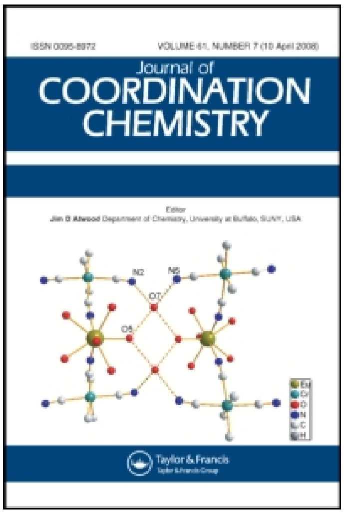

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AN N_2O_2 TETRADENTATE LIGAND 6,6'-BIS(ACYLAMINO)-2,2'-BIPYRIDINE. OXIDATION-REDUCTION PROPERTIES OF COBALT COMPLEXES

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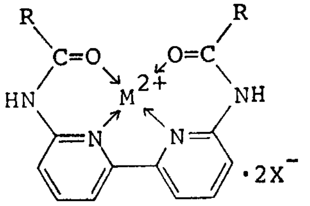
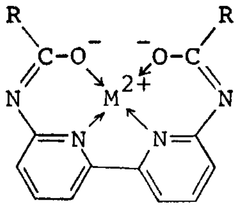
Recently, we reported the syntheses and the properties of a new type of N_2O_2 tetradentate ligands, 6,6'-bis(acylamino)-2,2'-bipyridines and their copper(II) complexes.[1] These ligands form two different types of square-planar complexes, i.e., Type 1 and Type 2, depending on the pH of the solution.[1,2] In addition, the deprotonated complexes (Type 2) are suggested to have strong ligand field, and are regarded as analogues of salen complexes. In this paper, we report syntheses and properties of cobalt complexes of 6,6'-bis(benzoylamino)-2,2'-bipyridine (babpH_2), and the interaction of the Type 2 complex with molecular oxygen.

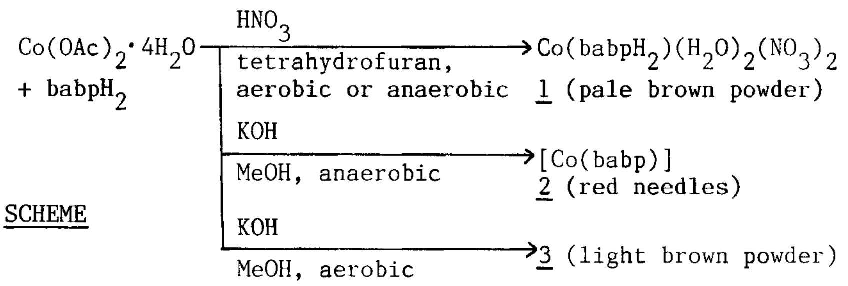


Type 1



Type 2

The reaction of babpH_2 with cobalt(II) acetate and subsequent anion exchange with nitric acid gave a pale brown powder 1 under either aerobic or anaerobic atmosphere, which was confirmed to be Type 1 complex. The reaction with cobalt(II) acetate in methanol in the presence of twice molar potassium hydroxide under anaerobic atmosphere gave red needles, 2, which was confirmed to be Type 2 complex, [Co(babp)], with no other component. The elemental analyses and the characteristic i.r. bands (Type 1; 1611 cm^{-1}, Type 2; 1557 cm^{-1}) confirmed that these two complexes have the square-planar structure analogous to the corresponding copper(II) complexes, in which babp(H_2) coordinates as N_2O_2 tetradentate ligand.[1] When the reaction in the presence of KOH was carried out under aerobic conditions, a light brown powder 3 was obtained. The i.r. spectrum of 3 was quite similar to that of 2 but a strong band near 1400 cm^{-1} was observed in 3; the e.s.r. spectrum was quite different from that of 2. The preparation procedures are summarized in Scheme.



SCHEME

Solvent effects were observed in the electronic spectra and the redox potentials of complex 2 under anaerobic conditions. The absorption band at longer wavelengths extended the absorption tail to around 700 nm in dimethyl sulfoxide (DMSO) or pyridine, which have strong electron donating abilities. In acetonitrile (AN), on the other hand it extended only to 600 nm (Figure 1). The electronic spectrum of 1 did not show such solvent effects. The redox potentials of a cobalt(II) / cobalt(III) couple of 2 were determined by cyclic voltammetry, and the values were ca. 0.4 V vs SCE in AN and ca. 0.1 V vs SCE in DMSO. The tailing of the absorption band and lowering of the redox potentials indicate that DMSO or pyridine molecule coordinates at the axial position of 2.

The coordination of molecular oxygen to complex 2 in DMSO and pyridine was investigated by the e.s.r. spectrometry at room temperature. Complex 2 showed no e.s.r. signals in solid state nor in an AN solution under aerobic and anaerobic conditions. In DMSO or pyridine, any spectra were neither observed under anaerobic conditions. After oxygen-bubbling, however, an octet of the ca. 15 G spacing was observed near g=2 due to isotropic ^{59}Co (I=2/7) hyperfine-splitting (Figure 2-A): it supports the formation of a cobalt(III)-superoxide type oxygen adduct of [Co(babp)].[3] The appearance of the spectrum was reversible on repeating the deaeration and oxygen-bubbling cycles at room temperature. Complex 1 showed no e.s.r. signals even after oxygen-bubbling. Black powder 4

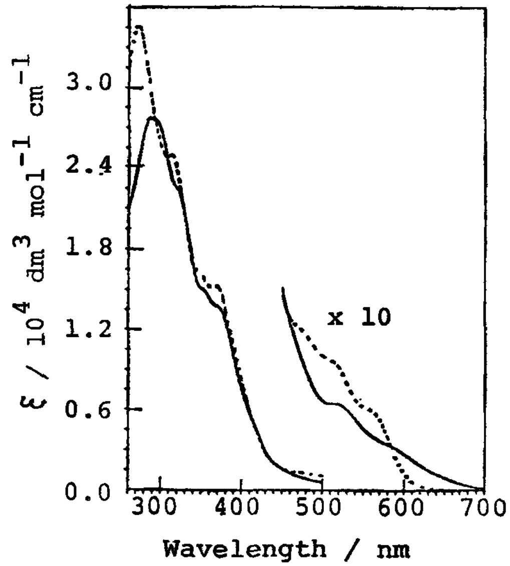


FIGURE 1. The electronic spectra of 2 under anaerobic conditions at 20 °C; in DMSO (———), in AN (- - - -).

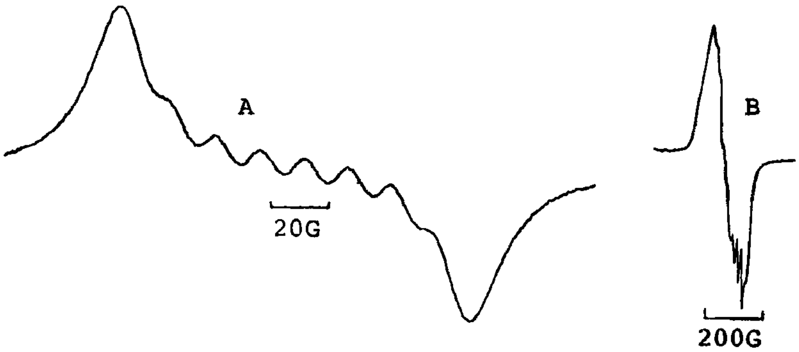


FIGURE 2. The e.s.r. spectra of cobalt complexes at room temperature. A: 2 in DMSO after oxygen-bubbling, B: 3 in solid state.

was recovered from a oxygen-bubbled pyridine solution of 2, while, similar treatment of 2 in DMSO afforded only the starting 2. As evolution of oxygen was observed by flash thermolysis of 4 at 300 °C this complex was confirmed to be the oxygen adduct of [Co(babp)]. The residue recovered was proved to be 2. Complex 2 itself was stable enough up to 300 °C even in aerobic atmosphere.

Complex 3 showed strong e.s.r. signals near g=2 having hyperfine structure in solid state at room temperature (Figure. 2-B). Thermal degradation of 3 showed an approximately 12% of weight loss up to 140 °C, and the resultant residue was found to be 2. Flash thermolysis at 300 °C revealed that methanol was incorporated in the complex 3, but oxygen was not detected. The composition of 3 has not yet been clarified.

In conclusion, coordination of molecular oxygen to Type 2 complex of cobalt(II), [Co(babp)], was confirmed in a solvent having strong coordination ability, while, Type 1 complex showed no evidence of such interaction. Oxygen molecule may coordinate reversiblly forming the cobalt(III)-superoxide type complex, and this complex was stable at room temperature. This properties resemble those of the molecular oxygen adducts of cobalt complexes of some salen derivatives.[3]

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