Tableau 2. *Distances interatomiques* (Å) *et angles* (°)

Tétraèdre $P(1)O_4$

| P(1) | O(*E*11) | O(*E*12) | O(*L*11) | O(*L*12) |
|---|---|---|---|---|
| O(*E*11) | 1,478 (3) | 2,573 (4) | 2,492 (4) | 2,474 (4) |
| O(*E*12) | 120,1 (2) | 1,491 (3) | 2,506 (4) | 2,531 (4) |
| O(*L*11) | 107,5 (2) | 107,7 (2) | 1,611 (2) | 2,486 (4) |
| O(*L*12) | 107,5 (2) | 110,5 (2) | 102,0 (2) | 1,588 (3) |

⟨P(1)–O⟩ = 1,542 Å

Tétraèdre $P(2)O_4$

| P(2) | O(*E*21) | O(*E*22) | O(*L*12) | O(*L*12) |
|---|---|---|---|---|
| O(*E*21) | 1,487 (4) | 2,556 (6) | 2,481 (4) | 2,481 (4) |
| O(*E*22) | 119,8 (3) | 1,467 (4) | 2,550 (5) | 2,550 (5) |
| O(*L*12) | 106,1 (2) | 111,5 (2) | 1,616 (3) | 2,473 (5) |
| O(*L*12) | 106,1 (2) | 111,5 (2) | 99,9 (2) | 1,616 (3) |

⟨P(2)–O⟩ = 1,547 Å

| | |
|---|---|
| P(1)–O(*L*11)–P(1) | 136,0 (3) |
| P(1)–O(*L*12)–P(2) | 131,7 (2) |
| P(1)–P(1)–P(2) | 59,28 (2) |
| P(1)–P(2)–P(1) | 61,45 (5) |
| P(1)–P(1) | 2,988 (2) |
| P(1)–P(2) | 2,924 (2) |

Octaèdre $CoO_6$

| | |
|---|---|
| 2 × Co–O(*E*21) | 2,056 (4) |
| 4 × Co–O(*W*1) | 2,127 (3) |
| 4 × O(*E*21)–O(*W*1) | 2,865 (4) et 3,049 (4) |
| 2 × O(*W*1)–O(*W*1) | 3,029 (5) et 2,987 (5) |
| 4 × O(*E*21)–Co–O(*W*1) | 86,4 (1) et 93,6 (1) |
| 2 × O(*W*1)–Co–O(*W*1) | 89,2 (1) et 90,8 (1) |

Polyèdre $Rb(1)O_8$

| | |
|---|---|
| 2 × Rb(1)–O(*E*11) | 3,082 (3) |
| 2 × Rb(1)–O(*E*12) | 2,898 (3) |
| 2 × Rb(1)–O(*E*22) | 3,028 (2) |
| 2 × Rb(1)–O(*W*2) | 3,291 (3) |

Polyèdre $Rb(2)O_{10}$

| | |
|---|---|
| Rb(2)–O(*L*11) | 3,348 (5) |
| Rb(2)–O(*L*11) | 3,077 (5) |
| 2 × Rb(2)–O(*E*11) | 3,397 (3) |
| 2 × Rb(2)–O(*E*12) | 3,007 (3) |
| Rb(2)–O(*E*22) | 3,232 (5) |
| 2 × Rb(2)–O(*W*1) | 2,911 (3) |
| Rb(2)–O(*W*2) | 3,230 (7) |

entre les deux composés. L'octaèdre de coordination du cobalt est distordu; en effet la liaison Co—O varie de 2,056 à 2,127 Å et les angles sont compris entre 86,43 et 93,57°. La molécule d'eau O(*W*2) participe exclusivement à l'environnement oxygéné du rubidium. En se limitant à une sphère de rayon 3,5 Å, les atomes Rb(1) et Rb(2) ont respectivement les coordinences huit et dix. L'agencement des polyèdres $Rb(1)O_8$ et $Rb(2)O_{10}$ est représenté sur la Fig. 2. Les polyèdres $Rb(1)O_8$ partagent les deux arêtes O(*E*22)—O(*E*22) et O(*W*2)—O(*W*2) et se développent en chaînes infinies parallèlement à l'axe binaire. Les polyèdres $Rb(2)O_{10}$ sont groupés par paires en mettant en commun l'arête O(*L*11)—O(*L*11) et servent de pont reliant les chaînes $[Rb(1)O_8]_\infty$ par les deux arêtes O(*E*11)—O(*W*2) et O(*E*12)—O(*E*22). Les paires $[Rb(2)O_{10}]_2$ sont connectées par l'octaèdre $CoO_6$ à travers l'arête O(*W*1)—O(*W*1).

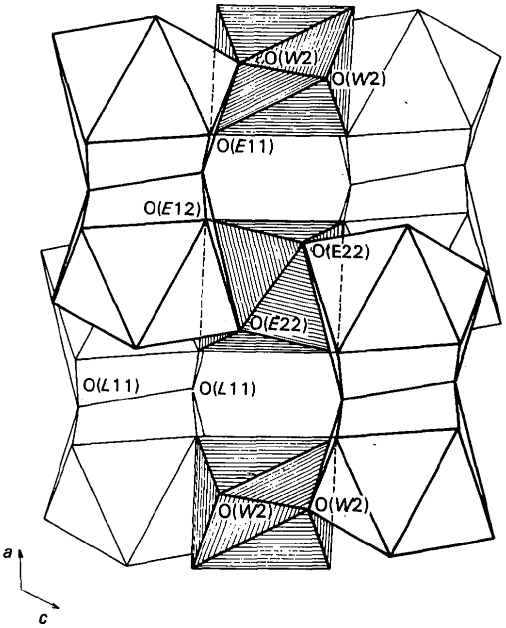

Fig. 2. Agencement des polyèdres $Rb(1)O_8$ (hachurés) et $Rb(2)O_{10}$ dans la structure de $Rb_4Co(P_3O_9)_2.6H_2O$.

### Références

Belkhiria, M. S., Ben Amara, M. & Dabbabi, M. (1987). *Acta Cryst.* C**43**, 609–610.

Enraf–Nonius (1980). *Structure Determination Package.* Enraf–Nonius, Delft, Les Pays Bas.

*International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

Jouini, A. & Dabbabi, M. (1986). *Acta Cryst.* C**42**, 268–270.

Jouini, A. & Durif, A. (1983). *C. R. Acad. Sci. Sér* II, **297**, 573–575.

Seethanen, D., Durif, A. & Averbuch-Pouchot, M. T. (1978). *Acta Cryst.* B**34**, 14–17.

Seethanen, D., Tordjman, I. & Averbuch-Pouchot, M. T. (1978). *Acta Cryst.* B**34**, 2387–2390.

---

*Acta Cryst.* (1987). C**43**, 2272–2275

# Structure of a Rhodium(III) Complex with Trimethyltriethylenetetramine

By James A. Muir, Grisell M. Gomez, Marisol Rodriguez, Mariel M. Muir and Lourdes M. Torres

*Departments of Chemistry and Physics, University of Puerto Rico, Rio Piedras, PR* 00931, *USA*

(*Received* 26 *March* 1987; *accepted* 14 *July* 1987)

**Abstract.** Λ-*cis*-β-(*SS*)-Dichloro[(2*S*,5*R*,9*S*)-5-methyl-4,7-diazadecane-2,9-diamine]rhodium(III) chloride monohydrate, $[RhCl_2(C_9H_{24}N_4)]Cl.H_2O$, $M_r = 415{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}538\ (2)$, $b = 9{\cdot}625\ (2)$, $c = 20{\cdot}655\ (4)$ Å, $V = 1697{\cdot}4$ Å$^3$, $D_x = 1{\cdot}62$, $D_m = 1{\cdot}59$ g cm$^{-3}$ (flotation), $Z = 4$, $\lambda$(Mo $K\alpha$)

0108-2701/87/122272-04$01.50

$= 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 13.5$ cm$^{-1}$, $F(000) = 848$, $T = 296$ K, final $R = 0.049$ for 1870 observed reflections. The Rh atom has a nearly regular octahedral geometry with an average Rh—N length of 2·36 (1) Å. The outer chelate rings of (2*S*,5*R*,9*S*)-Me$_3$trien assume distorted skew $\delta$ conformations and the central chelate ring assumes an envelope conformation. The configuration of each of the coordinated secondary N atoms is *S*, and the overall absolute configuration of the cationic complex is $\Lambda$.

**Introduction.** Complexes with chiral ligands can be very useful in the elucidation of reaction mechanisms. The chiral tetraamine ligand, (2*S*,5*R*,9*S*)-trimethyltriethylenetetramine (Me$_3$trien), whose formula is $H_2N—CH(CH_3)—CH_2—NH—CH_2—CH(CH_3)—NH—CH_2—CH(CH_3)—NH_2$, has been used to prepare a series of complexes of Co$^{III}$ and Rh$^{III}$ for which kinetic and photochemical studies have been carried out (Muir & Diaz, 1981; Torres, 1982).

The tetradentate ligand can coordinate with three different geometries, *cis*-α, *cis*-*β*, or *trans*. The ligand was prepared by a stereospecific route (Muir, Rechani & Diaz, 1981), so the configuration at the three chiral C atoms is known. However, the two secondary N atoms, which become chiral upon coordination to the Rh, can each have either *R* or *S* configuration, while each of the chelate rings can have a $\lambda$ or $\delta$ skew or an envelope conformation. The three methyl groups can have considerable influence in determining which of the possible conformations can be isolated. Only three of the possible isomers of [Rh{(2*S*,5*R*,9*S*)-Me$_3$trien}Cl$_2$]$^+$ were isolated (Muir, Torres & Zinner, 1987), one of which was originally assigned as the $\Delta$-*cis*-*β*-*RS* isomer based on comparison of ORD and UV–visible spectra with Co$^{III}$ complexes of known configuration. However, there was some doubt about that assignment for the *β* isomer, so the determination of the structure of the title complex, $\Lambda$-*cis*-*β*-(*SS*)-[Rh{(2*S*,5*R*,9*S*)-Me$_3$trien}Cl$_2$]Cl.H$_2$O, was carried out in order to establish the correct assignment.

**Experimental.** The tetraamine ligand (Muir, Rechani & Diaz, 1981) and the complex (Muir, Torres & Zinner, 1987) were prepared as described previously. The complex was dissolved in freshly distilled methanol. Crystals were obtained after the solution was kept in the dark for two months.

Diffraction data were collected by the Molecular Structure Corporation and the structural solution determined in this laboratory. Yellow prismatic crystal, $D_m = 1.59$ g cm$^{-3}$ by flotation in chloroform–1,2-dibromoethane, 0·30 × 0·30 × 0·20 mm, Enraf–Nonius CAD-4 diffractometer, monochromated Mo *K*α, $\omega$–$\theta$ scan, scan speed 2–20° min$^{-1}$ in $\omega$, scan width $(0.7 + 0.35 \tan\theta)°$, $2\theta_{\max} = 60°$, lattice parameters from least-squares fit of 25 reflections in the range of $3 < \theta < 7°$. Systematic absences $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$) and $00l$ ($l = 2n + 1$); $+h+k+l$ with $h \leq 12$, $k \leq 13$, $l \leq 27$; three standard reflections, intensities constant within experimental error; total unique reflections measured 2798, 1870 with $F^2 > 2\sigma(F_o)^2$ observed, $\sigma(F_o)^2 = [\sigma(I_{\text{raw}})^2 + (0.04F_o^2)]^{1/2}$. No absorption corrections were made. Structure was solved with the Enraf–Nonius *Structure Determination Package* (B. A. Frenz & Associates Inc., 1986), heavy-atom and difference Fourier methods; isotropic then anisotropic refinement on *F* of all non-H atoms, H atoms refined isotropically at calculated positions [C—H 0·95 Å]; 163 parameters refined, $wR = 0.057$, $w = 4(F_o)^2/[\sigma(F_o)^2]^2$, $S = 1.3$; difference syntheses showed no densities above 0·65 e Å$^{-3}$ except two peaks of 1·1 e Å$^{-3}$ at positions close to the Rh atom (min. −1·21 e Å$^{-3}$); max. $\Delta/\sigma = 0.01$. Neutral-atom scattering factors were used, except for Rh$^{III}$ [all from *International Tables for X-ray Crystallography* (1974)], and were corrected for anomalous dispersion (Cromer & Liberman, 1970). No correction for secondary extinction.

**Discussion.** The atomic coordinates and equivalent isotropic temperature factors for non-H atoms are listed in Table 1, and bond lengths and angles in Table 2.* An *ORTEP* plot (Johnson, 1976) of the complex cation and the atom numbering are shown in Fig. 1, and the packing of the ions in the *PLUTO* plot (Motherwell, 1976) in Fig. 2.

The Rh is coordinated to two Cl and four N atoms in approximately octahedral geometry. Since the two Cl atoms are *cis* and the tetraamine has three of the four N nearly coplanar, the cation is the *cis*-*β* isomer, as originally assigned. The absolute configuration of the complex is $\Lambda$, assigned by selection of the isomer with the correct configuration for the ligand, which was prepared stereospecifically from (*S*)-alanine and (*R*)-1,2-diaminopropane (Torres, 1982). Both secondary N atoms of the tetraamine have *S* configuration in the complex.

None of the three chelate rings of the complex has ideal symmetric skew geometry. Selected torsion angles are listed in Table 3. Both outer rings have asymmetric $\delta$ conformations with the methyl groups approximately equatorial. The central ring, coordinated through N(2) and N(3), has an envelope conformation. The C(5) methyl on that ring is best described as equatorial and is attached to C(4), adjacent to the so-called 'flat' secondary NH, rather than on C(6) adjacent to the 'apical' secondary NH. Other known structures which

---

* Lists of H-atom coordinates, anisotropic thermal factors, least-squares planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44247 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å²) *for* Λ-*cis*-β-(*SS*)-[Rh{(2*S*,5*R*,9*S*)-$Me_3$trien}$Cl_2$]Cl.$H_2O$

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(cos\ \alpha)B(2,3)]$.

| | *x* | *y* | *z* | *B*(Å²) |
|---|---|---|---|---|
| Rh | 0·14302 (8) | −0·31612 (6) | −0·81831 (3) | 2·709 (9) |
| Cl(1) | −0·1048 (3) | −0·3091 (3) | −0·7685 (1) | 3·58 (4) |
| Cl(2) | 0·2675 (4) | −0·2749 (3) | −0·7175 (1) | 4·37 (6) |
| Cl(3) | 0·2699 (3) | −0·3331 (3) | −1·0194 (1) | 3·95 (5) |
| N(1) | 0·1609 (9) | −0·1032 (7) | −0·8337 (4) | 3·3 (2) |
| N(2) | 0·3486 (8) | −0·3269 (7) | −0·8639 (3) | 2·5 (1) |
| N(3) | 0·1751 (8) | −0·5270 (7) | −0·8143 (3) | 2·8 (1) |
| N(4) | 0·0241 (8) | −0·3612 (7) | −0·9021 (3) | 2·6 (1) |
| C(1) | 0·302 (1) | −0·0782 (9) | −0·8750 (4) | 3·4 (2) |
| C(2) | 0·363 (1) | 0·0683 (9) | −0·8665 (5) | 4·4 (2) |
| C(3) | 0·422 (1) | −0·185 (1) | −0·8593 (5) | 3·8 (2) |
| C(4) | 0·450 (1) | −0·442 (1) | −0·8381 (5) | 3·7 (2) |
| C(5) | 0·545 (1) | −0·505 (1) | −0·8924 (6) | 5·8 (3) |
| C(6) | 0·346 (1) | −0·5515 (9) | −0·8033 (4) | 3·6 (2) |
| C(7) | 0·119 (1) | −0·5909 (9) | −0·8760 (4) | 2·9 (2) |
| C(8) | −0·022 (1) | −0·511 (1) | −0·8985 (4) | 3·0 (2) |
| C(9) | −0·078 (1) | −0·566 (1) | −0·9648 (4) | 4·0 (2) |
| O(1) | 0·074 (1) | −0·4303 (8) | −0·6018 (4) | 5·9 (2) |

Table 2. *Bond lengths* (Å) *and angles* (°) *in* Λ-*cis*-β-(*SS*)-[Rh{(2*S*,5*R*,9*S*)-$Me_3$trien}$Cl_2$]Cl.$H_2O$

| | | | |
|---|---|---|---|
| Rh—Cl(1) | 2·354 (2) | N(3)—C(6) | 1·50 (1) |
| Rh—Cl(2) | 2·372 (3) | N(3)—C(7) | 1·49 (1) |
| Rh—N(1) | 2·080 (7) | N(4)—C(8) | 1·50 (1) |
| Rh—N(2) | 1·995 (7) | C(1)—C(2) | 1·51 (1) |
| Rh—N(3) | 2·050 (7) | C(1)—C(3) | 1·49 (1) |
| Rh—N(4) | 2·053 (7) | C(4)—C(5) | 1·51 (2) |
| N(1)—C(1) | 1·49 (1) | C(4)—C(6) | 1·56 (1) |
| N(2)—C(3) | 1·50 (1) | C(7)—C(8) | 1·50 (1) |
| N(2)—C(4) | 1·50 (1) | C(8)—C(9) | 1·54 (1) |

| | | | |
|---|---|---|---|
| Cl(1)—Rh—Cl(2) | 90·82 (9) | C(3)—N(2)—C(4) | 113·8 (7) |
| Cl(1)—Rh—N(1) | 96·0 (2) | Rh—N(3)—C(6) | 107·0 (5) |
| Cl(1)—Rh—N(2) | 177·3 (2) | Rh—N(3)—C(7) | 109·2 (5) |
| Cl(1)—Rh—N(3) | 97·5 (2) | C(6)—N(3)—C(7) | 112·2 (6) |
| Cl(1)—Rh—N(4) | 86·0 (2) | Rh—N(4)—C(8) | 106·9 (5) |
| Cl(2)—Rh—N(1) | 86·3 (2) | N(1)—C(1)—C(2) | 111·1 (7) |
| Cl(2)—Rh—N(2) | 91·7 (2) | N(1)—C(1)—C(3) | 108·6 (7) |
| Cl(2)—Rh—N(3) | 94·0 (2) | C(2)—C(1)—C(3) | 112·4 (9) |
| Cl(2)—Rh—N(4) | 175·8 (2) | N(2)—C(3)—C(1) | 108·9 (8) |
| N(1)—Rh—N(2) | 85·1 (3) | N(2)—C(4)—C(5) | 110·1 (8) |
| N(1)—Rh—N(3) | 166·5 (3) | N(2)—C(4)—C(6) | 109·7 (7) |
| N(1)—Rh—N(4) | 96·6 (3) | C(5)—C(4)—C(6) | 111·9 (8) |
| N(2)—Rh—N(3) | 81·4 (3) | N(3)—C(6)—C(4) | 112·2 (7) |
| N(2)—Rh—N(4) | 91·5 (3) | N(3)—C(7)—C(8) | 108·1 (7) |
| N(3)—Rh—N(4) | 83·8 (3) | N(4)—C(8)—C(7) | 107·4 (7) |
| Rh—N(1)—C(1) | 107·8 (5) | N(4)—C(8)—C(9) | 111·4 (7) |
| Rh—N(2)—C(3) | 106·9 (5) | C(7)—C(8)—C(9) | 110·4 (8) |
| Rh—N(2)—C(4) | 112·2 (5) | | |

have a methyl on the central five-membered chelate ring of a trien derivative and also have the methyl group adjacent to the 'flat' N are Δ-*cis*-$β_2$-(*RR*)-[Co{(2*S*,5*S*,9*S*)-$Me_3$trien}{(*S*)-alanine}]$^{2+}$ (J. A. Muir, Muir, Saez & Campana, 1987), Λ-*cis*-$β_2$-(*SS*)-[Co{(2*S*,5*R*,9*S*)-$Me_3$trien}{(*S*)-ala}]$^{24}$ (M. M. Muir, Muir, Saez & Campana, 1987), and Λ-*cis*-β-(*SS*)-[Co{(5*R*)-Metrien}$(NO_2)_2$]$^+$ (Tanaka, Marumo & Saito, 1973). The planes defined by Rh, N(1) and N(2), and by Rh, N(2) and N(3) are coplanar, with a dihedral angle of 0·0 (0·2)°, while the plane defined by Co, N(3) and N(4) has a dihedral angle of 87·5 (0·2)° with the other two planes.

The bond distances and angles in Table 2 all fall in the expected ranges. The average Rh—N distance is 2·04 (4) Å and the average Rh—Cl distance is 2·36 (1) Å. These compare closely with values in the literature for other complexes of Rh, such as 2·076 (4) Å for Rh—N in [Rh(chxn)$_3$]$^{3+}$ (Miyamae, Sato & Saito, 1977), 2·054 (8) and 2·072 (7) Å for Rh—N in [Rh(en)$_3$]$^{3+}$ (Whuler, Brouty, Spinat & Herpin, 1976), 2·334 (5) and 2·06 (1) Å for Rh—Cl and Rh—N in *mer*-Rhpy$_3$Cl$_3$ (Acharya, Tavale & Guru Row, 1984), and 2·331 (1) and 2·06 (1) Å, respectively, in [Rhpy$_4$Cl$_2$]$^+$ (Roziere, Lehmann & Potier, 1979). No evidence of a *trans* influence could be seen in the Rh—N or Rh—Cl distances, which may imply that the steric requirements of the tetraamine are more important than a possible *trans* influence. The C—C and C—N distances, 1·52 (3) and 1·50 (1) Å, respectively, show no evidence of steric problems. However, possible strain can be seen in some of the angles. The N(1)—Rh—N(3) bond is 166·5 (0·3)°, significantly smaller than the 180° for a true octahedron. The three chelate rings have N—Rh—N angles of 85·1, 81·4 and 83·8°. The latter two are smaller than the averages observed for the corresponding angles in Δ-*cis*-$β_2$-(*RR*)-[Co{(2*S*,5*S*,9*S*)-$Me_3$trien}{(*S*)-alanine}]$^{2+}$ [85·9 (0·5)°] (J. A. Muir, Muir, Saez & Campana, 1987), Λ-*cis*-$β_2$-(*SS*)-[Co{(2*S*,5*R*,9*S*)-$Me_3$trien}{(*S*)-alanine}]$^{2+}$ [85 (2)°] (M. M. Muir, Muir, Saez & Campana, 1987), and Λ-*cis*-β-(*SS*)-[Co{(5*R*)-Metrien}$(NO_2)_2$]$^+$ [85·9(5)°] (Tanaka *et al.*, 1973). Neither the water molecule nor the chloride anion is close enough for significant interactions with the cation.

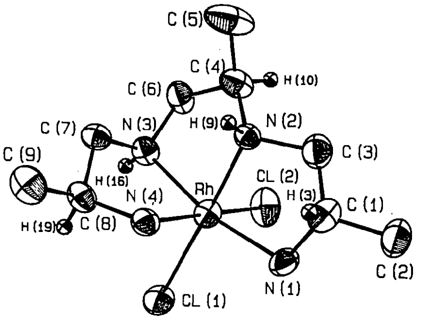

Fig. 1. Atom numbering for the Λ-*cis*-β-(*SS*)-[Rh{(2*S*,5*R*,9*S*)-$Me_3$trien}$Cl_2$]$^+$ cation including the H atoms on chiral atoms.

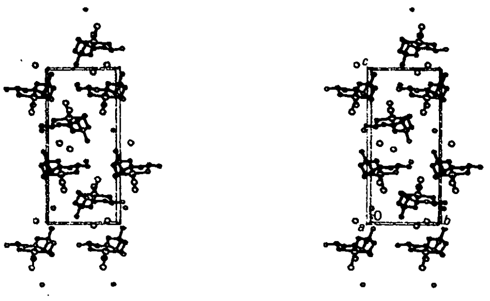

Fig. 2. Packing diagram for the title compound.

Table 3. *Selected torsion angles* (°) *in* $\Lambda$-*cis*-$\beta$-(*SS*)-[Rh{(2*S*,5*R*,9*S*)-$Me_3$trien}$Cl_2$]Cl.$H_2O$

| | | | |
|---|---|---|---|
| RhN(1)C(1)C(3) | −32·5 (8) | N(2)RhN(1)C(1) | 6·0 (5) |
| N(1)C(1)C(3)N(2) | 52·2 (9) | RhN(1)C(1)C(2) | 23·3 (6) |
| C(1)C(3)N(2)Rh | −45·5 (8) | N(2)C(3)C(1)C(2) | −4·4 (7) |
| C(3)N(2)RhN(1) | 21·0 (5) | N(2)C(3)C(1)H(3) | −67·5 (11) |
| RhN(2)C(4)C(6) | 21·4 (8) | N(3)RhN(2)C(4) | −33·4 (5) |
| N(2)C(4)C(6)N(3) | 9·7 (9) | RhN(2)C(4)C(5) | −34·8 (6) |
| C(4)C(6)N(3)Rh | −34·9 (8) | N(3)C(6)C(4)C(5) | 67·3 (8) |
| C(6)N(3)RhN(2) | 37·4 (5) | N(3)C(6)C(4)H(10) | 51·1 (10) |
| RhN(3)C(7)C(8) | −35·7 (7) | N(4)RhN(3)C(7) | 8·2 (5) |
| N(3)C(7)C(8)N(4) | 54·2 (8) | RhN(4)C(8)C(9) | 13·2 (5) |
| C(7)C(8)N(4)Rh | −45·9 (7) | N(3)C(7)C(8)C(9) | −4·1 (7) |
| C(8)N(4)RhN(3) | 20·8 (5) | N(3)C(7)C(8)H(19) | −65·7 (12) |

This research was supported by NIH grant RR-8102, the NIH MARC Honors Undergraduate Program, and the NSF RIMI program. We thank Dr C. L. Barnes for useful discussions and the Cornell University Chemistry Department for hospitality during the writing of this paper.

## References

Acharya, K. R., Tavale, S. S. & Guru Row, T. N. (1984). *Acta Cryst.* C**40**, 1327–1328.

B. A. Frenz & Associates Inc. (1986). *Enraf–Nonius Structure Determination Package*. College Station, Texas, USA, and Enraf–Nonius, Delft, Holland.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

*International Tables for X-ray Crystallography* (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Miyamae, H., Sato, S. & Saito, Y. (1977). *Acta Cryst.* B**33**, 3391–3396.

Motherwell, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Muir, J. A., Muir, M. M., Saez, R. & Campana, C. F. (1987). *Acta Cryst.* C**43**, 1487–1490.

Muir, M. M. & Diaz, J. A. (1981). *Synth. React. Inorg. Met. Org. Chem.* **11**, 333–344.

Muir, M. M. Muir, J. A., Saez, R. & Campana, C. F. (1987). *Inorg. Chim. Acta*. In the press.

Muir, M. M., Rechani, P. R. & Diaz, J. A. (1981). *Synth. React. Inorg. Met. Org. Chem.* **11**, 317–332.

Muir, M. M., Torres, L. M. & Zinner, L. B. (1987). *Synth. React. Inorg. Met. Org. Chem.* **17**. In the press.

Roziere, J., Lehmann, M. S. & Potier, J. (1979). *Acta Cryst.* B**35**, 1099–1102.

Tanaka, K., Marumo, F. & Saito, Y. (1973). *Acta Cryst.* B**29**, 733–738.

Torres, L. M. (1982). PhD Thesis, Univ. of Puerto Rico, Rio Piedras, USA.

Whuler, A., Brouty, C., Spinat, P. & Herpin, P. (1976). *Acta Cryst.* B**32**, 2542–2544.

---

*Acta Cryst.* (1987). C**43**, 2275–2277

# Structure of Triammonium $\mu$-Formato-(*O*,*O*′)-di-$\mu$-oxo-bis[diformato(oxo)molybdate(V)]

By Boris Kamenar,* Maja Penavić and Berislav Marković

*Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, PO Box* 153, 41001 *Zagreb, Yugoslavia*

(*Received* 24 *April* 1987; *accepted* 7 *July* 1987)

**Abstract.** $[NH_4]_3[Mo_2O_4(CHO_2)_5]$, $M_r = 535·08$, orthorhombic, *Pnma*, $a = 7·566$ (3), $b = 17·958$ (6), $c = 11·816$ (4) Å, $V = 1605$ (1) Å$^3$, $Z = 4$, $D_x = 2·19$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 15·84$ cm$^{-1}$, $F(000) = 1056$, $T = 293$ K, $R = 0·026$ for 1846 observed reflections. The structure consists of $NH_4^+$ cations and binuclear $[Mo_2O_4(HCOO)_5]^{3-}$ anions with crystallographically imposed mirror-plane symmetry. The octahedrally coordinated Mo atoms are bridged by two oxo O and one formato ligand. The Mo—O bond lengths are 1·695 (2) Å (from the terminal oxo O atom), 1·934 (2) and 1·935 (2) Å (from the bridging oxo O atoms), 2·302 (2) Å (from the bridging formato ligand), and 2·085 (2) and 2·130 (2) Å (from the monodentately linked formato ligands). The Mo···Mo distance is 2·549 (1) Å.

**Introduction.** $Mo^V$ has a distinct tendency to form dimeric species usually bridged by one or two oxo O atoms (Spivack & Dori, 1975; Kamenar & Penavić, 1977). However, there are structures in which two Mo atoms are triply bridged by an additional alkoxo or carboxylato bridging ligand (Głowiak, Sabat, Sabat & Rudolf, 1975; Głowiak, Rudolf, Sabat & Jeżowska-Trzebiatowska, 1977; Kamenar, Penavić & Marković, 1984). We report here the structure of such a dimeric complex anion in which a triple bridge between two Mo atoms is realized by two oxo O atoms and supplemented by the bidentate formato ligand.

**Experimental.** The red crystals of the title complex were prepared as described by Rosenheim & Nernst (1933). A prism-like crystal (0·35 × 0·38 × 0·19 mm) was chosen for data collection on a Philips PW1100 automatic diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters and standard

---

* To whom correspondence should be addressed.

0108-2701/87/122275-03$01.50