Aromatic Iodine-Assisted Self-assembly of a Cobalt(II) Complex of Ferron (Ferron = 7-iodo-8-hydroxyquinoline-5-sulfonate)

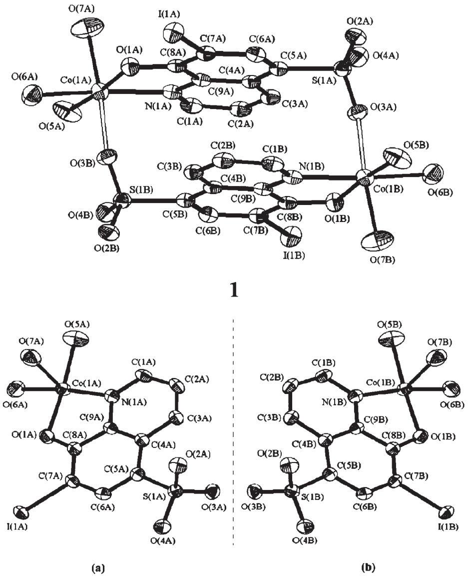
Feng Zhang,[†,††] Yi-Zhi Li,[†] Xu Gao,[††] Hui-Lan Chen,[†] Qi-Tao Liu,[††] Akira Odani,[†††] and Osamu Yamauchi*[††††]
[†]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*
[††]*Institute of Chemical Science and Engineering, Liaoning University, Shenyang 110036, P. R. China*
[†††]*Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602*
[††††]*Faculty of Engineering, Kansai University, Suita, Osaka 564-8680*

(Received January 26, 2004; CL-040096)

A dimeric Co(II) complex of ferron (=7-iodo-8-hydroxyquinoline-5-sulfonate) was isolated as crystals and structurally characterized. Weak I···H and I···C interactions involving the iodoquinoline rings and complementary steric requirements for I···I contacts led to self-assembly of the complex, which indicates versatile nature of the iodine atom in intermolecular interactions.

Iodine is the heaviest element among the essential biological elements. It is used by nature as a functional group in thyroid hormones,[1] which are iodinated derivatives of the tyrosine residues from thyroglobin. The iodophenol moieties are important for keeping the hormones' semi-rigid configurations[2] and contribute remarkably to the hormone–protein binding affinity,[3] but specifically what role the iodo groups play in the hormone–receptor binding event is still obscure. In view of this and the fact that aromatic chloro compounds, dioxins and polychlorinated biphenyls, are known as endocrin-disrupting chemicals which bind hormone receptors,[4] information on the intermolecular interactions of aromatic halo compounds is of urgent importance.

Attractive interactions of the iodine atom with aromatic rings and nucleophiles containing atoms such as O, N, S, and Se have been observed in a variety of systems.[5] The iodine–iodine contacts for various extended polyiodide anions in macrocyclic thioethers,[6] helical complex templates,[7] and iodophosphonium salts[8] exhibit a wide range of distances and geometries accommodating the steric requirements. Iodine has been used in the synthesis of donor–acceptor charge-transfer materials with unusual electrical behavior.[9] These findings indicate that iodine is versatile in interacting with various groups through noncovalent or weak interactions and adaptable to the stereochemistry of a given environment. To date, there are few examples of self-assembled structures containing iodo-substituted aromatic rings as building blocks, and structural information on the functions of the iodo groups in the thyroid hormone–receptor binding process is still lacking. We studied previously the Cu(II) complexes of 3-iodo- and 3,5-diiodotyrosinates[10] and revealed various weak interactions of the iodo groups leading to molecular assembly. The aromatic iodo group which is covalently bound to an aromatic ring may serve as an efficient template and knot in supramolecule construction. Here we report the Co(II) complex of a chelating reagent, ferron (=7-iodo-8-hydroxyquinoline-5-sulfonate) having the same local structure as Chinoform (Clioquinol), and its self-assembly assisted by the aromatic iodo group both as an electron donor and acceptor and a structure-supporting template.



1

Figure 1. ORTEP views of the homobimetallic complex $[Co(ferron)(H_2O)_3]_2$ (**1**) formed by the complementary sulfonato coordination to enantiomers **a** and **b**. Selected bond lengths [Å] and angles [°]: Co(1A)–O(1A), 2.065(2); Co(1A)–N(1A), 2.092(3); Co(1)–O(3B), 2.191(2); Co(1A)–O(5A), 2.088(17); Co(1A)–O(6A), 2.039(2); Co(1A)–O(7A), 2.132(3); O(7A)–Co(1A)–O(3B), 175.9(1); S(1A)–O(3A)–Co(1B), 139.9(1).

Single crystals of $[Co(ferron)(H_2O)_3]_2 \cdot 4H_2O$ (**1**) suitable for X-ray structure analysis were obtained in 54% yield.[11] X-ray structure analysis[12] showed that complex **1** is a dimeric cobalt (II) complex having an octahedral coordination geometry with an axial position complementarily occupied by one of the sulfonato oxygens (Figure 1). The quinoline rings symmetrically stacked with each other in a face-to-face manner with the average distance of 3.11 Å. The complex is composed of enantiomers **a** and **b** bound through the axial coordination of the sulfonate oxygen. The most striking structural feature is that the iodo groups are arranged in pairs with a distance of 4.08 Å according to their complementary steric requirements and located just between the hydrogen atoms of quinoline C(1) and C(6) from the neighboring complex molecule (Figure 2). The I···I distance is slightly longer than the van der Waals distance determined by Bondi (3.96 Å)[13] but shorter than that by Pauling (4.30 Å),[14] and the contact may be regarded as a spatial shape-fitting of the iodine atoms or as a weak interaction. The I···H distances (3.02 and 3.09 Å) are distinctly shorter than the van der Waals distance of 3.18 Å, indicating weak bonding interactions between the two atoms. The complex molecules were further tightly packed with one another by self-recognition of enantiomers **a** and **b** through partial face-to-face zig-zag stacking of the quinoline rings and iodine–quinoline ring contacts (Figure 3).

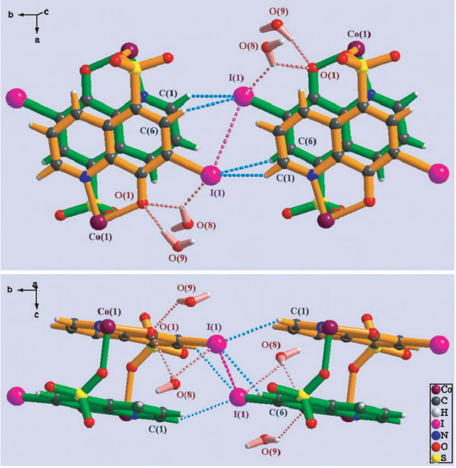


Figure 2. Modes of complementary iodine–iodine interactions and hydrogen bonds between the phenoxide oxygen and water molecules. The enantiomers **a** and **b** are colored orange and green, respectively. The coordinated water molecules were omitted for clarity. Selected distances [Å]: I(1)···I(1)[a], 4.08(1); I(1)···H(6)[a], 3.088(3); I(1)···C(6)[a], 3.807(5); I(1)···H(1)[b], 3.016(1); I(1)···C(1)[b], 3.712(2) [symmetry codes: [a] 1.5−x, 1.5−y, 1−z; [b] x, 1+y, z].

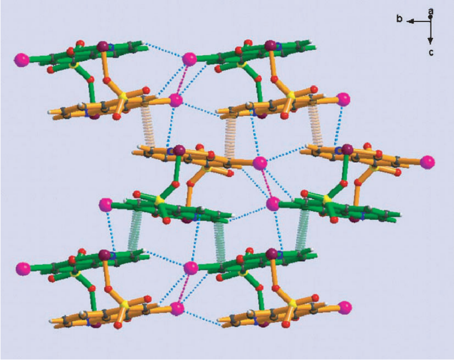


Figure 3. Intermolecular shape-fitting embedding of the stacked rings.

The stacked rings of the dinuclear complex molecules are tilted to each other by an angle of 16.5°, with the closest C···C distance of 3.30 Å. The iodine atom contacts with C(3) of the neighboring quinoline with a distance of 3.78 Å, which is in between the reported van der Waals distances of 3.68[13] and 3.85 Å.[14] These weak interactions are supported by the zig-zag oriented hydrogen bonds between the sulfonato oxygens and coordinated water molecules, leading to the characteristic complex layer construction. Efficient bridging by the sulfonato group may be attributed to the iodine's template effect and the quinoline–quinoline stacking interaction.

These results suggest that the aromatic iodo group in metal complexes may play an important role in intermolecular interactions and thus in stabilizing supramolecular structures by I···H, I···C, and I···I interactions as well as other interactions we reported previously.[10] The modes of the interactions involving the iodine atom may also be important for the recognition process of the self-assembly in solution and the thyroid hormone–receptor binding event. The present study shows that the iodine atom is an effective binding site and structural factor in molecular architecture and suggests that the halo groups of endocrine-disrupting chemicals may contribute to the receptor binding in similar manners.

This work was supported by the State Postdoctoral Research Grant (No. 0205003021 to F.Z.), the Natural Science Foundation of China (No. 29971014 to F.Z. and No. 20071017 to H.L.C.), and the Grant-in-Aid for Scientific Research (No. 13440202 to O.Y.) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 a) R. M. Evans, *Science*, **240**, 889 (1988). b) R. L. Wagner, J. W. Apriletti, M. E. McGrath, B. L. West, J. D. Baxter, and R. J. Fletterick, *Nature*, **378**, 690 (1995).

2 a) T. A. Andrea, S. W. Dietrich, W. J. Murray, P. A. Kollman, and E. C. Jorgensen, *J. Med. Chem.*, **22**, 221 (1979). b) V. Cody, *Endocr. Rev.*, **1**, 140 (1980). c) N. Okabe, T. Fujiwara, Y. Yamagata, and K.-I. Tomita, *Biochim. Biophys. Acta*, **717**, 179 (1982).

3 T. A. Andrea, R. R. Caralieri, I. D. Golafine, and E. C. Jorgensen, *Biochemistry*, **19**, 55 (1980).

4 A. Soto, C. Sonnenschein, and T. Colborn (Eds), *Comments Toxicol.* (Special Issue), **5**, 315 (1996).

5 a) V. Cody, *J. Mol. Struct.*, **112**, 189 (1984). b) P. Y. Cheng, D. Zhong, and A. H. Zewail, *Chem. Phys. Lett.*, **242**, 369 (1995). c) M. C. Aragoni, M. Arca, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, and G. Verani, *Coord. Chem. Rev.*, **184**, 271 (1999).

6 A. J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek, and M. Schröder, *Chem. Soc. Rev.*, **27**, 195 (1998).

7 C. J. Horn, A. J. Blake, N. R. Champness, A. Garau, V. Lippolis, C. Wilson, and M. Schröder, *Chem. Commun.*, **2003**, 312.

8 W. W. Du Mont and F. Ruthe, *Coord. Chem. Rev.*, **189**, 101 (1999).

9 J. R. Ferraro and J. M. Williams, "Introduction to Synthetic Electrical Conductors," Academic Press, New York (1987).

10 a) F. Zhang, A. Odani, H. Masuda, and O. Yamauchi, *Inorg. Chem.*, **35**, 7148 (1996). b) F. Zhang, T. Yajima, H. Masuda, A. Odani, and O. Yamauchi, *Inorg. Chem.*, **36**, 5777 (1997). c) F. Zhang, T. Yajima, A. Odani, and O. Yamauchi, *Inorg. Chim. Acta*, **278**, 136 (1998).

11 $[Co(ferron)(H_2O)_3]_2 \cdot 4H_2O$ (**1**) was synthesized by dropping 1.0 equiv of 0.050 M $CoCl_2$ into an aqueous MeOH solution (50 v/v%) of ferron·HCl (193.8 mg, 0.50 mmol) obtained from Sigma. Yield: 134.5 mg, 54%. Anal. Calcd for $C_{18}H_{28}N_2Co_2I_2O_{18}S_2$: C, 21.70; H, 2.83; N, 2.81%. Found: C, 21.84; H, 2.27; N, 2.77%.

12 X-ray structure determination of **1** was performed on a Siemens Apex SMART-CCD diffractometer with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was carried out at room temperature in the range of $2.24° \le \theta \le 26.00°$. Absorption correction was applied by SADABS (Bruker, 2000). The structure was solved by the direct method and refined using full-matrix least-squares (on F^2) (SHELXTL, Bruker, 2000). All nonhydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically, and refined isotropically. Crystal data: $C_{18}H_{28}Co_2I_2N_2O_{18}S_2$, $M_r = 996.21$, monoclinic, $C2/c$ space group, $a = 22.350(2)$, $b = 10.011(2)$, $c = 13.386(3)$ Å, $\beta = 102.030(10)°$, $V = 2929.3(9)$ Å^3, $Z = 4$, $D_{calcd} = 2.259$ mg·cm^{-3}, $\mu = 3.467$ mm^{-1}, $R_1 = 0.0265$ for 2615 reflections [$I > 2\sigma(I)$], and $wR_2 = 0.0755$ for all 2883 unique reflections (209 parameters). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-231992.

13 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

14 L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca (1960), p 260.

Published on the web (Advance View) April 12, 2004; DOI 10.1246/cl.2004.556