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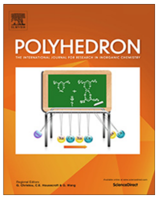

In(CH_3COO)$_3$: The first example of group 13 elements triacetate with an infinite chain crystal structure

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ABSTRACT

Single crystals of In(CH_3COO)$_3$ have been prepared by dissolution of basic indium carbonate In(OH)CO_3 in a mixture of anhydrous acetic acid and acetic anhydride. The crystal structure of In(CH_3COO)$_3$ has been solved and refined for the first time using single crystal X-ray diffraction data. It has a unique crystal structure buildup of 1D chains of InO_7 pentagonal bipyramids running along [0 1 0]. The compound has been characterized by ^{115}In NMR and NQR spectroscopy. Rather high values of quadrupole constant (C_Q = 182(1) MHz) and asymmetry parameter (η = 0.38) extracted from numerical simulation of experimental ^{115}In NMR and NQR spectra agree with large distortion and asymmetric coordination of In^{3+} in the crystal structure of In(CH_3COO)$_3$.

1. Introduction

Oxosalts of M^{3+} cations belonging to group 13 elements of the Periodic Table are easily hydrolysed and frequently form oxo- and hydroxy-salts. Despite the fact that the existence of anhydrous Al(CH_3COO)$_3$ is known from inorganic chemistry textbooks, no crystal structure data is available to our knowledge. Among cations of group 13 elements In^{3+} has the largest basicity and Redox stability and, therefore, one may expect the formation of unhydrolysed carboxylates. Neutral indium formiate In(HCOO)$_3$ could be an example and is known to exist with isolated octahedrally coordinated In^{3+} cations in the crystal structure [1].

Indium "acetate" has been prepared for the first time in 1869 by Meyer [2] by dissolution of indium hydroxide in acetic acid. Later Linden and Huber have reported the synthesis of In(CH_3COO)$_3$ by reaction of metallic In or (CH_3)$_3$In with anhydrous acetic acid [3]. They have failed to isolate single crystals appropriate for the crystal structure refinement but based on IR-spectra data have proposed that coordination number of In^{3+} in In(CH_3COO)$_3$ is 8. Later the crystal structures of indium(III)triacetate in complexes with 2,2′-dipyridine (bipy) and 1,10-phenanthroline (phen) have been refined [4]. In both In(CH_3COO)$_3$·bipy and In(CH_3COO)$_3$·phen complexes the acetate ligands and the N-donor ligand are bidentate and In^{3+} cations form a distorted dodecahedron with a coordination number (CN) 8.

Basic acetate In(μ-OH)(μ-O_2CCH_3)$_2$ is known to exist and poses 1D chain crystal structures [5]. Chain structures are also known for organoindium complexes with acetate In(CH_3)$_2$(CH_3COO) [6], In(C_2H_5)$_2$(CH_3COO) [7] and thioaceatate In(C_2H_5)$_2$(CH_3COS) [8]. Other examples of indium(III) acetates with additional chelate ligands are In(oep)(OAc) [9], In(tpyp)(OAc), In(tmpp)(OAc) [10], In(tpp)(OAc) [11].

One can expect that anhydrous indium triacetate may have the crystal structure similar to anhydrous rare-earth triacetates due to rather close ionic radius of In^{3+} (0.92 Å, CN = 8 [12]) and heavy lanthanides like Yb^{3+} (0.985 Å, CN = 8) and Lu^{3+} (0.977 Å, CN = 8). M(CH_3COO)$_3$ have 1D chain crystal structures. However, M^{3+} cations like M = Tm–Lu have capped trigonal prism (CN = 7) coordination, while larger cations like M = Sm–Er have CN = 8 [13].

In the present paper we report for the first time on crystal structure of indium triacetate In(CH_3COO)$_3$ solved and refined from single crystal data and its ^{115}In NMR and NQR spectroscopy studies.

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2. Experimental

Synthesis of $In(CH_3COO)_3$ was performed by dissolution of basic indium carbonate $In(OH)CO_3$ in a mixture of anhydrous acetic acid and acetic anhydride in 1:1 volume ratio boiled at 140 °C with stirring for 1 h. Obtained colorless solution was heated in evacuated and sealed glass ampoule at 150 °C followed by slow cooling down to room temperature for 10 days. Obtained colorless needle crystals were very fragile and could be destroyed by weak pressure. Single crystals thicken in air due to hydrolysis, therefore, all other manipulations with them were performed in a glove box.

The crystal structure of $In(CH_3COO)_3$ was determined by single-crystal X-ray diffraction. For this purpose, colorless needle crystal with dimensions ca. 0.45 × 0.10 × 0.10 mm was selected. Bruker SMART APEX II single-crystal diffractometer (graphite monochromatized Mo K radiation, λ = 0.71073 Å) at 173 K using ω scan mode was used for the data collection. Absorption correction based on measurements of equivalent reflections was applied. The structure was solved by direct methods and refined by full matrix least-squares on F^2 using shelxl-97 program package [14] with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined using a ridged model. Crystallographic data and structure refinement results are summarized in Table 1. X-ray diffraction studies were performed at the Centre of Shared Equipment of IGIC RAS. CCDC 1870126 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The field sweep NMR spectrum of ^{115}In nuclei (nuclear spin $I = 9/2$; natural abundance NA = 95.72%; gyromagnetic ratio $\gamma/2\pi = 9.30$ MHz/T; quadrupole moment $Q = 0.81$ barn) was measured at 5 K using a conventional phase-coherent pulsed NMR spectrometer (Tecmag-Apollo) at fixed frequency of 59.3 MHz. ^{115}In NQR spectrum was measured utilizing a home-built phase coherent pulsed NQR spectrometer at 4.2 K using a frequency step point-by-point spin-echo technique. The NMR and NQR spectra were obtained by integration over the spin echo magnitude envelope in the time domain at a given field and averaging over scan accumulation number which depends on temperature and type of experiment (NMR or NQR).

3. Results and discussion

3.1. Crystal structure of $In(CH_3COO)_3$

The crystal structure of $In(CH_3COO)_3$ viewed along unit cell axes is given in Fig. 1a–c. Selected interatomic distances are given in Table 2. The crystal structure of $In(CH_3COO)_3$ consists of infinite 1D chain of InO_7 pentagonal bipyramids running along [0 1 0]. In pentagonal bipyramid InO_7 oxygens O1—O4 are positioned in the equatorial plane, while O5 and O6 are in axial positions (Fig. 1d). In comparison with $M(CH_3COO)_3$, M = Tm–Lu [13] mentioned above, despite similar CN of M^{3+} cation, they have a different coordination polyhedron. InO_7 bipyramids are connected with each other by common corner (oxygen O1). Acetate fragments may be divided in two different groups. One group contains carbon atoms C3 and C5 with O3, O4 and O5, O6 oxygen atoms, respectively, which are connected to two different InO_7 bipyramids (μ_2-$\eta^1\eta^1$ *ZZ*). For these oxygen atoms short interatomic In-O distances ranging between 2.123(3) and 2.175(3) Å are observed. Oxygen atoms O1 and O2 belonging to C1 form edge of InO_7 bipyramid (μ_2-$\eta^2\eta^1$). This leads to a much longer In-O1 and In-O2 bond lengths and distorted C1-O interatomic distances in the acetate group (see Table 2) and a much smaller O1—C1—O2 angle of 118.5(4)° in comparison with that in O3—C3—O4 (126.9(4)°) and O5—C5—O6 (126.1(4)°). Surprisingly, only very week intermolecular interactions are observed between neighboring InO_6 chains.

Table 1
Crystallographic data and structure refinement results for $In(CH_3COO)_3$.

Fw	291.95
T (K)	173
Crystal System	monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	8.0770(10)
b (Å)	7.6481(10)
c (Å)	8.0859(10)
β (°)	116.825(2)
V (Å^3)	445.74(10)
Z	2
D_c (g cm^{-3})	2.175
μ (Mo Kα) (mm^{-1})	2.647
F(0 0 0)	284
Number of total reflections	3779
Number of unique reflections	1967
Number of observed reflections	1921
R_{int}	0.0255
R_1 [$I > 2\sigma(I)$], wR_2 (all data)	0.0268, 0.0666
GOF, Flack parameter	1.044, 0.06(4)

3.2. ^{115}In NMR and NQR studies

Experimental field sweep ^{115}In NMR spectrum of $In(CH_3COO)_3$ powder measured at 5 K at fixed frequency of 59.3 MHz is presented in Fig. 2. It demonstrates a very broad spin echo intensity distribution corresponding to a complicated powder pattern of $I = 9/2$ nuclei in the second order quadrupole perturbation. The position of the Larmor field $\mu_0H_L = 6.356$ T of ^{115}In nuclei at a given frequency is indicated by vertical solid red line. Narrow peak at 5.38 T is an extrinsic ^{27}Al signal originated from the NMR probe. To retrieve parameters of quadrupole interactions on In site in $In(CH_3COO)_3$ crystal structure we performed computer simulation of the experimental ^{115}In NMR spectrum using the SIMUL program which solves numerically the nuclear Hamiltonian including Zeeman and quadrupole interactions for our particular case of the powder field-sweep NMR spectrum at fixed frequency. The resulting theoretical spectrum shown in Fig. 2 by the green solid line demonstrates satisfactory resemblance with the experimental ^{115}In NMR spectrum. The extracted quadrupole parameters at In site (quadrupole constant $C_Q = e^2Qq_{zz}/h$ and asymmetry parameter η) are listed in Table 3. Knowledge of these values provides us an initial guess for the frequency range of approximately 7–30 MHz for searching the ^{115}In NQR lines with a-priory unknown frequency positions. Indeed, for $I = 9/2$ nuclei and axial symmetrical case with $\eta = 0$ the lowest $|\pm1/2\rangle \leftrightarrow |\pm3/2\rangle$ quadrupole transition frequency should occur at $\nu_Q = 3e^2Qq_{zz}/2I(2I\text{-}1)h = C_Q/24 = 7.2$ MHz with higher quadrupole transitions ($|\pm3/2\rangle \leftrightarrow |\pm5/2\rangle$, $|\pm5/2\rangle \leftrightarrow |\pm7/2\rangle$, $|\pm7/2\rangle \leftrightarrow |\pm9/2\rangle$) at $2C_Q/24 = 14.4$ MHz, $3C_Q/24 = 21.6$ MHz and $4C_Q/24 = 28.8$ MHz, respectively (see Insert in Fig. 3). ^{115}In NQR experimental spectrum measured at 4.2 K is presented in Fig. 3.

To our knowledge, this is the first direct observation of ^{115}In NQR spectrum in organic indium coordination complexes. Unexpectedly, it consists of five lines instead of four which one would expect to see in NQR spectrum of $I = 9/2$ nuclei. It is also quite unusual to observe a broad spin echo intensity distribution in wide frequency range of 10–33 MHz. Fortunately, the relative frequency values of NQR transition lines are strictly determined by asymmetry parameter η as shown in the Inset in Fig. 3. This simplifies essentially the spectrum analysis and line assignment. The numerical simulation of the observed ^{115}In NQR spectrum was performed by means of the SIMUL program used in the "NQR" mode. The

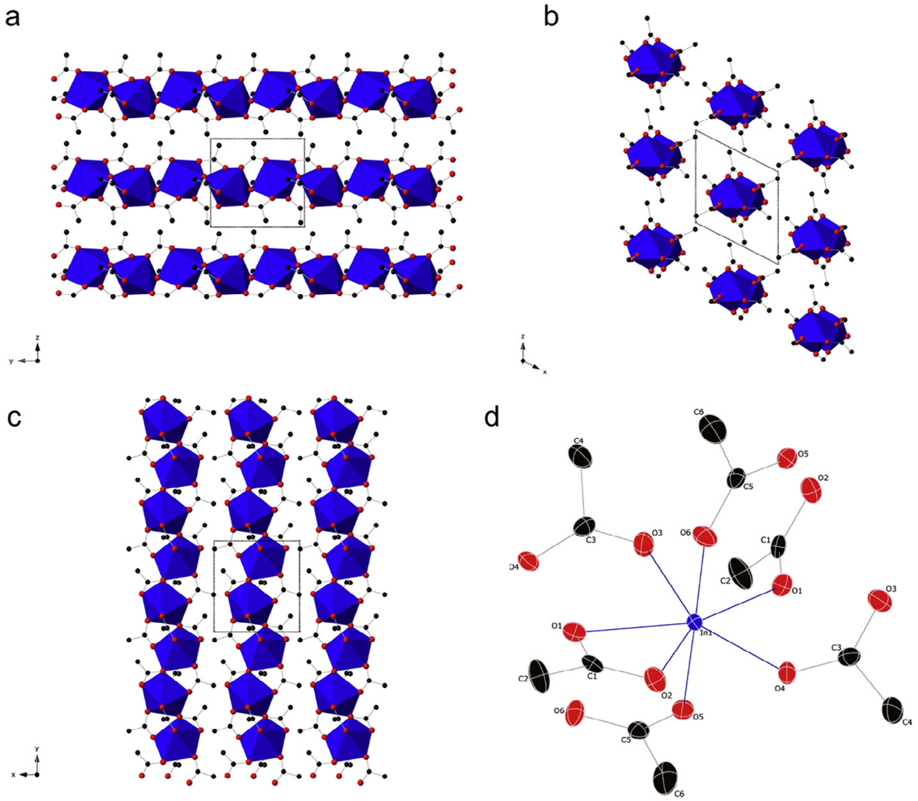

Fig. 1. Crystal structure of $In(CH_3COO)_3$ viewed along [1 0 0] (a), [0 1 0] (b), [0 0 1] (c) and the fragment around indium site drawn with displacement ellipsoids at the 50% probability level (d). Hydrogen atoms are omitted for clarity.

Table 2
Selected interatomic distances (Å) in the crystal structure of $In(CH_3COO)_3$.

In…In	3.9560(5)	In—O3	2.175(3)	C1—O1	1.297(5)
In—O1	2.236(3)	In—O4*	2.155(3)	C1—O2	1.235(6)
In—O1*	2.368(3)	In—O5	2.123(3)	C3—O3	1.249(5)
In—O2	2.273(3)	In—O6*	2.142(3)	C3—O4	1.245(6)
				C5—O5	1.261(5)
				C5—O6	1.253(5)

* Symmetry transformation: $1-x$, $-0.5+y$, $1-z$.

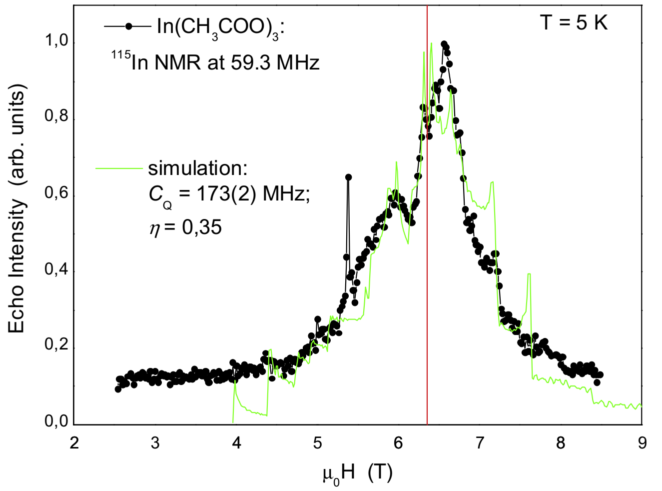

Fig. 2. ^{115}In NMR spectrum of the $In(CH_3COO)_3$ powdered sample measured at 5 K at fixed frequency of 59.3 MHz. Vertical solid red line is the position of the Larmor field $\mu_0 H_L = 6.356$ T of ^{115}In nuclei at 59.3 MHz. Green solid line is the calculated theoretical spectrum as discussed in the text. (Color online.)

Table 3
Parameters of quadrupole interactions on In site in $In(CH_3COO)_3$.

Experiment	Quadrupole constant $C_Q = e^2Qq_{zz}/h$ MHz	Asymmetry parameter η
NMR	173(2)	0.35
NQR	182(1)	0.38

resulting calculated spectrum including proper line broadening is shown in Fig. 3 by solid blue line. The frequency positions of the NQR transitions are indicated by thin vertical red lines. As seen from this figure the numerically calculated ^{115}In NQR spectrum demonstrates reasonable correspondence with the experimental one. The remarkable feature of these spectra is very close position of $|\pm 3/2\rangle \leftrightarrow |\pm 1/2\rangle$ and $|\pm 5/2\rangle \leftrightarrow |\pm 3/2\rangle$ NQR transitions resulting in unresolved intensive doublet at 14.0 MHz in perfect agreement with the η-dependence of the NQR transition frequencies shown in the Inset in Fig. 3. The quadrupole frequency and asymmetry parameter values extracted from the simulation spectrum are listed in Table 3. The remaining peaks at 10.2 MHz and 17.1 MHz as well as a broad spin echo intensity distribution observed between NQR peaks may originate from amorphous In-containing phase not registered by the X-ray powder diffraction.

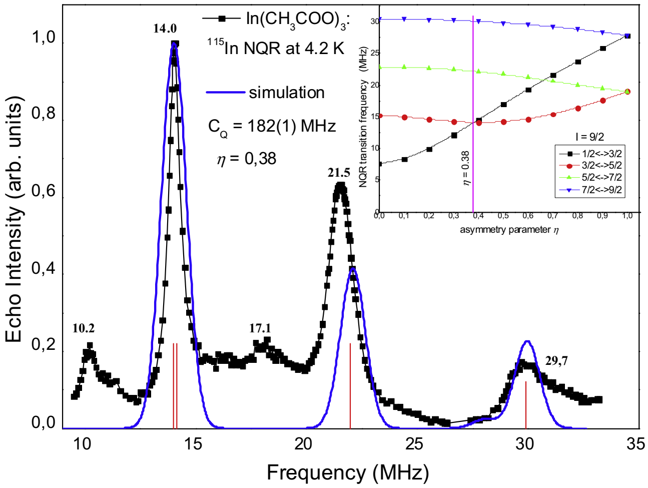

Fig. 3. ^{115}In NQR spectrum of In(CH$_3$COO)$_3$ measured at 4.2 K. Blue solid line is the calculated theoretical spectrum as discussed in the text. Vertical red lines are calculated frequencies of the NQR transitions. Inset: calculated relative values of the NQR transition frequencies as a function of asymmetry parameter η. The $\eta = 0.38$ value obtained for In(CH$_3$COO)$_3$ compound is indicated by vertical solid line. (Color online.)

It is worth to mention a surprisingly good agreement between quadrupole parameters extracted for the same In(CH$_3$COO)$_3$ sample by means of completely independent NMR and NQR experiments performed on different spectrometers which increases significantly a reliability of the obtained results. Moreover, the extracted quadrupole constant value for ^{115}In in 7-coordinated In^{3+} in In(CH$_3$COO)$_3$ is consistent with those observed using high field NMR in several In^{3+} organic complexes [15]. Indeed, in indium acetylacetonate (In(acac)$_3$) In^{3+} is in the center of a distorted octahedron with smaller and almost axially symmetric EFG ($\eta = 0.14$ [15]). This leads to reduced value of quadrupole constant $C_Q(^{115}\text{In}) = 106(2)$ MHz [15]. In contrast, In^{3+} coordination in I$_3$In[OP(p-Anis)$_3$]$_2$ is highly distorted trigonal bipyramid InI$_3$O$_2$ with high value of quadrupole constant $C_Q(^{115}\text{In}) = 200(4)$ MHz [15]. The experimental $C_Q(^{115}\text{In})$ values obtained by us for 7-coordinated In^{3+} in In(CH$_3$COO)$_3$ (Table 3) are only slightly higher than those found by Chen et al. [15] in indium *tris*(tropolonate) (In(trop)$_3$) with 6-coordinated In^{3+} (160(2) MHz) which also has high EFG due to rather large distortion of In coordination polyhedron. Moreover, relatively high value of asymmetry parameter $\eta = 0.38$ (3) is consistent with the lack of axial symmetry in InO$_7$ pentagonal bipyramid in In(CH$_3$COO)$_3$ in contrast to zero or low η values in 6-coordinated indium complexes reported by Chen et al. [15].

4. Conclusions

Single crystals of anhydrous In(CH$_3$COO)$_3$ were successfully prepared. In(CH$_3$COO)$_3$ has 1D chain crystal structure buildup of corner-shared InO$_7$ pentagonal bipyramids running along [010]. Results of ^{115}In NMR and NQR studies performed on powdered sample of In(CH$_3$COO)$_3$ showed rather high value of quadrupole constant $C_Q(^{115}\text{In})$ which is in agreement with large distortion of InO$_7$ polyhedron in the crystal structure.

Acknowledgment

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Appendix A. Supplementary data

CCDC 1870126 contains the supplementary crystallographic data for In(CH$_3$COO)$_3$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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