Preparation and Crystal Structure of [Ni(H_2tmtaa)][$AlCl_4$]$_2$: A Tetraazamacrocyclic Complex with Isolated Diimine Units in the Six-Membered Chelate Rings

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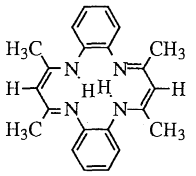
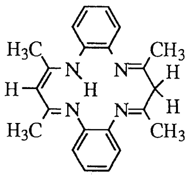
A nickel-tetraazamacrocyclic complex, Ni(H_2tmtaa), with a novel structure was synthesized from the reaction of Ni(tmtaa) with 1,3-dibenzenedicarbonyl dichloride in the presence of $AlCl_3$. The title compound losses proton readily in basic solution.

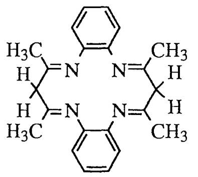
A large number of tetraaza-macrocycles have been synthesized and characterized.[1] Among them the dibenzotetraaza[14]annulene (H_2tmtaa) has been considered as a model due to its relationship to mimic the naturally occurring porphyrin in biologic system.[2] The normal structure of H_2tmtaa is as shown **I**[3] with two hydrogen atoms bound to nitrogen. In addition to type **I**, an odd structure **II** with a proton shift from one of the nitrogen atoms to a ring carbon atom is also observed for several complexes.[4] Although Dabrowiak[5] has prepared several brominated nickel macrocyclic complexes having structure type **III** on the basis of spectroscopic evidence, however no crystal structure was reported our knowledge. In this paper, we report a novel structure of this ligand with two protons shift from nitrogen atoms to both ring carbon atoms, thus generating two 1,3-diimino propane units, in which nickel is bonded to both diimino units.



(I)



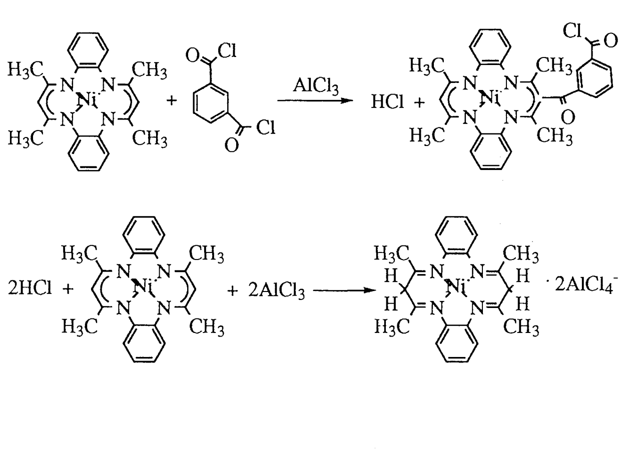
(II)



(III)

The title compound was obtained[6] from the reaction of Ni(tmtaa) ({6,8,15,17]-tetramethyl-7H,16H-5,9,14,18-tetraaza-dibenzo[b,i]-cyclotetradecenato(2-)-κ^4-N,N',N'',N'''}nickel(II)) with a mixture of $AlCl_3$ and 1,3-dibenzedicarbonyl dichloride in CH_2Cl_2 according to scheme **1**. The reactions of acid chlorides with Ni(tmtaa) to give HCl were observed in a number of reactions.[7] ^{1}H-NMR of the title compound (δ($CDCl_3$); 2.173, 2.175 (CH_2), 2.38 (CH_3), 6.7-7.1 (aro)) is different to that of Ni(HBrtmtaa)[6] ((δ($(CD_3)_2O$); 2.38 (CH_3), 6.5 (aro)) and that of $(CO)_4$Mo(H_2tmtaa)[4] ((δ($CDCl_3$); 1.86, 1.99 (CH_3), 3.59, 4.19 (CH_2) 7.1 (aro))

Scheme 1.



Proton NMR studies reveal that the title compound is rather stable in acidic solution, but losses both hydrogen atoms on the propylene units to form Ni(tmtaa) under basic solution even in acetonitrile or dimethylsulfoxide solution. The title compound was not observed in the reaction of Ni(tmtaa) with HCl. However it can be obtained in high yield by the reaction of Ni(tmtaa) with benzoic acid, trifluoroacetic acid and sulfuric acid. The answer to this question is still remained mystery Further studies of this work are pursuing.

The ORTEP diagram of [Ni(H_2tmtaa)]$^{2+}$ cation is illustrated in Figure 1. The side view of the molecule is given in Figure 2 which reveals the planarity of the NiN_4 plane in the molecule. The complex crystallizes[8] in the centrosymmetric orthorhombic space group Pccn (No. 56). Ni atom is sitting on the crystallographic C_2 axis. The coordination geometry around Ni is approximately a square planar with the displacement of Ni atom is only 0.036 Å above N(1)N(2)N(1a)N(2a) plane which is similar to that of Ni(tmtaa),[9] but is much differ to all of other known M(tmtaa) complexes in which metal atom is above N_4 plane ranged from 0.07 Å to 0.300 Å.[10] The evidences for this abnormal macrocyclic complex with four imine units coordinating on nickel are described as below. The distances between N(1)-C(2) and N(2)-C(4), are 1.278(5), 1.289(5) respectively for the indication of double bond characters between N(1)-C(2) and

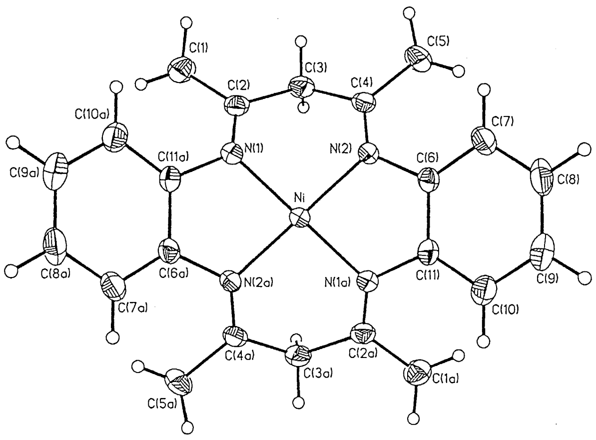


Figure 1. Structure of Ni(H_2tmtaa)$^{2+}$ cation with atomic numbering scheme. Bond distances (Å) are as follows: Ni-N(1) 1.854(3), Ni-N(2) 1.856(3), N(1)-C(2) 1.278(5), N(2)-C(4) 1.289(5), N(2)-C(6) 1.441(5), C(1)-C(2) 1.495(6), C(2)-C(3) 1.507(6), C(3)-C(4) 1.499(6), C(4)-C(5) 1.496(6), N(1)-C(11a) 1.439(5).

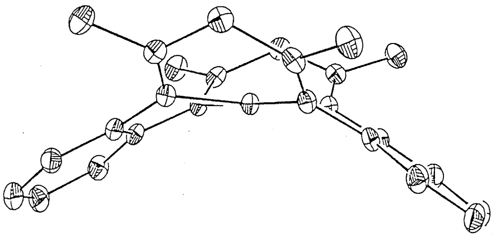


Figure 2 A side view of one $[Ni(H_2tmtaa)]^{2+}$ cation illustrating the planarity of NiN(1)N(2)N(1A)N(2A) of the molecule. The displacement of Ni atom is only 0.036 Å above N4 plane.

N(2)-C(4). The distances between C(2)-C(3) and C(3)-C(4) are 1.507(6) and 1.499(6) Å respectively, which show a normal single bond character. H(3a) and H(3b) attached on C(3) were revealed from a difference Fourier map but were idealized and used in fixed structure factor as (C-H: 0.96 Å) in subsequent calculation. Mean deviations from planes C(1)C(2)C(3)N(1) and C(3)C(4)C(5)N(2) are 0.0123 Å and 0.0091 Å respectively. The distances between Ni-N(1) and Ni-N(2) are 1.854(3), and 1.856(3) Å respectively, which are within the normal range for the Ni-N bond in Ni-tetraazamacrocyclic complexes.[3] The dihedral angle between the N_4 plane and C(6)-C(11) plane at 34.4° is much larger than the average dihedral angle (22°) between the N_4 plane and phenyl ring plane of M(tmtaa) complexes,[9] but is compatible to that of H_2tmtaa free ligand. The dihedral angle between the N_4 plane and C(2)N(1)C(4)N(2) plane is 32.9°. The bond angle of C(2)-C(3)-C(4) (120.6° (4)) of the title compound is much smaller than that of Ni(tmtaa) (127.2° (4)). Al-Cl distances range from 2.125(2) to 2.138(2) Å, which are within the normal range for an Al-Cl bond.[11]

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References and Notes

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6 *Experimental procedures* To a CH_2Cl_2 solution (50 ml) containing $AlCl_3$ (0.73 g, 5.5 mmol), and 1,3-dibenzenedicarbonyl dichloride (0.56 g, 2.75 mmol), Ni(tmtaa) (1.10 g, 2.75 mmol) in CH_2Cl_2 (40 ml) was added. The mixture was stirred at 27 °C for 6 h. A dark green solution was filtered. Dark green needle crystals were obtained after the filtrate was cooled to -30 °C. Yield: 0.10 g (5.4 %). ^{1}HNMR ($CDCl_3$, ppm): 6.7-7.1 (m, 8H), 2.38(s, 12H), 2.173(s, 2H), 2.175 (s, 2H). Calc: C, 35.7; H, 3.3; N, 7.6. Found: C, 35.5; H, 3.5; N, 7.6. mp: 140 - 141 °C (dec.).

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8 *Crystal data* for $[Ni(H_2tmtaa)][AlCl_4]_2$: $C_{22}H_{24}Al_2Cl_8N_4Ni$, orthorhombic, space group Pccn, a = 20.283(2), b= 11.344(2), c=13.540(2) Å, V=3115.4(6) Å^3, and D_c=1.579 Mg/M^3 for Z=4. Of 3927 data collect (Siemens R3m/V, 2q ranged from 4-50°, Mo-K_α), 1935 were observed at F > 4.0σ(F). Refinement converged with R = 0.041 and R_w = 0.053.

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