UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION AND REACTIONS OF COPPER (II) - GLYCEROL COMPLEX

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FPP 1998 12

CHARACTERIZATION AND REACTIONS OF COPPER (II) - GLYCEROL COMPLEX

BY

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Dissertation Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Science and Environmental Studies
Universiti Putra Malaysia

FOR

Mak and Abah

Ghani and Our Children

Nur Suriyana Abd Ghani
Ariff Ehsan Abd Ghani
Mohammad Asyraf Aslam Abd Ghani

ACKNOWLEDGEMENTS

Special Acknowledgement

I would like to express my sincere gratitute and appreciation to Associate Professor Dr Karen Badri for her continuous optimism, persistence, compassion, support and understanding, Professor Dr. Badri Muhammad for his vision, creativity, interest, support and patience, Dr Abd Rahman Manas for understanding, discussion, encouragement and support and Professor Dr. Md. Nordin Lajis for suggestion and discussion. Their contributions have been an inspiration in the completion of this thesis.

Acknowledgement

I am also greatly indebted to collegues, friends and staff of Department of Chemistry, UPM for friendship, encouragement, assistance and laughter which were invaluable through out the course of the study.

Chong Fai Kait (for her earlier involvement in this project), Nor Hadiani, Kamaliah and Yii Mei Woo.

Roila Awang for proof reading.

Academic and general staffs of Department of Chemistry, UPM especially Dr Mohd Toffazal Mohd Tarafder for his constant interest and support during group meetings.

Director General of PORIM for approval of study leave, Universiti Putra Malaysia, Public Service Department (JPA) and Ministry of Science, Technology and Environment, Malaysia (IRPA Project No. 03-04-03-0001).

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Abstract of the dissertation presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Doctor of Philosophy.

CHARACTERIZATION AND REACTIONS OF COPPER (II) - GLYCEROL COMPLEX

by

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July 1998

Chairman: Associate Professor Dr Karen Badri

Faculty: Science and Environmental Studies

In solution, either aqueous or methanolic, the colour of copper(II)-glycerol complex (Cu-Gly) is deep midnight blue. Its presence was confirmed by its UV-VIS spectrum, which was a broad unsymmetrical band with a λ_{max} ~625 nm. The Na_2SO_4 bisalt of the complex was successfully isolated and characterized. The detailed characterization studies revealed interesting behaviours of the complex and its unique chemistry. The coordination of glycerol to Cu(II) was evidenced by the absorption frequencies in the region 1500-1200 cm^{-1} of the IR spectrum of the complex. The CHN analysis of the complex led to a proposed molecular formula of $Na_2Cu(C_3H_6O_3)_2$. $2H_2O$. Na_2SO_4. xNaOH (x = 0.1 or 0.2).

The uv-visible spectra showed absorption maxima at 381 nm and 625 nm with a shoulder at 531 nm. The calculated 10Dq for the complex fell in the range of strong ligands. The structure of Cu-Gly complex ion was therefore suggested to be a

tetragonally distorted octahedron, with the two glycerolate ions lying in a square plane. The two water molecules were assumed to be weakly bonded at the axial positions. The study also indicated that coordination of glycerol to Cu(II) was *via* its 1,2-hydroxyl positions.

Oxidations of Cu-Gly complex were carried out *in-situ*, either in aqueous or methanolic media, using the following oxidants: HNO_3, Br_2, CrO_3, pyridiniumchlorochromate (PCC), H_2O_2, $KMnO_4$ and $K_2Cr_2O_7$. Four of these gave oxidative products such as CO_2, formic acid, oxalic acid and glyceric acid. These products were identified spectroscopically and confirmed by simple chemical tests, where necessary. To further understand the chemistry of Cu-Gly complex, the oxidations were also carried out on its insoluble intermediate and pure glycerol (uncomplexed). The results from this study, supported further by the identified products and the proposed mechanisms for the reactions, have shown that the coordination of Cu(II) was indeed at the 1,2-position of glycerol.

The relative activities of the oxidants are parallel to the E^o of their half-reactions. Therefore a general trend in predicting the products (cleavage or non-cleavage) can be postulated. The results of the study also show that Cu(II) does play a major role in the reactions of Cu-Gly complex especially those involving electron transfer. The GC technique developed in this study is shown to be simple, reliable, practical and, hence, suitable for direct analyses of glycerol and its derivatives. No derivatization was required.

Abstrak disertasi yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi keperluan Ijazah Doktor Falasafah.

PENCIRIAN DAN TINDAK BALAS KOMPLEKS KUPRUM (II) - GLISEROL

Oleh

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Julai 1998

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Kompleks kuprum(II)-gliserol (Cu-Gly) membentuk larutan berwarna biru tua di dalam larutan akueus atau metanol. Kehadiran kompleks ini boleh dipastikan dengan kaedah spektroskopi ultralembayung-nampak yang memberi serapan yang tak simetri dengan λ_{maks} 625 nm. Kompleks Cu-Gly berjaya dimendak dan diasing. Ia diasingkan sebagai dwi garam bersama Na_2SO_4. Pencirian terperinci menunjukkan kompleks ini mempunyai sifat kimia yang menarik dan unik. Serapan inframerah (IR) pada panjang gelombang 1500-1200 cm^{-1} membuktikan pengkoordinatan gliserol kepada Cu(II). Analisis CHN mencadangkan formula molekul bagi ion kompleks Cu-Gly ialah $Na_2Cu(C_3H_6O_3)_2$. $2H_2O$. Na_2SO_4. xNaOH (x = 0.1 atau 0.2).

Spektrum ultralembayung-nampak memberikan serapan maksima pada 381 nm dan 625 nm, dengan satu bahu pada 531 nm. Pengiraan nilai 10Dq menunjukkan ia berada dalam lingkungan nilai 10Dq bagi ligan kuat. Oleh itu struktur ion kompleks Cu-Gly dirumuskan sebagai oktahedron tetragonal terherot, dengan dua ion gliserolat di kedudukan empatsegi sesatah. Manakala dua molekul air terikat secara lemah pada kedudukan menegak.

Pengoksidaan kompleks Cu-Gly dilakukan dalam keadaan *in-situ*, samaada di dalam larutan akueus atau metanol. Pengoksida berikut telah digunakan: HNO_3, Br_2, $KMnO_4$, CrO_3, piridiniumklorokromat (PCC), $K_2Cr_2O_7$ dan H_2O_2. Cuma HNO_3, Br_2, $KMnO_4$ dan H_2O_2 sahaja yang memberikan hasil tindak balas, seperti asid formik, asid oksalik, CO_2 dan asid gliserik. Kajian tindak balas terhadap gliserol tulen dan bahantara kompleks Cu-Gly juga dilakukan. Keputusan yang diperolehi serta sokongan daripada hasil tindak balas yang dikenalpasti dan cadangan mekanisma tindak balas, menunjukkan pengkoordinatan kuprum(II) adalah pada kedudukan 1,2- kumpulan hidroksil gliserol.

Aktiviti relatif reagen pengoksida adalah selari dengan keupayaan elektrod piawai dari tindak balas separa reagen itu. Kereaktifan pengoksida bertambah dengan nilai keupayaan elektrod piawai. Oleh itu hasil tindak balas samaada melibatkan pemutusan ikatan karbon-karbon (C-C) atau tidak, boleh dijangka melalui hubungan pengoksida dan E^o. Keputusan analisis juga menunjukkan ion

Cu(II) memainkan peranan penting dalam tindak balas kompleks Cu-Gly terutama dalam pemindahan elektron. Teknik kromatografi gas (GC) yang dibangunkan di dalam kajian ini didapati amat mudah, boleh dipercayai, praktikal dan sesuai untuk analisis terus gliserol dan terbitannya. Penerbitan kepada sebatian lain tidak perlu dilakukan.

CHAPTER 1

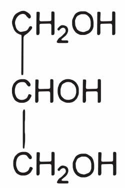
INTRODUCTION

Since the price of petroleum has increased nearly sixfold during the past 25 years and considering that petroleum is a non-renewable resource, the move to find alternatives for this feedstock was timely. Animal and vegetable oils and fats have been shown to be suitable substitutes for petrochemicals for certain applications. They are now the preferred base stock for many uses as they are renewable. Interest in researching production and utilization of oleochemicals continues to expand as a result of what seems to be an ever-increasing supply of vegetable oils especially in developing nations (Tsushima, 1997).

Oleochemicals are simply defined as the chemicals derived from animal or vegetable fats and oils, and five of them are considered as basic: fatty acids, fatty amines, fatty alcohols, methyl esters and glycerol. In addition to their price advantage, oleochemicals are often described as being more "environmentally friendly" than raw materials derived from petroleum.

Palm oil and palm kernel oil are well poised to assume a major role since they occupy an advantageous position with respect to tallow and coconut oil, which are the prime source of natural fats and oils. This is mainly because of their production economics, stable supply and freedom from religious taboos (Ministry of Primary Industries, 1997).

Among the basic oleochemicals, glycerol is considered as the primary base, since the preparation of all others must somehow yield glycerol at one point or other. In terms of composition, glycerol is the simplest of all the five basics. It is a simple trihydric alcohol, of molecular weight 92.09 having the structure I. It is a clear, odourless viscous liquid, has a sweet taste and is hygroscopic in nature. It is a tonnage chemical in the world market largely due to its numerous applications and its long record of safety in use (Whalley, 1993; Monick, 1960).



glycerol

I

When cold, glycerine can be supercooled and it resists freezing. Due to its miscibility with water and alcohol, it is a good solvent especially for many industrial