Zn—O2	2.000 (5)	N2—C11	1.28 (1)
Cu—O1	1.939 (5)	C6—C7	1.44 (1)
Cu—O2	1.949 (5)	C8—C9	1.49 (1)
Cu—N1	1.963 (7)	C9—C10	1.49 (1)
Cu—N2	1.969 (6)	C11—C12	1.43 (1)
O1—C1	1.330 (8)		
I1—Zn—I2	119.77 (4)	Zn—O1—C1	125.8 (4)
I1—Zn—O1	113.9 (1)	Cu—O1—C1	130.9 (5)
I1—Zn—O2	111.8 (1)	Zn—O2—Cu	103.1 (2)
I2—Zn—O1	111.5 (1)	Zn—O2—C17	126.7 (4)
I2—Zn—O2	116.3 (1)	Cu—O2—C17	130.0 (4)
O1—Zn—O2	75.4 (2)	Cu—N1—C7	124.2 (5)
O1—Cu—O2	78.1 (2)	Cu—N1—C8	120.8 (6)
O1—Cu—N1	91.2 (2)	C7—N1—C8	115.0 (7)
O1—Cu—N2	169.9 (2)	Cu—N2—C10	122.0 (5)
O2—Cu—N1	169.4 (2)	Cu—N2—C11	123.2 (5)
O2—Cu—N2	91.8 (2)	C10—N2—C11	114.6 (7)
N1—Cu—N2	98.7 (3)	O1—C1—C2	120.0 (7)
Zn—O1—Cu	103.3 (2)	O1—C1—C6	121.2 (6)

Table 2. *Structural data and bridging (φ) and dihedral (κ) angles (Å, °) for seven homo- and hetero-dinuclear metal complexes*

Complex	Bridging M(Cu,Ni)—O	M(Cu,Ni)···M(Cu,Zn)	φ	κ
(I)	1.941 (5)–1.950 (4)	2.994 (2)	100.6 (2)	5 (1)
(II)	1.930 (1)–1.982 (9)	3.073 (2)	103.5 (4)	11.3 (8)
(III)	1.885 (3)–1.976 (3)	3.021 (2)	102.8 (1)	2.9 (9)–8.0 (3)
(IV)	1.938 (3)–1.955 (3)	3.047 (6)	103.4 (1)	12.7 (2)
(V)	1.973 (3)–1.974 (2)	3.1013 (7)	102.5 (1)–102.7 (1)	11.4 (4)
(VI)	2.030 (3)–2.039 (2)	3.0753 (7)	98.8 (1)–99.7 (1)	3.5 (9)
(VII)	1.939 (5)–1.949 (5)	3.0933 (7)	103.1 (2)–103.3 (2)	1.9 (3)

Notes: (I) is $[Cu_2(C_{11}H_{10}ClNO_2)_2]$ (Tahir *et al.*, 1996), (II) is $[Cu_2(C_{14}H_{11}NO_2)_2]$ (Ülkü *et al.*, 1997), (III) is $[Cu_2(C_{12}H_{13}NO_2)_2]$ (Atakol *et al.*, 1997), (IV) is $[Cu_2(C_{12}H_{13}NO_2)_2]$ (Ülkü *et al.*, 1998), (V) is $[Cu\{Zn(C_{23}H_{21}I_2N_3O_2)\}]$ (Ercan *et al.*, 1999), (VI) is $[Ni\{Zn(C_{31}H_{34}I_2N_4O_2)\}]$ (Arıcı *et al.*, 1999) and (VII) is $[Cu\{Zn(C_{17}H_{16}I_2N_2O_2)\}]$ (this work).

The H81, H82, H91, H92, H101 and H102 atoms were taken from difference maps, while other H atoms were placed geometrically 0.95 Å from their parent C atoms. A riding model was then used for all H atoms [$U_{iso}(H) = 1.3U_{eq}(C)$]. The highest peak in the final ΔF synthesis was located 0.87 Å from the I2 atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *PLATON* (Spek, 1998). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1298). Services for accessing these data are described at the back of the journal.

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Bromotricarbonyl(3,3′-dimethylene-2,2′-biquinoline)rhenium(I)

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Abstract

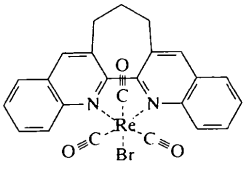
The mononuclear title compound, bromotricarbonyl(6,7-dihydro-13,14-diazapentaphene-*N,N′*)rhenium(I), [ReBr($C_{20}H_{14}N_2$)$(CO)_3$], presents a rhenium environment with a slightly distorted octahedral geometry: Re—C 1.905 (9), 1.909 (8) and 1.927 (6), Re—N 2.187 (6) and 2.201 (6), and Re—Br 2.6295 (12) Å.

Comment

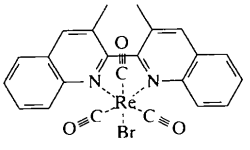
In the last two decades, a number of structural and coordination chemistry studies on transition metal complexes with polypyridinic ligands have been published (Guerrero *et al.*, 1998, and references therein), the interest being driven both by their interesting photophys-

ical and photochemical behaviour, and by the fact that they are deemed to be potential candidates for use as models in photosynthetic processes. In these, as in many other structural families with interesting physicochemical properties, slight modifications in structure might lead to dramatic changes in behaviour. We have thus undertaken the study of a series of compounds of general formula $BrRe(CO)_3$(3,3′-*R*-2,2′-biquinoline), with the aim of looking for the structural effect that 3,3′-substitutions might have on the 2,2′-biquinoline, as these particular substitutions have been shown to bestow interesting steric properties on these compounds, which may lead to an improvement of their catalytic and photophysical properties.

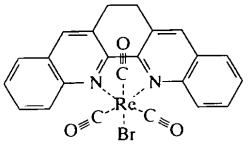
The structures of $BrRe(CO)_3$(3,3′-trimethylene-2,2′-biquinoline), (1) (Moya *et al.*, 1994), and $BrRe(CO)_3$-(3,3′-dimethyl-2,2′-biquinoline), (2) (Guerrero *et al.*, 1998), have already been reported. We present here an analysis of the crystal structure of a third member of this series, namely $BrRe(CO)_3$(3,3′-dimethylene-2,2′-biquinoline), (3). Like (1) and (2), compound (3) is mononuclear with two similar independent molecules, *A* and *B*, in the asymmetric unit. Molecule *B* appears to be well ordered, while molecule *A* shows disorder in the central ring involving the substituent methylene groups. The two conformations were detected by the appearance of unusually large anisotropic atomic displacement parameters for atoms C4*A* and C23*A*, whose parameters would not refine properly. The conformation of the major fraction (60%) of molecule *A* is the same as that of molecule *B*.



(1)



(2)



(3)

In both independent molecules, the rhenium environment is a slightly distorted octahedron, with the Br atom and C1 of a carbonyl group occupying apical positions, and an equatorial plane defined by C2 and C3 of the other carbonyls, and N1 and N2 of the biquinoline ligand. In both molecules, and in compounds (1) and (2), the metal atom is slightly displaced from this equatorial plane away from the negatively charged bromine [0.155 (1) and 0.143 (1) Å in molecules *A* and *B*, and 0.141 (2) and 0.113 (1) Å in compounds (1) and (2), respectively], thus forming a depressed square pyramid. The Br, Re and C1 atoms are nearly collinear [Br—Re—C1 177.3 (3) and 178.1 (3)° in molecules *A* and *B*, and 175.4 (4) and 179.2 (2)° in compounds (1) and (2), respectively]. The Re—C—O angles are in the range 175–178°.

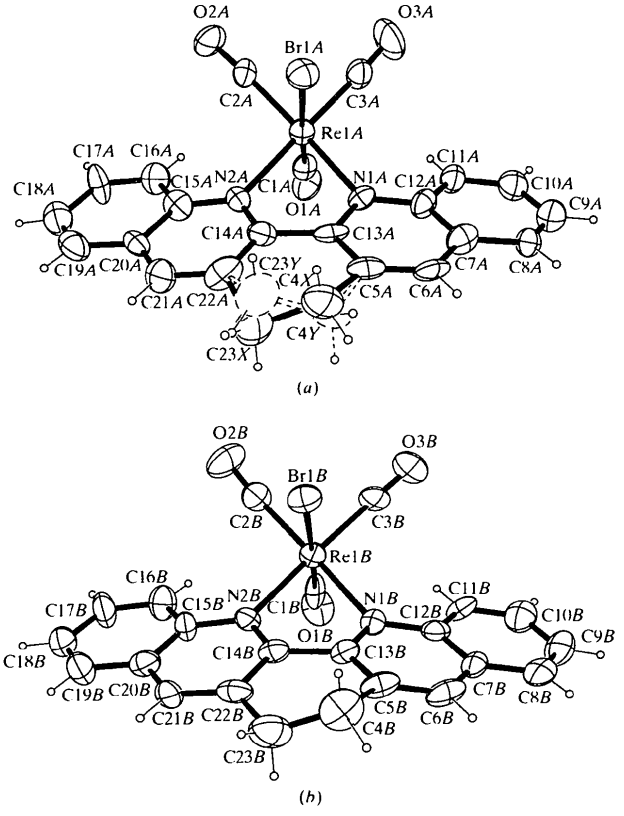


Fig. 1. The molecular structures of (*a*) molecule *A* (note the disordered central ring) and (*b*) molecule *B* of (3). Displacement ellipsoids are drawn at the 50% probability level.

In all the compounds in the series, the biquinoline ligand binds to the cation in a bidentate fashion, with a very significant inclination with respect to the equatorial plane of the octahedron. This inclination is mainly due to the steric hindrance between the outermost H atoms and the equatorial carbonyl groups. The ligand itself is not planar. The dihedral angles between the quinoline planes (N1/C5–C13 and N2/C14–C20) and the equatorial plane of the octahedron are 28.7 (2) and 27.3 (2)° in molecule *A*, and 33.8 (2) and 29.3 (2)° in molecule *B*, and the dihedral angle between the quinoline planes themselves is 12.5 (3)° in molecule *A* and 17.4 (2)° in molecule *B*. In all cases, the ligand is tilted towards the Br atom. The torsion angle C5—C13—C14—C22 is −4.8 (11) and −6.4 (13)° in molecules *A* and *B*, respectively, where these atoms are

part of a highly rigid six-membered ring (including C23 and C4) which prevents further deformation; it is in this ring that some disorder is seen in molecule *A*. The presence of an additional methylene group in this ring in compound (1) leads to a torsion angle of −26.7 (7)°. Finally, the breakage of the link between C23 and C4 gives the largest torsion angle of −44.9 (6)° in compound (2).

Crystal stabilization is provided by normal van der Waals forces, as well as by five short Br···H—C contacts (calculated values in the range 2.90–3.00 Å).

Experimental

The title complex was obtained according to the method of Guerrero *et al.* (1998).

Crystal data

[$ReBr(C_{20}H_{14}N_2)(CO)_3$]
M_r = 632.47
Triclinic
$P\bar{1}$
a = 10.045 (3) Å
b = 14.347 (5) Å
c = 15.606 (6) Å
α = 99.24 (2)°
β = 100.22 (2)°
γ = 108.76 (2)°
V = 2037.8 (12) Å^3
Z = 4
D_x = 2.06 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.5–12.5°
μ = 7.952 mm^{-1}
T = 293 (2) K
Polyhedral
0.30 × 0.30 × 0.20 mm
Dark red

Data collection

Siemens *R3m* diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (Sheldrick, 1994)
T_{min} = 0.10, T_{max} = 0.16
7654 measured reflections
7370 independent reflections
5447 reflections with $I > 2\sigma(I)$

R_{int} = 0.041
θ_{max} = 25.25°
$h = -12 \rightarrow 11$
$k = -17 \rightarrow 16$
$l = 0 \rightarrow 18$
2 standard reflections every 98 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.077
S = 1.064
7370 reflections
563 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 10.26P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond distances (Å)*

Re1*A*—C3*A*	1.905 (9)	Re1*B*—C2*B*	1.914 (8)
Re1*A*—C1*A*	1.909 (8)	Re1*B*—C3*B*	1.947 (8)
Re1*A*—C2*A*	1.927 (8)	Re1*B*—C1*B*	1.959 (10)
Re1*A*—N1*A*	2.187 (6)	Re1*B*—N2*B*	2.192 (6)
Re1*A*—N2*A*	2.201 (6)	Re1*B*—N1*B*	2.203 (6)
Re1*A*—Br1*A*	2.6295 (12)	Re1*B*—Br1*B*	2.6265 (14)

The data were collected using a variable scan speed of 4.2–29.3° min^{-1}. The structure were solved by direct methods and refined by full-matrix least squares in F^2 with the *SHELXL*97 package (Sheldrick, 1997). Anisotropic displacement parameters were used for non-H atoms, while H atoms (all of which were unambiguously defined by the stereochemistry) were included in idealized positions and allowed to ride on their host atoms. Some difficulties were found in dealing with the organic ligand in molecule *A*; unusually prolate anisotropic displacement ellipsoids for atoms C4*A* and C23*A* were interpreted as indicating disorder, and so a split model for the central ring with restrained C—C distances was set up, which refined satisfactorily with final occupation factors of 0.60 (6)/0.40 (6). Although the structural differences found suggested a genuine difference between the two moieties, the fact of having Z = 4 in space group $P\bar{1}$ suggested a careful search for any eventual higher symmetry which might have been overlooked. This was performed at the end of the refinement and proved unsuccessful.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *CSD* (Allen & Kennard, 1993), *SHELXL*97 and *PARST* (Nardelli, 1983).

Data collection was performed at the Universidad de Chile on a single-crystal diffractometer purchased by Fundación Andes.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1240). Services for accessing these data are described at the back of the journal.

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