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COMMUNICATION

A singlet ground state for a cobalt(II)-anilinylsalen radical complex

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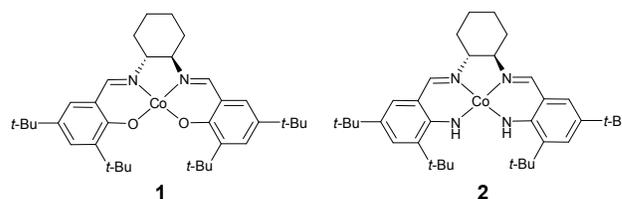
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The cobalt(II) anilinosalen complex [Co^{II}(L)] was prepared and subsequently oxidized by one electron. The resulting cation comprises a square planar low spin Co(II) ion anti-ferromagnetically exchange coupled to an anilinyl radical.

Cobalt(II)-salen complexes, in particular Jacobsen's complex **1**, have attracted a considerable interest in the past few years for catalytic purposes. They indeed show a remarkable catalytic activity for a broad range of reactions, the most representative being hydrolytic kinetic resolution of epoxides,^[1] CO₂/epoxide copolymerization^[2] and oxidation of alcohols.^[3] Noteworthy, in these reactions the active species is not the neutral Co(II) complex but its one-electron oxidized counter-part, which is generated either by air incubation (in the presence of acetic acid) or addition of a chemical reagent such as ferrocenium.^[1] The one-electron oxidized species was initially believed to be a cobalt(III) complex,^[1,4] although it could be in principle alternatively described as a metal–ligand radical complex. We recently showed that *ca.* 30% of the spin density is distributed over the aromatic rings in **1**⁺, thus conferring to it a non-negligible phenoxyl radical character, in addition to its main Co(III) character (*ca.* 70 % of spin density located at the metal center).^[5] Our proposal, which appeared to be seemingly contradictory with previous ones, was afterwards corroborated by a convincing NMR investigation by Fujii et al.^[6] Both in Fujii's work and our studies the metal ion changes its geometry from square planar to square pyramidal during oxidation. In the absence of a strong donor in the medium, the fifth position is indeed occupied by either the counter-ion of the oxidant or adventitious water, evidencing a high propensity of the complex to bind at least one axial ligand. As underlined in our previous work, axial ligation may contribute to the stabilization of the Co(III) valence isomer through charge compensation mechanism.

We synthesized a derivative of the Jacobsen's catalyst, namely **2**, wherein the phenolate donors are replaced by anilido ones. We show here that the stronger field provided by the anilido units^[7] sufficiently decreases the affinity of axial ligands for the complex so that the metal ion retains its square planar geometry in its one-

electron oxidized form. Magnetic measurements, Vis-NIR and DFT calculations support the description of the complex as square planar Co(II)-anilinyl radical species.



Scheme 1. Structures of the unactivated Jacobsen's catalyst **1** and its anilinosalen counter-part **2**.

The ligand and the cobalt(II) complex **2** were synthesized according to published procedures.^[8-9] The one-electron oxidized complex (**2**)⁺ was generated either electrochemically or chemically by addition of AgSbF₆ (both methods gave similar results). The cation (**2**)⁺ was found to be diamagnetic in solution, as judged by the sharp resonances observed over a small spectral width in the ¹H NMR spectrum (Fig. S1). A full assignment of the ¹H resonances is provided in ESI. Of particular interest is the chemical shift of the methine hydrogens of the cyclohexyl, which shift up to 11.44 ppm in the cation. Diffusion of pentane into a CH₂Cl₂ solution of the chemically oxidized complex resulted in the formation of single crystals of (**2**)⁺ • SbF₆⁻. The crystal cell of (**2**)⁺ • SbF₆⁻ contains two distinct molecules A and B. The solid state structure of one, arbitrary chosen, is shown in Fig. 1. In (**2**)⁺ • SbF₆⁻ the cobalt ion resides in a square planar geometry. This feature contrasts with the square pyramidal geometry observed in its salen counterpart complexes (**1**)⁺ • SbF₆⁻^[5] and (**1**)⁺ • OTf.^[6] In (**2**)⁺ • SbF₆⁻, the bond lengths in the plane Co1A-N1A, Co1A-N2A, Co1A-N3A and Co1A-N4A are 1.862(7), 1.850(7), 1.829(5) and 1.814(5) Å, respectively (the corresponding ones in molecule B are Co1B N1B 1.867(6), Co1B N2B 1.863(5), Co1B N3B 1.832(5) and Co1B N4B 1.810(5) Å,

respectively), with a very small angle between the N1A-Co1A-N4A and N2A-Co1A-N3A planes of 3° (10° in molecule B). When compared to the neutral complex **2** the Co1-N3 and Co1-N4 bond lengths in **(2)⁺** are significantly shorter (mean Co-N bond distance in **2** = 1.843(3) Å) while the Co1-N1 and Co1-N2 bond lengths are almost identical (mean Co-N bond distance in **2** = 1.858(3) Å). It is significant that the bond lengths within the aromatic framework remain essentially unchanged upon oxidation. Such behaviour may be understood by considering that i) the ligand radical is delocalized over both aromatic rings (mixed valence compound) [10] and ii) the magnitude of the bonding rearrangement resulting from one-electron oxidation of anilido moieties is smaller than that classically observed for phenolato groups [8]. This structure is consistent with a ^{LS}Co(II)-anilanyl character for **(2)⁺**, but the Co(III)-anilido electronic isomer still remains a valuable alternative at this point to describe the electronic structure of the cation.

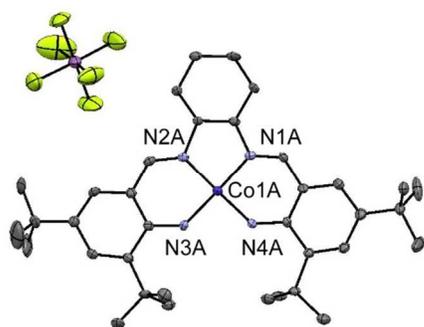


Figure 1. X-ray crystal structure of **(2)⁺ • SbF₆⁻** shown with 30% thermal ellipsoids. H atoms are omitted for clarity.

DFT geometry optimizations were performed at the BP86 level of theory for **(2)⁺**. [11] When a closed-shell singlet spin state is considered for **(2)⁺** (diamagnetic cobalt(III) metal ion) calculations predict a symmetrical structure with shortened metal-ligand bonds as compared to **2** (the Co1-N1/N2 and Co1-N3/N4 bonds are shortened by *ca.* 0.007 Å and 0.028 Å, respectively, Table S1, Fig. S5). Despite the fact that the calculated bond changes by considering a closed-shell singlet state may match the experimental ones, the singlet is found to be energetically disfavored by 7.0 and 5.6 kcal.mol⁻¹ over the triplet and the broken-symmetry singlet (obtained from a BS(1,1) calculation), respectively, thus ruling out a low spin Co(III)-anilido character for **(2)⁺**. Calculations performed by considering a triplet state for **(2)⁺** (either ^{LS}Co(II)-anilanyl radical or high spin Co(III)-anilido complex) predict a symmetrical structure with shortening of the Co1-N3 and Co1-N4 bonds by *ca.* 0.023 Å and elongation of the Co1-N1 and Co1-N2 ones by *ca.* 0.035 Å, which reasonably matches the features observed experimentally (Table S1, Fig. S3). We also considered a quintet spin state of **(2)⁺** but the predicted bond distances and the distortion at the metal center are far from the experimental ones in that case (Fig S7). In addition, the quintet is found to be located 25 kcal.mol⁻¹ over the triplet, thus making it irrelevant.

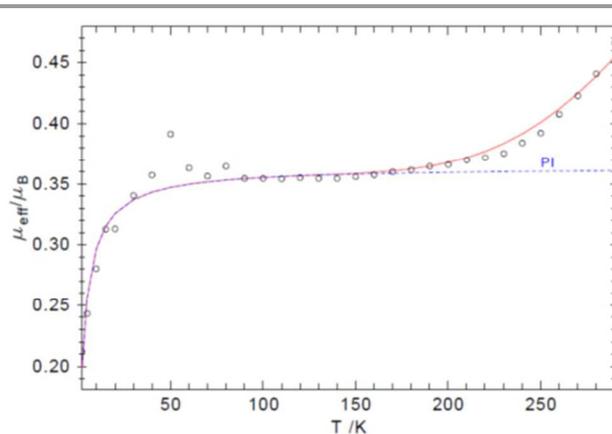


Figure 2. Temperature dependence of the magnetic moment of **(2)⁺ • SbF₆⁻**; PI is from a weak 4.3% paramagnetic impurity (assuming $S_{PI}=1/2$), and the red line represents a simulation using the parameters given in the text.

Magnetic susceptibility measurements were performed for **(2)⁺** both in solid state and in CH₂Cl₂ solution. The temperature dependence of the magnetic moment μ_{eff} of a powder sample of **(2)⁺ • SbF₆⁻** shows vanishing values below 200 K (except for a weak paramagnetic impurity), whereas μ_{eff} increases above 200 K, indicating thermal population of excited spin states (Fig. 2). The data could be fitted by using a model for two exchange coupled spins ($S = 1/2$) described by the spin Hamiltonian $H = -2 J S_1 \cdot S_2$. Parameter optimization yields $g_1 = g_2 = 2.00$, $J = -574 \text{ cm}^{-1}$ and $\chi_{\text{TIP}} = 7.8 \cdot 10^{-5} \text{ e.m.u.}$ Thus, a strong intramolecular antiferromagnetic spin coupling prevails in **(2)⁺ • SbF₆⁻**, which can arise only from a system with dominant ^{LS}Co(II)-anilanyl radical character. Solution measurements (see ESI) lead to similar results, *i.e.* antiferromagnetic coupling, showing that the complex preserves its electronic and geometric structure in CH₂Cl₂.

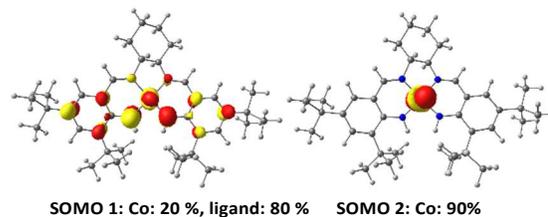


Figure 3. Localized SOMOs for **(2)⁺** ($S = 0$) obtained from a BS(1,1) B3LYP calculation. UHF corresponding orbitals were used to depict these orbitals.

The localized SOMOs of the broken-symmetry singlet state for **(2)⁺** obtained from a BS(1,1) B3LYP calculation are depicted in Fig. 3. [10] One SOMO has mainly a metal character (78% d_{2z} , 4% d_{xz} , 8% d_{yz}), while the other one has both an anilanyl (80%) and metal (15% d_{2z} , 3% d_{xz} , 2% d_{yz}) character. The broken symmetry calculation is essentially isoenergetic with the triplet state, which is favored by 1.4 kcal.mol⁻¹. This is well within the accuracy of the DFT method and may be the result of the small energetic gap between SOMOs.

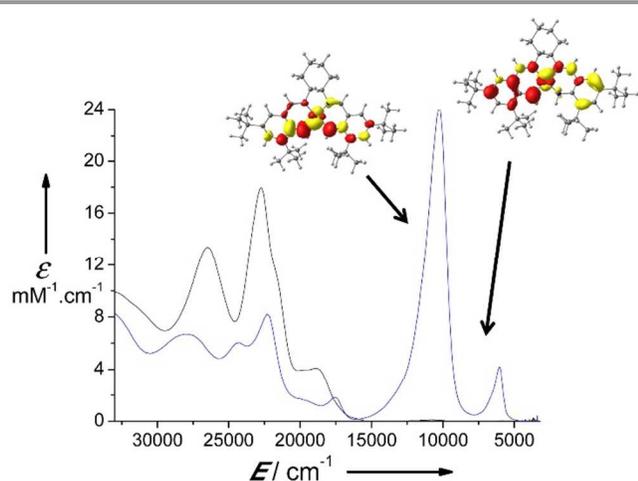


Figure 4. UV-visible spectra of the neutral and monooxidized complexes in 0.05 mM CH_2Cl_2 solutions: **2** (black) and $(\mathbf{2})^+ \cdot \text{SbF}_6^-$ (blue). $T = 298\text{K}$. Inserts: TD-DFT assignment of the electronic transitions of $(\mathbf{2})^+$ in the singlet state obtained from a BS(1,1) B3LYP calculation ($\nu_{\text{calc}} = 13\,189\text{ cm}^{-1}$ ($f = 0.25$), $\nu_{\text{calc}} = 7705\text{ cm}^{-1}$ ($f = 0.15$). The diagrams give the difference electron densities where red corresponds to positive density and yellow to negative density.

The visible-NIR spectrum of $(\mathbf{2})^+ \cdot \text{SbF}_6^-$ shows two remarkable NIR features at $10\,245\text{ cm}^{-1}$ ($24\,142\text{ M}^{-1}\text{ cm}^{-1}$) and 6024 cm^{-1} ($4195\text{ M}^{-1}\text{ cm}^{-1}$) that are absent in the spectrum of **2** (Fig. 4).^[12] Owing to their high intensity they necessarily originate from charge transfer (CT) transitions. The exact nature of the orbitals involved in the CT transitions was investigated by TD-DFT calculations for the broken symmetry state, which is found to be the only relevant form in CH_2Cl_2 solution by magnetic susceptibility measurements.^[13] The two electronic excitations of lowest energy are calculated at $13\,189\text{ cm}^{-1}$ ($f = 0.25$) and 7705 cm^{-1} ($f = 0.15$). Each calculated transition corresponds predominately to a ligand-to-ligand charge transfer (LLCT) transition. According to the difference in transition densities (Fig. 4), the donor and acceptor molecular fragments for the transition calculated at 13189 cm^{-1} display both a metal (with d_{xz} , d_{yz} contributions) and a ligand character (delocalized π orbital involving the two anilido/anilinyll moieties). In the transition calculated at 7705 cm^{-1} , the donor molecular fragment also exhibits a metal character (d_{xz} , d_{yz}) with a contribution from a π orbital, but in this case it involves a single anilido group. The acceptor orbital is a delocalized π orbital involving the other anilido moieties with a contribution from the d_{xz} and d_{yz} orbitals. Although the highest energy transition is slightly overestimated, the computed energy for the transitions are in reasonable agreement with the experimental ones.

Conclusions

In summary, we unequivocally identified complex $(\mathbf{2})^+$ in the present work to be a square planar $^{\text{LS}}\text{Co(II)}$ -anilinyll radical complex, which is based on a modified salen platform. In contrast with other square planar and tetrahedral one-electron oxidized Co(II) -amido complexes, which can be regarded as paramagnetic Co(III) species,^[14] $(\mathbf{2})^+$ possesses a rare singlet ground state that is attained via antiferromagnetic coupling between the ligand radical and the metal spins. Although the metal-centered SOMO2 does not overlap (due to orthogonality) with the organic part of SOMO1, the latter orbital also exhibits a

non-negligible metallic character that may contribute to the observed antiferromagnetic interaction (mutual spatial overlap of $S = 0.45$). Due to the absence of axial ligation $(\mathbf{2})^+$ exhibits an electronic structure different than that of the cobalt-anilido and anilinyll complexes described previously by Wiegardt *et al.* and Verani *et al.* (low spin octahedral Co(III) ion).^[15] It has to be emphasized that oxidation of **2** occurs readily (**2** is slowly oxidized into $(\mathbf{2})^+$ by air), making it a promising candidate for catalytic purposes (hydrolytic kinetic resolution of epoxides^[1] and aerobic oxidation of alcohols).^[16] Finally, the crystal structure of $(\mathbf{2})^+$ provides insight on the geometric features of anilinyll radicals, which became a matter of debate after the recent paper by Chen *et al.* on the structure of the tri-*tert*-butyl-aniline radical cation.^[17]

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Notes and references

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- Geometry optimizations were performed both without counter ion ($\mathbf{2}^+$) and including the counter-ion ($(\mathbf{2})^+ \cdot \text{SbF}_6^-$) (Figures S3-S6 and Figures S8-S9). The optimized geometries of neither the singlet nor the triplet states are significantly affected by the presence of the counter ion, thus the discussion is limited to $(\mathbf{2}^+)$.

- 12 UV-Vis-NIR data for the complexes in CH₂Cl₂ solution ($T = 298$ K):
 ν_{\max} , cm⁻¹ (ϵ , M⁻¹ cm⁻¹); **2**: 26 596 (13 390), 22 676 (17 927), 21 598
sh (12 656), 18 832 (4042); (**2**)⁺: 28 090 (6692), 24 272 (6044),
22 321 (8227), 17 606 (1823), 10 245 br (24 142), 6024 br (4195).
- 13 The predicted electronic excitations by considering the triplet state and singlet ¹Co(III) are provided in ESI. The latter does not reproduce satisfactorily the experimental spectrum.
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