Structure of Sodium Acetylacetonate Monohydrate,* Na[C$_5$H$_7$O$_2$].H$_2$O

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Abstract. $M_r = 140 \cdot 12$, $P2_1/c$, $T = 140$ K, $a = 11 \cdot 102$ (3), $b = 6 \cdot 058$ (2), $c = 10 \cdot 287$ (3) Å, $\beta = 104 \cdot 50$ (2)°, $Z = 4$, $V = 669 \cdot 8$ (3) Å^3, D_m(298 K) = $1 \cdot 36$, D_x(140 K) = $1 \cdot 39$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 1 \cdot 57$ cm^{-1}, $R = 0 \cdot 033$, 1372 unique observed reflections, $F(000) = 288$, recrystallized from absolute ethanol/diethyl ether. The coordination about the Na$^+$ ion is distorted octahedral. Two *trans* water molecules act as symmetrical bridges between adjacent Na$^+$ ions with Na–O separation of $2 \cdot 423$ (1) and $2 \cdot 422$ (1) Å. Two other O atoms from a chelated acetylacetonate ligand have Na–O of $2 \cdot 318$ (1) and $2 \cdot 325$ (1) Å. Two additional O atoms from two neighboring chelate groups have Na–O of $2 \cdot 387$ (1) and $2 \cdot 382$ (1) Å and complete the coordination around the Na$^+$ ion. The Na$^+$ ions themselves form a zigzag chain parallel to the b axis of the crystal with Na$\cdots$Na of $3 \cdot 057$ (1) Å and an Na$\cdots$Na$\cdots$Na angle of $164 \cdot 4$ (1)°. The crystals are highly hygroscopic and decompose rapidly when exposed to air.

Introduction. Among the wide variety of metal complexes of β-diketonates, acetylacetonate (acac) complexes of closed-shell diamagnetic metal ions have received considerable attention for their spectroscopic behavior (Kelmo, Neilson & Shepherd, 1977; Kelmo & Shepherd, 1977; Clark & Conners, 1974; Sahbari & Tinti, 1983). Of the alkali-metal complexes, only the structures of Li(acac) (Schröder & Weber, 1975; Onuma & Shibata, 1978) and K(acac).$\frac{1}{2}$H$_2$O (Shibata, Onuma, Matsui & Motegi, 1975) have been reported. No information regarding the structures of the acac complexes of Na is available in the literature. During our solid-state spectroscopic investigation of the acac complexes of alkali-metal cations it was desirable to solve the crystal and molecular structure of the Na complex. This report presents the structure of the monohydrate, Na(acac)(H$_2$O).

Experimental. Obtained by addition of freshly distilled 2,4-pentanedione to a sodium ethoxide solution (West & Riley, 1958); colorless plate, freshly grown by slow evaporation of an absolute ethanol/diethyl ether solution and coated with epoxy resin while still wet with mother liquor, dimensions $0 \cdot 09 \times 0 \cdot 25 \times 0 \cdot 62$ mm; Syntex $P2_1$ diffractometer. $T = 140$ K, Mo $K\alpha$

radiation, graphite monochromator; unit-cell dimensions from a least-squares fit of nine reflections having $18° < 2\theta < 23°$; space group $P2_1/c$ based on conditions $0k0$, $k = 2n$; $h0l$, $l = 2n$; absorption correction factors $1 \cdot 02$ to $1 \cdot 07$, absorption ignored; ω scan (60° min^{-1}) (Hope & Nichols, 1981), $1 \cdot 0°$ range, $1 \cdot 0°$ offset for background, $2\theta_{max} = 55°$ in the positive quadrant with maximum h,k,l of 14, 8, 13, respectively; two check reflections, monitored every 100 reflections, displayed a random fluctuation of $< 2\%$; solved by direct methods, 1539 unique reflections, 1372 observed $[F > 3\sigma(F)]$ used in the solution and refinement (based on F); full-matrix least-squares refinement, anisotropic thermal parameters for non-hydrogen atoms, $R = 0 \cdot 033$, $R_w = 0 \cdot 037$, $w = 1/[\sigma^2(F_o) + 0 \cdot 00025F_o^2]$, $S = 1 \cdot 60$, ratio of maximum least-squares shift to error of $0 \cdot 191$ for U_{33} of O(3), average ratio of shift to error of $0 \cdot 035$, maximum and minimum heights in final difference Fourier map of $0 \cdot 28$ and $-0 \cdot 19$ e Å^{-3}, respectively, atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from the *SHELXTL* (version 3) package (Sheldrick, 1981).

Discussion. The final atomic fractional coordinates and equivalent isotropic thermal parameters are given in Table 1.† Bond angles and bond distances are listed in Table 2. The structure (Fig. 1) consists of zigzag chains of Na atoms with Na$\cdots$Na of $3 \cdot 057$ (1) Å and an Na$\cdots$Na$\cdots$Na angle of $164 \cdot 4$ (1)°. The chain has a direction parallel to **b** and is situated on the twofold screw axis. The c glide generates another chain separated by a distance of $0 \cdot 5c$ which is weakly cross-linked to the first *via* hydrogen bonds between the water H atoms and the acac carbonyl O atoms. Each Na atom is octahedrally coordinated to six O atoms, two of which belong to two *trans* water molecules. These water molecules bridge adjacent Na atoms in the chain with Na–O(1) of $2 \cdot 423$ (1) and Na–O(1^i) of $2 \cdot 422$ (1) Å. Of the remaining four O atoms, two belong to a chelated acac ligand with Na–O of

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† Lists of structure factors, anisotropic thermal parameters and bonds and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38561 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* *catena*-Poly{[μ_3-(2,4-pentanedionato-*O:O,O′:O′*)sodium]-μ-aqua}.

Table 1. *Fractional atomic coordinates and isotropic thermal parameters* ($\mathring{A}^2 \times 10^3$)

	x	y	z	U
Na	1·0193 (1)	0·0009 (1)	0·2554 (1)	16 (1)*
O(1)	0·9997 (1)	0·2506 (2)	0·0673 (1)	19 (1)*
O(2)	0·8551 (1)	−0·2055 (2)	0·1300 (1)	18 (1)*
O(3)	0·8536 (1)	0·2077 (2)	0·2900 (1)	18 (1)*
C(1)	0·6561 (1)	−0·3300 (3)	0·0124 (1)	22 (1)*
C(2)	0·7393 (1)	−0·1709 (2)	0·1076 (1)	15 (1)*
C(3)	0·6817 (1)	0·0000 (2)	0·1625 (1)	17 (1)*
C(4)	0·7381 (1)	0·1711 (2)	0·2495 (1)	15 (1)*
C(5)	0·6531 (1)	0·3262 (3)	0·2998 (1)	24 (1)*
H(AW)	0·941 (2)	0·235 (3)	0·003 (2)	45 (6)
H(BW)	1·056 (2)	0·258 (3)	0·029 (2)	54 (7)
H(1A)	0·672 (1)	−0·484 (3)	0·041 (2)	34 (5)
H(1B)	0·670 (2)	−0·316 (3)	−0·076 (2)	44 (5)
H(1C)	0·568 (2)	−0·310 (4)	0·008 (2)	43 (5)
H(3)	0·597 (2)	0·001 (3)	0·139 (2)	29 (4)
H(5A)	0·669 (2)	0·473 (3)	0·277 (2)	40 (5)
H(5B)	0·672 (2)	0·323 (4)	0·394 (2)	46 (5)
H(5C)	0·565 (2)	0·297 (3)	0·261 (2)	51 (6)

* Equivalent value of the anisotropic temperature factor coefficients (Willis & Pryor, 1975).

Table 2. *Interatomic distances* ($\mathring{A}$) *and angles* (°)

Na—O(1)	2·423 (1)	O(2)—C(2)	1·265 (2)
Na—O(2)	2·318 (1)	O(3)—C(4)	1·265 (1)
Na—O(3)	2·325 (1)	C(1)—C(2)	1·513 (2)
Na—O(3^i)	2·387 (1)	C(2)—C(3)	1·407 (2)
Na—O(2^{ii})	2·382 (1)	C(3)—C(4)	1·409 (2)
Na—O(1^i)	2·422 (1)	C(4)—C(5)	1·512 (2)
Na···Na^i	3·057 (1)	O(1)···O(3^{iii})	2·918 (1)
		O(1)···O(2^{iv})	2·904 (1)

O(1)—Na—O(2)	89·5 (1)	C(2)—O(2)—Na^i	131·0 (1)
O(1)—Na—O(3)	82·5 (1)	Na—O(3)—C(4)	129·1 (1)
O(2)—Na—O(3)	80·4 (1)	Na—O(3)—Na^{ii}	80·9 (1)
O(1)—Na—O(1^i)	170·2 (1)	C(4)—O(3)—Na^{ii}	131·8 (1)
O(2)—Na—O(1^i)	82·9 (1)	O(2)—C(2)—C(1)	116·1 (1)
O(3)—Na—O(1^i)	90·0 (1)	O(2)—C(2)—C(3)	126·3 (1)
O(1)—Na—O(2^{ii})	81·6 (1)	C(1)—C(2)—C(3)	117·6 (1)
O(2)—Na—O(2^{ii})	163·7 (1)	C(2)—C(3)—C(4)	128·4 (1)
O(3)—Na—O(2^{ii})	84·8 (1)	O(3)—C(4)—C(3)	126·2 (1)
O(1^i)—Na—O(2^{ii})	104·2 (1)	O(3)—C(4)—C(5)	116·5 (1)
O(1)—Na—O(3^i)	104·3 (1)	C(3)—C(4)—C(5)	117·3 (1)
O(2)—Na—O(3^i)	84·9 (1)	O(1)—H(AW)···O(3^{iii})	149 (2)
O(3)—Na—O(3^i)	163·8 (1)	O(1)—H(BW)···O(2^{iv})	156 (2)
O(1^i)—Na—O(3^i)	81·3 (1)	Na—O(1)—H(AW)	118 (2)
O(2^{ii})—Na—O(3^i)	110·5 (1)	Na—O(1)—H(BW)	119 (2)
Na—O(1)—Na^{ii}	78·3 (1)	H(AW)—O(1)—H(BW)	100 (2)
Na—O(2)—C(2)	129·3 (1)	H(AW)—O(1)—Na^{ii}	119 (2)
Na—O(2)—Na^i	81·1 (1)	H(BW)—O(1)—Na^{ii}	123 (2)

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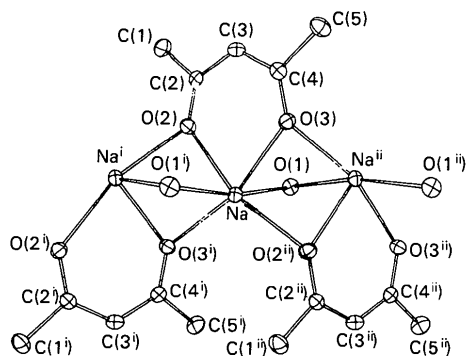

Fig. 1. A view of the structure normal to the *ab* plane showing how Na(acac)(H$_2$O) is propagated along the *b* direction and the atom labeling scheme.

2·318 (1) and 2·325 (1) Å, and two are from carbonyl O atoms of adjacent chelating acac groups with Na—O of 2·382 (1) and 2·387 (1) Å. Within the coordination environment, the chelated acac ligand has the shortest Na—O separations. The Na atom is 0·015 (1) Å out of the plane of the chelated ligand, but it is 1·759 (1) and 1·779 (1) Å out of the planes of the bridged acac groups (*i.e.* the C$_5$O$_2$ skeleton).

Recently (Sahbari & Olmstead, 1983) we reported the structure of the *cis*-octahedral complex [Ca(acac)$_2$(H$_2$O)$_2$].H$_2$O. Considering the similarity in ionic radii between Na (1·02 Å) and Ca (1·00 Å) for coordination number six (Shannon & Prewitt, 1969), similar *M*—O bond distances and bite angles would be expected. Some lengthening of the Na—O bonds due to bridging by every O atom might also occur. In fact, only the bonds to the water molecules seem to be much affected by bridging, while the bonds to the carbonyl O atoms are quite similar in length in the two metal complexes. The average values (average deviations in square brackets) are Na—O(acac), 2·353[32]; Ca—O(acac), 2·328[8]; Na—O(H$_2$O), 2·422[1]; Ca—O(H$_2$O), 2·356 (2) Å. As expected, the chelate bite angles are similar, with O—Na—O of 80·4 (1) and O—Ca—O of 76·2 (1)°.

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