Hetero-Ligand Assembly onto Cobalt(III) Complexes

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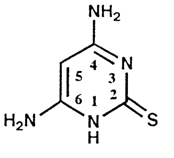
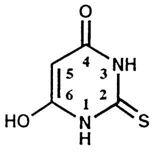
Novel cobalt(III) complexes with two kinds of dimerized ligands dapymt-tbba(2-) and tbba-dapymt(1-) are obtained from the mixed system containing Hdapymt and H_3tbba ligands (Hdapymt = 4,6-diamino-2-thiouracil and H_3tbba = thiobarbituric acid).

Recently we found an interesting reaction that two molecules of 6-amino-2-thiouracil (H_2atuc) self-assemble onto cobalt(III) complex to give the dimerized ligand 5-[6'-amino-4'-oxo-(1'*H*)-pyrimidin-2'-yl]thio-6-amino-2,3-dihydro-2-thioxo-(1*H*)-pyrimidin-4-one [atuc-atuc(2-)] in good yield.[1] This reaction was inferred to proceed through the electrophillic substitution reaction at the 5-carbon atom of pyrimidine ring.[2] In order to explore other ligand assemblies, we attempted here similar reactions in two ligand systems, 4,6-diamino-2-thiouracil (Hdapymt) and thiobarbituric acid (H_3tbba). In each system no complex with an assembled homo-ligand such as dapymt-dapymt or tbba-tbba, however, was identified. Surprisingly, the complexes with assembled hetero-ligands such as dapymt-tbba (2-) and tbba-dapymt(1- or 2-)[3] were found only in the mixed system containing both dapymt and tbba ligands. we describe the characterization of these novel complexes in this paper.



Hdapymt



H_3tbba

To an aqueous solution (100 cm^3) of H_3tbba (10 mmol, 1.44 g) and NaOH (10 mmol, 0.4 g) was added an aqueous solution of *trans*-$[CoCl_2(en)_2]Cl$ (10 mmol, 2.85 g) and the mixed solution were heated at 80 °C for 2 h. Activated charcoal (ca. 1 g) and an aqueous solution (50 cm^3) of Hdapymt (10 mmol, 1.51 g) and NaOH (10 mmol, 0.4 g) was added to the above reaction solution and the mixture was heated at 60 °C with stirring for 2 h under air-bubbling. During this reaction a considerable amount of green precipitate (complex **4**, yield ca. 30%) appeared. After filtration of the activated charcoal and the green precipitate, the filtrate was poured onto a column of cation exchanger (SP-Sephadex C-25, Na^+ form; ϕ 4 × 40 cm). Elution with 0.1 mol dm^{-3} NaCl gave three major bands with 1+ charge [red (**1**, 17%), red (**2**, 10%), red (**3**, 8.5%)]. Each red eluate was concentrated with a vacuum evaporator and after removal of NaCl complex was crystallized as the chloride salt. Complex **2** {Found: C, 24.36; H, 5.66; N, 21.16%. Calcd for $[Co(Htbba)(en)_2]Cl\cdot 2H_2O = C_8H_{22}ClCoN_6O_4S$: C, 24.47; H, 5.65; N. 21.40%}: UV-vis (water) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 506(135) 360sh(240) 297(10800) 265sh(9800) 240(22000) 214sh(31000). Complex **3** {Found: C, 24.84; H, 5.35; N, 24.20%. Calcd for $[Co\{dapymt\text{-}tbba(2\text{-})\}(en)_2]Cl\cdot 4H_2O = C_{12}H_{30}ClCoN_{10}O_6S_2$: C, 24.94; H, 5.41; N. 24.23%}: UV-vis (water) 507(134) 370sh (260) 303(13500) 267(18200) 244(24100) 215(61000). Complex **4**: UV-vis (2-methoxy-ethanol) λ_{max}/nm 588 480sh 338(14900) 276sh(32600) 250(44000).[4] Complex **1** was decomposed during the isolation process. The isolation of pure complex **4** was still unsuccessful but it was identified based on the ^1H and ^{13}C NMR spectra in DMSO-d_6.

Complex **2** is assigned to $[Co(Htbba)(en)_2]^+$ based on the UV-vis absorption and ^{13}C NMR spectra: eight signals, four in the tbba chemical shift region and four in the en region.

UV-vis absorption spectrum of complex **3** is very similar to that of complex **2** (Figure 1). It should, however, be noted that

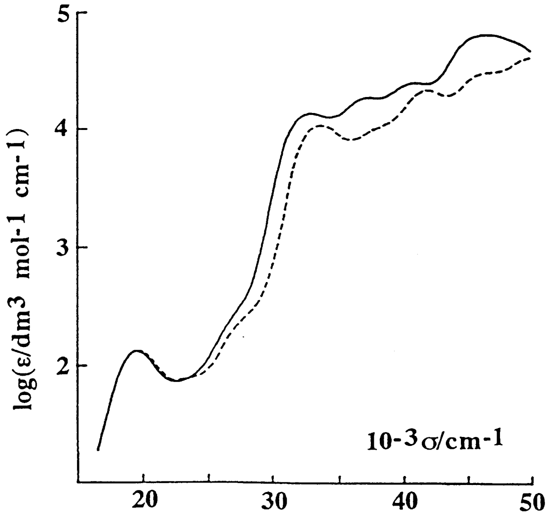


Figure 1. UV-vis absorption spectra of complexes **2**(dotted line) and **3**(solid line).

Figure 2. Proton NMR spectra of complexes **3**(left) and **4**(right).

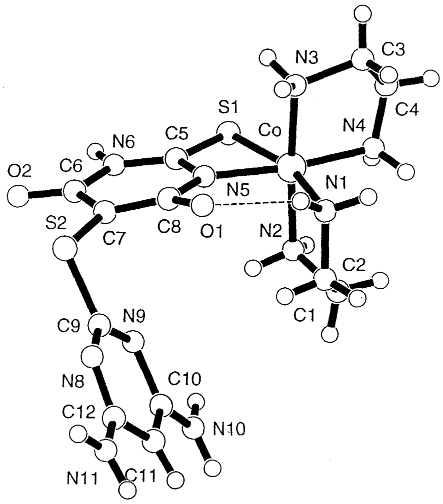


Figure 3. The structure of the cation of $[Co\{dapymt\text{-}tbba\text{-}(2\text{-})\}(en)_2]ClO_4 \cdot 3H_2O$.

the molar absorption coefficients of complex **3** are considerably larger than those of complex **2** only in the UV region. This is a common feature for the assembled complex.[1] Elemental analysis shows that complex **3** contains both dapymt and tbba ligands. Carbon-13 NMR spectrum confirms the result: seven signals appear in the pyrimidine chemical shift region. In the proton NMR spectrum only one signal is observed for 5-H (1H) and also for NH_2 (4H) in Figure 2, which means that C5 participates into the new bond formation and dapymt is freely rotating. The downfield shift of one amine proton (δ 8.16) indicates the existence of a N-H···O intramolecular hydrogen bond and the direct coordination of tbba to a cobalt(III) ion.[5] Figure 3 shows the cation of $[Co\{dapymt\text{-}tbba(2\text{-})\}(en)_2]ClO_4 \cdot 3H_2O$ complex **3**.[6] As expected by the NMR spectra complex **3** has an assembled dapymt-tbba ligand: a new bond is formed between the C(7) atom of tbba and the S(2) atom of dapymt. Coordination occurs through the S(1),N(5) donors of tbba. The coordinating four-membered plane of Co-S(1)-C(5)-N(5) is slightly bent from the tbba plane: the angle between two planes is 8.11 °. The dihedral angle between the pyrimidine ring of tbba and the pyrimidine ring of dapymt is 66.6 °, which is different from that of $[Co\{atuc\text{-}atuc(2\text{-})\}(en)_2]^+$ (ca. 90 °).[1] The protonation at N(6) of tbba [angle C(5)-N(6)-C(6) = 123(2) °] is inferred by a Singh's rule that the nitrogen valence angles with an extra-annular hydrogen atom are within 125 ±3 ° for a six-membered ring.[8] The same result is obtained by the crystal structure analysis of $[Co(Htbba)(en)_2]ClO_4$.[9]

The green precipitate **4** was not soluble in water but soluble in DMSO, and the NMR spectra were measured in DMSO. The UV-vis absorption spectra is very similar to that of *trans(S)*-$[Co(dapymt)_2(en)]^+$ [581 nm (ε 123) 460sh(170) 334(14900) 273(19100)] except for the relatively high molar absorption coefficients in the UV region.[10] Complex **4** showed eight ^{13}C NMR signals, one in the en chemical shift region and seven in the pyrimidine region, which means the presence of a C2 axis. This complex exhibits only one proton signal for 5-H (1H) and two amine signals (2H each) in Figure 2. The results indicate the direct coordination of dapymt. Thus we conclude that complex **4** is *trans(S)*-$[Co\{tbba\text{-}dapymt(1\text{-})\}_2(en)]^+$ where a new bond is formed between the 5-carbon atom of dapymt and the 2-sulfur atom of tbba. The high yield of this complex is responsible for the high stability of *trans(S)*-$[Co(dapymt)_2(en)]^+$ due to the double intramolecular hydrogen bondings.[10] Complex **1** may be $[Co\{tbba\text{-}dapymt(2\text{-})\}(en)_2]^+$ but decomposed easily.

The two ligands dapymt and tbba are expected to have analogous reactivities to that of atuc. In fact, the assembled hetero-ligands dapymt-tbba and tbba-dapymt were produced in the mixed system of both ligands: a new bond is formed between the 5-carbon atom of one ligand and the 2-sulfur atom of the other ligand as found in atuc-atuc. However, such an assembled ligand was not identified in the individual system of dapymt or tbba. These facts suggest that some kind of intermolecular interaction besides the reactivity at the 5-carbon atom is responsible for the assembled ligand formation.

References and Notes

1 K. Yamanari, M. Kida, M. Yamamoto, T. Fujihara, A. Fuyuhiro and S. Kaizaki, *Chem. Lett.*, **1993**, 1865.

2 R. M. Acheson, An Introduction to the Chemistry of Heterocyclic Compounds, John Wiley & Sons, 1976, ch. 8.

3 Nomenclature for complex with an assembled hetero-ligand $[Co\{L1\text{-}L2(2\text{-})\}]$: L2 indicates the coordinated ligand to Co(III) ion and L1 binds to the L2 ligand. The charge of L1-L2 is shown in parenthesis.

4 The molar absorption coefficients of complex **4** were determined based on the assumption that $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ value at 338 nm is the same as that at 334 nm of *trans(S)*-$[Co(dapymt)_2(en)]^+$.

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6 Crystal data for $[Co(C_8H_6N_6O_2S_2)(C_2H_8N_2)_2]ClO_4 \cdot 3H_2O$ at 296 K: Mw = 614.9, 0.25 × 0.20 × 0.30 mm, trigonal, $P3_121$ (no.152), a = 17.660(3), c = 13.484(3) Å, V = 3642.03(3) $Å^3$, Z = 6, R(Rw) = 0.109(0.110) for 1874 independent reflections with $I > 3\sigma(I)$. Selected bond distances (Å): Co-S(1) = 2.32(1), Co-N(1) = 1.91(1), Co-N(2) = 1.94(2), Co-N(3) = 1.96(2), Co-N(4) = 1.97(3) and Co-N(5) = 1.94(2). The structure was solved by direct methods and refined by full-matrix least-squares. The hydrogen atoms are located in calculated positions. All calculations were performed using the TEXSAN[7] crystallographic software package.

7 TEXRAY Structure Analysis Package, Molecular Structure Corporation: 3200A Research Forest Drive, The Woolands, TX 77381, 1985.

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