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Mercury–carbon bond formation promoted by the co-ordinated ligand reaction of a β-diiminate chelate

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Reaction between [Ni(tmtaa)] and $HgBr_2$ in dichloroethane afforded the mercury–carbon bonded tetranuclear complex $[Ni(tmtaa)HgBr]_2[Hg_2Br_6]$ (H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine).

Tetraaza macrocyclic complexes derived by metal-template reactions from acetylacetone and diamines (or linear tetra-amines) contain charge delocalized β-diiminate six-membered chelate rings. It has been shown that the central carbon atom on the diiminate chelate ring has nucleophilic character, and some unique co-ordinated ligand reactions originating from this feature have been reported, *e.g.* acid–base reaction[1,2] and C–C bond formation.[2–4] This suggests that chelate rings of this type may undergo metal–carbon bond formation under appropriate conditions. We report here Hg–C bond formation in Jäger macrocyclic complexes[5a] which have two such nucleophilic centers within a molecule.

Reaction of [Ni(tmtaa)] **1**[5a] (H_2tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine) with HgX_2 (X = Cl^-, Br^- or I^-) in 1,2-dichloroethane or diethyl ether at room temperature afforded dark red needles or plates. Single crystals suitable for X-ray study were obtained in the **1**–$HgBr_2$ reaction,‡ and the product was found to be $[Ni(tmtaa)HgBr]_2[Hg_2Br_6]{\cdot}5C_2H_4Cl_2$ (**2**$[Hg_2Br_6]{\cdot}5C_2H_4Cl_2$).§

Fig. 2 shows an ORTEP[8] drawing of **2**$[Hg_2Br_6]$. Complex cation **2** consists of two $[Ni(tmtaa)HgBr]^+$ asymmetric units related by a crystallographic inversion center. Two [Ni(tmtaa)] units are linked by the $Hg_2Br_2^{2+}$ group *via* Hg–C bonds with distances of 2.266(9) Å for Hg(1)–C(1) and 2.257(9) Å for Hg(1)–C(10′). In **2**, C–N and C–C bond distances in the chelate rings are 1.30(1)–1.32(1) Å and 1.44(2)–1.47(2) Å, respectively, whereas in **1**, C–N = 1.324–1.342 and C–C = 1.394–1.408 Å.[5b] Correspondingly, **2**$[Hg_2Br_6]$ shows a strong ν(C=N) at 1600 cm^{-1} in its IR spectrum, while parent compound **1** shows no imine bands at frequencies higher than 1550 cm^{-1}. This suggests that, upon Hg–C bond formation, the delocalized β-diiminate chelate rings are transformed into the isolated diimine form with the central carbon atom being of sp^3 type. The C–N and C–C distances in **2**, however, are obviously longer and shorter, respectively, as compared to those in protonated $[Ni(H_2tmtaa)]^{2+}$ [C–N = 1.278(5)–1.289(5) Å, C–C = 1.499(5)–1.507(5) Å], in which the relevant carbon atoms are normal sp^3 hybrid.[9] Furthermore, the Hg–C distances found in **2** are significantly longer than normal Hg–C bonds, which usually fall in the range 2.00–2.15 Å.¶ In view of this, a delocalized β-diiminate structure contributes, to some extent, to the bonding in the six-membered chelate rings in **2**. A similar discussion has also been given for $[Rh_2(C_5Me_5)_2(acac)_2]^{2+}$ (Hacac = acetylacetone).[11]

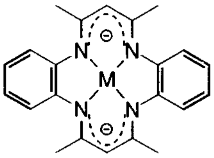

Fig. 1 Structure of [Ni(tmtaa)] (M = Ni)

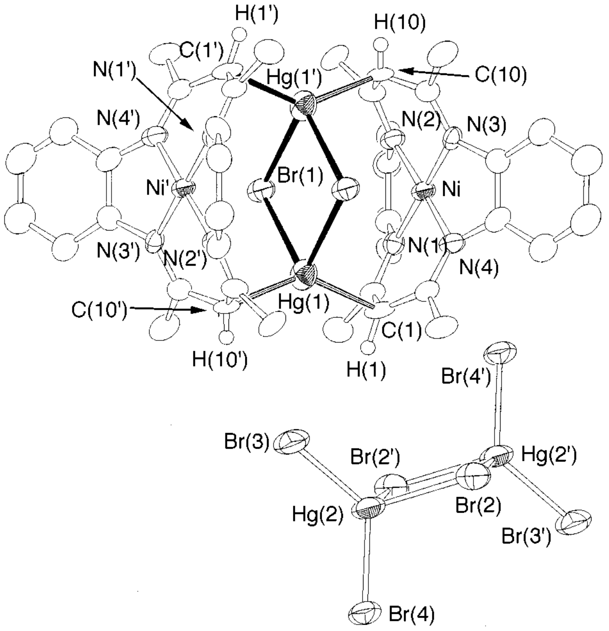

Fig. 2 An ORTEP drawing of **2**$[Hg_2Br_6]$ with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hg(1)–Br(1) 2.821(1), Hg(1)–Br(1′) 2.843(1), Hg(1)–C(1) 2.266(9), Hg(1)–C(10′) 2.257(9), Hg(1)–Hg(1′) 4.0544(8); Br(1)–Hg(1)–Br(1′) 88.60(4), Br(1)–Hg(1)–C(1) 105.3(2), Br(1)–Hg(1)–C(10′) 104.2(3), Br(1′)–Hg(1)–C(1) 105.1(3), Br(1′)–Hg(1)–C(10′) 103.8(3), C(1)–Hg(1)–C(10′) 138.8(3)

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‡ Reaction of complex **1** (0.21 mmol) in 1,2-dichloroethane (40 cm^3) with $HgBr_2$ (0.42 mmol) in the same solvent (60 cm^3) gave dark red crystalline material, **2**$[Hg_2Br_6]$ (yield 35%).

§ Crystal data: $C_{58}H_{72}Hg_4Br_8Cl_{14}Cu_2N_8$, $M = 2936.57$, crystal size = 0.25 × 0.15 × 0.20 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.416(1)$, $b = 15.711(2)$, $c = 12.180(2)$ Å, $\alpha = 92.310(5)$, $\beta = 99.479(7)$, $\gamma = 111.475(5)°$, $U = 2167.6(1)$ Å^3, $Z = 1$, $D_c = 2.250$ g cm^{-3}, μ(Mo-Kα) = 197.05 cm^{-1}. With the use of 5209 unique reflections [$I > 4\sigma(I)$] collected at 180 K with Mo-Kα radiation (λ = 0.710 69 Å) on a Mac Science DIP2020 diffractometer, the structure was solved by the Patterson method (DIRDIF 94 PATTY[6]), refined by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms and an absorption correction (DIFABS[7]) was applied. The final R value was 0.044 ($R' = 0.052$). CCDC reference number 186/595.

¶ Results of three-dimensional search and research using the Cambridge Structural Database.[10]

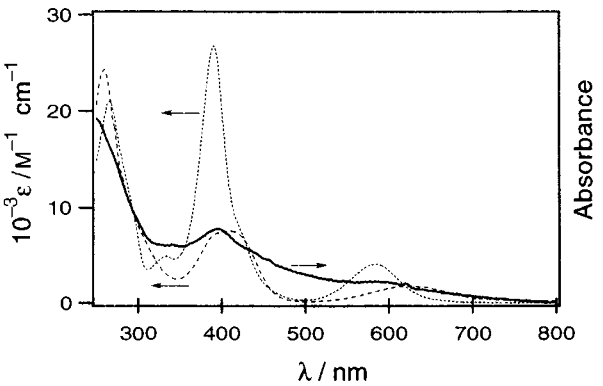

Fig. 3 Electronic spectra of [Ni(tmtaa)] (· · ·) and $[Ni(H_2tmtaa)]^{2+}$ (– – –) in MeCN, and $2[Hg_2Br_6]$ (——) in the solid state (KBr disk)

Deep red $2[Hg_2Br_6]$ dissolves in co-ordinating solvents such as acetone or acetonitrile to regenerate deep green **1**, as evidenced by spectral changes. Fig. 3 shows the electronic spectra of $2[Hg_2Br_6]$ in the solid state along with those of **1** and its protonated form $[Ni(H_2tmtaa)]^{2+}$ in solution. Complex **1** shows intense absorptions at 394 nm and 584 nm in acetonitrile solution. Upon protonation, the band maxima are shifted to 410 nm and 632 nm and concomitantly their intensities decrease. The major features of the solid-state spectrum of $2[Hg_2Br_6]$ resemble the solution spectrum of $[Ni(H_2tmtaa)]^{2+}$. This reveals that a change in π delocalization has been induced by protonation or C–Hg bond formation at the central carbon atoms.

We have succeeded in making Hg–C bonds by utilizing the reaction of the co-ordinated ligand of β-diiminate chelates. The result suggests that this type of compound may be a potential building block for making polynuclear frameworks. In fact, Hg–C bonded trinuclear and hexanuclear complexes, $[Ni(tmtaa)Hg_2I_4]$ and $[Cu(tmtaa)Hg_2Cl_4]_2$, have been obtained from similar reactions, which have similar C–Hg bonds.[12] Further, we have preliminarily found that similar tetraaza macrocyclic complexes such as $[M([14]dienato)]^+$ {[14]dienato = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato(1−)} and [M(omtaa)] (H_2omtaa = 5,14-dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b*,*i*][1,4,7,11]tetraazacyclotetradecine) (M = Ni^{II} or Cu^{II}) undergo facile M–C bond formation with soft metal ions such as Ag^+, Pd^{2+} or Pt^{2+} to give polynuclear metal complexes. It is well documented that metal-free β-diketonates, or acetylacetonate chelates in limited cases, undergo similar M–C bond formation.[13] To the best of our knowledge, however, this is the first example of M–C bond formation in β-diiminate chelates. Such research is now in progress in our laboratories.

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