}$, indicating that the tetrahedral aggregation of four *fac*-$[Ir(aet)_3]$ sub-units stabilizes the $[Co_4O]^{6+}$ core.

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