Marshing:
Past, Present and Future

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to be Marshed; Marshing

- My first encounter with the missionary work of Dick Marsh on missed higher symmetry was with the 1979 note in Inorganic Chemistry entitled:

  'Some Incorrect Space Groups in Inorg. Chem, Volume 16'.

- Since then many Marsh and 'look-alike' papers appeared, correcting many more SG-assignments.
- New Verb: to be Marshed
- However: MS-Word will change 'Marshing' into 'Mashing' .. as happened initially in the ACA-office to the title of my submitted abstract…

25 Years of Marshing

- Obvious Question:

  Is the Missed Symmetry Issue now Solved after 25 years ?

- Answer:

  -Yes: For Publications in the IUCr Journals.

  - No: For Publications in Chemical Journals.

Illustrative Example

- A survey by Dick Marsh in 1997 of all structures published in space group Cc showed that about 10% of the assignments was wrong.
- A new survey by Dick Marsh in 2004 surprisingly showed that this percentage is still around 10%.
- Note: none of the additional 164 corrected assignments were from Acta Cryst. journals.
- Revisions to C2/c, Fdd2, R-3c etc.

ORGANOMETALLICS

- Automatic Analysis with PLATON/ADDSYM
- Release: CSD 2003 + 2 UPDATES
- # of Alerts for missed or pseudo-symmetry:

Year-Range	Entries	Space Group Alerts
1982-1989	2687	28
1990-1995	5194	62
1996-1999	5688	88
2000-2004	6550	117

Examples from OM

Organometallics: Fdd2 ↙ I-42d

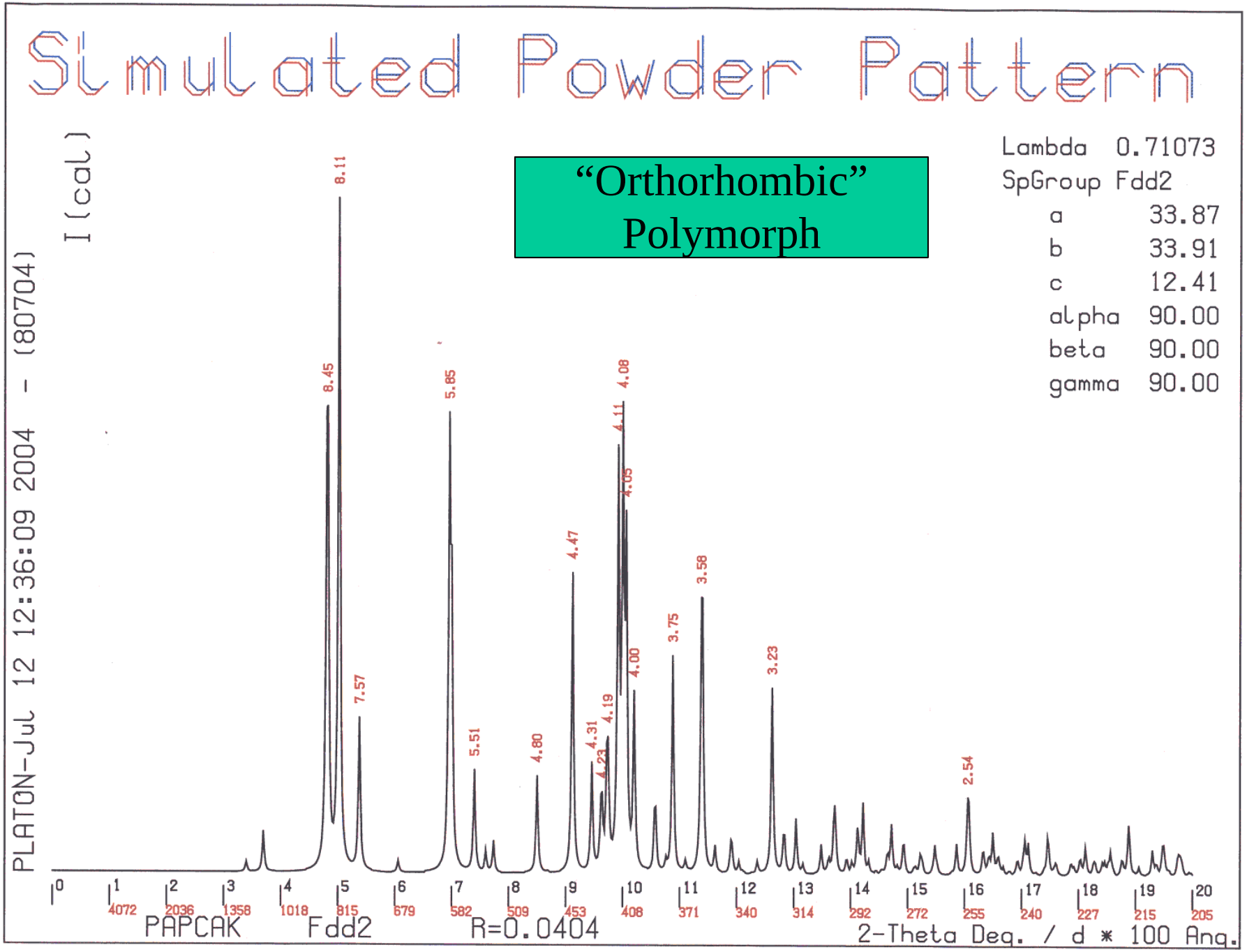
‘Orthorhombic Polymorph’: PAPCAK

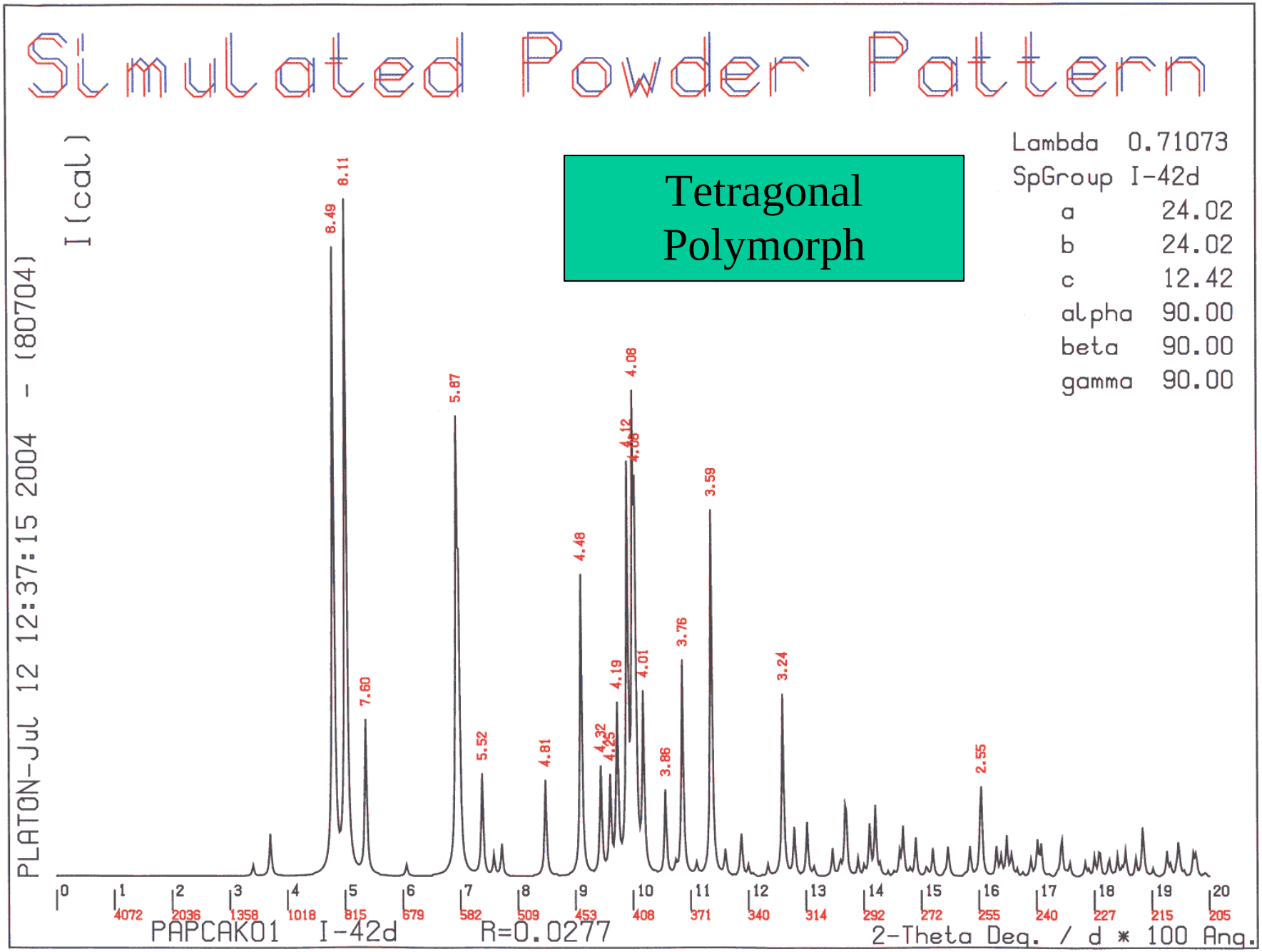
Private Communication to the CSD: I-42d

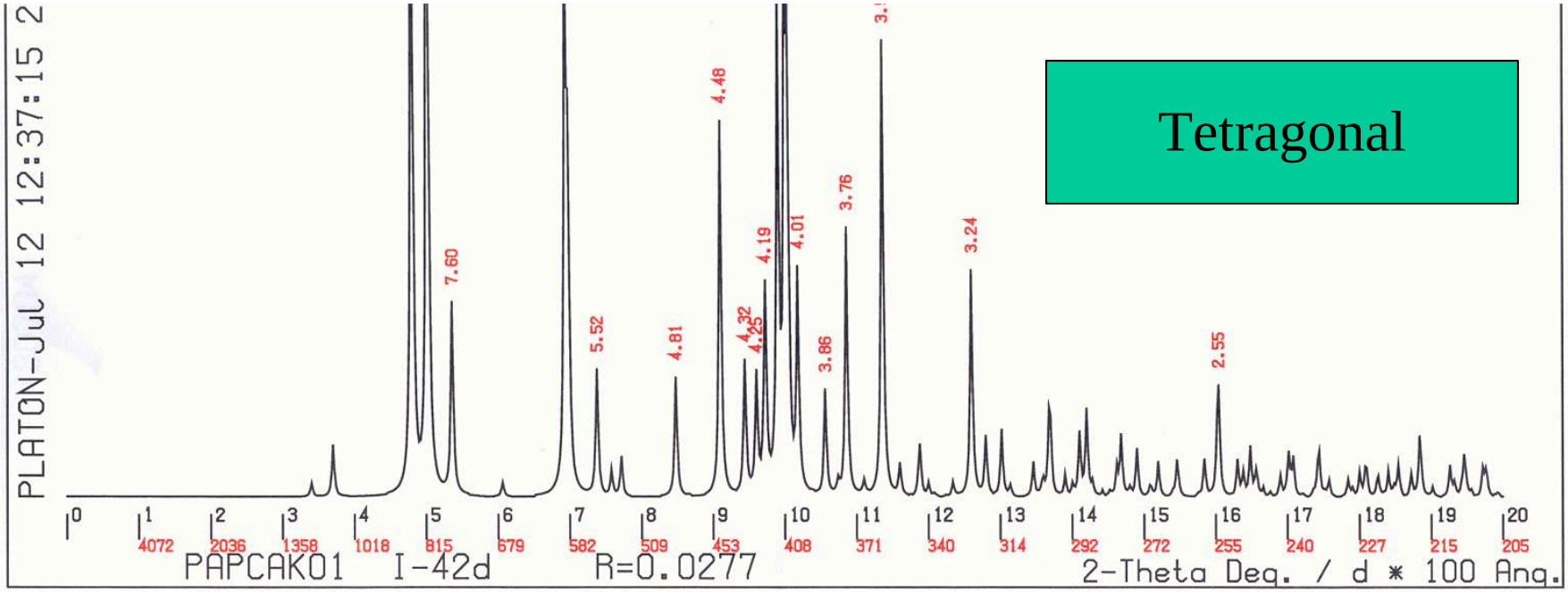
Tetragonal Polymorph: PAPCAK01

Identical Simulated Powder Patterns !!

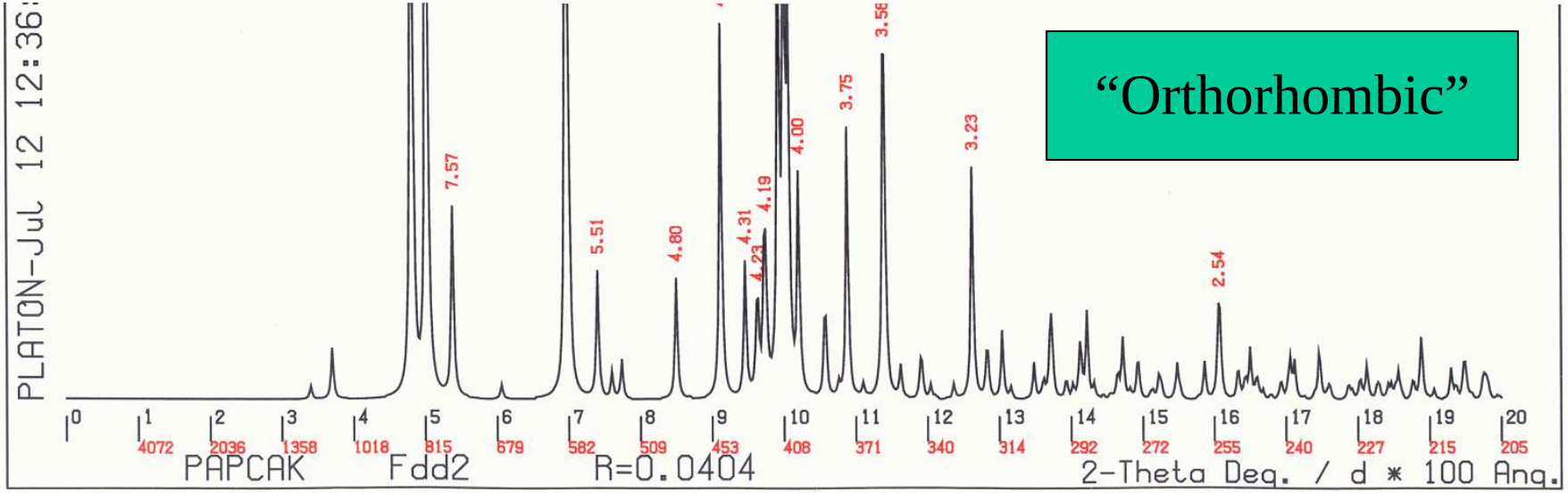
Simulated Powder Pattern




Simulated Powder Pattern
Tetragonal Polymorph
Lambda 0.71073
SpGroup I-42d
a 24.02
b 24.02
c 12.42
alpha 90.00
beta 90.00
gamma 90.00
I(cal)
PLATON-Jul 12 12:37:15 2004 - (80704)
8.49
8.11
7.60
5.87
5.52
4.81
4.48
4.32
4.25
4.19
4.12
4.08
4.01
3.86
3.76
3.59
3.24
2.55
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
4072 2036 1358 1018 815 679 582 509 453 408 371 340 314 292 272 255 240 227 215 205
PAPCAK01 I-42d R=0.0277
2-Theta Deg. / d * 100 Ang.



Tetragonal



"Orthorhombic"

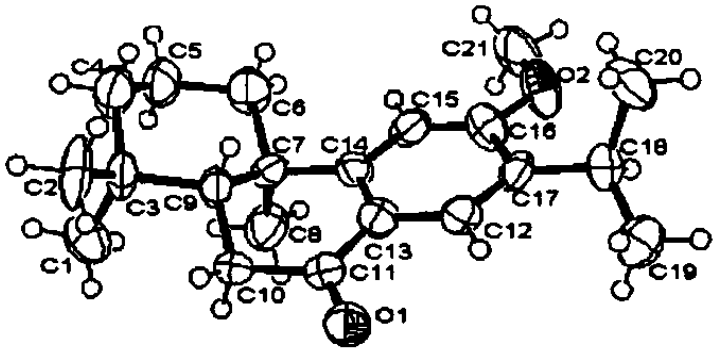
RECENT CSD UPDATES

- Version: CSD Nov 2003 + 2 Updates
- 22530 Entries for 2003 & early 2004 papers
- Default PLATON/ADDSYM run ↙ 458 New Hits requiring close examination (2%).

… Subset of 19 out of 458 Alerts …

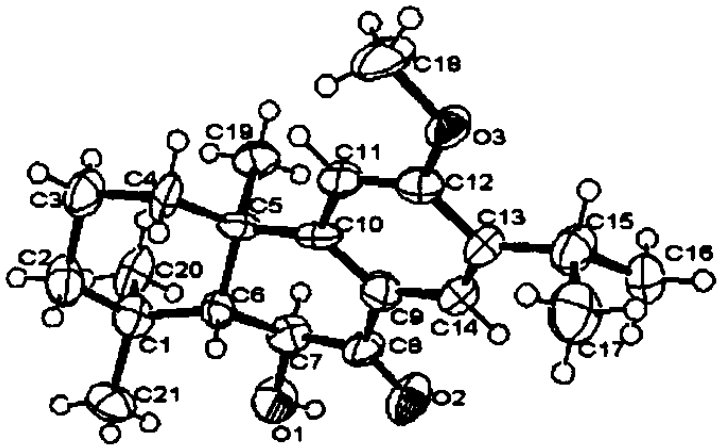
WUSDOD	Cc	R=0.070	mC=>mC	0.0	0	0	0.000	0.00	0.000		98%	C2/c
WUSLIF	Cc	R=0.049	mC=>mC	0.0	0	0	0.000	0.00	0.000		100%	C2/c
WUSLIF01	Cc	R=0.049	mC=>mC	0.0	0	0	0.000	0.00	0.000		100%	C2/c
WUWNAD	Cc	R=0.054	mC=>mC	0.0	0	0	0.000	0.00	0.000		100%	C2/c
WUXTOY	P21	R=0.059	mP=>mP	0.0	0	0	0.000	0.00	0.000		80%	P21/c
WUYXAP	I2	R=0.063	mI=>mC	0.0	0	0	0.000	0.00	0.000		91%	C2/m
WUYZIZ	I4	R=0.065	tI=>tI	0.0	0	0	0.000	0.00	0.000		100%	I4/m
WUZQIR	P21	R=0.039	mP=>mP	0.0	0	0	0.000	0.00	0.000		90%	P21/c
WUZXAQ	P1	R=0.056	aP=>aP	0.0	0	0	0.000	0.00	0.000		85%	P-1
XABFAI	P21	R=0.089	mP=>mP	0.0	0	0	0.000	0.00	0.243		93%	P21/c
XUMDUE	P21/c	R=0.047	mP=>mC	0.0	0	0	0.000	0.00	0.248	S	100%	C2/m
XURVUB	Cc	R=0.136	mC=>mC	0.0	0	0	0.000	0.00	0.000		100%	C2/c
XUSMAZ	P212121	R=0.038	oP=>oP	0.0	0	0	0.000	0.00	0.000		85%	Pnma
XUSZOA	C2/c	R=0.092	mC=>tI	0.0	0	0	0.000	0.03	0.062		100%	I41/acd
XUVGUQ	P1		aP=>oC	0.0	0	0	0.000	0.00	0.000		97%	Cmc21
XUVNAD	P-1	R=0.040	aP=>aP	0.0	0	0	0.000	0.00	0.000	S	100%	P-1
XUVNAD01	P-1	R=0.041	aP=>aP	0.0	0	0	0.000	0.00	0.000	S	100%	P-1
XUYDOK	C2	R=0.024	mC=>mC	0.0	0	0	0.000	0.00	0.000		100%	C2/c
XUYKOR	P63/m	R=0.038	hP=>hP	0.0	0	0	0.000	0.00	0.094		100%	P63/mmc

EKOCIY
Pc -> P21/c



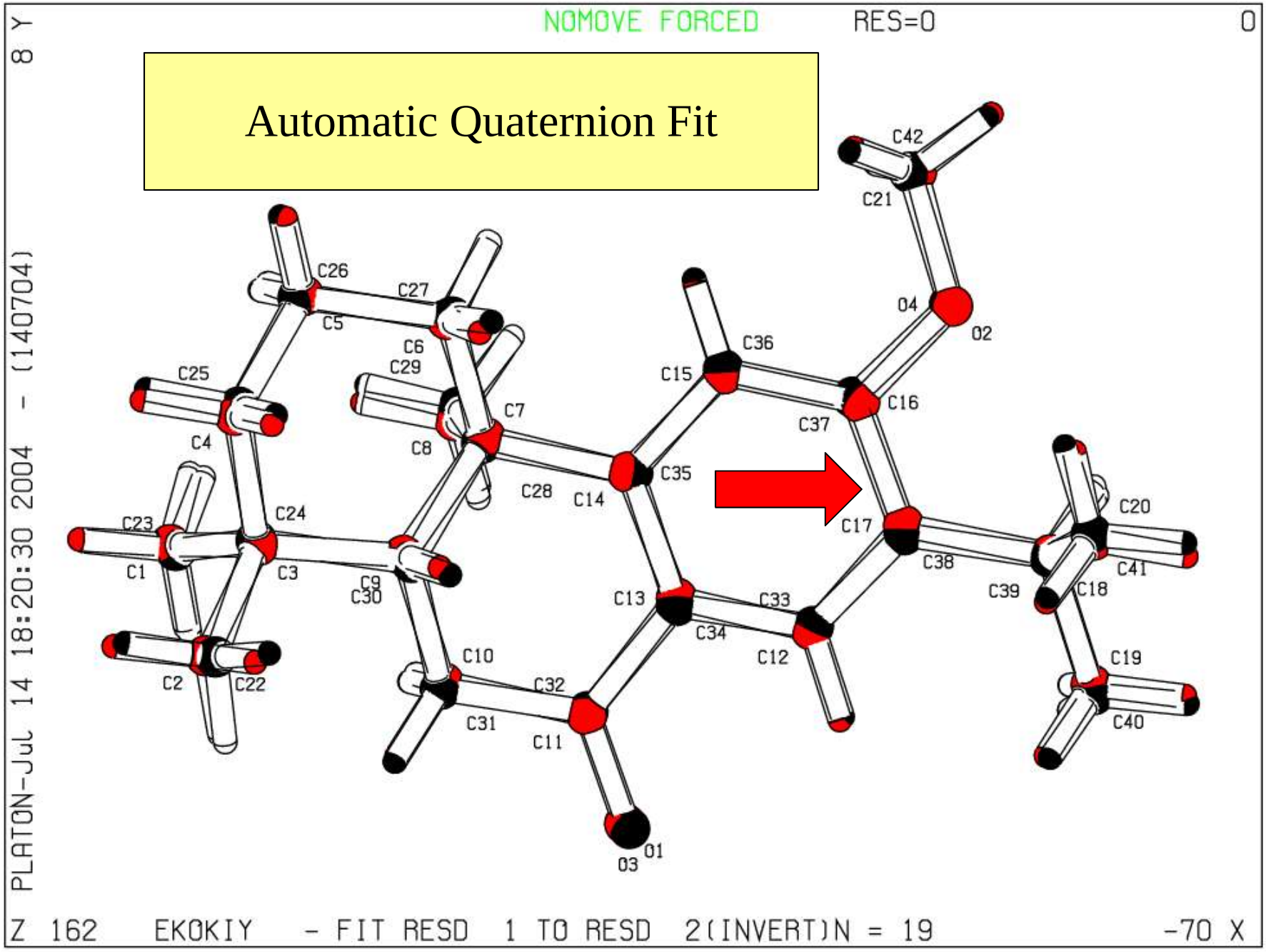
X-ray structure of **2** (CCDC 209202)

EKOKOE
P1 -> P-1



X-ray structure of **8** (CCDC 209203)

Tetrahedron, 59 (2003) 5737-5741


NOMOVE FORCED
RES=0
0
8 Y
PLATON-Jul 14 18:20:30 2004 - (140704)
Automatic Quaternion Fit
C42
C21
C26
C27
C5
C6
04
02
C36
C15
C25
C29
C7
C16
C37
C4
C8
C35
C28
C14
C17
C20
C23
C24
C1
C3
C9
C30
C38
C41
C39
C18
C13
C33
C34
C12
C10
C19
C2
C22
C32
C31
C11
C40
03
01
Z 162 EKOKIY - FIT RESD 1 TO RESD 2(INVERT)N = 19
-70 X

Comparison of the Bonds of the Fitted Residues for EKOKIY

Resd#1	Resd#2	Dist#1	Dist#2	Diff	Diff/Sig	
O(1) -C(11)	O(3) -C(32)	1.188(11)	1.264(11)	-0.076	-4.9	
O(2) -C(16)	O(4) -C(37)	1.360(12)	1.362(14)	-0.002	-0.1	
O(2) -C(21)	O(4) -C(42)	1.427(14)	1.406(17)	0.021	1.0	
C(1) -C(3)	C(23)-C(24)	1.551(18)	1.498(15)	0.053	2.2	
C(2) -C(3)	C(22)-C(24)	1.475(16)	1.614(16)	-0.139	-6.1	<
C(3) -C(4)	C(24)-C(25)	1.536(12)	1.550(17)	-0.014	-0.7	
C(3) -C(9)	C(24)-C(30)	1.506(14)	1.608(12)	-0.102	-5.5	
C(4) -C(5)	C(25)-C(26)	1.558(16)	1.405(19)	0.153	6.2	
C(5) -C(6)	C(26)-C(27)	1.484(16)	1.577(15)	-0.093	-4.2	
C(6) -C(7)	C(27)-C(28)	1.473(14)	1.575(10)	-0.102	-5.9	
C(7) -C(8)	C(28)-C(29)	1.567(16)	1.530(14)	0.037	1.7	
C(7) -C(9)	C(28)-C(30)	1.561(14)	1.543(11)	0.018	1.0	
C(7) -C(14)	C(28)-C(35)	1.494(13)	1.569(10)	-0.075	-4.6	
C(9) -C(10)	C(30)-C(31)	1.551(11)	1.513(12)	0.038	2.3	
C(10)-C(11)	C(31)-C(32)	1.493(13)	1.514(13)	-0.021	-1.1	
C(11)-C(13)	C(32)-C(34)	1.506(12)	1.426(13)	0.080	4.5	
C(12)-C(13)	C(33)-C(34)	1.411(13)	1.405(13)	0.006	0.3	
C(12)-C(17)	C(33)-C(38)	1.421(13)	1.317(12)	0.104	5.9	
C(13)-C(14)	C(34)-C(35)	1.372(12)	1.417(11)	-0.045	-2.8	
C(15)-C(16)	C(36)-C(37)	1.414(13)	1.344(13)	0.070	3.8	
C(16)-C(17)	C(37)-C(38)	1.329(13)	1.490(11)	-0.161	-9.5	<
C(17)-C(18)	C(38)-C(39)	1.528(15)	1.503(13)	0.025	1.3	
C(18)-C(19)	C(39)-C(40)	1.47(2)	1.554(14)	-0.084	-3.4	
C(18)-C(20)	C(39)-C(41)	1.479(18)	1.552(16)	-0.073	-3.0	

BAMYEU

Dalton Trans 2003,134-140

Cc

Dick ?

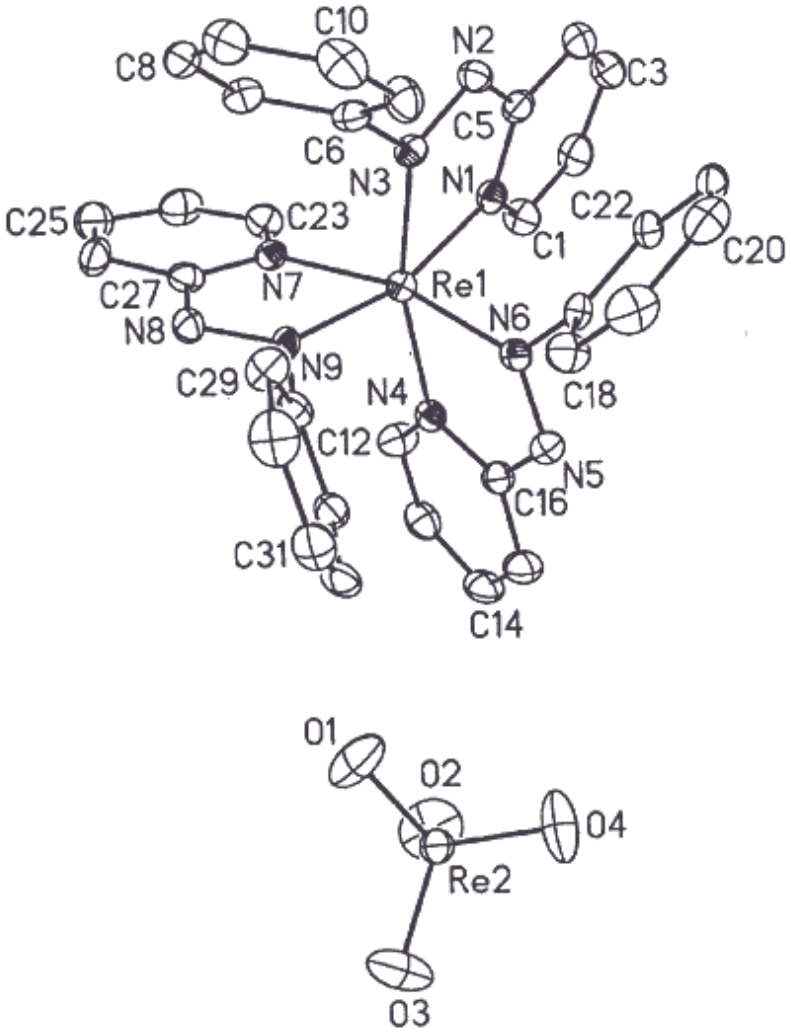


Fig. 4 A perspective view of $[Re(L^5)_3]ReO_4$ **4a**. The atoms are represented by their 30% thermal probability ellipsoids.

PLATON/ADDSYM for BAMYEU C c

ADDSYM Search on ALL NON-H Chemical Types [Max NonFit 20 Perc]

Criteria: 1.00 Deg (Metric), 0.25 Ang (Rot.), 0.45 Ang (Inv), 0.45 Ang (Transl)

Symm. Elem	Input Cell Row	Reduced Cell Row	(Ang) d	Typ	Dot	(Deg) Angle	( ) Flt	(Ang) MaxDev.		Input Cell x	y	z
3 *	[0 0 1]	[-1 0 0]	10.94	6	1	0.08	100 C5	0.019 -C27	through	0	1/6	0
c	[0 1 0]	[0 1-2]	22.31	2	2	0.00	100	0	through	0	1/2	0
									Glide =	0	0	1/2
c *	[3-1 0]	[0 2-1]	22.30	2	2	0.07	100 C5	0.019 -C27	through	5/8	1/8	0
									Glide =	0	0	1/2
c *	[3 1 0]	[0-1-1]	22.30	2	2	0.07	100 C27	0.019 -C5	through	3/8	1/8	0
									Glide =	0	0	1/2

Reduced-to-Convent Input-to-Reduced T = Input-to-Convent: a' = T a

$$\begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ -1/2 & -1/2 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ -1/2 & -1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \text{Det(T) = 0.500}$$

Cell	Lattice	a	b	c	Alpha	Beta	Gamma	Volume	CrystalSystem	Laue
Input	mC	12.876	22.313	10.938	90.00	90.08	90.00	3143	Monoclinic	2/m
Reduced	P	10.938	12.876	12.881	60.01	89.96	89.92	1572		
Convent	hP	12.876	12.881	10.938	90.04	89.92	119.99	1571	Trigonal	-3m

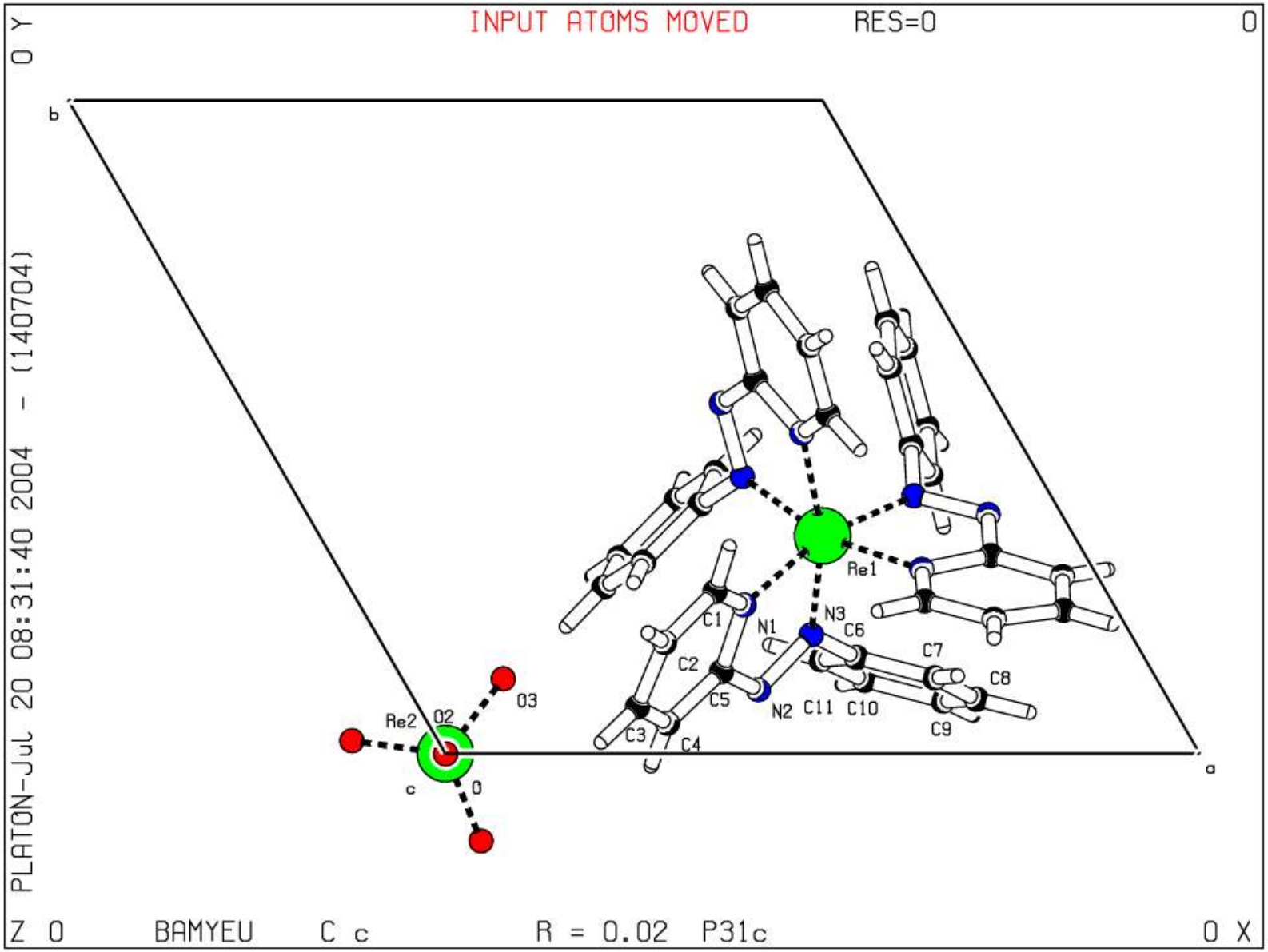
Origin shifted to: 0.500, 0.000, 0.000 after transformation

Missed/Additional Symmetry : Suggested SPGR = P31c (No 159)

ADDSYM MENU
NonFitPerc
TolMetric
TolRotAxis
TolInvers
TolTransl
NFTPercImpl
NoSubCell
KeepMon-I-n
ListDetails
ADDSYMEqual
ADDSYMElmnt
ADDSYMExact
ADDSYM-PLOT
ADDSYM-SHX
End
Exit
MenuActive

INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

Additional (Pseudo)Symmetry Found (See Listing for details)


INPUT ATOMS MOVED
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0
0 Y
PLATON-Jul 20 08:31:40 2004 - (140704)
b
a
c
Re1
Re2
O2
O3
O
N1
N2
N3
C1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
Z 0
BAMYEU
C c
R = 0.02
P31c
0 X

Sources of the Problem

- Education: Acta Cryst. Author query:

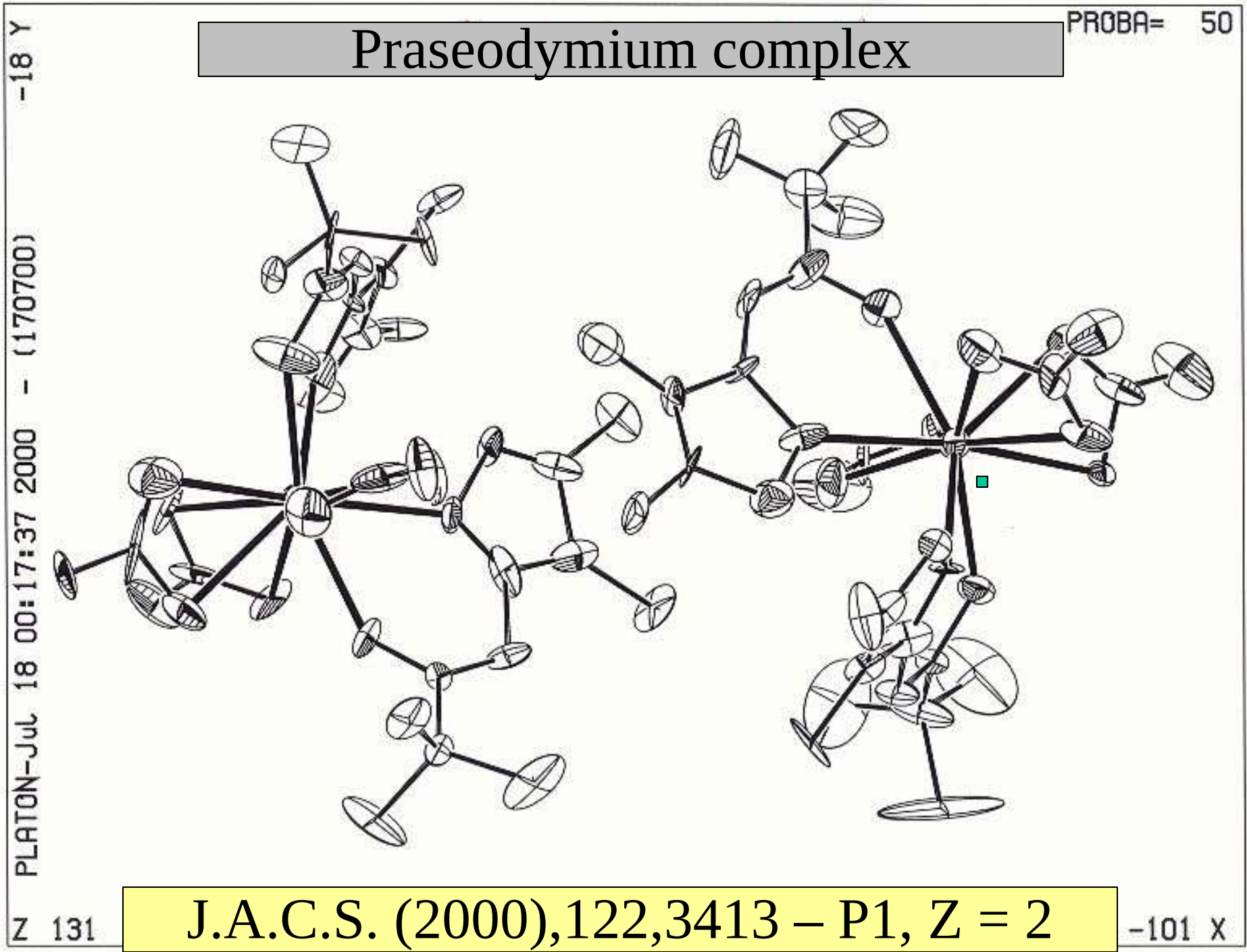
  Please teach me: what does it mean 'space group incorrect'

- Structures often solve only in lower symmetry space groups (e.g. P1)
- Authors either forget to check for or do not know how to manage transformation to higher symmetry space groups
- E.g. the origin shift (P-1) or origin choise (C2/c) problems.

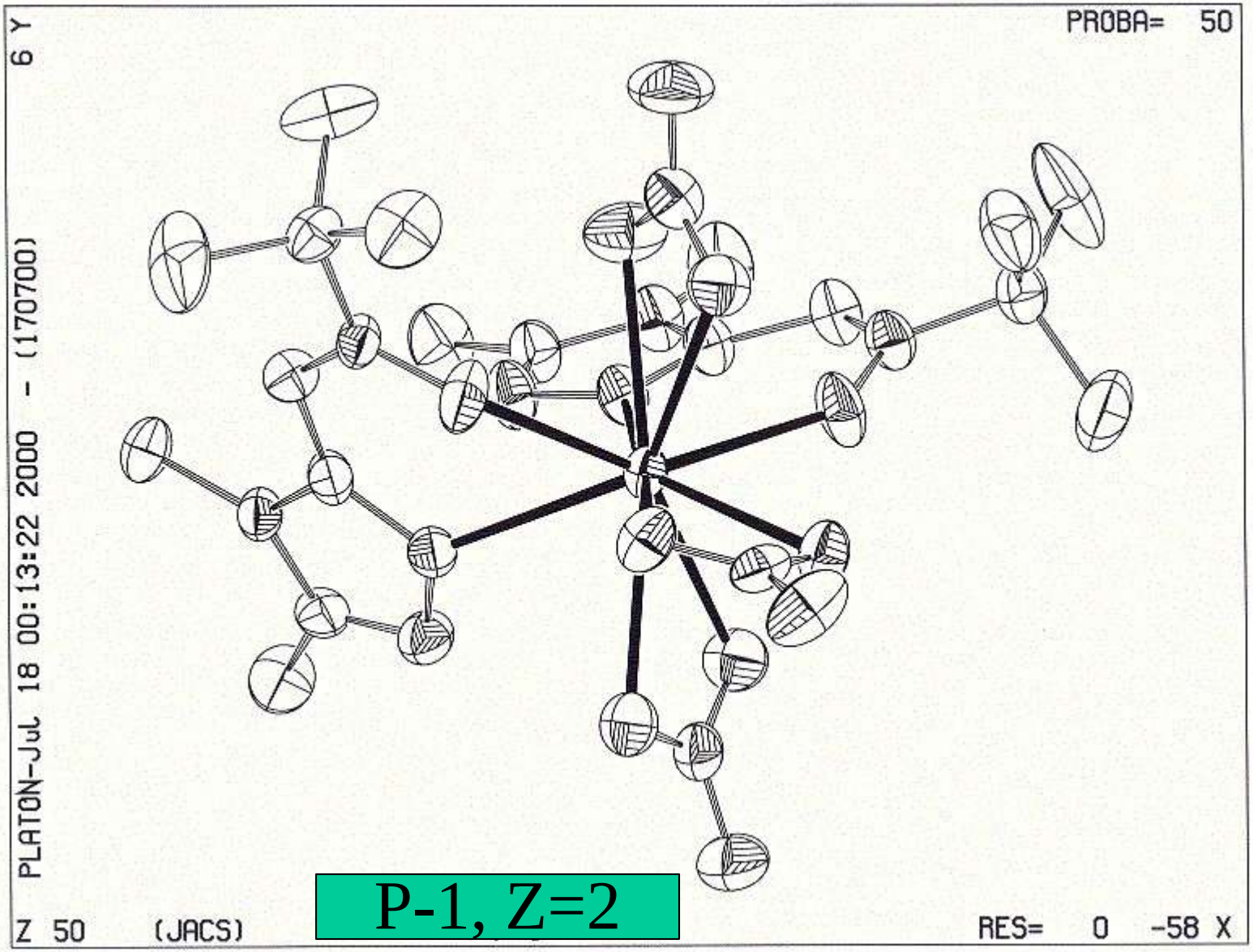
Residual Problems

- Chemists Perception: Space Group Terror ….
- Crystallographic data ‘hidden’ in suppl.mat. and not readily available for the referee.
- Pseudo-symmetry:
  - chiral molecules with Z’=2,
  - Angle close to 90 degrees but not exactly.
    e.g. ‘Orthorhombic with 90 90 89.50(1)
- No observed structure factors etc. available for detailed analysis.
- Interesting author response !

Praseodymium complex



J.A.C.S. (2000),122,3413 – P1, Z = 2


PROBA= 50
6 Y
PLATON-Jul 18 00:13:22 2000 - (170700)
Z 50 (JACS)
RES= 0 -58 X
P-1, Z=2

Concluding Remarks

- All Journals should implement an automated validation scheme for crystal structures
- Free IUCr – CHECKCIF server
- Use Free Software in-house
- (Space Group) ALERTS should be addressed by Authors and validated by knowledgeable referees.
- Structure Factors should be deposited being the primary data (required for detailed analysis).
- We need the expertise of Dick Marsh for the final word

Thanks !

- Dick Marsh – For his sustained efforts and service to the crystallographic community
- Yvon LePage – For the MISSYM algorithm, the basis of ADDSYM
- The Organisers of this Symposium

  Larry Falvello & Alberto Albinati