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An examination of bent semi-bridging metal carbonyl bonding

II *. Polymorphism and multiple independent molecules in $[H_2Ru_4(CO)_{13}]$

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Abstract

A triclinic polymorph of $[H_2Ru_4(CO)_{13}]$ has been crystallographically characterized: $P\bar{1}$, a 9.062(2), b 9.155(2), c 26.649(6) Å, α 81.80(2), β 88.03(2), γ 67.76(2)°, V 2024.9(8) Å^3, $Z = 4$, R_F 2.31%. Both this polymorph and a previously studied monoclinic polymorph [D.B.W. Yawney and R.J. Doedens, Inorg. Chem., 11 (1972) 838] crystallize with two independent molecules in the asymmetric units. A wide range of bond parameters are found for the two bent semi-bridging μ-CO ligands in each of the four chemically identical molecules in the two polymorphs. However, despite the wide range of values, which are attributed to crystal packing forces, each μ-CO group conforms exactly to the linear Crabtree–Lavin relationship [R.H. Crabtree and M. Lavin, Inorg. Chem., 25 (1986) 805].

Introduction

A common feature of 60-electron tetranuclear metal carbonyl clusters and cluster anions containing entirely or predominantly group 8 metal atoms is the extraordinary prevalence of polymorphism and multiple-independent molecules in their solid-state structures. Both situations arise from the roughly spherical equipotential surfaces of these tetrahedral structures and the absence of strong intermolecular (or interionic) forces compelling specific packing arrangements. When either polymor-

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* For part I see ref. 1.

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phism or multiple-independent molecules occurs, an opportunity exists to examine the relationship between structural features (intramolecular) and crystal packing forces (intermolecular). For metal carbonyls, the presence of and type of bridging CO ligands are particularly sensitive to crystal packing forces. We recently compared four molecules of $[H_2RuOs_3(CO)_{13}]$, arising from two polymorphs, each with two independent molecules and found a wide range of bent semi-bridging metal carbonyl bond parameters [1]. However, despite the range of parameters, all conformed closely to the Crabtree–Lavin empirical relationships discussed below [2].

We now report a similar study of two polymorphs of $[H_2Ru_4(CO)_{13}]$ which are both isomorphs of the structures of $[H_2RuOs_3(CO)_{13}]$ we reported. A monoclinic polymorph of $[H_2Ru_4(CO)_{13}]$ (**I(m)**), was reported in 1972 and refined to a conventional *R* factor of 5.9% [3]. The structure was obtained from a small crystal of questionable quality with only 1134 observed data; the bridging μ-H ligands were not located. We have determined the structure of the triclinic polymorph, (**I(t)**), with 5503 observed data and refinement to *R* 2.3%; the bridging μ-H ligands were located.

Experimental

The compound $H_2Ru_4(CO)_{13}$ was isolated as a minor product from the reaction of $Ru_3(CO)_{12}$ (4.5 g, 7.0 mmol) with PhNO (900 mg, 8.4 mmol) in THF (200 ml; 50 °C, 5h). Evaporation of solvent left a red residue which was extracted with hexane (300 ml) to leave a residue of $Ru_3(CO)_{12}$ (2.1 g). The extract was chromatographed on SiO_2 using hexane as eluent to give first a yellow band of $Ru_3(CO)_{12}$ (30 mg) followed by a light orange band of $H_2Ru_4(CO)_{13}$ (50 mg, 1.0%) followed by two orange bands of the desired products [4] $Ru_3(\mu_3\text{-NPh})_2(CO)_9$ (230 mg, 8.3%) and $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ (1.23 g, 48%). It may be that $H_2Ru_4(CO)_{13}$ was not actually formed in this reaction but instead was carried over as a minor impurity in the $Ru_3(CO)_{12}$ reagent since the preparation of this latter species via the literature route [5], involving carbonylation of $RuCl_3 \cdot nH_2O$ (125 °C, 1000 psi, 8 h), invariably gives $Ru_3(CO)_{12}$ contaminated with small quantities of $H_2Ru_4(CO)_{13}$.

Crystallographic data are summarized in Table 1. Red crystals of **I(t)** were obtained by slow evaporation from pentane. Photographic characterization revealed that the unit cell was isomorphous with that determined for $[H_2RuOs_3(CO)_{13}]$ [1]. The hemisphere of data collected was empirically corrected for absorption (six ψ-scan reflections, 216 data in 10° increments) which reduced *R*(int) for 5.2 to 1.0% for these reflections.

The coordinates for the eight heavy-atoms in the two independent molecules of $[H_2RuOs_3(CO)_{13}]$ were used to initialize refinement. The remaining atoms, including the two μ-H ligands were located in subsequent difference maps. All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were found and isotropically refined.

The atomic coordinates for **I(t)** are given in Table 2 and bond distances and angles are given in Table 3, and are compared to equivalent parameters for **I(m)**. Additionally, observed and calculated structure factors, anisotropic thermal parameters and a complete list of bond distances and angles are available from one of the authors (ALR).

Results and discussion

The triclinic polymorph of $[H_2Ru_4(CO)_{13}]$ (**I(t)**) crystallizes as discrete molecules with two crystallographically independent molecules forming the asymmetric unit. The molecules are shown in Fig. 1 and Fig. 2. Except for differences in the semi-bridging CO ligands, the two molecules are very similar. Both are, additionally, very similar to the two independent molecules found in the monoclinic ($P2_1/c$) polymorph, **I(m)** [3]. The differences in the arrangements of molecules of **I(t)** in the lattice are slight; the location of the screw axis in **I(m)** intersects the inversion center

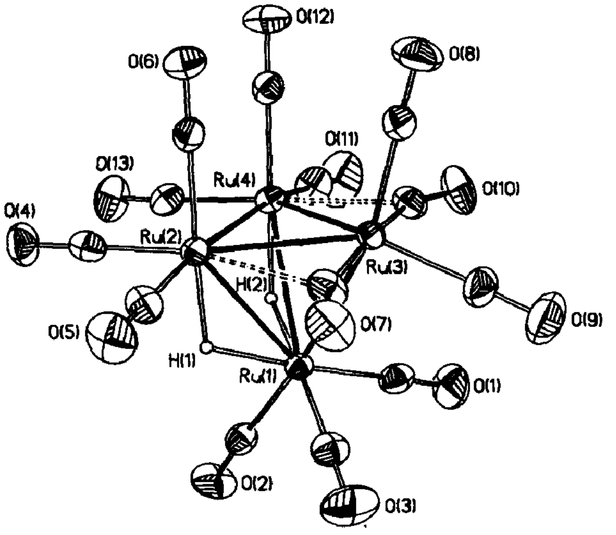

Fig. 1. Molecular structure and labeling scheme for molecule A of **I(t)** drawn with 40% thermal ellipsoids.

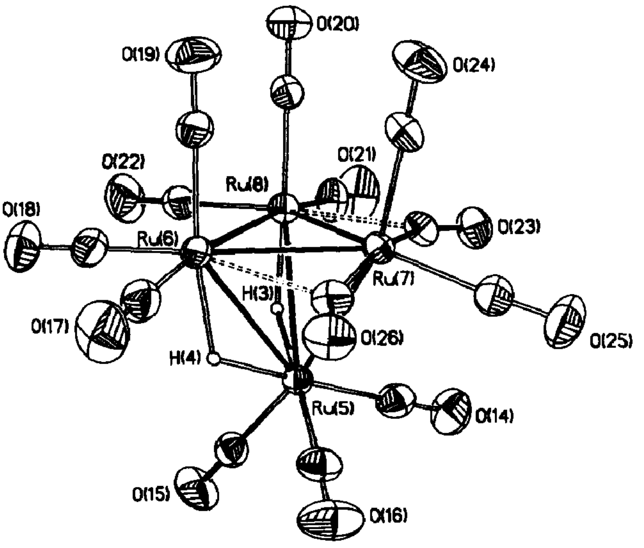

Fig. 2. Molecular structure and labeling scheme for molecule B of **I(t)** drawn with 40% thermal ellipsoids.

Table 1

Crystal data for complex **I(t)**

(a) Crystal data	
Formula	$H_2Ru_4(CO)_{13}$
Space group	$P\bar{1}$
a, b, c, Å	9.062(2), 9.155(2), 26.649(6)
α, β, γ, deg	81.80(2), 88.03(2), 67.76(2)
V, Å^3	2024.9(8)
Z	4
d(calcd), g cm^{-3}	2.527
Crystal size, mm	$0.21 \times 0.36 \times 0.38$
Color	red
(b) Data collection	
Diffractometer	Nicolet R3m
Radiation	Mo-K_α (λ 0.71073 Å)
Temperatures, ° C	23
μ, cm^{-1}	29.36
Scan method	θ-2θ
Scan limits	$4 \leqslant 2\theta \leqslant 48$
Data collected	$\pm h$, $\pm k$, $+l$
Independent data	(6543 collected)
Observed ($F_0 \geqslant 5\sigma(F_0)$)	5503
(c) Data reduction and refinement	
Standard reflections	3 std/197 rflns (< 2% decay)
R(int)	1.58%
R_F, R_{wF}(%), GOF	2.31, 2.18, 1.44
g ($W^{-1} = \sigma^2(F_0) + gF_0$)	0.001
Δ/σ(max), final cycle	0.209
$\Delta(\rho)$ e Å^{-3}	0.48

in **I(t)**. The overall effect is to shorten the c axis by approximately one half in **I(t)** while leaving the a and b axes only slightly changed.

In the previously determined structure of **I(m)**, the μ_2-H ligands were not located, but were placed along the longest Ru–Ru edges. In **I(t)** we have unambiguously located all four bridging hydrided ligands in the anticipated positions along the longest Ru–Ru edges [6*]. The average Ru–H distance (1.72(3) Å) agrees closely to that found for $[Ru_4(CO)_{10}(diphos)(\mu\text{-}H)_4]$ (av. Ru–H 1.76(3) Å) [7], $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Br)]$ (av. Ru–H 1.8 Å) [8], and $[Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COMe)]$ (av. Ru–H 1.75(4) Å) [9]. In **I(t)** the Ru–H–Ru planes are depressed below the bridged Ru_3 plane by ~ 57° away from the apical, unbridged Ru atom. Both **I(m)** and **I(t)** possess the same idealized C_s symmetry.

Crabtree and Lavin [2], in a statistical analysis of 35 iron carbonyl compounds containing semi-bridging CO ligands, derived the empirical relationship, $\theta = n\psi + m$ where θ and ψ are defined in Table 3. They obtained the values $n = 1.51$ and $m = 64.5$; in our previous study of $H_2RuOs_3(CO)_{13}$, which contained eight semi-bridging CO ligands (from two isomorphs each containing two independent mole-

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **I**(t)

	x	y	z	U [a]
Ru(1)	982.5(5)	3909.8(5)	1437.6(2)	29.5(2)
Ru(2)	2815.5(5)	3192.3(5)	504.2(2)	30.5(2)
Ru(3)	4300.6(5)	2788.8(5)	1433.9(2)	31.7(2)
Ru(4)	2925.0(5)	641.1(5)	1262.0(2)	32.3(2)
Ru(5)	5915.6(5)	8990.4(6)	3807.9(2)	35.4(2)
Ru(6)	8627.1(6)	8167.9(6)	3120.7(2)	39.2(2)
Ru(7)	9054.1(5)	8060.5(5)	4156.3(2)	34.1(2)
Ru(8)	8224.4(6)	5712.3(5)	3814.8(2)	36.4(2)
C(1)	1079(7)	3538(7)	2163(2)	48(3)
O(1)	1106(6)	3326(6)	2593(2)	82(3)
C(2)	−1288(8)	4434(7)	1384(2)	42(3)
O(2)	−2614(5)	4761(6)	1382(2)	72(2)
C(3)	786(7)	6055(8)	1423(2)	47(3)
O(3)	604(6)	7360(6)	1424(2)	83(3)
C(4)	1640(7)	2607(7)	44(2)	44(2)
O(4)	959(5)	2333(5)	−254(2)	63(2)
C(5)	2585(7)	5072(7)	38(2)	46(3)
O(5)	2467(6)	6176(5)	−239(2)	70(2)
C(6)	4813(7)	1920(7)	256(2)	39(2)
O(6)	6002(5)	1164(5)	108(1)	55(2)
C(7)	4033(7)	4705(7)	956(3)	47(3)
O(7)	4100(6)	5920(5)	808(2)	68(2)
C(8)	6539(7)	1705(7)	1318(2)	44(3)
O(8)	7862(5)	1051(6)	1258(2)	74(2)
C(9)	4563(8)	3840(8)	1976(2)	63(3)
O(9)	4698(7)	4454(8)	2295(2)	109(4)
C(10)	4262(7)	1035(7)	1951(2)	48(3)
O(10)	4538(6)	320(6)	2355(2)	74(2)
C(11)	2659(8)	−842(8)	1805(3)	60(3)
O(11)	2496(8)	−1699(7)	2140(2)	105(4)
C(12)	4888(8)	−823(7)	1056(2)	44(3)
O(12)	6072(5)	−1723(5)	941(2)	69(2)
C(13)	1669(7)	116(7)	801(2)	45(3)
O(13)	940(6)	−274(6)	557(2)	70(3)
C(14)	5216(8)	8696(8)	4483(2)	58(3)
O(14)	4799(6)	8487(6)	4884(2)	87(3)
C(15)	3914(7)	9359(7)	3488(2)	48(3)
O(15)	2723(5)	9556(6)	3314(2)	79(2)
C(16)	5533(7)	11183(7)	3803(2)	53(3)
O(16)	5274(7)	12506(7)	3785(3)	91(3)
C(17)	8707(8)	10031(8)	2712(2)	59(3)
O(17)	8749(7)	11115(6)	2462(2)	96(3)
C(18)	8031(8)	7544(8)	2547(2)	61(3)
O(18)	7674(7)	7234(6)	2176(2)	88(3)
C(19)	10839(8)	6881(8)	3082(2)	53(3)
O(19)	12144(6)	6127(6)	3055(2)	84(3)
C(20)	10359(7)	4223(7)	3812(2)	49(3)
O(20)	11626(5)	3297(5)	3815(2)	74(2)
C(21)	7554(10)	4239(9)	4270(3)	59(4)
O(21)	7197(8)	3371(6)	4529(2)	98(3)
C(22)	7670(7)	5048(7)	3227(2)	54(3)
O(22)	7309(7)	4562(7)	2911(2)	88(3)

Table 2 (continued)

	x	y	z	U [a]
C(23)	8488(7)	6413(7)	4596(2)	44(3)
O(23)	8249(5)	5871(5)	4998(2)	58(2)
C(24)	11343(7)	7080(7)	4223(2)	47(3)
O(24)	12700(5)	6554(6)	4251(2)	75(2)
C(25)	8749(7)	9003(8)	4768(2)	56(3)
O(25)	8598(6)	9498(6)	5140(2)	85(3)
C(26)	9078(7)	9948(7)	3743(2)	47(3)
O(26)	9141(5)	11203(5)	3630(2)	62(2)
H(1)	1014(49)	4151(70)	776(12)	110(25)
H(2)	1113(39)	1983(29)	1444(15)	30(13)
H(3)	6315(41)	7045(31)	3789(19)	66(18)
H(4)	6736(49)	9408(67)	3237(18)	149(31)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor, except for the H atoms.

Table 3

Bond distances (Å) and angles (°) for **I(t)** and **I(m)**

	I(t)		**I(m)**	
	mol. A	mol. B	mol. A	mol. B
Bond distances				
Ru(1)–Ru(2)	2.955(1)	2.940(1)	2.915(7)	2.924(7)
Ru(1)–Ru(4)	2.937(1)	2.936(1)	2.947(6)	2.935(8)
Ru(1)–Ru(3)	2.786(1)	2.793(1)	2.785(7)	2.771(7)
Ru(2)–Ru(3)	2.771(1)	2.783(1)	2.764(7)	2.786(7)
Ru(3)–Ru(4)	2.789(1)	2.801(1)	2.762(6)	2.778(7)
Ru(2)–Ru(4)	2.835(1)	2.828(1)	2.818(7)	2.805(8)
Ru(2)–C(7)	2.511(8)	2.627(7)	2.47(5)	2.42(5)
Ru(4)–C(7)	1.955(6)	1.919(6)	1.90(5)	2.01(7)
Ru(3)–C(10)	1.971(6)	1.988(7)	1.89(5)	1.94(5)
Ru(4)–C(10)	2.375(7)	2.309(7)	2.31(5)	2.40(4)
Ru–C(term) (ave.)	1.914(7)	1.909(7)	1.90(8)	1.88(8)
Ru(1)–H(1)	1.74(3)	1.73(5)		
Ru(2)–H(1)	1.72(3)	1.71(4)		
Ru(1)–H(2)	1.72(3)	1.68(3)		
Ru(4)–H(2)	1.74(3)	1.69(3)		
C(7)–O(7)	1.150(9)	1.168(7)	1.13(4)	1.23(6)
C(10)–O(10)	1.159(7)	1.165(7)	1.25(5)	1.22(6)
Bond Angles				
Ru–Ru–Ru	(all 60 ± 3°)			
Ru–C–O (term)	(all 173 ± 3°)			
Ru(2)–C(7)–O(7)	126.9(5)	126.1(4)	129(4)	133(5)
Ru(3)–C(7)–O(7) (θ)	157.5(6)	160.3(5)	154(5)	144(5)
Ru(3)–C(10)–O(10) (θ)	152.0(7)	149.5(6)	149(4)	152(5)
Ru(4)–C(10)–O(10)	128.7(6)	129.5(6)	130(4)	129(4)
Ru(2)–C(7)–Ru(3)	75.6(3)	73.6(2)	82(2)	79(2)
Ru(3)–C(10)–Ru(4)	79.3(2)	81.0(2)	77(2)	77(2)
Ru(1)–H(1)–Ru(2)	117(2)	118(2)		
Ru(1)–H(2)–Ru(4)	116(2)	121(2)		
Ru(2)–Ru(3)–C(7) (ψ)	61.3(2)	56.8(2)	60.5(14)	55.8(10)
Ru(4)–Ru(3)–C(10) (ψ)	64.92(2)	54.5(2)	57.8(15)	58.0(13)

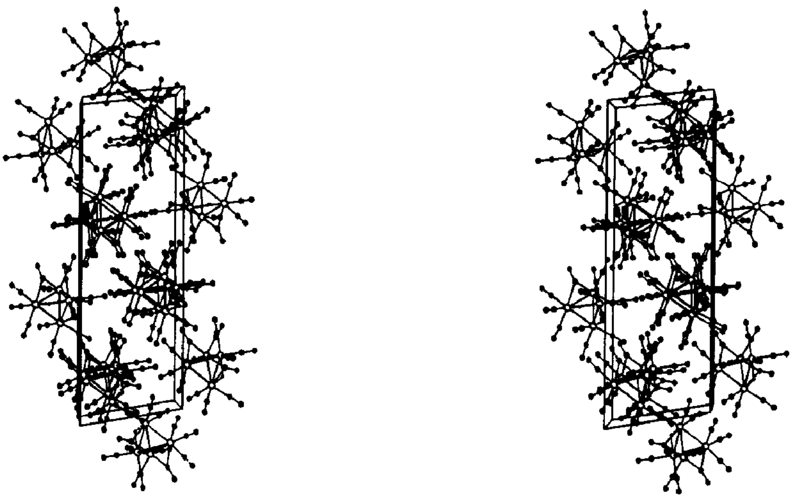

Fig. 3. Stereoview of the unit-cell packing for **I(t)** as viewed down the *b*-axis.

cules), we obtained $n = 1.52$ and $m = 64.6$ (the two sets of values are statistically identical) [1]. The θ and ψ parameters for the four semi-bridging CO ligands in **I(t)** all obey this linear relationship with deviations less than the errors in their measurements, despite wide ranges in their individual values: θ varies from 149.5 to 160.3° and ψ from 54.5 to 64.9°. Unfortunately, the θ and ψ parameters for **I(m)** were not accurately enough determined to include (some of the relevant angles have ±5° estimated standard deviations); nonetheless, three of the four values do, within the specified error limits, also fall on the line.

Conclusions

Wide range for the θ and ψ values for **I(t)**, **I(m)** and $[H_2RuOs_3(CO)_{13}]$ are found indicating that bent semi-bridging CO ligands may, in chemically identical sites, adopt a continuum of angular relationships [10]. The range is likely due to crystal packing forces as the energetic differences between the various μ-CO structures is undoubtedly very small. However, despite the variation in individual values, all of the semi-bridging CO ligands in these group 8 clusters exactly conform to the now well-established linear Crabtree–Lavin relationship. Thus, it would appear that while crystal packing forces may contribute to substantial differences among chemically identical bond parameters, the distortions are not arbitrary, but instead, at least with regard to μ-CO ligands, conform to simple linear relationships.

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