Unusual Solvent-dependent Syntheses of Mononuclear and Binuclear Cobalt(II) Complexes

Robert P. Kreh,*† Alfredo E. Rodriguez, and Stephen P. Fox

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

The ethylenediamine Schiff base derivatives of 1-phenylhexane-1,3,5-trione and 2,2-dimethyloctane-3,5,7-trione each provide two distinct binding sites for cobalt(II) ions, and in the presence of additional ligands (methanol, pyridine) mononuclear isomers with cobalt in the four-oxygen (O_4) site are favoured while in the absence of these ligands, mononuclear isomers with cobalt in the N_2O_2 site as well as a binuclear cobalt complex were isolated.

Complexes which contain more than one type of transition metal in close proximity are fascinating owing to their potential for magnetic coupling phenomena, intramolecular and multi-electron charge transfer, biological modelling, and homogeneous and heterogeneous catalysis.[1] There are few examples of well defined heterobinuclear complexes, particularly those which are catalytically active, largely because they require rather tedious synthetic procedures[2] or need binucleating ligands which contain two different co-ordination

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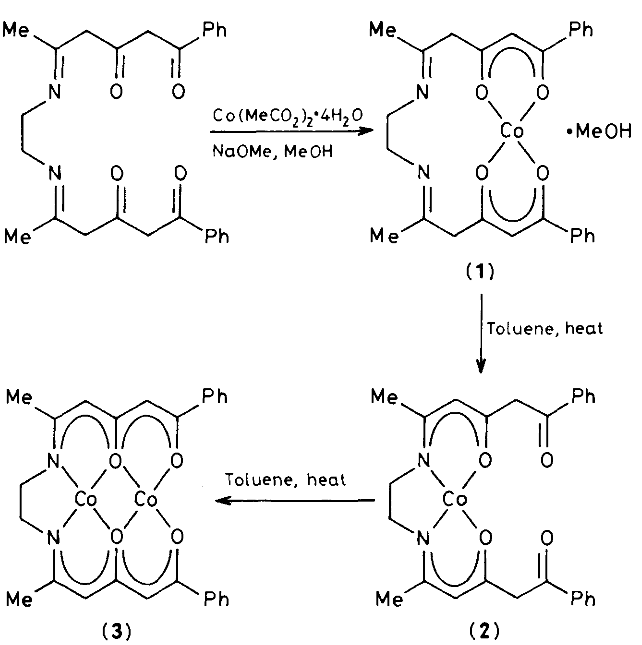
† *Present Address*: Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, Maryland 21227, U.S.A.

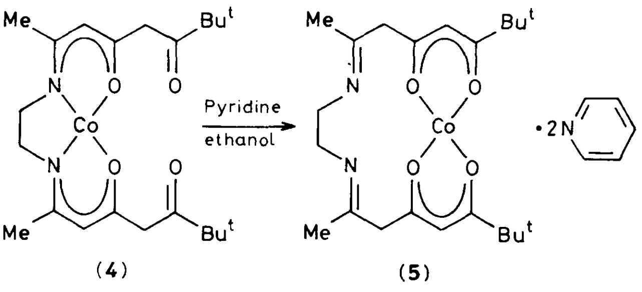


Scheme 1

sites for the selective binding of each metal ion.[3,4] In a programme to synthesize dioxygen-reactive heterobinuclear complexes, we have discovered new synthetic methods in which the solvents play pivotal roles in selecting between possible positional isomers in mononuclear cobalt complexes as well as in the synthesis of binuclear analogues.

The initial synthesis of the mononuclear cobalt complex (**1**) as a brown microcrystalline solid was straightforward (Scheme 1), [‡] but surprisingly, complex (**1**) contains the cobalt ion in the four-oxygen (O_4) co-ordination site, identified by the lack of an unchelated carbonyl i.r. band in the region 1650—1800 cm^{-1}.[3] Also the lack of reactivity toward dioxygen (pyridine solution)[§][5,6] and the magnetic moment of 4.90 μ_B at 291 K[¶][6,7] confirm the position of the cobalt in (**1**). Although a crystallographic analysis has not yet been performed on (**1**), it is likely to contain six-co-ordinate cobalt(II), utilizing methanol and ketone [bridging from a second molecule of (**1**)] oxygen atoms as axial ligands.[8]

Remarkably, the removal of the methanol from (**1**) by dissolution with heating in a non-co-ordinating solvent, toluene, resulted in the movement of cobalt from the O_4 site to the N_2O_2 site (Scheme 1). The isolated compound (**2**) (red crystals)[‡] was identified as the N_2O_2 isomer by an intense unchelated carbonyl i.r. band at 1675 cm^{-1} and by reactivity toward dioxygen in toluene solution and in the solid state. The magnetic moment for (**2**) is 2.09 μ_B at 295 K,[¶] and the structure is likely to contain square pyramidal[8,9] or square-planar[10] cobalt(II), similar to analogous low-spin mononuclear cobalt(II) complexes.[5,11]



Scheme 2

Remarkably, upon extensive (2—3 h) reflux of a concentrated toluene solution of (**2**) a novel 'disproportionation' occurs, generating the binuclear complex (**3**), which precipitates as a purple crystalline solid (Scheme 1).[‡] Its identity as (**3**) is confirmed by elemental analysis, the absence of an unchelated carbonyl i.r. band (1650—1800 cm^{-1}), and reactivity toward dioxygen in solution (dimethylformamide, ethanol, or pyridine). The exact structure around each cobalt atom in (**3**) is unknown, but the magnetic moment of 5.77 μ_B at 291 K[¶] is in agreement with low spin (N_2O_2) and high spin (O_4) cobalt(II) ions in each molecule. Binuclear cobalt[12] and nickel[13] complexes with mixed spin states have been reported for similar ligand systems.

In a manner analogous to (**2**), the mononuclear complex (**4**) was synthesized and characterized as the N_2O_2 isomer ($\mu_{eff.}$ = 2.73 μ_B at 291 K[¶]). Addition of pyridine to an ethanol solution of (**4**) resulted in the precipitation of (**5**) (Scheme 2). Complex (**5**) was identified as the O_4 isomer by the lack of an unchelated carbonyl i.r. band; the cobalt is probably six-co-ordinate, being bound by two axial pyridine ligands ($\mu_{eff.}$ = 4.65 μ_B at 291 K[¶]).[6] While (**4**) exhibits an unchelated carbonyl i.r. absorption at 1720 cm^{-1} in toluene solution, this band is absent in a pyridine solution of (**5**) indicating the existence of the O_4 isomer (pyridine adduct) in solution as well as in the solid state. The movement of cobalt from the N_2O_2 site into the O_4 site is surprising on both kinetic and thermodynamic grounds, but may be the result of the reluctance of cobalt(II) in the N_2O_2 site to assume six-co-ordination (with two added pyridines), possibly owing to the instability of a high-spin d^7 ion in this site.[**][12] Note that the hole size of this site is restricted by the ethylene bridge and by any hydrogen bonding between ketone oxygen atoms and enol protons across the second site. Crystallographic results on analogous systems show substantially longer (by at least 0.13 Å) Co–N and Co–O bond lengths for high-spin (six-co-ordinate) cobalt(II) compared to low-spin (four- or five-co-ordinate) cobalt(II).[**][6,8—11,14—16] Thus, although suffering from an apparent loss of σ donation from the imine nitrogen atom, the cobalt(II) ion gains stability in the O_4 site by binding two additional pyridine ligands, which is apparently unfavourable in the N_2O_2 site.[**]

Positional isomerization has apparently been observed with copper and possibly vanadyl complexes of compartmental ligands,[17] but the present example is the first case of reversible isomerization between isolated and characterized complexes. More importantly, these results have permitted the generation

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[‡] All syntheses were performed in a nitrogen atmosphere (<2 p.p.m. of O_2) in a glove box (Vacuum Atmospheres Co.). The reported complexes gave satisfactory analyses for C, H, N, and Co.

[§] Dioxygen reactivity was assessed by the measurement of O_2 uptake on a high-vacuum line.

[¶] Magnetic susceptibilities given are per molecule and have been corrected for diamagnetism but not for temperature-independent paramagnetism.

[**] An analogous four-co-ordinate complex containing only one available site (N_2O_2) for cobalt, Co(salen) (salen = *N,N'*-ethylenebis-salicylideneaminato), will readily bind one additional pyridine ligand, leading to a *low-spin* cobalt(II) complex[10] in which only slightly longer (by *ca.* 0.5 Å) Co–N (imine) and Co–O bond lengths were observed.[8,14] The binding of an additional pyridine to achieve six-co-ordination around cobalt was observed only in very concentrated pyridine solutions and again the cobalt(II) ion was *low spin.*[14]

of the first dioxygen-reactive cobalt complexes with this ligand system.[12,18]

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