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Di-μ-nitrosyl-*trans*-bis[bis(acetylacetonato)ruthenium](*Ru–Ru*)

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Abstract. [{Ru(CH$_3$COCHCOCH$_3$)$_2$}$_2$(μ-NO)$_2$], triclinic, $P\bar{1}$, $a = 10.853$ (3), $b = 12.115$ (3), $c = 9.931$ (3) Å, $\alpha = 89.29$ (2), $\beta = 97.17$ (2), $\gamma = 82.91$ (2)°, $D_c = 1.70$, $D_m = 1.70$ Mg m^{-3}, $Z = 2$, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $\mu = 1.20$ mm^{-1}, 3107 reflections with $I > 3\sigma(I)$, $R = 0.040$, $R_w = 0.069$. Two *cis*-[Ru(acac)$_2$] (acac = acetylacetonato) fragments are connected by a double μ-N(O) bridge so that each Ru is octahedrally coordinated by four O and two N atoms. The Ru(μ-NO)$_2$Ru unit is planar and the [Ru(acac)$_2$] fragments are *trans* to one another, giving effective D_2 symmetry to the dimer. The Ru–O distances average 2.031 (24) Å, Ru–N 1.918 (3) Å. The latter distance is indicative of delocalized π-bonding over the Ru(μ-NO)$_2$Ru unit. The Ru–Ru distance is 2.614 (1) Å, the shortest distance yet reported for an apparently single Ru–Ru bond.

Introduction. One of us recently obtained an oligomeric ruthenium nitrosyl of empirical formula [Ru(acac)$_2$(NO)]$_n$ (acac = acetylacetonato, $n = 2$ or 4) apparently containing bridging nitrosyl groups (Mukaida, Nomura & Ishimori, 1975). Because of the stability of the {RuNO}^{6} unit bridging nitrosyls are very rare in ruthenium chemistry (Bottomley, 1978), being so far confined to two trimeric clusters, [Ru$_3$(CO)$_{10}$(μ-NO)$_2$] (Norton, Collman, Dolcetti & Robinson, 1972) and [Ru$_3$(CO)$_7${PO(CH$_3$)$_3$}$_3$(μ-H)(μ-NO)] (Johnson, Raithby & Zuccaro, 1980). In view of the unusual nature of [Ru(acac)$_2$(NO)]$_n$ we have investigated it crystallographically and shown it to be [{Ru(acac)$_2$}$_2$(μ-NO)$_2$], this formulation being one of those previously suggested (Mukaida *et al.*, 1975).

Examination of Weissenberg and precession photographs revealed no systematic absences or symmetry elements. Successful refinement was accomplished in $P\bar{1}$. The crystal used for the intensity determination was 0.58 × 0.42 × 0.33 mm. Intensities of 3345 independent reflections ($2\theta < 45°$) were measured using graphite-monochromatized Mo $K\alpha$ radiation on a Picker FACS-1 diffractometer, of which 3107 were considered to be observed [$I > 3\sigma(I)$]. These were corrected for absorption (transmission factors ranged from 0.52 to 0.68). Initial atomic coordinates for ruthenium were obtained using the *MULTAN* procedure (Main, Woolfson & Germain, 1971) and the

structure solved subsequently by standard Fourier and difference Fourier syntheses. Refinement, with anisotropic thermal parameters for all atoms except H, using the program suite of Larson & Gabe (1978) converged at $R_1 [= (\sum |\Delta F| / \sum |F_o|)] = 0.040$, $R_2 [= (\sum w|\Delta F|^2 / \sum w|F_o|^2)^{1/2}] = 0.069$. The same functions including unobserved were $R_1' = 0.043$ and $R_2' = 0.073$. There were 420 variables and the function minimized was $\sum w(\Delta F)^2$, with $w = 1/[\sigma^2(|F|) + 0.005(|F|)^2]$. A final difference Fourier synthesis had a highest positive peak of 0.87 e Å^{-3} and a lowest negative of -0.67 e Å^{-3}. The scattering factors were taken from Cromer & Waber (1974), those for ruthenium being corrected for anomalous dispersion (Cromer & Ibers, 1974). The

Table 1. *Atomic coordinates and isotropic thermal parameters of the non-H atoms*

	x	y	z	B_{iso}^* (Å^2)
Ru(1)	0.23393 (2)	0.75005 (2)	0.33062 (3)	3.309 (12)
Ru(2)	−0.00485 (2)	0.75162 (2)	0.24920 (2)	3.066 (12)
N(1)	0.0866 (2)	0.7881 (2)	0.4177 (3)	3.13 (12)
O(2)	0.0637 (2)	0.8213 (2)	0.5225 (2)	4.68 (13)
N(3)	0.1417 (2)	0.7161 (2)	0.1619 (3)	3.05 (12)
O(4)	0.1655 (2)	0.6884 (2)	0.0539 (2)	4.64 (13)
O(11)	0.2304 (2)	0.9119 (2)	0.2712 (2)	4.45 (12)
C(12)	0.2736 (5)	1.0618 (4)	0.1476 (5)	6.74 (27)
C(13)	0.3012 (4)	0.9433 (3)	0.1913 (4)	4.94 (20)
C(14)	0.3991 (4)	0.8797 (4)	0.1426 (4)	5.81 (24)
C(15)	0.4448 (4)	0.7719 (4)	0.1751 (4)	5.29 (26)
C(16)	0.5585 (4)	0.7202 (5)	0.1208 (5)	7.37 (36)
O(17)	0.3978 (2)	0.7071 (2)	0.2534 (3)	4.66 (13)
O(21)	0.3433 (2)	0.7887 (2)	0.5018 (3)	4.86 (13)
C(22)	0.4597 (5)	0.7678 (5)	0.7125 (5)	7.43 (38)
C(23)	0.3874 (3)	0.7178 (3)	0.5970 (4)	4.45 (20)
C(24)	0.3773 (4)	0.6055 (4)	0.5970 (4)	5.34 (24)
C(25)	0.3157 (3)	0.5466 (3)	0.4968 (4)	4.22 (18)
C(26)	0.3180 (4)	0.4232 (3)	0.5147 (5)	5.77 (26)
O(27)	0.2538 (2)	0.5880 (2)	0.3877 (2)	3.98 (11)
O(31)	−0.0248 (2)	0.9100 (2)	0.1740 (2)	3.68 (11)
C(32)	−0.0941 (4)	1.0993 (3)	0.1472 (4)	5.60 (25)
C(33)	−0.1009 (3)	0.9872 (3)	0.2096 (3)	3.55 (15)
C(34)	−0.1884 (4)	0.9779 (3)	0.2988 (4)	4.41 (18)
C(35)	−0.2166 (3)	0.8810 (3)	0.3538 (4)	4.18 (17)
C(36)	−0.3180 (4)	0.8858 (4)	0.4437 (5)	6.33 (25)
O(37)	−0.1654 (2)	0.7822 (2)	0.3365 (2)	4.20 (12)
O(41)	−0.1140 (2)	0.7207 (2)	0.0744 (2)	3.89 (11)
C(42)	−0.2104 (4)	0.6154 (3)	−0.0932 (4)	4.92 (21)
C(43)	−0.1439 (3)	0.6254 (3)	0.0447 (3)	3.49 (16)
C(44)	−0.1199 (3)	0.5316 (3)	0.1281 (4)	4.27 (18)
C(45)	−0.0548 (3)	0.5195 (3)	0.2564 (3)	3.49 (16)
C(46)	−0.0424 (4)	0.4105 (3)	0.3305 (4)	4.80 (20)
O(47)	−0.0034 (2)	0.5950 (2)	0.3210 (2)	3.65 (11)

* B_{iso} is defined as the arithmetic mean of the principal axes of the thermal ellipsoid.

Table 2. *Selected bond distances* (Å)

Ru(1)—Ru(2)	2.6143 (9)	Ru(2)—N(3)	1.910 (3)
Ru(1)—N(1)	1.921 (3)	Ru(2)—O(31)	2.0268 (21)
Ru(1)—N(3)	1.918 (3)	Ru(2)—O(37)	2.0373 (24)
Ru(1)—O(11)	2.0349 (23)	Ru(2)—O(41)	2.0421 (23)
Ru(1)—O(17)	2.035 (3)	Ru(2)—O(47)	2.0160 (20)
Ru(1)—O(21)	2.0420 (25)	N(1)—O(2)	1.165 (3)
Ru(1)—O(27)	2.0149 (23)	N(3)—O(4)	1.178 (3)
Ru(2)—N(1)	1.922 (3)		

Table 3. *Selected bond angles* (°)

| N(1)—Ru(1)—N(3)	93.94 (11)	Ru(1)—N(1)—Ru(2)	85.74 (10)
N(1)—Ru(2)—N(3)	94.16 (11)	Ru(1)—N(3)—Ru(2)	86.14 (11)
Ru(1)—N(1)—O(2)	136.9 (2)	Ru(1)—N(3)—O(4)	136.4 (2)
Ru(2)—N(1)—O(2)	137.3 (2)	Ru(2)—N(3)—O(4)	137.4 (2)
N(1)—Ru(1)—O(11)	90.46 (11)	N(1)—Ru(2)—O(31)	93.23 (10)
N(1)—Ru(1)—O(21)	90.15 (11)	N(1)—Ru(2)—O(37)	88.48 (10)
N(1)—Ru(1)—O(27)	94.25 (10)	N(1)—Ru(2)—O(47)	89.82 (10)
N(3)—Ru(1)—O(11)	92.06 (10)	N(3)—Ru(2)—O(31)	90.41 (10)
N(3)—Ru(1)—O(17)	90.26 (11)	N(3)—Ru(2)—O(41)	89.97 (11)
N(3)—Ru(1)—O(27)	89.58 (10)	N(3)—Ru(2)—O(47)	94.04 (10)
O(11)—Ru(1)—O(17)	91.23 (11)	O(31)—Ru(2)—O(37)	91.43 (10)
O(11)—Ru(1)—O(21)	86.01 (10)	O(31)—Ru(2)—O(41)	84.91 (9)
O(17)—Ru(1)—O(21)	85.71 (11)	O(37)—Ru(2)—O(41)	87.46 (10)
O(17)—Ru(1)—O(27)	83.93 (10)	O(37)—Ru(2)—O(47)	83.96 (10)
O(21)—Ru(1)—O(27)	91.99 (10)	O(41)—Ru(2)—O(47)	91.70 (9)
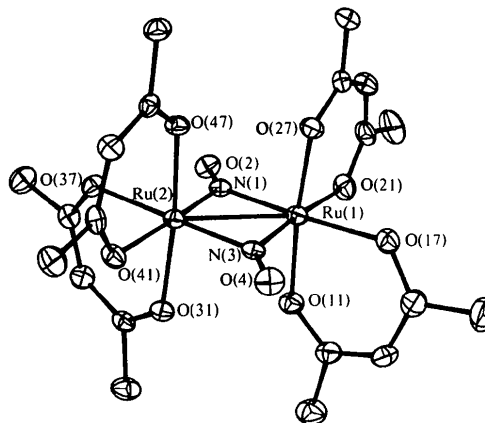
Fig. 1. Molecular architecture of [{Ru(acac)$_2$}$_2$(μ-NO)$_2$], showing the numbering scheme for the inner coordination sphere.

final atomic coordinates for the non-H atoms are given in Table 1, and a selection of important bond distances and angles in Tables 2 and 3.* The numbering scheme is given in Fig. 1.

Discussion. The crystals of [{Ru(acac)$_2$}$_2$(μ-NO)$_2$] consist of well separated molecular units of the dimeric molecule, the shortest non-bonded contact being 2.34 (9) Å between H atoms of CH$_3$ groups on the acetylacetonato ligand. From the distances and angles in Tables 2 and 3 it is seen that each ruthenium is approximately octahedrally coordinated by the four O atoms of two *cis*-(acetylacetonato) ligands and the N atoms of the nitrosyl bridges. The angles between the mean planes defining the octahedra have maximum deviations of ± 2.8 (1)° from 90°. The acetylacetonato ligands in the two halves of the dimer are arranged in a *trans* relationship to each other, so that the effective symmetry is D_2 within experimental error. The Ru—O

distances to the acetylacetonato ligands average 2·031 (24) Å. It is difficult to compare this average distance to other Ru—O distances because if the nitrosyl group is regarded as a three-electron donor the formal oxidation state of the ruthenium is I which is very rare. The only Ru^{I}—O distance in the literature appears to be the 2·13 (1) Å observed in [{Ru(CO)$_2$}$_2$(μ-O$_2$CCH$_2$CH$_2$CH$_3$)$_2${P(*tert*-Bu)$_3$}$_2$] (Schumann, Opitz & Pickardt, 1977). In [Ru(acac)$_3$] the Ru—O distances average 2·00 (2) Å (Chau, Sime & Sime, 1973). The C—C and C—O distances and all angles in the acetylacetonato ligand are normal.

The Ru(μ-NO)$_2$Ru unit is approximately planar with deviations within ±0·021 (2) Å from the mean plane. The Ru—N distances average 1·918 (3) Å. Again, detailed comparison with other Ru—N distances is difficult. The distance is considerably longer than the Ru—NO distance observed in {RuNO}^{6} complexes {*e.g.* in *trans*-[Ru(OH)(NH$_3$)$_4$(NO)]Cl$_2$, Ru—N is 1·735 (3) Å} but shorter than a simple Ru—N single bond [in the same nitrosyl the average Ru—NH$_3$ distance is 2·102 (3) Å (Bottomley, 1974)]. It can be concluded that some double-bond character is present in the Ru(μ-NO)$_2$Ru plane. In the other two known nitrosyl-bridged dimers of ruthenium the average Ru—N distance is longer than in [{Ru(acac)$_2$}$_2$(μ-NO)$_2$], being 1·981 (7) Å in [Ru$_3$(CO)$_7${P(OCH$_3$)$_3$}$_3$(μ-H)(μ-NO)] (Johnson *et al.*, 1980) and 2·03 (1) Å in [Ru$_3$(CO)$_{10}$(μ-NO)$_2$] (Norton *et al.*, 1972). However, these distances are associated with longer Ru—Ru distances, 2·816 (2) and 3·150 (1) Å respectively. The relationship between the Ru—N and Ru—Ru bond distances is discussed elsewhere (Bottomley, 1982). The N—O distances [1·165 (3) and 1·178 (3) Å] are in the range usually observed for bridging nitrosyls (Johnson *et al.*, 1980).

The most striking feature of the structure of [{Ru(acac)$_2$}$_2$(μ-NO)$_2$] is the Ru—Ru bond distance of 2·614 (1) Å. If [{Ru(acac)$_2$}$_2$(μ-NO)$_2$] is considered as being of general formula [(L_4M)$_2$(μ-AB)$_2$], where L is a unidentate or one-electron-pair donor from a polydentate ligand and AB is a π-acceptor molecule, then it may be compared to *trans*-[{Cp(CO)Ru}$_2$(μ-CO)$_2$] [Ru—Ru 2·735 (2) Å (Mills & Nice, 1967)], *cis*-[{Cp(CO)Ru}$_2$(μ-CO)(μ-C=CH$_2$)] [Ru—Ru 2·695 (1) Å] and *cis*-[{Cp(CO)Ru}$_2$(μ-CO)(μ-CCH$_3$)] [Ru—Ru 2·714 (1) Å, both from Davies, Dyke, Endesfelder, Knox, Naish, Orpen, Plaas & Taylor (1980)]. It is seen that the Ru—Ru distance in the present dimer is 0·1 Å shorter than these values, which have been considered as single-bond distances. Complexes of general formula [(L_3Ru)$_2$(μ-X)$_2$] where X is a π-donor ligand have Ru—Ru distances of 2·65–2·72 Å (Schumann, Opitz & Pickardt, 1977, 1980; Mason, Thomas, Gill & Shaw, 1972), and are also generally considered to have an Ru—Ru single bond. A double bond is proposed in [{Ru(NO)}$_2${P(CH$_3$)(C$_6$H$_5$)$_2$}$_2${μ-P(C$_6$H$_5$)$_2$}$_2$] for

which the Ru—Ru distance is 2·629 (2) Å (Reed, Schultz, Pierpont & Eisenberg, 1973), and the Ru—Ru distances of 2·25–2·62 Å in the tetracarboxylate dimers of ruthenium have been interpreted in terms of bond orders of 2–3 (Bino, Cotton & Felthouse, 1979; Warren & Goedken, 1978; Bennett, Caulton & Cotton, 1969; Togano, Mukaida & Nomura, 1980; Mukaida, 1982). It is clear that the Ru—Ru distance in [{Ru(acac)$_2$}$_2$(μ-NO)$_2$] is very short, particularly if it is considered to represent a single bond. We will present a theoretical approach to the metal—metal bonds in [(L_3M)$_2$(μ-AB)$_2$] and [(L_4M)$_2$(μ-AB)$_2$] dimers elsewhere (Bottomley, 1982).

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