383. *The Stereochemistry of Metallic Phthalocyanines.*

By R. P. Linstead and J. Monteath Robertson.

It was pointed out by Dent, Linstead, and Lowe (J., 1934, 1037) that the phthalocyanine molecule should lie in one plane, and that co-ordination of a metal normally exhibiting tetrahedral symmetry could only occur by a change either in the configuration of the organic portion of the molecule or in the direction of the valencies of the metal. An *X*-ray investigation of single crystals of nickel, copper, and platinum phthalocyanines showed that the metal atom and the four surrounding nitrogens lay in one plane (Robertson, J., 1935, 613). The whole molecule of metal-free phthalocyanine has since been proved to be planar to within a few hundredths of an Ångstrom unit (Robertson, this vol., p. 1195).

X-Ray measurements have now been made on single crystals of beryllium, manganese, iron, and cobalt phthalocyanines. These substances are closely isomorphous with phthalocyanine and its copper and nickel derivatives. The cell measurements and crystal data are in the table.

	Phthalocyanine derivative.							
	(Free.)	Be.	Mn.	Fe.	Co.	Ni.	Cu.	Pt.
At. no. of metal	0	4	25	26	27	28	29	78
a, A.	19·85	21·2	20·2	20·2	20·2	19·9	19·6	23·9
b, A.	4·72	4·84	4·75	4·77	4·77	4·71	4·79	3·81
c, A.	14·8	14·7	15·1	15·0	15·0	14·9	14·6	16·9
β	122·2°	121·0°	121·7°	121·6°	121·3°	121·9°	120·6°	129·6°
Space-group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
Mols. per cell	2	2	2	2	2	2	2	2
Mol. symmetry	Centre	Centre	Centre	Centre	Centre	Centre	Centre	Centre
Vol. of unit cell, A.^{3}	1173	1293	1233	1231	1235	1186	1180	1186
Density (calc.)	1·445	1·33	1·52	1·52	1·53	1·59	1·61	1·97
M	514	521	567	568	571	571	576	707
Electrons per cell, $F(000)$	532	536	578	580	582	584	586	684

A survey of the reflections from the (*h*0*l*) zones of the manganese, iron, and cobalt compounds was made by visual inspection of moving-film photographs, taken as nearly as possible under identical conditions. No difference in the intensities of corresponding reflections was observed, and further, they are practically identical with the intensities of the copper and nickel compounds already described. The atomic number of the central metal atom in this series varies from 25 in manganese to 29 in copper, and these atoms make positive contributions to the structure amplitudes, in accordance with the general principles previously given (*idem, ibid.*). Minute differences in the intensities from these compounds must, therefore, exist, but they are too small to be recorded. The similarity of the cell dimensions of these five metallic phthalocyanines shows that the over-all dimensions of the molecules and their relative arrangement in the crystals are practically identical, while the similarity of the intensities shows that the finer details of the structures, including all the interatomic distances and valency angles, must also be practically the same.

Beryllium phthalocyanine is particularly interesting in view of the stereochemistry of the metal atom. The cell dimensions are slightly changed, the *a* and *b* axes being longer by a small but measurable amount, with a consequent increase in the molecular volume. The intensities of the (*h*0*l*) zone are in general very closely similar to those of metal-free phthalocyanine, as might be expected from the low scattering power of the beryllium atom (at. no. 4). A careful inspection, however, reveals a few interesting differences between the two compounds. The (200) plane in beryllium phthalocyanine is represented by a weak reflection, but in the metal-free compound it is absent even on long-exposure films. In beryllium phthalocyanine the (2,0,10), $(2,0,\overline{11})$, and (601) reflections are all a little weaker, and the (607), (600), and $(20\overline{2})$ reflections all a little stronger, than the corresponding reflections from metal-free phthalocyanine. These observations can be explained by referring to the phase constants derived for free phthalocyanine (*idem, ibid.*). The (2,0,10), $(2,0,\overline{11})$, and (601) structure factors are of negative sign, whereas the (607), (600), and (202) are positive. The small positive contribution of the beryllium atom will decrease the amplitude of the negative structure factors, and increase the positive—changes which can be seen in the above reflections, because they are all relatively weak. Such differences as can be observed may therefore be explained by the additional scattering from the beryllium atom. There is no evidence from the intensities (by visual estimate) of any structural change in the molecule due to the presence of the beryllium atom.

The alteration in the cell dimensions noted above, however, shows that there is a small change in the relative positions of the molecules in the crystal. The nature of this change, and whether it is accompanied by any *small* change of structure, may be elucidated by careful measurement and Fourier analysis of the intensities from beryllium phthalocyanine, but in the meantime experimental difficulties prevent such work.

From the standpoint of general stereochemistry, the most important fact which arises is that all the compounds have centro-symmetrical molecules. From this it follows that the metal atoms lie in the same plane as the four nitrogen atoms which carry them. Hence bivalent, 4-co-ordinate beryllium, manganese, iron, cobalt, nickel, copper, and platinum all exhibit planar symmetry in the crystals of their phthalocyanine derivatives.

It is already well established that 4-co-ordinate bivalent platinum exhibits planar symmetry (Cox, J., 1932, 1912; Morgan and Burstall, J., 1934, 1498; Mills and Quibell, J., 1935, 839; Cox, Wardlaw, Webster, *et al.*, J., 1935, 459, 1475; etc.), and it appears that nickel frequently but not invariably occurs in the same condition (Sugden, J., 1932, 246; Cavell and Sugden, J., 1935, 621; Cox, Wardlaw, Webster, *et al.*, *loc. cit.*). The phthalocyanines of these metals are therefore normal. Copper is tetrahedral in the (cuprous) $[Cu(CN)]_4'''$ ion, and may be so in the (cupric) derivative of benzoylpyruvic acid (Mills and Gotts, J., 1926, 3121). The demonstration of the planar distribution of valencies of quadricovalent cupric copper in the phthalocyanine derivative (*loc. cit.*) was followed almost immediately by a similar discovery for the copper derivatives of various diketones (Cox and Webster, J., 1935, 731), and another example has since come to light (Cox, Sharratt, Wardlaw, and Webster, this vol., p. 129). On the other hand, cobalt is tetrahedral in the group $CoCl_4$ (Powell and Wells, J., 1935, 359), and the phthalocyanine derivative provides the first example of this metal exhibiting planar symmetry. As far as we are aware, nothing has so far been reported on the stereochemistry of 4-co-ordinate bivalent manganese or iron. In the 6-co-ordinate state, iron and cobalt are well known to have an octahedral arrangement of valencies; in the phthalocyanine derivatives, two of these positions become dormant, leaving a planar arrangement.

The most remarkable result is provided by beryllium, for which a tetrahedral symmetry is well established by investigations of its benzoylpyruvic acid derivative (Mills and Gotts, *loc. cit.*) and of its basic acetate (Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437).

Pauling's application of wave-mechanics to stereochemistry (*J. Amer. Chem. Soc.*, 1931, **53**, 1367) led him to expect a planar distribution of valencies only from transitional elements in which the electrons of the *d* levels were taking part in the formation of valencies. On this basis there is nothing remarkable in the planar arrangement found for iron, cobalt, manganese, and copper. That the very simple atom of beryllium, which normally contains no *d* electrons, should adopt a similar symmetry appears inexplicable on Pauling's theory. It is true that the theoretical difficulty can be avoided by the assumption that in beryllium phthalocyanine the metal is combined with only two nitrogen atoms, but there seems to us no justification for arbitrarily differentiating between this compound and the other covalent metallic phthalocyanines which resemble it so closely in crystalline form. The planar arrangement appears to be very unstable, for the anhydrous beryllium compound readily forms a dihydrate even in moist air (Barrett, Dent, and Linstead, this vol., p. 1720). This behaviour is not paralleled by other phthalocyanines except the magnesium derivative.

It seems highly probable that the molecules of all other covalent metallic phthalocyanines, of the type R, Metal$^{\bullet\bullet}$, will be planar. The monoclinic crystals of the zinc and the (anhydrous) magnesium derivative, indeed, appear to be exactly similar to those of the compounds discussed above.

Our general conclusions are (i) that in the metallic phthalocyanines, and probably also in the corresponding porphyrins, the rigid, planar, organic portion of the molecule imposes its steric requirements upon the metal, and (ii) that there is more tolerance in the distribution of valencies about 4-co-ordinate metal atoms than has hitherto been realised.

Finally, it may be pointed out that the stereochemistry of the four *iso*indole nitrogen atoms, which carry the metallic atoms, is novel. The three valencies from each of these lie in one plane and are inclined to each other at approximately 110°, 125°, and 125°. This is only possible owing to the peculiar "aromatic" behaviour of the great ring; if the double and single bonds had fixed positions, the third valency of the imino-nitrogen atoms would be inclined to the general plane.

EXPERIMENTAL.

Single crystals of the metallic phthalocyanines were obtained by low-pressure sublimation in carbon dioxide at about 550° (Barrett, Dent, and Linstead, *loc. cit.*). The specimens selected were in the form of thin laths, with cross sections about 0·3 × 0·1 mm., and several mm. long, with the (001), (100), (20$\bar{1}$), and (10$\bar{1}$) faces developed. The *b* axes were measured by rotation photographs about the lath axes with Cu-$K\alpha$ radiation. The other axial lengths and the β angles were obtained by analysis of moving-film photographs of the $(h0l)$ zones of reflections, taken on the two-crystal spectrometer.

Anhydrous beryllium phthalocyanine is difficult to handle on account of its hygroscopic nature. Some good crystals were taken directly from the sublimation apparatus and sealed up in thin-walled glass tubes. The lath-like crystal was then shaken to the end of the tube, which was touched with a small flame, causing part of the crystal to melt and fix the remainder in an upright position, suitable for the *X*-ray work. The glass walls of the tube cause extra scattering of the *X*-ray beam, and this, combined with the absorption effect, reduces the accuracy of the intensity observations.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.
DAVY FARADAY RESEARCH LABORATORY, THE ROYAL INSTITUTION, LONDON, W. 1.

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