

Space-Group Changes – Revised Structures of Seven Compounds

BY MOSHE KAPON AND GEORGE M. REISNER*

Department of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel

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Abstract. Revised structures are reported for seven crystalline compounds, based on space groups of higher symmetry than originally reported. In two cases the crystal class is revised, in five cases only centres of symmetry are added. For one of the latter cases the original F values have been used and least-squares refinement has been carried out in the centrosymmetric space group with more satisfactory results than originally reported.

Introduction. We present revised crystal structures of seven compounds based on space groups of higher symmetry than previously reported. In six cases centres of symmetry have been added, in one of these the crystal class is also revised from monoclinic ($C2$) to tetragonal ($I4/m$). In one case the Laue symmetry is increased from $2/m$ to mmm .

Addition of centres of symmetry removes the singularities associated with refining a centrosymmetric structure in a non-centrosymmetric space group and highly significant parameter changes usually result (Schomaker & Marsh, 1979; Marsh & Herbststein, 1988). For one of the cases involving just an addition of a centre of symmetry we have carried out a successful refinement based on the original structure factors. Details follow.

Category 1: centre of symmetry added, no refinement

Four such cases are reported. Information concerning the compound, the original and revised space groups, and the necessary revisions of the structural parameters is given in Table 1.

Category 2: centre of symmetry added, structure re-refined

N,N'-Trimethylenebis(2-hydroxyacetophenone iminato)copper(II), $[\text{Cu}(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2)]$. The structure of the compound was described (Iida, Oonishi, Nakahara & Komiyama, 1970) in space group Cc (four molecules in the unit cell) and refined to $R_F = 0.093$ for 1220 visually measured reflections. The authors note that 'the six-membered chelate ring has approximately a twofold axis of rotation through the central copper atom and the central atom C(10) of

the ligand'. The structure is better described in space group $C2/c$. The $C2/c$ coordinates were obtained by shifting the origin by $z = 0.2488$, thus placing the Cu and C(10) atoms on the twofold axis (0, y , 0.25) and averaging the coordinates of the other atoms, related in pairs, by this axis.

Values of 1217 reflections were recovered from the original paper and the structure refined using the *SHELX77* system of programs (Sheldrick, 1977). Full-matrix least squares [unit weights, 123 parameters refined (scale factor, anisotropic displacement factors for the non-H atoms and isotropic for the H atoms) converged at $R_F = 0.088$.† The $C2/c$ parameters are considerably more precise than those

† Final positional parameters and equivalent displacement factors of the non-H atoms (Table 5A), anisotropic displacement factors of the non-H atoms (Table 6A), coordinates of the H atoms (Table 7A) and a list of structure factors for $[\text{Cu}(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2)]$ together with the revised coordinates of the remaining compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52370 (17 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Pertinent information concerning the four compounds of category 1

Compound	Original space group	Revised space group	Reference
$\text{Mg}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}^*$	$P1$	$P\bar{1}$	Matveeva, Varfolomeev, Šamraj & Lunk (1986)
<i>N</i> -(1-(1-Adamantyl)propyl)acetamide†	$P1$	$P\bar{1}$	Tafeenk, Prozorovskii, Rybakov & Kovalev (1987)
NdTaO_4 ‡	Pa	$P2/a$	Yamnova, Pushcharovskaya Bogdanova & Leonyuk (1986)
(1,2,5,6-η-Cycloocta-1,5-diene)bis(2-methoxy-methyl-6-methylphenyl)-platinum(II)§	Cc	$C2/c$	Debaerdemaeker, Baumgärtner & Brune (1987)

* The $P\bar{1}$ coordinates [Table 1A (deposited)] are obtained by shifting the origin to $x = -0.4908$, $y = -0.4896$ and $z = -0.5083$ so that the Re atoms relate as xyz and $\bar{x}\bar{y}\bar{z}$.

† The $P\bar{1}$ model [Table 2A (deposited)] is derived by symmetrizing pairs of atoms of molecules 1 and 2 and also 3 and 4 [$x' = \frac{1}{2}(x_1 + x_2)$, etc.]. The resulting centre of symmetry is at $x' = 1.1298$, $y' = 0.3432$, $z' = 0.4011$ which becomes the origin in space group $P\bar{1}$.

‡ The $P2/a$ coordinates [Table 3A (deposited)] are obtained by shifting the origin by $x = 0.2527$ and $z = -0.0029$ so that atoms Ta and Nd lie on twofold axes and then averaging O(1) with O(3) and O(2) with O(4).

§ The $C2/c$ coordinates [Table 4A (deposited)] are derived by translating the origin to $x = 0.2487$ and $z = 0.4736$ thus placing the Pt atom on the twofold axis (0, 0.6398, 0.25) and averaging (in pairs) the coordinates of the other atoms related by this axis.

* To whom correspondence should be addressed.

reported for the *Cc* refinement (the e.s.d.'s are about half as large). The geometry of the molecule was found to be close to that previously reported.

Category 3: centre of symmetry added and crystal class revised, no further refinement

Aquatetrakis(3,5-dimethylpyrazole)copper diperchlorate, $[\text{Cu}(\text{C}_5\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})](\text{ClO}_4)_2$. The crystal structure of the complex was reported (Pervukhina, Podberezhskaya, Lavrenova, Larionov & Bakakin, 1986) in space group *C2* [$a = 19.783$ (5), $b = 16.271$ (6), $c = 13.994$ (6) Å, $\beta = 134.98$ (3)°, $Z = 4$]. The lattice vectors [001], [101] and [010] define an *I*-centred tetragonal cell ($a' = 13.994$, $b' = 13.994$, $c' = 16.217$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 89.96$ °, $Z = 4$). The corresponding coordinate transformations $x' = \bar{x} + z$, $y' = x$, $z' = y$ led to a structure that conforms quite closely to the symmetry of *I4/m* (No. 87). The *I4/m* coordinates have been deposited (Table 8A). Since in space group *I4/m* the Cl atom lies on a mirror with one of the Cl—O vectors almost perpendicular to this plane, the perchlorate group must be disordered. The structure is characterized by two types of hydrogen bonding both involving the ClO_4^- O atoms as acceptors with the water molecule and N(2) acting as donors [*i.e.* O(4)⋯N(2) = 2.808 Å and O(2)⋯O(9)(x, y, z) = 2.721 Å].

Category 4: change in Laue group

Tris(methyltrimethylsilylphosphino)phosphine, $\text{P}[\text{P}(\text{SiMe}_3)\text{Me}]_3$. The structure of this compound was described (Fritz, Stoll, Hönle & Schnering, 1986) in space group *Cc* [monoclinic, $a = 9.844$ (11), $b = 19.650$ (40), $c = 26.054$ (27) Å, $\beta = 100.91$ (9)°, $Z = 8$] and refined to $R_F = 0.09$ ($wR = 0.07$) using 2051

reflections with $I \geq 3\sigma(I)$. It is properly described as orthorhombic, space group *Fdd2* (No. 43). The lattice vectors $[0\bar{1}0]$, $[102]$ and $[\bar{1}00]$ define a cell with $a' = 19.650$, $b' = 51.166$, $c' = 9.844$ Å, $\alpha' = 89.98$, $\beta' = 90.00$, $\gamma = 90.00$ °, $Z = 16$. The corresponding transformations $x' = \bar{y}$, $y' = z/2 + 0.0665$, $z' = \bar{x} + z/2$ yield coordinates for atom pairs that are compatible (within three times the reported e.s.d.'s) with space group *Fdd2*. The *Fdd2* coordinates have been deposited (Table 9A).

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The Structure of Hexaaquanickel(II) Chlorate

BY JUDITH C. GALLUCCI AND ROGER E. GERKIN*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

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Abstract. Hexaaquanickel(II) chlorate, $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_3)_2$, $M_r = 333.69$, cubic, $Pa\bar{3}$, $a = 10.3159$ (5) Å, $V = 1097.80$ (5) Å³, $Z = 4$, $F(000) = 680$, $D_x = 2.02$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $T = 296$ K, $\mu = 23.13$ cm⁻¹, $R = 0.026$ for 388 unique reflections having $I > \sigma_I$. The single type of Ni ion is coordi-

nated by six water-molecule O atoms, each at an observed distance 2.054 (1) Å, in an almost regular octahedral array. The single type of chlorate ion has a Cl—O bond length 1.487 (1) Å and O—Cl—O bond angle 106.45 (6)°. The Ni—O complex, but not the chlorate ion, manifested rigid-body behavior. The Ni—O distance corrected for rigid-body motion is 2.060 Å. Location and refinement of the two

* To whom all correspondence should be addressed.