

A New Class of Low-spin Cobalt(II) Chelates. Molecular Structure and Properties of Bis(1-ethyl-3-phenyltriazene-1-olato)cobalt(II) and Related Complexes

Mikołaj F. Rudolf,* Juliusz Wolny, Zbigniew Ciunik, and Piotr Chmielewski

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

1-Aryl-1-hydroxy-3-X-phenyltriazenes bind to cobalt(II) to yield the first examples of centrosymmetric bis-bidentate $\text{Co}^{\text{II}}\text{N}_2\text{O}_2$ chromophores as shown by magnetic, X-ray crystallographic, and e.s.r. studies; a new type of spin-state isomerism was found.

Most low-spin Co^{II} complexes consist of square-planar chelates with the Co^{II} ion bound to tetradentate macrocycles such as porphyrins (CoN_4) and Schiff's bases derived from salicylic aldehydes or β -diketones (*cis*- CoN_2O_2), 2-aminobenzaldehyde (*cis*- CoN_2N_2), monothio(seleno)diketones [*cis*- $\text{CoN}_2\text{S}_2(\text{Se})_2$],¹ as well as their five-co-ordinate Lewis base adducts.² The few exceptions known are the six-co-ordinate $[\text{Co}(\text{CNPh})_6]\text{X}_2$,³ $[\text{Co}(\text{hexathio-18-crown-6})]\text{X}_2$,⁴ and the four-co-ordinate $\text{Co}(\text{pto})_2$,⁵ $\text{M}^{\text{I}}_2[\text{Co}(\text{mnt})_2]$,⁶ $\text{Co}(\text{sacsac})_2$,⁷ and $\text{Co}(\text{mesityl})_2(\text{PEt}_2\text{Ph})_2$ ⁸ chelates.[†]

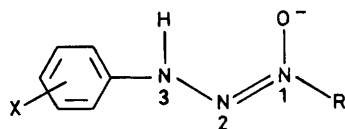
Our previous studies of spin-state transitions in four- and five-co-ordinate complexes have shown that 1-alkyl-1-hydroxy-3-X-phenyltriazene (1) monoanions[‡] favour strongly the low-spin states of mixed ligand (R,X) (*N*-alkylsalicylideneamino Ni^{II} chelates irrespective of the magnitude of steric hindrance imposed by the nitrogen-bound alkyl substituents.^{9a}

Angular overlap analysis of the above-mentioned spin-state equilibria for d^8 electron systems indicated that the (R,X) ligands are much stronger σ -donors than salicylideneamines.^{9b}

As all known bis-bidentate Co^{II} chelates derived from Schiff's bases are invariably high-spin pseudotetrahedral in the solid state and pseudotetrahedral or associated pseudo-octahedral in non-co-ordinating solvents¹⁰ an intriguing question arose: would the much stronger σ -donor monoanions (1) stabilize the low-spin state of Co^{II} in $[\text{Co}^{\text{II}}(\text{1})_2]$ type chelates.

The ligands (1) (5 mmol), prepared by the method in ref. 11, were dissolved in hot MeOH (15 cm^3), and a hot solution of cobalt acetate tetrahydrate (2.5 mmol) in a minimum amount of MeOH was added. After refluxing for 15 min, the solution was allowed to cool slowly, whereupon the crystalline complexes were deposited. The products were collected by filtration, washed with MeOH, and dried *in vacuo*. All manipulations were carried out in an inert atmosphere. The solid complexes are stable towards oxidation and oxygenation in air.[§]

The $\text{Co}^{\text{II}}(\text{R,X})_2$ chelates show two types of magnetic properties. The $\text{Co}(\text{Me}, 2\text{-Me})_2$, $\text{Co}(\text{Et}, \text{H})_2$, $\text{Co}(\text{Et}, 4\text{-Me})_2$,



(1) (R,X)

[†] Pto⁻ = 1-(6-chloro-*o*-tolyl)-3-methyltriazene 3-*N*-oxide, H_2mnt = dimercaptomaleodinitrile, Hsacsac = pentane-2,4-dithione, H_2salen = *N,N'*-ethylenebis-salicylideneamine, H_2saloph = *N,N'*-*o*-phenylenebis-salicylideneamine.

[‡] For simplicity the (R, X) notation will be used for the monoanionic ligands (1) throughout the paper.

[§] Satisfactory analytical data were obtained for all complexes.

$\text{Co}(\text{Et}, 3\text{-Me})_2$, $\text{Co}(\text{Et}, 4\text{-Br})_2$, $\text{Co}(\text{Bu}^t, \text{H})_2$ and $\text{Co}(\text{Bu}^t, 4\text{-Me})_2$ chelates are low-spin with temperature independent magnetic moments of 1.86, 2.08, 1.99, 2.03, 1.95, 2.02, and 1.75 μ_B respectively. The structure of the $\text{Co}(\text{Et}, \text{H})_2$ complex was determined by X-ray crystallography, and an ORTEP drawing is shown in Figure 1.

The ligands and Co form two five-membered chelate rings in a *trans*-configuration with Co^{II} occupying the inversion centre. The $\text{Co}(\text{Et}, \text{H})_2$ molecule represents the first well documented case of stabilization of the low-spin d^7 configuration, in a bis-bidentate, square-planar $\text{Co}^{\text{II}}\text{N}_2\text{O}_2$ chromophore. The remaining low-spin chelates most probably possess similar structures. Besides the strict planarity there are important differences in the Co-ligand bond distances compared with those found in low-spin tetradentate Schiff's base Co^{II} chelates. The Co-O bond length, 1.813(3) Å in $\text{Co}(\text{Et}, \text{H})_2$, is 0.04 Å shorter than those found in $\text{Co}(\text{salen})\text{CHCl}_3$ ^{12a} and $\text{Co}(\text{saloph})$ ^{12b} and 0.1 Å shorter than those found in $[\text{Co}(\text{salen})]_2$ ^{12c} and $\text{Co}(\text{salen})(\text{pyridine})$ ^{12d}

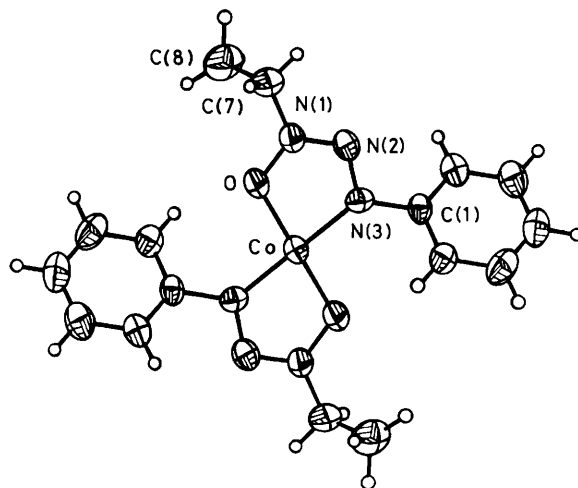


Figure 1. Perspective view of the complex $\text{Co}(\text{Et}, \text{H})_2$, showing 50% probability thermal ellipsoids. Crystal data: $\text{C}_{16}\text{H}_{20}\text{CoN}_6\text{O}_2$, $M = 387.38$, monoclinic, space group $P2_1/c$, $a = 5.795(2)$, $b = 9.223(3)$, $c = 17.555(5)$ Å, $\beta = 107.77(2)^\circ$, $U = 903.6(5)$ Å³, $Z = 2$, $D_c = 1.42$, $D_m = 1.42$ g cm^{-3} , $F(000) = 402$ electrons, graphite-monochromated Mo- K_α X-radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 10.1$ cm^{-1} . $R = 0.042$ for 944 independent reflections collected at room temperature in the range $4^\circ \leq 2\theta \leq 50^\circ$ with $I \geq 3\sigma(I)$ on a Syntex P2₁ four-circle diffractometer. The structure was solved by the heavy-atom method. Important bond distances and angles: Co-N(3) 1.861(3), Co-O 1.813(3), N(1)-O 1.340(4), N(1)-N(2) 1.278(5), N(2)-N(3) 1.322(5), N(1)-C(7) 1.448(6), N(3)-C(1) 1.430(5) Å; O-Co-N(3) 82.4(1), N(1)-O-Co 111.4(2), O-N(1)-N(2) 119.9(3), N(1)-N(2)-N(3) 110.9(3), N(2)-N(3)-Co 115.3(2)°. Torsion angles: Co-O-N(1)-N(2) -2.3(3), O-N(1)-N(2)-N(3) 0.65(4), N(1)-N(2)-N(3)-Co 1.3(3), N(2)-N(3)-C(1)-C(2) -39.2(5)°.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

representing the shortest Co–O bond distance known for low-spin Co^{II} complexes.

The e.s.r. spectrum of Co(Et,H)₂ also indicates a low spin state for the metal ion. For CH₂Cl₂/toluene frozen glasses at 77 K a rhombic e.s.r. spectrum, showing well resolved ⁵⁹Co hyperfine structure in the high-field part of the spectrum, was observed with g_1 2.700, g_2 2.047, g_3 1.968, A_2 Co 28.5, A_3 Co 41G (1 G = 10⁻⁴ T).[¶]

At least one of the studied chelates is capable of binding dioxygen reversibly. After passing air for 10 min at –40 °C through a CH₂Cl₂/toluene solution of the Co(Bu^t, 4-Me)₂ complex at a chelate to pyridine ratio of 1 : 1.5 a rhombic e.s.r. spectrum was observed at 77 K with g_x 2.009, g_y 2.079, g_z 1.984, A_x Co 7.4, A_y Co 18.7, A_z Co 10.0 G, α = 28.4°, most likely due to the monomeric dioxygen adduct Co(Bu^t, 4-Me)₂(pyridine)O₂. No significant loss in the dioxygen adduct e.s.r. signal intensities was observed during 10 subsequent oxygenation–deoxygenation cycles.

The isolated Co(Me,H)₂, Co(Me,4-Me)₂, and Co(Me,4-Br)₂ chelates are high-spin with nearly temperature-independent magnetic moments of 5.30, 4.88, and 4.66 μ_B respectively. The high-spin states of these chelates most likely are stabilized by crystal packing effects resulting in pseudo-tetrahedral distortion of the Co^{II}N₂O₂ chromophore or molecular association in the solid state as observed for the [Co(salen)]₂ dimer.¹² We have found that the high-spin complex Co(Me,H)₂ is completely converted to the low-spin isomer in solution in non-co-ordinating solvents, e.g. CCl₄, CHCl₃, or CH₂Cl₂, yielding a magnetic moment of 1.97 μ_B (CCl₄, room temp.) and a low-spin rhombic e.s.r. spectrum with g_1 2.704, g_2 2.064, g_3 2.004, A_2 Co 28.8, A_3 Co 38.3 G. If recrystallized from dimethylformamide/H₂O the high-spin Co(Me,4-Br)₂ is converted to the low-spin isomer characterised by a nearly temperature-independent magnetic moment of 2.55 μ_B (4.2–300 K) and g_1 2.72, g_2 2.07, g_3 1.98 (powder, 77 K). These results are unexpected because the high-spin states of bis-bidentate Co^{II} complexes were generally found to be more stable in solution.¹⁰ The foregoing high-spin Co(R,X)₂ complexes provide, besides the known

five-² and six-co-ordinate¹³ chelates, a new case of spin-state isomerism in Co^{II} d⁷ systems.

In conclusion, the present results establish the Co(Et,H)₂ complex as the first characterized example of a centrosymmetric, low-spin bis-bidentate Co^{II} complex with a CoN₂O₂ chromophore and 1-aryl-3-X-phenyltriazene-1-olato anions as ligands, imposing a much stronger in-plane ligand field compared with *N*-alkylsalicylideneaminato ligands.

Single crystal e.s.r. studies of the Co(Et,H)₂ complex and X-ray diffraction studies of the high-spin Co(Me,4-Me)₂ and five-co-ordinate Co(Me,4-Br)₂(pyridine) monoadduct are in progress.

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[¶] If not indicated otherwise e.s.r. spectral parameters refer to CH₂Cl₂/toluene glasses at 77 K. E.s.r. spectra were recorded on a JES-ME ESR 3X spectrometer (x-band). The remaining Co^{II} chelates studied show rhombic e.s.r. spectra with g_1 2.698–2.707, g_2 2.047–2.068, g_3 1.968–2.023, A_2 Co 28, A_3 Co 40 G, values which were not markedly dependent on the ligand.