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The disordered crystal structure of $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$

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Abstract

The crystal structure of $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$ has been determined. The cluster has a $\text{Co}_4(\text{CO})_{12}$ -like carbonyl geometry with three carbonyls bridging the basal cobalt atoms and a $\text{Co}_3(\mu_3\text{-H})$ hydride ligand. The disorder observed in the crystal arises because the carbonyl oxygen positions are nearly the same for two orientations of the cluster.

Tetranuclear dodecacarbonyl mixed metal clusters of cobalt, rhodium and ruthenium, $[\text{M}_4\text{H}_x(\text{CO})_{12}]$ ($x = 0-4$), constitute a large and well defined group of isoelectronic cluster compounds. The parent carbonyl clusters of this group have been synthesized and characterized [1–6] except for $[\text{CoRh}_3(\text{CO})_{12}]$, which is unstable [7]. These compounds are suitable for studying the influence of various metal combinations on the cluster properties, especially because most of the compounds have similar $[\text{Rh}_4(\text{CO})_{12}]$ -like carbonyl arrangements.

Of these clusters $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$ has been known since 1968, and has been characterized spectroscopically [8,9]. Several derivatives have been prepared with N [10], P [11], S [12], Se [13] or Te [14] donor ligands as well as with $[\text{MPPh}_3]^+$ ($\text{M} = \text{Cu}$ or Au) [15] or $[\text{HgCo}(\text{CO})_4]^+$ [16] groups replacing the hydride ligands. However, there has been no report of the crystal structure of $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$, and so we decided to determine it.

Results and discussion

$[\text{RuCo}_3\text{H}(\text{CO})_{12}]$ (1) crystallises in space group Cc , with three molecules in the asymmetric unit. The structure is disordered, which was not unexpected since disorder has been previously observed for $[\text{Co}_x\text{Rh}_{4-x}(\text{CO})_{12}]$ ($x = 0-4$) clusters [17–19] and $[\text{RuRh}_3\text{H}(\text{CO})_{12}]$ [6]. All the three complementary disordered clusters (marked with \star) are upside down “inside” the dominant molecule. Molecule B is shown in Fig. 1. The three independent cluster molecules (A, B and C) in the asymmetric unit have refined site occupation factors of 87, 57 and 84%, respectively, and the metal atoms of the complementary disordered clusters (A^\star , B^\star and C^\star) were also refined and the metals assigned.

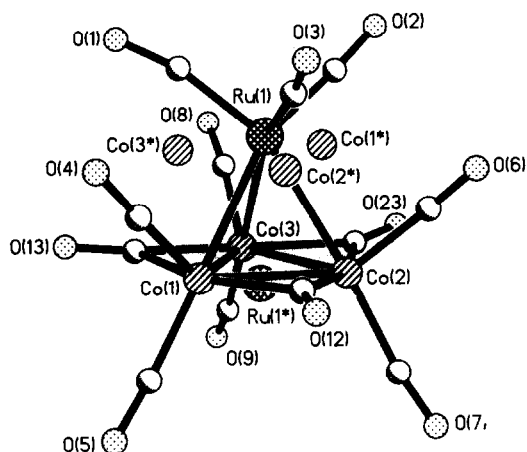


Fig. 1. Crystal structure and numbering scheme of $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$. The disordered metal atoms are marked *.

Compound **1** has a closed tetrahedral metal core with ruthenium in the apical position and three bridging carbonyls connecting the basal cobalt atoms (Fig. 1). This carbonyl geometry is common to all the known $[\text{Ru}_x\text{Co}_y\text{Rh}_z\text{H}_x(\text{CO})_{12}]$ ($x + y + z = 4$, $x = 0-2$) structures. The same geometry is also found with minor variations in derivatives of **1**.

Atomic coordinates are shown in Table 1, metal–metal distances in Table 2, metal–carbon and carbon–oxygen bond lengths in Table 3, and structurally im-

Table 1

Crystallographic data for $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$

Formula weight	663.07
Crystal system	Monoclinic
Space group	Cc
a (Å)	38.99(4)
b (Å)	11.827(8)
c (Å)	11.76(1)
α (deg)	90
β (deg)	94.35(8)
γ (deg)	90
V (Å ³)	5408.75
Z	12
D_{calc} (g cm ⁻³)	2.00
Crystal dimensions (mm)	0.6 × 0.5 × 0.3
Centering 2θ	5-18
No. centering reflections	25
2θ -limits	5-55
No. of unique reflections	6228
Observed data $I \geq 3\sigma(I)$	3436
μ (mm ⁻¹)	3.58
No. parameters	446
R^a	0.0571
GOOF	6.6050

^a $R = (\sum \|F_o\| - |F_c|) / \sum |F_o|$.

Table 2

Atomic coordinates for $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$

Atom	x	y	z
Ru(1a)	0.4913	0.6642(3)	0.2952
Co(1a)	0.5479(2)	0.7737(5)	0.2542(6)
Co(2a)	0.5265(2)	0.7869(4)	0.4516(6)
Co(3a)	0.4943(2)	0.8877(5)	0.2874(6)
Ru(1a [*])	0.5320(5)	0.838(2)	0.340(2)
Co(1a [*])	0.474(2)	0.725(6)	0.378(6)
Co(2a [*])	0.5262(6)	0.609(2)	0.350(2)
Co(3a [*])	0.4975(7)	0.717(2)	0.178(2)
O(1a)	0.4663(7)	0.620(2)	0.051(3)
O(2a)	0.4250(9)	0.622(3)	0.408(3)
O(3a)	0.5248(8)	0.426(3)	0.353(3)
O(4a)	0.5580(5)	0.5711(15)	0.121(2)
O(5a)	0.6107(11)	0.875(4)	0.217(4)
O(6a)	0.5066(5)	0.614(2)	0.601(2)
O(7a)	0.5664(6)	0.916(2)	0.620(2)
O(8a)	0.4226(8)	0.855(3)	0.210(3)
O(9a)	0.4908(6)	1.135(2)	0.275(2)
O(12a)	0.5911(5)	0.644(2)	0.439(2)
O(13a)	0.5093(5)	0.870(2)	0.052(2)
O(23a)	0.4585(5)	0.892(2)	0.498(2)
C(1a)	0.4764(12)	0.629(4)	0.157(4)
C(2a)	0.437(3)	0.654(11)	0.339(10)
C(3a)	0.511(2)	0.507(7)	0.329(6)
C(4a)	0.5518(6)	0.651(2)	0.168(2)
C(5a)	0.5825(13)	0.856(4)	0.248(4)
C(6a)	0.5105(6)	0.680(2)	0.539(2)
C(7a)	0.5493(8)	0.860(3)	0.565(3)
C(8a)	0.4527(13)	0.866(5)	0.232(5)
C(9a)	0.5048(8)	1.043(3)	0.287(3)
C(12a)	0.5639(10)	0.675(3)	0.399(3)
C(13a)	0.5189(12)	0.841(4)	0.139(4)
C(23a)	0.4845(5)	0.8772(16)	0.4490(16)
Ru(1b)	0.1946(2)	0.8385(5)	0.3448(6)
Co(1b)	0.1403(3)	0.7138(8)	0.3767(10)
Co(2b)	0.1954(3)	0.6151(9)	0.3385(10)
Co(3b)	0.1613(3)	0.7201(8)	0.1816(9)
Ru(1b [*])	0.1609(2)	0.6620(6)	0.2918(6)
Co(1b [*])	0.2153(3)	0.7896(8)	0.2586(9)
Co(2b [*])	0.1937(3)	0.7808(8)	0.4559(9)
Co(3b [*])	0.1592(3)	0.8860(8)	0.2998(9)
O(1b)	0.1605(7)	1.0680(3)	0.302(3)
O(2b)	0.2635(8)	0.903(3)	0.242(3)
O(3b)	0.2207(8)	0.883(3)	0.597(3)
O(4b)	0.1291(7)	0.899(2)	0.527(2)
O(5b)	0.0780(7)	0.585(2)	0.418(2)
O(6b)	0.2622(9)	0.652(3)	0.439(3)
O(7b)	0.1950(6)	0.365(2)	0.336(2)
O(8b)	0.1768(8)	0.917(3)	0.054(3)
O(9b)	0.1269(6)	0.614(2)	-0.017(2)
O(12b)	0.1754(6)	0.604(2)	0.574(2)
O(13b)	0.0937(8)	0.852(3)	0.220(3)

Table 2 (continued)

Atom	x	y	z
O(23b)	0.2291(6)	0.627(2)	0.108(2)
C(1b)	0.1774(8)	0.985(3)	0.324(3)
C(2b)	0.2367(7)	0.874(2)	0.280(2)
C(3b)	0.2118(6)	0.861(2)	0.500(2)
C(4b)	0.1333(6)	0.824(2)	0.472(2)
C(5b)	0.1019(6)	0.630(2)	0.401(2)
C(6b)	0.2379(6)	0.636(2)	0.394(2)
C(7b)	0.1929(9)	0.457(3)	0.334(3)
C(8b)	0.1729(7)	0.843(3)	0.111(2)
C(9b)	0.1393(5)	0.645(2)	0.0596(17)
C(12b)	0.1750(6)	0.632(2)	0.4815(19)
C(13b)	0.1196(5)	0.795(2)	0.2376(17)
C(23b)	0.2070(6)	0.639(2)	0.178(2)
Ru(1c)	0.3636(1)	0.3352(3)	0.3386(2)
Co(1c)	0.3064(2)	0.2259(5)	0.3773(6)
Co(2c)	0.3594(2)	0.1122(5)	0.3476(5)
Co(3c)	0.3281(2)	0.2139(5)	0.1838(6)
Ru(1c *)	0.3274(4)	0.1594(14)	0.2915(14)
Co(1c *)	0.3822(4)	0.2728(14)	0.2548(13)
Co(2c *)	0.3636(6)	0.284(2)	0.444(2)
Co(3c *)	0.3293(10)	0.375(3)	0.281(3)
O(1c)	0.3394(5)	0.576(2)	0.283(2)
O(2c)	0.4338(7)	0.383(3)	0.243(3)
O(3c)	0.3911(7)	0.399(3)	0.583(3)
O(4c)	0.2997(7)	0.405(2)	0.538(2)
O(5c)	0.2429(7)	0.111(2)	0.432(2)
O(6c)	0.4288(7)	0.136(2)	0.445(2)
O(7c)	0.3525(6)	-0.136(2)	0.356(2)
O(8c)	0.3579(6)	0.381(2)	0.044(2)
O(9c)	0.2935(6)	0.095(2)	-0.008(2)
O(12c)	0.3382(6)	0.117(2)	0.593(2)
O(13c)	0.2716(6)	0.374(2)	0.208(2)
O(23c)	0.3900(5)	0.089(2)	0.119(2)
C(1c)	0.3475(5)	0.4854(16)	0.305(2)
C(2c)	0.4067(4)	0.3654(14)	0.2772(14)
C(3c)	0.3807(7)	0.370(2)	0.496(2)
C(4c)	0.3055(14)	0.353(5)	0.467(5)
C(5c)	0.2671(5)	0.1561(16)	0.4073(15)
C(6c)	0.4024(9)	0.137(3)	0.400(3)
C(7c)	0.3610(6)	-0.041(2)	0.350(2)
C(8c)	0.3456(11)	0.332(4)	0.118(4)
C(9c)	0.3038(7)	0.125(3)	0.081(3)
C(12c)	0.3397(5)	0.143(2)	0.494(2)
C(13c)	0.2889(5)	0.2955(15)	0.2354(15)
C(23c)	0.3764(12)	0.143(4)	0.183(4)

portant bond angles in Table 4. Comparison of the average bond distances and bond angles of **1** with those of some other clusters with RuCo₃ metal core can be made on the basis of data presented in Table 5.

The hydride site can be inferred from the data in Table 2, 3 and 5. The average Co-Co-C_{ax} angle in **1** is 118°, which is typical to structures in which the M₃(μ-H)

Table 3

Selected bond lengths (pm) for $\{\text{RuCo}_3\text{H}(\text{CO})_{12}\}$

	Molecule		
	A	B	C
Ru(1)–Co(1)	263.5(8)	263.0(13)	264.7(8)
Ru(1)–Co(2)	264.3(7)	264.4(12)	264.5(7)
Ru(1)–Co(3)	264.7(7)	262.8(12)	262.9(7)
Co(1)–Co(2)	253.3(11)	251.5(16)	251.3(10)
Co(1)–Co(3)	254.4(10)	249.4(16)	249.3(11)
Co(2)–Co(3)	252.1(10)	252.0(15)	250.9(9)
Ru(1)–C(1)	174(5)	187(3)	192(2)
Ru(1)–C(2)	220(1)	190(3)	191(2)
Ru(1)–C(3)	204(8)	191(2)	197(3)
Co(1)–C(4)	178(3)	175(3)	184(6)
Co(1)–C(5)	167(5)	184(4)	180(2)
Co(1)–C(12)	212(4)	201(2)	207(2)
Co(1)–C(13)	188(5)	201(2)	194(2)
Co(2)–C(6)	177(3)	175(3)	177(4)
Co(2)–C(7)	177(3)	187(4)	181(2)
Co(2)–C(12)	210(4)	193(3)	197(2)
Co(2)–C(23)	195(2)	199(3)	213(5)
Co(3)–C(8)	172(5)	175(3)	176(4)
Co(3)–C(9)	188(3)	184(2)	182(3)
Co(3)–C(1)	213(5)	201(2)	194(2)
Co(3)–C(23)	197(2)	202(3)	206(5)
Ru(1*)–Co(1*)	269(8)	265.7(13)	259(2)
Ru(1*)–Co(2*)	271(3)	264.0(12)	265(3)
Ru(1*)–Co(3*)	267(3)	265.1(12)	255(3)
Co(1*)–Co(2*)	249(8)	253.1(16)	240(3)
Co(1*)–Co(3*)	258(8)	254.5(15)	243(4)
Co(2*)–Co(3*)	257(3)	252.1(14)	250(4)
O(1)–C(1)	128(5)	120(5)	114(3)
O(2)–C(2)	105(12)	122(4)	117(4)
O(3)–C(3)	112(9)	120(4)	113(4)
O(4)–C(4)	113(3)	112(4)	108(6)
O(5)–C(5)	121(7)	110(4)	114(3)
O(6)–C(6)	108(3)	107(4)	112(4)
O(7)–C(7)	111(4)	109(5)	118(3)
O(8)–C(8)	119(6)	113(4)	118(5)
O(9)–C(9)	122(4)	105(3)	115(4)
O(12)–C(12)	118(4)	113(3)	121(3)
O(13)–C(13)	112(5)	122(4)	118(3)
O(23)–C(23)	122(3)	124(4)	114(5)

hydride opens these angles ($[\text{RuCo}_3\text{H}(\text{CO})_{11}(\text{PR}_3)]$ clusters in Table 5). The corresponding value in $[(\text{Ph}_3\text{P})_2\text{N}][\text{RuCo}_3(\text{CO})_{12}]$, **2**, is 113.1° . The small Co–Ru–C (Av. 102°) and Ru–Co–C_{eq} (Av. 78°) angles indicate the absence of Ru(μ -H)Co bonds. Computer-simulated space-filling models of the cluster were also used to locate the hydrides [22]. The models shows a “hole” in the carbonyl coverage only on the Co₃-face of the cluster tetrahedron.

The packing disorder is similar for all the three molecules in the asymmetric unit. It is suggested that the oxygen positions of the two disordered molecules must be

Table 4

Selected bond angles ($^{\circ}$) for $[\text{RuCo}_3\text{H}(\text{CO})_{12}]$

	Molecule		
	A	B	C
Co(1)–Ru(1)–C(1)	99.9(16)	104.7(11)	102.8(6)
Co(2)–Ru(1)–C(1)	154.5(16)	158.2(11)	155.9(6)
Co(3)–Ru(1)–C(1)	102.7(16)	104.1(10)	102.4(6)
Co(1)–Ru(1)–C(2)	154(3)	155.0(9)	158.8(5)
Co(2)–Ru(1)–C(2)	109(3)	101.3(9)	105.1(5)
Co(3)–Ru(1)–C(2)	96(3)	102.6(9)	105.8(5)
Co(1)–Ru(1)–C(3)	100(2)	99.8(8)	99.7(8)
Co(2)–Ru(1)–C(3)	102(2)	99.4(7)	100.7(8)
Co(3)–Ru(1)–C(3)	155(2)	152.3(8)	152.9(8)
Ru(1)–Co(1)–C(4)	79.2(8)	80.8(8)	76(2)
Co(2)–Co(1)–C(4)	128.2(9)	129.5(9)	125(2)
Co(3)–Co(1)–C(4)	128.7(8)	130.0(9)	126(2)
Ru(1)–Co(1)–C(5)	170(2)	178.5(9)	177.7(7)
Co(2)–Co(1)–C(5)	109(2)	119.6(9)	120.2(7)
Co(3)–Co(1)–C(5)	112(2)	119.0(9)	120.4(7)
Ru(1)–Co(1)–C(12)	77.3(11)	81.2(7)	81.5(6)
Co(2)–Co(1)–C(12)	52.7(11)	48.9(7)	49.9(6)
Co(3)–Co(1)–C(12)	111.3(11)	109.2(8)	109.9(7)
Ru(1)–Co(1)–C(13)	82.7(14)	84.0(7)	83.7(6)
Co(2)–Co(1)–C(13)	114.5(15)	111.8(8)	110.3(6)
Co(3)–Co(1)–C(13)	55.2(15)	51.5(7)	50.1(6)
Ru(1)–Co(2)–C(6)	80.0(8)	82.0(9)	77.8(12)
Co(1)–Co(2)–C(6)	130.1(8)	131.6(10)	129.2(13)
Co(3)–Co(2)–C(6)	127.3(8)	129.4(10)	125.7(13)
Ru(1)–Co(2)–C(7)	175.1(11)	176.3(12)	174.2(8)
Co(1)–Co(2)–C(7)	122.5(11)	115.1(12)	124.1(8)
Co(3)–Co(2)–C(7)	122.6(11)	116.5(11)	120.5(7)
Ru(1)–Co(2)–C(12)	77.5(10)	82.2(8)	83.3(6)
Co(1)–Co(2)–C(12)	53.6(11)	51.6(7)	53.3(6)
Co(3)–Co(2)–C(12)	113.0(11)	110.9(8)	112.7(7)
Ru(1)–Co(2)–C(23)	84.3(6)	83.5(8)	76.6(14)
Co(1)–Co(2)–C(23)	110.8(6)	111.1(9)	110.6(13)
Co(3)–Co(2)–C(23)	50.3(6)	51.7(8)	52.0(13)
Ru(1)–Co(3)–C(8)	80(2)	77.0(10)	70.9(14)
Co(1)–Co(3)–C(8)	129(2)	125.2(11)	121.9(15)
Co(2)–Co(3)–C(8)	128.3(18)	128.0(10)	122.5(14)
Ru(1)–Co(3)–C(9)	169.9(10)	175.6(8)	177.4(10)
Co(1)–Co(3)–C(9)	109.6(10)	122.5(8)	116.5(10)
Co(2)–Co(3)–C(9)	111.6(9)	121.4(8)	115.6(10)
Ru(1)–Co(3)–C(13)	78.1(12)	83.9(7)	84.1(6)
Co(1)–Co(3)–C(13)	46.4(12)	51.8(7)	50.0(6)
Co(2)–Co(3)–C(13)	106.1(12)	111.9(8)	110.3(6)
Ru(1)–Co(3)–C(23)	83.8(6)	83.1(8)	78.0(13)
Co(1)–Co(3)–C(23)	109.7(6)	110.8(8)	113.7(13)
Co(2)–Co(3)–C(23)	49.7(6)	50.6(8)	54.4(13)
Ru(1)–C(1)–O(1)	171(4)	167(3)	177(2)
Ru(1)–C(2)–O(2)	135(8)	176(3)	178(2)
Ru(1)–C(3)–O(3)	172(7)	175(2)	174(3)
Co(1)–C(4)–O(4)	172(2)	176(2)	158(5)
Co(1)–C(5)–O(5)	152(5)	176(2)	177(2)
Co(2)–C(6)–O(6)	167(2)	171(3)	168(3)

Table 4

	Molecule		
	A	B	C
Co(2)–Co(7)–O(7)	167(3)	172(3)	161(2)
Co(3)–C(8)–O(8)	170(5)	110(3)	156(4)
Co(3)–C(9)–O(9)	141(2)	171(2)	156(3)
Co(1)–C(12)–O(12)	133(3)	134(2)	133(2)
Co(2)–C(12)–O(12)	135(3)	146(2)	148(2)
Co(1)–C(13)–O(13)	159(4)	133(2)	137(2)
Co(3)–C(13)–O(13)	122(3)	151(2)	139(2)
Co(2)–C(23)–O(23)	143(2)	146(2)	139(2)
Co(3)–C(23)–O(23)	132.7(16)	136(2)	135(3)

closely similar in these two orientations of the molecule, thus determining the packing of the structure. This disorder was studied by Chem-X molecular modeling program in order to gain quantitative information about the origin of the disorder. The refined clusters (A, B and C) and the complementary clusters (A*, B* and C*) were fitted together and the corresponding O–O* distances were determined. The data are presented in Tables 6 and 7. In Table 6 the metal atoms of the complementary clusters were fitted with the experimental disordered metal sites and, this fitting is shown in Fig. 2. It can be seen that the metal–metal distances, which show how well the metal cores fit together in each case. The average O–O* distances vary from 47 to 60 pm, which seems to not reflect a very good fit, but fitting was also made so that each molecule was rotated 120° around the three-fold axis of the C_{3v}-symmetry and then fitted to the original structure, and in this case the O–O* distances varied from 21 to 29 pm, allowing some measure of the experimental error in the fitting. On these grounds the original O–O* distances are about twice the experimental error. The distribution of O and O* atoms in the case A of Table 6 is shown in Fig. 3, which has space filling radii of 140 pm (van der Waals radius of oxygen) for the oxygen atoms. Attempts to fit the clusters together in other than the upside down orientation led to marked increase in the O–O* distances. An example is shown in Table 6 for which the average O–O* distances are 200 pm. This value serves as representative of a situation in which the oxygens atoms of the two structures are randomly distributed.

Table 5

Important bond distances (pm) and bond angles (°) in 1, [(Ph₃P)₂N][RuCo₃(CO)₁₂] (2) [9], [RuCo₃H(CO)₁₁(PMe₃)] (3) [11], [RuCo₃H(CO)₁₁(PMe₂Ph)] (4) [11] and [RuCo₃H(CO)₁₁(PPh₃)] (5) [10]

	1	2	3	4	5
Ru–Co	264.0	262.9	266.0	256.5	263.7
Co–CO	251.5	252.9	252.5	249.4	252.6
Ru–C(term)	194	191.3	193.4	188.5	191
Co–C(term)	179	170.2	181.7	178.9	178
Co–C(br)	201	195.8	198.8	195.1	196
Co–Ru–C	102	100.0	102.5	99.0	100.6
Ru–Co–C _{eq}	78	85.0	78.5	85.7	79.0
Co–Co–C _{ax}	118	113.1	120.0	116.8	119.2

Table 6

Average metal–metal and oxygen–oxygen distances (pm, range in parenthesis). Metals are fitted as shown. A, B, and C refer to the three molecules in the asymmetric unit

	A	B	C	"Random"
Ru–Ru *	5	1	5	
Co–Co *	4 (4–5)	1 (1–2)	7 (6–8)	
M–M *				8 (6–10) 6–10
O–O *	60 (12–93)	47 (19–75)	55 (20–81)	200 (116–245)
<i>120° rotation around the C_{3v} axis</i>				
Ru–Ru *	1	1	1	
Co–Co *	2 (1–2)	2 (1–2)	2 (1–2)	
O–O *	29 (19–41)	22 (8–41)	27 (9–42)	

Table 7 contains the same information as Table 6 except that oxygen atoms are fitted instead of the metal atoms. This results in an average 16 pm difference between the experimental and fitted metal sites. However, no significant difference can be observed between the O–O* distance data in Tables 6 and 7.

Previous results have shown that cluster stereochemistry can be successfully handled by studying the ligand polyhedra [21] or by using molecular mechanics [22]. The procedure we have adopted uses the experimental coordinates in studying the geometry of the ligand polyhedron. As a result the procedure gives distances, that show the differences between the two structures studied. This method seems to

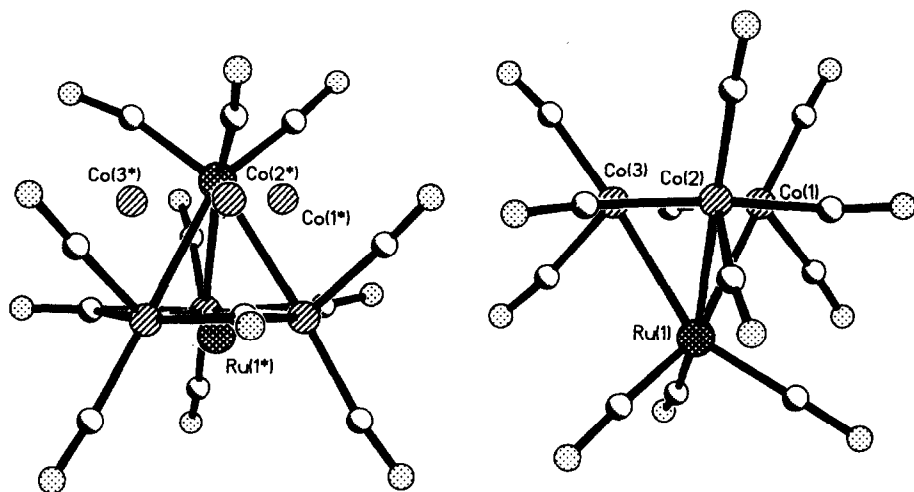


Fig. 2. The fitting procedure. The cluster on the right side is fitted into the disordered metal sites of the cluster on the left side. Alternatively (Table 7) oxygen atoms are fitted into oxygen sites.

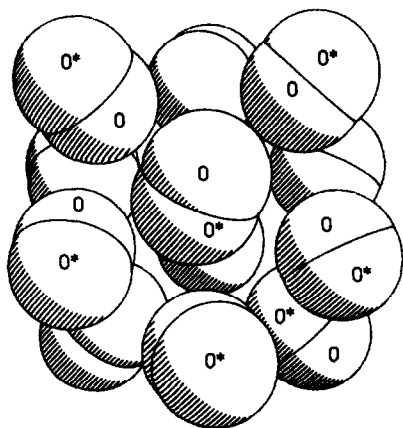


Fig. 3. Space-filling model of the two fitted structures; van der Waals radii (140 pm) are used for the oxygen atoms.

Table 7

Average metal–metal and oxygen–oxygen distances (pm, range in parenthesis). Oxygen atoms are fitted as shown

	Molecule		
	A	B	C
Ru–Ru *	18	14	16
Co–Co *	17 (14–18)	15 (14–16)	17 (14–21)
O–O *	55 (20–76)	49 (32–69)	52 (27–80)

provide an easy way of interpreting packing disorder, which is observed frequently in X-ray crystallography.

Experimental

The preparation of compound **1** has been described previously [10]. Suitable crystals were grown from CH_2Cl_2 /hexane mixtures by slow evaporation at room temperature.

Crystallography

Details of crystal parameters, data collection parameters, and refined data for **1** are summarized in Table 4. Intensity measurements were made on a Nicolet R3m diffractometer using graphite monochromatized Mo-K_α radiation (ω -scan mode with scan width 1° from $\text{K}_{\alpha 12}$ and scan speed $2.44\text{--}29.3^\circ/\text{min}$). All data sets were corrected for Lorentz and polarization effects. Empirical absorption corrections were made from ψ -scan data.

Structure analysis and refinement

The crystal structures were determined by direct methods and subsequent Fourier synthesis using SHELXTL program package [23]. Metal atoms were refined anisotropically, but only isotropic refinement was possible for the oxygen and carbon atoms

because of the low reflection to parameter ratio. The site occupation factors (SOFs) were refined independently for each of the three clusters so that the sum of the SOFs of the two complementary metal cores was fixed at 1.0. The SOFs were 87.1, 56.7 and 83.6% for the clusters A, B and C, respectively. Cluster cores A*, B* and C* are the complementary disordered cluster cores of A, B and C, respectively. The carbonyl groups were refined for the A, B and C clusters with site occupation factors of 1.0. The hydride ligand could not be located from final difference maps.

Cluster fitting

The fitting was made with the CHEM-X molecular modeling program [24]. All the experimental clusters (A, B and C) were fitted in three different ways.

- (1) The experimental metal core was fitted into the disordered metal sites (see Fig. 2).
- (2) The oxygen atoms of the experimental clusters were fitted into the oxygens of the disordered clusters with the same orientations of the clusters as in the (1) case.
- (3) The molecules were rotated 120° around the three-fold axis of the C_{3v} symmetry of the cluster.

The fitting was made as a rigid fit with the same weighting constant for all the superimposed atoms.

A table of anisotropic thermal parameters, a complete list of bond lengths and angles, and a list of observed and calculated structure factors are available from the authors.

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