Dinitrogen or Dichloromethane?

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A recent article[1] in this journal reports the crystal structure of (octaethylazaporphyrinato)iron(III) chloride, (OEP)Fe^{III}-Cl·CH$_2$Cl$_3$·N$_2$, at 130 K, in which the N$_2$ molecule is referred to as "unusual, but no other explanation for two equal-sized atoms separated by 1.21(2) Å could be found". Even more unusual is a "close contact" of 1.86 Å between two such molecules (related by a center of symmetry), forming an angle N—N≡N of 109° and thus leading to a sort of perazabuta-1,3-diene molecule. If this were a genuine new tetranitrogen molecules so gently produced, it would be a remarkable discovery, worth celebrating as a milestone in synthetic and structural chemistry and in nitrogen fixation. Since we were skeptical of the ability of these crystals, which were grown at room temperature, to capture and contain a nitrogen molecule (and to cause it to dimerize as well), we have undertaken a re-examination of the structure. Perhaps unfortunately, we have concluded that the earlier interpretation as dinitrogen is erroneous.

Our re-examination of the structure was based on the original X-ray diffraction data[1] (3054 reflections) and began with least-squares refinement of the earlier model but with an added parameter representing the occupancy of the dinitrogen sites. This parameter became 1.1 ($\sigma = 0.01$), suggesting that the atoms are something other than nitrogen. We then calculated an electron density map in the plane containing all four "nitrogen" atoms. This map (Figure 1) suggested an alternative explanation for the solvent of crystallization: a dichloromethane molecule, disordered across the center of symmetry. (The crystals had been grown from a dichloromethane solution, and one solvent molecule of dichloromethane had already been found in the original study.) Reasonable positions for the C and Cl atoms of such a molecule are indicated in Figure 1; note that the C atom of one molecule lies only about 0.65 Å from the Cl5 atom of the symmetry-related molecule, resulting in a broadened electron density peak.

Because of this overlap problem, least-squares refinement of this revised model was somewhat delicate; the problem was further exacerbated by apparent disorder involving the other dichloromethane molecules, which lie close by in a single, large solvent area. Eventually, C37 was placed in a fixed site, and it and Cl5 were given isotropic B values; only the well-resolved atom Cl4 was allowed to become anisotropic. The two hydrogen atoms were included but not refined. A population parameter for the Cl and C atoms converged at 0.382(4); a similar parameter for the other dichloromethane molecule converged at 0.851(5). Thus, the solvent region appears to be occupied by dichloromethane molecules only about 80% of the time; residual peaks in a difference map suggest that the other solvents are also present in small quantities, but we were unable to identify them. (Petroleum ether was present during the crystallization.) Other details of the refinement were as described earlier.[1]

Our final R was 0.0705, effectively identical to the 0.071 reported earlier[1]. Thus, we can offer no compelling experimental evidence that dichloromethane, rather than tetranitrogen, is the
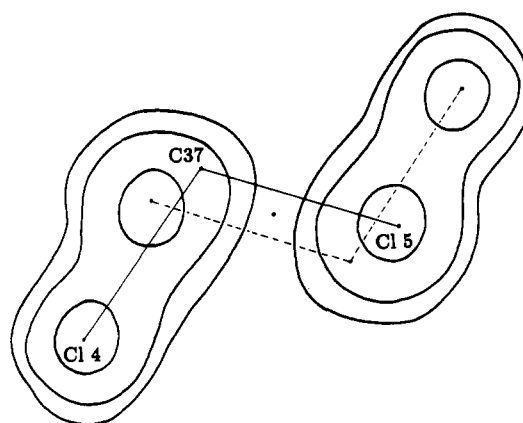

Figure 1. Electron density map in the plane of the disordered solvent molecules of the iron–prophyrin compound. Contours are drawn at 1, 2, and 4 e Å^{-3}.
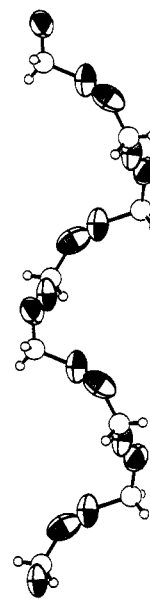

Figure 2. View of the solvent chain in crystals of the rhodium compound. The view is perpendicular to *c*, and the chain extends over two unit cells. Chlorine atoms are shown with shaded octants; pairs of adjacent chlorine atoms were originally interpreted as N$_2$ molecules. In the crystal, at least every other one of these solvent molecules is missing; the overall occupancy factor is 0.44(1).

second solvent molecule of crystallization; however, dichloromethane is a far more logical interpretation and is completely in accord with the experimental data.

In support of their conclusion that N$_2$ is present in these crystals, Balch *et al.*[1] noted "one other case where a molecule of dinitrogen has been found as an occlusion in the crystalline form of a metal complex", referring to [μ-(Ph$_2$P)$_2$py]$_2$Rh(μ-CO)(CO)$_2$(μ-Cl)$_2$-Cl$_2$·2CH$_2$Cl$_2$·2N$_2$ (Wood, Olmstead, and Balch[2]), with N–N = 1.19 Å. These crystals were also grown at room temperature, and again we were skeptical of the results. We have reexamined this structure as well, and here we find that the experimental evidence points quite conclusively to dichloromethane rather than dinitrogen. Once again our studies were based on the original *F$_o$* values, 2257 in number. Preliminary refinement showed a population parameter of about 1.4 if the solvent atoms are identified as nitrogen, and a difference map showed a relatively large peak at the position expected for the central carbon atom of CH$_2$Cl$_2$; in this case there was no problem of overlap. Refinement of the revised model (including fixed hydrogen atoms)

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(1) Balch, A. L.; Olmstead, M. M.; Safari, N. *Inorg. Chem.* **1993**, *32*, 291–296.

(2) Wood, F. E.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6332–6334.

led to an R of 0.044, compared to 0.048 for the earlier model; the population coefficient of the dichloromethane molecule was 0.44(1). In the original model, dinitrogen molecules spiral up a channel along a 4_3 axis. In the revised model (Figure 2), the chlorine atoms of a CH_2Cl_2 molecule replace one nitrogen atom in each of two successive N_2 molecules; to avoid impossible Cl---Cl contacts, the sites can be half-populated at best, in agreement with the population coefficient we found. As in the previous compound there is a second dichloromethane molecule present, this time in a fully-occupied site.

Coordinates for the added dichloromethane molecules in both crystal structures are given in Table I; coordinates of the remaining atoms are effectively unchanged from those found earlier.[1,2]

Solvent regions in crystals are a continual problem for crystallographers. Frequently the solvent molecules are disordered, are partially populated, are a mixture of different species, or all of the above. The solvent is of little or no interest to the synthetic chemist, but the interesting part of the crystal structure cannot be refined properly without adequate modeling of the solvent regions. Interpreting the solvent regions is often a difficult and unrewarding chore; moreover, as in the first example discussed here, a complete interpretation may not be available from the diffraction data alone. There is, then, a temptation to introduce atoms more or less at random, in such a way as to explain the major peaks in a difference Fourier map. If this is done, however, care must be taken to ensure that the resulting arrangement of atoms makes reasonable chemical sense in relation to the nature of the material, the composition of the solvent from which the crystals were grown, and other relevant circumstances. Dini-

Table I. Coordinates for the Added CH_2Cl_2 Molecules

atom	10^4x	10^4y	10^4z	$10^4U_{eq}{}^a$ or B
(Octaethylazaporphyrinato)iron(III) Chloride[b]				
Cl4	1400(11)	5682(10)	4864(9)	1131(39)
Cl5	−965(14)	5042(12)	4814(12)	11.9(5)
C37	540	4624	5333	7.0[c]
H37A	379	4403	6034	8.0[c]
H37B	1057	4029	5172	8.0[c]
$[\mu\text{-}(Ph_2P)_2py]_2Rh_4(\mu\text{-}CO)(CO)_2(\mu\text{-}Cl)_2Cl_2{}^d$				
Cl5	8095(5)	7624(5)	1740(20)	923(47)
Cl6	7728(9)	8307(7)	−167(19)	1165(61)
C33	8044(18)	8257(19)	1175(47)	5.1(10)[c]
H33A	8393	8395	1069	4.0[c]
H33B	7859	8466	1770	4.0[c]

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j[U_{ij}(a_i{}^*a_j{}^*)(\vec{a}_i\cdot\vec{a}_j)]$. [b] Bond lengths and angles: C37–Cl4, 1.72 Å; C37–Cl5, 1.67 Å; Cl4–C37–Cl5, 108° (no esd's, since the coordinates of C37 were assumed). [c] Isotropic displacement parameter, B. [d] Bond lengths and angles: C33–Cl5, 1.71(5) Å; C33–Cl6, 1.66(5) Å; Cl5–C33–Cl6, 115(3)°.

trogen—and, especially, "tetranitrogen"—molecules are unlikely candidates for crystal solvate molecules, particularly for compounds crystallized at room temperature (which is about 4 times the boiling point of nitrogen). Dichloromethane (bp 313 K) is a far more likely candidate.