UCRL-16549

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Submitted to Science

UCRL-16549

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CRYSTAL AND MOLECULAR STRUCTURE OF A DOUBLE COMPLEX OF MANGANESE WITH PHTHALOCYANATE AND PYRIDINE

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November 1965

Abstract. A crystalline solid, formed by oxidation of phthalocyanatomanganese(II) in pyridine, has been identified as phthalocyanatopyridinemanganese(III)-μ-oxo-phthalocyanatopyridinemanganese(III) dipyridinate ($C_{74}H_{42}ON_{18}Mn_2 \cdot 2C_5H_5N$) by X-ray diffraction methods. This novel molecule consists of two manganese complexes joined by a linear Mn-O-Mn bridge. Its structure may have some relation to oxidation processes in biological systems.

One approach to understanding the chemistry involved in complicated biological processes has been to study the physical and chemical properties of compounds which are related to, but less complex and more stable than those which occur in nature. The chemistry of phthalocyanatomanganese(II) (1,2) is of interest because of (a) the similarities between the structures of phthalocyanine and porphyrin rings, (b) the implication of manganese (possibly as a porphyrin complex) in biological oxidative processes, and (c) the report by Elvidge and Lever (1) that in pyridine solution the complex may reversibly combine with oxygen. Englesma, Yamamoto, Markham, and Calvin (2) did not detect oxygen evolution accompanying the reverse reaction. The absorption of oxygen takes place in two steps (2), ending in the formation of a complex which can be isolated as short, opaque, purple crystals with a metallic luster. Elvidge and Lever formulated this complex as $Mn^{IV}PcPyO$ (Pc = phthalocyanato, Py = pyridine). Because of the low solubility of the complex neither the molecular weight nor the magnetic susceptibility in solution was measured (2). Magnetic susceptibility measurements (2) on the solid indicated 0.71 B. M. instead of the expected 3.87 B. M. for Mn(IV). This fact suggested a different oxidation state or electronic interactions between Mn atoms in the solid.

By X-ray diffraction methods we have determined the structure of these crystals and have shown the molecules to be a novel double complex of manganese(III): $(Mn^{III}PcPy)_2O$. This complex (Fig. 1) consists of two approximately flat and parallel phthalocyanine ring systems, each with manganese at its center. These rings are bridged

by the oxygen atom which is midway between the manganese atoms. Each manganese also has a pyridine molecule coordinated opposite its oxygen atom. The crystals consist of these complex molecules together with other molecules of pyridine of crystallization which are not bonded in any direct way to the complex molecules.

We failed to get good diffraction patterns with crystals which were dried in air. To prevent loss of pyridine we grew crystals from pyridine solution and kept them in an atmosphere saturated with pyridine. We sealed a crystal of dimensions 0.15 × 0.15 × 0.30 mm in a thin-walled glass capillary with a drop of pyridine in the other end. We measured lattice dimensions and diffraction intensities with a General Electric XRD-5 diffractometer equipped with a goniostat and scintillation counter, with copper radiation, $\lambda(K\alpha_1) = 1.54051$ Å. We measured intensities of 3156 independent reflections by the stationary-crystal stationary-counter technique. Absorption was neglected ($\mu R \sim 1$).

The crystals are orthorhombic with cell dimensions:

$a = 22.635 \pm 0.005$,

$b = 23.850 \pm 0.005$,

$c = 12.808 \pm 0.003$ Å.

The space group is $P2_12_12_1$ with each cell containing four asymmetric units consisting of $(MnPcPy)_2O \cdot 2Py$ or $C_{84}H_{52}Mn_2N_{20}O$ (molecular weight 1467.3, 107 atoms excluding hydrogen). The molecular weight from the volume of the asymmetric unit and density measured by flotation (1.41 g/ml at 25°) is 1470.

The structure determination was surprisingly straightforward and lacked any special difficulty except excessive arithmetic. We guessed the two Mn positions correctly from the Patterson function. A sequence of least-squares and three-dimensional-Fourier calculations, coupled with the assumption that the phthalocyanine rings would have essentially the same shape as determined by Robertson (3) in other crystals, led to the structure. To refine the 107 atoms required 439 parameters including a scale factor, coordinates, anisotropic thermal parameters for each manganese atom, and individual isotropic thermal parameters for the other atoms. The least-squares program on our IBM-7044 (32K memory) computer can handle 160 parameters in a full-matrix calculation. We started the refinement procedure with this program, refining about a third of the structure at a time. At two hours per run, this procedure required six hours to shift each parameter at least once. We modified the program to neglect off-diagonal elements of the matrix. This change permitted all parameters to be shifted in one hour, and more refinement per hour of computer time was realized. The function:

$$R = \sum ||F_o|-|F_c||/\sum|F_o|,$$

which was 0.48 for the two Mn atoms, was reduced to 0.084 for 107 atoms. The anomalous dispersion effect of Mn was included in the calculations and was sufficient to establish the absolute configuration of the structure (4).

Most atoms shifted less than 0.002 Å in the last cycle. We

estimate the standard deviations of individual bond distances to be about 0.04 Å on the basis of the differences between bonds which are chemically equivalent and a comparison with the known dimensions of benzene rings. These estimates do not apply to the pyridine of crystallization, which appears to have very large and anisotropic thermal motion (B ~ 15-20 $Å^2$) and which may have some kind of disorder. Average values of the lengths and angles of some chemically-equivalent bonds are given in Fig. 2. We expect these average distances to have standard deviations of the order of 0.01 Å. They are in agreement with previous results on other phthalocyanines (3).

Each terminal pyridine (Figs. 1 and 2) is oriented so that its plane bisects two of the N—Mn—N angles of the adjacent phthalocyanato complex. One phthalocyanine ring is rotated 41° with respect to the other about the Mn-O-Mn axis so that its benzene rings are approximately between the benzene rings of the other. Except for the benzene rings the atoms of each ring system lie in a plane with the respective manganese atom. The benzene rings bend inward toward the empty spaces of the opposite half of the molecule by from 0.1 to 0.6 Å. We consider this bending to be the result of molecular packing forces in the crystal and assume it to have no chemical significance except as a reflection of the flexibility of such a large molecule.

The Mn—O distance of 1.71 ± 0.01 Å is shorter than we would have predicted for a single covalent bond. We expect that an explanation of the magnetic properties will involve electronic coupling between manganese atoms through this bond system.

The mechanisms proposed for the formation of this complex (1,2) need to be reexamined in the light of this new formulation.

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References and Notes

1. J. A. Elvidge and A. B. P. Lever, Proc. Chem. Soc. 195 (1959).

2. G. Englesma, A. Yamamoto, E. Markham and M. Calvin, J. Phys. Chem. 66, 2517 (1962).

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4. All molecules in one crystal are of the same handedness, but another crystal from the same preparation is as likely to right-handed as left-handed. Thus there is no general significance to the absolute configuration which we found.

5. One of us (L. H. V.) was National Institutes of Health Postdoctoral Fellow under the sponsorship of Prof. Melvin Calvin. We thank Prof. Calvin for bringing this very interesting substance to our attention. This work was done in part under the auspices of the U. S. Atomic Energy Commission.

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Fig. 1. Photograph of a cork-ball model of the $(MnPcPy)_2O$ molecule. Hydrogen atoms are omitted.

Fig. 2. Average bond distances and angles.

ZN-5293

Fig. 1

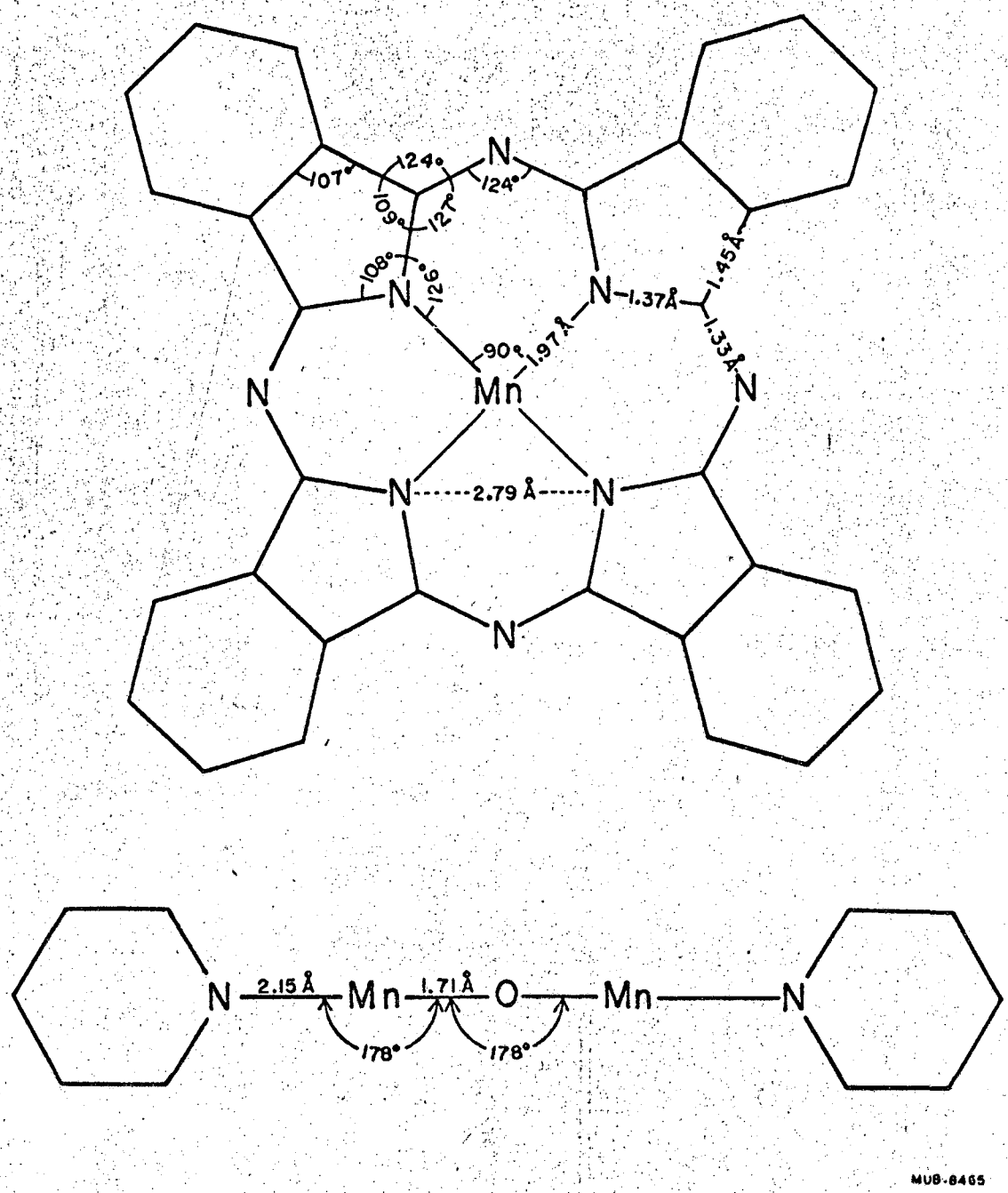
N
124°
107°
124°
109°
127°
108°
126°
N
N
1.37Å
1.45Å
1.97Å
1.33Å
90°
Mn
N
N
N
2.79 Å
N
N
N
2.15 Å
Mn
1.71 Å
O
Mn
N
178°
178°
MUB-8465

Fig. 2

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