

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5...O7	1.20 (4)	1.19 (4)	2.384 (3)	171 (4)
O1—H1...O7	0.80 (3)	1.96 (3)	2.764 (2)	178 (4)
O2—H2...O9 ⁱⁱ	0.75 (3)	1.99 (3)	2.729 (3)	170 (2)
O3—H3...O4 ⁱⁱⁱ	0.77 (3)	2.00 (3)	2.748 (3)	166 (3)
O8—H8...O4 ⁱⁱⁱ	0.82 (4)	2.08 (5)	2.856 (3)	158 (4)
O9—H7...O5 ^{iv}	0.87 (3)	1.90 (3)	2.764 (2)	178 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The structure was solved by heavy-atom and difference-Fourier methods, and refined by the full-matrix least-squares method. All H atoms were found in ΔF maps, but those connected to C atoms were placed at calculated positions using a riding model [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. H atoms from the H₂O molecules and COOH groups were refined isotropically. The intensities were corrected for absorption with the program *ABSORB* (DeTitta, 1985).

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: a local modification of *MolEN* (Fair, 1990). Program used to solve structure: *SHELXS86* (Sheldrick, 1990). Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP5f* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*. Weighted least-squares planes: *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1397). Services for accessing these data are described at the back of the journal.

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The red form of [Re(phen)(CO)₃(H₂O)]-CF₃SO₃·H₂O

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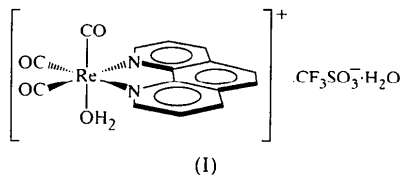
(Received 14 September 1998; accepted 26 January 1999)

Abstract

The coordination geometry of the cations in the red form of aquatricarbonyl(1,10-phenanthroline-*N,N'*)rhenium(I) trifluoromethanesulfonate hydrate, [Re(C₁₂H₈N₂)(CO)₃(H₂O)]CF₃SO₃·H₂O, is approximately octahedral, with a facial arrangement of the linearly coordinated carbonyl ligands. The phenanthroline (phen) ligands interleave to form a columnar π -stacked structure.

Comment

The water-soluble [Re(phen)(CO)₃(H₂O)]⁺ trifluoromethanesulfonate salt is a useful reagent for coupling [Re(phen)(CO)₃]⁺ to an imidazole group of a protein histidine (Connick *et al.*, 1995). We have found that the aqua complex forms both yellow and red crystalline solids, and that both materials dissolve to give spectroscopically indistinguishable yellow solutions. However, the room-temperature emission spectrum of the red crystals exhibits maxima near 550 and 670 nm. The high-energy yellow–green emission is characteristic of rhenium diimine tricarbonyl complexes and evidently arises from a film of yellow material formed on the surface of the red crystals. However, the red color and low-energy emission are less common for these complexes (Schanze *et al.*, 1993; Wrighton & Morse, 1974). In order to elucidate the origins of these spectroscopic properties, we have undertaken a structural study of the red form of this salt, (I).



The red crystals contain two crystallographically distinct cations, *A* and *B* (corresponding to Re1 and Re2, respectively), with nearly identical geometries (Fig. 1). The coordination geometry is approximately octahedral, with a facial arrangement of the linearly coordinated carbonyl ligands. Distances and angles in the phenanthroline (phen) ligand are normal (Orpen *et al.*, 1989). The structure of the cation is very similar to that of [Re(phen)(CO)₃(imidazole)]⁺ and related complexes (Connick *et al.*, 1995; Wallace *et al.*, 1995). As

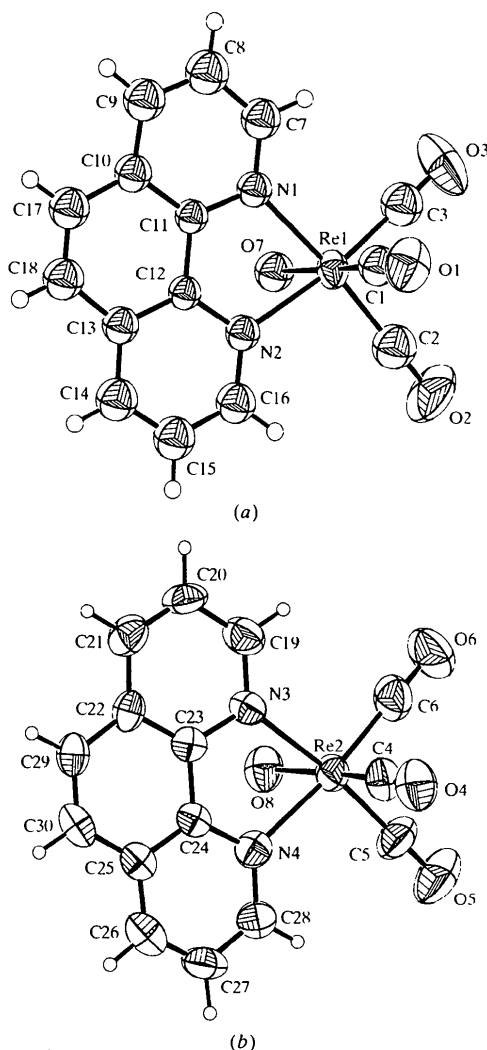


Fig. 1. ORTEPII (Johnson, 1976) drawings of the two independent cations, (a) *A* and (b) *B*, showing the atom-numbering system and 50% probability ellipsoids. H atoms are not shown.

expected, the Re—C distance *trans* to the water ligand [1.887 (10) and 1.868 (10) Å] is slightly shorter than found for related complexes with pyridyl [1.90 (2) Å; Wallace *et al.*, 1995] and imidazole ligands [1.915 (6) Å; Connick *et al.*, 1995]. The corresponding Re—O distance [2.214 (6) and 2.210 (6) Å] is longer than found for complexes with negatively charged *O*-donor ligands; 2.18 Å in [Re(bpy)(CO)₃(CF₃SO₃)] (Calabrese & Tam, 1987), 2.188 (13) Å in [Re(bpy)(CO)₃(PO₂F₂)] (Guilhem *et al.*, 1989) and 2.19 Å in [Re(bpy)(CO)₃(HCO₂)] (Horn & Snow, 1980). The coordination geometry within the equatorial plane exhibits approximate C₂ symmetry, with similar equatorial Re—C bond lengths [1.911 (10), 1.910 (11), 1.902 (10) and 1.909 (10) Å], as well as similar equatorial C—O bond lengths [1.149 (14), 1.152 (13), 1.154 (13) and 1.157 (13) Å]. In the case of [Re(phen)(CO)₃(imidazole)](SO₄)₂·4H₂O, steric and electronic effects due to twisting of the imidazole group about the Re—N bond result in significantly dissimilar equatorial Re—C bond lengths [1.907 (6) and 1.953 (6) Å], as well as dissimilar C—O bond lengths [1.149 (7) and 1.116 (8) Å].

Close intermolecular contacts (<3.0 Å) between the O atoms of the trifluoromethanesulfonate anion and the coordinated and solvent water molecules suggest extensive hydrogen bonding linking the cations, anions and water of crystallization. However, due to solvent disorder, this network was not fully elucidated.

The phenanthroline groups of the rhenium cations interleave to form a π -stacked columnar structure parallel to the *c* axis, with the equatorial carbonyl groups thrust to the periphery of the column. The cations are sequentially positioned along this chain forming an $\cdots A^i B^{ii} B \cdots$ motif [symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y+1, -z+1$] (Fig. 2). The interplanar spacing between the centrosymmetrically related (and hence parallel) phen ligands *B* and *Bⁱⁱ* is 3.45 Å, with closest contacts C21 \cdots C26 [3.466 (13) Å] and C23 \cdots C30 [3.504 (12) Å]. The spacing between the *A* and *Aⁱ* phen ligands is slightly larger (3.53 Å). Consecutive *A* and *Bⁱⁱ* (as well as *Aⁱ* and *B*) phen groups along the chain are not quite parallel, making a dihedral angle of 12.2 (1) $^\circ$; the shortest intermolecular contacts are C12 \cdots C30 [3.373 (12) Å] and C16 \cdots C26 [3.384 (14) Å]. Whereas there are ten intermolecular contacts less than 3.65 Å between consecutive *B* and *Bⁱⁱ* phen ligands, and seven contacts between consecutive *A* and *Bⁱⁱ* phen ligands, there are only two contacts as short between the *A* and *Aⁱ* phen groups (Table 2). Thus, this one-dimensional π -stacked structure may be regarded as a chain of *ABⁱⁱBAⁱ* tetrameric units with shortest phen \cdots phen contacts between cations *B* and *Bⁱⁱ*.

This packing arrangement suggests that the red color of these crystals is related to the interactions between phen ligands of adjacent cations. Similar π -stacked structures have been proposed to account for the per-

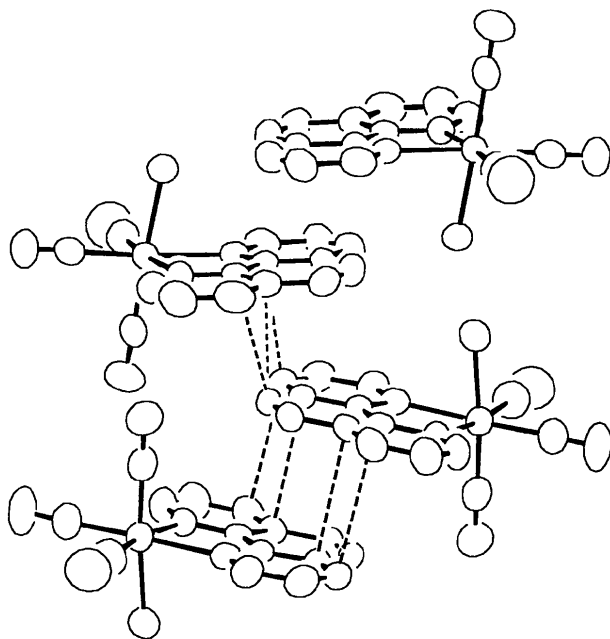


Fig. 2. A view showing four cations (A^iAB^iiB) stacked along the c axis. Intermolecular contacts ≤ 3.50 Å between phen ligands are shown as dashed lines. H atoms are not shown.

turbed absorption and emission properties of $[\text{Ru}(3,3\text{-biisoquinoline})_3](\text{PF}_6)_2$ crystals (Kato *et al.*, 1992) and platinum(II) diimine complexes (Bailey *et al.*, 1995; Kato *et al.*, 1996). The effects on the spectroscopy appear more pronounced for the extended π -stacked structure of $[\text{Re}(\text{phen})(\text{CO})_3(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3 \cdot \text{H}_2\text{O}$ than in the case of π -stacked dimers of platinum(II) diimine complexes (Kato *et al.*, 1997; Miskowski & Houlding, 1989).

Experimental

Crystals of (I) were grown by slow evaporation of an aqueous solution of $[\text{Re}(\text{phen})(\text{CO})_3(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3$ (Sullivan & Meyer, 1984).

Crystal data

$[\text{Re}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{CO})_3(\text{H}_2\text{O})]\text{CF}_3\text{SO}_3 \cdot \text{H}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 635.54$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 10\text{--}11^\circ$
$a = 12.922(2)$ Å	$\mu = 6.01$ mm $^{-1}$
$b = 13.914(2)$ Å	$T = 295$ K
$c = 14.263(6)$ Å	Irregular
$\alpha = 65.05(2)^\circ$	$0.41 \times 0.26 \times 0.22$ mm
$\beta = 73.30(3)^\circ$	Red–orange
$\gamma = 64.59(1)^\circ$	
$V = 2082.4(11)$ Å 3	
$Z = 4$	
$D_x = 2.027$ Mg m $^{-3}$	
D_m not measured	

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω scans
Absorption correction:
 ψ scan (North *et al.*,
1968)
 $T_{\min} = 0.172$, $T_{\max} = 0.267$
14 739 measured reflections
7218 independent reflections

5421 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 25^\circ$
 $h = -13 \rightarrow 15$
 $k = -13 \rightarrow 15$
 $l = -15 \rightarrow 16$
3 standard reflections
frequency: 150 min
intensity decay: 1.2%

Refinement

Refinement on F^2
 $R(F) = 0.058$
 $wR(F^2) = 0.075$
 $S = 1.66$
7218 reflections
560 parameters
H atoms: see below
 $w = 1/[\sigma^2(F_o^2)]$
 $(\Delta/\sigma)_{\max} = 0.04$

$\Delta\rho_{\max} = 2.06$ e Å $^{-3}$
 $\Delta\rho_{\min} = -1.86$ e Å $^{-3}$
Extinction correction:
(Larson, 1967)
Extinction coefficient:
 $1.4(14) \times 10^{-7}$
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Re1—N1	2.171 (7)	Re2—N3	2.164 (7)
Re1—N2	2.183 (7)	Re2—N4	2.178 (7)
Re1—O7	2.214 (6)	Re2—O8	2.210 (6)
Re1—C1	1.887 (10)	Re2—C4	1.868 (10)
Re1—C2	1.911 (10)	Re2—C5	1.902 (10)
Re1—C3	1.910 (11)	Re2—C6	1.909 (10)
N1—Re1—N2	75.9 (2)	N3—Re2—N4	75.8 (3)
N1—Re1—O7	82.1 (2)	N3—Re2—O8	79.4 (2)
N2—Re1—O7	80.3 (2)	N4—Re2—O8	80.7 (2)
C2—Re1—N2	98.2 (4)	C5—Re2—N4	98.0 (4)
C2—Re1—O7	95.7 (3)	C5—Re2—O8	95.2 (3)
C2—Re1—C3	88.4 (4)	C5—Re2—C6	87.8 (4)
C2—Re1—C1	87.1 (4)	C5—Re2—C4	87.2 (4)
C3—Re1—N1	97.3 (4)	C6—Re2—N3	98.3 (4)
C3—Re1—O7	93.1 (4)	C6—Re2—O8	96.0 (3)
C3—Re1—C1	88.5 (4)	C6—Re2—C4	88.6 (4)
C1—Re1—N1	95.0 (3)	C4—Re2—N3	97.8 (4)
C1—Re1—N2	97.9 (3)	C4—Re2—N4	94.5 (4)

Table 2. Intermolecular phen...phen contacts less than 3.65 Å

$A \cdots A^i$		$A \cdots B^{ii}$	
C10...C18 ⁱ	3.561 (13)	C10...C29 ⁱⁱ	3.531 (12)
C13...C17 ⁱ	3.645 (13)	C11...C30 ⁱⁱ	3.476 (12)
		C12...C25 ⁱⁱ	3.626 (12)
$B \cdots B^{ii}$		C12...C30 ⁱⁱ	3.373 (12)
C21...C26 ⁱⁱ	3.466 (13)	C13...C25 ⁱⁱ	3.583 (12)
C22...C25 ⁱⁱ	3.497 (12)	C15...C26 ⁱⁱ	3.537 (14)
C22...C26 ⁱⁱ	3.534 (13)	C15...C27 ⁱⁱ	3.535 (14)
C23...C25 ⁱⁱ	3.644 (12)	C16...C26 ⁱⁱ	3.384 (14)
C23...C30 ⁱⁱ	3.504 (12)	N2...C26 ⁱⁱ	3.603 (12)
C24...C29 ⁱⁱ	3.514 (12)	C17...C29 ⁱⁱ	3.624 (13)
C24...C30 ⁱⁱ	3.574 (12)		

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

The Re-atom positions were found from a Patterson map and the remaining heavy-atom coordinates were obtained from subsequent structure-factor Fourier calculations. H atoms were positioned by calculation (C—H 0.95 Å), assigned B values

1.1 times the average of the bound C atoms, and repositioned twice during refinement. The H atoms of the water molecules were ignored. Modeling the disordered water molecules was difficult and a three-site model was eventually adopted. The corresponding O atoms were assigned populations based on their heights in a Fourier map with fixed isotropic *B* values. The maximum (2.06 e Å⁻³) and minimum (-1.86 e Å⁻³) peaks in the final difference map are within 0.4 Å of the Re2 atom. Individual variances $\sigma^2(I)$ were derived from counting statistics plus an additional term (0.014I)², while variances of the merged intensities included propagation of error plus another additional term (0.014I)².

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *CRYM*. Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1449). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 916–918

Dibenzylbis(*tert*-butylimido)molybdenum(VI), containing both η^1 - and η^2 -benzyl ligands

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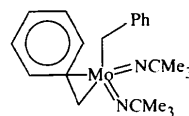
(Received 11 February 1999; accepted 2 March 1999)

Abstract

The title compound, [Mo(CH₂Ph)₂(C₄H₉N)₂], contains two slightly bent imido ligands and two benzyl ligands. One of these benzyl ligands is coordinated as a simple η^1 -alkyl ligand, while the other is η^2 -coordinated through the CH₂ group and the *ipso*-C atom, *i.e.* dibenzyl- κC^{α} ; $\kappa^2 C^1$, C ^{α} -bis(*tert*-butylimido- κN)molybdenum(VI). Considering the η^2 -benzyl ligand as occupying one coordination site, this gives a tetrahedral geometry around molybdenum, the main angular distortion being a mutual repulsion of the two strongly π -donating imido ligands. This complex is not crystallographically isostructural with its chromium analogue, but the two molecular structures are very similar.

Comment

As part of our work directed towards the development of new alkene polymerization catalysts based on complexes of imido ligands (Coles & Gibson, 1994), we have already reported the synthesis and crystallographic characterization of the chromium dibenzyl complex [Cr(CH₂Ph)₂(N^tBu)₂], (1) (Coles *et al.*, 1995). Although the possibility of α -agostic interactions between chromium and the CH₂ H atoms of the benzyl ligands was envisaged in this study, the structure revealed instead the presence of one η^1 - and one η^2 -benzyl ligand. In subsequent investigations of related complexes of chromium and molybdenum with different imido and alkyl ligands, we have prepared the molybdenum analogue of (1), complex (2), and report here its structure.



(2)