References

ARNOUX, B., PASCARD, C., RAYNAUD, L. & LUNEL, J. (1980). *J. Am. Chem. Soc.* **102**, 3605–3608.

BARTNER, P., BOXLER, D. L., BRAMBILLA, R., MALLAMS, A. K., MORTON, J. B., REICHERT, P., SANCILIO, F. D., SUPRENANT, H., TOMALESKY, G., LUKACS, G., OLESKER, A., THANG, T. T., VALENTE, L. & OMURA, S. (1979). *J. Chem. Soc. Perkin Trans.* 1, pp. 1600–1624.

FEUCHT, C. L., ALLEN, B. S. & CHALKER, D. K. (1980). *J. Am. Acad. Dermatol.* **3**, 483–491.

FURUHATA, K., OGURA, H., YOSHINORI, H. & IITAKA, Y. (1977). *Chem. Pharm. Bull. Jpn*, **25**, 2385–2391.

FURUSAKI, A., MATSUMOTO, T., FURUHATA, K. & OGURA, H. (1982). *Bull. Chem. Soc. Jpn*, **55**, 59–62.

HARRIS, D. R., MCGEACHIN, S. G. & MILLS, H. H. (1965). *Tetrahedron Lett.* **11**, 679–685.

IBERS, J. A. & HAMILTON, W. C. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 72–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

ROGERS, D. (1981). *Acta Cryst.* A**37**, 734–741.

SHELDRICK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Nicolet XRD Division, Madison, WI.

STRAUSS, J. S. & STRANIERI, A. M. (1984). *J. Am. Acad. Dermatol.* **11**, 86–89.

Acta Cryst. (1986). C**42**, 956–958

Structure of 2-Methylpyridinium *β*-Octamolybdate(VI)

BY P. ROMÁN* AND J. M. GUTIÉRREZ-ZORRILLA

Departamento de Quimica Inorgánica, Universidad del Pais Vasco, 48080 *Bilbao, Spain*

AND M. MARTÍNEZ-RIPOLL AND S. GARCÍA-BLANCO

Departamento de Cristalografía, Instituto Rocasolano, CSIC, Serrano 119, 28006 *Madrid, Spain*

(*Received* 25 *November* 1985; *accepted* 11 *March* 1986)

Abstract. $[C_6H_8N]_4[Mo_8O_{26}]$, $M_r = 1560{\cdot}05$, triclinic, $P\bar{1}$, $a = 10{\cdot}011$ (1), $b = 10{\cdot}453$ (3), $c = 10{\cdot}540$ (2) Å, $\alpha = 94{\cdot}83$ (2), $\beta = 84{\cdot}39$ (2), $\gamma = 113{\cdot}97$ (2)°, $V = 1001{\cdot}8$ (4) Å^3, $Z = 1$, $D_m = 2{\cdot}60$ (1), $D_x = 2{\cdot}59$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}459$ mm^{-1}, $F(000) = 748$, room temperature, $R = 0{\cdot}025$ for 4848 observed reflections. The title compound is the product of the reaction between 3-ethylpyridinium *β*-octamolybdate and 2-methylpyridine. The structure comprises $Mo_8O_{26}^{4-}$ anions in the well characterized conformation and 2-methylpyridinium cations. Eight MoO_6 distorted octahedra share edges with short terminal Mo—O bonds (1·693–1·749 Å), bonds of intermediate length (1·895–2·014 Å) and long bonds (2·156–2·484 Å). Octamolybdate polyanions are H-bonded [N···O: 2·82 (5) Å] to two crystallographically independent cations.

Introduction. This work forms part of a series of studies on molybdates of pyridinium, alkylpyridinium (Román, González-Aguado, Esteban-Calderón & Martínez-Ripoll, 1984; Román, Jaud & Galy, 1981; Román, Martínez-Ripoll & Jaud, 1982; Román, Vegas, Martínez-Ripoll & García-Blanco, 1982) and aminopyridinium ions (Gutiérrez-Zorrilla, 1984).

Reaction of 3-ethylpyridinium octamolybdate with pyridine (Esteban-Calderón, Martínez-Ripoll, García-Blanco & Román, 1984) and 3-methylpyridine (Román, González-Aguado, Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1983) gives the corresponding substituted octamolybdate. Attempts have been made to prepare single crystals of these salts from the reaction between MoO_3 with pyridine or *n*-alkylpyridine where $n = 2$, 3 and 4. The same octamolybdates have been obtained with both methods. This paper deals with the structure of the title compound.

Experimental. 3-Ethylpyridinium octamolybdate (3 g) heated under reflux for 8 h with water (800 ml); then 2-methylpyridine (3 ml) added with stirring during 1 h at the same temperature; resulting solution filtered and cooled. Colourless prismatic crystals separated after 48 h; stable to air, light and X-ray exposure. Density by method of Archimedes (CCl_4 +$CHBr_3$) (Román & Gutiérrez-Zorrilla, 1985); CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$; approximately 0·25 × 0·15 × 0·10 mm. Unit-cell parameters refined using 25 high-angle reflections ($20 < 2\theta < 40°$); $\omega/2\theta$ scans, $2\theta_{\max} = 60°$; two standard reflections, no intensity variation; 5731 reflections measured, 4848 with $I > 3\sigma(I)$, $h < 14$, $-14 < k < 13$, $-14 < l < 14$. No absorption corrections were made in spite of the rather high μ value. Coordinates of a group of four Mo atoms obtained from Patterson function, remaining non-H atoms from successive Fourier maps. Refinement: full-matrix least squares, unit weights [flat

---

* Author to whom correspondence should be addressed.

0108-2701/86/080956-03$01.50

Table 1. *Atomic coordinates and thermal parameters*

$U_{\rm eq} = \frac{1}{3}\sum_i\sum_j[U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j] \times 10^{-4}$.

	x	y	z	$U_{\rm eq}$
Mo(1)	0·05405 (4)	0·17412 (3)	0·95234 (3)	150 (1)
Mo(2)	0·30779 (4)	0·08194 (4)	1·02971 (3)	176 (1)
Mo(3)	0·21228 (4)	−0·17103 (4)	0·80777 (4)	204 (1)
Mo(4)	−0·04316 (4)	−0·07489 (4)	0·73420 (3)	185 (1)
O(1)	0·17377 (35)	0·28201 (34)	0·84146 (30)	254 (11)
O(2)	0·41965 (35)	0·19374 (36)	0·91494 (33)	288 (12)
O(3)	0·33358 (37)	−0·05515 (39)	0·70249 (33)	315 (13)
O(4)	0·08171 (38)	0·04763 (38)	0·63638 (32)	311 (12)
O(5)	−0·03486 (32)	0·27354 (31)	1·03366 (30)	221 (10)
O(6)	0·40919 (35)	0·11534 (37)	1·15752 (32)	285 (12)
O(7)	0·23967 (39)	−0·32286 (38)	0·77802 (35)	324 (13)
O(8)	−0·19417 (37)	−0·15848 (39)	0·64912 (32)	315 (13)
O(9)	0·18442 (30)	0·19108 (29)	1·08376 (27)	176 (9)
O(10)	0·30902 (32)	−0·09175 (32)	0·96319 (29)	220 (10)
O(11)	0·03458 (33)	−0·21539 (33)	0·72496 (29)	233 (11)
O(12)	−0·10575 (30)	0·05921 (30)	0·84680 (26)	173 (9)
O(13)	0·10343 (29)	−0·00743 (29)	0·90539 (26)	168 (9)
N(11)	0·40870 (41)	0·32463 (42)	0·66238 (36)	251 (13)
C(12)	0·51917 (50)	0·44835 (49)	0·69084 (44)	255 (15)
C(13)	0·64334 (55)	0·49086 (53)	0·60713 (52)	328 (17)
C(14)	0·65024 (56)	0·40952 (59)	0·49852 (53)	363 (19)
C(15)	0·53232 (60)	0·28389 (55)	0·47151 (49)	335 (18)
C(16)	0·41076 (54)	0·24215 (52)	0·55579 (47)	306 (16)
C(17)	0·49747 (67)	0·52937 (61)	0·80825 (55)	410 (21)
N(21)	0·68305 (42)	0·21773 (42)	0·76728 (38)	268 (13)
C(22)	0·79636 (53)	0·33559 (51)	0·79870 (50)	298 (16)
C(23)	0·92542 (59)	0·37005 (65)	0·72071 (65)	448 (22)
C(24)	0·93312 (63)	0·28531 (70)	0·61562 (62)	446 (23)
C(25)	0·81219 (63)	0·16654 (62)	0·58624 (51)	373 (20)
C(26)	0·68616 (58)	0·13254 (53)	0·66348 (50)	327 (17)
C(27)	0·77670 (73)	0·41975 (64)	0·91529 (62)	461 (24)

Table 2. Mo—O *distances* (Å) *within the octahedra, bond lengths* (Å) *and bond angles* (°) *within the 2-methylpyridinium cations*

Mo(1)–O(1)	1·710 (3)	Mo(2)–O(2)	1·730 (3)
–O(5)	1·749 (4)	–O(6)	1·693 (4)
–O(9)	1·944 (3)	–O(9)	2·012 (4)
–O(12)	1·950 (3)	–O(10)	1·895 (4)
–O(13)	2·156 (3)	–O(13)	2·354 (3)
–O(13′)	2·349 (3)	–O(12′)	2·312 (2)
Mo(3)–O(3)	1·715 (3)	Mo(4)–O(4)	1·713 (3)
–O(7)	1·717 (4)	–O(8)	1·707 (3)
–O(10)	1·933 (3)	–O(11)	1·914 (4)
–O(11)	1·925 (3)	–O(12)	2·014 (4)
–O(13)	2·484 (3)	–O(13)	2·317 (3)
–O(5′)	2·296 (3)	–O(9′)	2·371 (3)

	$X=1$	$X=2$
N(X1)–C(X2)	1·350 (5)	1·336 (5)
C(X2)–C(X3)	1·387 (7)	1·393 (8)
C(X3)–C(X4)	1·387 (7)	1·375 (10)
C(X4)–C(X5)	1·394 (7)	1·375 (7)
C(X5)–C(X6)	1·372 (7)	1·366 (8)
C(X6)–N(X1)	1·361 (6)	1·358 (7)
C(X2)–C(X7)	1·489 (8)	1·495 (9)

	$X=1$	$X=2$
N(X1)–C(X2)–C(X3)	117·3 (4)	117·2 (5)
C(X2)–C(X3)–C(X4)	120·4 (4)	120·5 (5)
C(X3)–C(X4)–C(X5)	120·4 (5)	119·9 (6)
C(X4)–C(X5)–C(X6)	118·7 (5)	119·5 (6)
C(X5)–C(X6)–N(X1)	119·2 (4)	119·0 (4)
C(X6)–N(X1)–C(X2)	124·1 (4)	123·9 (4)
N(X1)–C(X2)–C(X7)	117·6 (4)	118·1 (5)
C(X7)–C(X2)–C(X3)	125·1 (4)	124·7 (5)

dependence of $\langle w(\Delta F)^2\rangle$ on $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$], 280 variables [Mo, O, N and C anisotropic, H (located geometrically and not refined) isotropic], max. ratio of shift/error 0·07, $R = 0·025$. Largest peak in final difference map: 0·6 e Å^{-3}. Scattering factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), structure solution and refinement performed with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. Final atomic coordinates and thermal parameters are given in Table 1.* Mo—O bond lengths within the MoO_6 octahedra, and bond distances and bond angles within the 2-methylpyridinium cations are shown in Table 2. The O—O distances within the MoO_6 octahedra lie between 2·557 (4) and 3·150 (5) Å. Fig. 1 shows the atom labelling in the polyanion.

The structure solution confirms that the compound contains the centrosymmetric β-octamolybdate anion $Mo_8O_{26}^{4-}$ (Román, Jaud & Galy, 1981; McCarron & Harlow, 1984; Wilson, McKee, Penfold & Wilkins, 1984, and references therein) and 2-methylpyridinium cations, which occupy two crystallographically independent sites (Fig. 2).

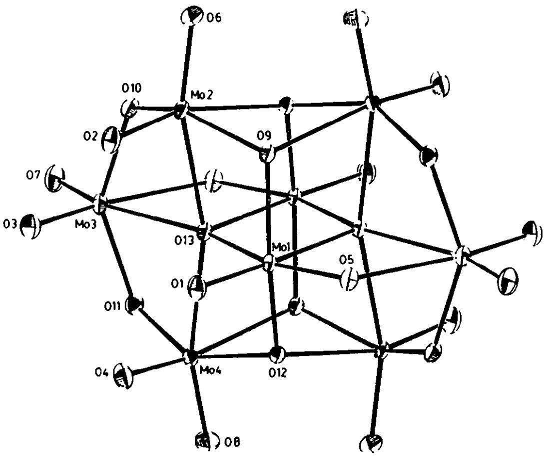

Fig. 1. The $Mo_8O_{26}^{4-}$ polyanion, with atom labelling.

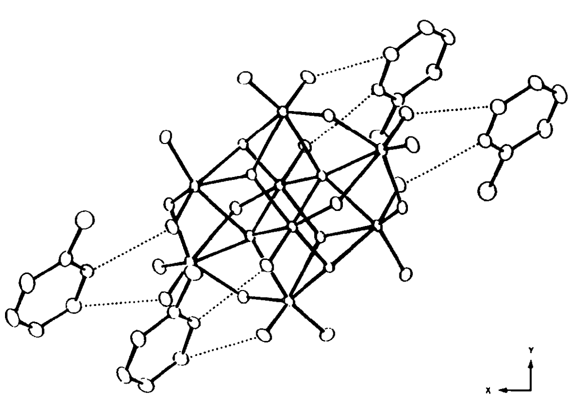

Fig. 2. Projection of the structural units, with hydrogen bonding.

---

* Lists of structure factors, anisotropic thermal parameters, hydrogen coordinates and hydrogen contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42854 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The octamolybdate anion is built up of eight distorted Mo—O octahedra linked together by bridging oxygen atoms. There are two types of Mo—Mo distances: (*a*) those between octahedra sharing edges (3·222—3·544 Å) and (*b*) octahedra sharing corners (4·593—4·619 Å). The Mo—O distances are classified in three types: short (1·693—1·749 Å), medium (1·895—2·014 Å) and long (2·156—2·484 Å), as commonly occurs in this kind of polyanion.

The distortions of MoO_6 octahedra have been evaluated by different equations (1–3). The results are shown in Table 3.

$$\Delta_1 = (1/6)\textstyle\sum_i[(R_i - R)/R]^2, \qquad (1)$$

$$\Delta_e = (1/12)\textstyle\sum_i[(D_i - D)/D]^2, \qquad (2)$$

$$\Delta_\alpha = (1/3)\textstyle\sum_i[(\alpha_i - 180)/180]^2, \qquad (3)$$

where R_i = individual Mo—O distances, R = mean MoO distance, D_i = individual O—O distances, D = mean O—O distance and α_i = individual $O—Mo—O_{trans}$ angles.

Plotting Δ_1 *versus* Δ_α we obtain the linear regression formula $\Delta_1 = 0{\cdot}0070 + 0{\cdot}671\Delta_\alpha$ with a correlation coefficient of $r = 0{\cdot}982$. Mo(2), Mo(3) and Mo(4) octahedra present a similar degree of distortion. The Mo(1) octahedron shows a lower degree of distortion as Mo(1) occupies a central position in the polyanion.

Two crystallographically independent 2-methylpyridinium cations have standard dimensions (Table 2). Two N—H···O [N···O = 2·778 (5), 2·857 (5) Å] and three C—H···O [C···O = 3·164 (5), 3·240 (6), 3·271 (6) Å] hydrogen contacts (Taylor & Kennard, 1982; McCarron & Harlow, 1983) have been detected in the structure (Fig. 2). No doubt the C—H···O contacts cannot be considered as hydrogen bonds, but they indicate some degree of polarization.

Table 3. *Octahedral distortion within the* MoO_6 *units*

Distortion	Mo(1)	Mo(2)	Mo(3)	Mo(4)
$\Delta_1 \times 10^4$	126	167	203	171
$\Delta_e \times 10^4$	10	18	24	19
$\Delta_\alpha \times 10^4$	154	188	206	181

References

Esteban-Calderón, M. C., Martínez-Ripoll, M., García-Blanco, S. & Román, P. (1984). *An. Quim.* **B80**, 470–473.

Gutiérrez-Zorrilla, J. M. (1984). PhD Thesis, Univ. of Pais Vasco, Spain.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

McCarron, E. M. III & Harlow, R. L. (1983). *J. Am. Chem. Soc.* **105**, 6179–6181.

McCarron, E. M. III & Harlow, R. L. (1984). *Acta Cryst.* C**40**, 1140–1141.

Román, P., González-Aguado, M. E., Esteban-Calderón, M. C. & Martínez-Ripoll, M. (1984). *Inorg. Chim. Acta*, **90**, 115–120.

Román, P., González-Aguado, M. E., Esteban-Calderón, M. C., Martínez-Ripoll, M. & García-Blanco, S. (1983). *Z. Kristallogr.* **165**, 271–276.

Román, P. & Gutiérrez-Zorrilla, J. M. (1985). *J. Chem. Educ.* **62**, 167–168.

Román, P., Jaud, J. & Galy, J. (1981). *Z. Kristallogr.* **154**, 59–68.

Román, P., Martínez-Ripoll, M. & Jaud, J. (1982). *Z. Kristallogr.* **158**, 141–147.

Román, P., Vegas, A., Martínez-Ripoll, M. & García-Blanco, S. (1982). *Z. Kristallogr.* **159**, 291–295.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, P. L., Heck, H. & Flack, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Wilson, A. J., McKee, V., Penfold, B. R. & Wilkins, C. J. (1984). *Acta Cryst.* C**40**, 2027–2030.

Acta Cryst. (1986). C**42**, 958–961

Structure of a (Ferra-β-diketonato)BF_2 Complex Containing a Methacryl Substituent*†

By P. Galen Lenhert, C. M. Lukehart and LouAnn Sacksteder

Departments of Chemistry and Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, *USA*

(*Received* 20 *August* 1985; *accepted* 11 *March* 1986)

Abstract. $(\eta\text{-}C_5H_5)(OC)Fe(MeCO)\{[H_2C{=}C(Me)]\text{-}CO\}BF_2$: $M_r = 309{\cdot}89$, monoclinic, $P2_1/c$, $a = 7{\cdot}8219\ (9)$, $b = 11{\cdot}794\ (2)$, $c = 15{\cdot}438\ (2)$ Å, $\beta = 111{\cdot}58\ (1)°$, $V = 1324{\cdot}40$ Å^3, $Z = 4$, $D_x = 1{\cdot}554$ g cm^{-3}, Mo $K\beta_1$, $\lambda = 0{\cdot}63225$ Å (for cell constants), Mo $K\alpha$ for data collection, $\mu = 11{\cdot}6$ cm^{-1}, $F(000) = 632$, $T = 294$ K, final $R = 0{\cdot}042$ for 3863 observed reflections. The ferra-β-diketonato ring adopts a boat-shaped conformation having the carbonyl ligand in an axial position. The Fe—C(acyl) distances of

---

* This paper is #43 in the series 'Reactions of Coordinated Molecules'.

† IUPAC name: difluoro[5-methyl-3-(carbonylcyclopentadienylferra)-5-hexene-2,4-dionato-*O,O'*]boron.

0108-2701/86/080958-04$01.50