A three-dimensional net of Δ-tris(1,10-phenanthroline)ruthenium(II) in the dual-metal self-assembly of bis[tris-(1,10-phenanthroline)ruthenium(II)] tetraisothiocyanatoiron(II) bis(per-chlorate)

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The title compound, $[Ru(C_{12}H_8N_2)_3]_2[Fe(NCS)_4](ClO_4)_2$, crystallizes in a tetragonal chiral space group ($P4_12_12$) and the assigned absolute configuration of the optically active molecules was unequivocally confirmed. The Δ-$[Ru^{II}(phen)_3]^{2+}$ complex cations (phen is 1,10-phenanthroline) interact along the 4_1 screw axis parallel to the c axis, with an $Ru\cdots Ru$ distance of 10.4170 (6) Å, and in the ab plane, with $Ru\cdots Ru$ distances of 10.0920 (6) and 10.0938 (6) Å, defining a primitive cubic lattice. The Fe atom is situated on the twofold axis diagonal in the ab plane. The supramolecular architecture is supported by C—H$\cdots$O interactions between the $[Ru^{II}(phen)_3]^{2+}$ cation and the disordered perchlorate anion. This study adds to the relatively scarce knowledge about intermolecular interactions between $[Ru(phen)_3]^{2+}$ ions in the solid state, knowledge that eventually may also lead to a better understanding of the solution state interactions of this species; these are of immense interest because of the photochemical properties of these ions and their interactions with DNA.

Comment

Dual-metal compounds that comprise both coordination and inorganic metal complexes as cationic and anionic modules have a growing significance in the self-assembly of supramolecular architectures (Adachi *et al.*, 2005; Luo *et al.*, 2004). We have recently reported on helices of Λ- and Δ-$[Ru^{II}(phen)_3]^{2+}$ (phen is 1,10-phenanthroline) observed in the dual-metal self-assembly of racemic $[Ru^{II}(phen)_3]^{2+}$ with $[M(NCS)_4]^{2-}$, where M is either Fe^{II} or Co^{II} (Ghazzali *et al.*, 2008). There are a number of structural studies on racemic $[Ru^{II}(phen)_3]^{2+}$ complexes (Nakamura *et al.*, 2004; Zheng *et al.*, 2006; Wu *et al.*, 2001; Otsuka *et al.*, 2001; Breu & Stoll,

1996), and the absolute configuration of the Λ enantiomers has been unambiguously assigned (Maloney & MacDonnell, 1997; Nakamura *et al.*, 2004; Rutherford *et al.*, 1998). We present here the structure of the title compound, (I), formed by the dual-metal assembly of the optically pure Δ-$[Ru^{II}(phen)_3]^{2+}$ with $[Fe(NCS)_4]^{2-}$ and ClO_4^- anions. Such assignment is significant, as it confirms earlier physicochemical studies for Λ and Δ enantiomers within complexes of this genre (Lincoln & Nordén, 1998).

(I)
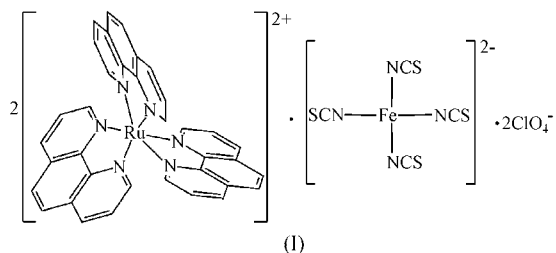
The overall geometries of the Ru^{II} and Fe^{II} complexes are slightly distorted octahedral and tetrahedral, respectively (Fig. 1). The Fe^{II} metal centre is situated on a twofold axis, which lies on the diagonal of the ab plane. In the Ru^{II} complex, the minimum and maximum interplanar angles between the three phenathroline ligands, defined by the 14-atom best-fit plane, are 74.10 (8) and 88.75 (9)°, respectively. The minimum and maximum bite angles for the chelating phen ligands are 79.55 (13) and 79.84 (13)°, respectively. The average Ru—N bond distance is 2.069 (3) Å and the average Fe—N bond distance is 1.992 (5) Å; selected bond distances are presented in Table 1. The maximum deviation from linearity in the SCN^- groups is 2.6 (5)°. The shortest $Ru\cdots Ru$, $Fe\cdots Fe$ and $Ru\cdots Fe$ distances are 10.0920 (6), 12.5275 (8) and 5.9761 (7) Å, respectively. While the bond angles and distances are typical of similar previously described complexes (Maloney & MacDonnell, 1997; Nakamura *et al.*, 2004; Rutherford *et al.*, 1998), the screw axis symmetry is higher than those reported earlier (2_1) for Λ enantiomers (Nakamura *et al.*, 2004; Rutherford *et al.*, 1998).

Elucidation of the intermolecular interactions of the $[Ru(phen)_3]^{2+}$ ions in the solid state may eventually lead to a better understanding of the solution state interactions of this species. This is of importance because of the photochemical properties of $[Ru(phen)_3]^{2+}$ and similar compounds (Bonnet *et al.*, 2006) and their interactions with DNA (Nordén *et al.*, 1996). Moreover, as the DNA chiral helices show some discrimination between the $[Ru(phen)_3]^{2+}$ enantiomers (Barton *et al.*, 1986; Yamagishi, 1983), it is of interest to compare racemic and optically pure materials.

An analysis of known $[Ru(phen)_3]^{2+}$ compounds indicates that the closest interaction between two such ions (less than 9 Å) found in *rac*-$[Ru^{II}(phen)_3](PF_6)_2\cdot0.5H_2O$ (Nakamura *et al.*, 2004), the anhydrous analogue *rac*-$[Ru^{II}(phen)_3](PF_6)_2$ (Breu & Stoll, 1996) and *rac*-$[Ru^{II}(phen)_3][Co(NCS)_4]$ (Ghazzali *et al.*, 2008) occurs between species of the same chirality, despite the fact that these compounds are all racemic.

metal-organic compounds
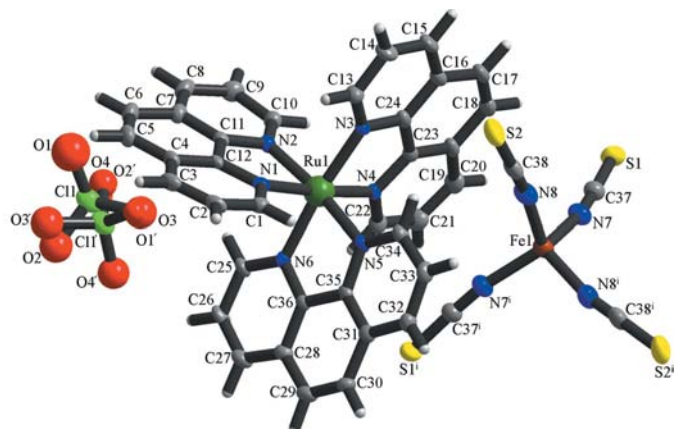
Figure 1
A perspective drawing showing the atomic-numbering scheme. The atomic displacement ellipsoids are shown at the 50% probability level. Both components of the disordered perchlorate anion are shown. [Symmetry code: (i) $y, x, -z$.]

An interaction similar to that in racemic $[Ru^{II}(phen)_3]$-$[Co(NCS)_4]$ can be found in the optically pure $[Ru^{II}(phen)_3]$-$(PF_6)_2 \cdot CH_3CN \cdot Et_2O$ (Maloney & MacDonnell, 1997), with an $Ru \cdots Ru$ distance only slightly longer than 9 Å (9.292 Å), and in both structures, supramolecular helices were revealed.

For the present compound, we find that in the *ab* plane the Δ-$[Ru^{II}(phen)_3]^{2+}$ cations interact through two very similar weak $C-H \cdots \pi$ interactions $[H2 \cdots C32^{ii} = 2.87$ Å and $H6 \cdots C25^{iii} = 2.95$ Å; symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z - \frac{1}{4}$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z - \frac{1}{4}]$, with $Ru \cdots Ru$ distances of 10.0920 (6) and 10.0938 (6) Å. Along the 4_1 screw axis parallel to the *c* axis, the tris(phenanthroline)ruthenium(II) complexes interact in a distinctively different manner that can be described as a 'tongue-and-groove' fit, giving an $Ru \cdots Ru$ distance of 10.4170 (6) Å (Fig. 2). In this interaction, the distances from atom H17 to the centre of gravity of the two closest six-membered rings [defined by atoms N1/C1–C4/C12 and N6/C25–C28/C36, both in the molecule at $(-y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{4})]$ are 2.68 and 2.98 Å. Together, these three interactions define a six-connected pcu-net (pcu is primitive cubic packing; O'Keeffe *et al.*, 2008; Öhrström & Larsson, 2005), as shown in Fig. 3. Similar examples of networks formed by such interactions, in certain cases called 'phenyl embraces', have been reported (Scudder & Dance, 2001; Dance, 2003). It is worth
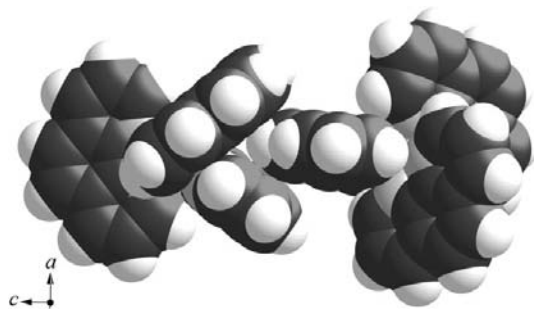
Figure 2
The interaction between two $[Ru^{II}(phen)_3]^{2+}$ ions in the *c* direction; the $Ru \cdots Ru$ distance is 10.4170 (6) Å.
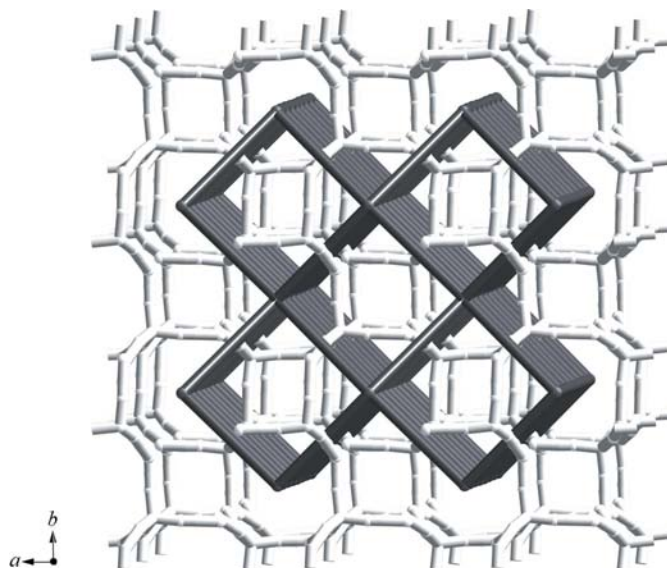
Figure 3
The pcu-net (primitive cubic packing) defined by $C-H \cdots \pi$ interactions (drawn in black); the $[Fe^{II}(NCS)_4]^{2-}$ ions are shown in light grey. The perchlorate ions (omitted for clarity) are situated in the smaller 'squares' between the isothiocyanate complexes.

noting that despite the phenanthroline complexes having the same charge, an overall attraction may result as the sum of many weak interactions, overriding this charge–charge repulsion.

A check of other reported $[Ru(phen)_3]^{2+}$ structures reveals that pcu-nets are also present in *rac*-$[Ru^{II}(phen)_3]$-$(PF_6)_2 \cdot 0.5H_2O$ (Nakamura *et al.* 2004) and *rac*-$[Ru^{II}(phen)_3]$-$(PF_6)_2$ (Breu & Stoll, 1996). However, at present, it is hard to judge the significance of these findings. We need more structural data for different types of $[Ru(phen)_3]^{2+}$ compounds and perhaps also theoretical studies that could indicate the preferred orientations of pairs of ruthenium–phenanthroline complexes.

The supramolecular architecture is consolidated by $C-S \cdots \pi$ interactions between the $[Fe^{II}(NCS)_4]^{2-}$ and $[Ru^{II}$-$(phen)_3]^{2+}$ ions, with an $S \cdots \pi$ distance of 3.680 (2) Å and a $C-S \cdots \pi$ angle of 145.2 (2)° [the acceptor ring is defined by atoms N5 and C31–C35 in the cation at $(-y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{4})]$, as well as by $C-H \cdots O$ interactions extending between the disordered perchlorate anion and the $[Ru^{II}(phen)_3]^{2+}$ cation (Table 2).

Experimental

A solution of iron(II) perchlorate hexahydrate (0.1 mmol, 0.03 g) and potassium thiocyanate (0.2 mmol, 0.02 g) in MeOH/EtOH/MeCN (1:1:1, 15 ml) was stirred for 30 min at room temperature under an N_2 stream and then filtered. Into the filtrate, an MeOH/EtOH (1:1, 20 ml) solution of Δ-tris(1,10-phenanthroline)ruthenium(II) chloride (0.1 mmol, 0.08 g), prepared as described previously (Lincoln & Nordén, 1998), was poured carefully. The resulting solution was set aside and crystallized at room temperature. Dark-red crystals were collected after one week and dried in air. **Caution:** perchlorate salts of

metal complexes are potentially explosive; only small quantities of the compound should be prepared and these should be handled with care. IR (γ, cm^{-1}, KBr): 717 (*s*, π_{CH}), 837 (*s*, σ_{CH}), 1091 (*s*, ClO$_4^-$), 1630 (*m*, C≡C), 2070 (*s*, SCN$^-$).

Crystal data

[Ru(C$_{12}$H$_8$N$_2$)$_3$]$_2$[Fe(NCS)$_4$](ClO$_4$)$_2$	$Z = 4$
$M_r = 1770.43$	Mo $K\alpha$ radiation
Tetragonal, $P4_12_12$	$\mu = 0.85$ mm^{-1}
$a = 13.3292$ (5) Å	$T = 153$ (2) K
$c = 41.668$ (2) Å	$0.45 \times 0.21 \times 0.15$ mm
$V = 7403.1$ (5) Å^3	

Data collection

Siemens SMART CCD area-detector diffractometer	132579 measured reflections
	13662 independent reflections
Absorption correction: multi-scan ($SADABS$; Sheldrick, 2003)	11006 reflections with $I > 2\sigma(I)$
$T_{min} = 0.701$, $T_{max} = 0.883$	$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	H-atom parameters constrained
$wR(F^2) = 0.200$	$\Delta\rho_{max} = 2.38$ e Å^{-3}
$S = 1.01$	$\Delta\rho_{min} = -0.60$ e Å^{-3}
13662 reflections	Absolute structure: Flack (1983), 3280 Friedel pairs
499 parameters	Flack parameter: 0.01 (3)
20 restraints	

Table 1
Selected bond lengths (Å).

Ru1—N2	2.064 (3)	Ru1—N1	2.071 (3)
Ru1—N6	2.067 (3)	Ru1—N4	2.071 (3)
Ru1—N3	2.069 (3)	Fe1—N7	1.981 (4)
Ru1—N5	2.070 (3)	Fe1—N8	2.003 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C30—H30$\cdots$O2$'^{iv}$	0.95	2.58	3.442 (12)	150
C13—H13$\cdots$O4^{iii}	0.95	2.35	3.262 (11)	160
C25—H25$\cdots$O3	0.95	2.41	3.154 (10)	135
C30—H30$\cdots$O4^{iv}	0.95	2.48	3.374 (9)	157

Symmetry codes: (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z - \frac{1}{4}$; (iv) $x, y - 1, z$.

The perchlorate anion was refined as disordered, with the two orientations related by pseudo-inversion and the major orientation having a site-occupation factor of 0.586 (9). The anion O atoms were refined isotropically. The highest peak of residual electron density is 1.56 Å from atom O4′. 20 distance and occupancy restraints were used to refine the model for the perchlorate anion. H atoms were constrained to an ideal geometry using an appropriate riding model [C—H = 0.95 Å and U_{iso}(H) = $1.2U_{eq}$(C)].

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXTL*.

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