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Space Groups of some Scandium Complexes

Ng Seikweng
(Institute of Postgraduate Studies & Research, University of Malaya, Kuala Lumpur 50603, Malaysia)
Hu Shengzhi
(Department of Chemistry, Xiamen University, Xiamen 361005, China)

Abstract The space group of $[(C_4H_9)_4N]_3[Sc(NCS)_6]\cdot 3.5\ H_2O$ is revised from orthorhombic *Pbca* to cubic $Pa\bar{3}$ by solving the cubic structure from the structure factors that are simulated from the orthorhombic structure. The space groups of three other scandium(III) structures that were originally reported in lower-symmetry settings are revised to higher-symmetry centrosymmetric settings: $Sc(PMBP)_3$(HPMBP = 1-phenyl-3-methyl-4-benzoylpyrazol-5-one)from $P\bar{1}$ to $C2/c$, $[(H_2O)_{10}(OH)_2Sc_2](C_6H_5SO_3)_4\cdot 4H_2O$ from $P\bar{1}$ to $C2/c$ and $[Sc(NO_3)_3(H_2O)_3]\cdot$18-crown-6 from $Pna2_1$ to *Pnma*.

Keywords: Space group revision, Simulated structure factors, Scandium complexes

A number of crystal structures have been incorrectly described by unnecessary lower-symmetry space groups; the structures are difficult to correct as their revisions require an extensive knowledge of crystallography, and such revisions are better left to the hand of specialists. Recently, a simple method[1] of space group revision has been reported, and non-specialists can easily revise the structures by making use of the lower-symmetry space group/atomic coordinates to calculate the structure factors. The simulated structure factors are then re-indexed match the higher-symmetry space group, and the structure then re-extracted from the simulated diffraction data. If a common temperature factor is used for all atoms in the calculation of structure factors, the temperature factors in the correct structure need not be refined. If anisotropic temperature factors are used (and even hydrogen atoms are included) in the calculations, the non-hydrogen atoms of the structure can be refined anisotropically. The calculations avoid the use of the original intensity data, which are not always available.

The majority of space group revisions involves the lower space groups; a report describes an unusual correction of an organic compound, from the orthorhombic *Pbca* to the cubic $Pa\bar{3}$[2]. We report the space group correction of a scandium(III) structure, again involving the same pair of space groups. Three other scandium(III)structures are also revised.

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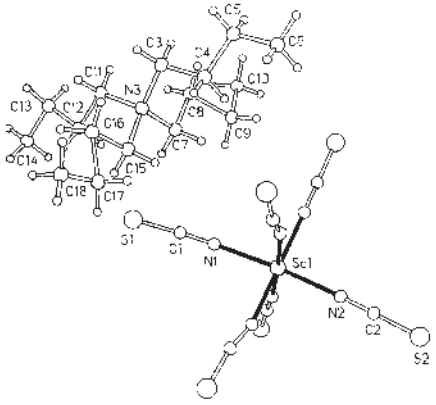

Fig. 1 Plot of the asymmetric unit of $[(C_4H_9)_4N]_3[Sc(NCS)_6]\cdot 3.5\,H_2O$

The water molecules not shown.

1 Calculations

The $[(C_4H_9)_4N]_3[Sc(NCS)_6]\cdot 3.5\,H_2O$, $C_{54}H_{115}N_9O_{3.5}S_6Sc$ **(1)**, complex is reported to crystallize in the orthorhombic *Pbca* space group [$a = 2.464(2)$, $b = 2.462(2)$, $c = 2.465(1)$ nm]; the structure has been refined to $R = 0.094$[3]. The structure factors were calculated by Crystallographica[4] for the $0-50°$ 2θ range; molybdenum radiation was assumed, and the temperature factors were set at 5×10^{-4} nm^2 for all atoms. Hydrogen atoms were not included in the calculations. The simulated data consisted of 13195 reflections, which were averaged to 4415 independent reflections ($R_{int} = 0.136$) in $Pa\bar{3}$ [$c = 2.464(2)$ nm]. The revision from *Pbca* to $Pa\bar{3}$ required a transformation of the unit cell and reflection indices by $(010, 100, 00\bar{1})$. The structure was solved by direct methods[5-7] and refined[8] on F^2 to $R = 0.076$. Atomic coordinates are listed in Table 1, and the structure is shown in Fig. 1.

Table 1 Atomic coordinates for $(C_4H_9)_4N]_3[Sc(NCS)_6]\cdot 3.5\,H_2O$ in $Pa\bar{3}$ [$a = 2.464(2)$ nm]

Atom	*x*	*y*	*z*
Sc1	0.3073	0.3073	0.3073
S1	0.3525	0.1627	0.1787
S2	0.2289	0.4348	0.4400
N1	0.3365	0.2442	0.2518
N2	0.2748	0.3653	0.3655
N3	0.2623	0.2580	0.0292
C1	0.3398	0.2117	0.2187
C2	0.2551	0.3946	0.3969
C3	0.2489	0.3050	−0.0106
C4	0.2107	0.3470	0.0160
C5	0.2088	0.3979	−0.0153
C6	0.1706	0.4382	0.0092
C7	0.2937	0.2770	0.0792
C8	0.3485	0.3071	0.0597
C9	0.3648	0.3385	0.1153
C10	0.4189	0.3584	0.0950
C11	0.2979	0.2165	−0.0023
C12	0.3180	0.1667	0.0296
C13	0.3624	0.1378	−0.0036
C14	0.3790	0.0861	0.0285
C15	0.2109	0.2276	0.0536
C16	0.1736	0.2075	0.0069
C17	0.1149	0.1976	0.0462
C18	0.0901	0.1709	0.0140
O1	0.0000	0.0000	0.0000
O2	0.4745	0.0822	0.4857

The incorrect symmetry for $Sc(C_{17}H_{13}N_2O_2)_3$, $C_{51}H_{39}N_6O_6Sc$ **(2)**, described in $P\bar{1}$ [a = 3.090(2), b = 1.2034(6), c = 1.2025(6) nm, α = 86.64(4), β = 81.13(5), γ = 81.11(5)°] [9] is evident from the similarity of two of the axes and two of the angles. The cell is transformed by (011, 01$\bar{1}$, $\bar{1}$00) to $C2/c$ [a = 1.7504(8), b = 1.6506(8), c = 3.090(2) nm, β = 102.25(5)°]. Atomic coordinates are listed in Table 2. As the atomic coordinates for $[(H_2O)_{10}(OH)_2Sc_2](C_6H_5SO_3)_4 \cdot 4H_2O$, $C_{24}H_{50}O_{28}S_4Sc_2$ **(3)** were not published, they were retrieved from the Cambridge Crystallographic Data Centre as refcode KERJEW. The cell in $P\bar{1}$ [a = 1.5518(5), b = 1.9827(7), c = 0.7493(2) nm, α = 100.90(3), β = 103.94(2), γ = 82.85(3)°] [10] was transformed by (201, 00$\bar{1}$, $\bar{1}$10) to the $C2/c$ cell [a = 3.012(1), b = 0.7493(2), c = 2.3608(9) nm, β = 124.73(3)°]; the matrix was also used to transform the reflection indices. The transformation of the cell of $[Sc(NO_3)_3(H_2O)_3]$ · 18-crown-6, $C_{12}H_{30}N_3O_{18}Sc$ **(4)**, in $Pna2_1$ [a = 1.5300(3), b = 1.0879(3), c = 1.4052(3) nm] [11] to $Pnma$ [a = 1.5300(3), b = 1.4052(3), c = 1.0879(3) nm] was effected by (100, 00$\bar{1}$, 010). Atomic coordinates for **(3)** and **(4)** are listed in Table 3 and Table 4.

Table 2 Atomic coordinates for $Sc(C_{17}H_{13}N_2O_2)_3$ in $C2/c$ [a = 1.7504(8), b = 1.6506(8), c = 3.090(2) nm, β = 102.25(5)°]

Atom	x	y	z	Atom	x	y	z
Sc1	0.4266	0.6877	0.6386	C7b	0.4360	0.5261	0.6840
O1a	0.3695	0.7944	0.6160	C8b	0.3654	0.4663	0.7289
O2a	0.3318	0.6374	0.5949	C9b	0.3076	0.4419	0.7569
N1a	0.2783	0.8757	0.5726	C10b	0.3810	0.5435	0.7119
N2a	0.2077	0.8686	0.5410	C11b	0.3540	0.6232	0.7154
C1a	0.3088	0.9553	0.5825	C12b	0.3087	0.6445	0.7498
C2a	0.3852	0.9653	0.6046	C13b	0.2428	0.6947	0.7352
C3a	0.4153	1.0448	0.6145	C14b	0.1986	0.7169	0.7679
C4a	0.3661	1.1135	0.6009	C15b	0.2256	0.6908	0.8116
C5a	0.2916	1.0994	0.5795	C16b	0.2903	0.6429	0.8251
C6a	0.2597	1.0225	0.5700	C17b	0.3344	0.6183	0.7931
C7a	0.3053	0.8029	0.5872	O1c	0.50157	0.6900	0.5951
C8a	0.1920	0.7914	0.5387	O2c	0.5097	0.7593	0.6766
C9a	0.1184	0.7638	0.5059	N1c	0.6104	0.7344	0.5693
C10a	0.2521	0.7446	0.5678	N2c	0.6721	0.7904	0.5816
C11a	0.2644	0.6632	0.5740	C1c	0.6034	0.6901	0.5296
C12a	0.2059	0.5994	0.5595	C2c	0.5696	0.6155	0.5258
C13a	0.2263	0.5306	0.5394	C3c	0.5715	0.5709	0.4855
C14a	0.1700	0.4670	0.5273	C4c	0.6057	0.6045	0.4532
C15a	0.0956	0.4777	0.5353	C5c	0.6383	0.6764	0.4581
C16a	0.0763	0.5438	0.5559	C6c	0.6399	0.7245	0.4968
C17a	0.1302	0.6079	0.5681	C7c	0.5618	0.7359	0.5984
O1b	0.4672	0.5756	0.6610	C8c	0.6618	0.8259	0.6183
O2b	0.3660	0.6787	0.6899	C9c	0.7222	0.8844	0.6392
N1b	0.4491	0.4465	0.6873	C10c	0.5926	0.7952	0.6301
N2b	0.4055	0.4081	0.7143	C11c	0.5634	0.8087	0.6684
C1b	0.5004	0.3974	0.6678	C12c	0.5858	0.8749	0.7011
C2b	0.5437	0.4355	0.6401	C13c	0.5960	0.8576	0.7457
C3b	0.5958	0.3830	0.6221	C14c	0.6104	0.9205	0.7769
C4b	0.6030	0.3031	0.6342	C15c	0.6130	1.0017	0.7611
C5b	0.5592	0.2675	0.6610	C16c	0.6011	1.0173	0.7170
C6b	0.5047	0.3169	0.6791	C17c	0.5890	0.9544	0.6843

Table 3 Atomic coordinates for $[(H_2O)_{10}(OH)_2Sc_2](C_6H_5SO_3)_4 \cdot 4H_2O$ in $C2/c$ [a = 3.012(1), b = 0.7493(2), c = 2.3608(9) nm, β = 124.73(3)°]

Atom	x	y	z
Sc1	0.0019	0.0351	0.1793
O1w	−0.0680	0.1850	0.0965
O2w	0.0039	0.0030	0.0859
O3w	−0.0380	−0.2184	0.1416
O4w	0.0750	−0.1265	0.2123
O5w	0.0427	0.2770	0.1868
O6w	0.0475	0.0513	0.2859
O7w	−0.0683	−0.1405	−0.0475
O8w	−0.0026	0.5374	0.0910
S1a	−0.1396	0.5189	0.1470
O1a	−0.1265	0.4242	0.1067
O2a	−0.1295	0.4286	0.2061
O3a	−0.1137	0.6896	0.1656
C1a	−0.2099	0.5597	0.0939
C2a	−0.2327	0.6550	0.1215
C3a	−0.2881	0.6919	0.0797
C4a	−0.3190	0.6269	0.0127
C5a	−0.2953	0.5302	−0.0134
C6a	−0.2401	0.4946	0.0269
S1b	−0.1134	0.3407	−0.0834
O1b	−0.1072	0.1900	−0.0411
O2b	−0.0898	0.5017	−0.0419
O3b	−0.0929	0.3063	−0.1242
C1b	−0.1831	0.3802	−0.1405
C2b	−0.2166	0.3273	−0.1210
C3b	−0.2721	0.3607	−0.1664
C4b	−0.2922	0.4385	−0.2293
C5b	−0.2580	0.4907	−0.2482
C6b	−0.2019	0.4614	−0.2027

2 Discussion

The original description of **(1)** in *Pbca* has four water molecules; one of these, which lies on a special position, is only 0.2 nm away from the other three. This water molecule must be disordered with respect to the other three. A check with *PLATON*[12] shows eight solvent accessible sites that exceed 0.04 nm^3 each, together with smaller holes near the butyl groups. The holes near the butyl groups, together with the larger temperature factors for the constituent carbon atoms, implicate disorder. However, the disorder was not adequately addressed in the original refinements. One procedure to redress the refinements, if real diffraction data were available, is to make use of the *SQUEEZE* option in *PLATON*, which is particularly effective handling structures having disordered solvents. The improper handling of the disordered lattice water molecules probably contributed to the high residual index. Because the scandium atom occupies a special position in the correct structure, the geometry of the scandium atom is a crystallographically-imposed O_h octahedron; this aspect of the structure was ignored in the original report because the authors had placed the scandium atom in a

general position. Similarly, for **(4)**, the scandium atom also lies on a special position in the correct structure, which is disordered in the 18-crown-6 portion; the authors had refined the structure, without disorder, in the non-centrosymmetric space group. Disorder in such polyethers is relatively common, and the bond distances and angles in such rings much be restrained for the refinements to converge. Disorder may not be detected by programs[12] that check for missing symmetry.

Table 4 Atomic coordinates for $[Sc(NO_3)_3(H_2O)_3]\cdot$18-crown-6 in *Pnma* [$a$ = 1.5300(3), b = 1.4052(3), c = 1.0879(3) nm]

Atom	x	y	z
Sc1	0.6092	−1/4	0.0283
O1	0.6145	−0.1742	0.2131
O2	0.6104	−1/4	0.3871
O3	0.7417	−0.3251	0.0360
O4	0.8668	−1/4	0.0321
O5	0.6013	−1/4	−0.3345
O6	0.5413	−1/4	−0.1551
O7	0.6783	−1/4	−0.1660
O8	0.5743	−0.4004	−0.0024
O9	0.4685	−1/4	0.0812
O10	0.6356	0.0514	0.1607
O11	0.6466	0.0960	−0.0953
O12	0.5378	−0.0247	−0.2410
N1	0.6136	−1/4	0.2751
N2	0.7852	−1/4	0.0335
N3	0.6078	−1/4	−0.2225
C1	0.5424	0.0294	0.3163
C2	0.5944	0.0943	0.2706
C3	0.6976	0.1207	0.1075
C4	0.7162	0.0903	−0.0040
C1a	0.5193	0.0579	0.3397
C2a	0.5927	0.0707	0.2789
C3a	0.6961	0.0917	0.0666
C4a	0.7313	0.0708	−0.0402
C5	0.6679	0.0532	−0.2134
C6	0.5970	0.0489	−0.2861

Examples **(2)** and **(3)** were originally indexed as triclinic cells, but whereas the similarity of the β and γ angles would have suggested higher symmetry, the cell axes and angles for **(3)** give little indication for incorrect symmetry, and only a close examination of the atomic coordinates reveals that the two independent monomers are related by $1/2 - x$, $1/2 - y$, z.

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若干 Sc 络合物的空间群

Ng Seikweng

（马来亚大学研究生院　50603　Kuala Lumpur. 马来西亚）

胡盛志

（厦门大学化学系，厦门　361005）

摘要　通过模拟结构因子计算将 $[(C_4H_9)_4N][Sc(NCS)_6]\cdot 3.5H_2O$ 的空间群从正交晶系的 *Pcab* 修正为立方晶系的 $Pa\bar{3}$. 将 $Sc(C_{17}H_{13}N_2O_2)_3$ 和 $[(H_2O)_{10}(OH)_2Sc_2](C_6H_5SO_3)_4\cdot 4H_2O$ 从 $P\bar{1}$ 修正为 $C2/c$. 还将 $[Sc(NO_3)_3(H_2O)_3]\cdot$18-Crown-6 的 $Pna2_1$ 修正为 *Pnma*.

关键词：空间群修正，模拟结构因子，钪络合物

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