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Notes

Two-Dimensional Polytypism of "Crystalline" $(C_5Me_5)ReO_3$

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Introduction

In a recent issue of *Inorganic Chemistry*, Burrell and coworkers[1] have reported the crystal structure determination of Cp^*ReO_3 ($Cp^* = \eta^5$-pentamethylcyclopentadienyl), originally synthesized by Hermann *et al.* in 1984,[2] which is an easily accessible precursor of many high-oxidation organorhenium compounds[3] and a powerful (and selective) oxidizing agent of alkenes and alkynes.[4] Their important work has apparently solved the long-standing problem of the solid state structure of Cp^*ReO_3 (for which diffraction experiments repeatedly showed unexpected difficulties)[3a,5] and shed a new light on the nature of the $[Tc_2O_3(Cp^*)]_n$ polymer,[6] which was eventually found to be an artifact.

At the same time we were also working on the same project, using a combination of single-crystal and powder diffraction techniques, coupled with computer simulations of faulted crystals, and reached similar conclusions on the nonexistence of the technetium polymer.[7]

Our results do not differ from those of Burrell *et al.*, as far as the local stereochemical features of the Cp^*ReO_3 molecule are concerned; however, we think to have reached a deeper understanding of the "crystalline" nature of the title compound by obtaining a detailed model of the *polytypic* nature of its crystals.

Experimental Section

Synthesis of Cp^*ReO_3. Cp^*ReO_3 was prepared by treatment of $Cp^*Re(CO)_3$[8] with hydrogen peroxide following reported procedures.[9] Crystals suitable for X-ray diffraction analysis were obtained by slow recrystallization from CH_2Cl_2/hexane 2:1. Larger crystals were also grown from amyl acetate solutions.

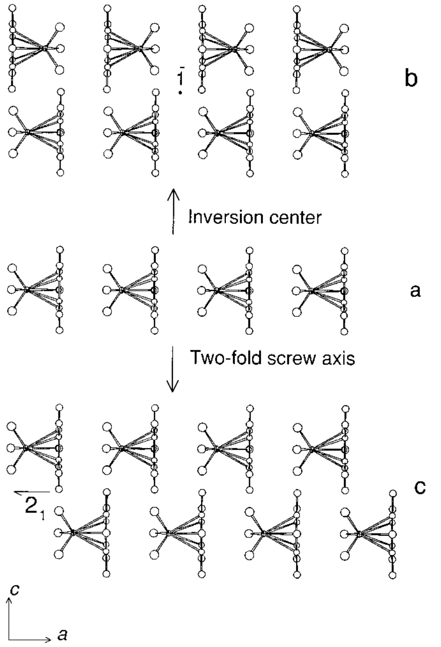

Figure 1. Rows of Cp^*ReO_3 molecules (a), packed in space by inversion centers (b) or 2-fold screw axes (c). In both cases, the packing sensitive oxo and methyl groups coincide.

Single-Crystal X-ray Analysis. Four crystals were mounted on purpose on different orientations on glass fibers and examined at room temperature on an Enraf-Nonius CAD4 automated diffractometer. For each crystal a full hemisphere of data was sampled by the ω-scan technique using a variable scan range with a 25% extension at each end for background evaluation. Standard reflections were measured at regular intervals during the data collections, and no decay was observed. Corrections for Lorentz, polarization, and absorption[10] effects were applied to all datasets.

In agreement with Burrell's observations, $00l$ reflections were absent for odd l values; however, for the $h0l$ subset, different patterns were found: crystal 1 clearly showed a systematic absence condition for $h + l = 2n + 1$, thus suggesting, as probable space groups, centric $Pmnm$ (*i.e.* that reported for $[Tc_2O_3(Cp^*)]_n$[6]) or acentric $P2_1nm$; the others (2−4) showed, in that order, increasing violations of such a pattern, suggesting monoclinic, rather than orthorhombic, symmetry ($P112_1/m$). Burrell's sample, therefore, ideally belongs to this last group.

Table 1 contains final agreement values (and other relevant crystal data and experimental figures) for the four datasets, each analyzed with the same structural model (*i.e.* anisotropic non-hydrogen atoms and isotropic H atoms riding on their methyl carbons) in five different ways, using twinned[11] and/or disordered models, as follows: model 1, orthorhombic $Pmnm$ symmetry, split oxygen atoms, 50:50 (symmetry imposed) disorder, (obviously) no twinning; model 2, monoclinic $P112_1/m$ symmetry, free Re atoms occupancy in two disordered sites, split oxygen atoms, no twinning (Burrell's first model); model 3, monoclinic $P112_1/m$ symmetry, free Re atoms occupancy in two disordered sites, split oxygen atoms, 50:50 twinning ratio (Burrell's second model); model 4, monoclinic $P112_1/m$ symmetry, free Re atoms occupancy in two disordered sites, split oxygen atoms, free twinning

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(11) The twinning plane, following Burrell's formulation, is [100].

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Table 1. Synoptic Collection of Selected Crystal Data and Refinement Parameters for Cp*ReO$_3$

	no. 1	no. 2	no. 3	no. 4	no. 5[a]
cryst dimens, mm	0.02 × 0.04 × 0.12	0.05 × 0.10 × 0.50	0.10 × 0.10 × 0.10	0.05 × 0.10 × 0.10	n.a.
θ range, deg	2−25	3−25	3−25	3−25	n.a.
octants explored	$\pm h, \pm k, l$	$\pm h, \pm k, l$	$\pm h, \pm k, l$	$\pm h, \pm k, l$	one hemisphere
min transm factor	0.73	0.78	0.68	0.90	0.63
scan mode	ω	ω	ω	ω	ω-θ
scan width, deg	$0.90 + 0.35 \tan \theta$	$1.20 + 0.35 \tan \theta$	$1.50 + 0.35 \tan \theta$	$1.20 + 0.35 \tan \theta$	n.a.
N_{refl}	1936	2040	2036	2040	n.a.
R_{merge} ($Pmnm$), N_{obs}	0.031, 540	0.017, 561	0.029, 558	0.034, 556	n.a.
R_{merge} ($P2_1nm$), N_{obs}	0.030, 935	0.012, 1016	0.026, 1002	0.032, 1007	n.a.
R_{merge} ($P112_1/m$), N_{obs}	0.020, 920	0.016, 1009	0.026, 999	0.026, 1005	0.032
model 1, *Pmnm*, 47 params					
R, wR^{2} [b]	0.030, 0.062	0.057, 0.141	0.088, 0.199	0.145, 0.375	n.a.
occupancy, fixed	0.50	0.50	0.50	0.50	0.50
model 2, $P112_1/m$, no twinning, 83 params					
R, wR^2	0.032, 0.060	0.068, 0.154	0.105, 0.228	0.161, 0.394	n.a., 0.25
occupancy	0.488(1)	0.486(1)	0.468(2)	0.377(4)	0.40
model 3, $P112_1/m$, 50:50 twinning, 83 params					
R, wR^2	0.029, 0.061	0.024, 0.056	0.032, 0.069	0.027, 0.073	n.a., < 0.10
occupancy	0.466(1)	0.449(1)	0.408(1)	0.294(1)	n.a.
model 4 $P112_1/m$, refinable twin ratio, 84 params					
R, wR^2	0.023, 0.047	0.024, 0.056	0.032, 0.069	0.025, 0.068	0.025, 0.061
occupancy	0.464(1)	0.450(1)	0.408(1)	0.295(1)	0.38
twin ratio,[c] (refined)	0.393(4)	0.499(2)	0.499(2)	0.478(2)	0.43
model 5, $P2_1nm$, 83 params					
R, wR^2	0.025, 0.052	0.034, 0.084	0.055, 0.121	0.103, 0.263	n.a.
occupancy	0.488(2)	0.461(2)	0.456(2)	0.431(4)	n.a.

[a] from ref 1. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $\text{wR}^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$. [c] Rigourously, for an occupancy value of 0.50 the monoclinic symmetry is lost and the *Pmnm* space group is restored, making the twin ratio mathematically undefined; therefore, for occupancy values close to 0.50, the twin ratio can be refined to values which are physically unsound, reflecting mainly the statistical fluctuations of the measured intensities and systematic errors, such as imperfect absorption correction.

ratio (Burrell's final model); model 5, orthorhombic $P2_1nm$ symmetry, free Re atoms occupancy in two disordered sites, split oxygen atoms.[12]

The data available from Burrell's paper have been included in Table 1 as crystal 5. All refinements were performed using the full-matrix least-squares method implemented into SHELX93,[13] using the TWIN and BASF options when needed, on a Silicon Graphics Personal Indigo computer running IRIX 4.01. The twin ratio (BASF) and the occupancy parameter were included, with all other refined parameters, in the same least-squares matrix until convergence was achieved (maximum Δ/σ value < 0.01). The correlation coefficients between occupancy and twin ratio parameters were rather small (maximum value 0.18 for crystal 1); indeed they address different physical events, *i.e.* interference (disorder) *vs* (incoherent) sum of intensities (twinning).

The coordinates of the (disordered) rhenium atoms were rather stable throughout all refinements, independently on the model used, with (false) Re−Re contacts ranging from 1.876(1) up to 1.899(8) Å. Of course, during the refinement with the poorest agreements, *i.e.* when the twin ratio and the rhenium occupancy parameters were not yet optimized, the sizes and orientations of some anisotropic thermal factors for the lighter atoms were refined to unphysical values.

Results and Discussion

Back in 1993,[7] on the basis of the only single crystal data available ("orthorhombic" crystal 1, see Table 1) *and* of a thorough analysis of the powder diffraction spectra,[14] we formulated the following structural model:

(a) Cp*ReO$_3$, a truly molecular compound, stacks in space in a head-to-tail sequence, along *a* (see Figure 1a), and the whole crystal is perfectly ordered along *a*.

(b) These *ordered* columnar moieties, of *beam group Lm*,[15] pack together in a pseudohexagonal fashion (see Figure 2) either by inversion centers or 2-fold screw axes (the −1 packing operator alone generates $P112_1/m$ ordered crystals; conversely, the 2_1 axis alone affords the $P2_1nm$ space group). In both cases, the location of the (packing sensitive) oxo and methyl groups coincide (see Figure 1b,c).

(c) The almost perfect matching of the Cp* and O$_3$-triangle sizes (and their possibility of acting as equivalent ligands on both sides) makes then the crystals grow as macroscopically perfect crystals, as also witnessed by the small mosaicity observed during the "single-crystal" data collection (see Table 1).

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(12) This model could be (very slightly) improved by considering racemic twins (with domains differing in their anomalous scattering contribution).

(13) Sheldrick, G. M. *SHELX 93: A program for crystal structure refinement*; University of Göttingen: Göttingen Germany, 1993.

(14) It is well-known that the simultaneous sampling of all reciprocal lattice nodes having the same 2θ makes the powder diffraction technique poorer (compared to standard single-crystal analysis), because severe (accidental or exact) overlaps of peaks occur. For the very same reason, however, (macro)twinning, i.e. the presence of two (or more) ordered macroscopic domains within each crystallite, does not affect the powder patterns, as long as preferred orientation of the crystallites is avoided (Li, J.; McCulley, F.; McDonnell, S. L.; Masciocchi, N.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1993**, *32*, 4829). In particular, the powder spectrum of the title compound shows the following: (*i*) the presence at low angles of broad, but well-defined, peaks (100 and 120) which are forbidden in *Pmnm*; (*ii*) a marked asymmetric broadening of some peaks (counterparted, in the "single-crystal" data collection, by *anomalous* peak widths of 1.8−2.0°); (*iii*) a structured background level. These features, which correspond to the streaks observed by Burrell on oscillation photographs, cannot be accounted for by ordinary twinning but are indicative of the paracrystalline and/or faulted nature of the crystals (Guinier, A. *X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies*; Freeman & Co.: San Francisco, CA, 1963. Reynolds, R. C. In *Modern Powder Diffraction*; Bish, D. L., Post, J. E., Eds.; Reviews in Mineralogy, 20.; The Mineralogical Society of America: Washington, DC, 1989; p 145). Consistently, we failed to satisfactory reproduce all such features by using, in a Rietveld refinement, any of the four structural models presented in the single-crystal analysis. However, some of these anomalies can be reproduced by our faulted model: (a) on nanocrystals, by the Debye interference function (Espinat, D.; Thevenot, F.; Grimound, J.; El Malki, K. *J. Appl. Crystallogr.* **1993**, *26*, 368) (b) on nanocrystals, by the explicit Fourier transform (Neder, R. B. *Z. Kristallogr.* **1994**, *Suppl. 8*, 744); (c) on infinitely thick crystals, by recursive algorithms (Treacy, M. M. J.; Newsam, J. M.; Deem, M. W. *Proc. R. Soc. London, A* **1991**, *433*, 499).

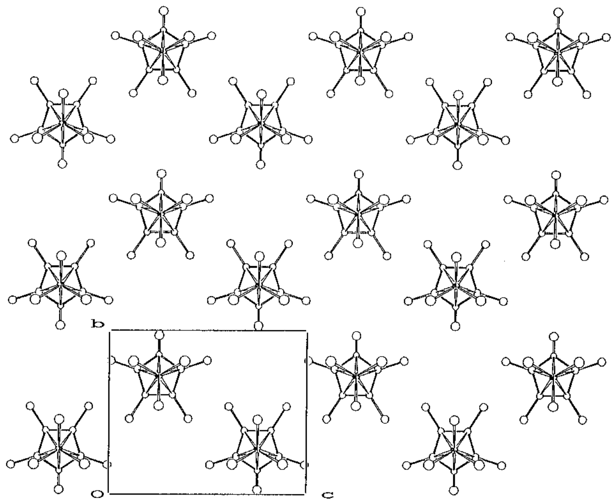

Figure 2. Pseudohexagonal crystal packing of Cp*ReO$_3$ columns viewed down [100].

(d) A random choice of the packing operator generates a paracrystalline sample (in the *bc* plane), with rhenium atoms *randomly located* in the geometrically equivalent holes between the *essentially ordered* Cp* and trioxo frames, which is reasonably approximated, in single-crystal terms, by the (disordered) *Pmnm* space group.

The appearance of Burrell *et al.* work, however, revealed that their were handling a slightly different sample, for which the (disordered) *Pmnm* model was not matching the observed intensities. This prompted us to reconsider the whole problem, by collecting newer datasets on different crystals (2$-$4). The results reported in Table 1 show that, despite the substantial *mmm* Laue symmetry presented by all samples,[16] their intensity patterns are heavily different. This led to the discovery that *morphologically homogeneous* samples contain crystals of different kinds and that none of them can be taken as representative of the bulk. This demonstrates, *inter alia*, that the observed disorder is not dynamic, *i.e.* that (cooperative) migration of the rhenium atoms through the O$_3$ fragments does not occur.

These observations require a slight modification of point d of the model presented above, as, in order to match quantitatively all observed data, *nonrandom*, *i.e. correlated*, growth by the same kind (-1 or 2_1) of operator must be present. The crystals should therefore be better described, in the *bc* plane, by a complex intergrowth of $P112_1/m$ and $P2_1nm$ microdomains, which, much like a leopard skin, tile the full space. If the size of such domains reduces to a single column, random intergrowth occurs and the crystal is reasonably well described in (disordered) *Pmnm* (crystal 1); on the other hand, if such domains become large enough, twinned and/or biphasic crystals are generated. Intermediate situations may be *partially* accounted for by relative amounts of disorder (which is a quantitative measure of the amount of boundary zones between ordered domains) and twinning.[17] Disordered but monophasic single-crystals correspond to models 1 (*Pmnm*), 2 (untwinned $P112_1/m$), and 5 ($P2_1nm$), for which poor agreement was found (apart from crystal 1).

Accordingly, a simple growth mechanism has been simulated, by introducing a parameter *p*, which accounts for the probability that a given molecule (and, thanks to the above considerations, also an ordered column along *a*) stacks with those surrounding it in the *bc* plane, by the -1 packing operator (conversely, $1 - p$ addresses the probability of the 2_1 operator).[18] A perfect growth of a $P112_1/m$ crystal would then be generated by a *p* value equal to 1, while $p = 0$ would generate a single crystal of acentric $P2_1nm$. Thermodynamically speaking, the small energy difference in the two packing modes, which, using a locally developed molecular mechanics program capable of minimizing the *intra-* and *inter*molecular steric energies of a molecule within its crystal lattice, has been evaluated to be less than 0.2 kcal mol^{-1},[19] would impose a *p* value close to 0.50, and growth of a paracrystal containing randomly oriented columns, *i.e.* that described in *Pmnm*.

However, as crystal growth is a nonequilibrium process, kinetic effects such as nucleation rate, local supersaturation, and concentration and temperature gradients may locally affect the *p* value, which, therefore, cannot be taken as a thermodynamic parameter but represents, instead, the phenomenological (kinetic) description of that particular growth site. Accordingly, the growth of long-period one-dimensional polytypes and coexistence, in the same macrocrystal, of different polytypes or even polymorphs for mica,[20] long chain alcohols and carboxylic acids,[21] and organic polymers,[22] as well as different nucleation fronts on the same crystal surface is well documented on the basis of diffraction, optical, and HRTEM microscopical evidence. Indeed, in the present case, we have found that crystals from the same preparation and even fragments of the same crystal show different diffraction patterns, *i.e.* have different (polytypic) intergrowths motifs.

Conclusions

Crystals of Cp*ReO$_3$ have been shown to present a rare case of two-dimensional polytypism. They consist of a polytypic packing (in the *bc* plane) of ordered polar chains of *three-legged piano-stool* Cp*ReO$_3$ molecules, stacked head-to-tail along the *a* axis. The two-dimensional polytypism (*i.e.* polytypic aggregation, in two dimensions, of 1D rods) is a generalization of the more common polytypic, monodimensional, stacking of 2D layers,[23] and, in the present case, arises from the possibility of building a similar motif both with 2-fold screw axes and inversion centers as packing operators, *i.e.* from the possibility of packing together neighboring chains of equal or different polarity. A similar model, which also accounts for the shape and the intensities of "forbidden" reflections and/or streaks was proposed, on α-isotactic polypropylene, by Hikosaka *et al.*[24] who evidenced ordered domains of two crystallographically different phases coexisting within the same crystal (block-type distribution of structural defects).

The common use of "disordered" fragments in "molecular" single-crystal analysis is normally associated with completely

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(15) Thompson, J. B., Jr. *Am. Mineral.* **1978**, *63*, 239. Niggli, A. *Z. Kristallogr.* **1959**, *111*, 288.

(16) A simulation of the diffraction intensities of Burrell's crystal based on the *published* coordinates and isotropic thermal parameters, shows that also its sample possessed substantial *mmm* Laue symmetry ($R_{\text{merge}} = 0.034$ and 0.032,[1] for orthorhombic and monoclinic merging, respectively).

(17) Biphasic crystals cannot be simulated by conventional single-crystal refinement programs.

(18) A similar approach to polytypic macromolecular structures can be found in: Corradini, P.; Giunchi, G.; Petraccone, V.; Pirozzi, B.; Vidal, H. M. *Gazz. Chim. Ital.* **1980**, *110*, 413, and references therein.

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(21) Amelinckx, S. *Acta Crystallogr.* **1955**, *8*, 530; **1956**, *9*, 16; **1956**, *9*, 217.

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(23) Zvyagin, B. B. *Comput. Math. Appl.* **1988**, *16*, 569.

(24) Hikosaka, M.; Seto, T. *Polym. J.* **1973**, *5*, 111.

uncorrelated (*i.e.* statistical) orientations or occupancies of moieties not affecting the local topology or connectivity; however, even is such a simple and ideal case, weak "forbidden" peaks are likely to occur, as local correlations (short range order) may arise. When the random nature of such disorder is not maintained (for example, by partial or total ordering in one or two dimensions, as in the present case), the single-crystal approximation (*i.e.* the assumption of Laue's conditions and of rigorous space group symmetry) becomes poorer and non-Bragg scattering (which can only be accounted by faulted models or defective structures) larger. In such cases, the single-crystal approximation requires *numerical* massaging (*i.e.* the combined use of twinning and disorder) in order to model the diffracted intensities about the lattice nodes and to obtain reliable stereochemical molecular features;[1] however, the *physical* reality can only be matched by a paracrystalline description.

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Supporting Information Available: A comparative list of *observed* structure factor moduli for crystals 1−4, a plot of raw XRPD data and DiffaX[14] simulation, and maps of crystal intergrowth for different stacking probabilities ($p = 0.00, 0.02, 0.50, 0.98$, and 1.00) (20 pages). See any current masthead page for ordering information.

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