

Correspondence to:

*Professor B K Nicholson,  
Chemistry Department,  
University of Waikato,  
Private Bag 3105, Hamilton 3240,  
New Zealand.  
Email: b.nicholson@waikato.ac.nz  
Fax: 64 7 838 4219  
Phone: 64 7 856 2889*

*(p-Cymene)thioglycollatoruthenium(II) dimer; a complex with an ambi-basic S,O-donor ligand.*

William Henderson, Tracey D. Kilpin and Brian K Nicholson.

*Chemistry Department, University of Waikato, Private Bag 3105, Hamilton, New Zealand.*

Running title: *(p-Cymene)thioglycollatoruthenium(II) dimer*

## Abstract

The title compound was prepared from the (*p*-cymene)ruthenium chloride dimer and thioglycollic acid. The structure is a centrosymmetric dimer bridged by the soft-base S atoms, with the hard-base O atoms of the carboxylate group chelating to form a five-membered twisted-ring. The coordination of the ruthenium atoms is completed by a  $\eta^6$ -*p*-cymene ligand, giving an 18-electron count. The Ru-S bonds are essentially equal at 2.396(1) Å.

**Keywords:** Ruthenium, thioglycollate, crystal structure, S-bridged dimer

## Introduction.

We and others have recently been exploring the coordination chemistry of the thiosalicylate ligand which combines a soft S<sup>-</sup> donor site with a hard O<sup>-</sup> one [1, 2]. It forms complexes with metals with both high [e.g. Mo(VI)] and low [e.g. Mn(I)] oxidation states [3, 4], as S- or O-bonded only or more commonly as S,O-bidentate chelating [1,2, 5-7]. Higher aggregates are possible through bridging via the S atom, or by it acting as a doubly monodentate ligand to two separate metal atoms [1-5]. A less-explored S,O donor ligand is the thioglycollate dianion, <sup>-</sup>SCH<sub>2</sub>COO<sup>-</sup> which differs from thiosalicylate in that it forms five- (rather than six-) membered chelate rings, and has a potentially more flexible chain of atoms compared with the rigidity imposed for the thiosalicylate by the phenyl ring. The only previous reports of structurally characterised organometallic complexes containing the thioglycollate ligand appear to be a mixed Mo-Zr species with one chelating and one bridging ligand

[8], and  $[\text{Cp}^*\text{Mo}(\text{SCH}_2\text{COO})_2]\text{S}$  with chelating/bridging ligands [9]. We now report the structure of  $[(p\text{-cymene})\text{Ru}(\text{SCH}_2\text{COO})_2]$ , **1**, for comparison with that of the previously-described thiosalicylate analogue **2** [2]. Arene-ruthenium(II) complexes with chelating ligands are of extra interest because of their established anticancer properties [10].

### Experimental.

*Preparation:*  $[(p\text{-Cymene})\text{RuCl}_2]_2$  (102 mg, 0.17 mmol) and thioglycollic acid (BDH, 5 drops, excess) were suspended in methanol (25 mL), and triethylamine (1 mL, excess) was added. The resulting yellow mixture was refluxed for 30 min., water (70 ml) added, and the mixture cooled to room temperature. After concentration of the solution to ca. 3 mL, and cooling to 4 °C for 2 days, orange-brown block crystals formed. After decantation and washing with a small quantity of water, the product was isolated in 12% yield. ESI MS (positive ion, cone voltage 20V, methanol)  $[\text{M} + \text{H}]^+$  ( $m/z$  652),  $[\text{M} + \text{Na}]^+$  ( $m/z$  675),  $[2\text{M} + \text{Na}]^+$  ( $m/z$  1326). IR  $\nu_{\text{CO}}$  1606  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta$  1.28 [d, 6H,  $\text{CHMe}_2$ ,  $J(\text{HH})$  6], 2.16 (s, 3H, Me), 2.75-2.80 [m, 1H,  $\text{CHMe}_2$ ,  $J(\text{HH})$  6], 3.23 [d, 1H,  $\text{CH}_2$ ,  $^3J(\text{HH})$  15], 3.34 [d, 1H,  $\text{CH}_2$ ,  $^3J(\text{HH})$  15], 5.35, 5.27, 5.18 and 5.09 [4xd, CH of cymene,  $^3J(\text{HH})$  6].

*Structure determination:* Crystal data for **1** are summarised in Table 1. Data were collected on a Bruker SMART CCD diffractometer and processed using standard software. Absorption corrections were carried out with SADABS [11].

The structure was solved with SHELXS-97 and refined (on  $F^2$ ) using SHELXL-97 [12], operated under WinGX [13]. All non-hydrogen atoms were treated anisotropically and hydrogen atoms were included with a riding model with  $d(\text{C-H})$

0.95 Å,  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$  for aromatic and 0.98 Å,  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$  for CH<sub>3</sub> groups.

ORTEP-3 was used for the Figure [14].

## Results and Discussion.

The preparation and spectroscopic characterisation of the complex [(*p*-cymene)Ru(SCH<sub>2</sub>COO)]<sub>2</sub>, **1**, was straightforward, by reaction of [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> with HSCH<sub>2</sub>CO<sub>2</sub>H and Et<sub>3</sub>N in hot methanol. Crystals of the product were obtained in low yield by addition of water, followed by concentration and cooling of the reaction mixture. The product shows [M + H]<sup>+</sup>, [M + Na]<sup>+</sup> and [2M + Na]<sup>+</sup> ions in the electrospray mass spectrum, a carbonyl stretch at 1606 cm<sup>-1</sup> in the IR spectrum, and the expected resonances in the <sup>1</sup>H NMR spectrum. As a result of the asymmetry at the Ru centre, the CH<sub>2</sub> protons of the thioglycollate ligand appear as two inequivalent AB doublets at δ 3.23 and 3.34 with a geminal coupling of 15 Hz, and the aromatic protons of the cymene ligand appear as four distinct doublet resonances.

The compound crystallises as centrosymmetric dimers, as shown in Figure 1.

The <sup>-</sup>SCH<sub>2</sub>COO<sup>-</sup> ligand is chelated to the Ru atom to form a five-membered ring. This ring is slightly twisted, with atoms displaced up to ±0.28 Å from the least-squares plane through the five atoms. The S atom is further coordinated to the other Ru atom to form the dimer linked by a planar Ru<sub>2</sub>S<sub>2</sub> ring. The two independent Ru1-S1 distances are not significantly different at 2.3992(10) and 2.3943(11) Å. The least-squares plane through the five atoms of the chelate ring makes an angle of 89.86(7)° to the Ru<sub>2</sub>S<sub>2</sub> plane. The coordination sphere of the Ru is completed by an η<sup>6</sup>-cymene ligand with Ru...C distances ranging from 2.188(4)-2.232(4) Å. The Ru...Ru

distance of 3.653 Å is too long to involve any direct bonding, consistent with the 18-electron count achieved without it.

The 'piano-stool' geometry around the Ru atom is regular with the three S-Ru-S and S-Ru-O angles covering the narrow range of 80.7-81.7° despite the different types of atoms involved. Larger angles are more usual in symmetrical complexes (e.g. 87° for Cl-Ru-Cl in [(*p*-cymene)RuCl<sub>3</sub>]<sup>+</sup>, [15]) and a larger range for less symmetrical ones (e.g. 82-87° for [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>, [16]).

A comparison of the bond parameters of **1** with those of the thiosalicylate complex **2** [2] shows remarkable consistency; the Ru-S, Ru-O and Ru...Ru distances are essentially the same in both molecules despite the larger, and more puckered, chelate ring for **2**, with only a small asymmetry in the Ru<sub>2</sub>S<sub>2</sub> ring for **2** distinguishing the core geometry.

The chelating/S-bridging mode found for the thioglycollate in **1** has direct precedent in some Mo and Co complexes [17] and is also related to other Mo complexes in which the bridging S supports a direct Mo-Mo bond [9, 18]. Other examples have the thioglycollate as a simple chelating ligand [19], or simultaneously chelating and bridging metals through both the S and O atoms [20], so it clearly is a versatile ligand.

There are only weak intermolecular interactions between the dimers of **1**, the closest being non-classical C-H...O hydrogen bonds involving the C=O group of the thioglycollate ligand (C-H4...O1 2.414 Å, C-H1c...O1 2.427 Å, C-H11a...O1 2.707 Å).

## Supplementary material

CCDC 662225 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html), or from the Cambridge Crystallographic Data Centre, 12 Union Rd, Cambridge CB2 1EZ, UK; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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Table 1. Crystal data and structure refinement details for **1**.

Molecular formula	C <sub>24</sub> H <sub>32</sub> O <sub>4</sub> Ru <sub>2</sub> S <sub>2</sub>
Formula weight	650.18
Temperature	89(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /n
Unit cell dimensions	
a (Å)	8.3622(2)
b (Å)	17.7630(4)
c (Å)	8.5426(2)
β (°)	110.02(1)
Volume (Å <sup>3</sup> )	1192.22(9)
Z	2
Density (calc.) g cm <sup>-3</sup>	1.813
Absorption coefficient (mm <sup>-1</sup> )	1.471
F(000)	656
Crystal size (mm <sup>3</sup> )	0.26 x 0.20 x 0.14
θ range for data collection (°)	2.29 to 26.31 deg.
Reflections collected	6941
Unique reflections	2421 [R(int) = 0.0481]
Completeness to θ = 26.31	99.5 %
Absorption correction	multi-scan
Max. and min. transmission	0.821 and 0.701
Data / restraints / parameters	2421 / 0 / 148

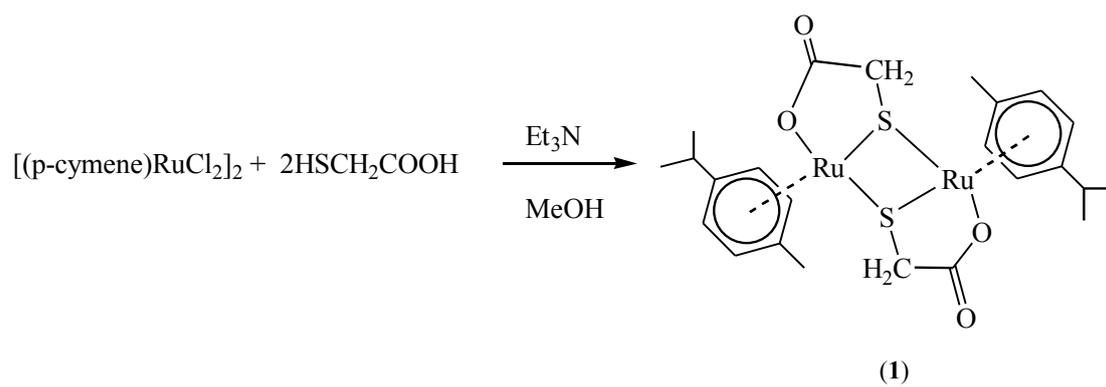
Goodness-of-fit on $F^2$	1.025
R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0434$ , $wR_2 = 0.1047$
R indices (all data)	$R_1 = 0.0551$ , $wR_2 = 0.1120$
Largest diff. features ( $e \text{ \AA}^{-3}$ )	1.49 and -1.89

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

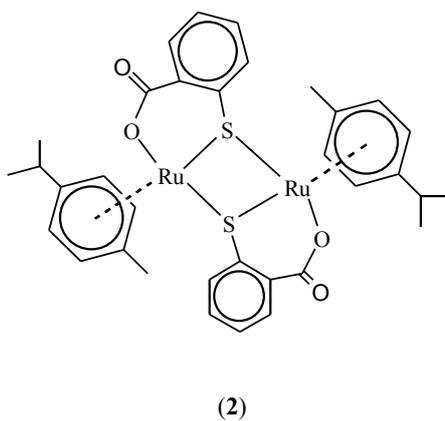
Ru1-S1	2.3992(10)
Ru1-S1'	2.3943(11)
Ru1-O2	2.096(3)
S1-C11	1.818(4)
C11-C12	1.537(6)
C12-O1	1.229(6)
C12-O2	1.299(5)
Ru1-C <sub>arene</sub>	2.209(4) (av.)
Ru1-S1-Ru1'	99.29(4)
S1-Ru1-O2'	81.27(9)
S1'-Ru1-O2'	81.74(9)
S1 -Ru1-S1'	80.71(4)
C11-S1-Ru1'	94.58(14)
C11-S1-Ru1	106.80(14)
C12-C11-S1	113.0(3)
O1-C12-O2	124.0(4)
O1-C12-C11	119.8(4)
O2-C12-C11	116.1(4)
Ru1'-O2-C12	122.3(3)

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Symmetry transformation to generate equivalent atoms: 1-x,-y,1-z



Scheme 1



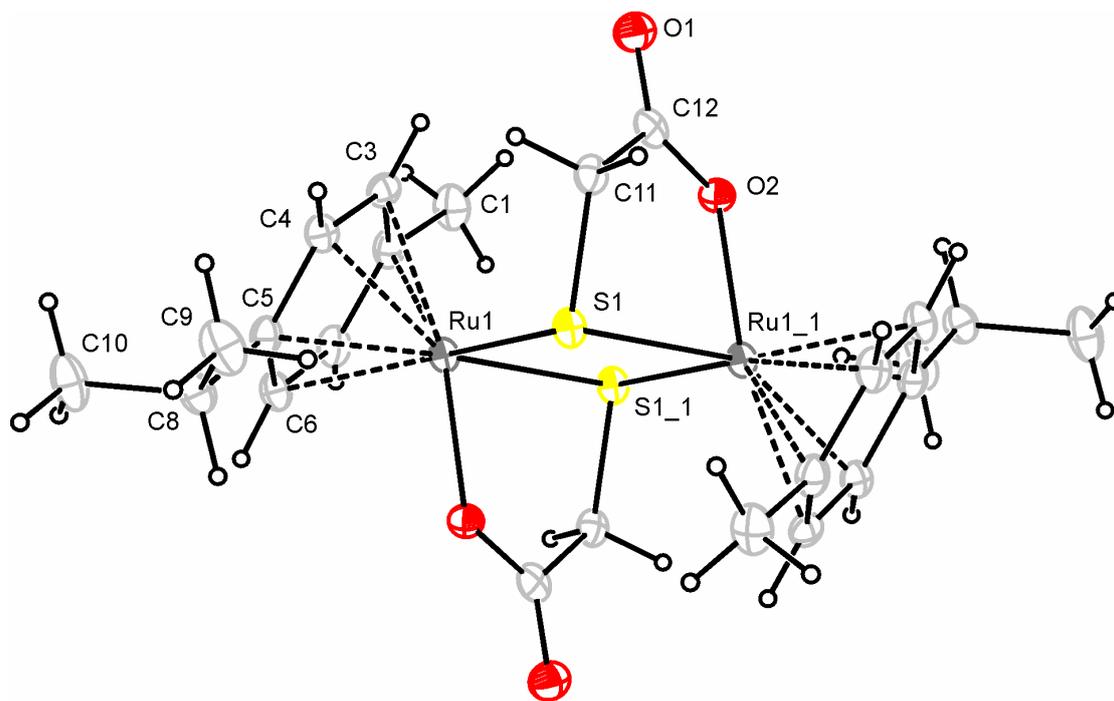


Figure 1. The structure of the centrosymmetric (*p*-cymene)thioglycollatoruthenium(II) dimer, with ellipsoids plotted at the 50% level.