

**Symmetry relations among coefficients of the anisotropic temperature factor.** By HENRI A. LEVY,  
*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

In the least-squares refinement of crystal structures involving anisotropic temperature motion, individual atom temperature factors  $\exp(-M_{\mathbf{h}})$  are conveniently introduced by expressing  $M_{\mathbf{h}}$  in the form

$$M_{\mathbf{h}} = \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} h_i h_j, \quad \beta_{ij} = \beta_{ji}, \quad (1)$$

where  $\mathbf{h} = \sum_{i=1}^3 h_i \mathbf{b}_i$  is the reciprocal-lattice vector for the

reflection. Two problems which arise are (1) the determination of relations among the  $\beta_{ij}$  for symmetry-related atoms, and (2) the determination of restrictions among the  $\beta_{ij}$  for an atom in a position of special symmetry.

The following rules thus give the desired relationships:

Rule 1.—The quantities  $\beta_{ij}$  for distinct positions, general or special, related by a symmetry operation are related as are the quadratic products of atomic coordinates, translational terms being ignored, for general positions related by the symmetry operation.

Rule 2.—The quantities  $\beta_{ij}$  associated with a position of special symmetry are restricted as required by the invariance of all  $\beta_{ij}$ , when transformed as described by Rule 1 above, under all symmetry operations leaving the position invariant.

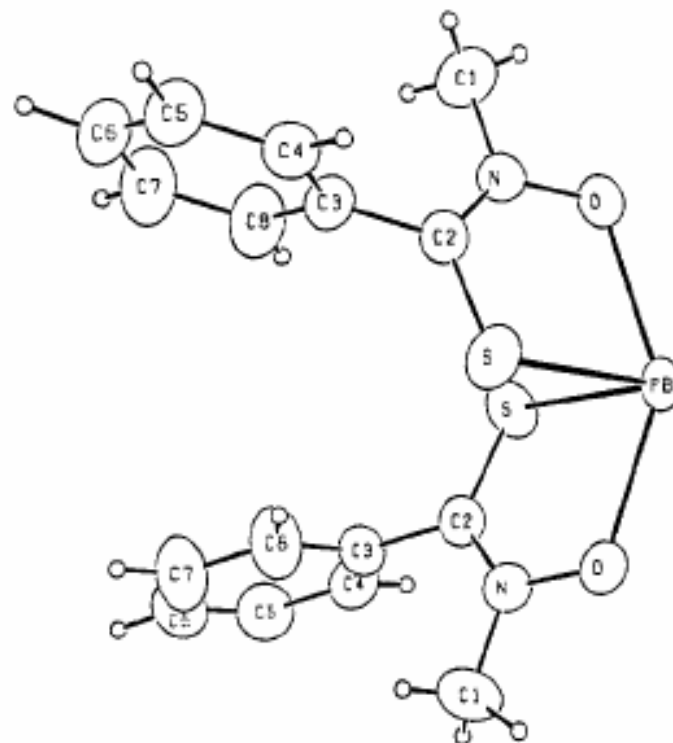
## Lead Sequestering Agents. 1. Synthesis, Physical Properties, and Structures of Lead Thiohydroxamato Complexes

Kamal Abu-Dari,<sup>†</sup> F. Ekkehardt Hahn, and Kenneth N. Raymond\*

### What are the constraints on the Pb thermal parameters?

**Table I.** Summary of Crystallographic Data and Parameters for Bis(*N*-methylthiobenzohydroxamato)lead(II) (**2**) and Bis(*N*-methylthioacetohydroxamato)lead(II) (**5**)<sup>a,b</sup>

	<b>2</b>	<b>5</b>
formula	Pb(C <sub>8</sub> H <sub>8</sub> NOS) <sub>2</sub>	Pb(C <sub>3</sub> H <sub>6</sub> NOS) <sub>2</sub>
fw	539.62	415.49
space group	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	18.067 (2)	7.958 (2)
<i>b</i> , Å	12.518 (2)	7.445 (1)
<i>c</i> , Å	8.103 (1)	19.007 (3)
$\beta$ , deg	101.93 (1)	98.74 (2)
<i>V</i> , Å <sup>3</sup>	1792.9 (7)	1113.1 (6)
<i>Z</i>	4	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	2.00	2.48
<i>d</i> <sub>obsd</sub> , g/cm <sup>3</sup>	1.98 <sup>c</sup>	2.47 <sup>c</sup>



**Figure 1.** Perspective view of compound **2** with the numbering scheme of the non-hydrogen atoms. The crystallographic and molecular 2-fold axis is horizontal while the vertical axis is what would be the 3-fold axis of a trigonal-bipyramidal geometry. The non-hydrogen atoms are drawn at 50% probability contours of the thermal motion, while the hydrogen atoms have an arbitrary size. The vacant coordinate position to the right is interpreted as being occupied by the nonbonding electron pair of Pb<sup>2+</sup>.

$C2/c$

No. 15

UNIQUE AXIS  $b$ , CELL CHOICE 1

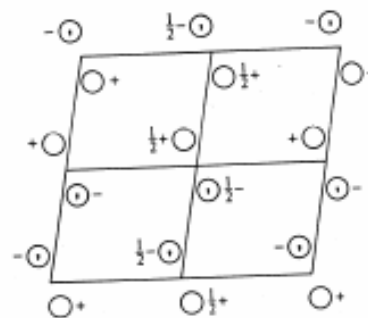
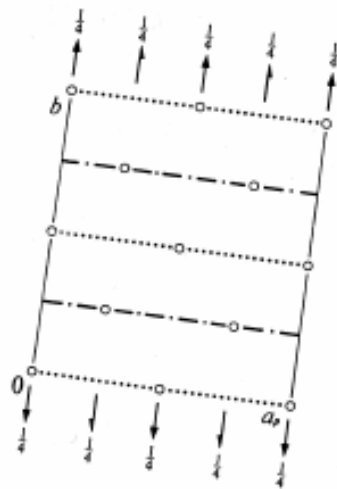
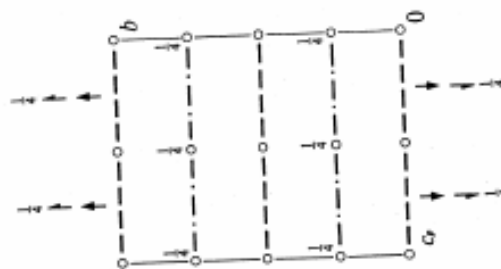
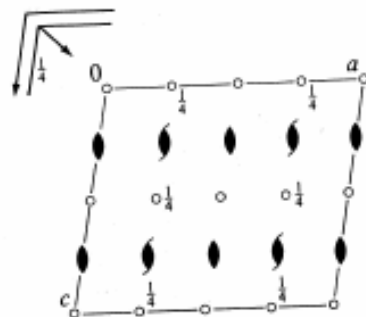
$C_{2h}^6$

$C12/c1$

$2/m$

Monoclinic

Patterson symmetry  $C12/m1$



**Generators selected** (1);  $t(1,0,0)$ ;  $t(0,1,0)$ ;  $t(0,0,1)$ ;  $t(\frac{1}{2},\frac{1}{2},0)$ ; (2); (3)

**Positions**

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates

$(0,0,0)+$   $(\frac{1}{2},\frac{1}{2},0)+$

8 *f* 1 (1)  $x,y,z$  (2)  $\bar{x},y,\bar{z}+\frac{1}{2}$  (3)  $\bar{x},\bar{y},\bar{z}$  (4)  $x,\bar{y},z+\frac{1}{2}$

Reflection conditions

General:

- $hkl : h+k=2n$
- $h0l : h,l=2n$
- $0kl : k=2n$
- $hk0 : h+k=2n$
- $0k0 : k=2n$
- $h00 : h=2n$
- $00l : l=2n$

Special: as above, plus

no extra conditions

4 *e* 2  $0,y,\frac{1}{2}$   $0,\bar{y},\frac{1}{2}$

4 *d*  $\bar{1}$   $\frac{1}{2},\frac{1}{2},\frac{1}{2}$   $\frac{1}{2},\frac{1}{2},0$

4 *c*  $\bar{1}$   $\frac{1}{2},\frac{1}{2},0$   $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

4 *b*  $\bar{1}$   $0,\frac{1}{2},0$   $0,\frac{1}{2},\frac{1}{2}$

4 *a*  $\bar{1}$   $0,0,0$   $0,0,\frac{1}{2}$

$hkl : k+l=2n$

$hkl : k+l=2n$

$hkl : l=2n$

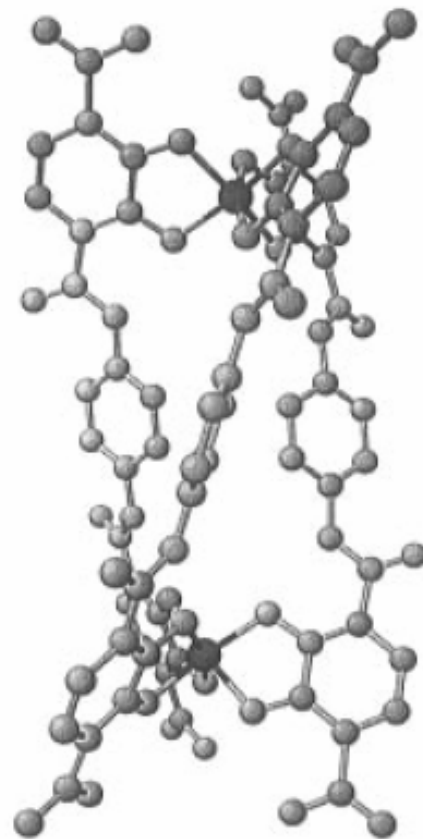
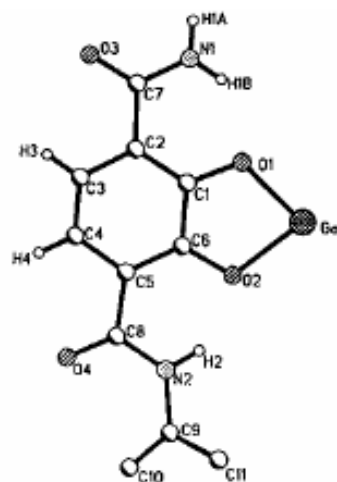
$hkl : l=2n$

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**Table 1.** Crystal Data and Structure Refinement for  $(\text{N}(\text{CH}_3)_4)_6\text{Ga}_2(\text{L}^3)_3 \cdot 6\text{DMF} \cdot 4\text{H}_2\text{O}$ 

formula	$\text{Ga}_4\text{C}_{216}\text{H}_{328}\text{N}_{48}\text{O}_{68}$
fw	2482.07
$T$ , °C	−148 °C
cryst system	hexagonal
space group	$P\bar{3}1c$ (No. 163)
$a$ , Å	14.283(2)
$c$ , Å	42.966(2)
$V$ , Å <sup>3</sup>	7591(2)
$Z$	2
$D_{\text{calcd}}$ , g cm <sup>−3</sup>	1.05

**Figure 4.** Structure of the  $\text{Ga}_2(\text{L}^3)_3^{6-}$  anion of  $(\text{N}(\text{CH}_3)_4)_6\text{Ga}_2(\text{L}^3)_3 \cdot 6\text{DMF} \cdot 4\text{H}_2\text{O}$  as determined by X-ray diffraction. (See Chart 1 for the ligand formulation.)

**What are the constraints on the Ga thermal parameters?**

$P\bar{3}1c$

No. 163

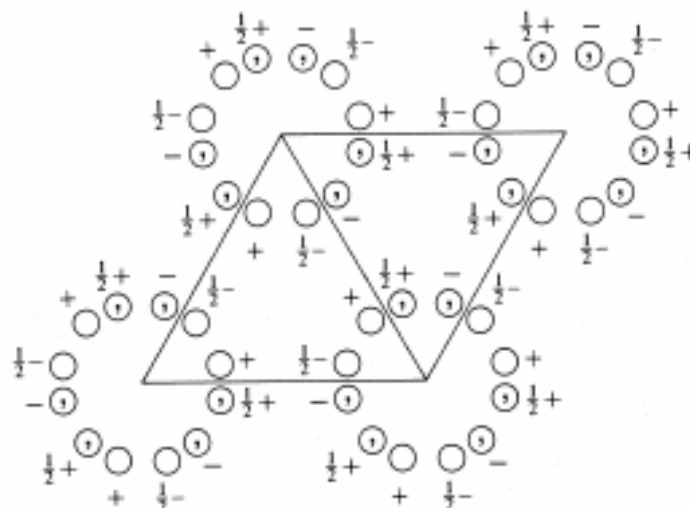
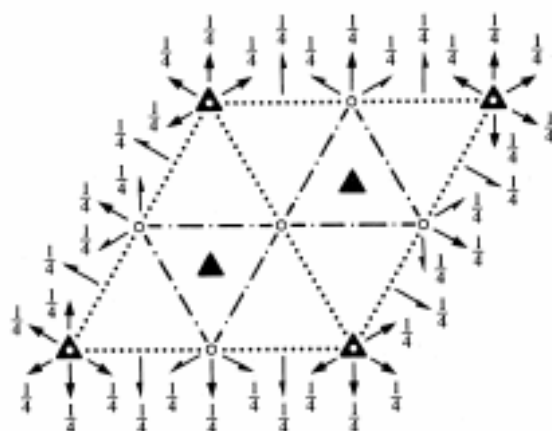
$D_{3d}^2$

$P\bar{3}12/c$

$\bar{3}1m$

Trigonal

Patterson symmetry  $P\bar{3}1m$



Origin at centre ( $\bar{3}$ ) at  $\bar{3}1c$

## Positions

Multiplicity,  
Wyckoff letter,  
Site symmetry

## Coordinates

12	<i>i</i>	1	(1) $x, y, z$ (4) $\bar{y}, \bar{x}, \bar{z} + \frac{1}{2}$ (7) $\bar{x}, \bar{y}, \bar{z}$ (10) $y, x, z + \frac{1}{2}$	(2) $\bar{y}, x - y, z$ (5) $\bar{x} + y, y, \bar{z} + \frac{1}{2}$ (8) $y, \bar{x} + y, \bar{z}$ (11) $x - y, \bar{y}, z + \frac{1}{2}$	(3) $\bar{x} + y, \bar{x}, z$ (6) $x, x - y, \bar{z} + \frac{1}{2}$ (9) $x - y, x, \bar{z}$ (12) $\bar{x}, \bar{x} + y, z + \frac{1}{2}$			
6	<i>h</i>	..2	$x, \bar{x}, \frac{1}{2}$	$x, 2x, \frac{1}{2}$	$2\bar{x}, \bar{x}, \frac{1}{2}$	$\bar{x}, x, \frac{1}{2}$	$\bar{x}, 2\bar{x}, \frac{1}{2}$	$2x, x, \frac{1}{2}$
6	<i>g</i>	$\bar{1}$	$\frac{1}{2}, 0, 0$	$0, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
4	<i>f</i>	3..	$\frac{1}{2}, \frac{2}{3}, z$	$\frac{1}{2}, \frac{2}{3}, \bar{z} + \frac{1}{2}$	$\frac{2}{3}, \frac{1}{2}, \bar{z}$	$\frac{2}{3}, \frac{1}{2}, z + \frac{1}{2}$		
4	<i>e</i>	3..	$0, 0, z$	$0, 0, \bar{z} + \frac{1}{2}$	$0, 0, \bar{z}$	$0, 0, z + \frac{1}{2}$		
2	<i>d</i>	3.2	$\frac{2}{3}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{2}{3}, \frac{1}{2}$				
2	<i>c</i>	3.2	$\frac{1}{2}, \frac{2}{3}, \frac{1}{2}$	$\frac{2}{3}, \frac{1}{2}, \frac{1}{2}$				
2	<i>b</i>	$\bar{3}$ ..	$0, 0, 0$	$0, 0, \frac{1}{2}$				
2	<i>a</i>	3.2	$0, 0, \frac{1}{2}$	$0, 0, \frac{1}{2}$				

## Reflection conditions

General:

$$hh\bar{2}hl : l = 2n$$

$$000l : l = 2n$$

Special: as above, plus

no extra conditions

$$hkil : l = 2n$$

$$hkil : l = 2n$$

$$\text{or } h - k = 3n + 1$$

$$\text{or } h - k = 3n + 2$$

$$hkil : l = 2n$$

$$hkil : l = 2n$$

$$\text{or } h - k = 3n + 1$$

$$\text{or } h - k = 3n + 2$$

$$hkil : l = 2n$$

$$\text{or } h - k = 3n + 1$$

$$\text{or } h - k = 3n + 2$$

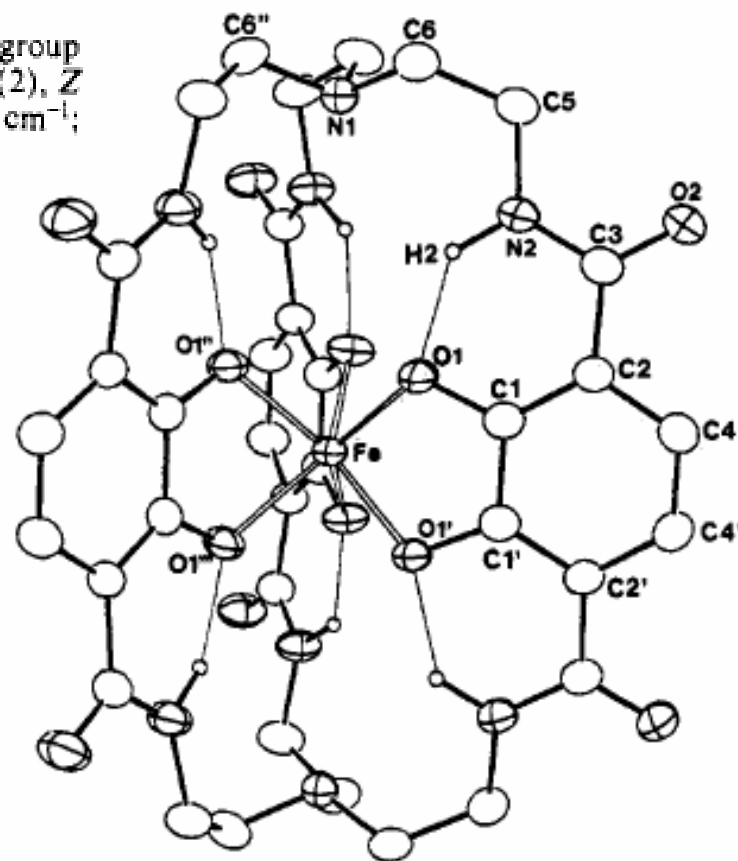
$$hkil : l = 2n$$

$$hkil : l = 2n$$

Thomas J. McMurry, Mir Wais Hosseini,  
Thomas M. Garrett, F. Ekkehardt Hahn, Zelideth E. Reyes,  
and Kenneth N. Raymond\*

(22) Hexagonal red needles 0.13 mm × 0.13 mm × 0.44 mm; space group  $P6_3/m$  ( $C_{6h}$ , no. 176),  $a = 13.785$  (3) Å,  $c = 16.244$  (5) Å,  $V = 2673$  (2),  $Z = 2$ ,  $D_m = 1.45$ ,  $D_c = 1.51$  g/cm<sup>3</sup>,  $\lambda$  (Mo K $\alpha$ ) = 0.71073 Å,  $\mu = 3.97$  cm<sup>-1</sup>;

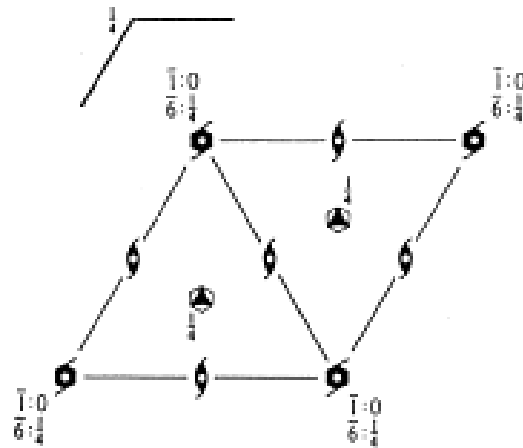
What are the constraints on the Fe thermal parameters?



**Figure 3.** ORTEP of ferric (bicapped TREN CAM). The ellipsoids are scaled to represent the 50% probability surface. Select bond distances (Å) and angles (deg): Fe–O1, 2.012 (2); C1–O1, 1.333 (3); C3–N2, 1.332 (4); N2–H2, 0.89 (4); O1...O1', 2.526 (4); O1...O1'', 2.713 (3); O1...N2, 2.620 (3); O1...H2, 1.89 (4); O1–Fe–O1', 77.75 (11); O1–Fe–O1'', 84.78 (8); O1–Fe–O1''', 134.18 (4); O1...H2–N2, 138 (4).

$P 6_3/m$

No. 176



Origin at centre ( $\bar{3}$ ) on  $6_3$

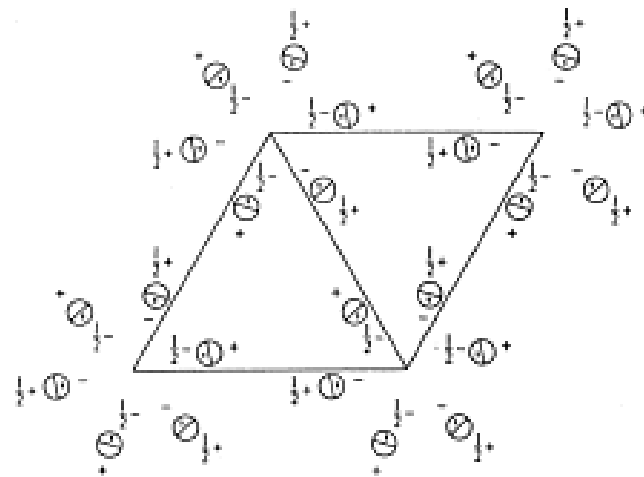
$C_{6h}^2$

$P 6_3/m$

$6/m$

Hexagonal

Patterson symmetry  $P 6/m$



Generators selected (1);  $t(1,0,0)$ ;  $t(0,1,0)$ ;  $t(0,0,1)$ ; (2); (4); (7)

## Positions

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates

Reflection conditions

12	$i$	1	(1) $x, y, z$	(2) $\bar{y}, x-y, z$	(3) $x+y, x, z$
			(4) $x, \bar{y}, z+\frac{1}{2}$	(5) $y, x+y, z+\frac{1}{2}$	(6) $x-y, x, z+\frac{1}{2}$
			(7) $x, \bar{y}, \bar{z}$	(8) $y, x+y, \bar{z}$	(9) $x-y, x, \bar{z}$
			(10) $x, y, \bar{z}+\frac{1}{2}$	(11) $\bar{y}, x-y, \bar{z}+\frac{1}{2}$	(12) $x+y, x, \bar{z}+\frac{1}{2}$

General:

$$000l : l = 2n$$

Special: as above, plus

6  $h$   $m..$   $x, y, \frac{1}{2}$   $\bar{y}, x-y, \frac{1}{2}$   $x+y, x, \frac{1}{2}$   $x, \bar{y}, \frac{1}{2}$   $y, x+y, \frac{1}{2}$   $x-y, x, \frac{1}{2}$

no extra conditions

6  $g$   $\bar{1}$   $\frac{1}{2}, 0, 0$   $0, \frac{1}{2}, 0$   $\frac{1}{2}, \frac{1}{2}, 0$   $\frac{1}{2}, 0, \frac{1}{2}$   $0, \frac{1}{2}, \frac{1}{2}$   $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

$$hkil : l = 2n$$

4  $f$   $3..$   $\frac{1}{2}, \frac{1}{2}, z$   $\frac{1}{2}, \frac{1}{2}, z+\frac{1}{2}$   $\frac{1}{2}, \frac{1}{2}, \bar{z}$   $\frac{1}{2}, \frac{1}{2}, \bar{z}+\frac{1}{2}$

$$hkil : l = 2n$$

$$\text{or } h-k = 3n+1$$

$$\text{or } h-k = 3n+2$$

4  $e$   $3..$   $0, 0, z$   $0, 0, z+\frac{1}{2}$   $0, 0, \bar{z}$   $0, 0, \bar{z}+\frac{1}{2}$

$$hkil : l = 2n$$

2  $d$   $\bar{6}..$   $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$   $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

$$hkil : l = 2n$$

$$\text{or } h-k = 3n+1$$

$$\text{or } h-k = 3n+2$$

2  $c$   $\bar{6}..$   $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$   $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

$$hkil : l = 2n$$

$$\text{or } h-k = 3n+1$$

$$\text{or } h-k = 3n+2$$

2  $b$   $\bar{3}..$   $0, 0, 0$   $0, 0, \frac{1}{2}$

$$hkil : l = 2n$$

2  $a$   $\bar{6}..$   $0, 0, \frac{1}{2}$   $0, 0, \frac{1}{2}$

$$hkil : l = 2n$$

# Synthesis and Characterization of a Series of Vanadium–Tunichrome B 1 Analogues. Crystal Structure of a Tris(catecholamide) Complex of Vanadium

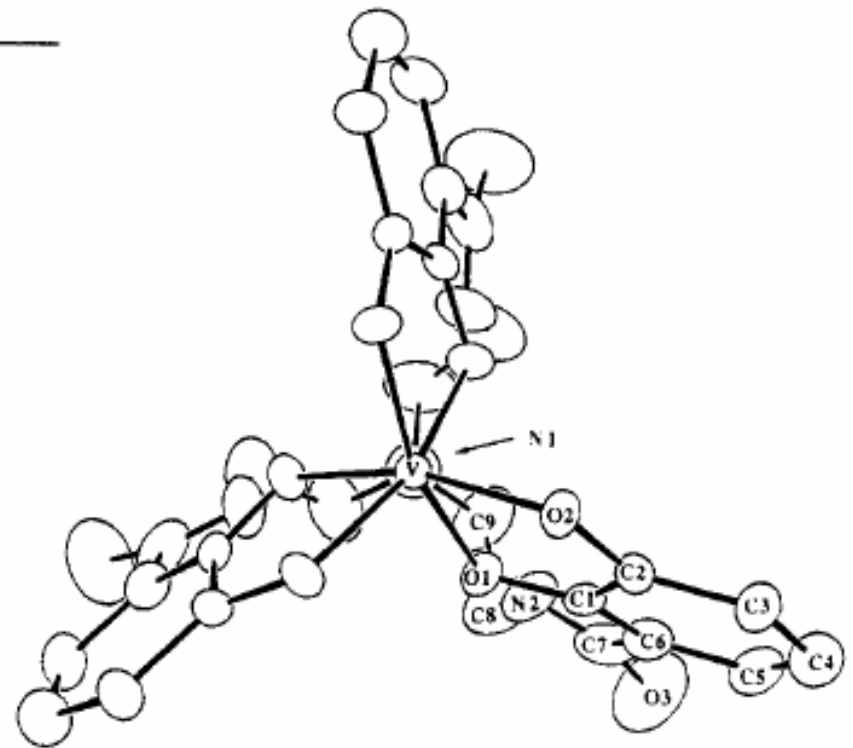
A. Ray Bulls, C. Greg Pippin, F. Ekkehardt Hahn, and Kenneth N. Raymond\*

*J. Am. Chem. Soc.* **1990**, *112*, 2627–2632

**Table I.** Data Collection, Solution, and Refinement Parameters for  $K_3[V(\text{TRENCAM})] \cdot 4\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$

empirical formula	$\text{VK}_3\text{C}_{27}\text{N}_4\text{O}_9\text{H}_{24} \cdot 4\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$
fw,	824.92
temp, K	150
cell param, Å	15.961
space group	$P2_13$
Z	4

What are the constraints on the V thermal parameters?



**Figure 4.** Molecular structure of the complex anion in  $K_3[V(\text{TRENCAM})] \cdot 4\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$  as observed down the 3-fold axis.

$P 2_1 3$

$T^4$

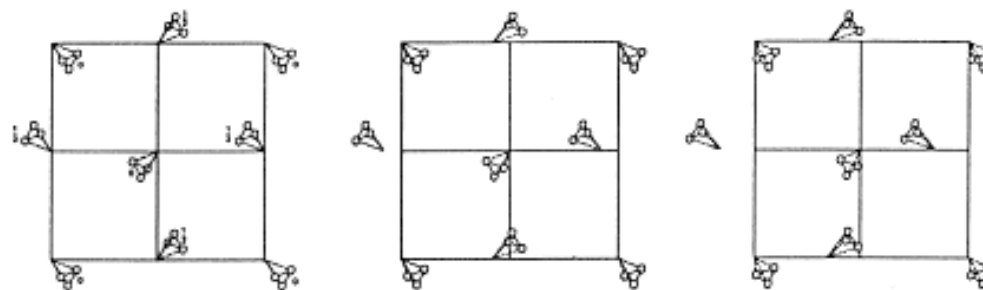
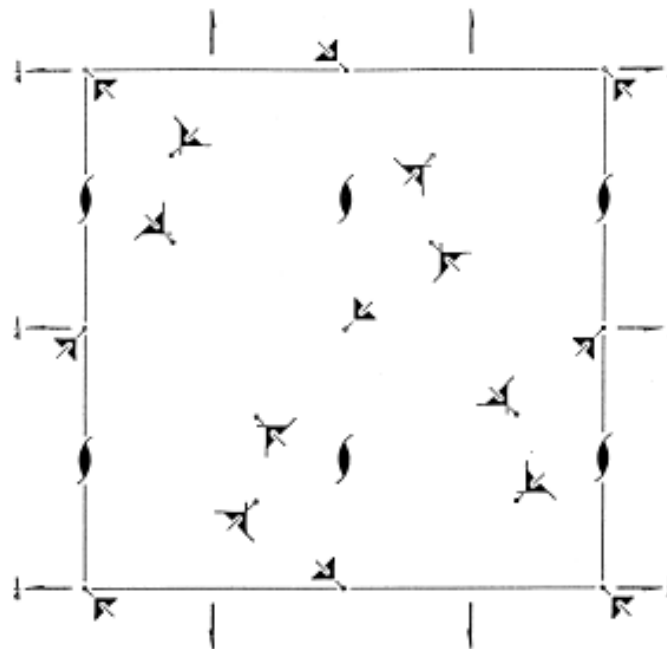
23

Cubic

No. 198

$P 2_1 3$

Patterson symmetry  $Pm\bar{3}$



Origin on  $3[111]$  at midpoint of three non-intersecting pairs of parallel  $2_1$  axes

CONTINUED

No. 198

P 2, 3

Generators selected (1);  $t(1,0,0)$ ;  $t(0,1,0)$ ;  $t(0,0,1)$ ; (2); (3); (5)

## Positions

Multiplicity,  
Wyckoff letter,  
Site symmetry

Coordinates

Reflection conditions

 $h, k, l$  cyclically permutable

General:

 $h00: h = 2n$ 

12	<i>b</i>	1	(1) $x, y, z$	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	(3) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$
			(5) $z, x, y$	(6) $z + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{y}$	(7) $\bar{z} + \frac{1}{2}, \bar{x}, y + \frac{1}{2}$	(8) $\bar{z}, x + \frac{1}{2}, \bar{y} + \frac{1}{2}$
			(9) $y, z, x$	(10) $\bar{y}, z + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(11) $y + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{x}$	(12) $\bar{y} + \frac{1}{2}, \bar{z}, x + \frac{1}{2}$

Special: no extra conditions

4	<i>a</i>	.3.	$x, x, x$	$\bar{x} + \frac{1}{2}, \bar{x}, x + \frac{1}{2}$	$\bar{x}, x + \frac{1}{2}, \bar{x} + \frac{1}{2}$	$x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x}$
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