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# Crystal structure of *catena*-diaqua-sodium (3,6-dioxopiperazine-2-yl)-acetate, $Na(H_2O)_2(C_6O_4N_2H_7)$

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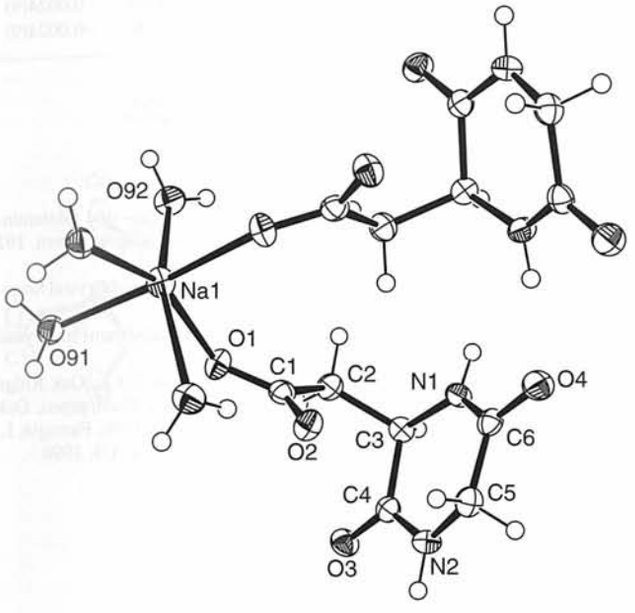


**Abstract**

$C_6H_{11}N_2NaO_6$, monoclinic, $P12_1/c1$ (No. 14), $a = 13.9552(5)$ Å, $b = 10.7372(3)$ Å, $c = 6.2156(2)$ Å, $\beta = 93.981(1)°$, $V = 929.1$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.100$, $T = 200$ K.

**Source of material**

The title compound was obtained as a by-product from the reaction of the dipeptide diester H–Gly–L–Asp(OMe)$_2$ with $NiCl_2$ and NaOMe in methanol and water (at 333 K) and was recrystallized from water [1].

**Discussion**

Recently, a facile synthesis of cyclotetrapeptide complexes by cyclocondensation of non-activated dipeptide esters at planar metal templates ($Cu^{2+}$, $Ni^{2+}$, $Pd^{2+}$) was reported [2,3]. Also dipeptide esters with functional side chains (Asp, Glu, Lys residues) could be condensated at a metal ion to cyclotetrapeptides [1]. During attempts to synthesize water soluble cyclotetrapeptide complexes the title compound was obtained from a reaction mixture of H–Gly–L–Asp(OMe)$_2$, NaOMe, $NiCl_2$ in methanol and water.

The carboxylate ligand with a diketopiperazine moiety in the sodium compound is formed by cyclocondensation of the terminal amino groups in the glycine residue with the $\alpha$-$CO_2$Me group of the aspartic acid component in Gly-L-Asp(OMe)$_2$ and by hydrolysis of the second carboxylic ester. The sodium ion is surrounded by six oxygen atoms (four water molecules and two carboxylate groups) in a distorted octahedral fashion. O91, O92, and O1 form the planes of the plane-linked octahedra along the *c* axis. A similar chain structure is formed by potassium hydrogen L-aspartate dihydrate [4,5]. The Na—O bond lengths are between 2.325(2) Å and 2.460(2) Å. O2, O3, and O4 have no metal contacts but act as well as O1 as acceptors in hydrogen bonds with the donors O91, O92, N1 and N2. The crystal contains both the *S* and *R* enantiomers (space group $P2_1/c$), i.e. racemisation at the $\alpha$-carbon atom of H–Gly–L-Asp(OMe)$_2$ has occurred during the reaction.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colourless platelet, size 0.02 × 0.05 × 0.18 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 1.83 cm$^{-1}$ |
| Diffractometer, scan mode: | Nonius Kappa CCD, $\omega/\varphi$ |
| $2\theta_{max}$: | 54.96° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 19963, 2117 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 1493 |
| $N(param)_{refined}$: | 180 |
| Programs: | SHELXS-97 [6], SHELXL-97 [7], ORTEP-III [8] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(911) | 4*e* | 0.818(2) | 0.237(3) | –0.223(4) | 0.040(8) |
| H(912) | 4*e* | 0.847(2) | 0.120(3) | –0.164(5) | 0.047(9) |
| H(921) | 4*e* | 1.068(2) | 0.428(3) | –0.280(5) | 0.045(8) |
| H(922) | 4*e* | 0.988(2) | 0.485(3) | –0.259(5) | 0.06(1) |
| H(81) | 4*e* | 1.418(2) | 0.194(3) | –0.037(4) | 0.028(6) |
| H(82) | 4*e* | 1.348(2) | –0.207(3) | 0.066(4) | 0.034(7) |
| H(21) | 4*e* | 1.262(2) | 0.210(2) | –0.281(3) | 0.023(6) |
| H(22) | 4*e* | 1.226(2) | 0.091(2) | –0.402(4) | 0.023(6) |
| H(3) | 4*e* | 1.386(2) | 0.059(2) | –0.317(3) | 0.018(5) |
| H(51) | 4*e* | 1.438(2) | –0.095(2) | 0.317(4) | 0.031(6) |
| H(52) | 4*e* | 1.332(2) | –0.051(2) | 0.320(4) | 0.031(6) |

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**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Na(1) | 4*e* | 0.98943(6) | 0.26909(8) | 0.0432(1) | 0.0263(5) | 0.0292(5) | 0.0181(4) | –0.0012(4) | 0.0021(3) | –0.0009(3) |
| O(1) | 4*e* | 1.0896(1) | 0.1466(1) | –0.1795(2) | 0.0226(8) | 0.0316(9) | 0.0250(8) | 0.0060(7) | –0.0011(6) | 0.0010(6) |
| O(2) | 4*e* | 1.1888(1) | 0.0540(1) | 0.0682(2) | 0.0254(8) | 0.0312(9) | 0.0223(8) | 0.0031(7) | 0.0041(6) | 0.0074(7) |
| O(3) | 4*e* | 1.2887(1) | –0.1440(1) | –0.2928(2) | 0.0297(9) | 0.0256(8) | 0.0268(8) | –0.0025(7) | 0.0011(7) | –0.0070(7) |
| O(4) | 4*e* | 1.4548(1) | 0.1403(1) | 0.3367(2) | 0.038(1) | 0.0276(9) | 0.0251(8) | 0.0020(7) | –0.0060(7) | –0.0075(7) |
| O(91) | 4*e* | 0.8676(1) | 0.1868(2) | –0.2093(3) | 0.0230(9) | 0.0272(9) | 0.0300(9) | 0.0011(8) | 0.0028(7) | 0.0039(7) |
| O(92) | 4*e* | 1.0154(1) | 0.4154(2) | –0.2253(3) | 0.031(1) | 0.0278(9) | 0.0290(9) | 0.0012(8) | 0.0085(7) | 0.0035(7) |
| N(1) | 4*e* | 1.3985(1) | 0.1194(2) | –0.0107(3) | 0.025(1) | 0.0185(9) | 0.0226(9) | –0.0030(8) | 0.0004(7) | –0.0006(8) |
| N(2) | 4*e* | 1.3592(1) | –0.1275(2) | 0.0439(3) | 0.028(1) | 0.0177(9) | 0.025(1) | –0.0005(8) | 0.0030(7) | 0.0013(8) |
| C(1) | 4*e* | 1.1708(2) | 0.1064(2) | –0.1115(3) | 0.025(1) | 0.019(1) | 0.022(1) | –0.0008(9) | 0.0001(8) | –0.0035(9) |
| C(2) | 4*e* | 1.2515(2) | 0.1216(2) | –0.2613(4) | 0.024(1) | 0.025(1) | 0.021(1) | 0.0016(9) | 0.0012(9) | 0.0014(9) |
| C(3) | 4*e* | 1.3460(2) | 0.0560(2) | –0.1894(3) | 0.022(1) | 0.022(1) | 0.016(1) | –0.0015(9) | 0.0034(8) | –0.0006(8) |
| C(4) | 4*e* | 1.3284(2) | –0.0803(2) | –0.1451(3) | 0.018(1) | 0.023(1) | 0.023(1) | 0.0013(9) | 0.0058(8) | –0.0021(9) |
| C(5) | 4*e* | 1.3865(2) | –0.0544(2) | 0.2355(3) | 0.026(1) | 0.029(1) | 0.019(1) | 0.001(1) | 0.0006(9) | 0.0024(9) |
| C(6) | 4*e* | 1.4154(2) | 0.0769(2) | 0.1891(3) | 0.020(1) | 0.025(1) | 0.022(1) | 0.0044(9) | 0.0023(8) | –0.0024(9) |

## References


1. Schapp, J.; Haas, K.; Sünkel, K.; Beck, W.: Cyclopeptide Complexes of Nickel(II) and Palladium(II) by Template Synthesis from Dipeptide Esters with Functional Chains. Eur. J. Inorg. Chem., submitted.
2. Haas, K.; Ponikwar, W.; Nöth, H.; Beck, W.: Facile Snthesis of cyclic Tetrapeptides from Nonactivated Peptide Esters on Metal Centers. Angew. Chem. Int. Ed. **37** (1998) 1086-1089.
3. Haas, K.; Ehrenstorfer-Schäfers, E.-M.; Polborn, K.; Beck, W.: Bis(dipeptide ester) Complexes of Palladium(II) — Precursors for the Formation of Cyclotetrapeptides. Eur. J. Inorg. Chem. (1999) 465-469.
4. Schmidbaur, H.; Bach, I.; Wilkinson, D. L.; Müller, G.: Preparation and Crystal structures of Lithium Hydrogen L-Aspartate Hydrate and Potassium Hydrogen L-Aspartate Dihydrate. Chem. Ber. **122** (1989) 1427-1431.
5. Schmidbaur, H.; Classen, H. G.; Helbig, J.: Asparagin- und Glutaminsäure als Liganden für Alkali- und Erdalkalimetalle. Angew. Chem. **102** (1990) 1122-1136.
6. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
8. Burnett, M. N.; Johnson, C. K.: ORTEP-III version 1.0.2.: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge National Laboratory Report ORNL-6895, USA 1996; Farrugia, L. J.: Windows 32-bit version 1.04, University of Glasgow, UK 1998.