

represents the configuration of the complex cation together with the atom-labelling sequence. The central Cu^{2+} ion binds the NCS^- ion and the two bipy ligands *via* the N atoms, so that N(1), N(13) and N(25) are located in the equatorial plane of the trigonal bipyramid with the Cu^{2+} ion almost in this plane [max. deviation 0.023 (1) Å]; N(12) and N(24) occupy axial sites, with $\text{N}(12)\text{--Cu--N}(24) = 176.4 (1)^\circ$. The three equatorial N–Cu–N bond angles are close to 120° (Table 2), so that the distortion from a regular trigonal bipyramid is very small compared with the distortion found in the monoclinic $[\text{Cu}(\text{bipy})_2\text{NSC}]\text{BF}_4$ complex (Tyagi & Hathaway, 1981). In the tetrafluoroborate salt of the complex, the two Cu–N(bipy) equatorial distances are significantly different, which is not so in the present case (Table 2). There are no unusual bond lengths and bond angles in the bipy ligands. The individual pyridine rings are planar [max. deviation 0.011 (4) Å] and the pertinent dihedral angles for each bipy ligand are 5.4 and 7.1° (corresponding to 0.6 and 3.2° in the monoclinic analogous complex). The dihedral angle between the mean planes of the bipy ligands is 64.0° , which is significantly smaller than the value of 100.1° in the analogous complex. There is nothing unusual in the NCS^- ligand (Stults, Day, Marianelli & Day, 1979), but the Cu–N(25)–C(26) angle has the value of

$166.2 (2)^\circ$ compared with $174.2 (5)^\circ$ in the analogous complex.

The crystal packing is achieved with the uncoordinated nitrate ions and water molecules. There are no short intermolecular interactions that could correspond to hydrogen bonds.

This work was partially supported by the Programa Regional de Desarrollo Científico de la OEA en Chile and by a Grant from DIB, Universidad de Chile (E 2282 y Q 949-8455).

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Acta Cryst. (1988). **C44**, 1193–1196

***cis*-Dicarbonyl-*trans*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II) (1) and *cis*-Dicarbonyl-*cis*-dichloro[3,6-bis(2-pyridyl)pyridazine]ruthenium(II) (2)**

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(Received 2 September 1987; accepted 9 February 1988)

Abstract. $[\text{RuCl}_2(\text{CO})_2(\text{C}_{14}\text{H}_{10}\text{N}_4)]$. (1) $M_r = 462.3$, monoclinic, $P2_1/c$, $a = 15.004 (2)$, $b = 10.641 (1)$, $c = 10.849 (1)$ Å, $\beta = 94.31 (1)^\circ$, $V = 1727.3 (4)$ Å³, $Z = 4$, $D_x = 1.777$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 12.2$ cm⁻¹, $F(000) = 912$, $T = 298$ K, final conventional $R = 0.029$ for 2054 unique observed reflections. (2) $M_r = 462.3$, monoclinic, $P2_1/c$, $a = 7.152 (1)$, $b = 16.439 (2)$, $c = 14.708 (2)$ Å, $\beta = 93.46 (1)^\circ$, $V = 1726.0 (4)$ Å³, $Z = 4$, $D_x = 1.779$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 12.2$ cm⁻¹, $F(000) = 912$, $T = 298$ K, final conventional $R = 0.023$ for 2751 unique observed reflections. Both (1) and (2) have a six-coordinated Ru atom with a distorted

octahedral geometry, being bonded by two N atoms of the organic ligand, which acts as bidentate, by two Cl atoms and by two C atoms of CO groups. In (1) the Cl atoms are in *trans* position, the CO groups being *cis*; in (2) both Cl and CO groups are in *cis* position.

Introduction. Mono- and dinuclear ruthenium(II) complexes of chelating (Cole-Hamilton, 1980; Deacon, Patrick, Skelton, Thomas & White, 1984) and bis-chelating (Braunstein, Baker, Streckas & Gafney, 1984; Ruminski & Petersen, 1982) heterocyclic N-donor ligands are receiving much attention in view of their interesting photocatalytic properties. Among the ligands

of the above class, 3,6-bis(2-pyridyl)pyridazine (bppi) has been used to synthesize several mono- and bimetallic complexes, and the X-ray structures of some of them have been determined by us (Manotti Lanfredi, Tiripicchio, Ghedini & De Munno, 1982; De Munno, Denti & Dapporto, 1983; De Munno & Denti, 1984; De Munno & Bruno, 1984). We report here on two mononuclear isomeric species in which bppi chelates the Ru(CO)₂Cl₂ moiety.

Experimental. From a light-protected methanolic suspension of Ru(CO)₂Cl₂ and bppi in the molar ratio 1:1, a pale yellow microcrystalline precipitate of [Ru(bppi)-(CO)₂Cl₂] (1) was recovered. The X-ray structural analysis showed that (1) was the *cis*-dicarbonyl-*trans*-dichloro species. The *cis*-dicarbonyl-*cis*-dichloro species was prepared from a warm acetonitrile solution of the dinuclear (μ -bppi) [Ru(CO)₂Cl₂]₂ (Denti, De Rosa & Stillitani, 1987) compound. On cooling a gold-yellow microcrystalline compound was recovered. Crystals suitable for X-ray measurements were obtained from a warm ethanolic or acetonitrile solution for (1) and (2) respectively. Crystals 0.12 × 0.12 × 0.18 (1), 0.15 × 0.15 × 0.18 mm (2). Siemens-Stoe diffractometer, scan range 2 θ = 3–52°, graphite-monochromatized Mo K α radiation, ω -2 θ scan technique. 20 reflections with 16 < 2 θ < 30° (1) and 14 < 2 θ < 24° (2) used for measuring lattice parameters. No systematic loss of intensity of three standard reflections measured [1 $\bar{1}$ 3, 161, 16 $\bar{1}$ for (1); and 340, 341, 454 for (2)]. 3398 reflections measured with θ < 26°, 2054 unique with $I \geq 3\sigma(I)$, 0 ≤ $h \leq 14$, 0 ≤ $k \leq 14$, -19 ≤ $l \leq 19$ for (1). 3344 reflections measured with θ < 26°, 2751 unique with $I > 3\sigma(I)$, -18 ≤ $h \leq 18$, -20 ≤ $k \leq 0$, 0 ≤ $l \leq 9$ for (2). R_{int} (from merging equivalent reflections) 0.018 and 0.014 for (1) and (2) respectively. Absorption ignored. Lp corrections. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1974, p. 99) and for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, p. 149). Structures solved by Patterson and Fourier techniques and refined by a full-matrix least-squares procedure; $\sum w(|F_o| - |F_c|)^2$ minimized; anisotropic thermal parameters for Ru, C, N, Cl and O, H atoms (calculated) assigned isotropic U of 0.06 Å² and not refined; final $R = 0.029$, $wR = 0.034$, $w = 0.5480/[\sigma^2(F_o) + 0.002108(F_o)^2]$; $S = 0.77$, max. $\Delta/\sigma = 0.01$, max. and min. $\Delta\rho$ excursions in ΔF synthesis 0.49 and -0.11 e Å⁻³ for (1). Final $R = 0.023$, $wR = 0.028$, $w = 0.3777/[\sigma^2(F_o) + 0.002057(F_o)^2]$; $S = 0.77$, max. $\Delta/\sigma = -0.13$, max. and min. $\Delta\rho$ excursions in ΔF synthesis 0.34 and -0.52 e Å⁻³ for (2). VAX/VMS computer of the Università della Calabria and IBM 4341 computer of the Università di Messina; *SHELX* (Sheldrick, 1976) and *PARST* programs (Nardelli, 1983). Final atomic

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Hamilton, 1959) (Å² × 10³) for non-hydrogen atoms of compound (1)

	x	y	z	U_{eq}
Ru	1874 (1)	472 (1)	1252 (1)	42 (1)
Cl(1)	568 (1)	529 (1)	2387 (1)	57 (1)
Cl(2)	3217 (1)	223 (1)	211 (1)	57 (1)
N(1)	1561 (2)	-1432 (3)	830 (3)	43 (1)
N(2)	2530 (2)	-498 (3)	2724 (3)	44 (1)
N(3)	2986 (2)	111 (4)	3631 (3)	44 (1)
N(4)	4157 (3)	-438 (4)	6549 (4)	69 (2)
C(1)	1026 (3)	-1836 (5)	-138 (5)	54 (2)
C(2)	839 (3)	-3080 (5)	-330 (5)	61 (2)
C(3)	1194 (4)	-3950 (5)	484 (6)	67 (2)
C(4)	1752 (3)	-3570 (5)	1488 (5)	57 (2)
C(5)	1923 (3)	-2285 (4)	1632 (4)	45 (1)
C(6)	2486 (3)	-1763 (4)	2674 (4)	41 (1)
C(7)	2955 (3)	-2470 (4)	3590 (4)	51 (2)
C(8)	3415 (3)	-1866 (4)	4534 (4)	50 (1)
C(9)	3413 (3)	-540 (4)	4536 (4)	44 (1)
C(10)	3885 (3)	201 (4)	5531 (4)	47 (2)
C(11)	4011 (3)	1467 (5)	5418 (5)	61 (2)
C(12)	4445 (4)	2111 (6)	6372 (6)	77 (2)
C(13)	4733 (4)	1480 (6)	7410 (6)	74 (2)
C(14)	4566 (5)	211 (6)	7464 (5)	82 (3)
C(15)	2179 (4)	2103 (5)	1815 (5)	54 (2)
C(16)	1288 (3)	1217 (5)	-159 (5)	52 (2)
O(1)	2331 (3)	3088 (4)	2147 (4)	84 (2)
O(2)	935 (3)	1657 (4)	-1011 (4)	84 (2)

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Hamilton, 1959) (Å² × 10³) for non-hydrogen atoms of compound (2)

	x	y	z	U_{eq}
Ru	1646 (1)	1816 (1)	707 (1)	289 (1)
Cl(1)	4836 (1)	1961 (1)	1356 (1)	372 (2)
Cl(2)	1304 (1)	542 (1)	1483 (1)	463 (2)
N(1)	2839 (3)	1307 (1)	-442 (1)	315 (6)
N(2)	2241 (3)	2835 (1)	-25 (1)	283 (6)
N(3)	2026 (3)	3576 (1)	321 (1)	306 (7)
N(4)	2729 (3)	5668 (1)	-249 (2)	368 (7)
C(1)	3155 (2)	513 (2)	-594 (2)	401 (9)
C(2)	4031 (4)	252 (2)	-1354 (2)	464 (11)
C(3)	4569 (4)	815 (2)	-1979 (2)	473 (11)
C(4)	4219 (4)	1626 (2)	-1846 (2)	410 (8)
C(5)	3327 (4)	1863 (1)	-1064 (2)	303 (8)
C(6)	2948 (3)	2719 (2)	-843 (2)	283 (7)
C(7)	3289 (4)	3382 (2)	-1399 (2)	340 (8)
C(8)	3014 (4)	4143 (2)	-1066 (2)	332 (8)
C(9)	2462 (3)	4219 (1)	-175 (2)	320 (8)
C(10)	2310 (3)	5027 (2)	273 (2)	320 (8)
C(11)	1801 (4)	5104 (2)	1167 (2)	393 (9)
C(12)	1737 (4)	5881 (2)	1539 (2)	419 (10)
C(13)	2146 (4)	6537 (2)	1014 (2)	433 (9)
C(14)	2623 (4)	6405 (2)	130 (2)	431 (9)
C(15)	572 (4)	2380 (2)	1673 (2)	391 (9)
C(16)	-742 (4)	1628 (2)	123 (2)	363 (9)
O(1)	-96 (4)	2718 (2)	2236 (1)	616 (9)
O(2)	-2116 (3)	1477 (1)	-226 (2)	574 (8)

coordinates for (1) and (2) are given in Tables 1 and 2 respectively,* and bond lengths and angles in Table 3. Views of the compounds are given in Figs. 1 and 2.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44760 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atom is *trans* to a CO group, in the second it is *trans* to a Cl atom. A similar behaviour is observed for the Ru—Cl(1) distance, which is longer in (2) than in (1). In (2) the Cl atom is *trans* to a CO group, whereas in (1) it is *trans* to Cl. It is in accordance with the expected *trans* influence order and with that previously reported for *cis*-bis(2,2'-bipyridyl)carbonylchlororuthenium(II) perchlorate (Clear, Kelly, O'Connell, Vos, Cardin, Costa & Edwards, 1980). It seems that the uncoordinated pyridine does not have an important influence on the shortening of N(2)—Ru with respect to N(1)—Ru. This effect is present in both complexes, but it is more evident in the *cis*—*cis* compound [Ru—N(1) = 2.112 (2), Ru—N(2) = 2.049 (2) Å]. On the other hand the shorter Ru—N(2) distances with respect to the Ru—N(1) ones in both complexes are in agreement with the greater π acidity of the pyridazine ring. The C—O distances [1.126 (7), 1.132 (7) Å in (1) and 1.127 (4), 1.109 (4) Å in (2)] and the Ru—C—O angles [177.6 (5), 179.5 (5)° in (1) and 178.6 (3), 176.4 (3)° in (2)] are close to previously reported values (Clear, Kelly, O'Connell, Vos, Cardin, Costa & Edwards, 1980). The shortening of the C—O distance for the axial positions in the *cis*—*cis* compound with respect to the equatorial one in the *cis*—*trans* is noticeable.

Acta Cryst. (1988). **C44**, 1196–1198

The Determination of Absolute Structure. VI.* The Structure of Zinc Digold(III) Octapropionate Dihydrate: Absolute Structure and Ghost Peaks

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(Received 8 January 1988; accepted 8 March 1988)

Abstract. [Au₂Zn(C₃H₅O₂)₈(H₂O)₂], $M_r = 1079.9$, tetragonal, $I\bar{4}$, $a = 9.092$ (2), $c = 22.540$ (8) Å, $V = 1863.3$ Å³, $Z = 2$, $D_x = 1.925$ Mg m⁻³, $F(000) = 1040$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 8.6$ mm⁻¹, $T = 293$ K. The structure was refined to $R = 0.030$ for 1631 unique observed reflections. The absolute structure was determined with an η refinement [$\eta = +1.06$ (3)]. A two-dimensional polymeric structure is observed; the Zn atom is coordinated octahedrally by four propionate oxygens and two *trans* waters, and the Au is coordinated by four propionate oxygens in a square plane. One propionate bridges Zn and Au, the other is only bonded to Au and has one non-coordinated O. The refinement of the wrong absolute structure led to a large

difference peak at 0, 0, 0.5, which could be successfully refined as an O atom. Incorrect absolute structure can thus lead to incorrect stoichiometry.

Introduction. In the course of our studies of gold(III) carboxylate complexes we have reported the structure of strontium digold(III) octaacetate dihydrate (Jones, 1984a). A detailed report of several other acetato-gold(III) complexes is in preparation. Here we show that the synthetic and structural principles can be extended to propionate complexes.

Experimental. Zinc digold(III) octahydroxide was prepared as a grey powder from aqueous solutions of NaAu(OH)₄ and Zn(ClO₄)₂, and immediately dissolved in warm propionic acid. On standing for several days,

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