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LETTER

# Structure of *trans*-{[Cr(en)$_2$ONO]$_2$-(H$_3$O$_2$)}(ClO$_4$)$_3$, a Cr(III) nitrito complex with a $H_3O_2^-$ bridging group

**Anna G. McKenna**

*Department of Chemistry, College of St. Benedict, Collegeville, MN 56321 (U.S.A.)*

**William T. Pennington*** and **James C. Fanning***

*Department of Chemistry, Clemson University, Clemson, SC 29634-1905 (U.S.A.)*

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While investigating the reactivity of O-bound nitrite(nitrito) transition metal complexes [1], crystals of the compound, *trans*-{[Cr(en)$_2$ONO]$_2$-(H$_3$O$_2$)}(ClO$_4$)$_3$ (**1**) were prepared. The structure of **1**, which is the subject of this report, has two unique features, a nitrito group bound to a Cr(III) atom and dimeric cations with a hydrogen oxide, $H_3O_2^-$, bridge between the two Cr(III) atoms. Searches of the data bases of the Cambridge [2] and CRYSTDAT [3] files found only one reference of a Cr(III) nitrito complex, [Cr(py)$_3$(NO)(ONO)$_2$]·py [4]. Hitchman and Rowbottom [5] also mention this structure in their review of transition metal nitrite complexes.

No reports of binuclear Cr(III) complexes being bridged by a single $H_3O_2^-$ group have been found. Hydrogen oxide bridging ligand structures have been reviewed recently by Ardon and Bino [6]. This type of bridging ligand has been found in a number of octahedral complexes which were originally considered to be hydroxy–aquo complexes. The review points out three Cr(III) complexes with the potential of having $H_3O_2^-$ bridges. One is *cis*-{[Cr(bpy)]$_2$(H$_3$O$_2$)$_2$}I$_4$·2H$_2$O which is dimeric with two *cis* bridges between the Cr atoms [7]. The second, *trans*-{[Cr(NH$_3$)$_3$(OH)]$_2$(H$_3$O$_2$)}Br$_3$·2H$_2$O, is polymeric with chemically identical units bridged by $H_3O_2^-$ groups, ... (H$_3$O$_2$)[(NH$_3$)$_3$Cr(OH)$_2$Cr(NH$_3$)$_3$]-(H$_3$O$_2$)[(NH$_3$)$_3$Cr(OH)$_2$Cr(NH$_3$)$_3$]... [8]. The third compound, *cis*-[Cr(2-pyridylmethylamine)$_2$(H$_2$O)-(OH)]S$_2$O$_6$ has the potential to form $H_3O_2^-$ bridges, but yet is a genuine hydroxy–aquo complex without $H_3O_2^-$ ligands [9]. The only complexes mentioned in the review which are dimeric with one $H_3O_2^-$ bridge between two metal atoms are *trans*-{[Co(en)$_2$NO$_2$]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$·2H$_2$O and *trans*-{[Co(en)$_2$NCS]$_2$(H$_3$O$_2$)}(CF$_3$SO$_3$)$_3$·H$_2$O [10].

## Experimental

The preparation of **1** was a multistep synthesis involving the following compounds in order of preparation: *trans*-[Cr(en)$_2$F$_2$]Cl [11], *trans*-[Cr(en)$_2$-Br$_2$]Br·H$_2$O [11], *trans*-[Cr(en)$_2$(ONO)Br]-ClO$_4$·2H$_2$O [12] and **1** [12]. The overall % yield is approximately 0.2% starting with 30 g of CrCl$_3$·6H$_2$O and obtaining 0.10 g of **1** after recrystallization. *Anal.* Calc. for C$_8$H$_{35}$N$_{10}$O$_{18}$Cl$_3$Cr$_2$: C, 12.48; H, 4.58; N, 18.20. Found: C, 12.75; H, 4.62; N, 18.30%.

Crystals of **1** for the structure determination were grown by dissolving the recrystallized complex in absolute ethanol and allowing anhydrous diethyl ether to isotropically distill into the complex solution in the refrigerator for two days. The crystals were filtered from solution and dried under vacuum.

A crystal was selected and mounted on a glass fiber. Diffraction measurements were made on the crystal at 21 °C on a Nicolet R3mV diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained from 29 reflections in the range $28.55 < 2\theta < 42.99°$. Crystal data for **1** are: monoclinic space group *C*2/*c* (No. 15), $a = 22.336(9)$, $b = 8.128(3)$, $c = 15.486(5)$ Å, $\beta = 96.15(3)°$, $V = 2795(2)$ Å$^3$, $D_{calc} = 1.83$ g/cm$^3$, $Z = 4$. A total of 7286 reflections was measured ($\pm h$, $\pm k$, $\pm l$) of which 1835 were unique; 1643 of these were considered to be observed ($I > 3\sigma(I)$) and were used in subsequent calculations. Final residual values were: $R$, 0.046; $R_w$, 0.0738.

The structure was solved by direct methods (SHELXTL PLUS) [13] and refined using full-matrix least-squares; non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

## Results and discussion

The structure of **1** is shown in Fig. 1 and a packing view of the unit cell along the *b* axis is shown in Fig. 2. Some selected bond distances and bond angles are given in Fig. 1. The cationic portion of **1** consists of two bis-ethylenediaminenitritochromium(III) units bridged by an $H_3O_2^-$ anion; the central hydrogen atom of this bridging ligand lies on a crystallographic

*Authors to whom correspondence should be addressed.

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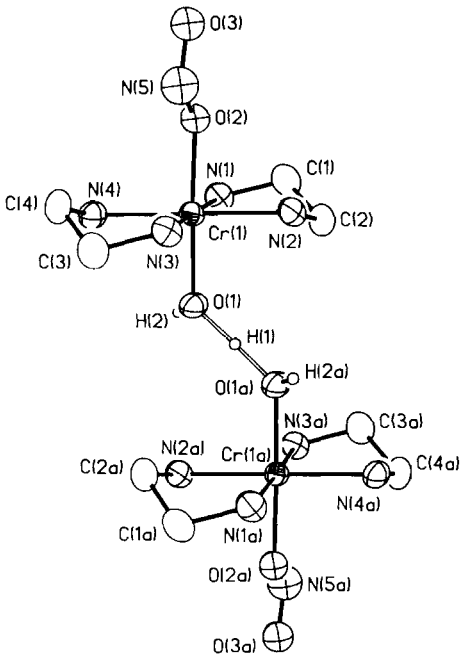


Fig. 1. Structure of *trans*-{[Cr(en)$_2$ONO]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$ showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Cr(1)–O(1), 1.957(3); Cr(1)–O(2), 1.974(6); Cr(1)–N(1), 2.078(4); Cr(1)–N(2), 2.073(4); Cr(1)–N(3), 2.066(4); Cr(1)–N(4), 2.080(4); O(2)–N(5), 1.308(10); O(3)–N(5), 1.228(10); O(1)–Cr–O(2), 171.7(2); N(1)–Cr(1)–N(3), 177.4(2); N(2)–Cr(1)–N(4), 177.6(2); Cr(1)–O(2)–N(5), 118.2(6); O(2)–N(5)–O(3), 117.4(8).

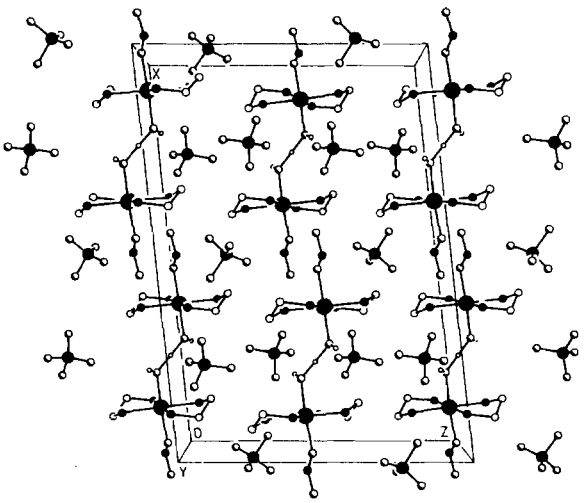


Fig. 2. Packing view of unit cell of *trans*-{[Cr(en)$_2$ONO]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$ down the *b* axis.

inversion center ($-\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{2}$) which relates the two halves of the dimeric cation. One of the perchlorate anions occupies a general position in the cell, while

TABLE 1. Comparison of structural data

| Nitrite data | M–ONO (Å) | MO–NO (Å) | MON–O (Å) | <MON (°) | <ONO (°) | *R* | Reference |
|---|---|---|---|---|---|---|---|
| *trans*-{[Cr(en)$_2$ONO]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$ | 1.976(7) | 1.316(11) | 1.221(12) | 118.2(6) | 117.4(8) | 0.046 | this work |
| | 1.968(12)[a] | 1.226(20)[a] | 1.196(10)[a] | 119.6(10)[a] | 120.1(14)[a] | | |
| [Cr(py)$_3$(NO)(ONO)$_2$]·py | 1.96(1) | 1.34(1) | 1.13(1) | 115.0(7) | 112(1) | 0.059 | 4 |
| *trans*-[Co(en)$_2$(ONO)(NCS)]I | 1.915(7) | 1.30(1) | 1.24(1) | 115.1(6) | 112.8(10) | 0.054 | 14 |
| *trans*-[Co(en)$_2$(ONO)(NCS)]ClO$_4$ | 1.875(7) | 1.30(1) | 1.25(1) | 115.0(6) | 112.8(9) | 0.081 | 14 |
| $H_3O_2^-$ bridge data | O–O($H_3O_2^-$) (Å) | M–O($H_3O_2^-$) (Å) | M...M (Å) | <MOO($H_3O_2^-$) (°) | MO...OM (°) | | |
| *trans*-[Cr(en)$_2$ONO]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$ | 2.410(3) | 1.957(4) | 5.77 | 130.0(3) | 180 | 0.046 | this work |
| *cis*-{[Cr(bpy)]$_2$(H$_3$O$_2$)$_2$}I$_4$·2H$_2$O | 2.446(5) | 1.925(3) | 5.03 | 127.1(2) | 64.9 | 0.037 | 7 |
| | | 1.928(3) | | 126.2(2) | | | |
| *trans*-{[Cr(NH$_3$)$_3$(OH)]$_2$(H$_3$O$_2$)}Br$_3$·2H$_2$O | 2.450(5) | 1.983(3) | 5.64 | 123.5(1) | 147.2 | 0.048 | 8 |
| | | 1.975(4) | | 125.4(1) | | | |
| *trans*-{[Co(en)$_2$(NO$_2$)]$_2$(H$_3$O$_2$)}(ClO$_4$)$_3$·2H$_2$O | 2.412(9) | 1.906(6) | 5.67 | 129.8(3) | 180 | 0.063 | 10 |
| *trans*-{[Co(en)$_2$(NCS)]$_2$(H$_3$O$_2$)}(CF$_3$SO$_3$)$_3$·H$_2$O | 2.415(6) | 1.911(5) | 5.77 | 135.9(3) | 174.3 | 0.037 | 10 |
| | | 1.916(5) | | 132.3(3) | | | |

[a]The values for the minor component of the dimer.

over two possible sites which are occupied in a 60:40 ratio (as determined by refinement of occupacy factors in the latter stages of refinement). The packing is influenced by extremely weak hydrogen bonding involving ethylenediamine N–H groups and perchlorate oxygen atoms (N...O distances ranging from 2.934–3.106 Å).

The nitrito group is bound to the Cr in a *trans* arrangement with O(3) far removed from the metal. The bond distance and angle values of the ONO ligand are compared to values of similar complexes in Table 1. There are some minor differences between the values for **1** and those of the Cr and Co compounds. The ONO ligand of **1** and the Co complexes have smaller differences between the NO distances of the nitrito group than does the Cr nitrito/nitrosyl complex. This difference of NO bond lengths was noted in the report on the Cr nitrito/nitrosyl complex, but was not explained [4].

Data describing the $H_3O_2^-$ bridges in two Cr(III) and two Co(III) complexes are given in Table 1 along with similar data for **1**. As mentioned above the two Co(III) complexes are the only ones with a $H_3O_2^-$ bridge like that of **1** and the data closely compare. The two Cr(III) complexes which have two bridges per complex have bond angles and distances which do not match those of **1**.

The two types of $ClO_4^-$ ions in the crystal – those in the proximity of the $H_3O_2^-$ bridges and those close to the ONO groups – have different bond parameters (Fig. 2). The former have Cl–O bond distances ranging from 1.42–1.44 Å and < OClO values of 109(1)°. The latter show greater variability in bond distances and bond angles: 1.2–1.5 Å and 109(9)°. The $ClO_4^-$ ions near the $H_3O_2^-$ probably experience a directional force which decreases the anisotropy in the bond parameters, while those near the nitrite ligand have an absence of such forces and are distorted through both static and dynamic disorder. The latter effect was observed with the $ClO_4^-$ ion in *trans*-$[Co(en)_2(ONO)(NCS)]ClO_4$ [14].

## Supplementary material

A figure showing the nitrito disorder and tables of crystallographic details, bond distances and angles, anisotropic and thermal parameters, refined hydrogen atom coordinates, and observed and calculated structure factors for **1** (12 pages total) may be obtained from author W.T.P.

## Acknowledgement

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