

N2—C12—C13	107.9 (3)	N2—C14—C15	112.7 (3)
O9B—C9—C8	116.0 (4)	O11B—C11—C10	117.0 (3)
O13B—C13—C12	114.6 (3)	O15B—C15—C14	116.9 (3)
C9—O9B—Fe1	121.1 (2)	C11—O11B—Fe1	123.6 (3)
C13—O13B—Fe1	121.9 (3)	C15—O15B—Fe1	121.6 (3)
C10—N1—Fe1	104.9 (2)		

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XRAY72* (Stewart, Krüger, Ammon, Dickinson & Hall, 1972). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

We wish to thank the Education Council of the Canary Islands Government (Grant N 33/01.06.88) and the Spanish Ministry of Education and Science, Spain (DGICYT, Grant N PB89–0401) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1280). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Azuma, S., Nakasuka, N. & Tanaka, M. (1986). *Acta Cryst.* **C42**, 673–677.
- Brito, F., Mederos, A., Herrera, J. V., Domínguez, S. & Hernández-Padilla, M. (1988). *Polyhedron*, **7**, 1187–1195.
- Cohen, G. H. & Hoard, J. L. (1966). *J. Am. Chem. Soc.* **88**, 3228–3234.
- Cromer, D. T. & Liberman, J. B. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
- Hehre, W. J., Random, L., Schleyer, P. R. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*, p. 386. New York: Wiley.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Lind, M. D., Hamor, M. J., Hamor, T. A. & Hoard, J. L. (1964). *Inorg. Chem.* **3**, 34–43.
- López-Alcalá, J. M., Puerta-Vizcaíno, M. C., González-Vilchez, F., Duesler, E. N. & Tapscoott, R. E. (1984). *Acta Cryst.* **C40**, 939–941.
- McCandlish, E. F. K., Michael, T. K., Neal, J. A., Lingafelter, E. C. & Rose, N. J. (1978). *Inorg. Chem.* **17**, 1383–1394.
- Mederos, A., Gili, P., Domínguez, S., Benítez, A., Palacios, M. S., Hernández-Padilla, M., Martín-Zarza, P., Rodríguez, M. L., Ruíz-Pérez, C., Lahoz, F. J., Oro, L., Brito, F., Arrieta, J. M., Vlasi, M. & Germain, G. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1477–1491.
- Mederos, A., Herrera, J. V. & Felipe, J. M. (1987). *Ann. Quím.* **83**, 22–25.
- Mederos, A., Herrera, J. V., Felipe, J. M. & Quesada, M. L. (1984). *Ann. Quím.* **80B**, 281–287.
- Mizuno, M., Funahashi, S., Nakasuka, N. & Tanaka, M. (1991). *Inorg. Chem.* **30**, 1550–1553.
- Nakasuka, N., Azuma, S., Katayama, C., Honda, M., Tanaka, J. & Tanaka, M. (1985). *Acta Cryst.* **C41**, 1176–1179.
- Nakasuka, N., Azuma, S. & Tanaka, M. (1986a). *Acta Cryst.* **C42**, 1482–1485.
- Nakasuka, N., Azuma, S. & Tanaka, M. (1986b). *Acta Cryst.* **C42**, 1736–1739.
- Nakasuka, N. & Shiro, M. (1989). *Acta Cryst.* **C45**, 1487–1490.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- Nesterova, Ya. M., Polynova, T. N. & Porai-Koshits, M. A. (1975). *Koord. Khim.* **1**, 966–974.
- Ruiz-Pérez, C., Rodríguez, M. L., Rodríguez Romero, F. V., Mederos, A., Gili, P. & Martín-Zarza, P. (1990). *Acta Cryst.* **C46**, 1405–1407.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Solans, X., Font-Altaba, M. & García-Orcaín, J. (1984). *Acta Cryst.* **C40**, 635–638.
- Stewart, J. M., Krüger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). *The XRAY72 System*. Version of June 1972. Technical Report TR-192. Computer Science Center, University of Maryland, College Park, Maryland, USA.
- Weakliem, H. E. & Hoard, J. L. (1959). *J. Am. Chem. Soc.* **81**, 549–561.
- Acta Cryst.* (1996). **C52**, 1621–1624

5,5'-(2-Hydroxy-1,3-propandiyldiamino)bis(1-phenyl-1,3-hexanedionato-O,O')oxovanadium(IV), [VO(C₂₇H₂₈N₂O₅)]

HÅKON HOPE^a AND LONDA L. BORER^b

^aDepartment of Chemistry, University of California, Davis, CA 95616, USA, and ^bDepartment of Chemistry, California State University, Sacramento, CA 95819, USA

(Received 1 August 1995; accepted 21 February 1996)

Abstract

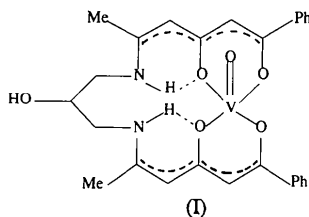
Schiff base ligands derived from triketones form stable complexes with VO. In the mononuclear vanadyl complex of 5,5'-(2-hydroxy-1,3-propandiyldiamino)bis(1-phenyl-1,3-hexanedione), vanadium is five-coordinate, equatorially bonded to four carbonyl O atoms in a nearly square-planar arrangement and axially to one other O atom. N atoms are not involved in complex formation. The hydroxy group is disordered.

Comment

It is well known that complexes such as molybdenum or vanadyl acetylacetonate catalyze the epoxidation of alkenes in the presence of organic hydroperoxides. (Sheldon & Kochi, 1981; Talsi, Chinakov, Babenko & Zamarev, 1993). Previously, we prepared the dinuclear Mo^{VI} complex of a triketone (Borer & Sinn, 1990) and reported the epoxidation of some bicyclic olefins using this complex (DiAmico, Rasmussen, Sisneros, Magnussen, Wade, Russell & Borer, 1992). Results of epoxidation reactions indicated that only one of the olefin bonds was oxidized in the ring, even though two metal sites were available on the catalyst.

It is also well established that Schiff base ligands derived from triketones readily form vanadyl complexes (Lintvedt, Glick, Tomlonovic, Gavel & Kuscaj, 1976; Lintvedt, Glick, Tomlonovic & Gavel, 1976; Adams, Bailey, Fenton, Gonzalez & Phillips, 1983). The paper by Adams *et al.* (1983) describes the syntheses and structures of several complexes of this general type.

As a continuation of the Mo-based project, we attempted the preparation of an analogous dinuclear vanadyl complex of a triketone. The ultimate goal of our experiment was to attach the complex to a Merrifield's polymer that had been modified to contain acid chloride groups. To this end, we chose a diamine with a hydroxy group positioned between the amine moieties; this would allow reaction between the secondary alcohol and the acid chloride. However, even upon addition of excess vanadyl acetylacetonate, we were unable to introduce a second vanadium atom; the present mononuclear structure, (I), represents the end result of our synthetic efforts.



The core region of one of the compounds described by Adams *et al.* (1983) (their structure 4*b*) is similar to the one presented here. There is close agreement between all relevant geometric parameters. In the context of our synthetic endeavor, we note that the H atoms of the two NH groups participate in strong hydrogen bonds to carbonyl O atoms [N(1)—O(2) 2.608 (6), N(2)···O(4) 2.651 (6), H(1N)···O(2) 1.86 (6),

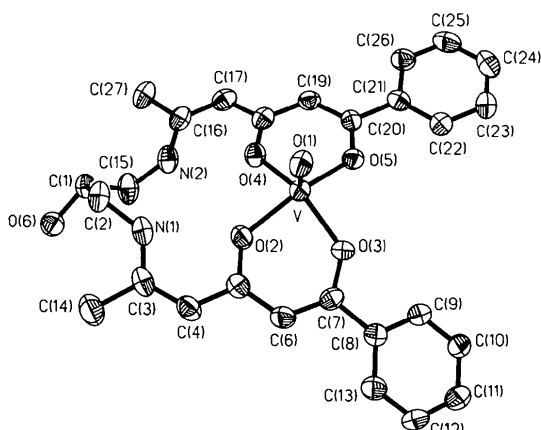


Fig. 1. Perspective drawing of the structure of the title vanadyl complex, with atomic numbering. Ellipsoids are shown at 50% probability. For clarity, H atoms and the minor component of the disordered region are not shown.

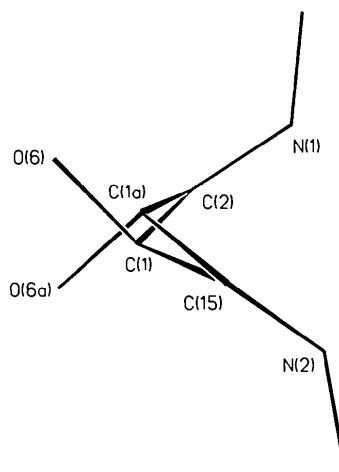


Fig. 2. Detail of disorder at C(1).

H(2N)···O(4) 1.89 (6) Å], forming planar six-membered ring systems. (The two H atoms were conspicuously apparent in a difference map and their positional and displacement parameters were refined freely.) We believe the stability of these internal hydrogen-bonded rings and the stabilization resulting from extended delocalization over the complexing parts of the ligand provide an explanation for the difficulty in adding the second vanadium.

Experimental

1-Methyl-1,5-phenyl-1,3,5-pentanetrione (1 g, 0.0049 mol) was heated and dissolved in 10 ml of methanol. 2-Hydroxydi-aminopropane (0.22 g, 0.0025 mol) was dissolved by heating in 10 ml of methanol and then added to the triketone in a 50 ml round-bottomed flask equipped with a condenser. This mixture was heated for 15 min. Vanadyl acetylacetonate (0.66 g, 0.0025 mol) was dissolved in 25 ml of methanol and added to the ligand solution. After two hours of reflux, the solution was allowed to cool slowly to room temperature. The crystals were recovered by vacuum filtration, washed with hot methanol and dried. Crystals large enough for X-ray analysis were recovered from the reaction mixture.

Crystal data

[VO(C₂₇H₂₈N₂O₅)]

M_r = 527.45

Triclinic

*P*1

a = 9.360 (2) Å

b = 9.845 (2) Å

c = 15.216 (4) Å

α = 85.18 (2)°

β = 77.79 (2)°

γ = 63.75 (2)°

V = 1229.0 (5) Å³

Z = 2

D_x = 1.425 Mg m⁻³

Cu *K*α radiation

λ = 1.54178 Å

Cell parameters from 24

reflections

θ = 20–30°

μ = 3.762 mm⁻¹

T = 118 (1) K

Plate

0.12 × 0.10 × 0.04 mm

Greenish yellow

Data collection

Siemens P4/R diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 refined form ΔF (XABS2;
 Parkin, Moezzi & Hope,
 1995)
 $T_{\min} = 0.54$, $T_{\max} = 0.86$
 3010 measured reflections
 3010 independent reflections

2285 observed reflections
 $[I > 2\sigma(I)]$
 $\theta_{\max} = 55^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = 0 \rightarrow 16$
 2 standard reflections
 monitored every 200
 reflections
 intensity variation: $\pm 1\%$

Refinement

Refinement on F^2
 $R(F) = 0.065$
 $wR(F^2) = 0.147$
 $S = 1.054$
 3010 reflections
 336 parameters
 H atoms included as riding
 (H on N free)
 $w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 1.33P]$
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e } \text{Å}^{-3}$
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0008 (4)
 Atomic scattering factors
 from *International Tables*
 for X-ray Crystallography
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
V	0.4545 (1)	0.7181 (1)	0.8064 (1)	0.034 (1)
O(1)	0.3048 (5)	0.8696 (5)	0.7843 (3)	0.044 (1)
C(1)†	0.9939 (8)	0.9102 (9)	0.7095 (4)	0.042 (2)
C(2)	0.8570 (7)	0.9562 (7)	0.6590 (5)	0.048 (2)
N(1)	0.8080 (6)	0.8423 (6)	0.6412 (4)	0.043 (2)
C(3)	0.8510 (7)	0.7603 (8)	0.5665 (4)	0.044 (2)
C(4)	0.7909 (8)	0.6570 (8)	0.5603 (4)	0.045 (2)
C(5)	0.6784 (7)	0.6284 (7)	0.6278 (4)	0.041 (2)
O(2)	0.6311 (5)	0.6993 (5)	0.7042 (3)	0.041 (1)
C(6)	0.6219 (7)	0.5219 (7)	0.6133 (4)	0.041 (2)
C(7)	0.5187 (7)	0.4818 (7)	0.6774 (4)	0.037 (2)
O(3)	0.4473 (5)	0.5489 (5)	0.7550 (3)	0.039 (1)
C(8)	0.4843 (7)	0.3521 (7)	0.6616 (4)	0.038 (2)
C(9)	0.4087 (8)	0.2962 (7)	0.7354 (4)	0.042 (2)
C(10)	0.3805 (8)	0.1722 (7)	0.7260 (4)	0.044 (2)
C(11)	0.4285 (8)	0.0999 (7)	0.6437 (4)	0.046 (2)
C(12)	0.5022 (8)	0.1542 (7)	0.5701 (4)	0.046 (2)
C(13)	0.5312 (8)	0.2781 (8)	0.5793 (4)	0.047 (2)
C(14)	0.9645 (9)	0.7857 (9)	0.4883 (5)	0.062 (2)
C(15)	1.0036 (7)	0.7826 (8)	0.7765 (4)	0.052 (2)
N(2)	0.8521 (6)	0.8128 (7)	0.8358 (4)	0.047 (2)
C(16)	0.8099 (7)	0.8510 (7)	0.9235 (4)	0.041 (2)
C(17)	0.6812 (7)	0.8372 (7)	0.9794 (4)	0.042 (2)
C(18)	0.5748 (7)	0.7870 (7)	0.9542 (4)	0.038 (2)
O(4)	0.5865 (5)	0.7680 (5)	0.8687 (3)	0.038 (1)
C(19)	0.4627 (7)	0.7545 (7)	1.0197 (4)	0.037 (2)
C(20)	0.3691 (7)	0.6882 (7)	1.0010 (4)	0.034 (2)
O(5)	0.3709 (5)	0.6524 (5)	0.9207 (3)	0.037 (1)
C(21)	0.2574 (7)	0.6519 (7)	1.0745 (4)	0.036 (2)
C(22)	0.1716 (7)	0.5792 (7)	1.0510 (4)	0.041 (2)
C(23)	0.0600 (8)	0.5501 (8)	1.1154 (4)	0.047 (2)
C(24)	0.0325 (8)	0.5923 (8)	1.2037 (5)	0.052 (2)
C(25)	0.1184 (8)	0.6614 (8)	1.2283 (4)	0.052 (2)
C(26)	0.2293 (8)	0.6919 (8)	1.1638 (4)	0.044 (2)
C(27)	0.9119 (8)	0.9084 (8)	0.9591 (5)	0.052 (2)
O(6)†	1.1392 (7)	0.8596 (7)	0.6448 (4)	0.047 (2)
O(6A)†	1.0230 (22)	1.0052 (15)	0.7154 (12)	0.050 (7)
C(1A)†	1.0187 (8)	0.8711	0.6939 (5)	0.050

† Partial occupancy (see text).

Table 2. Selected geometric parameters (Å , $^\circ$)

V—O(1)	1.602 (5)	C(10)—C(11)	1.380 (8)
V—O(3)	1.932 (4)	C(11)—C(12)	1.384 (8)
V—O(5)	1.933 (4)	C(12)—C(13)	1.385 (8)
V—O(4)	1.943 (4)	C(15)—N(2)	1.430 (7)
V—O(2)	1.969 (4)	C(15)—C(1A)	1.486 (5)
C(1)—O(6)	1.408 (8)	N(2)—C(16)	1.345 (7)
C(1)—C(2)	1.510 (4)	C(16)—C(17)	1.373 (7)
C(1)—C(15)	1.533 (4)	C(16)—C(27)	1.507 (7)
C(2)—N(1)	1.449 (7)	C(17)—C(18)	1.418 (7)
C(2)—C(1A)	1.555 (5)	C(18)—O(4)	1.305 (7)
N(1)—C(3)	1.334 (7)	C(18)—C(19)	1.414 (7)
C(3)—C(4)	1.380 (7)	C(19)—C(20)	1.385 (7)
C(3)—C(14)	1.503 (7)	C(20)—O(5)	1.294 (6)
C(4)—C(5)	1.414 (7)	C(20)—C(21)	1.498 (7)
C(5)—O(2)	1.296 (7)	C(21)—C(26)	1.385 (7)
C(5)—C(6)	1.417 (7)	C(21)—C(22)	1.400 (7)
C(6)—C(7)	1.383 (7)	C(22)—C(23)	1.385 (7)
C(7)—O(3)	1.299 (6)	C(23)—C(24)	1.377 (8)
C(7)—C(8)	1.496 (7)	C(24)—C(25)	1.379 (8)
C(8)—C(13)	1.389 (7)	C(25)—C(26)	1.388 (8)
C(8)—C(9)	1.403 (7)	O(6A)—C(1A)	1.406 (9)
C(9)—C(10)	1.382 (7)		
O(1)—V—O(3)	107.9 (2)	C(9)—C(8)—C(7)	118.1 (5)
O(1)—V—O(5)	104.8 (2)	C(10)—C(9)—C(8)	120.9 (5)
O(3)—V—O(5)	85.9 (2)	C(11)—C(10)—C(9)	120.3 (5)
O(1)—V—O(4)	110.1 (2)	C(10)—C(11)—C(12)	119.6 (5)
O(3)—V—O(4)	141.8 (2)	C(11)—C(12)—C(13)	120.3 (6)
O(5)—V—O(4)	87.6 (2)	C(12)—C(13)—C(8)	121.0 (5)
O(1)—V—O(2)	103.0 (2)	N(2)—C(15)—C(1A)	123.2 (6)
O(3)—V—O(2)	87.3 (2)	N(2)—C(15)—C(1)	113.1 (5)
O(5)—V—O(2)	152.1 (2)	C(1A)—C(15)—C(1)	15.6 (4)
O(4)—V—O(2)	81.3 (2)	C(16)—N(2)—C(15)	127.6 (5)
O(6A)—C(1)—O(6)	82.3 (10)	N(2)—C(16)—C(17)	122.2 (5)
O(6A)—C(1)—C(2)	111.0 (11)	N(2)—C(16)—C(27)	117.1 (5)
O(6)—C(1)—C(2)	106.9 (5)	C(17)—C(16)—C(27)	120.7 (6)
O(6A)—C(1)—C(15)	128.2 (12)	C(16)—C(17)—C(18)	126.2 (6)
O(6)—C(1)—C(15)	108.8 (6)	O(4)—C(18)—C(19)	121.0 (5)
C(2)—C(1)—C(15)	113.2 (5)	O(4)—C(18)—C(17)	117.9 (5)
N(1)—C(2)—C(1)	118.4 (5)	C(19)—C(18)—C(17)	121.1 (6)
C(3)—N(1)—C(2)	128.5 (5)	C(18)—O(4)—V	130.7 (3)
N(1)—C(3)—C(4)	121.1 (5)	C(20)—C(19)—C(18)	124.3 (5)
N(1)—C(3)—C(14)	118.1 (5)	O(5)—C(20)—C(19)	123.8 (5)
C(4)—C(3)—C(14)	120.7 (6)	O(5)—C(20)—C(21)	115.0 (4)
C(3)—C(4)—C(5)	125.7 (6)	C(19)—C(20)—C(21)	121.2 (5)
O(2)—C(5)—C(4)	118.4 (5)	C(20)—O(5)—V	128.8 (3)
O(2)—C(5)—C(6)	120.8 (5)	C(26)—C(21)—C(22)	118.3 (5)
C(4)—C(5)—C(6)	120.9 (6)	C(26)—C(21)—C(20)	123.6 (5)
C(5)—O(2)—V	131.2 (3)	C(22)—C(21)—C(20)	118.1 (5)
C(7)—C(6)—C(5)	124.3 (5)	C(23)—C(22)—C(21)	120.6 (6)
O(3)—C(7)—C(6)	124.1 (5)	C(24)—C(23)—C(22)	120.2 (5)
O(3)—C(7)—C(8)	114.8 (4)	C(23)—C(24)—C(25)	119.9 (5)
C(6)—C(7)—C(8)	121.1 (5)	C(24)—C(25)—C(26)	120.1 (6)
C(7)—O(3)—V	130.3 (3)	C(21)—C(26)—C(25)	120.9 (6)
C(13)—C(8)—C(9)	117.9 (5)	O(6A)—C(1A)—C(15)	110.3 (9)
C(13)—C(8)—C(7)	123.8 (5)	O(6A)—C(1A)—C(2)	93.7 (8)

The crystal was mounted on a glass fiber with vacuum grease and cooled with a modified Siemens LT-2 low-temperature attachment. Indexing, cell refinement and data collection: *P3/PC Diffractometer Program* (Siemens, 1989). Data reduction, structure solution and graphics: *SHELXTL-Plus* (Sheldrick, 1991). Refinement and tables: *SHELXL93* (Sheldrick, 1993). Site occupancy factor for atoms C(1) and O(6) refined to 0.75 (1); total occupancy was constrained to 1.00.

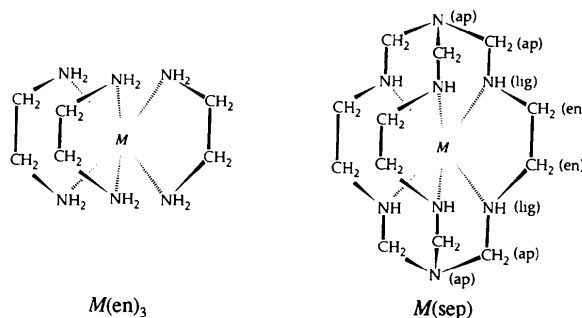
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1216). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Adams, M., Bailey, N. A., Fenton, D. A., Gonzalez, M. S. L. & Phillips, C. A. (1983). *J. Chem. Soc. Dalton Trans.* pp. 371–379.
- Borer, L. L. & Sinn, E. (1990). *Inorg. Chem.* **29**, 2514–2518.
- DiAmico, M. L., Rasmussen, L., Sisneros, D., Magnussen, C., Wade, H., Russell, J. G. & Borer, L. L. (1992). *Inorg. Chim. Acta*, **191**, 167–170.
- Lintvedt, R. L., Glick, M. D., Tomlonovic, B. K. & Gavel, D. P. (1976). *Inorg. Chem.* **15**, 1646–1653.
- Lintvedt, R. L., Glick, M. D., Tomlonovic, B. K., Gavel, D. P. & Kuscaj, J. M. (1976). *Inorg. Chem.* **15**, 1633–1645.
- Parkin, S., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.
- Sheldon, R. A. & Kochi, J. K. (1981). In *Metal-Catalyzed Oxidation of Organic Compounds*. New York: Academic Press.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1989). *P3/PC Diffractometer Program*. Version 3.13. Siemens Analytical instruments Inc., Madison, Wisconsin, USA.
- Talsi, E. P., Chinakov, V. D., Babenko, V. P. & Zamarev, K. I. (1993). *J. Mol. Catal.* **81**, 235–254.

Comment

Sepulchrate (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) is a cage ligand with six secondary amine N—H groups which can encapsulate a metal cation in an octahedral coordination arrangement. The complex molecule *M*(sep) can be thought of as derived from a trisethylendiamine metal complex *M*(en)₃, with two N(CH₂)₃ systems capping two opposite N—N—N faces of the octahedron.



Acta Cryst. (1996). **C52**, 1624–1627

Conformation and Packing of Cobalt(III) Sepulchrate Dihydrogentriphosphate Hexahydrate

ALESSIA BACCHI,^a FRANCESCO FERRANTI^b AND GIANCARLO PELIZZI^a

^aDipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università degli Studi di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy, and

^bDipartimento di Chimica Fisica ed Inorganica, Università degli Studi di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy

(Received 28 October 1994; accepted 31 January 1996)

Abstract

In cobalt(III) sepulchrate dihydrogentriphosphate hexahydrate (sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane), [Co(C₁₂H₃₀N₈)](H₂P₃O₁₀).6H₂O, the cation adopts the *lel*₃ [$\Delta(\lambda\lambda\lambda)$] optically active conformation. The overall geometry of the cation is not significantly different from that found in other salts. A strong symmetric O··H··O hydrogen bond is responsible for the cyclic conformation of the anion, the geometry of which is described by an eight-membered puckered ring. The entire crystal packing is dominated by hydrogen bonds. The cations and the anions are linked together in a three-dimensional network with six-membered meshes; the water molecules are situated in the voids, and interact only with the anions.

The compound is optically active and presents potential *D*₃ point symmetry, with the *C*₃ axis passing through N(ap)—*M*—N(ap), and the three *C*₂ axes bisecting the three C(en)—C(en) bonds. The cobalt(III) sepulchrate cation has been studied in different crystalline environments (Creaser *et al.*, 1977, 1982; Bacchi, Ferranti & Pelizzi, 1993*a,b*; Bacchi, 1995) and its conformation has been shown to be practically invariant in all compounds. The preferred geometry for Co(sep)³⁺ is that which allows the formation of hydrogen-bonded Co(sep)ABC moieties (A, B, C = hydrogen-bond acceptors). Pairs of N—H groups belonging to one cation are bridged by hydrogen-bonding anions or water molecules. In order to make this possible, the six amine N—H groups of a cation must point, in pairs, towards three different positions around the cation; this is accomplished by orienting the C(en)—C(en) bonds in directions almost parallel to the N(ap)—Co—N(ap) pseudo-threefold axis. Following the chirality independent *lell*ob classification proposed by Corey & Baley (1959), the geometry of the cation is *lel*₃. A perspective view of the Co(sep)³⁺ cation and the H₂P₃O₁₀ anion is shown in Fig. 1. The angles α formed by the C(en)—C(en) bonds and the N(ap)—Co—N(ap) vector range from 4.0 (3) to 5.4 (3)° for the cation. The overall absolute configuration of the cation is Λ , while the conformations of the puckered Co—N(lig)—C(en)—C(en)—N(lig) rings are all δ ; a $\Lambda(\delta\delta\delta)$ cation results, in accord with the *lel*₃ geometry. The geometry of the cation was compared with that of cation *A* in (\pm)-Co(sep)Cl₃.H₂O (Bacchi *et al.*, 1993*a*) by performing a half-normal probability plot on all the interatomic distances between non-H atoms (Abrahams & Keve, 1971). The least-squares regression line through the data points is $y = -0.36(4) + 3.28(4)x$, with a correlation coefficient of 0.98. The