Extended Linear Metal–Metal Interactions in an Anionic Rhodium(I) Complex. *X*-Ray Structure of $NMe_4[Rh(ox)(CO)_2]$ (ox = oxalato)

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The complex $NMe_4[Rh(ox)(CO)_2]$ (**2**) (ox=oxalato) was prepared from $NMe_4[Rh(ox)(cod)]$ (**1**) (cod=cyclo-octa-1,5-diene) by bubbling carbon monoxide and, complex (**1**) was prepared from $Rh_2Cl_2(cod)_2$, oxalic acid, and NMe_4OH; the solid state structure of (**2**) consists of infinite chains of metal atoms [Rh · · · Rh · · · Rh 175.01(3)°] with equal rhodium–rhodium distances of 3.243(1) Å, the shortest distance found in a stacked rhodium complex.

Although Rh^I square-planar stacked complexes have been known for many years, few have been structurally characterized. The best known example is the complex $Rh(acac)(CO)_2$ (acac = acetyacetonate), which has been shown to behave as an intrinsic semiconductor.[1] Attempts partially to oxidize this species or its iridium analogue to form one-dimensional synthetic metals have proved unsuccessful.

The interest in new anisotropic materials has led to the preparation of new neutral rhodium complexes containing azolate ligands, with stacking arrangements of square-planar rhodium units along one axis, forming nearly linear chains of metal atoms.[2] Very recently, it has been found that anionic complexes of iridium and azolate or carboxyazolate ligands readily form stacked structures.[3] Some of these compounds can be electrochemically partially oxidized to yield conductive materials. The oxalato ligand offers interesting possibilities in this field, since it can be strictly planar; the methyl groups of the acetylacetonate ligand should increase its 'thickness' compared to oxalate. Oro and co-workers[4] have reported on the chemistry of some non-strictly planar μ-oxalato rhodium(I) complexes, including the interesting $[Rh_2(ox)(CO)_4]_x$ (ox = oxalato), which is dark in colour and dichroic. However, the reported 'complex' IR spectrum of this compound in the carbonyl region seems to preclude a simple planar structure.[4] For our purposes we find anionic complexes more appealing; they should be simpler and easier partially to oxidize.

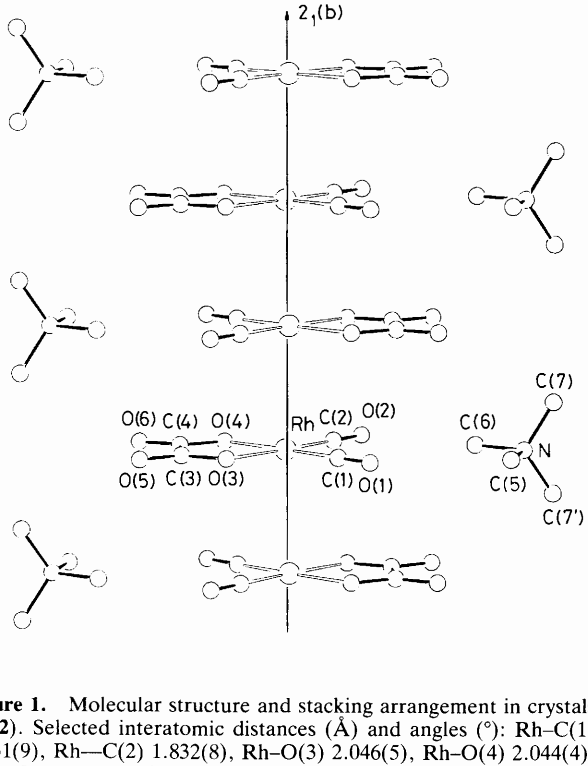

Figure 1. Molecular structure and stacking arrangement in crystals of (**2**). Selected interatomic distances (Å) and angles (°): Rh–C(1) 1.831(9), Rh—C(2) 1.832(8), Rh–O(3) 2.046(5), Rh–O(4) 2.044(4), C(1)–O(1) 1.123(10), C(2)–O(2) 1.131(10), C(3)–O(3) 1.269(10), C(3)–O(5) 1.225(10), C(3)–C(4) 1.554(12), C(4)–O(4) 1.291(9), C(4)–O(6) 1.210(10); C(1)–Rh–C(2) 89.7(4), O(3)–Rh–O(4) 81.0(2), C(1)–Rh–O(3) 95.3(3), C(2)–Rh–O(4) 94.0(3), C(1)–Rh–O(4) 176.3(3), C(2)–Rh–O(3) 175.1(3), Rh–C(1)–O(1) 178.1(8), Rh–C(2)–O(2) 178.2(8).

The reaction of $Rh_2Cl_2(cod)_2$ (cod = cyclo-octa-1,5-diene) with $H_2ox{\cdot}2H_2O$ and two equivalents of NMe_4OH in MeCN affords the yellow, crystalline $NMe_4[Rh(ox)(cod)]{\cdot}1/2$ MeCN (**1**) in good yield (*ca.* 80%).† Bubbling CO through ice cold concentrated MeOH/MeCN solutions of (**1**) causes displacement of the cod ligand and crystallization of the carbonyl $NMe_4[Rh(ox)(CO)_2]$ (**2**), which is isolated in good yield (*ca.* 80%).† Crystals of (**2**) are dichroic, appearing dark olive green in bulk. MeCN (or MeOH) solutions are pale yellow. Finely precipitated (**2**) (by addition of ether to MeCN or MeOH solutions) is dark blue.

These facts indicated some kind of solid state interaction, which was confirmed by a crystal structure determination.‡ The complex anion $[Rh(ox)(CO)_2]^-$ is strictly planar, lying on a crystallographic symmetry plane. The anions are stacked along the 2_1 crystallographic axis (Figure 1), forming practically linear chains of metal atoms [Rh · · · Rh · · · Rh angle of

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† Satisfactory elemental analyses were obtained for all new compounds. NMR data for (**1**): $^{13}C\{^1H\}$ 100 MHz (CD_3OD) δ 170.0 (ox), 76.8 (cod, =CH, d, $^1J_{Rh-C}$ 15 Hz), 56.0 (NMe_4^+), 31.5 (cod, $-CH_2$); ^1H 400 MHz (CD_3OD) δ 4.15 (br., cod, =CH), 3.38 (NMe_4^+), 2.63 (br., cod, $-CH_2$), 1.95 (pseudo d, *J* 8 Hz, cod, $-CH_2$). IR data for (**1**): (KBr pellet) ν(COO) 1592 cm^{-1} (v st, br.).

NMR data for (**2**): $^{13}C\{^1H\}$ 100 MHz (CD_3OD) δ 185.1 (CO, d, $^1J_{Rh-C}$ 73 Hz), 167.8 (ox), 56.0 (NMe_4^+). IR data (MeCN solution, cm^{-1}): ν(CO) 2077, 2000; ν(COO) 1704, 1685, 1666. Nujol mull: ν(CO) 2068, 2002; ν(COO) 1703, 1667 (br.).

‡ *Crystal data* for (**2**): orthorhombic, space group *Pnma* (No. 62), a = 16.7669(7), b = 6.4806(2), c = 11.3930(4) Å, U = 1237.96(8) $Å^3$, Z = 4, D_c = 1.723 g cm^{-3}. A black needle (0.19 × 0.19 × 0.42 mm, sealed in a capillary) was mounted on a Siemens AED-2 diffractometer with graphite monochromated Mo-K_α radiation; 4797 reflections were measured ($3 \leqslant 2\theta \leqslant 50°$) using the ω/2θ scan technique. Data were corrected for Lorentz, polarization, and absorption effects (ψ-scan method, 3 reflections, μ = 13.67 cm^{-1}). 714 unique reflections with $F \geqslant 5.0\sigma(F)$ were considered observed. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions, riding upon carbon atoms and included in the last cycle of refinement. Final agreement indices were R = 0.029 and R_w = 0.031. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

175.01(3)°] with equal Rh · · · Rh distances of 3.243(1) Å. This distance is slightly shorter (0.02 Å) than that in the related acac complex, probably because of the strict planarity of the anion in (**2**). An intriguing feature of the packing is the eclipsed configuration of adjacent anions in the stack, with a relative rotation angle of 180°, which produces the overlap of the carbon atoms of the carbonyl ligands and the O-donor atoms of the oxalato ligands; as far as inter-anion repulsions are concerned this seems quite an unfavourable arrangement. The most direct interpretation is that there must be an interaction between carbonyl and oxalato ligands of adjacent complex anions, which stabilizes the eclipsed configuration. It should be pointed out that in most cases Rh^I and Ir^I stacked complexes adopt this type of eclipsed configuration. However, partially oxidized bis-oxalato platinates stack with rotation angles ranging from 45 to 60° due to inter-molecular HOMO–LUMO interactions.[5]

Distances and angles within the oxalate are normal for this ligand acting as bidentate.[6] In spite of the anionic character of (**2**), back donation of the metal to the CO ligands appears to be smaller than in the neutral $[Rh(acac)(CO)_2]$ complex [with Rh–C 1.76(2) and 1.75(2); carbonyl C–O 1.21(3) and 1.26(3)], as revealed by the longer Rh–C and shorter C–O distances found in (**2**).

Preliminary results indicate that it is not easy to obtain characterizable materials from the oxidation of (**2**); further attempts are under way and will be reported in due course.

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