Triple-Decker Sandwich Structure of a New Rubidium(I) Tetraimino Macrocyclic Complex

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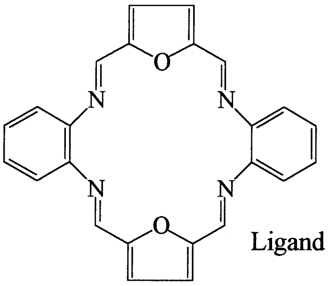
A new triple-decker type rubidium(I) complex containing 18-membered macrocyclic ligands has been synthesized and characterized by X-ray crystallography. Linear stacks of the triple-decker units have been revealed in the crystal.

Phthalocyanine and porphyrin complexes having either a sandwich or a triple-decker type structure have been intensively studied[1] due to their redox,[2] semiconducting,[3] and electrochromic properties.[4] Sandwich type complex, $[BaL_2](BPh_4)_2$, where L is a 18-membered macrocyclic ligand containing two furan units, was first reported by Nelson et al.[5] A number of complexes containing tetraimino macrocyclic ligands of similar structures have been prepared, but almost all of them are monomeric.[6] Recently, we have re-examined the reaction products of L with various metal ions and have found that this macrocycle affords a wide variety of complexes depending upon the metal ion to be encapsulated. In this communication, we wish to report the synthesis and the crystal structure of a triple-decker type complex, $[Rb_2L_3](BPh_4)_2$.



Ligand L

A solution of 2,5-diformylfuran (0.5 mmol)[7], *o*-phenylenediamine (0.5 mmol), and RbBr (0.25 mmol) dissolved in a minimum quantity of methanol was refluxed with stirring for 1.5 h. Cooling and concentration of the solution yielded orange solid, which has the formula $[RbL]Br_2$. The orange product was redissolved in 50 mL of methanol, and to the solution was added $NaBPh_4$ (0.2 mmol) dissolved in a minimum quantity of methanol. After a day, orange precipitates deposited were collected by filtration. From the filtrate, orange crystals of $[NaL(CH_3OH)]_2(BPh_4)_2$[8] were deposited after 2 weeks on standing at 5°C. Recrystallization of the orange precipitates from acetonitrile gives dark red crystals of $[Rb_2L_3](BPh_4)_2$.

X-ray analysis of the complex, $[Rb_2L_3](BPh_4)_2$,[9] revealed a triple-decker structure of the complex cation as shown in Figure 1. A crystallographic inversion center lies at the centre of the inner ligand (L_i) of the complex. Each Rb atom is surrounded by N_8O_4 coordination sphere, but the Rb atom is more strongly connected with outer ligand(L_o) than with L_i. The average length of the six Rb-L_o coordination bonds is 3.05 Å, whereas that of Rb-L_i is 3.30 Å. The Rb-Rb interatomic distance is 3.818(1) Å. The L_i and L_o are in a staggered configuration with an angle of 50° from the eclipsed configuration. Both L_i and L_o show considerably planer conformations, although the ligand in the $[BaL_2]^{2+}$ sandwich complex[5] and the analogous macrocycles containing the pyridine moieties[6] usually show fairly bent conformations. The dihedral angle between the two furan rings is 17.7° and that between the two phenyl rings is 3.7° for L_i. L_i and L_o are approximately parallel with each other, where the dihedral angle between the best N_4O_2 planes of L_i and L_o is 3.1°. The interligand distance between L_i and L_o measured at the centre of the ligands is estimated as 3.19 Å, which implies strong π-π interactions.

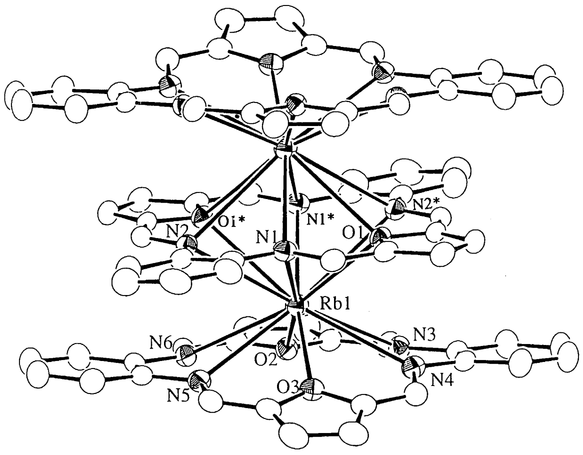


Figure 1. An ORTEP drawing of triple-decker structure of $[Rb_2L_3]^{2+}$. Selected interatomic distances; Rb-O(1) = 3.112(3), Rb-O(1)* = 3.094(3), Rb-O(2) = 2.884(3), Rb-O(3) = 2.847(4), Rb-N(1) = 3.609(4), Rb-N(1)* = 3.233(4), Rb-N(2) = 3.466(3), Rb-N(2)* = 3.270(4), Rb-N(3) = 3.175(1), Rb-N(4) = 3.136(1), Rb-N(5) = 3.129(5), Rb-N(6) = 3.125(4) Å.

The molecular alignment of the Rb complex is shown in Figure 2. The complex forms a one-dimensional infinite structure along the c axis by intermolecular π-stacking achieved between the adjacent L_o ligands. The distance between the L_o rings is estimated as 3.14 Å. The planes of the macrocycles are inclined from the right angle with the direction of the infinite chain by 26°.

Finally we want to note the redox properties of the complexes. Cyclic voltammograms[10] of the rubidium complex indicate two-steps of quasi-reversible redox couples. The current study presents these macrocyclic complexes have a potential to become a new series of low-dimensional compounds.

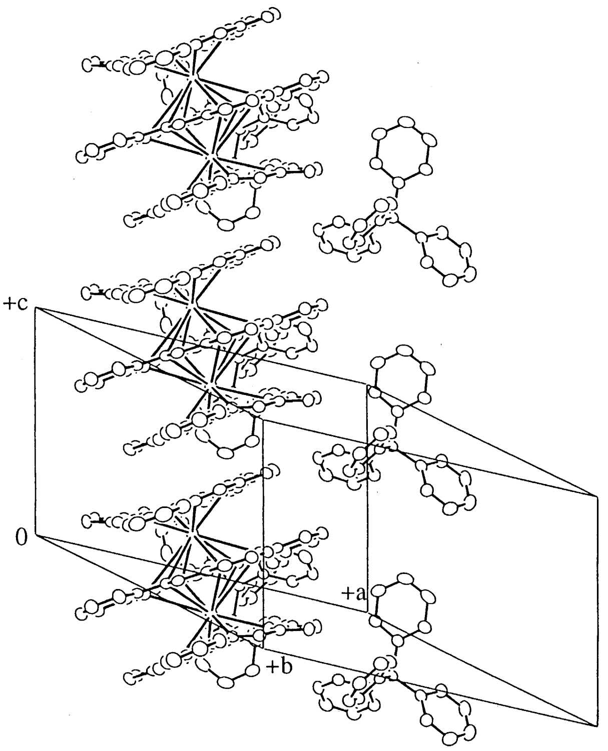


Figure 2. Linear chain structure of $[Rb_2L_3]^{2+}$.

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References and Notes

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8 The preliminary X-ray study has revealed thath the ligand L forms a 1 : 1 complex with a Na ion. Two molecules of the complex cation are closely located facing each other. Crystal data; $C_{98}H_{80}B_2N_8Na_2O_6$, M = 1533.36, triclinic, space group $P\bar{1}$, a = 16.265(4), b = 19.129(3), c =15.780(5) Å, α = 98.31 (2), β = 118.93(2), γ = 73.75(2) °, V = 4125 (2) Å^3, Z = 2, D_c = 1.23 g cm^{-3}.

9 Crystal data. $C_{120}H_{88}B_2N_{12}O_6Rb_2$, M = 1986.65, triclinic, space group $P\bar{1}$, a = 16.383(1), b = 16.514(1), c =10.589(1) Å, α = 108.409(6), β = 102.322(5), γ = 60.660(5) °, V = 2363(1) Å^3, Z = 1, D_c = 1.40 gcm^{-3}, μ(Cu-Kα) = 1.87 mm^{-1}, λ = 1.54178 Å. R = 0.045 (Rw = 0.033) for 5232 absorption corrected data with $I \geq 3\sigma(I)$.

10 Quasi-reversible redox couples are found at -1.10 and -1.20 (V) (ΔE_p = 0.08 and 0.07V, respectively) for $[Rb_2L_3](BPh_4)_2$, (Platinum working electrode, 0.1M TBAP in DMSO solution).