Table 3. *Selected torsion angles* (°) *in Λ-cis-β-(SS)-* $[Rh\{(2S,5R,9S)\text{-}Me_3trien\}Cl_2]Cl.H_2O$

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)

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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 *μ*-Formato-(*O,O'*)-di-*μ*-oxo-bis[diformato(oxo)molybdate(V)]

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Abstract. $[NH_4]_3[Mo_2O_4(CHO_2)_5]$, $M_r = 535{\cdot}08$, orthorhombic, *Pnma*, $a = 7{\cdot}566$ (3), $b = 17{\cdot}958$ (6), $c = 11{\cdot}816$ (4) Å, $V = 1605$ (1) Å^3, $Z = 4$, $D_x = 2{\cdot}19$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 15{\cdot}84$ cm^{-1}, $F(000) = 1056$, $T = 293$ K, $R = 0{\cdot}026$ 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 *Kα* radiation. Cell parameters and standard

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deviations from 20 reflections ($9 < 2\theta < 16°$). The intensities of 1977 unique reflections ($2\theta \leq 64°$, ω–2θ scan, range of hkl $0 \leq h \leq 10$, $0 \leq k \leq 25$, $0 \leq l \leq 16$, scan rate 0·04° s^{-1}, scan width 1·60°) were corrected for Lorentz and polarization effects. 131 reflections with $I \leq 3\sigma(I)$ were considered unobserved. Intensities of three standard reflections ($\bar{3}02$, $\bar{2}30$, 024) each measured every 2 h showed no significant crystal decomposition. The Mo-atom position was derived from a Patterson synthesis, all non-H atoms from a subsequent electron density summation using scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974). Full-matrix least squares of positional and anisotropic thermal parameters for non-H atoms based on the F magnitudes gave a final $R = 0·026$, $wR = 0·032$ [$w = 0·2953/(\sigma^2|F| + 0·003688F^2)$], $(\Delta/\sigma)_{\max} = 0·48$, max. and min. peak heights in final difference Fourier synthesis: +0·63 and −1·14 e Å^{-3}. H atoms located either in the difference Fourier maps or generated at fixed positions. Calculations performed on a Univac 1110 computer of the University Computing Centre in Zagreb using programs written by Domenicano, Spagna & Vaciago (1969) and the *SHELX*76 system (Sheldrick, 1976).

Discussion. Final atomic coordinates are given in Table 1,* bond lengths and angles in Table 2. The structure of the dimeric anion is shown in Fig. 1. The structure of the title compound is built up of NH_4^+ cations and binuclear $[Mo_2O_4(HCOO)_5]^{3-}$ anions; the dimer as well as one [N(1)] of the NH_4^+ cations has crystallographically imposed mirror-plane symmetry. Each Mo atom is octahedrally coordinated by three oxo O atoms, one terminal at 1·695 (2) Å and two bridging at 1·934 (2) and 1·935 (2) Å, one O atom from the bridging formato ligand at 2·302 (2) Å and two O atoms from two monodentately linked formato ligands at 2·085 (2) and 2·130 (2) Å. Due to the *trans* influence of the terminal oxo ligand the Mo—O (from the formato ligand) bond is longer than one would expect for an Mo—O single bond (Schröder, 1975). The octahedron is significantly distorted, the angles at Mo ranging from 76·7 (1) to 103·3 (1)°. The Mo atom is displaced out of the equatorial O(2), O(3), O(4), O(5) plane towards the terminal O by 0·36 Å. The Mo_2O_2 four-membered ring is folded along a line connecting the two bridging O, the dihedral angle between the Mo, O(2), O(3) and Mo^{i}, O(2), O(3) planes being 162·6°. The Mo···Mo bond distance of 2·549 (1) Å corresponds to the value considered as an Mo—Mo single bond (Cotton, 1977).

Both NH_4^+ ions are involved in hydrogen bonding to the dimeric anion. At N(1) the interactions N—H(13)···O(8^{i}) and N—H(11)···O(3^{ii}) of 2·842 (3) and 2·746 (4) Å, and at N(2) the interactions N—H(21)···O(7), N—H(22)···O(8^{iii}), N—H(23)···O(4^{iv}) and N—H(24)···O(5^{v}) of 2·802 (3), 2·882 (2),

Table 1. *Atomic positional parameters* (×10^4) *and equivalent isotropic thermal parameters* (×10^{4}Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo	2895 (0·3)	1790 (0·1)	317 (0·2)	185 (0·3)
O(1)	752 (3)	1596 (1)	22 (2)	323 (4)
O(2)	2824 (3)	2500	1549 (2)	235 (3)
O(3)	3537 (3)	2500	−843 (2)	195 (2)
O(4)	3292 (3)	935 (1)	1483 (2)	305 (4)
O(5)	3924 (3)	936 (1)	−745 (2)	275 (3)
O(6)	5895 (3)	1872 (1)	615 (2)	281 (3)
O(7)	3880 (4)	445 (1)	3162 (2)	380 (4)
O(8)	2887 (3)	1256 (1)	−2458 (2)	356 (4)
C(1)	3740 (4)	978 (1)	2526 (2)	303 (5)
C(2)	3732 (4)	853 (1)	−1816 (2)	258 (4)
C(3)	6637 (5)	2500	687 (4)	297 (4)
N(1)	590 (5)	2500	−2240 (3)	351 (4)
N(2)	2652 (4)	497 (2)	5398 (2)	325 (4)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mo—O(1)	1·695 (2)	C(1)—O(4)	1·281 (4)
Mo—O(2)	1·935 (2)	C(1)—O(7)	1·221 (4)
Mo—O(3)	1·934 (2)	C(2)—O(5)	1·285 (3)
Mo—O(4)	2·085 (2)	C(2)—O(8)	1·228 (4)
Mo—O(5)	2·130 (2)	C(3)—O(6)	1·263 (3)
Mo—O(6)	2·302 (2)	Mo···Mo′	2·549 (0·5)
O(1)—Mo—O(3)	103·3 (1)	C(1)—O(4)—Mo	129·0 (2)
O(1)—Mo—O(5)	94·6 (1)	C(2)—O(5)—Mo	128·5 (2)
O(2)—Mo—O(3)	96·1 (1)	C(3)—O(6)—Mo	120·3 (2)
O(2)—Mo—O(6)	82·6 (1)	O(4)—C(1)—O(7)	124·6 (3)
O(4)—Mo—O(5)	78·8 (1)	O(5)—C(2)—O(8)	126·9 (3)
O(4)—Mo—O(6)	78·7 (1)	O(6)—C(3)—O(6)′	126·6 (4)
Mo—O(2)—Mo′	82·4 (1)	O(1)—Mo—O(6)	171·1 (1)

Primed atoms are related to unprimed atoms by mirror-plane symmetry.

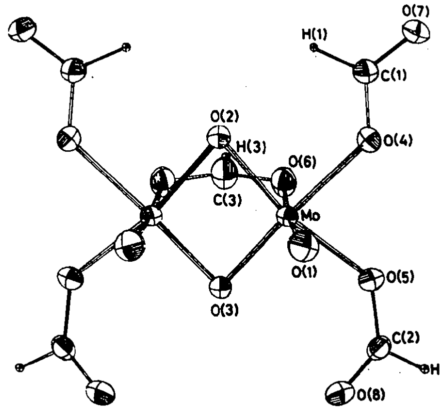

Fig. 1. An *ORTEP* (Johnson, 1971) view of the binuclear $[Mo_2O_4(HCOO)_5]^{3-}$ anion showing the atom-numbering scheme. Ellipsoids at 50% probability level.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44220 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2·960 (2) and 2·956 (3) Å, respectively, may be considered as hydrogen bonds [(i) $x, \frac{1}{2}-y, z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}-z$; (iii) $x, y, 1+z$; (iv) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (v) $-\frac{1}{2}+x, y, \frac{1}{2}-z$].

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References

Cotton, F. A. (1977). *J. Less-Common Met.* **54**, 3–12.

Domenicano, A., Spagna, R. & Vaciago, A. (1969). *Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend.* **47**, 331–336.

Głowiak, T., Rudolf, M. F., Sabat, M. & Jeżowska-Trzebiatowska, B. (1977). *J. Less-Common Met.* **54**, 35–50.

Głowiak, T., Sabat, M., Sabat, H. & Rudolf, M. F. (1975). *J. Chem. Soc. Chem. Commun.* p. 712.

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

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Kamenar, B. & Penavić, M. (1977). *Izvj. Jugosl. Cent. Kristallogr. (Zagreb)*, **12**, 81–104.

Kamenar, B., Penavić, M. & Marković, B. (1984). *Croat. Chem. Acta*, **57**, 637–643.

Rosenheim, A. & Nernst, C. (1933). *Z. Anorg. Allg. Chem.* **214**, 209–224.

Schröder, F. A. (1975). *Acta Cryst.* B**31**, 2294–2308.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Spivack, B. & Dori, Z. (1975). *Coord. Chem. Rev.* **17**, 99–136.

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Structures of (Aniline)(alkyl)[3,3′-(1,3-propanediyldinitrilo)di(2-butanone oximato)(1−)]cobalt(III) Hexafluorophosphate with Alkyl = Ethyl (I), Trifluoroethyl (II)

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Abstract. (I) $[Co(C_2H_5)(C_6H_7N)(C_{11}H_{20}N_4O_2)]PF_6$, $M_r = 565·4$, triclinic, $P\bar{1}$, $a = 8·034$ (2), $b = 10·847$ (2), $c = 14·942$ (4) Å, $\alpha = 87·29$ (2), $\beta = 81·15$ (2), $\gamma = 71·30$ (2)°, $V = 1218·7$ (5) Å^3, $Z = 2$, $D_x = 1·54$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 8·4$ cm^{-1}, $F(000) = 584$, $T = 293$ K, $R = 0·043$ for 3736 reflections $I > 3\sigma(I)$. (II) $[Co(C_2H_2F_3)(C_6H_7N)(C_{11}H_{20}N_4O_2)]PF_6$, $M_r = 619·4$, triclinic, $P\bar{1}$, $a = 8·107$ (2), $b = 10·828$ (2), $c = 15·065$ (3) Å, $\alpha = 85·99$ (2), $\beta = 79·51$ (2), $\gamma = 70·53$ (2)°, $V = 1225·9$ (5) Å^3, $Z = 2$, $D_x = 1·68$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 8·6$ cm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0·034$ for 4671 reflections with $I > 3\sigma(I)$. In both structures, the geometry around the Co atom may be described as a distorted octahedron, the equatorial positions being occupied by the tetradentate ligand (DO)(DOH)pn = 3,3′-(1,3-propanediyldinitrilo)di(2-butanone oximato). The axial fragment is characterized by Co—C(alkyl) and Co—N(aniline) bond lengths of 2·030 (4) and 2·174 (3) Å in (I) and 2·010 (2) and 2·130 (2) Å in (II), respectively. The two chemically equivalent halves of the equatorial ligand bend towards aniline, with a dihedral angle, α, of 7·1 (2) (I) and 5·6 (3)° (II). The aniline phenyl group lies above one of the five-membered rings of the equatorial moiety.

Introduction. As part of an extensive investigation of the properties of simple organocobalt complexes, we have recently extended previous studies on cobaloximes, the trivial name of the $LCo(DH)_2R$ complexes, where DH = monoanion of dimethylglyoxime, R = alkyl group and L = neutral ligand (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985), to the so-called Costa models,′ $[LCo\{(DO)(DOH)pn\}R]PF_6$ (Costa, Mestroni & Savorgnani, 1969). The latter complexes have been claimed to mimic the type of reactions involved in B_{12}-dependent enzymic processes: in certain cases, they present electrochemical behaviour closer to that of cobalamins than cobaloximes (Finke, Schiraldi & Mayer, 1984).

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