Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1316). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1054–1055

A Crown-Linked Donor–Acceptor Assembly Containing Re^{I}(diimine)$(CO)_3Cl$ and Nitrobenzene Components

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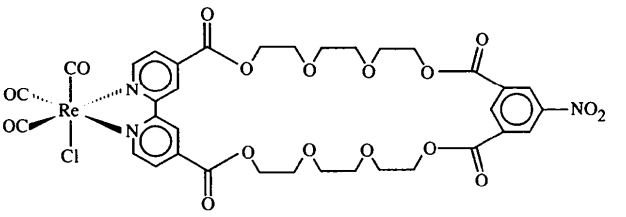
(*Received 6 February 1996; accepted 9 January 1997*)

Abstract

The structure of the title assembly, tricarbonylchloro-[16-nitro-3,6,9,12,20,23,26,29-octaoxa-34,37-diazatetracyclo[34.3.1.1^{14,18}.1^{31,35}]dotetraconta-1(39),14,16,18(41),-31,33,35(42),36(40),37-nonaene-2,13,19,30-tetrone]-rhenium(I), [$ReCl(C_{32}H_{33}N_3O_{14})(CO)_3$], has been determined *via* a single-crystal diffraction study. The rhenium ion is octahedrally coordinated. The bidentate bipyridine/crown ether/nitrobenzene assembly is folded such that the pyridyl rings and nitrobenzene moiety are almost coplanar.

Comment

In earlier work, Wrighton and co-workers introduced the complex *fac*-(bpy)$Re(CO)_3Cl$ (bpy is 2,2′-bipyridine) and its derivatives as metal-to-ligand charge-transfer (MLCT) excited-state emitters (Wrighton & Morse, 1974). Subsequently, crystal and molecular structures for difluorophosphato (Horn & Snow, 1980) and bicarbonato (Guilhem, Pascard, Lehn & Ziessel, 1989) derivatives were reported. In addition, the crystal and molecular structure of a 2,2′:6′2″-terpyridine analogue, *fac*-(σ^2-terpy)$Re(CO)_3Cl$, has been reported (Anderson, Keene, Horn & Tiekink, 1990; Civitello *et al.*, 1993). We have utilized the Wrighton & Morse synthetic chemistry to prepare covalently linked donor–crown–acceptor complexes of Re^{I} in order, ultimately, to understand how non-covalently bound material in a cavity (crown) can modulate and facilitate intermediate to long-range electron-transfer (ET) kinetics. Recently, we reported on the synthesis and photo-redox reactivity of crown ether linked assemblies featuring various *fac*-tricarbonylrhenium(bi)pyridine moieties as donors and nitrobenzene as an acceptor (Yoon, Berg-Brennan, Lu & Hupp, 1992; Berg-Brennan, Yoon & Hupp, 1993). Studies revealed that the rate of light-induced forward ET is strongly dependent on the initial assembly conformation, and that the conformation is strongly dependent on temperature. We report here the crystal structure of the title compound, (1). While the MLCT excited state of (1) is insufficiently reducing to transfer an electron to the tethered acceptor, the compound is closely related structurally to bipyridine assemblies which do display such reactivity (Kazala, Yoon & Hupp, 1995).



(1)

A view of (1) together with our atomic numbering scheme is shown in Fig. 1. The Re atom lies at the center of a slightly distorted octahedron formed by three carbonyl groups (facial configuration), two *cis* N atoms of bipyridine, and a Cl atom. It is also observed that the assembly is folded with an offset rather than a cofacial bipyridine/nitrobenzene configuration. The structure is significantly disordered in the vicinity of C56 and C57. Since no restraints were applied, the disorder and associated large displacement parameter almost certainly account for the unrealistically short C56—

C57 bond distance (apparent distance). No unusual intermolecular interactions were revealed by the crystal packing structure.

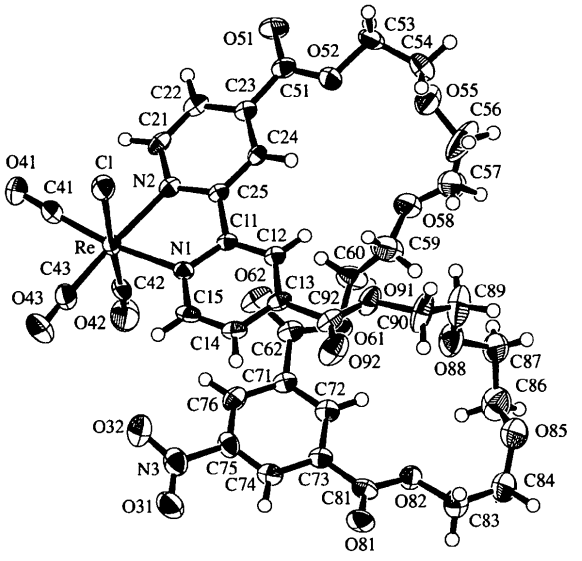


Fig. 1. A perspective view of the molecular structure of the title assembly, (1), with atom-numbering scheme, excluding the H atoms. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The synthesis of the title compound is described elsewhere (Yoon *et al.*, 1992). The crystal used for data collection was recrystallized from methylene chloride layered with hexanes.

Crystal data

$[ReCl(C_{32}H_{33}N_3O_{14})(CO)_3]$
M_r = 989.32
Monoclinic
$C2/c$
a = 28.818 (7) Å
b = 21.357 (2) Å
c = 13.668 (6) Å
β = 116.29 (3)°
V = 7542 (8) Å^3
Z = 8
D_x = 1.742 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7.7–11.8°
μ = 3.41 mm^{-1}
T = 153 K
Prismatic
0.5 × 0.3 × 0.2 mm
Yellow–orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: analytical
T_{min} = 0.36, T_{max} = 0.59
6736 measured reflections
6439 independent reflections
4847 reflections with $I > 3\sigma(I)$

R_{int} = 0.016
θ_{max} = 24.5°
h = −35 → 35
k = 0 → 26
l = −17 → 0
3 standard reflections
frequency: 90 min
intensity decay: 0.2%

Refinement

Refinement on F
R = 0.030
wR = 0.035
S = 1.51
4847 reflections
515 parameters
H atoms not refined
$w = 4F_o^2/\sigma^2(F_o)^2$
$(\Delta/\sigma)_{max}$ = 0.26

$\Delta\rho_{max}$ = 1.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}
Secondary extinction correction: *TEXSAN* (Molecular Structure Corporation, 1985)
Secondary extinction coefficient: 0.8909 × 10^{-8}
Scattering factors from Cromer & Waber (1974)

Table 1. *Selected geometric parameters (Å, °)*

Re—Cl	2.460 (2)	Re—C41	1.913 (6)
Re—N1	2.171 (4)	Re—C42	1.950 (6)
Re—N2	2.165 (4)	Re—C43	1.924 (6)
Cl—Re—N1	85.1 (1)	Cl—Re—C42	177.6 (1)
Cl—Re—N2	83.3 (1)	Cl—Re—C43	92.2 (2)
Cl—Re—C41	90.4 (2)	N1—Re—N2	75.0 (1)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Additional program used: *AGNOST* (de Meulenaer & Tompa, 1965).

The authors gratefully acknowledge the US National Science Foundation (Grant CHE-9303682) and the Dreyfus Foundation (Teacher–Scholar Award to JTH) for support of our work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1234). Services for accessing these data are described at the back of the journal.

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