Hexaaquamagnesium bis\([\text{trans-}[\text{nitrilotriacetato}(2-)\cdot\kappa^3\text{O}^1,\text{N},\text{O}^2]-\mu\text{-oxo-cis-dioxomolybdate(VI)}]\) hexahydrate

Both the cation and anion in the title compound, \([\text{Mg(H}_2\text{O})_6][\text{Mo}_2\text{O}_5\text{(C}_6\text{H}_7\text{NO}_6)_2]\cdot6\text{H}_2\text{O}\), lie on centers of symmetry, and their metals are both six-coordinate in octahedral environments.

Comment

Oxomolybdate(VI) complexes are of interest as possible models for molybdenum sites in metalloenzymes (Chan et al., 1993; Hille, 1996; Stiefel, 1977). Among the complexes, those chelated by tridentate ligands derive their stability through the binding of the ligand to vacant coordination sites (Gebreyes et al., 1985). The deprotonated nitrilotriacetato ligand, which functions as a tetradeionate entity in a number of metal complexes, is only tridentate in the dipyridinium (Matsumoto et al., 1984), monohydrated bis(tetrabutylammonium) (Liu et al., 1990) and octahydrated disodium \(\mu\text{-oxobis(hydrogen-nitrilotriacetato-cis-dioxomolybdates)}\) (Knobler et al., 1980, 1983). In the peroxo complex, potassium nitrilotriacetato-(oxo)(peroxo)molybdate monohydrate, the ligand behaves as a tetradeionate chelate (Won et al., 1994). On the other hand, as the hexaaquamagnesium(II) cation has been used to balance the charges of a number of organic (Arranz Mascarós et al., 2000; Castellari et al., 1999, 1994; Solans, Font-Altaba, Aguilo et al., 1983) and inorganic (Coiro & Mazza, 1991; Kariuki & Jones, 1989; Maslen et al., 1988; Solans, Font-Altaba, Oliva & Herrera, 1983) derivatives, we have used this dication as counter-ion in the title compound, (I).

Both the cation and anion lies on centers of symmetry; for the anion, this symmetry requires the Mo—O—Mo unit to be linear. The Mo—O bond distance is similar to that [1.880 (1) Å] found in the sodium salt (Knobler et al., 1983), which is also centrosymmetric. In the related dipotassium tetrassodium oxobis(citratodioxomolybdate), the Mo—O—Mo unit is bent [Mo—O—Mo = 144.7 (2)°; Zhou et al., 1997]. In the title compound, the anions and the water-coordinated cations are linked by hydrogen bonds into a three-dimensional network motif.
Experimental

Magnesium molybdate (10 mmol) dissolved in water (10 ml) was added to nitritolactiaceic acid (20 mmol) dissolved in water (5 ml) and the mixture was stirred for several hours. The solution was concentrated to about 10 ml; colorless crystals of the title hydrate, (I), separated from the solution in 35% yield when it was set aside for several days.

Crystal data

\[ \text{[Mg(H}_2\text{O)}_6]\text{[Mo}_2\text{O}_5(C}_6\text{H}_7\text{NO}_6}_2]\text{]}\cdot6\text{H}_2\text{O} \]

\[ M_r = 890.63 \]

Triclinic, \( \text{PT} \)

\[ a = 6.4787 (3) \text{ Å} \]

\[ b = 9.2555 (6) \text{ Å} \]

\[ c = 13.9995 (6) \text{ Å} \]

\[ \alpha = 91.014 (4) ^\circ \]

\[ \beta = 101.315 (3) ^\circ \]

\[ \gamma = 106.592 (4) ^\circ \]

\[ V = 786.44 (7) \text{ Å}^3 \]

Data collection

Enraf-Nonius CAD-4

do scans

Absorption correction: empirical

via \( \psi \) scans (North et al., 1968)

\[ T_{\text{min}} = 0.618, T_{\text{max}} = 0.716 \]

3339 measured reflections

3079 independent reflections

2877 reflections with \( I > 2\sigma(I) \)

Refinement

Refinement on \( F^2 \)

\[ R[F^2 > 2\sigma(F^2)] = 0.028 \]

\[ wR(F^2) = 0.076 \]

\[ S = 1.11 \]

3079 reflections

215 parameters

H atoms treated by a mixture of

independent and constrained refinement

\[ w = 1/[\sigma^2(F^2) + (0.0442P)^2 + 0.3336P] \]

where \( P = (F^2 + 2F^2)/3 \)

\[ (\Delta F)^2_{\text{max}} = 0.001 \]

\[ \Delta F_{\text{max}} = 0.38 \text{ e Å}^{-3} \]

\[ \Delta F_{\text{min}} = -0.52 \text{ e Å}^{-3} \]

The acid H atom was located and refined. The H atoms of the water molecules were located in difference maps, but these were not refined. For the O3w water, one of its H atoms is disordered over two positions.

Data collection: \( \text{CAD-4 VAX/PC Fortran System} \) (Enraf-Nonius, 1988); cell refinement: \( \text{CAD-4 VAX/PC Fortran System} \); data reduction: \( \text{XCAD4} \) (Harms, 1997); program(s) used to solve structure: \( \text{SHELX97} \) (Sheldrick, 1997); program(s) used to refine structure: \( \text{SHELXL97} \) (Sheldrick, 1997); molecular graphics: \( \text{ORTEPII} \) (Johnson, 1976); software used to prepare material for publication: \( \text{SHELXL97} \).

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References


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