A Mononuclear *cis*-Cobaloxime: *X*-Ray Crystal Structure of Di-trifluoroacetoxybis(butane-2,3-dione dioxime)cobalt(II)

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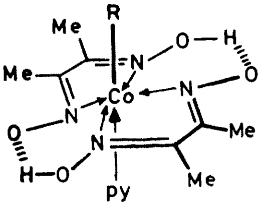
Summary Treatment of several alkyl(pyridine)cobaloximes with an excess of trifluoroacetic acid in chloroform gives the crystalline *cis*-cobaloxime(II) complex di-trifluoroacetoxybis(butane-2,3-dione dioxime)cobalt(II) identified by single crystal analysis

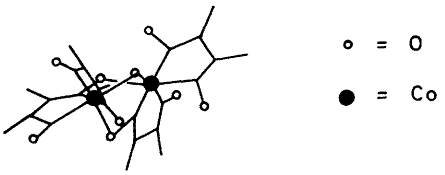
All mononuclear cobaloximes hitherto described exist as the *trans*-isomers.[1-3] The fifth and sixth ligands to cobalt are perpendicular to the plane of the four nitrogen atoms [*cf.* structure (**1a**) for methyl(pyridine)cobaloxime][2]. Ablov reported[4] that treating *trans*-hydroxoaquocobaloxime(III) with conc. aqueous KOH gives a *cis*-cobaloxime, subsequently formulated as a binuclear complex after a crystal structure analysis.[5] Acidification with nitric acid gave the binuclear *cis*-cobaloxime (**2**).[6]



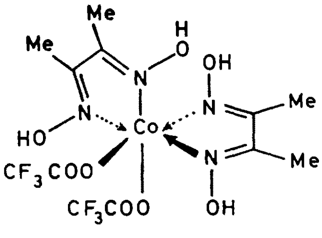
(1)

a; R = Me
b; R = CH_2Cl
c; R = $CHCl_2$
d; R = Et
e; R = Pr^i
f; R = Bu^n
g; R = $CH_2{=}CHCH_2CH_2$
h; R = $CH_2{=}CHCHMeCH_2$

We have found that addition of trifluoroacetic acid (TFA) to a series of alkylcobaloximes (**1b**—**h**) in chloroform causes sequential protonation of the cobaloxime and loss of pyridine, and with 8—10 mol. equiv. of TFA leads eventually to the deposition of a red crystalline solid. This is the first mononuclear *cis*-cobaloxime (**3**), identified by a single crystal structure analysis (Figure).† Cobaloxime (**3**) is a cobalt(II) complex as indicated by the presence of two uninegative ligands (trifluoroacetates). A powdered sample of (**3**) showed a molar magnetic susceptibility of 8350 × 10^{-6} c.g.s. units at 24 °C corresponding to a moment of 4·45 μ_B.



(2)



(3)

For clarity, only certain non-hydrogen atoms are shown in (2) (*cf.* ref. 6).

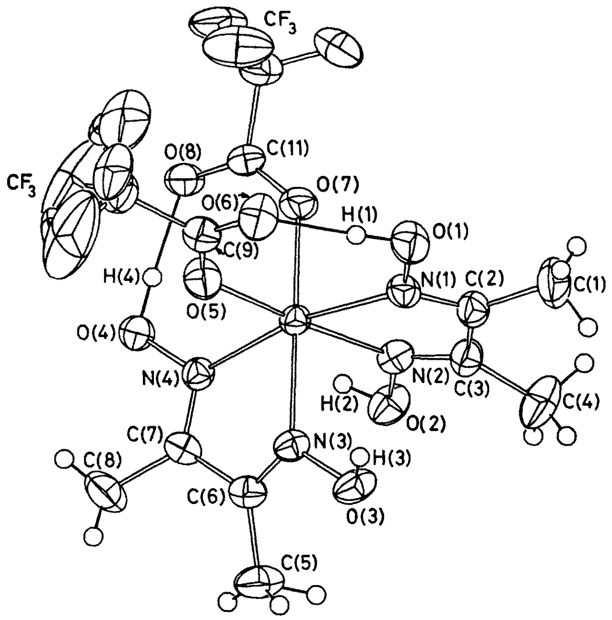


Figure. View of the molecule (3), showing the atomic numbering and the internal hydrogen bonds. Selected bond lengths are Co–O = 2·057(2), Co–N = 2·126(3), 2·138(2), 2·139(3), and 2·149(3) Å.

The complete location of the molecule's hydrogen atoms shows that the *cis*-cobaloxime (**3**) has a hydrogen bonding system completely different from that typical of the *trans*-species.[1-3] Both dimethylglyoxime ligands are neutral, rather than uninegative, and it is clearly their additional protons which prohibit the classical *trans*-cobaloxime geometry. Instead, each dimethylglyoxime forms one intramolecular and one intermolecular O–H · · · O bond to the free oxygen atoms of a co-ordinated trifluoroacetate ligand.

In the formation of (**3**), the first step is monoprotonation of one dimethylglyoximato oxygen, which is followed, rapidly, by the loss of pyridine (as pyridinium trifluoroacetate) and its replacement by trifluoroacetate or trifluoroacetic acid. A slower subsequent stage (over a period of days at room temperature) involves loss of R as RH followed by crystallisation of (**3**). Pyridinium trifluoroacetate was identified by monitoring the decompositions of (**1b**—**h**) by ^1H n.m.r. spectroscopy. For (**1c**) the formation

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† *Crystal data:* $C_{12}H_{16}N_4O_8F_6Co.CHCl_3$, M = 636·6, triclinic, space group $P\bar{1}$, with a = 10·068(3), b = 10·706(6), c = 13·030(3) Å, α = 100·15(3), β = 116·76(3), γ = 88·97(3)°, U = 1232·6(8) $Å^3$, D_c = 1·714 g cm^{-3} for Z = 2; Mo-K_α radiation (λ = 0·71069 Å), μ(Mo-K_α) = 9·88 cm^{-1}.

R = 0·053 for 1873 reflections [$I/\sigma(I) > 3{\cdot}0$] collected at −80 °C by a four-circle diffractometer, corrected for absorption, all atoms except H with anisotropic temperature factors. One CF_3 group is disordered. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

of CH_2Cl_2 (RH) was detected by ^{1}H n m r spectroscopy and for (**1e**) formation of propane (RH) was shown by g l c

It is significant that formation of Ablov's binuclear *cis*-cobaloxime[5] requires extreme pH conditions, and there can be no doubt that this involves the destruction of the *trans*-cobaloxime hydrogen-bonding system by proton *abstraction*, in contrast with the proton *addition* reported here

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[6] S T Malinovskii Y A Simonov A V Ablov T I Malinovskii I D Samus and O A Bologa *Dokl Akad Nauk SSSR* 1977 **232** 326 (*Chem Abs* 1977 **86** 99424b)