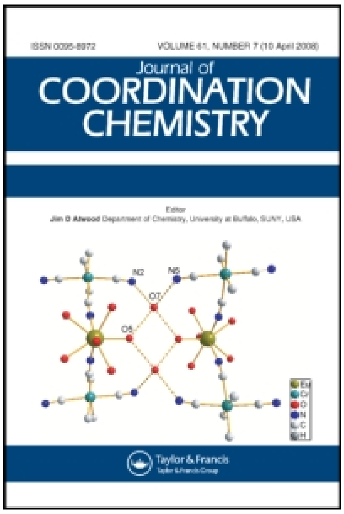

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SHORT COMMUNICATION

The Synthesis and Structure of a Novel Dimetallic Tetraazaannulene: μ-[dibenzo[b,i][1,4,8,11]tetraaza[14]annulenato]-bis[tricarbonyl rhenium(I)]

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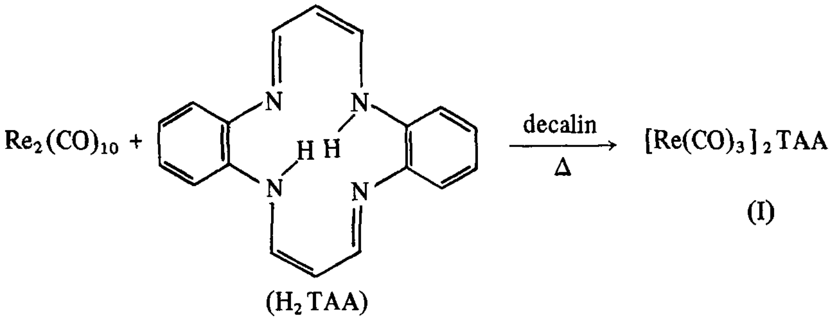
The first dinuclear metallotetraazaannulene complex, μ-[dibenzo-[b,i] [1,4,8,11] tetraaza[14] annulenato]-bis [tricarbonyl rhenium(I)], with an unusual geometry was synthesized by reaction of dirhenium decacarbonyl and 1,8-dihydrodibenzo[b,i][1,4,8,11]tetraazaannulene. This compound was characterized via visible, infrared, and mass spectral methods as well as elemental analysis. Structural data were obtained by single crystal x-ray diffraction. The distance between the rhenium atoms is 3.345(1) Å. This is a significant increase (.219(1) Å) from the corresponding porphyrin compounds. The dibenzotetraazaannulene ring is puckered a significant amount from planarity.

We would like to report the synthesis and x-ray diffraction anaylsis of the first dinuclear metallotetraazaannulene in which one tetraazaannulene ligand binds with 2 metal atoms. There is growing interest in synthetic macrocyclic ligands because of their obvious similarity with porphyrins which have importance as biological models,[1] because of their catalytic ability,[2] and because of their unique nature in coordinating metals.[3-12] Homodinuclear complexes of porphyrins have been well studied.[13-22] To our knowledge, no stable homodinuclear metallotetraazaannulenes with this novel geometry have been prepared. Such a compound would prove useful in comparing the effect of the central "hole" or "core" size of the macrocyclic ligand on the rhenium-rhenium distance as well as on the degree of puckering of the ligand. We have synthesized μ-[dibenzo[b,i] [1,4,8,11] tetraaza [14] annulenato]-bis-[tricarbonyl rhenium(I)] (I), and we have obtained crystals suitable for x-ray study.

The compound I was prepared by refluxing dirhenium decacarbonyl[23] in equimolar quantities with 1,8-dihydrodibenzo[b,i] [1,4,8,11] tetraaza-[14] annulene[24] in refluxing decalin for 24 hours under argon. After cooling, the resulting precipitate was centrifuged out and washed with decalin and hexane. The washed precipitate was then introduced into a neutral alumina column using chloroform as the elutant. Compound I, the wine-red fraction, was collected and evaporated to dryness (36% yield). The red residue was crystallized from a dichloromethane-chloroform-cyclohexane solution to give ruby-red crystals of I, m.p. 278–279°C. Analysis[25] calculated for $Re_2C_{24}H_{14}N_4O_6$: C, 34.87; H, 1.70; N, 6.78; Re, 45.04. Found: C, 34.62; H, 2.27; N, 6.64; Re, 46.03. The visible spectrum of I in chloroform has a broad absorption band centered at 455 nm (log ϵ 3.52). The infrared spectrum of I in the solid phase (KBr) shows two strong metal-carbonyl bands at 2020 and 1900 cm^{-1} as well as



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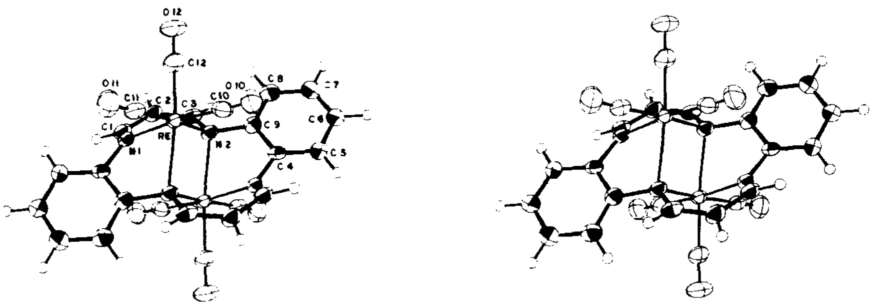

FIGURE 1 An ORTEP stereographic view of the molecular structure of μ-[dibenzo[b,i][1,4,8,11]tetraaza[14]-annulenato]-bis[tricarbonyl rhenium(I)] (I).

the 739^{-1} band characteristic of the tetraazaannulene ligand. The mass spectrum[26] of I shows the parent peak at m/e 829.9 (M^+). In addition, the $(M-2CO)^+$, $(M-3CO)^+$, $(M-4CO)^+$, $(M-5CO)^+$, and $(M-6CO)^+$ peaks are also observed. Since naturally occurring rhenium has two common isotopes, 185 Re and 187 Re, the triplet at $(M)^+$, $(M+2)^+$, and $(M+4)^+$ as well as this same type of triplet pattern at the major peaks gives further evidence that there are two rhenium atoms per molecule.

Crystals of I are triclinic, space group P$\bar{1}$ with a = 8.031(3), b = 8.575(3), c = 4.550(1) Å, α = 104.73(2), β = 102.32(2), γ = 74.08(2) and V= 287.9(1) Å^3 ; Z = ½ for D_{meas} = 2.36 g·cm^{-3} and D_{calc} = 2.38 g·cm^{-3}.

The data crystal dimensions are 0.11 × 0.14 × 0.09 mm, with μ = 111.6 cm^{-1} (Mo Kα: λ = 0.71069 Å). A total of 1382 independent reflection intensities was measured by the stationary crystal/stationary counter method using a manual General Electric XRD-700 diffractometer equipped with balanced Zr/Y filters ($2\theta_{max}$ = 60.00°). Ten second counts were recorded for each filter. The intensity data were processed by calculations described previously.[27] An experimentally determined absorption correction was applied to the data as a function of the diffractometer setting angles of ϕ and 2θ. The points were measured by rotating the crystal about the ϕ axis at the respective reflection 2θ angles with χ set at 90.00°. A maximum of 20% was noted for intensity variation. 1083 of the reflections were classed to be significantly above background.

The correct phase angles were determined by the heavy-atom technique. Atom coordinates and anisotropic temperature factors were refined to convergence by full-matrix least-squares calculations to R = 0.020 and R_w = 0.022. Hydrogen atoms could not be located in a difference Fourier map, but their scattering contribution was included in the final cycles of refinement by assuming idealized C–H geometry. Hydrogen atom parameters were not allowed to refine. The largest residual peak in a final difference map is 0.50 e·Å^{-3}, located 0.7 Å from the rhenium atom. Most of the crystallographic calculations were done with the SHELX system of programs.[28]

The molecule lies on a crystallographic center of symmetry, and provides confirmation of the centrosymmetric space group. The figure is an ORTEP stereographic view of the molecular structure. The Table lists some interatomic distances with estimated standard deviations. Some pertinent torsional angles are listed to show the non-planarity of the dibenzotetraazaannulene ligand.

The tricarbonylrhenium(I) groups are located on opposite sides of the dibenzotetraazaannulene ligand. Interatomic distances indicate each rhenium is bonded to three nitrogen atoms and that they both bond in common to N2 and N2′. The bond distances within the organic ligand clearly show the non-delocalization of the macrocycle. The distances of nitrogen atoms N1 and N2 from the center of the ligand are 2.236(8) and 1.555(8) Å respecitvely. This compares with 2.26(1) and 1.81(2) Å for a similar dirhenium structure with a tetraphenylporphine ligand.[13] The deviation of the rhenium atom from the best least-square plane containing the N1, N2, N1′, and N2′ atoms is 1.50 Å.

It is significant to note that the smaller "hole" size of the dibenzotetraazaannulene ligand has caused the rhenium atoms to be farther apart (.219(1) Å) than in the porphyrin analogs. Like the porphyrin ligand in these complexes, the dibenzotetraazaannulene ligand also shows a significant amount of twisting in its complex with two rhenium tricarbonyl moieties.

The crystal lattice appears to be disordered. An ordered lattice of space group P$\bar{1}$ required one

TABLE I
Interatomic distances^{a}

Re–N1	2.130(6) Å	N1–C1	1.30(1) Å
Re–N2	2.232(6)	N1–C4′	1.45(1)
Re–N1′	3.325(7)	N2–C3	1.42(1)
Re–N2′	2.334(6)	N2–C9	1.45(1)
Re–Re′	3.345(1)	C1–C2	1.48(1)
Re–C10	1.910(8)	C2–C3	1.34(1)
Re–C11	1.910(8)	C4–C5	1.38(1)
Re–C12	1.916(8)	C4–C9	1.39(1)
C10–O10	1.16(1)	C5–C6	1.42(1)
C11–O11	1.15(1)	C6–C7	1.38(1)
C12–O12	1.14(1)	C7–C8	1.37(1)
N1–N2	2.827(8)	C8–C9	1.39(1)
N1–N2′	2.615(8)		

Torsional angles

N1′–C4–C9–N2	–1.4(1.1)°	C3–C2–C1–N1	27.2(1.2)°
C4–C9–N2–C3	–153.8(8)	C2–C1–N1–C4′	–157.2(6)
C9–N2–C3–C2	–170.2(8)	C1–N1–C4′–C9′	131.7(8)
N2–C3–C2–C1	–10.8(1.3)		

[a] The prime (′) after an atom label indicates the atom generated by the inversion symmetry operation.

molecule per unit cell, whereas packing considerations and a density measurement indicate one-half molecule per cell. The least-squares calculations were done using half-occupancy for all atoms. A search was undertaken for reflections which may have been overlooked, but none were located. No satisfactory explanation for the apparent lattice disorder has been found.

During the workup of I, a second dark brown band was eluted from the neutral alumina column. It was formulated as [monohydrogen dibenzo[b,i] [1,4,8, 11] tetraaza[14] annulenato] tricarbonyl rhenium(I) in analogy to the prophyrin systems already known, but attempts to obtain analytical purity of this compound have failed.

We are continuing our studies of molecules of these types.

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