Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Sodium citrate dihydrate doped with Mn^{3+} ions

Dejan Poleti,[a] Ljiljana Karanović,[b]* Tamara Đordjević[c] and Katarina Đuriš[d]

[a]Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia, [b]Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia, [c]Institut für Mineralogie und Kristallographie, Universität Wien-Geozentrum, Althanstrasse 14 A, 1090 Vienna, Austria, and [d]Institute for Multidisciplinary Research, Kneza Višeslava 1, 11000 Belgrade, Serbia
Correspondence e-mail: ljika2002@yahoo.com

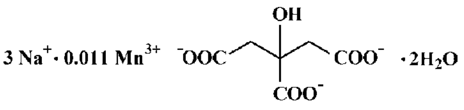
Received 26 June 2009
Accepted 31 July 2009
Online 19 August 2009

Sodium citrate dihydrate doped with Mn^{3+} ions, namely trisodium(I) managnese(III) citrate(3−) dihydrate, $[Na_3Mn_{0.011}(C_6H_5O_7)(H_2O)_2]_n$, was obtained during attempts to prepare some complex Mn^{III} citrates from a concentrated strong alkaline solution containing Na^+, Mn^{3+} and citrate ions. The compound is isostructural with the recently described $Na_3(C_6H_5O_7)\cdot 2H_2O$ [Fischer & Palladino (2003). *Acta Cryst.* E**59**, m1080–m1082]. The essential difference between these two structures is the presence of a very small proportion (0.205 wt%) of Mn^{3+} ions, which are positioned at the special 4*e* Wyckoff position in *C*2/*c*, where they are in a highly distorted octahedral environment of O atoms from two citrate anions.

Comment

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) belongs to the group of polycarboxylic acids present in biological fluids and playing very important roles in biochemical processes. Complexes of citric acid also attract considerable attention in the production of special materials, such as high-conductive $LaNiO_3$ and $LaMnO_3$ (Počuča *et al.*, 2007; Đuriš *et al.*, 2007), using a modification of Pechini's method (Pechini, 1967; Keishi & Toshio, 2005; Petrykin & Kakihana, 2005). In spite of this, not many citrate complexes have been structurally characterized. For example, only three Mn compounds – polymeric $\{K[Mn^{III}(C_6H_5O_7)(H_2O)]\}_n$ (Xie *et al.*, 2005), as well as mononuclear $(NH_4)_4[Mn^{II}(C_6H_5O_7)_2]$ and $(NH_4)_5[Mn^{III}(C_6H_4O_7)_2]\cdot 2H_2O$ (Matzapetakis *et al.*, 2000) – have been reported so far. No Na-containing analogues of these complexes have been described.

During attempts to prepare single crystals of complex Mn^{III} citrates from a strongly alkaline aqueous solution (pH ∼ 13) containing Na^+ ions, crystals of the title compound, (I), were obtained together with the already described sodium citrate salts $Na_3(C_6H_5O_7)\cdot 2H_2O$ (Fischer & Palladino, 2003) or $Na_3(C_6H_5O_7)\cdot 5.5H_2O$ (Viossat *et al.*, 1986). The presence and oxidation state of Mn were confirmed by a qualitative energy dispersive X-ray spectroscopy (EDX) analysis and crystal colour, respectively.



(I)

The structure analysis indicated that the investigated compound is isostructural with the recently described $Na_3(C_6H_5O_7)\cdot 2H_2O$ (Fischer & Palladino, 2003). The minor discrepancies in the unit-cell dimensions and volume (∼0.1%) are negligible (see Table 2). The two structures are essentially identical with no significant differences in bond distances and angles. Both structures contain three Na^+ ions bonded to a triply deprotonated citrate anion and two water molecules (Fig. 1). The citrate anion acts as a heptadentate ligand coordinated to two Na1, three Na2 and four Na3 cations. In addition to O atoms from COO and OH groups, the Na^+ ions also coordinate two water O atoms (O8 and O9) and are in a distorted octahedral environment. The Na polyhedra create very narrow channels extending parallel to the [101] and [001] directions (Fig. 2). These channels accommodate H atoms from the citrate ions and water molecules.

The only difference between these two structures is the presence of a very small proportion (0.205 wt%) of Mn^{3+} ions positioned on the twofold rotation axis at special Wyckoff site 4*e* in *C*2/*c*. The Mn^{3+} ions are in a highly distorted octahedral

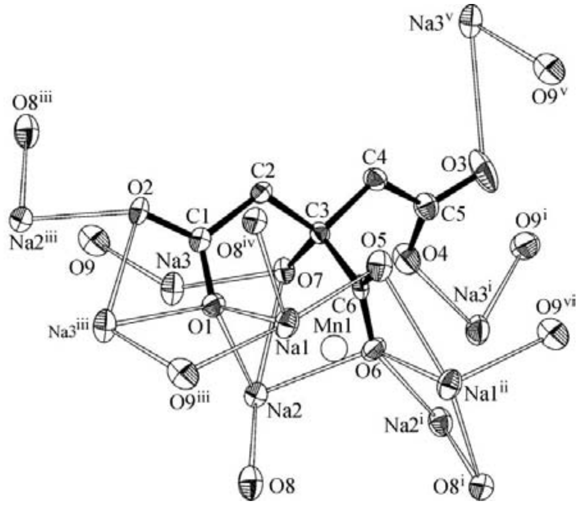


Figure 1
The binding of the citrate anion (dark bonds) coordinated to Na^+ in $Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O$, showing the atomic numbering scheme (50% probability displacement ellipsoids). H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iv) $x, -y+1, z-\frac{1}{2}$; (v) $-x+1, -y, -z$; (vi) $x-\frac{1}{2}, y+\frac{1}{2}, z$.]

doi:10.1107/S0108270109030595

environment of O atoms (O4, O6 and O7) arising from two citrate anions (Fig. 3). The Mn—O distances range from 1.9514 (15) to 2.585 (10) Å (Table 1). Four of them are close to the expected value of 2.045 Å, calculated from ionic radii (Shannon, 1976). However, the remaining two distances (Mn—O6) are much longer than the longest distance observed, for example, in $(NH_4)_5[Mn^{III}(C_6H_4O_7)_2]\cdot 2H_2O$ [2.224 (1) Å; Matzapetakis *et al.*, 2000]. Values comparable to those observed here are found in the low-temperature form of the mineral bixbyite, Mn_2O_3, where three of the five independent Mn^{3+} ions have one Mn—O distance of about 2.50 Å (Geller, 1971).

At first sight the distortion of the Mn octahedron can be attributed to the Jahn–Teller effect, but in that case the two long Mn—O bonds are expected to be in *trans* positions. Nevertheless, a theoretical study of $MnPO_4$ using density functional theory calculations confirmed that the existence of two long (about 2.50 Å) Mn—O bonds in *cis* positions is also possible (Osorio-Guillen *et al.*, 2004). Another, probably better, explanation is that the shape of the Mn polyhedron is determined by the packing of the O atoms based on the existing sodium citrate framework. This is confirmed by calculating the centroid position of the corresponding set of O atoms in the structure reported by Fischer & Palladino (2003) and in our structure when the Mn ion is and is not included in the refinement. In all three cases, the position of the centroid almost coincides with the reported position of the Mn ion.

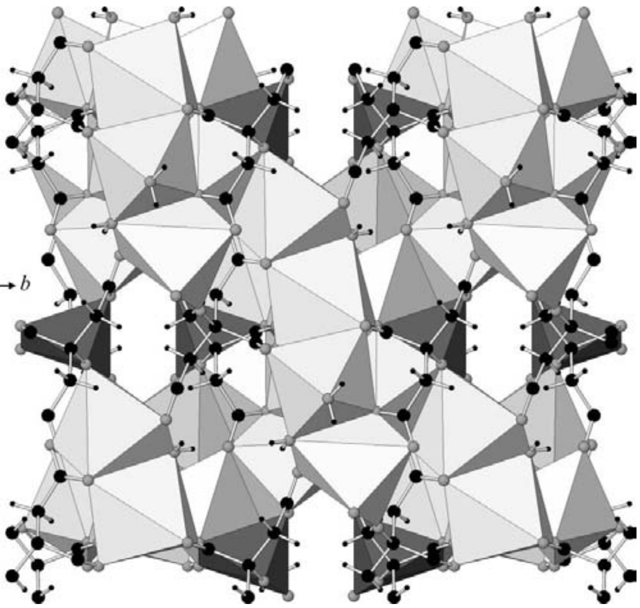


Figure 2
The narrow channels extending parallel to the [101] and [001] directions accommodating H atoms from the citrate ligand and water molecules in $Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O$ (C and H atoms are black, O atoms are grey, Na polyhedra are light grey and Mn polyhedra are dark grey).

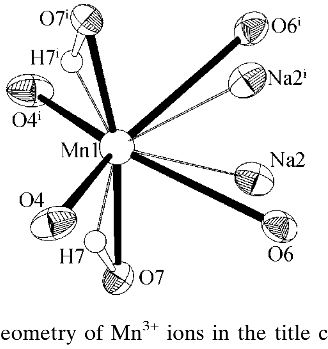


Figure 3
The coordination geometry of Mn^{3+} ions in the title compound. Atoms Na2 and H7, which must be absent when Mn1 is present, are also shown (50% probability displacement ellipsoids for non-H atoms). [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.]

It is notable that Mn^{3+} in $Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O$ occupies a similar environment compared to Mn^{3+} in $(NH_4)_5[Mn(C_6H_4O_7)_2]\cdot 2H_2O$ (Matzapetakis *et al.*, 2000). Both ions are in a distorted octahedral coordination formed by O atoms from two citrate ligands. Each citrate ion uses the central hydroxy and carboxylate groups, as well as one of the terminal carboxylate groups, to achieve coordination around Mn^{3+}. In our case, the $(Mn1)O_6$ polyhedron shares two edges with adjacent $(Na3)O_6$ and two vertices with adjacent $(Na1)O_6$ polyhedra (Fig. 2).

Refinement of the Mn^{3+} site-occupancy factor yielded the empirical formula $Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O$, meaning that one Mn^{3+} ion exists in only one of about 23 unit cells, and only one of about 92 available Mn sites is occupied. At the same time, to maintain reasonable bond distances and charge balance, some Na2 and H7 atoms must be absent (Fig. 3). Therefore, when Mn^{3+} ions are present some O7—H7 groups in the neighbourhood should be ionized and some Na^+ sites should be vacant. This resembles the mechanism of aliovalent substitution characteristic of inorganic compounds but does not quite satisfy the charge balance. Attempts to resolve this ambiguity were unsuccessful;apparently the sensitivity of the available experimental data is insufficient for this purpose.

In this case, the crystallization occurred from very concentrated aqueous solution, allowing Mn^{3+} ions to enter the crystal lattice at a place characteristic for some other Mn^{III} citrates. Our study confirmed the presence of Mn^{3+} ions at a level of only 0.2 wt%, demonstrating that when a suitable combination of light and heavy elements exists and high-quality experimental data are available, X-ray analysis can be a very powerful tool for determination of small impurities/dopants in unusual cases.

Experimental

Into an aqueous solution containing an equimolar mixture of Mn^{2+} ions and citric acid (~1 mol l^{-1}), a solution of NaOH (~1 mol l^{-1}) was added slowly until a pH of ~13 was reached. The presence of Mn^{3+} ions in this solution was confirmed by UV–vis spectroscopy. After about a month, slow evaporation of the mother liquor resulted in colourless needle-like (up to 20 mm long) crystals. These crystals were assumed to be one of the known sodium citrates (Fischer & Palladino, 2003; Viossat *et al.*, 1986) and were not further characterized. However, after about two months, a few brown prismatic crystals were obtained from the honey-like slurry solution. They were picked out, quickly washed by putting them into a drop of water to remove the mother liquor and dried using filter paper. The presence of Mn was confirmed by a qualitative EDX analysis (a quantitative determination was not possible owing to crystal decomposition under the given experimental conditions).

Crystal data

$[Na_3Mn_{0.011}(C_6H_5O_7)(H_2O)_2]$
M_r = 294.71
Monoclinic, $C2/c$
a = 15.7072 (3) Å
b = 12.4989 (2) Å
c = 11.2710 (2) Å
β = 103.5991 (10)°
V = 2150.71 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.28 mm^{-1}
T = 295 K
0.68 × 0.64 × 0.38 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003)
T_{min} = 0.833, T_{max} = 0.902
9936 measured reflections
2661 independent reflections
2508 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.078
S = 1.04
2661 reflections
202 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—Na2	2.594 (9)	Mn1—O7	1.9514 (15)
Mn1—O4	2.150 (6)	Mn1···H7	1.35 (2)
Mn1—O6	2.585 (10)		
O4^{i}—Mn1—O4	121.2 (6)	O7^{i}—Mn1—O7	168.0 (7)
O4—Mn1—O6	88.87 (13)	O7—Mn1—O4^{i}	95.2 (2)
O4—Mn1—O6^{i}	144.4 (3)	O7—Mn1—O4	78.83 (18)
O6^{i}—Mn1—O6	72.3 (3)	O7—Mn1—O6^{i}	120.1 (4)
O6—Mn1—O7	70.6 (2)		

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

Table 2
Comparison of $Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O$ unit-cell parameters with literature data (space group $C2/c$).

Compound	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
$Na_3Mn_{0.011}(C_6H_5O_7)\cdot 2H_2O^1$	15.7072 (3)	12.4989 (2)	11.2710 (2)	103.5991 (10)	2150.71 (7)
$Na_3(C_6H_5O_7)\cdot H_2O^2$	15.7044 (4)	12.5010 (4)	11.2837 (4)	103.5841 (13)	2153.26 (12)

Notes: (1) this work; (2) Fischer & Palladino (2003).

With the exception of Mn, all non-H atoms were refined anisotropically. H atoms were located in difference Fourier maps and refined isotropically with restraints applied to O—H bond distances in water molecules [O—H = 0.85 (2) Å].

The Mn^{3+} ion was located at special Wyckoff position 4e as a maximum of 1.25 e Å^{-3} in a ΔF map (the next highest peak was ~0.7 e Å^{-3}). To avoid significant correlations, the occupancy and isotropic atomic displacement parameter of Mn1 were tested in subsequent cycles. The final cycles of refinement were performed keeping the Mn1 isotropic atomic displacement parameter at a reasonable value of 0.025 Å^2, yielding an atom site occupancy of 0.0224 (8). The final R value for $F^2 > 2\sigma(F^2)$ of 0.029 may be compared with that of 0.033 obtained when Mn1 is not included in the refinement.

The highest residual maxima and minima in the final difference Fourier map are located about 0.80 Å from atom O3, suggesting possible disorder, which was not further investigated.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO–SMN* (Otwinowski & Minor, 1997; Otwinowski *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2009).

This research was partially supported by the Ministry of Science and Technological Development of the Republic of Serbia (grant No. 142030) and the Austrian Science Foundation, FWF (grant No. T300-N19 to TĐ.)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3205). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.
Đuriš, K., Branković, G., Branković, Z., Počuča, M. & Poleti, D. (2007). *Mater. Sci. Forum*, **555**, 237–242.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fischer, A. & Palladino, G. (2003). *Acta Cryst.* E**59**, m1080–m1082.
Geller, S. (1971). *Acta Cryst.* B**27**, 821–828.
Keishi, N. & Toshio, T. (2005). *Sol–Gel Processing of Thin Films with Metal Salts*, in *Handbook of Sol-Gel Science and Technology: Processing, Characterization, and Applications*, edited by Saka Sumio, pp. 59–64. Boston: Kluwer Academic Publishers.
Matzapetakis, M., Karligiano, N., Bino, A., Dakanali, M., Raptopoulou, C. P., Tangoulis, V., Terzis, A., Giapintzakis, J. & Salifoglou, A. (2000). *Inorg. Chem.* **39**, 4044–4051.
Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
Osorio-Guillen, J. M., Holm, B., Ahuja, R. & Johansson, B. (2004). *Solid State Ionics*, **167**, 221–227.
Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003). *Acta Cryst.* A**59**, 228–234.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Pechini, M. P. (1967). US Patent No. 3 330 697.
Petrykin, V. & Kakihana, M. (2005). *Chemistry and Applications of Polymeric Gel Precursors*, in *Handbook of Sol-Gel Science and Technology: Processing, Characterization, and Applications*, edited by Saka Sumio, pp. 78–97. Boston: Kluwer Academic Publishers.
Počuča, M., Branković, G., Branković, Z., Vasiljević-Radović, D. & Poleti, D. (2007). *J. Eur. Ceram. Soc.* **27**, 1083–1086.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Viossat, B., Rodier, N. & Eberle, J. (1986). *Bull. Soc. Chim. Fr.* pp. 522–525.
Westrip, S. P. (2009). *publCIF*. In preparation.
Xie, F.-T., Duan, L.-M., Chen, X.-Y., Cheng, P., Xu, J.-Q., Ding, H. & Wang, T.-G. (2005). *Inorg. Chem. Commun.* **8**, 274–277.