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Trinuclear carbonyl clusters with capping sulphur ligands. crystal structures of $Ru_3(CO)_8(\mu_3\text{-}S)(\eta^1\text{-}L)$ and $RuCo_2(CO)_8(\mu_3\text{-}S)(\eta^1\text{-}L)$

Tiina M. Räsänen *, Sirpa Jääskeläinen, Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland

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Abstract

The reaction of 3-methyl-2-benzothiazolinethione ($PhN(CH_3)C((S)S)$ (L) with the tetrahedral clusters $H_4Ru_4(CO)_{12}$ and $HRuCo_3(CO)_{12}$ leads to coordination of the ligand to triangular faces of the clusters The structures are labile, however, and rearrange to trinuclear compounds $Ru_3(CO)_8(\mu\text{-}S)(\eta^1\text{-}L)$ (1) and $RuCo_2(CO)_8(\mu\text{-}S)(\eta^1\text{-}L)$ (2). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cobalt; Carbonyl clusters; Sulphur ligands

1. Introduction

The reactivity of thione ligands S(C(X)Y with mono- and di-nuclear transition metal complexes has been widely explored [1–5]. Usually the coordination is accompanied by the cleavage of C–X, C–Y or C=S bonds. Binding through the C=S (π-bond is also possible, leaving the ligand framework intact [6]. The X and Y groups have a significant effect on the way the ligand binds to multinuclear metal compounds. For example, ligands with nitrogen- or oxygen-containing groups, the binding may occur through either atom. Polydentate coordination of the ligand often causes cleavage of the C–S double bond and this further assists the reshaping of the cluster. In the reaction between $Ru_3(CO)_{12}$ and $S(C(NRH)_2$ the main product is tetranuclear $Ru_4(CO)_6(\mu_4\text{-}S)_2[C(NRH)_2]_2$ [7]. The reactions of thione ligands with polynuclear metal clusters with more than three metals has received little attention, and interest has been focused on $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [7–14].

In this paper we report the reactions of 3-methyl-2-benzothiazolinthione with tetrahedral mixed–metal clusters.

2. Results and discussion

$Ru_3(CO)_8(\mu_3\text{-}S)$[CN(Me)SPh] (1) was prepared from the reaction between $H_4Ru_4(CO)_{12}$ and 3-methyl-2-benzothiazolinthione in refluxing THF. $RuCo_2(CO)_8(\mu_3\text{-}S)$[CN(Me)SPh] (2) was synthesised from $HRuCo_3(CO)_{12}$ and 3-methyl-2-benzothiazolinthione in refluxing dichloromethane. The use of THF as solvent accelerates the reaction, but $HRuCo_3(CO)_{12}$ tends to fragment in refluxing in this solvent and therefore dichloromethane was used in the latter reaction. The reactions were relatively fast and yields were reasonable. The structures of (1) and (2) are presented in Figs. 1 and 2. Selected bond lengths are listed in Table 1 and selected bond angles in Table 2.

Compounds **1** and **2** both contain a triangular metal framework with μ_3-bonded sulphur atoms originating from the thione groups of the ligand. The remainder of the ligand is bound in terminal position through carbon atom. In both compounds the terminal ligand is attached to ruthenium. The two rings of the ligand form a plane. In **2** the plane of the ligand is nearly parallel to the metal triangle, but in **1** it is twisted so that the sulphur atom in the ligand ring is on the same side as the μ_3-coordinated sulphur atom. The distances be-

* Corresponding author.

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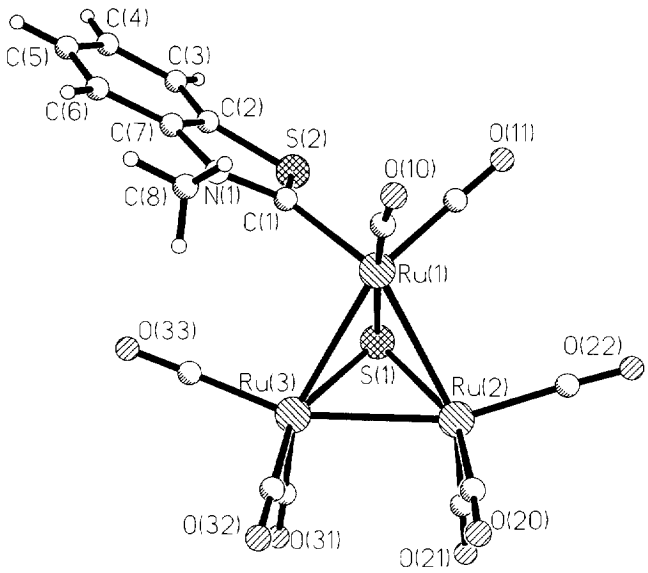


Fig. 1. Structure and numbering scheme of $Ru_3(CO)_8(\mu_3\text{-}S)(L)$ (1).

tween the cobalt atoms and sulphur in compound **2** are 218 and 219 pm, while the distance between ruthenium and sulphur is 235 pm. The average of the Ru–S bond lengths in compound **1** is 237 pm.

Compound **1** contains three terminal carbonyls at Ru(2) and at Ru(3) and two terminal carbonyls at Ru(1) where the ligand is bonded. Product **2**, in turn, has three terminal carbonyls at Co(1) and two terminal carbonyls at Ru(1) and Co(2). There is also an unsymmetrical carbonyl bridge between Ru(1) and Co(2). Semibridging carbonyls are uncommon in mixed metal clusters. This type of semibridges are known where the otherwise unequal charge distribution on the

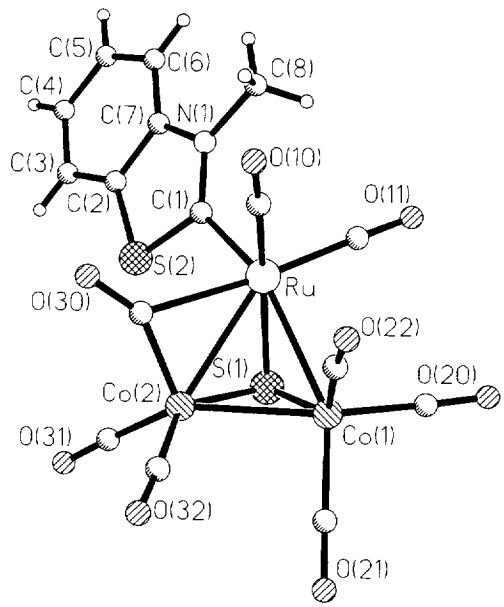


Fig. 2. Structure and numbering scheme of $RuCo_2(CO)_8(\mu_3\text{-}S)(L)$ (2).

Table 1
Bond lengths (pm) for $Ru_3(CO)_8(\mu_3\text{-}S)(\eta^1\text{-}L)$ (**2**)

(1)		(2)	
Ru(2)–Ru(1)	288.2(2)	Ru(1)–Co(1)	266.8(7)
Ru(3)–Ru(1)	288.35	Ru(1)–Co(2)	266.46(7)
Ru(2)–Ru(3)	274.52(11)	Co(2)–Co(1)	253.01
Ru(1)–S(1)	236.8(2)	Ru(1)–S(1)	235.09(11)
Ru(2)–S(1)	236.6(2)	Co(1)–S(1)	217.53(12)
Ru(3)–S(1)	235.55(15)	Co(2)–S(1)	217.53(12)
Ru(1)–C(1)	207.3(5)	Ru(1)–C(1)	204.6(4)
Ru(1)–C(10)	189.9(6)	Ru(1)–C(10)	189.3(4)
Ru(1)–C(11)	187.9	Ru(1)–C(11)	188.9
		Ru(1)–C(30)	232.6(4)
Ru(2)–C(20)	190.8(7)	Co(1)–C(20)	179.0(5)
Ru(2)–C(21)	190.8(6)	Co(1)–C(21)	179.9(5)
Ru(2)–C(22)	194.6(7)	Co(1)–C(22)	177.7(4)
Ru(3)–C(31)	190.2(7)	Co(2)–C(30)	181.5(4)
Ru(3)–C(32)	190.8(7)	Co(2)–C(31)	176.8(4)
Ru(3)–C(33)	191.4(7)	Co(2)–C(32)	177.5(5)
O(10)–C(10)	114.1(8)	O(10)–O(10)	113.9(5)
C(11)–O(11)	115.0(8)	O(11)–O(11)	111.2(5)
O(20)–C(20)	112.4(9)	C(20)–O(20)	114.2(6)
O(21)–O(21)	113.8(8)	O(21)–C(21)	113.2(6)
C(22)–O(22)	110.4(9)	O(22)–C(22)	113.7(5)
O(31)–C(31)	113.6(8)	O(31)–C(31)	114.4(5)
O(32)–C(32)	113.8(8)	C(32)–O(32)	112.0(5)
O(33)–C(33)	114.0(9)	O(30)–C(30)	115.9(5)
C(1)–S(2)	172.9(6)	S(2)–C(1)	173.2(4)
S(2)–C(2)	173.4(7)	S(2)–C(2)	173.7(4)
C(2)–C(3)	139.7(9)	C(2)–C(3)	138.7(6)
C(3)–C(4)	138.9(11)	C(3)–C(4)	137.9(7)
C(4)–C(5)	136.6(12)	C(5)–C(4)	137.4(7)
C(6)–C(5)	138.5(10)	C(5)–C(6)	138.1(6)
C(7)–C(6)	139.2(9)	C(7)–C(6)	138.6(6)
C(7)–C(2)	138.5(9)	C(2)–C(7)	138.9(6)
N(1)–C(7)	142.0(8)	N(1)–C(7)	139.8(5)
C(1)–N(1)	132.2(7)	C(1)–N(1)	132.5(5)
N(1)–C(8)	143.0(9)	N(1)–C(8)	147.3(5)

metal atoms involved is equalized by the semibridge [15–18]. The Ru(1)–C(30) bond is 232.6(4) pm, whereas the average bond length between ruthenium and terminal carbonyl groups at cobalt is over 300 pm. In the normal bridging carbonyl the distance is about 210 pm [19]. The corresponding values for cobalt are 181.5(1) for this semibridge compared with averages of 180 pm for terminal carbonyl groups and 195 pm for normal bridges [20]. Only a few tetranuclear Ru–Co compounds with semibridging carbonyls are known. One of them is the tetrahedral compound $HRu_3Co(CO)_{10}$(trithiacyclohexane) [21] where the corresponding Ru–C distances are 213–217 pm and Co–C distances are 188–186 pm. In the butterfly structure $HRu_3Co(CO)_{12}(SMe_2)$ [22] the distances are 226 pm for Ru–C and 184 pm for Co–C.

The formation of the trinuclear products possibly proceeds via tetranuclear intermediates. Our earlier studies have shown that in mixed metal clusters containing ruthenium and cobalt, sulphur has a greater

Table 2
Bond angles (°) for $Ru_3(CO)_8(\mu_3\text{-}S)(\eta^1\text{-}L)$ (1) and $RuCo_2(CO)_8(\mu_3\text{-}S)(\eta^1\text{-}L)$ (2)

Ru(3)–Ru(2)–Ru(1)	61.59(4)	Co(2)–Co(1)–Ru(1)	61.61(2)
Ru(2)–Ru(3)–Ru(1)	61.54(4)	Co(1)–Co(2)–Ru(1)	61.74(2)
Ru(2)–Ru(1)–Ru(3)	56.87(3)	Co(2)–Ru(1)–Co(1)	56.65(2)
Ru(2)–S(1)–Ru(1)	72.00(6)	Co(1)–S(1)–Ru(1)	71.86(4)
Ru(3)–S(1)–Ru(1)	75.24(5)	Co(2)–S(1)–Ru(1)	72.01(3)
Ru(3)–S(1)–Ru(2)	71.09	Co(2)–S(1)–Co(1)	70.83(4)
S(1)–Ru(1)–Ru(2)	52.47(4)	S(1)–Ru(1)–Co(1)	51.29(3)
S(1)–Ru(1)–Ru(3)	52.18(4)	S(1)–Ru(1)–Co(2)	50.94(3)
S(1)–Ru(2)–Ru(1)	52.53(5)	S(1)–Co(1)–Ru(1)	56.86(3)
S(1)–Ru(2)–Ru(3)	54.27(4)	S(1)–Co(1)–Co(2)	54.30(3)
S(1)–Ru(3)–Ru(1)	52.57(4)	S(1)–Co(2)–Ru(1)	57.05(3)
S(1)–Ru(3)–Ru(2)	54.64(4)	S(1)–Co(2)–Co(1)	54.87(4)
C(10)–Ru(1)–Ru(2)	117.2(2)	C(10)–Ru(1)–Co(1)	11.74(13)
C(10)–Ru(1)–Ru(3)	120.9(2)	C(10)–Ru(1)–Co(2)	13.88(13)
C(11)–Ru(1)–Ru(2)	100.1(2)	C(11)–Ru(1)–Co(1)	92.47(12)
C(11)–Ru(1)–Ru(3)	145.0(2)	C(11)–Ru(1)–Co(2)	143.33(13)
C(20)–Ru(2)–Ru(1)	111.2(2)	C(20)–Co(1)–Ru(1)	104.2(2)
C(20)–Ru(2)–Ru(3)	97.7(2)	C(20)–Co(1)–Co(2)	153.1(2)
C(21)–Ru(2)–Ru(1)	147.0(2)	C(21)–Co(1)–Ru(1)	153.83(15)
C(21)–Ru(2)–Ru(3)	94.4(2)	C(21)–Co(1)–Co(2)	92.22(14)
C(22)–Ru(2)–Ru(1)	101.6(2)	C(22)–Co(1)–Ru(1)	79.03(14)
C(22)–Ru(2)–Ru(3)	160.3(2)	C(22)–Co(1)–Co(2)	97.90(13)
C(31)–Ru(3)–Ru(1)	144.9(2)	C(31)–Co(2)–Ru(1)	128.88(14)
C(31)–Ru(3)–Ru(2)	95.7(2)	C(31)–Co(2)–Co(1)	141.69(15)
C(32)–Ru(3)–Ru(1)	113.2(2)	C(32)–Co(2)–Ru(1)	129.2(2)
C(32)–Ru(3)–Ru(2)	96.2(2)	C(32)–Co(2)–Co(1)	92.0(2)
C(33)–Ru(3)–Ru(1)	100.2(2)	C(30)–Co(2)–Ru(1)	58.97(13)
C(33)–Ru(3)–Ru(2)	159.0(2)	C(30)–Co(2)–Co(1)	109.94(13)
C(10)–Ru(1)–S(1)	169.1(2)	C(10)–Ru(1)–S(1)	160.57(13)
C(11)–Ru(1)–S(1)	93.2(2)	C(11)–Ru(1)–S(1)	95.38(13)
C(20)–Ru(2)–S(1)	151.1(2)	C(20)–Co(1)–S(1)	98.9(2)
C(21)–Ru(2)–S(1)	95.6(2)	C(21)–Co(1)–S(1)	109.03(15)
C(22)–Ru(2)–S(1)	108.1(2)	C(22)–Co(1)–S(1)	134.71(14)
C(31)–Ru(3)–S(1)	92.8(2)	C(31)–Co(2)–S(1)	97.27(15)
C(32)–Ru(3)–S(1)	150.5(2)	C(32)–Co(2)–S(1)	141.0(2)
C(33)–Ru(3)–S(1)	106.7(2)	C(30)–Co(2)–S(1)	111.71(13)
C(11)–Ru(1)–C(10)	92.4(3)	C(11)–Ru(1)–C(10)	94.8(2)
C(20)–Ru(2)–C(22)	98.2(3)	C(22)–Co(1)–C(20)	101.6(2)
C(21)–Ru(2)–C(20)	93.3(3)	C(20)–Co(1)–C(21)	99.7(2)
C(21)–Ru(2)–C(22)	96.2(3)	C(22)–Co(1)–C(21)	106.7(2)
C(31)–Ru(3)–C(32)	94.5(3)	C(31)–Co(2)–C(32)	99.2(2)
C(31)–Ru(3)–C(33)	94.8(3)	C(31)–Co(2)–C(30)	104.6(2)
C(32)–Ru(3)–C(33)	101.1(3)	C(32)–Co(2)–C(30)	97.9(2)
O(10)–C(10)–Ru(1)	174.4(6)	O(10)–C(10)–Ru(1)	175.6(4)
O(11)–C(11)–Ru(1)	178.2(6)	O(11)–C(11)–Ru(1)	178.8(4)
O(20)–C(20)–Ru(2)	175.8(7)	O(20)–C(20)–Co(1)	178.4(4)
O(21)–C(21)–Ru(2)	179.0(6)	O(21)–C(21)–Co(1)	179.3(4)
O(22)–C(22)–Ru(1)	175.7(7)	O(22)–C(22)–Co(1)	174.1(4)
O(31)–C(31)–Ru(3)	177.7(7)	O(31)–C(31)–Co(2)	177.9(4)
O(32)–C(32)–Ru(3)	178.9(6)	O(32)–C(32)–Co(2)	175.7(4)
O(33)–C(33)–Ru(3)	177.6(7)	O(30)–C(30)–Co(2)	149.9(3)
		Co(2)–C(30)–Ru(1)	79.05(15)
		C(30)–Ru(1)–Co(1)	91.38(10)
		C(30)–Ru(1)–Co(2)	41.98(10)
		C(30)–Ru(1)–S(1)	90.06(10)
		C(1)–Ru(1)–C(30)	85.40(14)
		C(10)–Ru(1)–C(30)	80.2(2)
		C(11)–Ru(1)–C(30)	174.5(2)
		C(11)–Ru(1)–Co(30)	131.0(3)
C(10)–Ru(1)–C(1)	96.7(2)	C(10)–Ru(1)–C(1)	97.2(2)
C(11)–Ru(1)–C(1)	92.7(3)	C(11)–Ru(1)–C(1)	93.2(15)
C(1)–Ru(1)–Ru(2)	142.9(2)	C(1)–Ru(1)–Co(1)	142.86(10)
C(1)–Ru(1)–Ru(3)	93.79(15)	C(1)–Ru(1)–Co(2)	104.72(10)
C(1)–Ru(1)–S(1)	92.5(2)	C(1)–Ru(1)–S(1)	96.68(13)

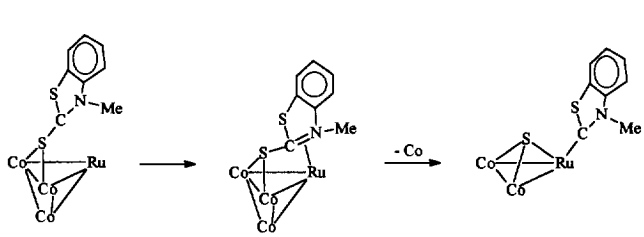
Table 2 (*Continued*)

S(2)–C(1)–Ru(1)	118.0(3)	S(2)–C(1)–Ru(1)	117.7(2)
N(1)–C(1)–Ru(1)	132.4(4)	N(1)–C(1)–Ru(1)	133.3(3)
N(1)–C(1)–S(2)	109.6(4)	N(1)–C(1)–S(2)	108.8(3)
C(1)–S(2)–C(2)	93.3(3)	C(1)–S(2)–C(2)	93.1(2)
C(7)–C(2)–S(2)	109.2(5)	C(7)–C(2)–S(2)	109.2(3)
C(7)–C(2)–C(3)	120.7(6)	C(3)–C(2)–C(7)	121.2(4)
C(3)–C(2)–S(2)	130.0(6)	C(3)–C(2)–S(2)	129.7(4)
C(4)–C(3)–C(2)	116.4(7)	C(4)–C(3)–C(2)	118.2(5)
C(5)–C(4)–C(3)	122.9(7)	C(5)–C(4)–C(3)	120.3(4)
C(4)–C(5)–C(6)	120.8(7)	C(4)–C(5)–C(6)	122.3(5)
C(5)–C(6)–C(7)	117.3(7)	C(5)–C(6)–C(7)	117.7(5)
C(2)–C(7)–C(6)	121.7(6)	C(6)–C(7)–C(2)	120.3(4)
C(6)–C(7)–N(1)	126.5(6)	C(6)–C(7)–N(1)	128.0(4)
C(2)–C(7)–N(1)	111.8(5)	C(2)–C(7)–N(1)	111.7(3)
C(1)–N(1)–C(7)	116.0(5)	C(1)–N(1)–C(7)	117.2(3)
C(1)–N(1)–C(8)	124.8(5)	C(1)–N(1)–C(8)	123.2(3)
C(7)–N(1)–C(8)	119.2(5)	C(7)–N(1)–C(8)	119.6(3)

tendency to bind to cobalt, while nitrogen favours ruthenium [23]. On that basis it would seem that the ligand first binds through the thione sulphur to two cobalt atoms in equatorial positions. The bonding opens the C=S π-bond and enhances the multiple bond C=N, and the remainder of the ligand then binds to ruthenium through the double bond between carbon and nitrogen. Evidence for this tetrahedral trisubstituted intermediate has been obtained from the IR spectra of the reaction solution. Although it is too unstable to be isolated it can be identified by the similarity of its IR spectrum with that of a RuCoCo-trisubstituted phosphine derivative [24]. The μ_2-S bridging coordination mode weakens the C–S bond and facilitates the C–S bond cleavage resulting in the formation of μ_3-S bridge. A similar progress of reaction has been proposed for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ clusters [11,14]. The remainder of the ligand coordinates via carbon atom (Scheme 1).

The slight shortening of the C–N distance (in products 132 pm and in free ligand 135 pm) shows that some of the (electron density of the S=C double bond has migrated to the C–N bond. As there is no significant change in the C–S bond of the ligand the electron density seems not to migrate to that bond.

The reactions of coordinated S–N ligands with $Os_3(CO)_{12}$ lead to the formation of an intermediate with a triply sulphido-bridging cluster, in which the sulphur is bridging two metal atoms and the nitrogen is coordinated to the third metal of the triangular metal core [6,25]. The subsequent reaction paths seem to be highly dependent on the properties of the metal compound as well as the other ligands coordinated to the cluster.



Scheme 1.

The results are reminiscent of the reaction of $Ru_3(CO)_{12}$ and mercaptobenzothiazole [26], which resembles 3-methyl-2-benzothiazolinethione. Mercaptobenzothiazole has a double bond between nitrogen and carbon rather than between sulphur and carbon. The free ligand molecule has two tautomeric forms, HN–C=S and N=C–SH, in a thione-thiol equilibrium. The latter form is easily broken down to give a coordinated sulphido-ligand and the rest of the ligand binds through both the unsaturated carbon atom and the nitrogen atom. Thus the coordination mode in the second step is dependent on the nitrogen environment and C–NR_2 groups prevent the binding through nitrogen.

$Co_2(CO)_8$ and $Fe_2(CO)_9$ also react with thioamides giving, among mono- and di-nuclear complexes, trinuclear compounds with a μ_3-S group and a bidentate ligand [2–5]. The coordinated heterocyclic group is in some cases desulphurized, but coordination without fragmentation is also observed.

3. Experimental

3.1. General comments

All reactions were carried out under nitrogen atmosphere with deoxygenated solvents. 3-Methyl-2-benzothiazolinthione was of commercial origin (Aldrich). $HRuCo_3(CO)_{12}$ [27] and $H_4Ru_4(CO)_{12}$ [28] were prepared by published methods.

Infrared spectra were recorded in dichloromethane on a Nicolet 750 spectrometer. ^{1}H-NMR spectra were measured on a Bruker AM-250 spectrometer with CDCl3 as solvent and TMS as reference.

Table 3
Crystal data and collection parameters for $Ru_3(CO)_8(\mu$-S)(CNMeSPh) (1) and $RuCo_2(CO)_8(\mu_3$-S)(L) (2)

	1	2
Formula	$Ru_3S_2NO_8C_{16}H_7$	$RuCo_2S_2NO_8C_{16}H_7$
Formula weight (g mol^{-1})	708.56	624.29
Colour, habit	Yellow	Black
Crystal size (mm)	0.5×0.6×0.3	0.3×0.3×0.2
Crystal system	Triclinic	Monoclinic
Space group	P−1	C2/c
Unit cell dimension		
a (Å)	8.168(2)	24.438(5)
b (Å)	11.597(2)	11.257(2)
c (Å)	13.231(3)	14.738(3)
α (°)	115.93(3)	90
β (°)	93.05(3)	95.00(3)
γ (°)	104.16(3)	90
V (Å^3)	1079.8(4)	4039.0(14)
Z	2	6
μ (mm^{-1})	2.306	2.613
Calculated density (g cm^{-3})	2.179	2.053
Number of centring reflections	25	24
Centring 2θ (°)	15–25	15–26
Scan range 2θ (°)	3.04–25	2.39–25
Scan speed (° min^{-1})	3–30	3–30
h, k, l range	9, ±13, ±15	29, 13, ±17
Number of unique reflections	3712	3474
Number of observed data ($F>4\sigma(F)$)	3577	3153
Number of parameters	271	271
R	0.0477	0.0372
Rw	0.1616	0.1182
GoF	1.518	1.033

3.2. Synthesis of $[Ru_3(CO)_8(\mu_3$-S)(CSNMePh)] (1)

A mixture of $H_4Ru_4(CO)_{12}$ (100 mg, 0.13 mmol) and 3-methyl-2-benzothiazolinthione (60 mg, 0.33 mmol) in 40 ml of THF was refluxed for 3 h. The solvent was evaporated in vacuum and the residue was chromatographed on a silica column. Elution with hexane gave a yellow fraction containing by-products. Elution with 1:1 hexane-$CHCl_2$ mixture gave an orange franction of (1) yield 42 mg, 35%. Orange crystals were obtained from dichloromethane at room temperature. IR ($CHCl_2$): 2078 m, 2046 vs, 2000 s, 1943 w. ^{1}H-NMR: 4.33 ppm (s, CH_3), 7.5 ppm (m, Ph). $Ru_3S_2NC_{15}O_8H_7$ Calc.: H 1.01%, C 25.97%, N 2.01%. Found: H 1.23, C 26.20, N 1.95%.

3.3. Synthesis of $[RuCo_2(CO)_8(\mu_3$-S)(CSNMePh] (2)

To a solution of $HRuCo_3(CO)_{12}$ (100 mg, 0.16 mmol) in dichloromethane (40 ml) was added 3-methyl-2-benzothiazolinthione (40 mg, 0.22 mmol). The solution was refluxed for 24 h. Chromatographic separation on silica plates with 1:1 hexane-CH_2Cl_2 as eluent gave three bands. The first and largest fraction contained product (2), yield 28 mg, 21%. The other two reddish-brown fractions contained tetranuclear compounds, as characterized by IR spectra. Black crystals for the X-ray study were obtained from CH_2Cl_2. IR ($CHCl_2$): 2075 m, 2036 s, 2022 s, 2006 m, 1960 w, 1880 w, 1822 w, 1796 w. ^{1}H-NMR: 4.38 ppm (s, CH_3), 7.5 ppm (m, Ph). $RuCo_2S_2NC_{15}O_8H_7$ Calc.: H 1.16, C 29.43, N 2.29%. Found: H 1.17, C 29.94, N 2.33%.

3.4. Crystallographic studies

Intensity data were collected on a Nicolet R3m diffractometer. Mo Kα radiation with $\lambda = 0.71073$ Å was used. Intensities were corrected for Lorentz, polarization and background effects. Table 3 presents further crystallographic data. The structures were solved by direct methods using the SHELXTL program [29] package. The subsequent least squares refinement was made with the SHELXL93 program [30]. Methyl and phenyl protons were placed in idealized positions with C–H distance of 96 pm and isotropic temperature factors of 0.08 Å^2.

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