Crystal and Molecular Structure of a Double Complex of Manganese with Phthalocyanato and Pyridine Ligands

Abstract. *A crystalline solid, formed by oxidation of phthalocyanatomanganese(II) in pyridine, has been identified as phthalocyanatopyridinemanganese(III)-μ-oxo-phthalocyanatopyridinemanganese(III)dipyridinate*($C_{74}H_{42}Mn_2N_{18}O \cdot 2C_5H_5N$) *by x-ray diffraction methods. This novel molecule consists of two manganese complexes joined by an essentially linear Mn—O—Mn bridge. Its structure may have some relation to oxidation processes in biological systems.*

One approach to understanding the chemistry of complicated biological processes has been the study of 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 (i) the similarities between the structures of phthalocyanine and porphyrin rings, (ii) the implication of manganese (possibly as a porphyrin complex) in biological oxidative processes, and (iii) the report by Elvidge and Lever (*1*) that, in pyridine solution, the complex may reversibly combine with oxygen. Englesma *et al.* (*2*) did not detect evolution of oxygen 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 indicates 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 Bohr magnetons instead of the expected 3.87 for Mn(IV). This fact suggested a different oxidation state or electronic interactions between Mn atoms in the solid.

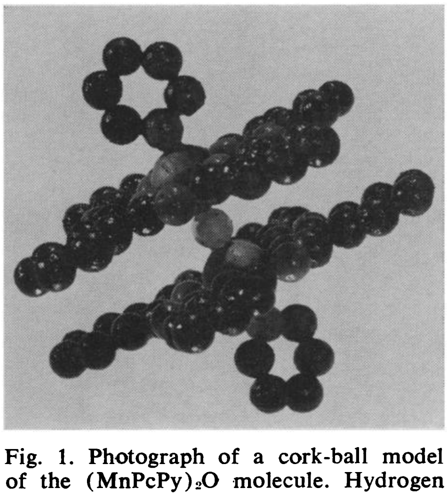

Fig. 1. Photograph of a cork-ball model of the $(MnPcPy)_2O$ molecule. Hydrogen atoms are omitted.

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 joined by the oxygen atom which is midway between the manganese atoms. Each manganese also has a pyridine molecule coordinated opposite to 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 (0.15 by 0.15 by 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 $CuK\alpha_1$ radiation (λ = 1.54051 Å). We measured intensities of 3156 independent reflections by the stationary-crystal, stationary-counter technique. Absorption was neglected.

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 that consist of $(MnPcPy)_2O \cdot 2Py$ or $C_{84}H_{52}Mn_2N_{20}O$ (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°C) is 1469 compared to 1467.3 calculated from the empirical formula.

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 (*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 2 hours per run, this procedure required 6 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 1 hour, and more refinement per hour of computer time was realized. The discrepancy index

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

which was 0.48 for the two manganese atoms, was reduced to 0.084 for 107 atoms. The anomalous dispersion effect of manganese 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

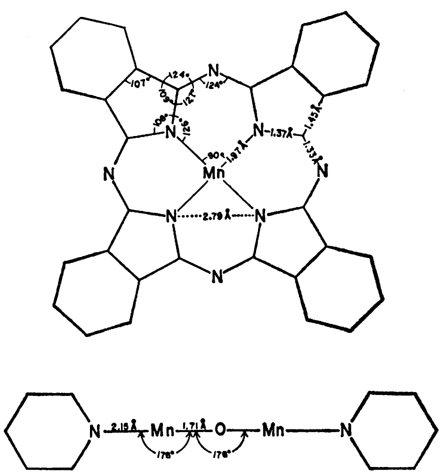

Fig. 2. Average bond distances and angles.

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* is about 15 to 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. The standard deviations of the bond angles are on the order of 1° or less. The bond distances and angles are in agreement with 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.* **1959**, 195 (1959).
2. G. Englesma, A. Yamamoto, E. Markham, M. Calvin, *J. Phys. Chem.* **66**, 2517 (1962).
3. J. M. Robertson, *J. Chem. Soc.* **1936**, 1195 (1936); ——— and I. Woodward, *ibid.* **1937**, 219 (1937); **1940**, 36 (1940).
4. All molecules in one crystal are of the same handedness, but another crystal from the same preparation is as likely to be 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 NIH postdoctoral fellow. We thank Prof. Calvin for bringing this very interesting substance to our attention. Partly supported by AEC.

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Distribution of Uranium in Some Natural Minerals

Abstract. *The advantages of the fission method over conventional autoradiography for studying the distribution of uranium in natural minerals is described. Relatively high concentrations of uranium associated with micro inclusions in the St. Marks enstatite chondrite have been observed and may account for the variation of the uranium concentrations in different samples of this meteorite.*

In order to study the distribution of uranium in various natural silicates by the fission method (*1*) a 700-million-year-old mica was selected as the detecting medium. An etching time of 40 minutes and 48 percent HF were used, which permitted removal of any surface contamination. After neutron irradiation, no clusters of tracks were seen, so that the mica was well-suited for localizing areas of uranium enrichment in the samples. The samples consisted of uncovered thin sections of rocks which were fixed to either plastic or silica mounts. After neutron irradiation, common minerals present in the sample can be arranged in order of decreasing uranium concentration as follows: accessory minerals, biotite, potassic feldspar, amphibole, pyroxene, olivine, and quartz. Exceptions to the sequence were observed, particularly in amphibole and quartz. In fine-grained volcanic rocks and granites that had been altered by pneumatolysis, uranium was often concentrated along intercrystal areas (Fig. 1, left). Accessory minerals, such as apatite from a ferrogabbro (Fig. 1, center), showed a fairly even distribution of tracks compared to sphene (Fig. 1, right) which shows the enrichment of uranium in some areas of the crystal.

The fission-track method has the distinct advantage over autoradiographic methods in that, for very small amounts of uranium, many tracks can be induced simply by increasing the irradiation exposure time.

Meteorites are known to contain very small amounts of total uranium, but zircon and the phosphate mineral, whitlockite (*2*), containing high concentrations of uranium, have been found in the Vaca Muerta (*3*) mesosiderite.

I have investigated the quartz-bearing enstatite chondrite St. Marks (*4*). After thermal neutron irradiation and etching, 95 percent of the exposed meteorite surface contained no significant track populations above the general track background. In one area of the sample, covering about 0.2 cm^2, a very high population of tracks was present; this suggested that the tracks were the mirror images of small uranium-bearing minerals. In Fig. 2*a*, a rectangular area of tracks forming a rim enclose a clear area which, in turn, contains a high-density spot in the center; in Fig. 2*b* the tracks clearly outline three sources having prismatic forms. In the same area of the sample, a high-density track population was associated with well-defined "sunbursts" (Fig. 2*c*), which Price and Walker (*1*) have related to surface contamination by dust that contained uranium. The spatial distribution of these tracks is a result of the passage of a fission fragment through air before being registered at the detecting mica surface.

I accept the interpretation of this feature, but in the study I present here, in which twenty thin sections of rock were examined, the "sunbursts" were associated with the meteorite sample, and this suggests some direct relation with the sample. To study this further, the sample was carefully washed in hot dilute nitric acid and boiled in demineralized water (distilled in quartz) for 15 minutes. The sample was then irradiated for a second time and, after etching, continued to show "sunbursts" in the same area, fewer in number and more dispersed, as shown in Fig. 2*d*; these samples were photographed at a lower magnification and etched for a