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NEW TYPE OF METALLO-ORGANIC POLYMER: BIMETALLOPORPHYRINS. INVS--ETC(U)

JAN 81 M TSUTSUI

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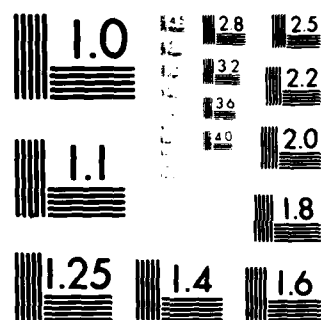
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18. ABSTRACT (Continue on reverse side if necessary and identify by block number) The creations (synthesis) of out of plane and skewered metalloporphyrins were reported. The structure of bis(phthalocyaninato)neodymium(III) was elucidated by the x-ray diffraction analysis. From the conductivity of $[\text{Pc}_2\text{Nd}]^+\text{Cl}^-$, a new hydrogen bonded polymer structure in crystal solid state without solvent was proposed.		

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April 1973 to June 1978

**NEW TYPE OF METALLO-ORGANIC POLYMER:
BIMETALLOPORPHYRINS**

July 1978 to December 1980

**INVESTIGATING A NEW CHEMISTRY OF
METALLOPHthalOCYANINES**

Submitted by the

TEXAS A&M RESEARCH FOUNDATION

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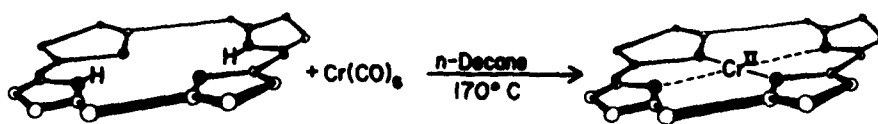
LIST OF CONTENTS

- I. Summary
- II. References
- III. List of Publications

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Summary

The use of metal carbonyls for the insertion of metal ions into porphyrins was first introduced by Tsutsui and his co-worker^{1,2} in 1966 (Figure 1). This method is probably one of the most important developments in porphyrin chemistry within the last two decades. In addition



Use of $\text{Cr}(\text{CO})_6$ for Insertion of Cr^{II} into Porphins

FIGURE 1

to a number of previously reported metalloporphyrins, the reaction of metal carbonyls and metal carbonyl halides³⁻¹⁰ with neutral porphyrins has led to the synthesis of new metalloporphyrin complexes of chromium, molybdenum, technetium, ruthenium, rhodium, rhenium and iridium.¹⁰⁻³² Except for the chromium and molybdenum complexes, carbonyl groups are retained by the metals in the new metalloporphyrin complexes.

By reaction of dirhenium decacarbonyl, $\text{Re}_2(\text{CO})_{10}$ or ditechne-
tium decacarbonyl, $\text{Tc}_2(\text{CO})_{10}$, with mesoporphyrin IX dimethylester, $\text{H}_2\text{MPiXDMe}$,
in refluxing decalin under argon, Tsutsui and his co-workers have suc-
cessfully prepared two unusual rhenium organometalloporphyrins^{22,23}
 $(\text{H-MP})\text{Re}(\text{CO})_3$, **I**, and $\text{MP}[\text{Re}(\text{CO})_3]_2$, **II**, a pair of technetium organometal-
loporphyrins,^{24,25} $(\text{H-MP})\text{-Tc}(\text{CO})_3$, **III**, and $\text{MP}[\text{Tc}(\text{CO})_3]_2$, **IV**, and a mixed

rhenum technetium organometalloporphyrin¹³, $(OC)_3ReMPTc(CO)_3$, V_L . A single crystal x-ray diffraction analysis of μ -[*meso*-tetraphenylporphinato] bis[tricarbonylrhenium(1)],²¹ $TPP[Re(CO)_3]_2$, V_L , (Figure 2), has shown

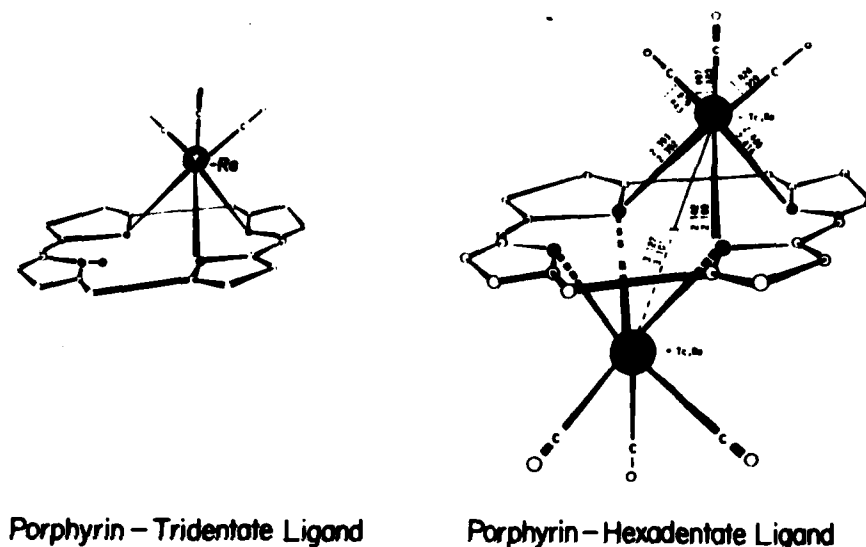


FIGURE 2

that each rhenium ion is bonded to three nitrogen atoms and that two rhenium atoms are bonded to one porphyrin on opposite sides of the plane of the porphyrin molecule.

The metal ions in these complexes, $I-V_L$, sit out of the plane of the porphyrin molecule. The monorhenium and monotchnetium complexes, I and III , where the porphyrin moiety acts as a tridentate ligand, resemble Fleischer's proposed "sitting-atop complex"^{26,27} and are good models for the intermediates in the insertion of a metal ion into porphyrin.²⁸ The dirhenium, ditechnetium, and mixed rhenium-technetium organometalloporphyrin complexes, II , IV , V , and V_L , where the porphyrin moiety acts as a hexa-

dentate ligand, are examples of the first isolated stable homo- and hetero-dinuclear organometalloporphyrin complexes.^{11,23} The monorhenium porphyrin complex,³¹ **II**, and the mixed rhenium technetium porphyrin complex,¹³ **V**, respectively. Replacement of the pyrrolic proton (N-H) of the monorhenium porphyrin complex by other metal ions such as Ag^+ , Hg^{2+} , and Pb^{2+} , has resulted in unstable complexes.³² The monotechnetium porphyrin complex, **III**, (Figure 3), behaves in a different manner by disproportionating to form a ditechnetium porphyrin complex, **IV**, and the free porphyrin, $\text{H}_2\text{MPIXIME}$, by heating in refluxing decalin.²⁵ This unusual coordination phenomenon has never been reported. Such a reaction was not observed on heating monorhenium porphyrin complex, **I**, in refluxing decalin.^{22,23} It seems that both the rhenium and technetium dimetalloporphyrin complexes are thermodynamically more stable than the monometalloporphyrin complexes, because a reverse reaction of $\text{MP}[\text{M}(\text{CO})_3]_2$ to $(\text{H-MP})-\text{M}(\text{CO})_3$, ($\text{M}=\text{Re}$ or Tc), could not be detected between $\text{MP}[\text{M}(\text{CO})_3]_2$ and $\text{H}_2\text{MPIXIME}$ in refluxing decalin for either the rhenium or technetium dimetalloporphyrin complexes.

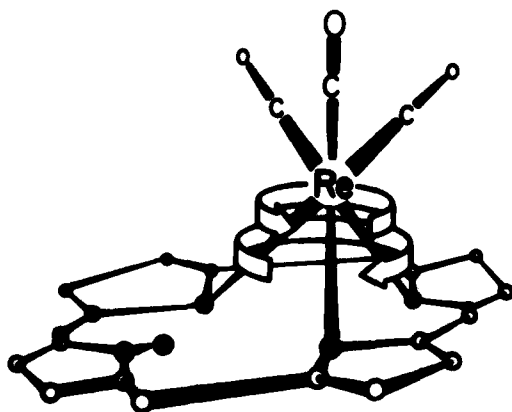
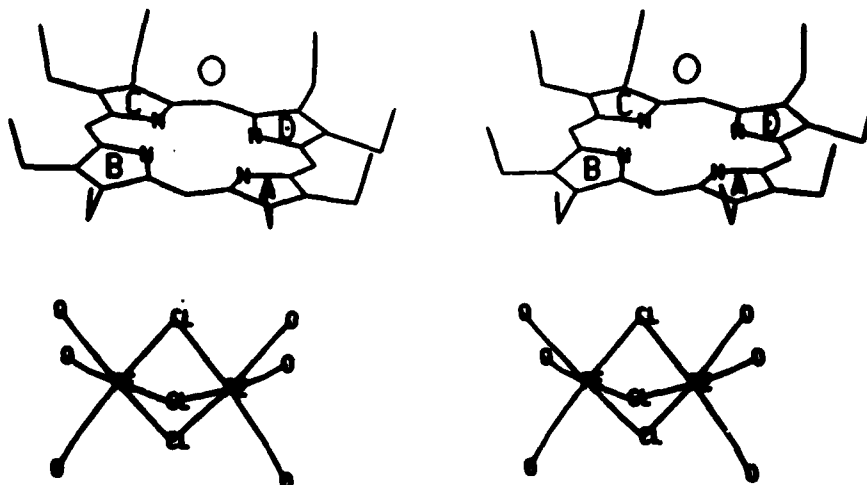


FIGURE 3

Temperature-dependent ^1H nmr spectral changes for $\text{HTPPRe}(\text{CO})_3$ and $\text{HMPRe}(\text{CO})_3$ dissolved in 1,1,2,2-tetrachlorethane showed fluxional behavior of $\text{Re}(\text{CO})_3$ group. This phenomenon is best explained by the intramolecular rearrangement of the metal carbonyl group among the four ring nitrogens of porphin and also movement of the N-H; it can also be regarded as intramolecular substitution at rhenium or technetium, (Figure 3).²⁹

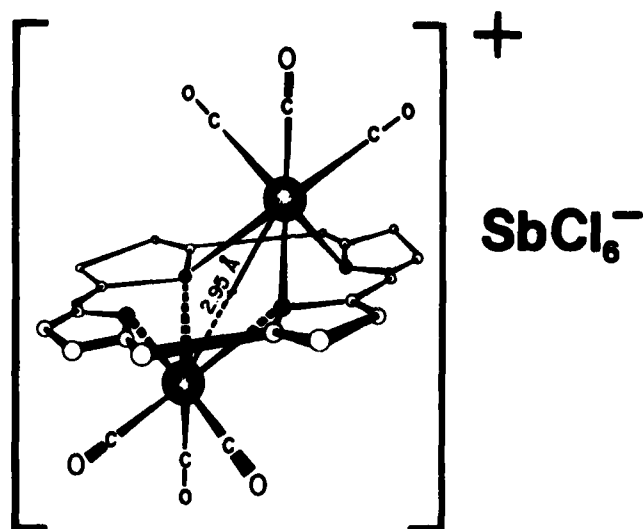
We have prepared a new salt type complex of porphyrins, monocation octaethylporphyrin tri- μ -halogeno-hexacarbonyldirhenate(I) from the reaction of $\text{Re}(\text{CO})_5\text{Cl}$ and H_2OEP in a 2:1 mole analysis method, (Figure 4).³⁰



Structure of $(\text{H}_3\text{OEP})^+[\text{Re}_2(\text{CO}_6)\text{Cl}_3]^- \cdot \text{H}_2\text{O}$

FIGURE 4

$[\text{Re}(\text{CO})_3]_2\text{TPP}$ has been oxidized by SbCl_5 in dichloromethane to yield $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{TPP} \cdot 2\text{SbCl}_6$ and $[\text{Re}(\text{CO})_3][\text{Re}(\text{CO})_3\text{Cl}] \cdot \text{SbCl}_6$. An x-ray determination of the structure of these complexes provides definite evidence for a "skewered complex", that is a metalloporphyrin in which a metal-metal bond exists through the "hole" of the macrocycle, (Figure 5).³¹



First Skewered Complex (Radical Metalloporphyrin)

FIGURE 5

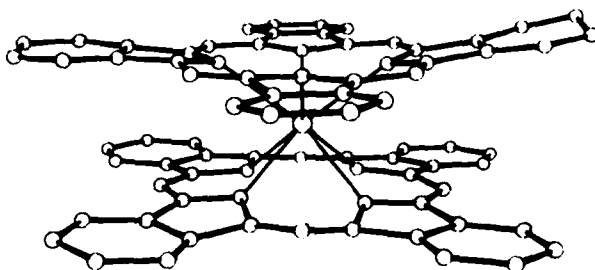
Tsutsui et al. used $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ for the preparation of $\text{Ru}(\text{CO})\text{Pc}$ and $\text{Os}(\text{CO})\text{Pc}$.³² The structure of $\text{Ru}(\text{CO})\text{Pc}$ was elucidated by x-ray diffraction analysis.³³ Carbon monoxide was found to be reversibly coordinated with Ru ion. $\text{Ru}(\text{CO})\text{Pc}$ has shown selective Fischer-Tropsch reaction.

Tsutsui and co-workers also investigated the ESCA of diphthalocyaninelanthanides, Pc_2LnH ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$ and Ga) and actinides, Pc_2An ($\text{An} = \text{Th}$ and U).³²⁻³⁴ As in copper(II) phthalocyanine, the nitrogen 1s spectra of these sandwich-type complexes show a single sharp peak.³⁵ This indicates that the central metal is equivalently surrounded by eight central nitrogen atoms and that the charge density of the central nitrogen atoms is accidentally the same as that of the outer-bridging aza nitrogen atoms. They also examined the satellites accompanying lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ signals.³⁶ In the case of Pc_2LnH , a shake-up satellite

was not observed in the $\text{Pr}^{\text{III}}(f^2)$ and $\text{Nd}^{\text{III}}(f^3)$ compounds which have sufficient vacant f -orbitals to receive electrons from ligands, whereas $\text{La}^{\text{III}}(f^0)$ and $\text{Ce}^{\text{III}}(f^1)$ compounds showed satellites. Analyzing the data carefully, they concluded that f -orbitals play an important role in the core-ionization process to give a sharp variation in intensity of the satellites.

The structure of $(\text{Pc})_2\text{Nd}^{\text{III}}\text{H}$ was elucidated by x-ray diffraction analysis and was also studied by esca.³⁶

The neodymium ion occupies a central position between two parallel but staggered (45°) phthalocyanine ligands (Figure 6).

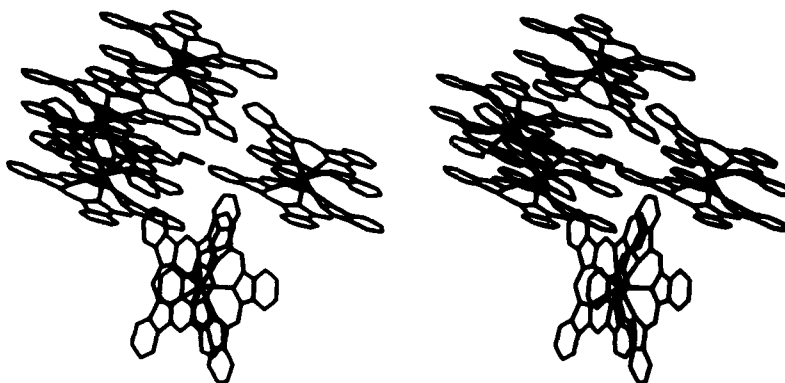


Molecular structure of bis(phthalocyaninato)neodymium(III)

FIGURE 6

The eight Nd-N bond distances vary from 2.39 to 2.49 Å. While one of the phthalocyanine macrocycles is slightly saucer shaped toward the neodymium atom, the other is planar; angles of tilt range from 2.5 to 7.0°. The pyrrole nitrogen atoms vary from the macrocyclic planes by distances ranging from 0.04 to 0.21 Å. The tilted benzimidazole group is an equal distance of 1.47(1) Å from each of the two least-squares planes containing the four pyrrole nitrogen atoms. An acidic hydrogen in this complex is known to play an important role in the electrochromic

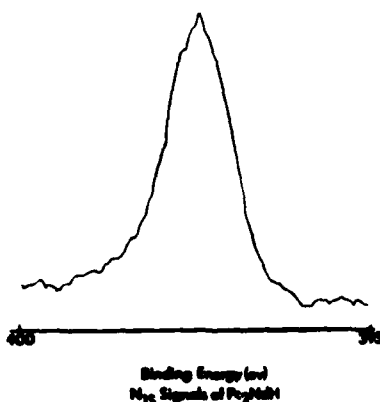
properties. Although an obvious distortion from macrocyclic planarity (13°) is manifest by one benzimidazole moiety, the elusive hydrogen is not directly revealed by the crystallographic results.³⁷ However, the molecules are packed in a three-dimensional "herringbone" pattern (Figure 7) with the molecule of solvation, dichloromethane, on the pseudomirror plane and between the benzimidazole rings of translationally related molecules; it is these rings which show the greatest distortion from symmetry.



Stereoscopic view of molecular packing cell of the structure

FIGURE 7

One may therefore conclude that the hydrogen occurs at this locus of asymmetry. In order to verify the location of the acidic hydrogen in the complex, we also obtained an N 1s X-ray photoelectron spectrum (Figure 8). The spectrum shows a sharp, single peak (at 398.8 eV with the width of 1.1 eV) in analogy with the spectra of usual types of metallophthalocyanines. The data imply that eight central nitrogen atoms are chemically equivalent to each other, and thereby the acidic hydrogen does not bind strongly to any of the nitrogen atoms in the complex though a possibility of a weak interaction between the hydrogen atom and the



An N 1s X-ray photoelectron spectrum of bis(phthalocyaninato)neodymium(III)

FIGURE 8

nitrogen atom(s) cannot be excluded. Recently, Moskalev et al. proposed a double-sandwich model of the neodymium(III) complex, $\text{PcNd}^{(\text{III})}\text{Pc}(\mu\text{-H}_2)\text{PcNd}^{(\text{III})}\text{Pc}$, to explain electrochromism. In their model, the acidic hydrogen has a weak intermolecular hydrogen bond, consistent with the result of the N 1s spectrum. Although the position of the acidic hydrogen of the complex could not be detected distinctly in this study, it is elucidated that the two phthalocyanine ring systems form the sandwich-type compound with the neodymium atom in the center and are oriented in the staggered configuration. We are studying electrochromism of bis-(phthalocyaninato)neodymium(III) in further detail by using ESR and cyclic voltametry, and the results will be described in a forthcoming paper.

Kirin and Moskalev reported that bis(phthalocyaninato)neodymium complex ($[\text{Pc}_2\text{Nd}]^-\text{H}^+$; Pc denotes a phthalocyanine dication) showed a semiconduction and considerably low resistivity (23 Ωcm at 25°C) and forbidden gap (0.122 eV) in the form of compressed disk.³⁸ The resistivity reported was extremely lower by about nine orders of magnitude than those

of usual metallophthalocyanines, which have resistivities of $10^{10} \sim 10^{13}$ Ωcm at room temperature.³⁹ The report, however, did not describe the detailed experimental conditions for the resistivity determination. In general, semiconductive properties of organic compounds are affected by experimental conditions.³⁹ Especially, the resistivity might be varied substantially by four orders of magnitude or more in the presence of trace amounts of oxygen for p-type semiconductors or impurities in the substance. Therefore, the resistivity should be measured in an oxygen-free ambient with a highly purified substance. Furthermore, the heat treatments should be done in a reducing gas such as hydrogen in order to remove oxygen completely absorbed in the substance.⁴⁰

Taking these factors into consideration, we attempted to reproduce their results. As a result of our experiments, the resistivity and activation energy for $[\text{Pc}_2\text{Nd}]^-\text{H}^+$ and $[\text{Pc}_2\text{Gd}]^-\text{H}^+$ compressed disks were found to have values between those of usual metallophthalocyanines and those reported by Kirin and Moskalev.

The values are close to those of the $[\text{Si}(\text{Pc})-\text{O}]_n$ polymer, 3.3×10^7 (Ωcm).⁴² It is possible that these decreases may be associated with the formation of an intermolecular hydrogen bond as shown in Figure 9.

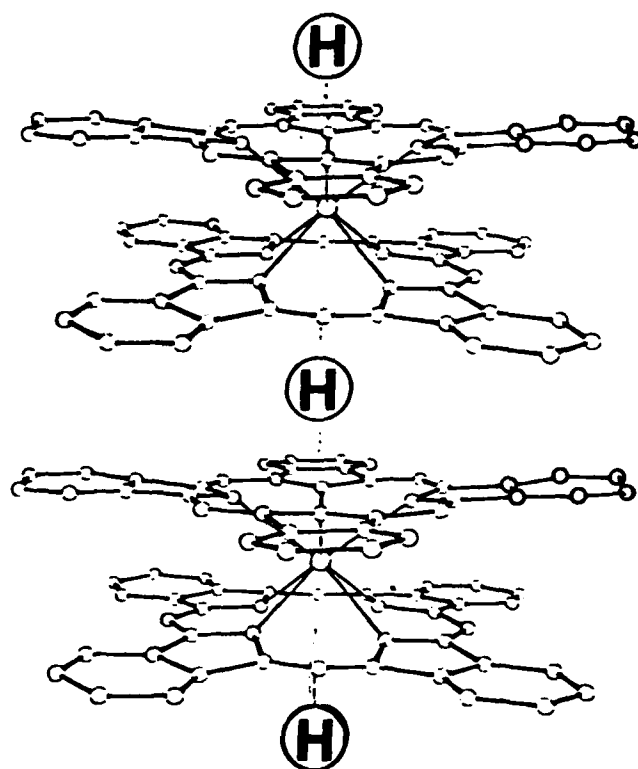


FIGURE 9

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