



Synthesis and characterization of a dipyridocatecholate silicon complex



David A. Lee, Sang K. Moon, Adrian N. Sizeland, Nicholas W. Gould, Eshere M. Gbarbea, Deborah Owusu, Daniel S. Jones, Thomas A. Schmedake*

Department of Chemistry, University of North Carolina-Charlotte, Charlotte, NC 28223, USA

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ABSTRACT

The reaction of $[\text{Si}(\text{bpy})_2\text{I}_2]$ with 1,10-phenanthroline-5,6-dione followed by metathesis provides various salts of $[\text{Si}(\text{bpy})_2(\text{dpcat})]^{+2}$ (**1**, bpy = 2,2'-bipyridine and dpcat = dipyridocatecholate). Recrystallization of $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{ClO}_4)_2$ from an aqueous solution of NaClO_4 afforded orange crystals of $\text{Na}[\text{Si}(\text{bpy})_2(\text{dpcatH})](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ (**2**), in which silicon possesses a distorted octahedral geometry. The dipyridocatecholate ligand is coordinated to the silicon through the oxygen atoms, and one of the nitrogen atoms is protonated. ²⁹Si NMR and ESI-mass spectroscopy indicate $[\text{Si}(\text{bpy})_2(\text{dpcat})]^{+2}$ maintains its hexacoordinate structure in solution. The complex is stable with respect to hydrolysis, and degassed aqueous solutions luminesce at 410 nm.

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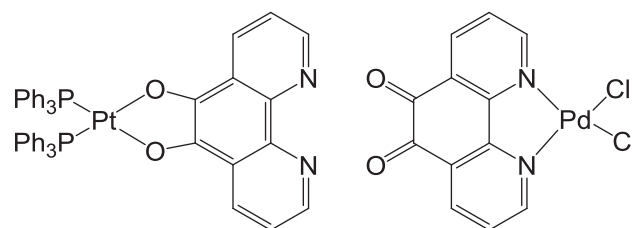
The ligand 1,10-phenanthroline-5,6-dione is a versatile ligand in transition metal coordination chemistry since it possesses both quinone and diimine functionality. The ambidentate bonding ability was demonstrated by Balch in synthesizing an O,O'-dipyridocatecholate complex of platinum and an N,N'-phenidione complex of palladium (Scheme 1) [1]. Transition metal complexes of phenidione have since been explored in applications such as catalysis [2–4], sensing [5], and non-linear optics [6]. Its role as a bridging ligand between metal centers has been demonstrated and explored [7–10]. Furthermore, N,N'-phenidione complexes can act as precursors for DNA-active dipyrrophenazine complexes [11] and tetrapyrrophenazine (tpphz) bridged polynuclear complexes [12].

Our group is interested in robust, redox active hexacoordinate silicon analogs of transition metal complexes, and reviews of the hexacoordinate silicon chemistry literature point to diimine and catecholate ligands as particularly good ligands for targeting such novel hydrolytically stable complexes [13,14]. We recently showed that $\text{Si}(\text{bpy})_3^{+4}$ and $\text{Si}(\text{terpyridine})_2^{+4}$ complexes can be reduced with up to six electrons, and that both species exhibit counter-ion dependent outer sphere charge transfer bands spanning the entire visible spectrum [15]. Xiang recently demonstrated $\text{Si}(1,10\text{-phenanthroline})_2(\text{arenediolate})^{+2}$ complexes have biological activity, with a high binding constant $1.7(\pm 0.6) \times 10^6 \text{ M}^{-1}$ for calf thymus DNA [16]. Silicon complexes of 1,10-phenanthroline-5,6-dione would be particularly interesting due to the ligands previously mentioned electronic, chemical, and bridging

properties. Consequently, we initiated the following study to explore the binding mode of phenidione in hexacoordinate silicon complexes.

Phenidione [17] was combined with $[\text{Si}(\text{bpy})_2\text{I}_2]$ [18] in pyridine and heated inside a sealed ampoule to generate a dark red precipitate in a 70% yield, determined to be $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{I}^-)(\text{I}_3^-)$ based on elemental analysis, ESI-mass spectroscopy, and NMR spectroscopy (Scheme 2) [19]. The product was consistent with a mechanism in which phenidione displaced iodides to generate an intermediate $[\text{Si}(\text{bpy})_2(\text{O}, \text{O-phenidione})]^{+4}$, which could then be reduced by two iodide ions to form $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{I}^-)(\text{I}_3^-)$. Alternatively, $[\text{Si}(\text{bpy})_2(\text{dpcat})]\text{I}_2$ can be synthesized by refluxing dipyridocatechol with $[\text{Si}(\text{bpy})_2\text{I}_2]$ in acetonitrile.

After many unsuccessful attempts to grow X-ray quality crystals of **1** with a variety of counter-ions and solvents, we were able to obtain suitable orange rectangular crystals (monoclinic, P2₁/c space group) from an aqueous solution of $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{ClO}_4)_2$ and excess NaClO_4 [20]. The crystal structure contains one protonated **1**,



O,O'-dpcat

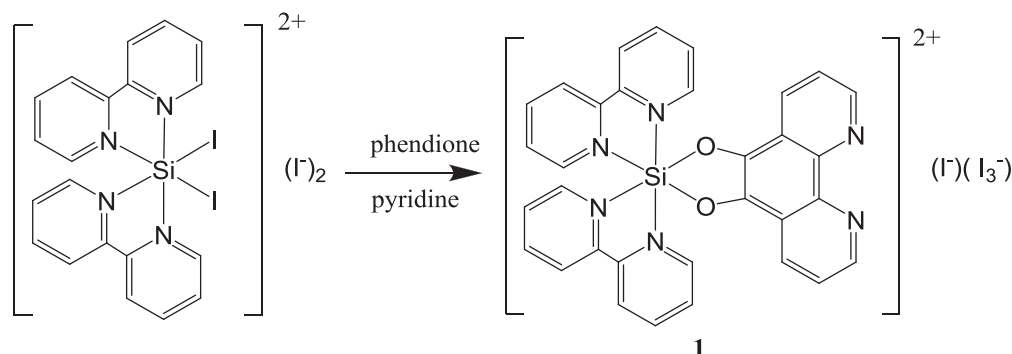
N,N'-phenidione

Scheme 1. Ambidentate bonding modes demonstrated by Balch.

* Corresponding author at: UNC Charlotte, Department of Chemistry, 9201 University City Blvd, Charlotte, NC 28223. Tel.: +1 704 687 4011; fax: +1 704 687 3151.

E-mail address: tschmeda@uncc.edu (T.A. Schmedake).

URL: <http://www.chemistry.uncc.edu> (T.A. Schmedake).



Scheme 2. Synthesis of $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{I}^-)(\text{I}_3^-)$.

$[\text{Si}(\text{bpy})_2(\text{dpcatH})]^{+3}$, in the asymmetric unit with 3 perchlorate counter-ions, along with 1 equivalent of NaClO_4 and 3 water molecules. The silicon has a distorted octahedral geometry with an O–Si–O bond angle of $92.17(4)^\circ$ (Fig. 1).

The hexacoordinate geometry of the $[\text{Si}(\text{bpy})_2(\text{dpcat})]^{+2}$ ion is maintained in solution. ESI-MS confirmed the presence of the $[\text{Si}(\text{bpy})_2(\text{dpcat})]^{+2}$ ion in solutions of $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{I})(\text{I}_3)$ in water and $[\text{Si}(\text{bpy})_2(\text{dpcat})](\text{PF}_6)_2$ in acetonitrile. ^{29}Si NMR data also was consistent with a hexacoordinate silicon complex in solution, with a peak at -148.3 ppm (vs. TMS). In addition, aqueous solutions of $[\text{Si}(\text{bpy})_2(\text{dpcat})]\text{Cl}_2$ showed no signs of ligand scrambling or hydrolysis after one week. UV–vis and fluorescence spectroscopy were

performed on aqueous solutions of $[\text{Si}(\text{bpy})_2(\text{dpcat})]\text{Cl}_2$ (4×10^{-5} M) (Figs. 2 and 3). The UV–vis spectrum shows several strong UV–vis peaks around 310 nm and a weaker band around 390 nm. The degassed aqueous solution emits with peaks in the UV region around 330 nm and a broad lower energy peak at 410 nm. In both spectra we tentatively attribute the lowest energy peak to an intraligand transition, based on previous assignment of an emission peak at 420 nm for (dpcat)Pt(dbbpy) and similar peaks observed in other complexes containing the (dpcat)Pt(dbbpy) moiety (dbbpy = 3,5-di-tert-butylcatecholate) [8].

In conclusion, the $[\text{Si}(\text{bpy})_2(\text{dpcat})]^{+2}$ ion has been synthesized and the crystal structure of $\text{Na}[\text{Si}(\text{bpy})_2(\text{dpcatH})](\text{ClO}_4)_4 \cdot 3\text{H}_2\text{O}$ was

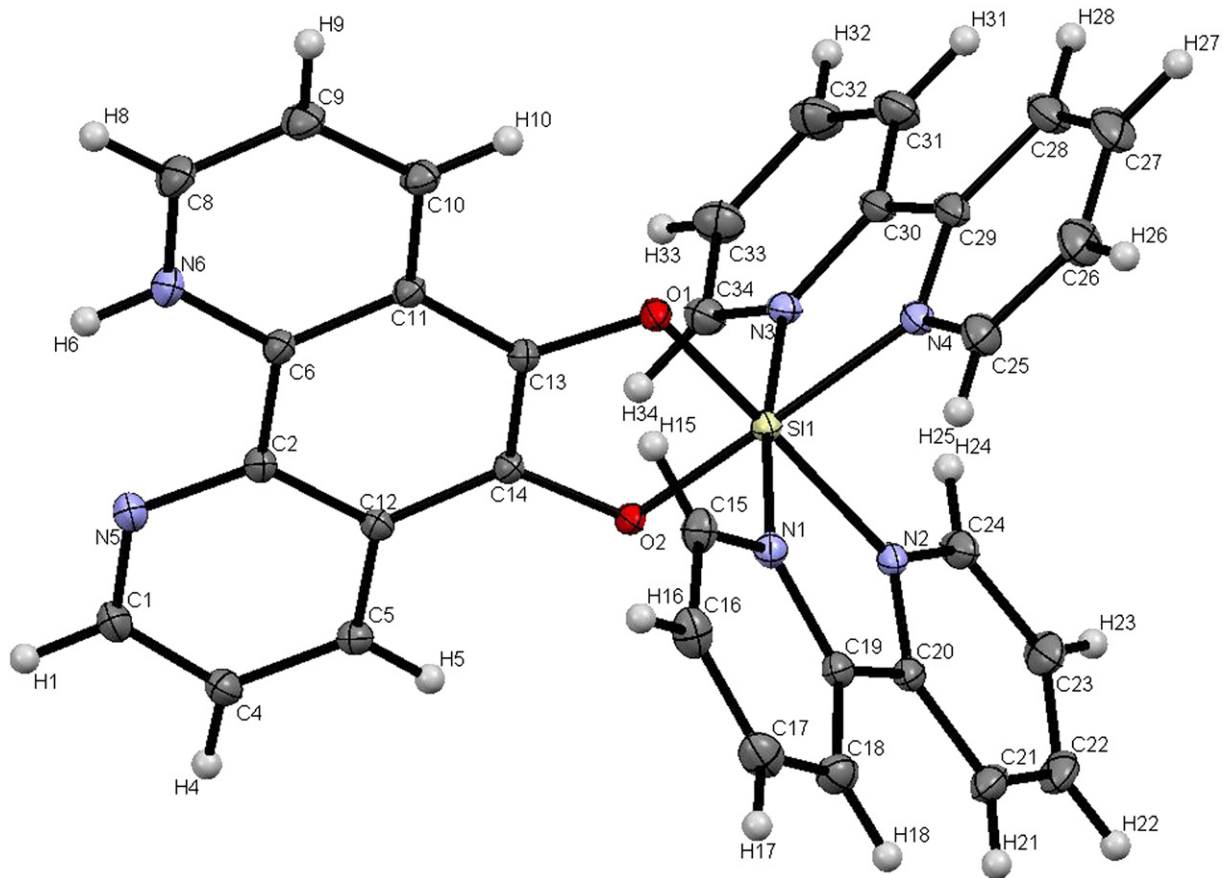


Fig. 1. Molecular structure of $[\text{Si}(\text{bpy})_2(\text{dpcatH})]^{+3}$ ion (other ions and solvent molecules excluded for clarity) and selected bond distances (Å) and angles ($^\circ$): N1–Si 1.923(1), N2–Si 1.929(1), N3–Si 1.907(1), N4–Si 1.924(1), O1–Si 1.7229(9), O2–Si 1.7491(9), C13–O1 1.359(1), C14–O2 1.368(1), N1–Si–N2 82.25(5), N1–Si–N4 93.23(5), N3–Si–N1 173.31(5), N3–Si–N2 92.40(5), N3–Si–N4 82.78(5), N4–Si–N2 90.74(5), O1–Si–N1 92.64(5), O1–Si–N2 174.79(5), O1–Si–N3 92.62(5), O1–Si–N4 88.53(4), O1–Si–O2 92.17(4), O2–Si–N1 90.64(4), O2–Si–N2 88.92(4), O2–Si–N3 93.29(5), O2–Si–N4 176.04(5).

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