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Acta Cryst. (1993). C**49**, 1619–1621

Structure of $Ru_4(CO)_8(O_2CCH_2CH{=}CH_2)_4(NMe_3)_2$

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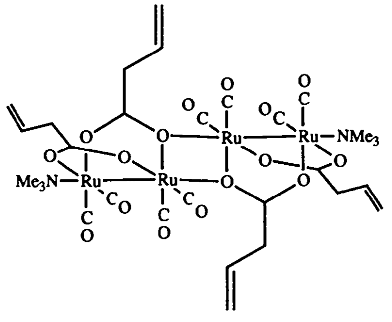
(*Received* 8 *January* 1993; *accepted* 8 *March* 1993)

Abstract

The tetranuclear ruthenium carboxylate complex, bis(μ_3-3-butenoato)-bis(μ-3-butenoato)-octacarbonylbis(trimethylammine)tetraruthenium(2 *Ru—Ru*), consists of a dimer of diruthenium carboxylates, $Ru_2(CO)_4(O_2CCH_2CH{=}CH_2)_2$, held together by O-atom bridge bonds. The two terminal Ru atoms complete their six-coordination with trimethylammine ligands.

Comment

Dodecacarbonyltriruthenium reacts with several carboxylic acids to provide polymeric compounds $[Ru(CO)_2(RCO_2)]_n$. Subsequent reactions of these polymeric derivatives with various Lewis bases result in the formation of dimeric carboxylate complexes of the type $Ru_2(CO)_4(RCO_2)_2L_2$ (Crooks, Johnson, Lewis, Williams & Gamlen, 1969). The X-ray structure of $(CH_3CO_2)_2Ru_2(CO)_4(C_5H_5N)_2$, as well as that of an analogous osmium complex, $(CH_3CO_2)_2Os_2(CO)_6$, have been determined (Kilbourn, 1971; Bullitt & Cotton, 1971). The overall structures of these complexes possess sixfold coordination about the metal atoms with *cis*-bridging acetate groups. We have isolated crystals of a ruthenium carboxylate complex (I) containing features of both the polymeric and dimeric carboxylate derivatives from the reaction of $Ru_3(CO)_{12}$ and 1-butenoic acid in the presence of trimethylamine *N*-oxide. The structure reported in this work is similar to that reported for the tetranuclear compound $(CH_3CO_2)_4Ru_4(CO)_8\{P[(CH_2)_3CH_3]_3\}_2$ (Bianchi, Frediani, Nardelli & Pelizzi, 1981).



(I)

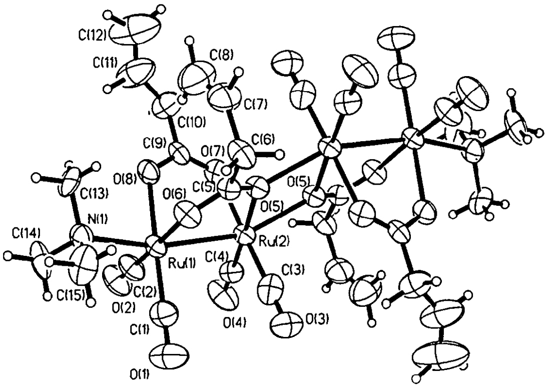


Fig. 1. Thermal ellipsoid plot (50% probability) of $Ru_4(CO)_8(O_2CCH_2CH{=}CH_2)_4(NMe_3)_2$. H atoms have been drawn as spheres with arbitrary radii. For clarity only one of the atoms of each of the disordered atomic pairs [C(13), C(13′); C(14), C(14′); C(15), C(15′)] is displayed.

Experimental

Crystal data

$[Ru_4(C_4H_5O_2)_4(C_3H_9N)_2(CO)_8]$
$M_r = 1086.91$
Monoclinic
$P2/c$
$a = 7.628\ (2)$ Å
$b = 19.526\ (4)$ Å
$c = 13.120\ (3)$ Å

$D_x = 1.863$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 19.89$–$34.23°$
$\mu = 1.568$ mm^{-1}
$T = 197$ K

$\beta = 97.45\ (2)°$
$V = 1937.7\ (8)\ \text{Å}^3$
$Z = 2$

Plate
0.32 × 0.20 × 0.11 mm
Yellow

Data collection

Siemens *R*3*m* diffractometer
ω (Wyckoff) scans
Absorption correction: semi-empirical
$T_{\min} = 0.777$, $T_{\max} = 0.997$
3637 measured reflections
3637 independent reflections
2823 observed reflections $[F > 2.0\sigma(F)]$

$R_{\rm int} = 0.069$
$\theta_{\max} = 25.00°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 16$
3 standard reflections monitored every 97 reflections intensity variation: 3%

Refinement

Refinement on *F*
Final $R = 0.0634$
$wR = 0.0622$
$S = 2.5814$
2823 reflections
248 parameters
Calculated weights $w = 1/[\sigma^2(F)+0.00001F^2]$

$(\Delta/\sigma)_{\max} = 0.0580$
$\Delta\rho_{\max} = 1.7310\ \text{e Å}^{-3}$
$\Delta\rho_{\min} = -0.7900\ \text{e Å}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: *P3VAX* (Siemens, 1990). Data reduction: *REFRED* (Reibenspies, 1992). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Ru(1)	0.2918 (1)	0.3800 (1)	0.7792 (1)	0.0354 (1)
Ru(2)	0.5162 (1)	0.4189 (1)	0.9406 (1)	0.0352 (1)
C(1)	0.2005 (13)	0.3064 (6)	0.8445 (8)	0.0523 (4)
O(1)	0.1499 (11)	0.2603 (4)	0.8839 (7)	0.0784 (4)
C(2)	0.4437 (13)	0.3210 (5)	0.7288 (8)	0.0491 (4)
O(2)	0.5418 (10)	0.2830 (4)	0.6972 (6)	0.0680 (3)
C(3)	0.4079 (13)	0.3700 (6)	1.0336 (8)	0.0510 (4)
O(3)	0.3352 (11)	0.3393 (4)	1.0907 (6)	0.0678 (3)
C(4)	0.6663 (12)	0.3449 (5)	0.9317 (8)	0.0432 (3)
O(4)	0.7501 (10)	0.2973 (4)	0.9255 (6)	0.0709 (3)
O(5)	0.3384 (7)	0.5044 (3)	0.9442 (5)	0.0382 (2)
O(6)	0.1254 (8)	0.4551 (3)	0.8355 (5)	0.0435 (2)
C(5)	0.1809 (11)	0.5025 (5)	0.8963 (7)	0.0340 (3)
C(6)	0.0554 (13)	0.5607 (5)	0.9079 (8)	0.0508 (4)
C(7)	0.0728 (18)	0.6201 (7)	0.8400 (10)	0.0707 (5)
C(8)	0.1492 (20)	0.6266 (8)	0.7697 (11)	0.0905 (7)
O(7)	0.6296 (7)	0.4805 (3)	0.8330 (5)	0.0430 (2)
O(8)	0.4033 (8)	0.4647 (3)	0.7069 (5)	0.0443 (2)
C(9)	0.5483 (12)	0.4929 (5)	0.7471 (8)	0.0398 (3)
C(10)	0.6238 (14)	0.5460 (6)	0.6823 (9)	0.0610 (4)
C(11)	0.5068 (19)	0.5822 (9)	0.6065 (12)	0.1015 (7)
C(12)	0.4797 (19)	0.6406 (9)	0.5802 (15)	0.1335 (9)
N(1)	0.0751 (10)	0.3780 (4)	0.6432 (6)	0.0470 (3)
C(13)	0.0600 (21)	0.4441 (8)	0.5888 (10)	0.0559 (6)
C(14)	0.1002 (20)	0.3232 (9)	0.5716 (12)	0.0668 (6)
C(15)	−0.0992 (17)	0.3641 (10)	0.6830 (12)	0.0689 (7)
C(13′)	0.1573 (73)	0.3859 (32)	0.5347 (40)	0.0887 (19)
C(14′)	−0.0251 (53)	0.3126 (20)	0.6242 (29)	0.0455 (12)
C(15′)	−0.0513 (69)	0.4361 (27)	0.6308 (39)	0.0705 (16)

Table 2. *Geometric parameters* (Å, °)

Ru(1)—Ru(2)	2.655 (1)	O(5)—Ru(2$^{\rm i}$)	2.306 (6)
Ru(1)—C(1)	1.854 (12)	O(6)—C(5)	1.259 (11)
Ru(1)—C(2)	1.819 (11)	C(5)—C(6)	1.507 (13)
Ru(1)—O(6)	2.133 (7)	C(6)—C(7)	1.479 (17)
Ru(1)—O(8)	2.136 (7)	C(7)—C(8)	1.160 (21)
Ru(1)—N(1)	2.270 (7)	O(7)—C(9)	1.238 (11)
Ru(2)—C(3)	1.829 (11)	O(8)—C(9)	1.286 (11)
Ru(2)—C(4)	1.858 (10)	C(9)—C(10)	1.502 (15)
Ru(2)—O(5)	2.155 (6)	C(10)—C(11)	1.433 (18)
Ru(2)—O(7)	2.122 (7)	C(11)—C(12)	1.201 (25)
Ru(2)—O(5$^{\rm i}$)	2.306 (6)	N(1)—C(13)	1.472 (17)
C(1)—O(1)	1.131 (15)	N(1)—C(14)	1.453 (18)
C(2)—O(2)	1.166 (13)	N(1)—C(15)	1.515 (16)
C(3)—O(3)	1.156 (14)	N(1)—C(13′)	1.636 (56)
C(4)—O(4)	1.137 (13)	N(1)—C(14′)	1.493 (40)
O(5)—C(5)	1.282 (9)	N(1)—C(15′)	1.484 (53)
Ru(2)—Ru(1)—C(1)	95.5 (3)	C(5)—O(5)—Ru(2$^{\rm i}$)	132.9 (6)
Ru(2)—Ru(1)—C(2)	95.5 (3)	Ru(1)—O(6)—C(5)	123.9 (5)
C(1)—Ru(1)—C(2)	88.4 (5)	O(5)—C(5)—O(6)	123.3 (8)
Ru(2)—Ru(1)—O(6)	83.0 (2)	O(5)—C(5)—C(6)	119.7 (8)
C(1)—Ru(1)—O(6)	95.5 (4)	O(6)—C(5)—C(6)	116.9 (7)
C(2)—Ru(1)—O(6)	175.9 (4)	C(5)—C(6)—C(7)	115.1 (9)
Ru(2)—Ru(1)—O(8)	83.1 (2)	C(6)—C(7)—C(8)	131.1 (14)
C(1)—Ru(1)—O(8)	178.5 (3)	Ru(2)—O(7)—C(9)	121.2 (6)
C(2)—Ru(1)—O(8)	91.1 (4)	Ru(1)—O(8)—C(9)	121.4 (6)
O(6)—Ru(1)—O(8)	84.9 (3)	O(7)—C(9)—O(8)	126.3 (9)
Ru(2)—Ru(1)—N(1)	163.8 (2)	O(7)—C(9)—C(10)	117.8 (8)
C(1)—Ru(1)—N(1)	94.1 (4)	O(8)—C(9)—C(10)	115.9 (8)
C(2)—Ru(1)—N(1)	97.9 (4)	C(9)—C(10)—C(11)	118.8 (10)
O(6)—Ru(1)—N(1)	83.0 (3)	C(10)—C(11)—C(12)	137.3 (15)
O(8)—Ru(1)—N(1)	87.4 (3)	Ru(1)—N(1)—C(13)	111.7 (7)
Ru(1)—Ru(2)—C(3)	94.7 (3)	Ru(1)—N(1)—C(14)	112.2 (7)
Ru(1)—Ru(2)—C(4)	93.8 (3)	C(13)—N(1)—C(14)	109.9 (10)
C(3)—Ru(2)—C(4)	88.3 (5)	Ru(1)—N(1)—C(15)	108.3 (7)
Ru(1)—Ru(2)—O(5)	84.1 (1)	C(13)—N(1)—C(15)	107.9 (10)
C(3)—Ru(2)—O(5)	92.9 (4)	C(14)—N(1)—C(15)	106.6 (11)
C(4)—Ru(2)—O(5)	177.6 (3)	Ru(1)—N(1)—C(13′)	111.1 (19)
Ru(1)—Ru(2)—O(7)	84.7 (2)	C(13)—N(1)—C(13′)	60.7 (23)
C(3)—Ru(2)—O(7)	176.4 (4)	C(14)—N(1)—C(13′)	53.8 (23)
C(4)—Ru(2)—O(7)	95.2 (4)	C(15)—N(1)—C(13′)	140.3 (20)
O(5)—Ru(2)—O(7)	83.6 (2)	Ru(1)—N(1)—C(14′)	116.8 (15)
Ru(1)—Ru(2)—O(5$^{\rm i}$)	156.0 (1)	C(13)—N(1)—C(14′)	131.5 (16)
C(3)—Ru(2)—O(5$^{\rm i}$)	97.0 (4)	C(14)—N(1)—C(14′)	50.9 (17)
C(4)—Ru(2)—O(5$^{\rm i}$)	107.4 (3)	C(15)—N(1)—C(14′)	56.7 (18)
O(5)—Ru(2)—O(5$^{\rm i}$)	74.5 (2)	C(13′)—N(1)—C(14′)	100.4 (26)
O(7)—Ru(2)—O(5$^{\rm i}$)	82.3 (2)	Ru(1)—N(1)—C(15′)	118.0 (19)
Ru(1)—C(1)—O(1)	177.6 (10)	C(13)—N(1)—C(15′)	42.9 (22)
Ru(1)—C(2)—O(2)	179.5 (10)	C(14)—N(1)—C(15′)	129.1 (21)
Ru(2)—C(3)—O(3)	178.2 (9)	C(15)—N(1)—C(15′)	65.7 (22)
Ru(2)—C(4)—O(4)	176.2 (9)	C(13′)—N(1)—C(15′)	98.6 (30)
Ru(2)—O(5)—C(5)	121.2 (6)	C(14′)—N(1)—C(15′)	108.9 (25)
Ru(2)—O(5)—Ru(2$^{\rm i}$)	105.5 (2)		

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

A suitable crystal was chosen and mounted on a glass fiber at room temperature with epoxy cement and cooled to 197 K. Inspection of photographs about each of the three axes confirmed axis length and Laue symmetry. ω scans of several intense reflections indicated an acceptable crystal quality. The ω-scan width was 2.0° with a variable ω-scan rate between 1.5 and 14.6° min^{-1}. Background measurement was by stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time.

C-bound H atoms were placed in idealized positions [C—H = 0.96 Å; U(H) = 0.08 Å^3 (fixed)].

Atoms C(13), C(14) and C(15) were seen to be disordered between two positions. This disorder was modelled by the addition of three new atomic positions, C(13′), C(14′) and C(15′). These were identified as disordered atoms and were refined isotropically. The site occupation factors of the original atomic positions were then refined as one number, 0.74 (2), and the complement of the refined site occupation factor was used as the site occupation factor of the new atomic positions.

An unusual electron density peak of 1.7 e Å^{-3} was seen near (1.05 Å) Ru(1) which may be due, in part, to errors in the Ru(1) absorption correction.

The X-ray diffraction and crystallographic computing system was purchased from funds provided by the US National Science Foundation grant CHE-8513273.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71187 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1057]

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Acta Cryst. (1993). C**49**, 1621–1623

catena-Poly[{aqua(cyanoacetato-κ*O*)(*N*,*N*-dimethylformamide-κ*O*)neodymium}-di-μ-cyanoacetato-κ*O*,κ*O*′:κ*O*′] Monohydrate

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(*Received* 12 *November* 1992; *accepted* 18 *March* 1993)

Abstract

The structure consists of polymeric neutral chains composed of aquatris(cyanoacetato)(dimethylformamide)-neodymium units and water of hydration. The neodymium environment consists of seven carboxylate O atoms, one dimethyl formamide O atom and one water O atom. There are no Nd—N bonds.

Comment

It was suggested recently (Vaidya, Deshpande, Jain & Jain, 1988) that the cyanoacetate anion can act as both an O- and an N-donor ligand towards lanthanide cations. Therefore, we decided to study the crystal structure of a lanthanide cyanoacetate in order to investigate the coordination properties of the anion. We could not obtain crystals of neodymium tris(cyanoacetate) from a pure water solution. Crystals of the title compound were obtained by adding a few drops of dimethylformamide (DMF) to an aqueous solution of neodymium cyanoacetate and then allowing the mixture to evaporate for a few days at ambient temperature.

The neodymium coordination environment consists of nine O atoms, of which seven are carboxylate O atoms, one a DMF O atom, and one a water O atom. All distances are within the previously observed range. The coordination figure is rather irregular. The best-fitted tricapped trigonal prism had Δ [defined as $\Sigma d_i^2/9$ where d_i is the distance between *i*th atom and the relevant vertex of the ideal least-squares-fitted polyhedron (Drew, 1977)] equal to 0.240 Å^2. For the best capped-square antiprism, Δ was 0.233 Å^2. The cyanoacetate ions are either bridging bidentate *O,O*′:*O* or unidentate *O* ligands. The cyano groups are either involved in hydrogen bonds (N3), or in van der

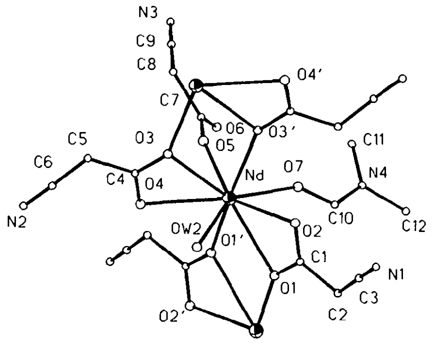

Fig. 1. Fragment of the polymeric chain.

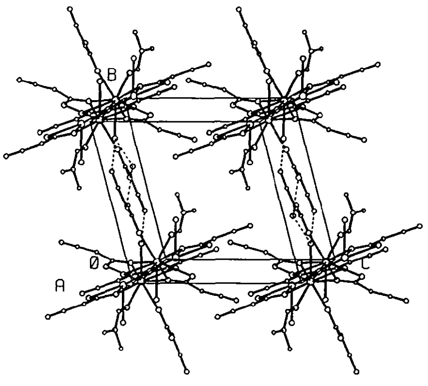

Fig. 2. View of the unit cell. The dashed lines represent the hydrogen bonds.