Coordination Chemistry

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Enticing Cobalt into Planarity: Can a Pair of Diolato Ligands Make It Happen?

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Molecular four-coordinate high-spin ($S = 2$) iron(II) centers with a more-or-less square-planar FeO_4 chromophore have recently been discovered.[1] The four oxygen donor atoms were provided by two diolato chelate ligands. For the high-spin d^6 Fe^{II} centers, we interpreted the flattening of a tetrahedral coordination environment towards a square-planar one as being driven by the tetrahedron's Jahn–Teller (JT) instability. Specifically, the spatial distribution of the oxygen donor atoms in, say, the xy plane and the only β-spin electron of the high-spin d^6 configuration in the z^2 orbital should result in a favorable separation of the negative charge. This charge separation helps to compensate the increased interligand repulsion within the square-planar motif.

It was therefore remarkable that, with the perfluoropinacolato chelator ($(FpinH_{-2})^{2-}$, Fpin = perfluoropinacol; for the sake of consistency with a previous work by our group,[2] we use this abbreviation; in Ref. [1b], the abbreviation ddfp is used instead of $(FpinH_{-2})^{2-}$), not only a second example of a planar high-spin bisdiolato iron(II) but also a high-spin d^7 cobalt(II) analogue was recently reported.[1b] Since a tetrahedral high-spin cobalt(II) complex is devoid of JT instability, the tetrahedral-to-square-planar transformation should be less favorable compared to the iron(II) case. The opposite, however, was reported. On the one hand, in line with our result, a smooth, flat curve was calculated for the iron(II) complex's tetrahedral-to-planar transition by a DFT approach (Figure 1, curve label Fe). On the other hand, a clear preference for the planar structure was found for the cobalt species for which the tetrahedral conformation is approximately 40 $kJ\,mol^{-1}$ less stable (Figure 1, curve label Co_{exc}). With their conclusion that the formation of a planar complex would be driven by the ligand's characteristics only, and not the specific electron configuration of the central metal, the authors of Ref. [1b] initiated a controversy that we wish to address herein. Our starting point was the most surprising result of Ref. [1b], namely the marked instability of the tetrahedral high-spin d^7 cobalt(II) conformer found by the DFT calculations.

We thus started our investigation with the computational part. For this, the same procedure as used by the authors of Ref. [1b] (BP/TZ2P, ADF program package in its default settings) was applied to calculate a relaxed [potential energy] surface scan from the planar to the tetrahedral form of the cobalt(II) complex. As a result, the same orbital population for the planar form depicted in the Supporting Information of Ref. [1b] was obtained. Moreover, the scan towards the tetrahedron (Figure 1) results in the same 40 $kJ\,mol^{-1}$ ascent depicted in Figure 4 of Ref. [1b]. At the end of the scan, however, the β-spin configuration of the tetrahedral species was one of the less stable configurations of the $(x^2-y^2,z^2)^1(xy,xz,yz)^1$ type. The x^2-z^2 and yz d orbitals were occupied by the β spins (standard Cartesian axes for tetrahedral species as defined in Figure 2 are used throughout).

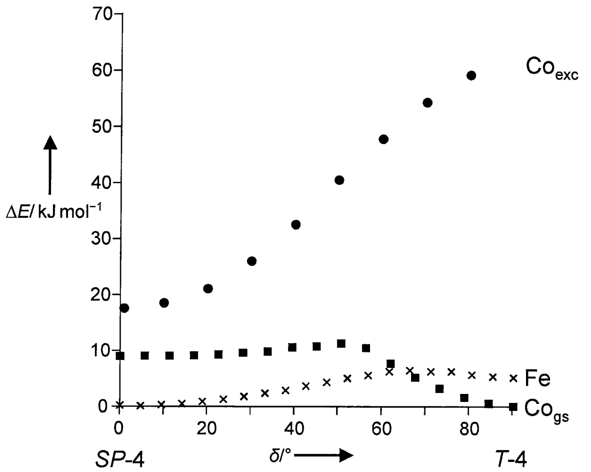

Figure 1. Relative energies of bis(perfluoropinacolato)metallate(II) species on the transition path from the planar (*SP*-4) to the tetrahedral (*T*-4) conformation. For details see the text. Abscissa: the dihedral angle $M(O_{diol1})_2/M(O_{diol2})_2$ (δ as in Ref. [1a], Θ in Ref. [1b]; 0° refers to a rectangularly distorted planar conformation, 90° refers to a distorted tetrahedral conformation); ordinate: relative energy; $\Delta E = 0$ for the most stable Fe or Co species.

Hence, an electronically excited configuration was obtained, particularly at the scan's end. More-stable species throughout the entire scan curve were obtained by starting the scan at the tetrahedral end (Figure 1, curve label "Co_{gs}"). The minimum resembled, in terms of the axes in Figure 2, an $(xz)^1(y^2)^1$ configuration of the two β spins, with the y^2 orbital carrying some s admixture to concentrate the spin in the xz plane. Proceeding towards the planar conformation, an intersection was crossed where the electronic configuration switched to a state that was derived from the $(x^2-y^2)^1(z^2)^1$ configuration for the β spins. As a result, by allowing for the electronic ground-state configuration at the cobalt center, a flat scan curve was obtained that does not show the unexpected instability of the tetrahedral conformation found in the Co_{exc} curve. Moreover, the expected differ-

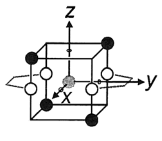

Figure 2. Choice of the Cartesian axes used in orbital assignments.

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ence, in terms of a JT influence between the iron and cobalt centers, is visible. Similar curves, but with a slight stabilization of the planar conformation, were obtained when a solvent correction was added that, to some extent, reduced the ligand–ligand repulsion (Figure 3).

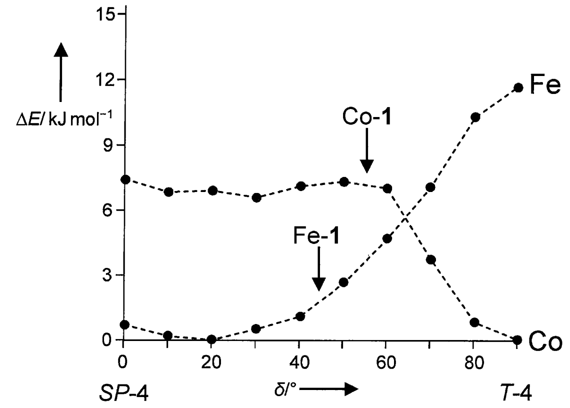

Figure 3. The flat *SP*-4-to-*T*-4 transformation curves of the [M-(FpinH$_{-2}$)$_2$]$^{2-}$ ions' C_2-symmetric conformation (C_{2h} for $\delta = 0°$) on the BP86/TZVP level of theory including a polarizable continuum model with the parameters for water. Fe-1 and Co-1 mark the experimentally determined angles for these compounds.

The fact that the tetrahedral conformer had been calculated approximately 60 kJ mol^{-1} too high in energy in Ref. [1b] at the chosen level of theory, affects the conclusions drawn there that "the lowest energy conformation for the [M(ddfp)$_2$]$^{2-}$ compounds is clearly much closer to square planar than tetrahedral" and that the observed planar conformation be "enforced by the ligands, and not any particular electron count at the metal center". With the corrected scan curves, however, the JT-driven planarization of the iron(II) complex remains the facile one, whereas the high-spin d^7 cobalt complex's planarization is energetically more demanding—as expected.

In addition, the corrected scan curves share a typical feature: they are flat. As such, they seem to be the result of the balance of various determining factors. Three of them can be recognized at the present state of investigation: 1) the metal's electron count and spin state, 2) the ligand's characteristics including its relatively small bite angle that supports the smaller O-M-O angles close to the *SP*-4 conformation, 3) secondary interactions, such as the metal center's bonding to counterions or hydrogen-bond donors. That the last factor is crucial is demonstrated by the compounds in Ref. [1b] where [K(dme)$_2$]$^+$ (dme = dimethoxyethane) counterions are bidentate chelated by the bis(perfluoropinacolato) complexes of iron(II), cobalt(II), and zinc(II). Even the zinc compound is flattened ($\delta = 65°$ instead of the expected 90°). As for iron and cobalt, the counterion chelation levels out the energetic differences between these metals and both end up in a planar conformation.

The experimental part of our study confirms the expected differences. By using bis(phosphoranediyl)iminium (PPN) and tetrakis(methanol)lithium counterions, we prepared the isotypic bis(perfluoropinacolato)metallates PPN[Li(MeOH)$_4$][M(FpinH$_{-2}$)$_2$] ([Fe-**1**], [Co-**1**]). In these metallates, there is no counterion chelation to support the planar conformation. Instead, the anions interact with hydrogen-bond donors and the corresponding O···O distance is larger. As the result of the crystals' isotypy, the major difference between the cobalt(II) and the iron(II) center is the first factor mentioned above, the metal's electronic configuration. In agreement with the lack of a JT contribution in the case of cobalt, the cobaltate is, in fact, "more tetrahedral". Specifically, δ is approximately 46° for the iron(II) complex and approximately 56° for the cobalt analogue (Figure 4 top).

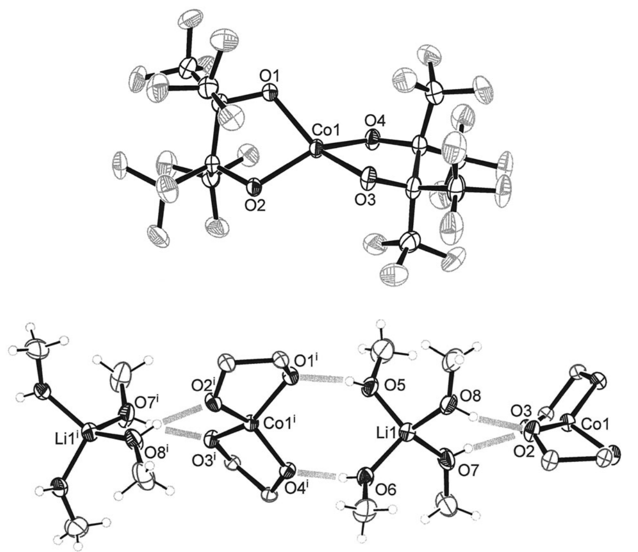

Figure 4. Top: Structure of the anion in crystals of [Co-**1**] (ORTEP representation with thermal ellipsoids set at 50% probability); the Co1-O1-O2/Co1-O3-O4 dihedral angle δ is 55.6(9)°. The dihedral angle in the isotypic ferrous compound Fe-**1** is 46.2(11)°. Interatomic distances [Å]: Co1–O1 1.948(2), Co1–O2 1.953(2), Co1–O3 1.952(2), Co1–O4 1.954(2); Fe1–O1 1.991(2), Fe1–O2 1.981(2), Fe1–O3 1.981(2), Fe1–O4 1.991(2). Bottom: The hydrogen-bonded polymer along [001] in crystals of [Co-**1**] (CF$_3$ groups omitted). Interatomic distances [Å]: Li1–O5 1.916(4), Li1–O6 1.905(4), Li1–O7 1.906(4), Li1–O8 1.914(4); hydrogen-bonded O···O contacts: O5···O1^{i} 2.669(2), O6···O4^{i} 2.691(2), O7···O3 2.640(2), O8···O2 2.680(2). Parameters for [Fe-**1**]: interatomic distances [Å]: from Li1–O5 1.912(5), Li1–O6 1.895(5), Li1–O7 1.916(5), Li1–O8 1.914(5); O5···O1^{i} 2.657(2), O6···O4^{i} 2.661(3), O7···O3 2.644(3), O8···O2 2.669(3). Symmetry code: $^{i}x, \frac{1}{2}-y, z-\frac{1}{2}$.

The interionic interaction that supports the larger O···O distance in the more-tilted pair of chelate rings in **1** is highlighted in Figure 4 bottom. In agreement with the 1:1 ratio of tetra(methanol)lithium cations and metallate anions, a hydrogen-bonded chain of alternating cations and anions extends along the [001] direction of the solid.

The actual distortions were mirrored by computational results: structure optimizations on the theoretical level used for the scans in Figure 3 led to a tetrahedral conformation starting with the parameters of Co-**1** but an almost planar conformation for the iron(II) center starting with the Fe-**1** parameters. Calculations that include the various counterions are in progress.

In conclusion, a pair of diolato ligands can contribute, as one of several factors, to the rare planar conformation of tetracoordinate high-spin metal(II) centers. Diolato chelators, however, do not override the rules of coordination chemistry. If the competing tetrahedral conformation is JT-destabilized as with iron(II), the tetrahedral-to-planar transformation proceeds on the JT path and is facilitated in terms of energy. If not, as with cobalt(II), planarization is energetically more demanding—and not less demanding as claimed in Ref. [1b]. In total, the metal's electronic configuration, the ligand's characteristics, and secondary interactions define the toolbox for the construction of these new types of complexes—not solely the ligands.

Experimental Section

A solution of cobalt or iron triflate–methanol (1:2; 1 mmol) and Fpin (2 mmol) in methanol (20 mL) was added to lithium methoxide (4 mmol) in methanol (10 mL) under stirring. PPN nitrate (4 mmol) was dissolved in methanol (6 mL) and added to the violet (Co) or blue (Fe) solution. Methanol was slowly distilled off under vacuum until a precipitate was observed. The precipitate was redissolved by heating and the solution and then left at 4 °C. Crystals of **1** formed within a few days. No attempts have been made to optimize the yield.

[Co-**1**]: $C_{52}H_{46}CoF_{24}LiNO_8P_2$, $M_r = 1396.71$ g mol^{-1}, red block, $0.243 \times 0.140 \times 0.136$ mm, monoclinic, $P2_1/c$, $a = 19.3947(7)$, $b = 17.6340(7)$, $c = 19.0096(7)$ Å, $\beta = 116.0836(10)$, $V = 5839.3(4)$ Å^3, $Z = 4$, $\rho = 1.589$ g cm^{-3}, $T = 200$ K, $\mu = 0.478$ mm^{-1}, multi-scan absorption correction, Bruker D8 Quest diffractometer, MoK_α radiation, $\lambda = 0.71073$ Å, θ range: 2.31–27.53°, 64798 reflections, 13140 independent and used in refinement, 10530 with $I \geq 2\sigma(I)$, $R_{\mathrm{int}} = 0.0271$, mean $\sigma(I)/I = 0.0225$, 819 parameters, $R(F_{\mathrm{obs}}) = 0.0388$, $R_w(F^2) = 0.1025$, $S = 1.023$, min./max. residual electron density: $-0.348/0.344$ e Å^{-3}, max. shift/error: 0.001.

[Fe-**1**]: $C_{52}H_{46}F_{24}FeLiNO_8P_2$, $M_r = 1393.63$ g mol^{-1}, blue block, $0.151 \times 0.144 \times 0.129$ mm, monoclinic, $P2_1/c$, $a = 19.5459(8)$, $b = 17.4775(6)$, $c = 18.8345(8)$ Å, $\beta = 116.7122(13)$, $V = 5747.4(4)$ Å^3, $Z = 4$, $\rho = 1.611$ g cm^{-3}, $T = 100$ K, $\mu = 0.449$ mm^{-1}, multi-scan absorption correction, Bruker D8 Venture diffractometer, MoK_α radiation, $\lambda = 0.71073$ Å, θ range: 2.75–27.52°, 70610 reflections, 13225 independent and used in refinement, 10071 with $I \geq 2\sigma(I)$, $R_{\mathrm{int}} = 0.0507$, mean $\sigma(I)/I = 0.0394$, 818 parameters, $R(F_{\mathrm{obs}}) = 0.0463$, $R_w(F^2) = 0.1215$, $S = 1.020$, min./residual electron density: $-0.738/1.289$ e Å^{-3}, max. shift/error: 0.001. Programs used: SHELXS, SHELXL, PLATON, ORTEP.[3] CCDC 921626 ([Co-**1**]) and 921627 ([Fe-**1**]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The DFT calculations for Figure 1 were performed, following Ref. [1b], with the ADF package (2012 version).[4] For the scan curves of Figure 3, Gaussian 09 was used (solvent model used: IEFPCM in its standard settings).[5]

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