# Dinuclear Rhodium and Iridium Complexes of Dicarboxyimidazolates; Crystal Structure of $[NBu_4][(cod)Rh(dcbi)Rh(cod)]\cdot 2Pr^iOH$ †

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Dinuclear complexes of rhodium and iridium with 4,5-dicarboxyimidazole ($H_3$dcbi) and 4,5-dicarboxy-2-methylimidazole ($H_3$dcbmi) are reported. In each case, the bridging carboxyimidazole ligand binds as the trianion. The auxiliary ligands are cyclo-octa-1,5-diene (cod), carbon monoxide, and triphenylphosphine. The CO complexes, such as $[NR_4][(OC)_2Ir(dcbi)Ir(CO)_2]$ which contains a planar dinuclear anion, exhibit strong colours which are caused by intermolecular stacking interactions and which are modulated by the counter cation. The *X*-ray crystal structure of $[NBu_4]$-$[(cod)Rh(dcbi)Rh(cod)]\cdot 2Pr^iOH$ is described.

In recent years, low-dimensional solids have received considerable attention. Square-planar $d^8$ metal complexes, such as Krogmann-type tetracyanoplatinates, have been widely investigated because they offer the opportunity of studying the influence of structural modifications on the conductivity of these materials.[1] However, the low-temperature instability inherent in one-dimensional systems prevents the attainment of a metallic state.[2] This problem has been surmounted by molecular structures which have a large number of polarizable atoms (*i.e.* sulphur or selenium) at the periphery of the stacking unit producing strong interchain electronic interactions. Such compounds retain the metallic state to low temperatures and in some cases exhibit superconductivity.[3]

We are engaged in the synthesis of a new type of $d^8$ metal complexes which combine both the simplicity of a one-dimensional chain of atoms and the possibility of strong inter-stack electronic interaction. These requirements can be satisfied by dinuclear, planar complexes which have strong interactions within the stacking unit. In order for such a compound to be highly conducting the band arising from the metal–metal interaction must not be completely filled. Electrochemical partial oxidation has been extensively used to provide the system with the charge carriers required to achieve the metallic state. For that reason many of the synthetic precursors of highly conducting materials are anionic species. The uncommon conditions of dinuclearity, planarity, and anionic character are met by some of the rhodium(I) and iridium(I) complexes of the ligands 4,5-dicarboxyimidazole ($H_3$dcbi) and 4,5-dicarboxy-2-methylimidazole ($H_3$dcbmi). We report here the synthesis of these new species along with some related compounds and their spectroscopic and structural characterization.

## Experimental

All syntheses of rhodium and iridium complexes were performed by standard Schlenk techniques under a nitrogen atmosphere. The complexes $[\{M(cod)Cl\}_2]$ and [Ir(cod)(acac)] (cod = cyclo-octa-1,5-diene, acac = acetylacetonate) were prepared by methods previously decribed.[4] Solvents were purified by standard procedures. All other reagents were used as commercially available.

*Measurements.*—Infrared spectra (Nujol mulls, KBr pellets, or solution) were obtained on a PU0510 spectrophotometer. Electronic spectra (solution or Nujol mulls) were recorded on a Shimadzu UV-240 spectrophotometer. Thermogravimetric and elemental analyses were performed on a Rigaku Thermoflex and a Perkin-Elmer 240-C instrument respectively. Proton n.m.r. spectra were recorded on a Varian XL-200 and $^{13}C$-$\{^1H\}$ n.m.r. spectra on a Bruker WP80SY spectrometer. Chemical shifts are relative to $SiMe_4$. A HP5985 GC/MS instrument was used for mass spectral analyses. Electrical conductivity was determined on compressed pellets between two copper pistons under a pressure of 30 bar ($3 \times 10^6$ Pa) and measured with a Keithley 503 electrometer.

*Synthesis of the Ligands.*—4,5-Dicyanoimidazoles were prepared from diaminomaleonitrile by the method of Woodward.[5] Hydrolysis of these molecules in basic media to form the diacids has been described,[6] but we found some amide as impurity following that procedure. For this reason we report an improved preparation. 4,5-Dicyanoimidazole (4 g) was refluxed 12 h in a mixture of sulphuric acid (18 mol $dm^{-3}$, 35 $cm^3$) and water (15 $cm^3$). Addition of cold water (150 $cm^3$) precipitated a white powder in the case of $H_3$dcbi and a white crystalline solid in the case of $H_3$dcbmi (yields above 80%): $H_3$dcbi, m.p. 290—292 °C (Found: C, 37.9; H, 2.65; N, 17.6. Calc. for $C_5H_4N_2O_4$: C, 38.5; H, 2.60; N, 17.9%); *m/z* 156, 139, 123, 112, 94, 67, and 45; $^{13}C$-$\{^1H\}$ n.m.r. ($LiOD$–$D_2O$) δ 137.1 ($C^{4,5}$), 142.6 ($C^2$), and 173.1 ($CO_2^-$); $H_3$dcbmi, m.p. 286—288 °C (Found: C, 41.9; H, 3.85; N, 16.5. Calc. for $C_6H_6N_2O_4$: C, 42.4; H, 3.55; N, 16.5%); *m/z* 170, 152, 126, 108, and 82.

*Synthesis of* $[NR_4][M_2(cod)_2L]$.—A 0.1 mol $dm^{-3}$ solution of $NR_4OH$ in isopropanol–methanol (1:1) (Merck) (12 $cm^3$) or $NEt_3$ (1.2 mmol) was slowly added dropwise *via* a syringe to a suspension of the ligand (0.4 mmol) and $[\{M(cod)Cl\}_2]$ (0.4 mmol) in $CH_3CN$ (25 $cm^3$). The yellow solution was stirred for 0.5 h and the solvents evaporated to 5—10 $cm^3$ at which time a yellow crystalline solid precipitated. Addition of isopropanol (15 $cm^3$) and further evaporation of the solvent improved the yield of the more soluble compounds.

$[NHEt_3][Rh_2(cod)_2(dcbi)]\cdot H_2O$ (yield 80%) (Found: C, 46.3; H, 5.95; N, 6.15. Calc. for $C_{27}H_{43}N_3O_5Rh_2$: C, 46.6; H, 6.25; N, 6.05%). I.r. (KBr): 1 650s,br $cm^{-1}$ ($CO_2$, asym). N.m.r. ($CDCl_3$): $^1H$, δ 6.35 (s, CH), 4.37, 4.05 (m, CH of cod), 2.41, 1.82 (m, $CH_2$ of cod); $^{13}C$-$\{^1H\}$, 171.4 ($CO_2$), 136.6 ($C^2$), 135.8 ($C^{4,5}$), 82.7 [d, CH of cod *trans* to N, *J*(Rh–C) = 13], 71.7 [d, CH of cod *trans* to O, *J*(Rh–C) = 14 Hz], 31.2, 30.0 ($CH_2$ of cod).

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† Tetrabutylammonium μ-imidazole-4,5-dicarboxylato(3−)-bis-[(η-cyclo-octa-1,5-diene)rhodate]–isopropanol (1/2).

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

$[NMe_4][Rh_2(cod)_2(dcbi)]\cdot 0.5CH_3CN$ (yield 80%) (Found: C, 47.0; H, 5.85; N, 7.35. Calc. for $C_{26}H_{38.5}N_{3.5}O_4Rh_2$: C, 46.6; H, 5.80; N, 7.30%).

$[NBu_4][Rh_2(cod)_2(dcbi)]\cdot 2H_2O$ (yield 80%) (Found: C, 52.1; H, 7.45; N, 4.95. Calc. for $C_{37}H_{65}N_3O_6Rh_2$: C, 52.1; H, 7.65; N, 4.90%). Under slow crystallization conditions single crystals were obtained containing two molecules of isopropanol of solvation.

$[NMe_4][Rh_2(cod)_2(dcbmi)]\cdot 0.5C_3H_8O\cdot H_2O$ (yield 80%) (Found: C, 46.1; H, 6.45; N, 5.85. Calc. for $C_{27.5}H_{45}N_3O_{5.5}Rh_2$: C, 46.4; H, 6.40; N, 5.90%). I.r. (KBr): 1 650s,br cm$^{-1}$ ($CO_2$, asym). $^1$H N.m.r. ($CDCl_3$): δ 1.68 (s, $CH_3$ of dcbmi), 4.26 (m, CH of cod), 2.44, 1.78 (m, $CH_2$ of cod).

$[NBu_4][Rh_2(cod)_2(dcbmi)]\cdot 0.5H_2O$ (yield 70%) (Found: C, 54.3; H, 7.95; N, 4.90. Calc. for $C_{38}H_{64}N_3O_{4.5}Rh_2$: C, 54.3; H, 7.65; N, 5.00%).

$[NMe_4][Ir_2(cod)_2(dcbmi)]\cdot 2H_2O$ (yield 60%) (Found: C, 35.2; H, 4.70; N, 4.65. Calc. for $C_{26}H_{43}Ir_2N_3O_6$: C, 35.6; H, 4.95; N, 4.80%). I.r. (KBr): 1 680s,br cm$^{-1}$ ($CO_2$, asym). N.m.r. ($CD_2Cl_2$): $^1$H δ 4.06 (m, CH of cod *trans* to N), 3.95 (m, CH of cod *trans* to O), 2.22, 1.56 (m, $CH_2$ of cod), and 1.88 (s, $CH_3$); $^{13}$C-{$^1$H} 158.3 ($C^2$), 128.5 ($C^{4,5}$), 66.1 (CH of cod *trans* to N), 54.9 (CH of cod *trans* to O), 33.6 ($CH_3$), and 30.5 ($CH_2$ of cod).

$[NBu_4][Ir_2(cod)_2(dcbmi)]$ (yield 55%) (Found: C, 45.5; H, 6.35; N, 4.35. Calc. for $C_{38}H_{63}Ir_2N_3O_4$: C, 45.2; H, 6.30; N, 4.15%).

*Synthesis of* $[NR_4][M_2(CO)_4L]$.—Carbon monoxide was slowly bubbled through saturated solutions of $[NR_4][M_2(cod)_2L]$ salts in $CH_3CN$ or $CH_2Cl_2$, producing fine dichroic needles (addition of diethyl ether was necessary in the case of $NBu_4^+$). Yields were about 70% for the rhodium compounds and about 50% for iridium.

$[NHEt_3][Rh_2(CO)_4(dcbi)]$ (Found: C, 31.8; H, 3.20; N, 7.30. Calc. for $C_{15}H_{17}N_3O_8Rh_2$: C, 31.4; H, 3.00; N, 7.35%). I.r. (Nujol): 2 095s, 2 070s, 2 040s, and 2 015s cm$^{-1}$.

$[NMe_4][Rh_2(CO)_4(dcbi)]\cdot H_2O$ (Found: C, 27.6; H, 2.70; N, 7.20. Calc. for $C_{13}H_{15}N_3O_9Rh_2$: C, 27.7; H, 2.70; N, 7.50%). I.r. (Nujol): 2 090s, 2 080s, 2 025s, and 2 010s cm$^{-1}$.

$[NEt_4][Rh_2(CO)_4(dcbi)]$ (Found: C, 33.8; H, 3.70; N, 6.90. Calc. for $C_{17}H_{21}N_3O_8Rh_2$: C, 34.0; H, 3.50; N, 7.00%). I.r. (Nujol): 2 090s,br, 2 030s, and 2 010s cm$^{-1}$.

$[NBu_4][Rh_2(CO)_4(dcbi)]\cdot H_2O$ (Found: C, 41.1; H, 5.95; N, 5.60. Calc. for $C_{25}H_{39}N_3O_9Rh_2$: C, 41.1; H, 5.35; N, 5.75%). I.r. ($CH_2Cl_2$): 2 085s and 2 020s cm$^{-1}$.

$[NMe_4][Ir_2(CO)_4(dcbi)]\cdot 2H_2O$ (Found: C, 20.5; H, 2.35; N, 5.35. Calc. for $C_{13}H_{17}Ir_2N_3O_{10}$: C, 20.5; H, 2.35; N, 5.35%). I.r. (Nujol): 2 070m,br and 1 995s,br cm$^{-1}$.

$[NEt_4][Ir_2(CO)_4(dcbi)]\cdot 3H_2O$ (Found: C, 24.4; H, 2.90; N, 5.05. Calc. for $C_{17}H_{27}Ir_2N_3O_{11}$: C, 24.5; H, 3.25; N, 5.05%). I.r. (Nujol): 2 080m,br and 1 990s,br cm$^{-1}$.

$[NMe_4][Rh_2(CO)_4(dcbmi)]\cdot 2H_2O$ (Found: C, 27.9; H, 3.05; N, 7.00. Calc. for $C_{14}H_{19}N_3O_{10}Rh_2$: C, 28.2; H, 3.20; N, 7.05%). I.r. (Nujol): 2 086s, 2 064s, 2 032s, and 2 019s cm$^{-1}$.

$[NBu_4][Rh_2(CO)_4(dcbmi)]$ (Found: C, 43.2; H, 5.40; N, 5.60. Calc. for $C_{26}H_{39}N_3O_8Rh_2$: C, 42.9; H, 5.40; N, 5.80%). I.r. ($CH_3CN$): 2 087 and 2 030 cm$^{-1}$. $^1$H N.m.r. ($CDCl_3$): δ 2.48 (s, $CH_3$ of dcbmi).

$[NMe_4][Ir_2(CO)_4(dcbmi)]\cdot 2H_2O$ (Found: C, 21.6; H, 2.40; N, 5.35. Calc. for $C_{14}H_{19}Ir_2N_3O_{10}$: C, 21.7; H, 2.45; N, 5.45%). I.r. (Nujol): 2 076m,br, 2 026s, and 2 008s cm$^{-1}$.

$[NBu_4][Ir_2(CO)_4(dcbmi)]$ (Found: C, 34.7; H, 4.55; N, 4.70. Calc. for $C_{26}H_{39}Ir_2N_3O_8$: C, 34.5; H, 4.30; N, 4.65%). I.r. (Nujol): 2 085s, 2 028s, and 2 009s cm$^{-1}$. $^1$H N.m.r. ($CDCl_3$): δ 2.50 (s, $CH_3$ of dcbmi).

*Synthesis of* $K[Ir_2(CO)_4(dcbi)]\cdot 2H_2O$.—The compounds [Ir(cod)(acac)] (0.5 mmol) and $K(H_2dcbi)$ (0.25 mmol) were stirred for 1 h at 60 °C in $CH_3CN$ (30 cm$^3$) producing a yellow precipitate. The sparingly soluble solid was dissolved in the same solvent and treated with carbon monoxide forming an insoluble dark blue solid (Found: C, 15.0; H, 0.95; N, 3.85. Calc. for $C_9H_5Ir_2KN_2O_{10}$: C, 14.9; H, 0.70; N, 3.85%). I.r. (Nujol): 2 075m,br and 1 995s,br cm$^{-1}$.

**Table 1.** *X*-Ray data for $[NBu_4][Rh_2(cod)_2(dcbi)]\cdot 2Pr^iOH$

| | |
|---|---|
| Formula | $C_{43}H_{77}N_3O_2Rh_2$ |
| *M* | 873.92 |
| Space group | *Fddd* (no. 70) |
| *a*/Å | 13.784(4) |
| *b*/Å | 27.189(9) |
| *c*/Å | 49.336(14) |
| α, β, γ/° | 90.0 |
| *U*/Å$^3$ | 18 490(9) |
| *Z* | 16 |
| $D_c$/g cm$^{-3}$ | 1.256 |
| μ/cm$^{-1}$ | 7.355 |
| Crystal dimensions (mm) | 0.64 × 0.31 × 0.20 |
| Data collected | 4 111 |
| Observed [$I > 3\sigma(I)$] | 2 153 |
| Number of parameters | 338 |
| $R^a$ | 0.046 |
| $R'^b$ | 0.041 |

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

**Table 2.** Fractional atomic co-ordinates

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Rh(1) | 0.805 0(0) | −0.014 6(0) | 0.033 9(0) |
| O(1) | 0.806 9(4) | −0.021 5(2) | 0.075 6(1) |
| O(2) | 0.832 6(4) | −0.073 2(2) | 0.109 7(1) |
| N(1) | 0.849 7(4) | −0.086 5(2) | 0.037 6(1) |
| C(1) | 0.859 9(5) | −0.101 4(2) | 0.064 3(1) |
| C(2) | 0.875 0(0) | −0.125 0(0) | 0.022 3(2) |
| C(3) | 0.831 6(5) | −0.063 7(3) | 0.085 6(2) |
| C(11) | 0.757 1(9) | −0.019 5(4) | −0.006 4(2) |
| C(12) | 0.851 9(9) | −0.000 6(3) | −0.005 9(2) |
| C(13) | 0.877 3(9) | 0.053 5(4) | −0.010 7(2) |
| C(14) | 0.871 7(12) | 0.084 0(5) | 0.014 2(3) |
| C(15) | 0.808 2(10) | 0.063 3(3) | 0.036 3(2) |
| C(16) | 0.713 4(10) | 0.048 1(3) | 0.034 1(3) |
| C(17) | 0.658 1(11) | 0.052 5(6) | 0.007 2(4) |
| C(18) | 0.666 6(10) | 0.009 1(6) | −0.011 2(3) |
| N | 0.875 0(0) | 0.057 3(3) | −0.125 0(0) |
| C(C1) | 0.804 1(7) | 0.088 7(4) | −0.109 3(2) |
| C(C2) | 0.845 4(8) | 0.123 6(4) | −0.088 6(2) |
| C(C3) | 0.767 8(10) | 0.144 1(5) | −0.070 6(3) |
| C(C4) | 0.808 0(11) | 0.177 8(5) | −0.049 1(3) |
| C(C5) | 0.066 2(7) | −0.025 8(3) | 0.105 8(2) |
| C(C6) | 0.121 2(8) | 0.010 8(4) | 0.088 3(2) |
| C(C7) | 0.051 1(8) | 0.041 9(3) | 0.071 7(2) |
| C(C8) | 1.006 1(10) | 0.078 7(5) | 0.091 4(3) |
| O(S)* | 0.868 1(5) | −0.001 3(2) | 0.148 1(1) |
| C(1S) | 0.808 0(14) | 0.061 1(6) | 0.178 0(3) |
| C(2S) | 0.449 0(14) | 0.037 2(5) | 0.098 1(3) |
| C(3S) | 0.529 9(16) | 0.034 7(8) | 0.107 5(4) |

* S denotes solvent.

*Synthesis of* $[NR_4][Rh_2(CO)_2(PPh_3)_2L]$.—An acetonitrile solution (10 cm$^3$) of $PPh_3$ (0.32 mmol) was added over a suspension of $[NMe_4][Rh_2(CO)_4L]$ (0.13 mmol) in the same solvent. After stirring for 2 h a pale yellow solid was formed. The product was collected by filtration and rinsed with diethyl ether.

$[NHEt_3][Rh_2(CO)_2(PPh_3)_2(dcbi)]\cdot H_2O$ (yield 90%)

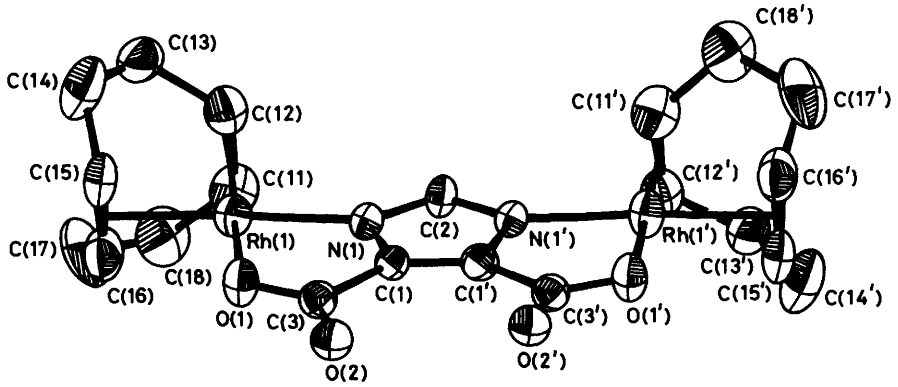


**Figure.** ORTEP diagram of $[Rh_2(cod)_2(dcbi)]^-$. Primed atoms are generated by the two-fold symmetry axis

(Found: C, 55.3; H, 4.65; N, 4.05. Calc. for $C_{49}H_{49}N_3O_7P_2Rh_2$: C, 55.5; H, 4.65; N, 3.95%). I.r. (Nujol): 1 970s $cm^{-1}$.

$[NMe_4][Rh_2(CO)_2(PPh_3)_2(dcbmi)]\cdot H_2O$ (yield 70%) (Found: C, 55.1; H, 4.65; N, 3.95. Calc. for $C_{48}H_{47}N_3O_7P_2Rh_2$: C, 55.1; H, 4.70; N, 4.00%). I.r. (Nujol): 1 978s $cm^{-1}$. $^1H$ N.m.r. $[(CD_3)_2SO]$: δ 2.50 ($CH_3$ of dcbmi) and 7.5 (m, $PPh_3$).

*X-Ray Structure Determination.*—Single crystals of $[NBu_4][Rh_2(cod)_2(dcbi)]\cdot 2C_3H_8O$ were grown by the slow evaporation of a saturated solution of the complex in isopropanol under a stream of nitrogen. A well formed crystal was sealed in a glass capillary and mounted on a Syntex $P\bar{1}$ four-circle diffractometer. Table 1 contains a summary of the data collection conditions and results. Intensity data were obtained using Mo-$K_\alpha$ radiation (λ = 0.710 69 Å) monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 50 reflections and their intensity was invariant. The data were reduced and corrected for absorption by procedures previously described.[7] Computations were carried out on an Amdahl 5860 computer, using programs for structural analysis from the SHELX package. Other programs used included ORTEP.

Least-squares refinement results using anisotropic thermal parameters for all non-hydrogen atoms are shown in Table 2. The positions of the hydrogen atoms of the cation and of cod were calculated and not refined.

## Results and Discussion

*Structure of the Rhodium Complex.*—The triprotic acids 4,5-dicarboxyimidazole ($H_3dcbi$) and its 2-methyl derivative ($H_3dcbmi$) react with $[M_2(cod)_2Cl_2]$ and base (3 mol equiv.) in acetonitrile to afford salts of the anionic dinuclear complex $[M_2(cod)_2L]^-$ (M = Rh or Ir; L = dcbi or dcbmi). Alternatively, reaction of the dinucleating ligand (1 mol) with [M(cod)(acac)] (2 mol) and further addition of base (1 mol) produces the same compounds, but we found the first method more convenient except in the cases where the side product tetra-alkylammonium chloride has a solubility similar to that of the complex salt.

The rhodium complexes are stable in the air over long periods (weeks) and they have greater resistance to aerial oxidation than their iridium analogues. However, both types of compounds are air sensitive in solution. Elemental and thermogravimetric analysis, and in some cases i.r. and n.m.r. spectroscopy, reveal solvation of many of these complex salts. The presence of water cannot be excluded from the preparative route described because of the use of alcoholic solutions of tetra-alkylammonium hydroxides. It is likely that water and alcohol molecules are linked by hydrogen bonds to the oxygen atoms (C=O) of the bridging ligand, where most of the negative charge of the anions probably resides.

The proton and $^{13}C$ n.m.r. spectra of $[Rh_2(cod)_2(dcbi)]^-$ in $CDCl_3$ show two distinct signals in the olefinic region {δ 4.37 and 4.05; coalescence temperature about 80 °C, $\Delta G^\ddagger = 17.4$ kcal $mol^{-1}$ (72.8 kJ $mol^{-1}$). Similar values were found for [Ir(tfpd)(cod)] (tfpd = 1,1,1-trifluoropentane-2,4-dionate},[8] which are in agreement with values reported for rhodium-co-ordinated cyclo-octadienes *trans* to N and to O respectively.[9] However, in the case of the dcbmi complex a single signal is observed in an intermediate position, indicating rapid exchange of the two olefinic co-ordination positions. This fact can be explained in terms of steric repulsion between the hydrogens of the methyl group of the imidazolic ligand and those of the double bond *trans* to O. It should be noted that the $^1H$ n.m.r. signal of the methyl group dramatically shifts when cyclo-octadiene is replaced by other ligands.

The molecular structure of the complex anion $[Rh_2(cod)_2(dcbi)]^-$ is shown in the Figure. Pertinent intramolecular bond distances and angles are presented in Table 3. The complex has an idealized $C_{2v}$ symmetry, although the only crystallographic symmetry element in the molecule is a mirror plane perpendicular to the best plane defined by the central ligand and the two metal atoms.

The co-ordination around each rhodium atom can be described as square planar, considering the olefinic midpoints of the cyclo-octadiene as co-ordination positions. The major distortion from the square-planar geometry is due to the bite angle (80°) of the chelating fragment O(1)–Rh–N(1) of the dcbi ligand. The best plane calculated for the Rh(1), O(1), O(2), N(1), C(1), C(2), C(3) atoms has a maximum deviation of only 0.04 Å for C(1). Thus the carboxyimidazole–metal core of this complex anion is an unstrained planar unit and derivatives in which cod is replaced by carbon monoxide should readily stack. The Rh–N distance (2.058 Å) is slightly shorter than values reported for related N-donor rhodium complexes, which normally are in the range 2.08—2.11 Å and are not significantly sensitive to the nature of the azole ligand nor the overall charge of the complex.[10]

The distances from the metal atom to the midpoints of the two olefins in the cyclo-octadiene ligand are almost the same as those found in [Rh(quin)(cod)] (quin = quinolin-8-olate).[11] Analogous to this complex, we observe a clear correlation between the longer distance Rh–M(22) (*trans* to N) and a shorter C(15)–C(16) distance for the corresponding olefin, implying that less electron density of this double bond is used for bond formation with the metal atom than is the case when the olefin

**Table 3.** Bond distances (Å) and angles (°)

| | | | |
|---|---|---|---|
| Rh(1)–O(1) | 2.065(05) | C(15)–C(16) | 1.375(13) |
| Rh(1)–N(1) | 2.058(05) | C(16)–C(17) | 1.536(17) |
| Rh(1)–C(11) | 2.100(09) | C(17)–C(18) | 1.492(17) |
| Rh(1)–C(12) | 2.105(08) | N–C(C1) | 1.510(09) |
| Rh(1)–C(15) | 2.121(08) | C(C1)[a]–C(C2) | 1.507(12) |
| Rh(1)–C(16) | 2.121(09) | C(C2)–C(C3) | 1.500(14) |
| O(1)–C(3) | 1.295(08) | C(C3)–C(C4) | 1.507(16) |
| O(2)–C(3) | 1.217(07) | C(C5)–C(C6) | 1.520(11) |
| N(1)–C(1) | 1.386(07) | C(C6)–C(C7) | 1.522(11) |
| N(1)–C(2) | 1.337(07) | C(C7)–C(C8) | 1.526(14) |
| C(1)–C(3) | 1.518(09) | C(1)–C(1′) | 1.350(09) |
| C(11)–C(12) | 1.405(12) | O(2) ··· O(2′) | 3.052(07) |
| C(11)–C(18) | 1.489(13) | M(11)[b] ··· Rh(1) | 1.982(11) |
| C(12)–C(13) | 1.530(12) | M(22)[c] ··· Rh(1) | 2.007(10) |
| C(13)–C(14) | 1.485(14) | Rh(1) ··· Rh(1′) | 6.306(05) |
| C(14)–C(15) | 1.509(15) | | |
| | | | |
| O(1)–Rh(1)–N(1) | 79.8(2) | Rh(1)–C(11)–C(12) | 70.7(5) |
| O(1)–Rh(1)–C(11) | 160.3(2) | Rh(1)–C(11)–C(18) | 112.5(8) |
| N(1)–Rh(1)–C(11) | 96.7(3) | C(12)–C(11)–C(18) | 126(1) |
| O(1)–Rh(1)–C(12) | 160.6(3) | Rh(1)–C(12)–C(11) | 70.3(5) |
| N(1)–Rh(1)–C(12) | 99.3(3) | Rh(1)–C(12)–C(13) | 112.8 (6) |
| C(11)–Rh(1)–C(12) | 39.0(3) | C(11)–C(12)–C(13) | 124(1) |
| O(1)–Rh(1)–C(15) | 91.9(3) | C(12)–C(13)–C(14) | 113.5(9) |
| N(1)–Rh(1)–C(15) | 159.6(4) | C(13)–C(14)–C(15) | 115(1) |
| C(11)–Rh(1)–C(15) | 97.1(4) | Rh(1)–C(15)–C(14) | 110.2(7) |
| C(12)–Rh(1)–C(15) | 82.3(4) | Rh(1)–C(15)–C(16) | 71.1(5) |
| O(1)–Rh(1)–C(16) | 94.3(4) | C(14)–C(15)–C(16) | 127(1) |
| N(1)–Rh(1)–C(16) | 160.2(4) | Rh(1)–C(16)–C(15) | 71.1(5) |
| C(11)–Rh(1)–C(16) | 82.4(4) | Rh(1)–C(16)–C(17) | 110.8(8) |
| C(12)–Rh(1)–C(16) | 92.4(5) | C(15)–C(16)–C(17) | 121(1) |
| C(15)–Rh(1)–C(16) | 37.8(3) | C(16)–C(17)–C(18) | 115(1) |
| Rh(1)–O(1)–C(3) | 117.5(5) | C(11)–C(18)–C(17) | 112(1) |
| Rh(1)–N(1)–C(1) | 113.0(4) | N–C(C1)–C(C2) | 117.3(7) |
| Rh(1)–N(1)–C(2) | 140.5(5) | C(C1)–C(C2)–C(C3) | 111.6(9) |
| C(1)–N(1)–C(2) | 106.4(6) | C(C2)–C(C3)–C(C4) | 112(1) |
| N(1)–C(1)–C(3) | 115.8(6) | C(C5)–C(C6)–C(C7) | 110.6(8) |
| O(1)–C(3)–O(2) | 124.2(7) | C(C6)–C(C7)–C(C8) | 106.3(8) |
| O(1)–C(3)–C(1) | 113.8(6) | C(C6)–C(C7)–C(C8) | 117(2) |
| O(2)–C(3)–C(1) | 122.0(7) | | |

[a] CC indicates cation carbon. [b] M(11) is the midpoint between C(11) and C(12). [c] M(22) is the midpoint between C(15) and C(16).

is *trans* to O. However, both double-bond distances in the quin complex are longer than those in $[Rh_2(cod)_2(dcbi)]^-$ which is unexpected considering the anionic character of the latter. Interestingly, the similarities do not extend to the Rh–N and Rh–O distances which in the case of $[Rh_2(cod)_2(dcbi)]^-$ are longer for Rh–O (2.065 Å) than for Rh–N (2.058 Å), but reversed in the quin complex (2.051 and 2.098 Å respectively).

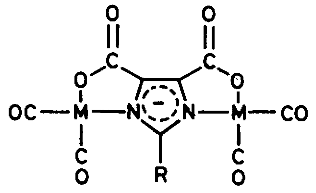
No short intermolecular interactions were found between the anions. Diagrams of the packing are cluttered by the unusually large number of symmetry operators present in this uncommon space group.

*Planar Carbonyl Complexes.*—Slow bubbling of carbon monoxide through $CH_2Cl_2$ or acetonitrile solutions of the cyclooctadiene complexes causes a rapid change in the colour from yellow to dark green or blue followed by the precipitation of fine dichroic needles in all cases except for the salts of $NBu_4^+$ which are very soluble in those solvents. The planarity of the dinuclear anions $[M_2(CO)_4L]^-$ favours the presence of extended intermolecular metal–metal interactions in the solid state. The colour of the salts of these anions strongly depends on the cation. Table 4 lists the wavelengths of the absorption maxima in the visible spectra. We have previously observed the same effect in rhodium and iridium mononuclear anionic complexes of 4,4′,5,5′-tetracyano-2,2′-bi-imidazole.[12]

**Table 4.** Visible absorption maxima[a] of $[NR_4][M_2(CO)_4L]$ complexes

| L | Cation | M | $\lambda_{max.}$/nm | M | $\lambda_{max.}$/nm |
|---|---|---|---|---|---|
| dcbi | $NMe_4$ | Rh | 650 | Ir | 760 |
| dcbmi | $NMe_4$ | Rh | 470 (sh) | Ir | 740 |
| dcbmi | $NHEt_3$ | Rh | 515 | Ir | 720 |
| dcbi | $NEt_4$ | Rh | 520 | Ir | 620 |
| dcbi | $NBu_4$ | Rh | 430[b] (320)<br>340 (3 300) | Ir | 435 (sh)[b] (380)<br>395 (sh) (650)<br>355 (sh) (1 470) |

[a] $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ in parentheses. [b] In acetonitrile solution.



M = Rh or Ir
R = H (dcbi) or $CH_3$ (dcbmi)

The i.r. spectra of $[M_2(CO)_4L]^-$ in acetonitrile solution show two equal-intensity absorptions characteristic of *cis* carbonyls bound to rhodium and iridium.[13] However, when the spectra are recorded in the solid state, in the case of the rhodium complexes each absorption splits, and for the iridium complexes drastic changes are observed in the broadness and intensity of the bands. This effect has been attributed to a lowering of symmetry upon close intermolecular contacts produced by metal–metal interactions[13] and, in accord with our results, they should be stronger in the iridium species.

The conductivities of pressed pellets of the salts $[NR_4][Ir_2(CO)_4L]$ (R = Me or Et; L = dcbi or dcbmi) are in the range of those of semiconductors ($10^{-7}$ S cm$^{-1}$), and comparable to that ($10^{-5}$ S cm$^{-1}$) reported for $[Ir(CO)_2(acac)]$ measured in a single crystal along the stacking axis.[14] To our knowledge, semiconductor behaviour has not been previously reported for any dinuclear complex. The conductivities should increase greatly with partial oxidation and experiments to determine this are in progress.

The complex anions $[Rh_2(CO)_4L]^-$ (L = dcbi or dcbmi) react at room temperature with $PPh_3$ to form species of the type $[Rh_2(CO)_2(PPh_3)_2L]^-$. The single absorption observed in the carbonyl region of the i.r. spectra reveals that the CO ligands are either both *trans* to O or both *trans* to N. It has recently been shown that in rhodium complexes the nitrogen atom of a chelate ring has a larger *trans* effect than does an oxygen atom and therefore substitution in a $[Rh(N–O)(CO)_2]$ system takes place at a position *trans* to N.[15] Furthermore, in our case substitution at both positions *trans* to O would produce steric hindrance because of the proximity of the two bulky phosphine ligands.

By adding $PPh_3$ to the anion $[Ir_2(CO)_4(dcbmi)]^-$ in $CH_2Cl_2$ or acetonitrile the colour of the solution fades to pale yellow, but no analytically pure compounds could be isolated. On the other hand, reaction of the dinucleating ligands with *trans*-$[IrCl(CO)(PPh_3)_2]$ in the presence of base also failed to yield pure products. In both cases spectroscopy and elemental analysis indicate formation of mixtures of four- and five-co-ordinated iridium species.

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