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Third
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Development
Programme

Photocatalytic Production of Energy-Rich Compounds

**Energy
from
Biomass
— 2 —**

Edited by G. Grassi and D.O. Hall

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PHOTOCATALYTIC PRODUCTION OF ENERGY-RICH COMPOUNDS

Edited by

G. GRASSI

Commission of the European Communities, Brussels, Belgium

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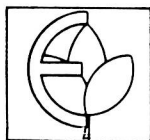
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**PHOTOCATALYTIC PRODUCTION
OF ENERGY-RICH COMPOUNDS**



Third EC Biomass Development Programme
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ENERGY FROM BIOMASS 2

*Proceedings of Second EC Workshop on Photochemical and Photobiological
Processes for the Production of Energy-Rich Compounds, Seville, Spain,
22-25 September, 1987*

Preface

This workshop comprises part of the four-year (1985–1988) non-nuclear energy R & D programme for the development of renewable energy sources which is being implemented by the Commission of the European Communities (Directorate-General Science, Research and Development—DG XII). The aim of the workshop was to present work by the contracting laboratories in addition to work by numerous other research laboratories in 11 European countries. Extensive discussions were also held on the present status of this basic, directed research in photochemistry, photoelectrochemistry and photobiology and where the future emphasis may usefully lie.

Thus the book presents the proceedings of all the papers presented and summarizes the recommendations made by the participants as to where future research support may be most effectively placed. It was emphasized in these recommendations that the interdisciplinary collaboration between photochemistry and photobiology had been quite successfully achieved in this European programme. There were both high quality basic research and practical benefits accruing from the work—these are elucidated in the report on proposed areas for future research.

We hope that this collaborative programme will continue in bringing together photochemists and photobiologists to help to ultimately devise practical systems for solar energy conversion and storage of useful compounds for energy and chemicals.

G. GRASSI

Commission of the European Communities

D. O. HALL

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2nd EEC Workshop on Photochemical and Photobiological Processes
for Producing Energy Rich Compounds
Seville, Spain; September 22nd-25th, 1987

*Recommendations from the participants for future research
in the R & D programme, DGXII/F-4*

The main areas proposed for further research support are:

1. Emphasise work on reaction centres and light-harvesting mechanisms, chemical and biological. Studies of light-activated reactions on surfaces and at interfaces. Synthesis and study of model compounds which mimic photosynthetic reaction centres, light-harvesting complexes and associated enzymes - this may provide very interesting new materials for further development.
2. The research programme should parallel and overlap research in photovoltaics and semiconductors, and thus provide a unique link and basis of information across the fields of photovoltaics, semiconductors and photosynthesis.
3. Research on multi-electron transfer reactions. These are different mechanisms from photovoltaics where single electron transfer reactions occur.
4. Activation and conversion of small molecules; photocatalysis. Production of H_2 from protons, N_2 fixation for ammonia production, CO_2 fixation for organics, sulphide (H_2S and Na_2S) oxidation, methane activation for methanol production, etc.
5. Photochemical processes for solving pollution problems. Removal of organic pollutants and inorganic molecules (e.g. NO_3 and NO_2) from water.
6. Genetic manipulation of cyanobacteria. Genetic engineering techniques with these micro-organisms are rapidly advancing and will make the understanding of photosynthetic reaction centre and water-splitting mechanisms easier, especially from the recent work in the USA and in Japan. However, there is no significant European group working in this field - this should be rectified.
7. Photobiotechnology. Photosynthetic micro-organisms specifically designed for the production of compounds such as carotenoids, ammonia, amino-acids, H_2 and possibly ethanol. Cyanobacteria, for example, are versatile micro-organisms whose growth and metabolism can be manipulated to preferentially excrete biochemicals.
8. Prevention of photodestruction. Many industrial products (e.g. paints and plastics) are destroyed by continuous exposure to the sun. Semiconductors and photoelectrodes are corroded in continuous light. Biological materials are also prone to photoinhibition. Understanding the mechanisms of photodecay (corrosion and inhibition) is essential to prevent such wasteful processes in chemical and biological systems.

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STABILISATION OF Si PHOTOANODES BY SILICON OXYNITRIDE COATINGS.

ATTEMPTED SYNTHESIS OF BINUCLEAR Co COMPLEXES FOR (PHOTO)ELECTROCHEMICAL
REDUCTION OF CO₂

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ABSTRACT

For the stabilisation of Si photoanodes by SiON coatings two routes are followed: the use of sufficiently thin (~ 2.5 nm) coating layers, prepared by etching techniques, so that electron-tunneling may occur and the doping of the thicker (~ 6.0 nm) layers with Pt to make them electronically conductive. The etching route gives limited success in that higher and rather stable photocurrents may be obtained than from photoanodes with thicker coatings. More reproducible results and higher photocurrents (still below 0.1%) occur upon Pt doping in the coating. This work is now in a final stage as specific funds have been used up.

The main emphasis of our EC project is in electrocatalytic CO₂ reduction, where we explore synthetic pathways for novel binuclear Co complexes with tetra-azamacrocyclic ligands and their use in electrochemical measurements and synthesis. Although several routes for ligand synthesis have been briefly described in the literature, we find upon repeated attempts that well-characterised samples are hard to obtain. In one case (bis-dioxo-cyclam [1]) we have obtained a pure product. In addition, the rotating-ring disk electrode has been introduced in this study for obtaining kinetic information on mono- and binuclear complexes. For their use in anhydrous media, water-free complexes have been prepared.

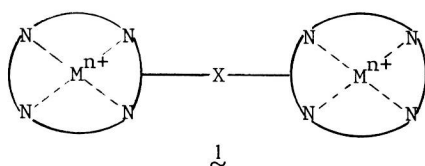
INTRODUCTION

The photo-electrochemical (PEC) cleavage of water to produce hydrogen and oxygen is still a long-term option for the storage of solar energy. No suitable photoelectrode material has yet been found. We have previously reported about titanates (TiO₂, SiTiO₃) and α -ferric oxide as unsuccessful candidates (Mackor et al., 1984a; Tinnemans et al., 1986). Thereupon, we have turned to the mass-produced n-Si, which is unstable as a photoanode. In this paper we report on results, which have been obtained by employing an insulating SiO_xN_y coating of appr. 6.0 nm thickness as a protective layer for n-Si. Two lines of research have been followed:

- 1) trying to obtain electron-tunneling thin layers via chemical etching techniques
- 2) doping the original layers with platinum to make them electronically more conductive.

The results are reported in the following section.

Our research on the electrocatalytic reduction of CO_2 is a continuation of previous research, sponsored by the EEC (Mackor et al., 1984b). In the referred study we showed the possibility of lowering the overvoltage for CO_2 reduction by using tetra-azamacrocyclic complexes of Co (and Ni) as electrocatalysts. This is due to the coordination of CO_2 to the metal ion in intermediate steps, whereby the $\text{O}=\text{C}=\text{O}$ bonding is weakened. It was felt that further reduction of this overvoltage is possible if one has two metal centers available at short distances for end-on or side-on coordination. Therefore we have considered the literature on the accessibility of ligands and possibly complexes of the type



in which M^{n+} is a transition-metal ion and X a bridging group, e.g. $(\text{CH}_2)_n$ ($1 \leq n \leq 5$). From this literature three pathways were selected for further study. These results are given in the next-following section.

Finally, we briefly report on the preliminary results of measurements with a rotating ring disk electrode.

STABILISATION OF Si PHOTOANODES BY SiO_n COATINGS

Results and discussion

While this research is part of the contract, it is mainly reported elsewhere (Mackor et al., 1987a and b). Here the main research lines and results are given.

Two sources of n-Si wafers, coated with 3.7–6.6 nm layers of SiO_xN_y ($x \approx y$), were used with comparable results. From Auger analysis, it follows that upon using these materials as photoanodes in wet PEC cells, the already low photocurrents (of the order of 10^{-8} A/cm^2) decrease upon operation by oxidation of the coated electrode, whereby x increases at the expense of y and by oxidation of Si. The starting SiO_xN_y layers already have a very high resistance ($1.9 \cdot 10^{13} \Omega \cdot \text{cm}^{-1}$). This resistivity must be diminished for more efficient operation. Two routes have been followed:

1. Chemical etching by a mixture of HCl , NH_4F and NH_4Cl to obtain a thinner layer with hopefully electron-tunneling properties at layer thickness below 3.0 nm
2. Doping of the coating layer by platinum atoms or clusters for making

them electronically more conductive by so-called resonance-tunneling at distances of appr. 1.5 nm.

Chemical etching experiments

A homogeneously coated 6.6 nm layer was used and part of the layer was removed by increasing etching times. Two (major) effects have been noted:

- higher photocurrents, up to a factor 100 higher than the original one in one case, over prolonged periods (hours);
- poor reproducibility.

Because of the latter effect, approach 1. was abandoned in favour of 2.

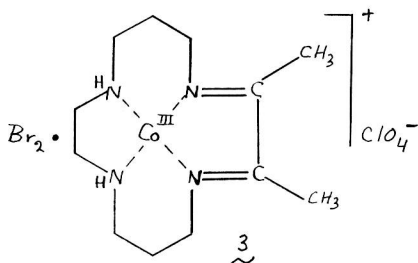
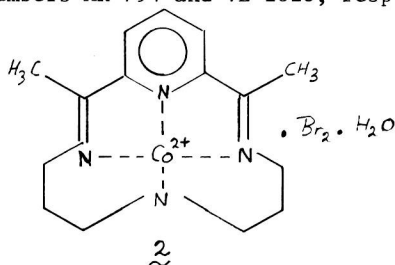
Doping SiO_xN_y layers with Pt clusters

A thin layer of Pt was sputtered onto a SiO_xN_y layer (6.6 nm) and thereupon the electrode was annealed at a certain temperature. Even at 300°C and short annealing time (30 min) a considerable increase in photocurrent has been routinely obtained at a current density of $14 \mu\text{A}/\text{cm}^2$, i.e. appr. 300 times larger than the original photoanode. In some cases an even ten times higher photocurrent density resulted. This is still a factor of 150 too low for practical use ($< 0.1\%$). Our final research in this area is aiming at getting a better understanding of these experiments. These results will be reported at the meeting in more detail.

ATTEMPTED SYNTHESIS OF BINUCLEAR Co COMPLEXES FOR (PHOTO)-ELECTROCHEMICAL REDUCTION OF CO_2

Mononuclear complexes

From previous research (Mackor et al., 1984b), the need had grown to dispose of water-free complexes CoL (or NiL), to be used in anhydrous solvents, e.g. acetonitrile. Two compounds were selected, viz. 2 and 3 (our code numbers MR 794 and VE 2828, resp.).



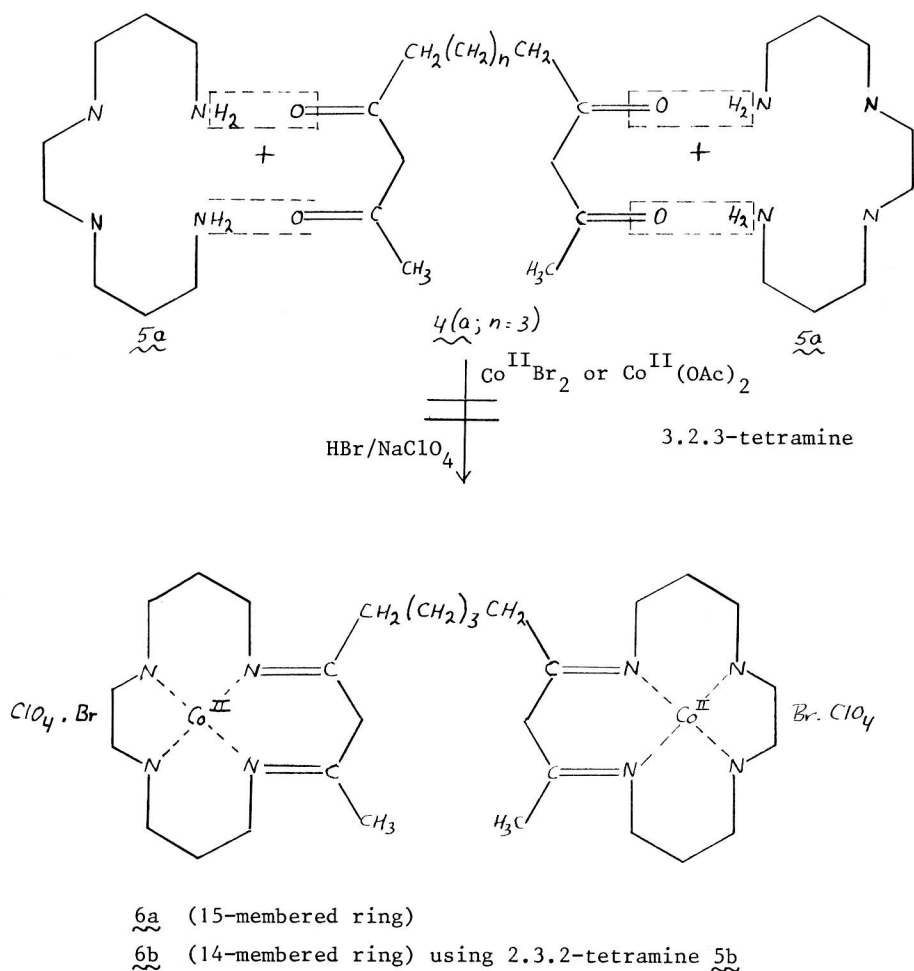
A previously prepared sample of 2 (Tinnemans et al., 1984) was dissolved in dimethylformamide and it was attempted to remove water by azeotropic distillation. Compound 2 was recovered unchanged, indicating the presence of coordinated water. The synthesis of compound 3 was carried out to give the

correct product and elemental analysis. (Tait et al., 1978).

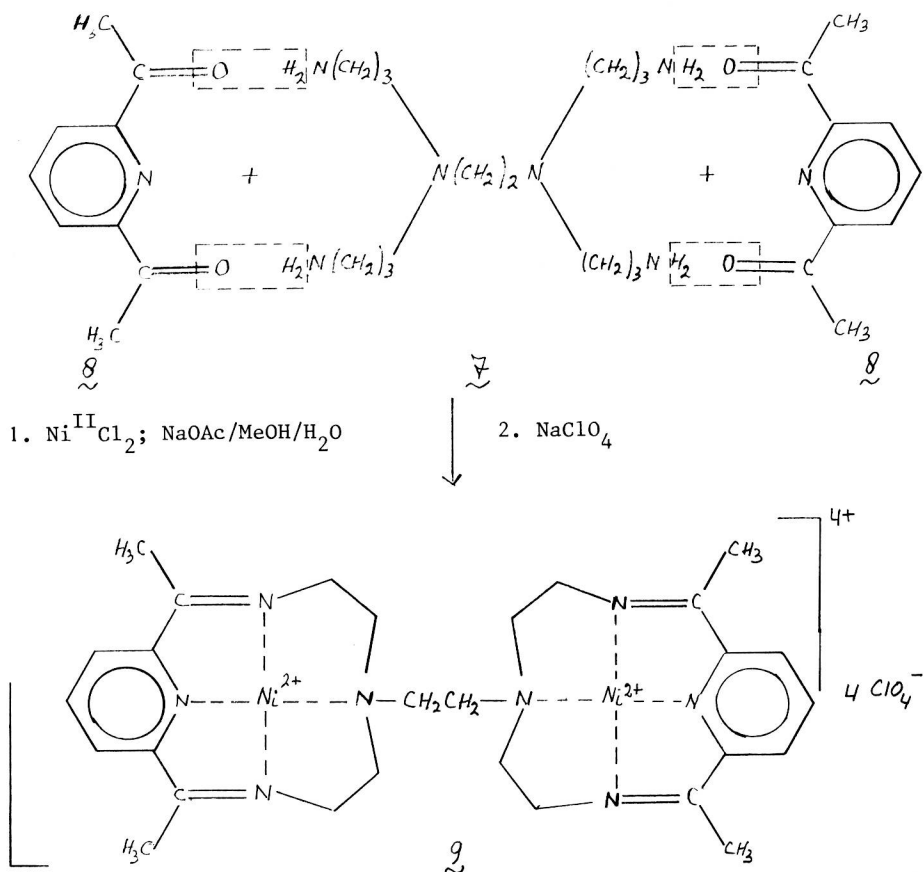
Dinuclear complexes

For the synthesis of dinuclear Co (or Ni) complexes of the type 1 the strategy of template synthesis was followed and worked out in two routes. Both principles were described in the literature (Murase et al., 1981, 1983, 1986).

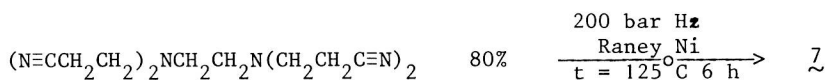
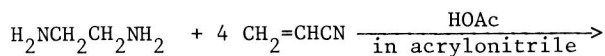
In route I, we synthesized various tetraketones 4 ($n = 2, 3$ or 6) and reacted 4a ($n = 3$) with a tetraamine 5a or 5b in the presence of a cobalt(II) salt in the hope of obtaining binuclear complex 6a or 6b.



In neither case could we obtain a well-defined and crystalline product. In route II, the building block for a dinuclear ligand was a hexaamine 7, which was reacted with 2,6-diacetylpyridine 8 and $\text{Ni}^{\text{II}}\text{Cl}_2$.

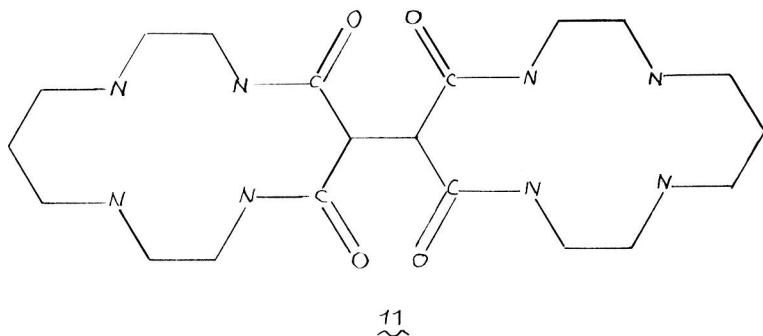


In this case some product was obtained, but the analysis of the product does not fit with pure compound 9. Moreover, unexpected problems occurred during the preparation of hexaamine 7:

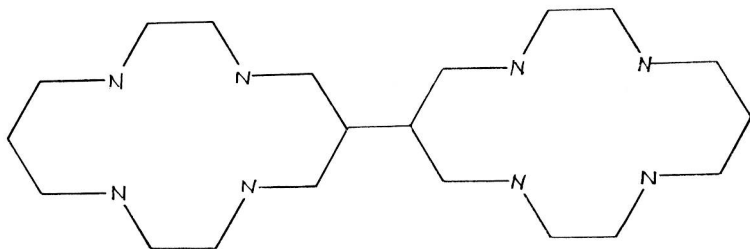


Two successive preparations in an autoclave exploded (or caused the safety plate in the autoclave to break) under these conditions, without personal injuries and without a clear cause. Thereupon the autoclave approach was

abandoned and other reducing agents (Redal, $\text{NaAlH}_2\cdot(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$; B_2H_6 /diglyme and B_2H_6 /THF) were used without much success. Fortunately, the autoclave method had yielded sufficient product to continue the synthesis. At this point a third pathway was examined to obtain dinuclear complexes (Fabbrizzi et al., 1984, 1986). Coupling of the 2.3.2-tetraamine 5b with a tetracarboxylic ester 10, yielded the bis-dioxocyclam 11.



The sample appears to be a mixture if NMR spectra are taken, e.g. one hour after dissolution in D_2O . However, elemental analysis is in good agreement with structure 11. Moreover, ^{13}C NMR spectra directly taken upon dissolution show only six ^{13}C signals, as expected. Compound 11 is a potential dinuclear ligand, which is now under study. It has been reduced by B_2H_6 to give the biscyclam 12, the analysis of which is underway.



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In conclusion, the synthesis of dinuclear complexes of Co (or Ni) is cumbersome and it has not yet been achieved. Earlier reports in the literature did not (always) refer to preparative-scale experiments, but rather to spectroscopic characterisation. It seems, however, feasible to obtain complexes of type 1 and therefore these experiments are continued.

RRDE experiments

A rotating ring disk electrode has been manufactured at TNO and it was successfully tested. Preliminary experiments with some old complexes (Tinnemans et al., 1984) showed that these materials had deteriorated over time. The new complexes were either not yet available in the pure state or were intended for use in anhydrous solvent (3 in MeCN), where stability problems occur during electrochemical operation.

ACKNOWLEDGEMENT

The research on water cleavage was supported by PEO, the Netherlands Project Office for Energy Research, by an extended contract, ending on September 30, 1987. The authors are grateful to Dr. W. Visscher of Eindhoven Technical University for supplying to them the drawings of a RRDE.

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