Chelating Ligands

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Stable Five- and Six-Coordinate Cobalt(III) Complexes with a Pentadentate Bispidine Ligand**

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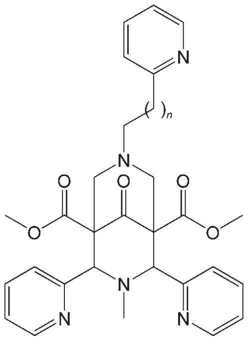
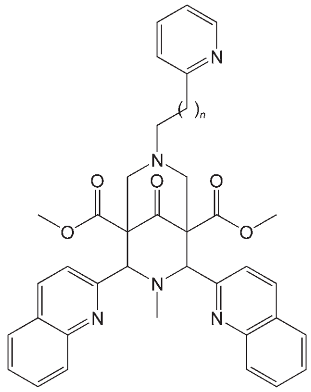
Cobalt(III) complexes are classics in coordination chemistry,[1–3] and pentaamine as well as hexaamine Co^{III} complexes generally have a low-spin d^6 electronic configuration with little distortion from an ideal octahedral coordination geometry.[4,5] Among the 2859 X-ray structures of {Co^{III}(N)$_5$(X)$_n$} species ($n = 0,1$) in the CSD[6] there are only 18 pentacoordinate complexes ($n = 0$). Most of these are systems with electron-rich, often anionic ligands, and many are derived from macrocyclic ligand systems,[7–11] largely as a result of extensive modeling studies of vitamin B$_{12}$.[12,13] Para- as well as diamagnetic square-pyramidal[14] and trigonal-bipyramidal[8] systems have been reported, and, in the course of the search for the elusive Co=O functional group,[15] a tetracoordinate amido–Co^{III} complex was also structurally characterized.[11] All these complexes have interesting reactivities that are not observed in classical Co^{III} systems, such as the efficient production of alkyl radicals[16] and C–H activation.[11]

Herein, we report the synthesis and structural characterization as well as an MM- and DFT-based interpretation (molecular mechanics, density functional theory) of the geometric and electronic structures of a pair of hexa- and pentacoordinate Co^{III} complexes of the same, electronically "innocent", pentadentate bispidine ligand L^1. Single-crystal X-ray structural analyses of the corresponding Co^{II}, Cu^{II}, and Zn^{II} complexes, as well as structures of the complexes with the quinoline-based ligand derivative L^2 are also reported. The amine–pyridine-based chelate ligand produces stable Co^{II} as well as five- and six-coordinate Co^{III} complexes. Interestingly, the bispidine derivatives L^{1a} and L^{2a} with a methylene- instead of an ethylene-bridged pyridine donor only produce the usual six-coordinate Co^{III} complexes, that is, the size of the corresponding chelate ring is a critical feature for the bond strength to the monodentate coligand in the sixth coordination site.



L^1: n=1
L^{1a}: n=0



L^2: n=1
L^{2a}: n=0

The study of first-row transition-metal coordination chemistry of a wide range of tetra-, penta-, and hexadentate bispidine-type ligands with various donor sets[17] has revealed a number of interesting properties (e.g., various types of isomerism, uncommon complex stabilities, unexpected electron-transfer properties, efficient Cu-catalyzed aziridination, novel Cu-, Fe-, and Co-based oxygen activation pathways). Many of these properties are the result of the coordination geometries enforced by the rigid bispidine backbone, as well as the potential energy surface, which shows steep walls and various minima with similar energy that may be stabilized by careful, ligand-based tuning (high elasticity of the coordination geometry). The facile switching between coordination numbers and electronic structures in classical Co^{III} coordination chemistry is another example of how structure and properties can be enforced by bispidine ligands.

Crystal-structural analysis of [Cu(L^2)]$^{2+}$ revealed an unusual geometry of the Cu^{II} center, with elongation of the N$_{ar1}$–Cu–N$_{ar2}$ bonds and short metal–donor bonds to N3, N7, and N$_{py3}$, but a missing coligand at the fourth in-plane site *trans* to N7 (Figure 1, Table 1).[18] Interestingly, two different species, a hexacoordinate diamagnetic and a pentacoordinate paramagnetic complex (color, NMR, magnetism; see the Supporting Information), could be trapped during synthesis (chemical oxidation of the Co^{II} precursor) and workup of the Co^{III} complexes of L^1, depending on the solvent, temperature, and type as well as concentration of anions present. The two species, [Co(L$^{1'}$)]$^{3+}$ and [Co(L$^{1''}$)(OH)]$^{2+}$, were analyzed by X-ray crystallography (Figure 1, Table 1).[19,20] In contrast to these observations, the structures of the Co^{II} and Zn^{II} complexes of L^1 and L^2 are six-coordinate, and the metal–

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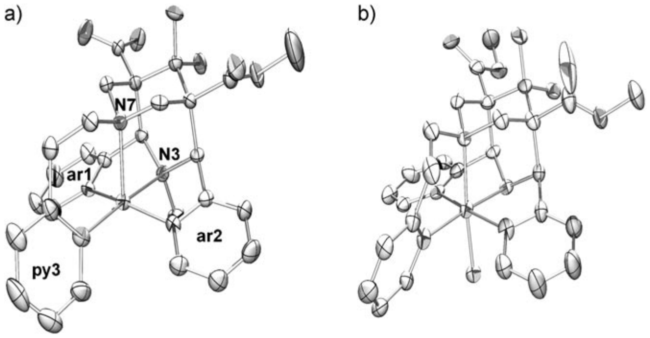

Figure 1. Structures of a) $[Co(L^{1'})]^{3+}$ and b) $[Co(L^{1''})(OH)]^{2+}$ (thermal ellipsoids set at 30% probability).

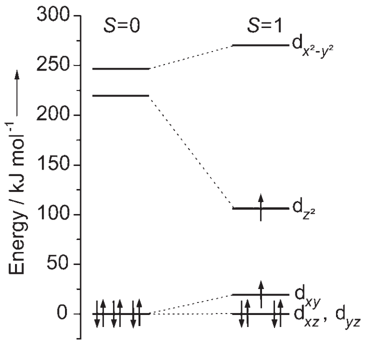

Figure 2. Simplified orbital scheme based on ADF calculations (BP86/TZP). The relative orbital energies are derived from the optimized hexacoordinate ($S=0$) and pentacoordinate ($S=1$) systems, respectively.

donor bond lengths are as expected from other bispidine complexes (Table 1).[17,21] There are no unusual coordination geometries with the parent ligands L^{1a} and L^{2a} with a smaller chelate ring involving N_{py3}.[17,18,20,21] Therefore, these experimental results suggest that the open N7–M–N_{py3} angle and the concomitant short M–N_{py3} bonds (specifically for Co^{III} and Cu^{II}) create a strong repulsive interaction between the α-H atom of py3 and the coligand X *trans* to N7. This repulsion is minimized by an elongation of the M–X bond, resulting in an increased splitting of the $d_{x^2-y^2}$ and d_{z^2} orbitals (stabilization of d_{z^2}). For Co^{III}, the resulting decrease of the energy gap between the t_{2g} and e_g orbitals (in O_h symmetry) stabilizes the intermediate-spin ($S=1$) excited state, which is further stabilized by elongation of the N7–Co–X axis (Figure 2). This pseudo-Jahn–Teller-derived mechanism (combination of steric and electronic preferences) eventually leads to dissociation of the monodentate coligand X. A similar situation is expected for Cu^{II} but not for high-spin Co^{II} and Zn^{II} complexes, which do not have an asymmetric occupation of the e_g orbitals (in O_h symmetry). In the case of Co^{III}, this effect stabilizes the unusual intermediate-spin electronic state, which for bispidine-type ligands is already relatively low in energy as a result of their relatively large ligand cavity.[17,20,22]

MM and DFT calculations were used to confirm these hypotheses. The quality of the DFT approach used (see the Experimental Section) is confirmed by the excellent agreement between computed and experimental structures and energetics (see Table 1 and the Supporting Information). On the B3LYP/TZVP level, the intermediate-spin pentacoordinate Co^{III} complex of L^1 is between 9 kJ mol^{-1} ($X = H_2O$) and 54 kJ mol^{-1} ($X = Cl^-$) higher in energy than the low-spin hexacoordinate state. An energy decomposition analysis (EDA, BP86/TZP) as a function of θ (N7-Co^{III}-N_{py3}) indicates that repulsion indeed is the reason for the destabilization of the diamagnetic ground state (Figure 3a), and this is supported both by the computed HOMO–LUMO energy barrier of $[Co(L^1)(NCCH_3)]^{3+}$ as a function of θ (Figure 3b) and by force-field calculations (Figure 3c).

Table 1: Selected experimental and computed structural data and relative energies of the transition-metal complexes of L^1 and L^2.[a]

Parameter	$[Co^{III}(L^{1'})]^{3+}$ *(comput: $S=1$)*	$[Co^{III}(L^{1''})(OH)]^{2+}$ *(comput: $S=0$; $X=OH_2$)*	$[Co^{II}(L^1)(Cl)]^+$ *(comput: $S=3/2$)*	$[Co^{II}(L^2)(Cl)]^+$ *(comput: $S=3/2$)*	$[Cu^{II}(L^1)]^{2+}$	$[Cu^{II}(L^2)]^{2+}$[b]	$[Zn^{II}(L^1)(OH_2)]^{2+}$	$[Zn^{II}(L^2)(OH_2)]^{2+}$
M–N3	1.998 (5)	1.904 (3)	2.186 (4)	2.167 (2)	2.0108 (10)	1.953 (2)	2.220 (6)	2.179 (2)
	1.99	*2.02*	*2.22*	*2.20*	*2.06*	*2.12*	*2.21*	*2.20*
M–N7	2.154 (5)	2.031 (3)	2.257 (3)	2.237 (2)	2.2355 (10)	2.095 (2)	2.248 (6)	2.250 (2)
	2.15	*2.09*	*2.34*	*2.40*	*2.33*	*2.20*	*2.18*	*2.27*
M–N_{ar1}	1.988 (6)	1.948 (3)	2.139 (3)	2.259 (2)	2.0408 (11)	2.311 (2)	2.124 (6)	2.345 (2)
	2.00	*1.99*	*2.18*	*2.45*	*2.08*	*2.44*	*2.16*	*2.35*
M–N_{ar2}	1.994 (6)	1.932 (4)	2.154 (3)	2.254 (2)	2.0232 (11)	2.269 (2)	2.140 (6)	2.301 (2)
	2.02	*2.00*	*2.21*	*2.33*	*2.10*	*2.66*	*2.16*	*2.34*
M–N_{py3}	1.977 (6)	2.006 (3)	2.166 (3)	2.205 (2)	1.9752 (11)	1.927 (2)	2.089 (6)	2.141 (2)
	1.96	*2.09*	*2.25*	*2.28*	*2.02*	*2.10*	*2.09*	*2.18*
M–X	–	1.958 (3)	2.4513 (12)	2.3693 (8)	–	–	2.200 (5)	2.0439 (17)
		(2.06)	*2.40*	*2.31*			*3.41*	*2.37*
Hα···M, X	2.877, –	2.932, 2.291	3.045, 2.679	3.102, 2.591	2.906, –	2.747, –	3.008, 2.434	2.987, 2.292
	2.81, –	*2.99, 2.20*	*3.01, 2.44*	*3.02, 2.43*	*2.87, –*	*2.87, –*	*2.99, 2.26*	*3.03, 2.25*
N7–M–N_{py3}	98.9 (2)	98.23 (14)	92.66 (13)	92.71 (8)	100.00 (4)	100.95 (7)	95.7 (2)	93.28 (8)
	99.3	*94.8*	*90.1*	*88.3*	*97.8*	*93.7*	*100.0*	*94.4*
$\Delta E_{ls\text{-}is}$	−6.5	9.2	−38.7					
$\Delta E_{HOMO-LUMO}$	–	263.2						

[a] Complete data tables are given in the Supporting Information; distances in Å, angles in °, energies in kJ mol^{-1}. [b] From reference [18].

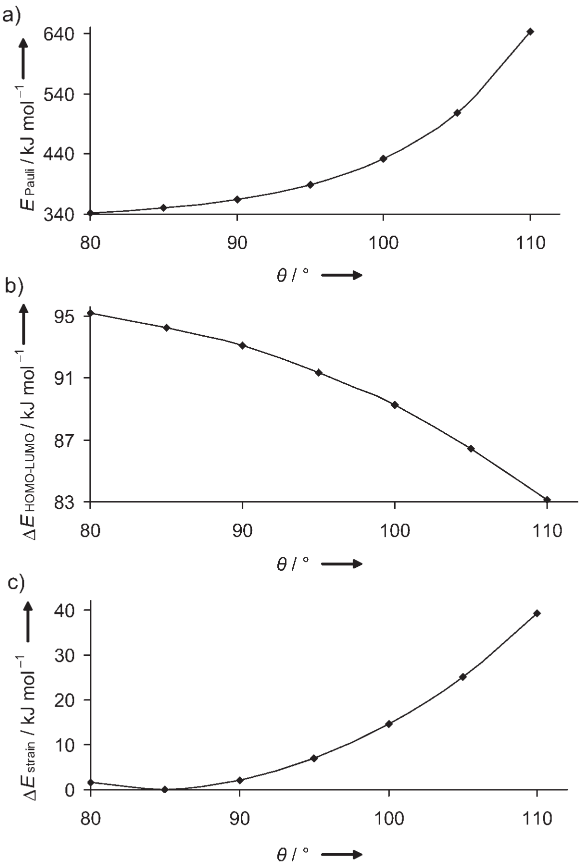

Figure 3. a) Pauli repulsion (BP86/TZP) of the hexacoordinate low-spin Co^{III}–L^1 system as a function of θ ($\theta = N7\text{-}Co^{III}\text{-}N_{py3}$; the ethylene bridge between N7 and N_{py3} is replaced by H atoms). b) HOMO–LUMO gap (BP86/TZP) of the Co^{III}–L^1 system as a function of θ. c) Strain energy (MOMEC) of the Co^{III}–L^1 system as a function of θ.

First experiments show that these complexes show uncommon reactivities.[23,24] An important feature for their thorough analysis and for possible applications is that the Co^{II} precursors as well as the penta- and hexacoordinate Co^{III} complexes are stable compounds. Moreover, their relative stabilities (redox potential, HOMO–LUMO gap of the low-spin configuration) are tunable through simple ligand modifications, such as the substitution of the α-position of py3, which, by analogy to other published bispidine systems, is expected to be a facile preparative task. Also of interest in this context are the structural differences between the complexes of L^1 and L^2: the quinoline-derived ligands lead to a repulsive interaction between ar1,2 and py3. This interaction generally leads to an elongation along N_{ar1}–M–N_{ar2}, as well as longer M−N_{py3} and shorter M−X bonds (see Table 1). This behavior is well reproduced by the DFT calculations (see Table 1 and the Supporting Information) and is another possible design principle for these systems.

Experimental Section

Chemicals (Aldrich, Fluka) were used without further purification. L^1 and L^2 were prepared as reported.[18] For details, see the Supporting Information.

DFT optimizations were performed with Gaussian 03[25] using the B3LYP method[26,27] and TZVP[28] basis set. Frequency calculations were performed on all optimized structures to verify that they are minima on the potential energy surface and to obtain zero-point energy corrections. The quoted energy differences are between intermediate-spin and low-spin configurations with low-spin state as the origin. The reported HOMO–LUMO gaps are related to the low-spin configurations. A simplified model system was used in all calculations, in which the ester groups on the ligand backbone were replaced by hydrogen atoms. The energy decomposition analysis (EDA) was performed with ADF[29] using BP86[30,31] and a triple-ζ basis set with an additional polarization function and a small core. Empirical force field calculations were obtained with the MOMEC97 program[32] and force field.[33]

Crystal-structure data were collected on a Bruker AXS Smart 1000 CCD diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å); semiempirical absorption correction (SADABS).[34] Structure solution was performed by the heavy atom method combined with structure expansion by direct methods,[35,36] conventional direct methods,[37–40] or direct methods with dual-space recycling.[41,42] Refinement was by full-matrix least squares methods based on F^2;[39,40] all non-hydrogen atoms anisotropic, hydrogen atoms at calculated positions (refined riding).[43–45] Geometrical restraints were applied to most of the BF_4^- and ClO_4^- ions. Owing to severe disorder or partial occupancy, some parts of the structures of $[Zn(L^2)OH_2](BF_4)_2$ and $[Co(L^{1''})OH](ClO_4)_2\cdot[Co(L^{1''})OH_2](ClO_4)_3\cdot[Na(H_2O)_6]\cdot 6\,H_2O$ (solvate water, anions, $Na(H_2O)_6]^+$) were removed from the data with the SQUEEZE procedure.[46,47]

Co^{II}, Cu^{II}, and Zn^{II} complexes: A suspension of the ligand (500–1000 mg) in MeOH (10–50 mL) was mixed with an equimolar solution of a metal salt ($Zn(BF_4)_2\cdot 6\,H_2O$, $Cu(BF_4)_2\cdot 6\,H_2O$, $CoCl_2\cdot 6\,H_2O$, or $Co(ClO_4)_2\cdot 6\,H_2O$) in the same solvent. The complexes precipitated from these solutions or were obtained by diffusion of diethyl ether, collected by filtration, and dried. Co^{III} complexes: $[Co(L^{1'})](ClO_4)_3\cdot 5\,H_2O$: Brown crystals were obtained according to published procedures and analyzed by X-ray crystallography and magnetic measurements ($\mu_{\text{eff}} = 3.5$ B.M.).[20] $[Co(L^{1''})Cl]Cl_2\cdot H_2O$: $[Co(L^1)](ClO_4)_2$ (804.4 mg, 1.0 mmol) was dissolved in 50 mL water at room temperature. Chlorine gas was bubbled through the solution for 10 min and then nitrogen was bubbled for 1 h to remove the excessive chlorine gas. The deep-red solution was adsorbed onto SP Sephadex C-25 and eluted readily with 0.3 M NaCl. A pink solid was isolated with a methanol–acetonitrile mixture from the eluent (383 mg, 53 %).

Details of the crystal-structure analysis and analytical data are given in the Supporting Information.

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