

## Review

# Organo-bridged dicobaloximes: Synthesis, structure and nuclear magnetic resonance study

B.D. Gupta<sup>a,b,\*</sup>, Kamlesh Kumar<sup>a</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

<sup>b</sup> Bahra University, Wahnaghat, Shimla Hills 173215, India

## ARTICLE INFO

## Article history:

Available online 3 February 2011

Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday

## Keywords:

Dicobaloxime  
X-ray structure  
Variable-temperature NMR  
Bridging ligands

## ABSTRACT

This short review describes the synthesis and structural characteristics of methylene, xylylene and biphenyl-bridged dicobaloximes. The bridged dicobaloximes are easily synthesized by oxidative alkylation method and the yield of dicobaloxime depends on many factors like reaction time, solvent, dihalide:Co(I) ratio and also on the nature of dihalide used. The NMR and structural studies have been described. The cobalt-bound CH<sub>2</sub> and dioxime protons in xylylene-bridged dicobaloximes become nonequivalent at sub-zero temperature and this is caused by the restricted rotation of the Co–C bond. However, the nonequivalence in biphenyl-bridged dicobaloximes is caused by atropisomerism and/or restricted rotation of C–Ph/Co–C bond. Two cobaloxime units of biphenyl-bridged dicobaloximes are symmetrical, and can be looked at as two independent benzyl cobaloximes and there is no direct or indirect interaction between them. In the xylylene-bridged dicobaloxime, one cobaloxime unit affects the structural parameters of the other unit through axially bridged benzyl group, which is sandwiched between two dioxime wings.

© 2011 Elsevier B.V. All rights reserved.



**B.D. Gupta** obtained his M.S. (Hons) from Panjab University Chandigarh, India, in 1970 and Ph.D. from the Flinders University, Adelaide, Australia, in 1975. After three years postdoctoral studies at University College London, England, he initially joined Roorkee University (now Indian Institute of Technology, Roorkee) and then moved to Indian Institute of Technology, Kanpur in 1980 where he has been a professor since 1988. He moved to IIT Ropar as Chair and Dean in 2009. At present he is the Vice Chancellor of Bahra University, Shimla Hills. He has been a visiting professor and taught undergraduate classes at various Universities in US and Japan. His research interests include modeling of vitamin B12, activation of small molecules, cobalt mediated organic reactions, organocobalt complexes with 2–5 cobalt centers.



**Kamlesh Kumar** received his B.Sc. (2004) and M.Sc. (2006) degrees from D.D.U. Gorakhpur University (Gorakhpur, India). After receiving a fellowship from UGC, India (2006), he joined Indian Institute of Technology, Kanpur as a doctoral fellow. His research interest includes synthesis and reactivity studies of Vitamin B12 model compounds.

\* Corresponding author at: Bahra University, Wahnaghat, Shimla Hills 173215, India. Tel.: +91 512 2597046, fax: +91 512 2597436.

E-mail address: [bdg@iitk.ac.in](mailto:bdg@iitk.ac.in) (B.D. Gupta).

## Contents

1. Introduction	9
2. Synthesis	10
2.1. Methylene-bridged dicobaloximes	10
2.2. Xylylene-bridged dicobaloximes	10
2.3. Biphenyl-bridged dicobaloximes	11
3. <sup>1</sup> H NMR studies	11
3.1. Methylene-bridged dicobaloximes	11
3.2. Xylylene-bridged dicobaloximes	12
3.3. Biphenyl-bridged dicobaloxime	13
4. X-ray structural studies	14
4.1. Methylene bridged dicobaloximes	14
4.2. Xylylene-bridged dicobaloximes	14
4.3. Biphenyl-bridged dicobaloximes	14
5. Concluding remarks	15
Acknowledgment	15
References	15

## 1. Introduction

Although the organometallic chemistry of cobalt has been known since 1949 when Ingles and Polya [1,2] reported the synthesis of  $RCoX_3$ ,  $RCoX_2$ , the real breakthrough came after the discovery of the B12 based enzymes, the only naturally occurring Co–C bond [3,4]. The scientists got interested in mimicking the chemistry and hence synthesized many simple model compounds. In some respect these simple models have been useful in understanding some of the basic features of the more complex bio-systems [5–9], thereby providing clues into the elusive mechanisms of B12 dependent enzymatic processes [10–13]. Among all the known models, two classic simple model compounds, cobaloximes (proposed by Schrauzer) [14–16] and iminocobaloximes (known as Costa complex) [17,18] have been the most studied systems (Fig. 1). Many complexes with Schiff-base type ligands like Salen, BAE [19] have

also been reported. Some of the recently appeared model compounds have been derived from Costa compound.

- Lariat model (Marzilli, 1992) [20].
- Advanced Costa's model (van der Baan, 1995) [21].
- Model with three membered ring (1996, Marzilli) [22].
- Model with hexadentate ligand (1997, Marzilli) [23].
- Tridentate imino-oximate model (Randaccio, 1996) [24].
- Amino-oxime model (Randaccio, 2001) [25].

Though the chemistry of mononuclear organocobaloximes is rich, well documented and reviewed periodically [5–8,26,27], surprisingly not much has been reported on the bridged dinuclear organocobaloximes. The bridging in the dicobalt system can occur in several ways, for example, it can occur through the neutral base ligand [28–34] or inorganic ligand [35–41], through axial organic ligand [42–47], it can even be through the equatorial ligand and a combination of processes [34,48–55]. Bridging through the equatorial ligands or mixed types of bridging is rare and mostly known with hetero bimetallic systems [56–62]. However, mainly two types of bridging viz. ligand-bridged and organo-bridged have been studied (Scheme 1).

Although the ligand-bridged bimetallic complexes including cobaloximes have been extensively studied and reviewed, not much work on the neutral organo-bridged dicobaloximes  $B(\text{dioxime})_2\text{Co}-R-\text{Co}(\text{dioxime})_2B$  bearing two reactive Co–C bonds have been carried out. In 1966, Schrauzer and Windgassen [42] were the first to mention the synthesis of neutral methylene-bridged dicobaloximes,  $\text{PyCo}(\text{dmgH})_2-(\text{CH}_2)_n-\text{Co}(\text{dmgH})_2\text{Py}$  (where  $n = 3, 4$ ) however, these complexes were only partially characterized. Formation of B12-dimer through a reaction of B12<sub>s</sub> with 1,4-dibromobutane was first suggested in 1964 by Smith et al. [63] although no evidence concerning its structure was given. They found that such dimeric coenzyme analogs were formed only when the bridging carbon chain length exceeded three units, as predicted by

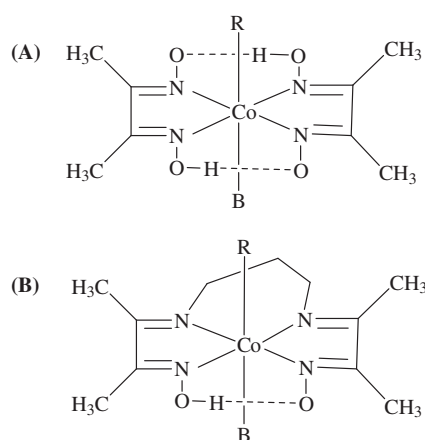
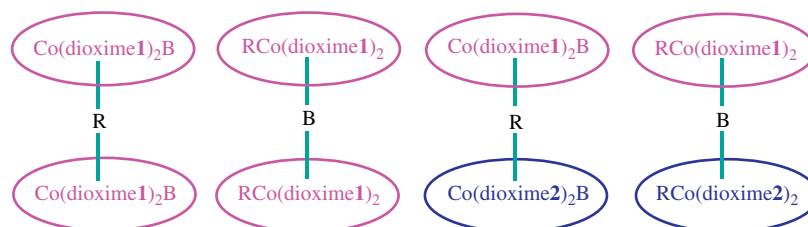


Fig. 1. Chemical structure of (A) Cobaloxime and (B) Costa's model.



Scheme 1. Schematic representation of bridged dicobaloxime.

Download English Version:

<https://daneshyari.com/en/article/1308866>

Download Persian Version:

<https://daneshyari.com/article/1308866>

[Daneshyari.com](https://daneshyari.com)