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New Type of Organocobalt Complexes Structure of η^2-Aminomethylenebis(2,2'-bipyridyl) Cobalt (III)

Short Communication

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The cations Co*bipy*$_2$(CH$_2$NH$_2$)$^{2+}$ formed through the photodecarboxylation of Co*bipy*$_2$(O$_2$CCH$_2$NH$_2$)$^{2+}$ have been shown by single-crystal X-ray diffraction to contain the three-membered Co—C—N cycles, with Co—C, Co—N, and C—N distances being 195, 194, and 141 pm respectively.

(Keywords: Cobalt(III), η^2-aminomethylene complex; Crystal structure; Organocobalt complexes; Photodecarboxylation)

Ein neuer Typ von Organo-Kobaltkomplexen. Struktur von η^2-Aminomethylenbis(2,2'-bipyridyl)-kobalt(III) (Kurze Mitteilung)

Die durch Photodecarboxylierung von Co*bipy*$_2$(O$_2$CCH$_2$NH$_2$)$^{2+}$ gewonnenen Kationen Co*bipy*$_2$(CH$_2$NH$_2$)$^{2+}$ enthalten einen dreigliederigen Ring Co—C—N der durch Einkristall-Röntgenstrukturanalyse bestätigt wurde. Die gefundenen Co—C-, Co—N- und C—N-Abstände betragen 195, 194 und 141 pm.

Organometallic compounds which were thought to contain three-membered Co—C—N rings formed through the photoelimination of carbon dioxide from five-membered glycinato rings of glycinatobis(diimine) cobalt(III), where diimine is 2,2'-bipyridyl (*bipy*) or 1,10-phenanthroline (*phen*) have been recently[1,2] reported. A proposed structure of photolysis products though plausible lacked certainty. Therefore an X-ray crystal study seemed advisable to demonstrate the structure conclusively.

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The perchlorate salt of $\mathrm{Co}\mathit{bipy}_2(\mathrm{CH_2NH_2})^{2+}$ was prepared as described previously[1,2]. Dark red crystals of $[\mathrm{Co}\mathit{bipy}_2(\mathrm{CH_2NH_2})](\mathrm{ClO_4})_2$ were obtained by slow cooling of an ethanol—water solution (1:1 *v*/*v*) saturated at 25 °C. Crystal data of $\mathrm{C_{11}H_{20}N_5O_8Cl_2Co}$, *M* 600.32: monoclinic, space group $P2_1/c$, $a = 967.1$ (2), $b = 1278.7$ (4), $c = 1984.9$ (7) pm, $Z = 4$, $d_{\mathrm{calc}} = 1.656\ \mathrm{g\,cm^{-3}}$.

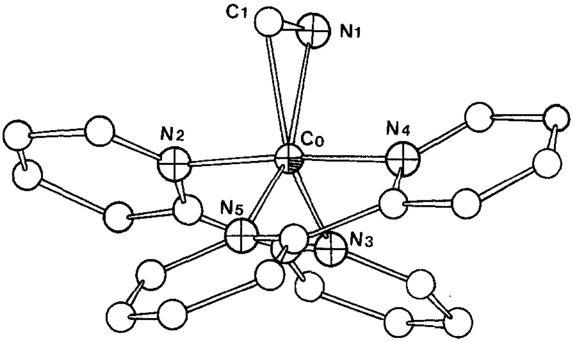

Fig. 1. The stereochemistry of $\mathrm{Co}\mathit{bipy}_2(\mathrm{CH_2NH_2})^{2+}$. The most relevant bond lengths and angles: Co—C(1) 196(2), Co—N(1) 194(2), Co—N(2) 193(2), Co—N(3) 203(2), Co—N(4) 197(2), Co—N(5) 193(2), C(1)—N(1) 141(3) pm; C(1)—Co—N(1) 43(1), C(1)—Co—N(5) 107(1), N(1)—Co—N(3) 103.4(9), N(2)—Co—N(3) 80.5(8), N(2)—Co—N(4) 175.5(9), N(2)—Co—N(5) 95.7(9), N(3)—Co—N(4) 96.3(9), N(3)—Co—N(5) 107.0(9), N(4)—Co—N(5) 82.0(9)°

Three-dimensional X-ray diffraction data were collected on an automated Syntex $P\bar{1}$ diffractometer by Cu-Kα radiation ($\lambda = 154.056$ pm) and a $\theta - 2\theta$ scan technique. From a set of 2332 reflections measured, 1945 ones were classified as observed [$I \geq 4\sigma(I)$]. The main features of the structure were obtained by applying *Patterson* and successive electron density calculations, only nonhydrogen atoms being localized. The positions of atoms were refined by the full-matrix least-square program with anisotropic thermal parameters to a final *R* factor of 0.128. The high value of the *R* factor results from the poor quality of the crystals and strong absorption of Cu-Kα radiation.

The crystal structure consists of complex cations $\mathrm{Co}\mathit{bipy}_2(\mathrm{CH_2NH_2})^{2+}$ and perchlorate anions. The structure of the complex cation together with some important bond parameters is shown in Fig. 1. Cobalt atom, N(1) and C(1) atoms of the aminoethylene group are approximately coplanar with two nitrogen atoms, N(3) and N(5), belonging to different *bipy* molecules. The remaining nitrogen atoms are in axial sites. The most interesting feature of the complex cation is the Co—N(1)—C(1) system, two canonical structure types of which may be considered.

According to the first one, the cation would be regarded as trigonal-bipyramidal Co(I) complex with π-bonded iminium cation $CH_2 = NH_2^+$. In the second extreme, we would regarded it as an octahedral Co(III) complex with a Co—C(1) σ-bond and a dative Co—N(1) bond.

The actual structure is an intermediate between each of the given extremes. The equatorial N(3)—Co—N(5) angle of 107^0, for example, is larger than that for an idealized octahedral geometry (90^0), but still far from the value of an idealized trigonal-bipyramidal structure (120^0). However, the C(1)—N(1) bond (141 pm), though shorter than that of a carbon—nitrogen single bond (150 pm), is much longer than a carbon-nitrogen double bond (124 pm). Some chemical properties of Co*bipy*$_2(CH_2NH_2)^{2+}$ or Co*phen*$_2(CH_2NH_2)^{2+}$ and its electron absorption spectra[1,2] as well as Co*en*$_2(CH_2NH_2)^{2+}$ spectra[3] are consistent with the lowspin cobalt (III) formulation (*en* = ethylenediamine). Therefore, the cation Co*bipy*$_2(CH_2NH_2)^{2+}$ is best viewed as containing an aminomethylene group acting as a three-electron donor to cobalt, and the unusually small C(1)—Co—N(1) angle of 43° results in a considerable distortion of what otherwise could be regarded as an octahedron of ligands about cobalt.

Several complexes with metal-nitrogen-carbon rings have been described in literature and the crystal structure of some of those were determined[4,5]. However, as far as our knowledge goes, compounds of Co*bipy*$_2(CH_2NH_2)^{2+}$ and Co*phen*$_2(CH_2NH_2)^{2+}$ are the first examples of cobalt η^2-aminomethylene complexes.

Generally, the photodecarboxylation of cobalt(III) aminocarboxylate complexes which follows irradiation in its ligand-to-metal charge-transfer band involves a complete oxidation-reduction decomposition. According to the currently accepted photolysis mechanism of these complexes, the redox photodecomposition occurs in the primary process which yields Co^{2+} and a free radical derived from the one-electron oxidation of a ligand[6,7]. In view of some findings, another primary process was assumed, namely, a contraction of the five-membered glycinato ring via elimination of carbon dioxide[8]. Co*bipy*$_2(CH_2NH_2)^{2+}$ is formed according to the following equation:

$$\mathit{bipy}_2\,\underline{\mathrm{CoO_2CCH_2N}}\mathrm{H_2}^{2+} \xrightarrow{h\nu} \mathit{bipy}_2\,\underline{\mathrm{CoCH_2N}}\mathrm{H_2}^{2+} + \mathrm{CO_2}$$

The organocobalt complexes formed in similar reactions from unmixed aminocarboxylate complexes could not be isolated because of their instability towards the thermal redox decomposition. It is noteworthy that cobalt(III) η^2-aminomethylene complexes are also involved in the UV otolysis of $\mathrm{Co}en_3{}^{3+}$ according to the following equation[3]:

$$en_2\,\underbrace{\mathrm{CoNH_2CH_2CH_2N}}\mathrm{H_2}^{3+} \xrightarrow{h\nu} en_2\,\underbrace{\mathrm{CoCH_2N}}\mathrm{H_2}^{2+} + \mathrm{CH_2NH_2}^{+}.$$

It is not inconceivable that the cyclophotoelimination will enable us to prepare compounds with three-membered metallocycles containing atoms other than nitrogen, for example, phosphorus, oxygen or sulfur.

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