Crystal Structure of Bis(benzo[*h*]quinolin-10-yl-C^{10},*N*)-dicarbonylruthenium(II) *

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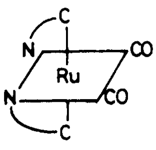
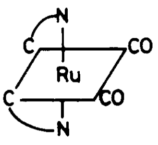
The crystal structure of the *cis* isomer of the title compound, *cis*-[Ru(CO)$_2$(bquin)$_2$] (bquin = benzo[*h*]quinolin-10-yl), has been established at 295 K by single-crystal *X*-ray diffraction methods, and refined by least squares to a residual of 0.037 for 1 242 independent 'observed' reflections. Crystals are monoclinic, space group *Pn*, with a = 13.682(4), b = 10.885(3), c = 7.497(2) Å, β = 104.05(2)°, and Z = 2. The two carbonyl groups [Ru–C 1.87(1) and 1.81(1) Å] lie *trans* to the two ligand nitrogen atoms [Ru–N 2.15(1) and 2.16(1) Å]; Ru–C(ligand) are 2.13(1) and 2.12(1) Å.

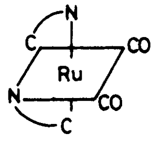
Reaction of benzo[*h*]quinoline (Hbquin) with dodecacarbonyltriruthenium yields the cyclometallated complex [Ru(CO)$_2$(bquin)$_2$], which contains C,N-chelating benzo[*h*]quinolin-10-yl groups, together with [Ru$_4$H$_4$(CO)$_{12}$].[1] Determination of the stereochemical arrangement from the possibilities (A)—(C) by spectroscopic data was not possible, but has now been shown to be (A) by the single-crystal structure determination described in this report.



(A)



(B)



(C)

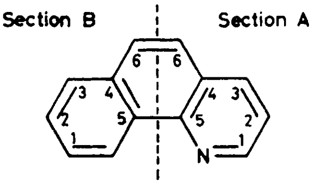
Experimental

The complex [Ru(CO)$_2$(bquin)$_2$] was prepared by the reported method,[1] m.p. 259—260 °C (decomp.) (lit.,[1] 257—261 °C), and its i.r. spectrum was in agreement with that reported. For the structure determination, the crystals were grown from dichloromethane–diethyl ether (1 : 1).

Crystallography.—Crystal data. C$_{28}$H$_{16}$N$_2$O$_2$Ru, M = 513.5, Monoclinic, space group *Pn* (variant of C_s^2, no. 7), a = 13.682(4), b = 10.885(3), c = 7.497(2) Å, β = 104.05(2)°, U = 1 083.1(5) Å^3, D_m = 1.55(1), Z = 2, D_c = 1.57 g cm^{-3}, $F(000)$ = 516, monochromatic Mo-K_α radiation (λ = 0.710 69 Å), μ = 6.9 cm^{-1}. Specimen: 0.20 × 0.20 × 0.05 mm. T = 295(1) K.

Structure determination. A unique data set, measured on a Syntex $P2_1$ four-circle diffractometer to $2\theta_{max.}$ = 45°, yielded 1 389 independent reflections, 1 242 with $I > 2\sigma(I)$ being considered 'observed' and used in the 9 × 9 block-diagonal least-squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U)_H$ were included as constrained estimates. At convergence, R and R' were 0.037 and 0.040; with the ligating C and N atoms interchanged these values rose to 0.040 and 0.044, with the thermal parameters of one of the ligating 'carbon' atoms becoming non-positive definite. The assignment of the *cis* configuration was therefore made with the carbonyl groups opposed to the ligand nitrogen atoms; this assignment is suggested by the ligand geometry associated with the ligating atoms. For the correct configuration, refinement of the structure in the opposite chirality gave R = 0.038. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[2]

Computation used the *X*-RAY 76 program system,[3] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Atom numbering within ligands 1 and 2 is as shown below.



Discussion

The unit-cell contents (Figure, Table 1) comprise discrete molecules of the required stoicheiometry, the asymmetric unit of the structure being a single molecule with no crystallographically imposed internal-symmetry elements. Assignment of the relative disposition of the carbonyl groups as *cis* is immediately apparent; assignment of the co-ordinating atoms of the benzoquinoline moiety as carbon or nitrogen can only be made on the basis of behaviour of thermal parameters and residuals in refinement and the resulting ligand geometries. The similarities in the metal–ligand distances (Table 2) are such that this is not a useful additional parameter in making the discrimination. Although the assignment is hindered by the dominance of the scattering by the ruthenium atom and

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* *Supplementary data available* (No. SUP 23620, 10 pp.): thermal parameters, H-atom co-ordinates, least-squares planes, ligand geometries, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Non-hydrogen atom-co-ordinates

	Ligand 1			Ligand 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru	$\frac{3}{4}$ *	0.851 89(7)	$\frac{3}{4}$ *			
Carbonyl ligands						
C	0.821 1(10)	0.726 9(11)	0.666 5(17)	0.864 9(10)	0.896 2(11)	0.914 5(17)
O	0.870 1(8)	0.656 3(10)	0.625 9(14)	0.937 2(7)	0.927 4(9)	1.020 5(14)
Benzoquinolyl ligands						
Section A						
N(1)	0.608 9(6)	0.795 8(7)	0.573 2(12)	0.668 3(7)	1.002 2(8)	0.834 5(12)
C(1)	0.569 2(8)	0.835 3(11)	0.403 5(15)	0.620 0(9)	1.001 8(11)	0.968 5(14)
C(2)	0.476 8(10)	0.793 1(12)	0.293 5(16)	0.571 8(9)	1.103 9(12)	1.017 2(17)
C(3)	0.423 4(8)	0.707 2(12)	0.368 4(16)	0.572 5(10)	1.210 1(12)	0.920 1(19)
C(4)	0.462 2(8)	0.667 5(9)	0.549 4(16)	0.621 2(9)	1.216 1(11)	0.774 7(18)
C(5)	0.555 5(8)	0.711 8(9)	0.646 2(14)	0.669 9(8)	1.106 6(9)	0.735 6(14)
C(6)	0.412 4(9)	0.579 3(10)	0.637 4(17)	0.627 4(11)	1.319 8(11)	0.663 8(23)
Section B						
C	0.695 7(8)	0.728 3(9)	0.925 2(15)	0.767 6(8)	0.991 8(11)	0.563 3(15)
C(1)	0.733 5(9)	0.688 1(10)	1.103 2(17)	0.819 5(9)	0.991 3(12)	0.422 6(15)
C(2)	0.680 5(11)	0.604 4(11)	1.185 5(16)	0.818 5(11)	1.097 5(15)	0.314 1(17)
C(3)	0.589 7(10)	0.556 8(11)	1.098 3(17)	0.773 8(11)	1.205 6(15)	0.346 7(18)
C(4)	0.548 0(10)	0.592 0(10)	0.918 2(16)	0.722 4(9)	1.211 4(11)	0.484 1(17)
C(5)	0.600 2(9)	0.675 9(8)	0.835 6(15)	0.720 6(8)	1.104 4(9)	0.591 0(15)
C(6)	0.452 8(10)	0.544 8(11)	0.814 1(18)	0.673 1(11)	1.320 0(12)	0.523 7(19)

* Defines origin.

Table 2. Ruthenium environment. The column *r* is the metal–ligand distance (Å). Other entries in the matrix are the angles (°) subtended at the metal atom by the two relevant ligand atoms. Carbonyl atoms are italicized

	r(Ru–L)	*C*(2)	N(A)	C(A)	N(B)	C(B)
C(1)	1.87(1)	89.2(6)	92.8(4)	92.0(5)	177.0(5)	98.6(5)
C(2)	1.81(1)		175.5(5)	97.1(5)	91.4(5)	92.3(5)
N(A)	2.148(8)			78.8(4)	86.8(3)	91.5(4)
C(A)	2.13(1)				90.8(4)	166.0(4)
N(B)	2.161(9)					78.4(4)
C(B)	2.12(1)					

also by the non-centrosymmetric space group, discrimination between C and N appears to be clear-cut, significant, and valid on the basis of the above indices.

The ligand geometries are largely as expected. Slight differences are observed between the internal ring angles at the co-ordinating carbon and nitrogen atoms; rather larger differences are observed in the exocyclic angles subtended by the ruthenium and neighbouring carbon atoms.

The knowledge of the stereochemistry provides further understanding of the reported ^{1}H n.m.r. spectrum.[1] First, the observation of a single set of resonances for H(2)—H(4) (other features were not clearly resolved) now appears to be a suitable criterion for eliminating the unsymmetrical arrangement (C). Secondly, the chemical shifts for the same protons are some 0.5—1 p.p.m. upfield of corresponding values for free benzo[*h*]quinoline,[1,4] bi(benzo[*h*]quinolin-10-yl),[1] and complexes such as [M(CO)$_4$(bquin)] (M = Mn or Re).[1] The shifts can now be attributed to through-space shielding between adjacent pyridine rings. Analogous but somewhat larger shifts have been observed for resonances of adjacent pyridine rings in *cis*-[Ru(CO)$_2$L$_2$]$^{2+}$ [L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline][5] and *cis*-[RuCl$_2$(bipy)$_2$][6] complexes.

The complex [Ru(CO)$_2$(bquin)$_2$] is one of the few known to contain two cyclometallated N-donor ligands. These include

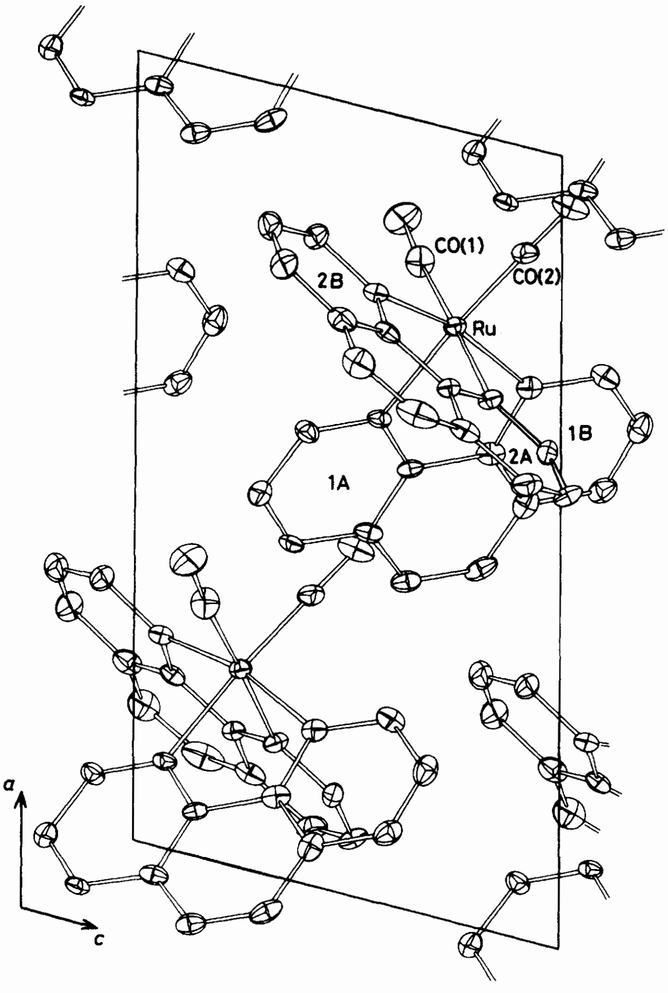

Figure. Unit-cell contents projected down *b*, showing 20% thermal ellipsoids for the non-hydrogen atoms

the palladium and platinum complexes [M(pap)$_2$] (M = Pd or Pt, pap = 2-phenylazophenyl-*C*,*N*′),[7] but the two closest analogues are the rhodium derivatives [Rh(O$_2$CMe)(pap)$_2$][8,9] and [(pap)$_2$Rh(μ-Cl)Rh(CO)$_2$].[8,10,11] In these, the two pap ligands chelate a rhodium(III) atom, although in contrast with our complex the two nitrogens are *trans*, as in (B).

Acknowledgements

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