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#### Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.015\text{ \AA}$

Disorder in solvent or counterion

$R$  factor = 0.038

$wR$  factor = 0.109

Data-to-parameter ratio = 13.2

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## ( $\mu$ -Benzenethiolato)bis[(bipyridine)tricarbonyl- rhodium(I)] perchlorate dichloromethane hemisolvate

The title binuclear  $\text{Re}^{\text{I}}$ -thiolate complex,  $[\text{Re}_2(\text{C}_6\text{H}_5\text{S})(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{CO})_6]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ , was isolated from the reaction between  $[\text{Re}(\text{bpy})(\text{CO})_3](\text{SC}_6\text{H}_5)$  and  $[\text{Cu}_2(\mu_2\text{-dppm})_2(\text{MeCN})_4](\text{ClO}_4)_2$  (bpy is bipyridine and dppm is diphenylphosphinomethane). The two rhenium–diimine moieties are bridged by one S-donor and each Re atom adopts a distorted octahedral geometry.

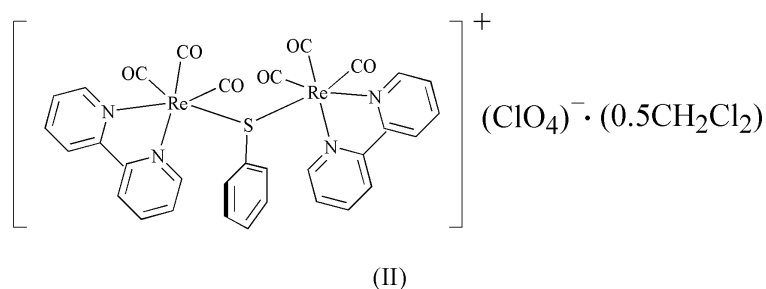
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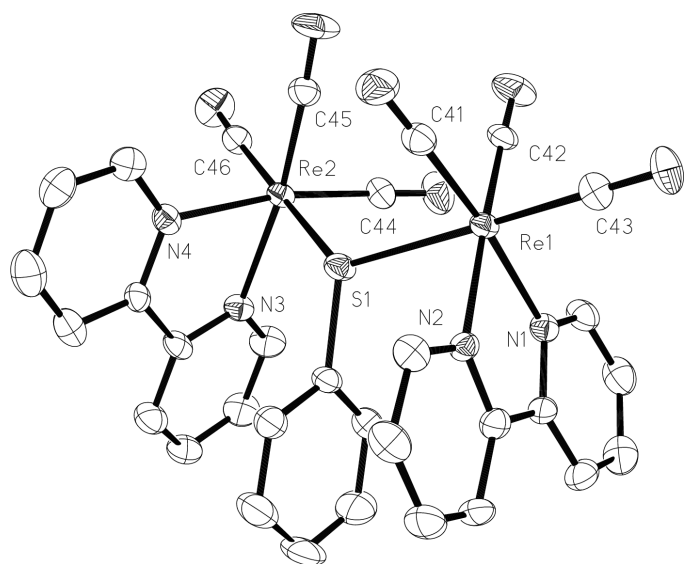
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#### Comment

There has been increasing interest in designing polymetallic complexes with mixed diimine and thiolate ligands, owing to their unique optical and optoelectronic properties (Yam *et al.*, 2000; Tang *et al.*, 2002). It is well known that thiolates as versatile bridging ligands can exhibit various bonding modes to produce metal cluster complexes with diverse structural topologies (Su *et al.*, 1998). We describe here a dinuclear rhenium(I) complex,  $[\{\text{Re}(\text{bpy})(\text{CO})_3\}_2(\mu\text{-SC}_6\text{H}_5)]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ , (II), which resulted from the self-assembly between the metal components  $\{\text{Re}(\text{bpy})(\text{CO})_3\}(\text{SC}_6\text{H}_5)$ , (I), and  $[\text{Cu}_2(\mu_2\text{-dppm})_2(\text{MeCN})_4](\text{ClO}_4)_2$ .



A perspective drawing of the complex cation of (II) with the atomic numbering scheme is shown in Fig. 1, and selected bonding parameters are given in Table 1. The two rhenium–diimine moieties are bridged by the S donor atom of the benzenethiolate ligand, with an  $\text{Re}2-\text{S}1-\text{Re}1$  angle of  $124.35(8)^\circ$ . The three carbonyl ligands at each Re atom are arranged in a facial configuration. Each Re atom adopts a slightly distorted octahedral geometry, with the  $\text{S}1-\text{Re}1-\text{C}43$  and  $\text{S}1-\text{Re}2-\text{C}46$  bond angles being  $174.8(2)$  and  $175.8(3)^\circ$ , respectively. The planes of the two bipyridyl ligands and the phenyl ring of the bridging thiolate ligand show a stacked conformation, with dihedral angles between the mean planes of each of the two bipyridyl units and the phenyl ring of  $14.1(2)$  and  $16.1(3)^\circ$ . Because of the steric effects of each chelating bipyridyl ligand, the  $\text{N}2-\text{Re}1-\text{N}1$  [ $75.3(2)^\circ$ ] and  $\text{N}4-\text{Re}2-\text{N}3$  [ $74.2(3)^\circ$ ] angles are far from  $90^\circ$  (Yam *et al.*, 1995, 1996). The average bond distances of  $\text{Re}-\text{S}$



**Figure 1**  
A view of the complex cation of (II), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

[2.526 (2) Å] and Re–C [1.918 (9) Å] are found to be comparable to those observed in [Re(CO)<sub>3</sub>SCH<sub>3</sub>]<sub>4</sub> (Abel *et al.*, 1970; Yam *et al.*, 1997).

## Experimental

The starting material [Re(bpy)(CO)<sub>3</sub>](μ-SC<sub>6</sub>H<sub>5</sub>), (I), was synthesized by modification of literature procedures (Yam *et al.*, 1997), using a large excess of benzenethiolate, to give (I) as a red–orange solid in good yield. Reaction between (I) and [Cu<sub>2</sub>(μ<sub>2</sub>-dppm)<sub>2</sub>(MeCN)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (Diez *et al.*, 1987) in an equimolar ratio in dichloromethane was carried out under anaerobic conditions for 12 h, during which a color change from red into yellow–orange was observed. Well shaped yellow crystals of (II) suitable for X-ray diffraction analysis were grown by layering of diethyl ether over the concentrated solution.

### Crystal data

[Re<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>S)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(CO)<sub>6</sub>]  
ClO<sub>4</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>  
*M<sub>r</sub>* = 1103.90  
Triclinic, P $\bar{1}$   
*a* = 9.7014 (3) Å  
*b* = 10.3257 (3) Å  
*c* = 17.8823 (5) Å  
 $\alpha$  = 85.994 (1)°  
 $\beta$  = 86.487 (1)°  
 $\gamma$  = 83.405 (1)°  
*V* = 1772.57 (9) Å<sup>3</sup>

### Data collection

Siemens SMART CCD  
diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.040, *T*<sub>max</sub> = 0.090  
9243 measured reflections

*Z* = 2  
*D<sub>x</sub>* = 2.068 Mg m<sup>-3</sup>  
Mo *K*α radiation  
Cell parameters from 6144  
reflections  
 $\theta$  = 1.1–25.1°  
 $\mu$  = 7.10 mm<sup>-1</sup>  
*T* = 293 (2) K  
Prism, yellow  
0.78 × 0.36 × 0.34 mm

6185 independent reflections  
5245 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.027  
 $\theta$ <sub>max</sub> = 25.1°  
*h* = –11 → 11  
*k* = –12 → 12  
*l* = –16 → 21

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.109  
*S* = 1.13  
6185 reflections  
470 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 6.9595P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho$ <sub>max</sub> = 1.35 e Å<sup>-3</sup>  
 $\Delta\rho$ <sub>min</sub> = –2.22 e Å<sup>-3</sup>  
Extinction correction: SHELXL97  
Extinction coefficient: 0.0061 (3)

**Table 1**

Selected geometric parameters (Å, °).

Re1–C43	1.912 (9)	Re2–C45	1.909 (9)
Re1–C41	1.921 (9)	Re2–C46	1.917 (8)
Re1–C42	1.922 (9)	Re2–C44	1.924 (9)
Re1–N2	2.165 (6)	Re2–N4	2.169 (7)
Re1–N1	2.175 (6)	Re2–N3	2.173 (7)
Re1–S1	2.529 (2)	Re2–S1	2.523 (2)
N2–Re1–N1	75.3 (2)	C46–Re2–S1	175.8 (3)
C43–Re1–S1	174.8 (2)	C44–Re2–S1	93.2 (3)
C41–Re1–S1	86.6 (3)	N4–Re2–S1	79.59 (18)
C42–Re1–S1	93.9 (2)	N3–Re2–S1	89.80 (18)
N2–Re1–S1	83.18 (17)	C31–S1–Re2	111.8 (3)
N1–Re1–S1	90.15 (17)	C31–S1–Re1	112.1 (3)
N4–Re2–N3	74.2 (3)	Re2–S1–Re1	124.35 (8)
C45–Re2–S1	87.5 (3)		

The positions of the H atoms were generated geometrically (C–H bond length fixed at 0.96 Å), assigned isotropic displacement parameters, and allowed to ride on their respective parent C atoms. The dichloromethane molecule lies near the center of symmetry and atom C01 has two possible positions with occupancies of 50%.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: XPREF in SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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