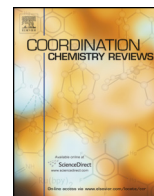




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Recent advances in hexacoordinate silicon with pyridine-containing ligands: Chemistry and emerging applications

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ABSTRACT

The chemistry of hexacoordinate silicon complexes containing one or more pyridine-like ligands is reviewed. Pyridine-containing ligands are excellent ligands for stabilizing hexacoordinate silicon complexes, and over 100 hexacoordinate silicon complexes containing at least one pyridine-like ligand have been deposited with the Cambridge Structural Database. This review focuses on advances since 2000

Abbreviations: ace, acetone; all, allyl; apip, 4-[[2-(methylamino)phenyl]imino]-2-pentanone; baquin, *N*-8-quinolinylbenzamide; B3LYP, Becke 3-parameter, Lee, Yang, and Parr basis set; binolato, 1,1'-binaphthalene-2,2'-diolato; bipy/bpy, 2,2'-bipyridine; Bn, benzyl; bp, 1,1'-biphenyl-2,2'-diolato; BP86, Becke 88, Perdew 86 basis set; bq, 1,2-benzoquinone-4,5-diolato; brcat, 4,5-dibromocatecholato; brpy, 3-bromopyridine; Bu, butyl; cat, catecholato; C≡CPh, 2-phenylethynyl; CD, circular dichroism; COSMO, conductor-like screening model; Cp*, pentamethylcyclopentadienyl; CP/MAS, cross polarization magic-angle spinning; CSD, Cambridge Structural Database; CV, cyclic voltammetry; DCM, dichloromethane; dcm, dichloromethyl; dcms, dichloro(methyl)silyl; DFT, density functional theory; diba, *N,N'*-diisopropylbenzamidine; Dipic, pyridine-2,6-dicarboxylate; DMAP, 4-(*N,N*-dimethylamino)pyridine; DMSO, dimethylsulfoxide; DNA, deoxyribonucleic acid; dpcaH, 1-*H*-1,10-phenanthroline-5,6-diolato; dped, *N,N'*-diphenylethylenediamine; dppz, dipyrido[3,2-*a*:2',3'-*c*]phenazine; DSC, differential scanning calorimetry; eg, 1,2-ethylenediolato; EL, electroluminescent; epy, 4-ethylpyridine; e.r., enantiomeric resolution; Et, ethyl; Fc, ferrocene; HOMO, highest occupied molecular orbital; imp, 2-(iminomethyl)-phenolato; LUMO, lowest unoccupied molecular orbital; lut, lutidine; icat, 4-iodocatecholato; ⁱPr, isopropyl; mbpy, 4,4'-dimethyl-2,2'-bipyridine; mcat, 4-methylcatecholato; Me, methyl; MeCN, acetonitrile; MLCT, metal-to-ligand charge transfer; mquin, 2-methyl-8-oxyquinolato; ncat, 4,5-dinitrocatecholato; NCO, isocyanato; NCS, isothiocyanato; NMR, nuclear magnetic resonance; OLED, organic light-emitting diode; OMe, methoxy; OPh, phenolato; OSiCl₃, trichlorosilyloxy; OTf, trifluoromethanesulfonato; PC, personal communication; pc, phthalocyanine; Pent, pentyl; Ph, phenyl; PhBP^{Ph}₃, tris[(diphenylphosphino)methyl](phenyl)borate; phen, 1,10-phenanthroline; phn, 9,10-phenanthrenediolato; phpy, 4-phenylpyridine; pic, picoline; pip, 4-[(2-phenolato)imino]-2-pentanone; PL, photoluminescent; Pr, propyl; Py/pyr, pyridine; pyre, pyrene-4,5-diolato; PYBOX, 2,6-bis(2-oxazolonyl)pyridine; PyS, pyridine-2-thiolato; qin, 1-[(8-quinolinylimino)methyl]-2-naphthalenolato; qip, 2-[(8-quinolinylimino)methyl]-phenolato; quin, 8-oxyquinolato; quinS, 8-thioquinolato; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; R.T., room temperature; TBAPF₆, tetra-*N*-butylammonium hexafluorophosphate; ^tBupy, 4-*tert*-butylpyridine; tcm, trichloromethyl; tcs, trichlorosilyl; tcsm, (trichlorosilyl)dichloromethyl; terpy, 2,2':6',2''-terpyridine; tfbm, α,α-bis(trifluoromethyl)benzenemethanolato; THF, tetrahydrofuran; TMEDA, tetramethylethylenediamine; tol, toluene; ttip, 4-[(2-thiophenolato)imino]-2-pentanone; TPP, tetraphenylporphyrin; TZ2P, triple zeta double polarization; VACP/MAS, variable amplitude cross polarization magic-angle spinning; vpy, 4-vinylpyridine; ZORA, zeroth order regular approximation.

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and covers complexes with substituted pyridines, pyridine-2-thiolates, oxyquinolates, thioquinolates, iminoquinolates, bipyridines, phenanthrolines, and terpyridines. Emerging applications in fluorescence, high-energy materials, biology, and electrochromism are discussed.

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1. Introduction

Pyridine-containing ligands are prevalent throughout the field of coordination chemistry. This review will focus on the chemistry and emerging applications of hexacoordinate silicon with one or more pyridine-containing ligands (Fig. 1). These ligands are particularly significant for a number of reasons. (1) Multidentate pyridine-containing ligands are particularly good at stabilizing hexacoordinate silicon compounds, and a wide variety of complexes have been isolated and structurally characterized (Tables 1–3). (2) Despite the hydrolytic susceptibility of the Si–N bond in tetrahedral silicon complexes, some of these complexes are quite resistant to hydrolysis and are even stable in aqueous solutions. (3) The non-innocence of pyridine-containing ligands provides opportunities to explore the ligand-localized redox activity of these complexes. (4) The complexes can act as d-electron free analogs of ubiquitous transition metal coordination complexes in applications where MLCT bands are not needed or are undesired. Much of the early (pre-2000) coordination chemistry of hexacoordinate silicon complexes with pyridyl-containing ligands has been extensively reviewed in a number of comprehensive reviews, and several more recent reviews have covered other significant areas of hexacoordinate silicon chemistry [1–10]. This comprehensive review covers the literature since 2000 on the subject of hexacoordinate silicon with pyridine-containing ligands and discusses possible future directions in the field. It also includes data and references on all of the structurally characterized hexacoordinate silicon complexes with one or more pyridine-containing ligands that have been deposited with the Cambridge Structural Database. The review is structured according to ligand type starting with monodentate pyridine and substituted pyridines along with bidentate 2-substituted pyridines. The next section reviews complexes with quinoline-type ligands. Finally, complexes with polypyridine ligands (2,2-bipyridine, phenanthroline, and terpyridine) are reviewed.

2. Pyridine-type ligands

2.1. Complexes with pyridine

Silicon tetrahalides are very Lewis acidic and readily form adducts through direct combination with pyridine. A search of

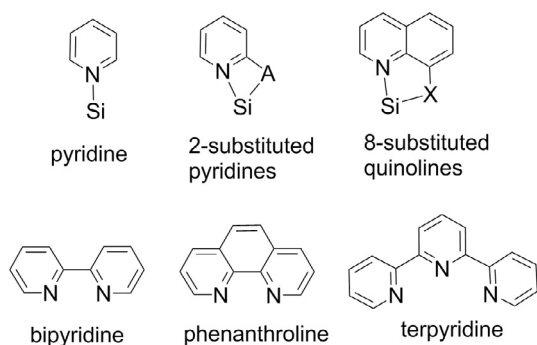


Fig. 1. Types of pyridine-containing ligands observed in hexacoordinate silicon complexes.

the CSD database produced crystal structures of 43 hexacoordinate silicon complexes containing at least one monodentate pyridine or substituted pyridine ligand (Table 1). For unsubstituted pyridine the range of Si–N bond lengths is quite small, 1.93–2.02 Å, with the shortest bond length reported for *trans*-tetrafluorobis(pyridine)silicon [11] and the longest bond in the pentafluoro(pyridine)silicate anion [12]. Significantly, all of the di-substituted complexes exist solely in the *trans* orientation. However, several tetra-substituted complexes demonstrate the ability of the silicon center to accommodate pyridine ligands separated by only 90°. The greater basicity of the 4-dimethylaminopyridine ligand (DMAP) is apparent in the shorter Si–N bond lengths (1.90–1.92), which is just outside the range of all other hexacoordinate pyridine-silicon complexes. The DMAP ligand was also shown to coordinate to the electrophilic silicon center of [PhBP^{Ph}₃]RuH(η^3 -H₂SiRR') (R,R' = Ph, Me or Ph, Ph) to form the corresponding hexacoordinate complexes [PhBP^{Ph}₃]Ru(μ -H)₃SiRR'(DMAP) [13].

The reactivity of hexacoordinate pyridine complexes has inspired a few potential applications. Besgubenko and coworkers explored the possibility of using *trans*-dichlorotetrakis(DMAP)silicon dichloride as an alternative to carbodiimides as a dehydrating agent for amide bond formation, but found it inferior to the analogous *N*-methylimidazole complex due to the latter's greater hydrolytic stability [14]. Likewise, Churakov and coworkers demonstrated Si(pyridine)₂F₄ along with other SiF₄ adducts as a potential precursor for fluorosilatrane [15,16].

Goldvasser has explored the reversible complexation of trifluorosilanes with pyridines for potential molecular self-assembly [17–19]. They report NMR evidence of complexation at low temperatures for phenyltrifluorosilane with pyridine and 4-methoxypyridine to form the hexacoordinate species. Complexation with pyridine and 4-methoxypyridine was observed at room temperature with the more electron deficient trifluoro(pentafluorophenyl)silane. Extensive multinuclear evidence indicates exclusive formation of the *trans*-pyridine isomers.

Pyridine ligands have also been used as axial ligands in silicon porphyrins and phthalocyanines. Cissell and coworkers synthesized two silicon(IV) tetraphenylporphyrins, Si(TPP)(pyridine)₂ and Si(TPP)Cl₂ [20,21]. Similar chemistry also afforded the phthalocyanine analog, Si(pc)(pyridine)₂ from Si(pc)Cl₂ [22]. As seen in Fig. 2, the TTP ligand in Si(TTP)Cl₂ possesses a fully oxidized –2 oxidation state (18 electrons), while the TTP ligand in the pyridine coordinated analog possesses a –4 oxidation state (20 electrons). The latter is synthesized by reducing Si(TPP)Cl₂ with 2 equiv. of Na/Hg in THF followed by precipitation and then dissolution in pyridine. Si(TPP)Cl₂ has a fluorescence yield of 2.7% and a lifetime of 1.8 ns, while the reduced pyridine analog has a fluorescence yield $\leq 0.04\%$ and a lifetime of 2.4 ps. The significantly shortened lifetime was attributed to the ruffled structure adopted by the antiaromatic 20 electron porphyrin system and the introduction of low-energy singlet states lying below the emissive state (Q-state).

2.2. Complexes with pyridine-2-thiolate

The ambidentate pyridine-2-thiolato (PyS) ligand has been used to obtain a range of stable, hexacoordinate silicon complexes (Table 1). The reaction of 2 equiv. of 2-mercaptopyridine and

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