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One-dimensional coordination polymers in the crystal structures of sodium and potassium acetylacetonates

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The mixed ligand complexes $[K_2(acac)_2(H_2O)]_{\infty}$ (I), $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (II), $[Na(acac)(H_2O)]_{\infty}$ (III), $[Na_3(acac)_3(^iPrOH)]_{\infty}$ (IV), $[Na_3(acac)_3(Py)]_{\infty}$ (V) and $[Na_2(acac)_2(phen)]_{\infty}$ (VI) (Hacac = pentane-2,4-dione; phen = 1,10-phenanthroline; $^iPrOH = iso$ -propanol; Py = pyridine) were synthesized by the reaction of the alkaline metal *tert*-butyloxide in dried solvent (iPrOH , benzene or Py) with Hacac and phen. The products were characterized by elemental analysis, 1H NMR and FTIR spectroscopy, and thermal analysis. The single-crystal structures were determined for the novel compounds II, IV and VI, and refined for I. The structures of I-VI consist of one-dimensional polymeric chains or ribbons which are described as a combination of formal binuclear structural blocks, $[M_2(acac)_2]$, of four types. Quantum chemical calculations on the four isomers of $[M_2(acac)_2]$ allowed us to explain different stabilities of the formal building blocks with M = Na and K.

Keywords: Sodium; Potassium; Acetylacetone; Beta-diketone; X-ray Crystal Structure; Coordination polymer; Mixed-ligand complex; Quantum chemical calculations.

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Introduction

Metal β -diketonates and their mixed-ligand complexes with different ancillary neutral ligands have successfully been used as precursors for vapor thin film deposition of functional materials [1-3] for the last thirty years. The advantages of β -diketonate complexes as precursors results from the easy control of the solubility or volatility by variation of substitutions and the introduction of different ancillary ligands. A great number of excellent experimental and theoretical works devoted to the synthesis, characterization and application of β -diketonates of transition metals [1], rare earth elements [2,4-5] and even alkaline earth elements [6-8] have been published describing the variety of superconductors, ferroelectric and magnetic thin films, etc. Among these functional materials there are a lot of alkaline metal-containing ones, such as $K_{1-x}Na_xNbO_3$ [9-10], $La_{1-x}K_yMnO_3$ [11], La_{1-x}Na_yMnO₃ [12] and (K, Rb, Cs)VO₃ [13]. However, the chemistry of alkaline metal β diketonates as precursors is practically unexplored. These complexes were not even mentioned in the comprehensive review by Fromm [14]. Besides, the capabilities of mixed-ligand complex formation with neutral donor ligands have not been studied systematically, despite this being an important approach to property modification. Only a few works devoted to the synthesis and structures of alkaline metal β -diketonates have been reported. The known crystal structures of sodium and potassium acetylacetonates hydrates were determined in 1970-80s [15,16]. In the case of $[K_2(acac)_2(H_2O)]$, the crystal structure determination was performed at room temperature by a photo method with low accuracy.

Examples of mixed-ligand complexes of sodium and potassium β -diketonates with organic ligands are also very limited. Practically all the known crystal structures were determined for incidental single-crystals: $[Na_4(bta)_4(pypzH)_2]$ (pypzH = 2-(3-pyrazonyl)pyridine) [18], [K(hfa)(18 $crown-6)]_{\infty}$ [20], [K(Etacac)(18-crown-6)] [21] (Etacac $C_2H_5OC(O)CHC(O)CH_3),$ = [Na(Etacac)(15-crown-5)] [22], [Na(hfa)(15-crown-5)] (hfa 1,1,1,5,5,5-= hexafluoroacetylacetonate) [23]; and polymer structures of $[Na_3(acac)_3(Py)]_{\infty}$ [17] and $[Na(bzac)(HOC_2H_4OH)]_{\infty}$ (bzac = benzoylacetonate) [19]. Most of these compounds were characterized only by X-ray diffraction, without detailed analysis of their bulk properties.

Here we report a systematic study of the synthesis, X-ray crystal structures, IR and ¹H NMR spectroscopy data, thermal analysis and quantum chemical calculations for $[K_2(acac)_2(H_2O)]_{\infty}$ (I), $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (II), $[Na(acac)(H_2O)]_{\infty}$ (III), $[Na_3(acac)_3(^iPrOH)]_{\infty}$ (IV), $[Na_3(acac)_3(Py)]_{\infty}$ (V) and $[Na_2(acac)_2(phen)]_{\infty}$ (VI). The compounds II, IV and VI have not been reported previously; in addition, we have determined the structure of I with a higher accuracy.

2. Experimental

2.1 Synthesis

All the chemical reagents and solvents were preliminarily purified. Acetylacetone was distilled under reduced pressure and dried over 3Å molecular sieves. 1,10-Phenanthroline (Aldrich, 99% purity) and the sodium and potassium *tert*-butyloxides (ChemPur, 95-99%) were purified by sublimation in a vacuum (at 130 and 165 °C). *Iso*-propanol was dried by boiling with aluminum isopropylate under reflux and distilled. Benzene was conventionally dried by mixing with anhydrous H_2SO_4 and distilled. Pyridine was dried over KOH and distilled over BaO. All solvents were stored over 3 and 4Å molecular sieves under Ar.

2.1.1 $K_2(acac)_2(H_2O)$ (I) and $Na(acac)(H_2O)$ (III)

A solution of Hacac (2 mmol, 0.200 g) in *iso*-propanol (2 ml) was added to MO^tBu (2 mmol, 0.192 or 0.224 g for M = Na or K) dissolved in *iso*-propanol (8 ml) under continuous stirring at 50 °C. The reaction mixture was cooled to room temperature and the colorless crystalline precipitate that formed was isolated by filtration and dried in a vacuum. Yield: 80-90%. All operations were carried out in air. X-ray quality single crystals were grown by slow recrystallization from *iso*-propanol.

Anal. Calc for C₁₀H₁₆K₂O₅: C, 40.8; H, 5.5. Found: C, 40.6; H, 5.6. ¹H NMR (d₆-acetone, δ ppm): 5.1 (broad, 1H, CH_{acac}), 1.8 (s, 6H, CH_{3 acac}). IR (cm⁻¹): 3500-3100 v(O–H); 3064, 2991, 2963, 2919 v(C–H); 1724 δ (H₂O); 1617 v(C=O); 1507 v(C=C), δ (C=CH); 1459 δ (CH₃), v(C=O); 1408 v(C=O), v(C=C); 1358 δ (CH₃); 1009 ρ (CH₃); 908 v(C–CH₃); 760 π (C–H); 655 π _{ring}.

Anal. Calc. for C₅H₉O₃Na: C, 42.9; H, 6.5; Found: C, 42.6; H, 6.5. ¹H NMR (d₆-acetone, δ ppm): 5.0 (s, 1H, CH_{acac}), 1.7 (s, 6H, CH_{3 acac}). IR (cm⁻¹): 3432 v_{as}(O–H); 3326 v_s(O–H); 3075, 2987, 2956, 2921 v(C–H); 1669 δ (H₂O); 1608 v(C=O); 1509 v(C=C), δ (C=CH); 1444 δ (CH₃), v(C=O); 1401 v(C=O), v(C=C); 1360 δ (CH₃); 1010 ρ (CH₃); 912 v(C–CH₃); 767 π (C–H); 656 π _{ring}.

2.1.2. $Na_3(acac)_3(^{\prime}PrOH)$ (IV) and $Na_3(acac)_3(Py)$ (V)

A solution of Hacac (2 mmol, 0.200 g) in *iso*-propanol or pyridine (2 ml) was added to 2 mmol (0.192 g) of NaO^tBu dissolved in *iso*-propanol/pyridine (8 ml) under continuous stirring at 50 °C. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. A colorless crystalline precipitate was isolated and dried in a vacuum. All operations were carried out under a dry Ar atmosphere using Schlenk techniques. Yield: 80-90%. The single crystals of Na₃(acac)₃(ⁱPrOH) were grown by slow recrystallization from *iso*-propanol in an evacuated sealed tube.

Anal. Calc. for C₁₈H₂₉O₇Na₃: C, 51.7; H, 7.0; Found: C, 51.5; H, 6.9. ¹H NMR (d₆-acetone, δ

ppm): 5.0 (s, 3H, CH_{acac}), 3.9 (m, 1H, CH_{iPrOH}), 3.4 (d, 1H, OH), 1.7 (s, 18H, CH_{3 acac}), 1.1 (d, 6H, CH_{3 iPrOH}). IR (cm⁻¹): 3435 v(O–H); 3071, 2977, 2918, 2850 v(C–H); 1615 v(C=O); 1512 v(C=C), δ (C=CH); 1457 δ (CH₃), v(C=O); 1404, 1387 v(C=O), v(C=C); 1011 ρ (CH₃); 911 v(C–CH₃); 767 π (C–H); 656 π ring; 1163, 1126, 1110, 816 (ⁱPrOH).

Anal. Calc. for $C_{20}H_{26}O_6Na_3N$: C, 53.9; H, 5.8; N, 3.2; Found: C, 53.7; H, 5.9; N, 3.1. ¹H NMR (d₆-acetone, δ ppm): 8.6 (s, 2H, CH_{Py}), 7.8 (m, 1H, CH_{Py}), 7.3 (m, 2H, CH_{Py}), 5.0 (s, 3H, CH_{acac}), 1.7 (s, 18H, CH_{3 acac}). IR (cm⁻¹): 2989, 2959, 2937, 2919, 2851 v(C–H); 1615 v(C=O); 1512 v(C=C), δ (C=CH); 1456 δ (CH₃), v(C=O); 1404, 1387 v(C=O), v(C=C); 1011 ρ (CH₃); 912 v(C–CH₃); 766 π (C–H); 660 π _{ring}; 3083, 3019, 3000, 1122, 1055, 705 (Py).

$2.1.3 K_2(acac)_2(phen)(H_2O)$ (II)

The solution of acetylacetone (1.98 mmol, 0.198 g) in *iso*-propanol (3 ml) was added to KO^tBu (1.89 mmol, 0.212 g) and 1,10-phenanthroline (0.99 mmol, 0.178 g) dissolved in the mixture *iso*-propanol:benzene (1:1, 20 ml) under continuous stirring at 50°C. The reaction mixture was cooled down to room temperature and small colorless crystals were obtained. Precipitate was filtrated of and dried in vacuum. The single crystals were grown by slow recrystallization from *iso*-propanol/benzene mixture.

Anal. Calc. for $C_{22}H_{24}K_2N_2O_5$: C, 55.7; H, 5.1; N, 5.9. Found: C, 55.2; H, 5.1; N, 6.0. ¹H NMR (d₆-Acetonte, δ ppm): 9.1 (q, 2H, CH_{phen}), 8.5 (q, 2H, CH_{phen}), 8.0 (s, 2H, CH_{phen}), 7.8 (q, 2H, CH_{phen}), 5.1 (broad, 1H, CH_{acac}), 1.8 (s, 6H, CH_{3acac}). **IR** (cm⁻¹): 3414 v_{as}(O–H); 3351 v_s(O–H); 3055, 2977, 2956, 2915, 2852 v(C–H); 1699 δ (H₂O); 1617 v(C=O); 1510 v(C=C), δ (C=CH); 1465 δ (CH₃), v(C=O); 1423 v(C=O), v(C=C); 1007 ρ (CH₃); 902 v(C–CH₃); 753 π (C–H); 650 π _{ring}; 1588, 1565, 1140, 1098, 843, 733, 708 (phen).

2.1.4 Na₂(acac)₂(phen) (VI)

Acetylacetone (1.66 mmol, 0.166 g) was added dropwise to NaO^tBu (1.66 mmol, 0.159 g) and 1,10-phenanthroline (1.66 mmol, 0.299 g) dissolved in an *iso*-propanol:benzene mixture (1:1, 10 ml) under continuous stirring at room temperature. The reaction mixture was placed into a Λ -like evacuated sealed tube and the solvent was slowly distilled off over 6 weeks. As a result, single crystals of **VI** were obtained together with crystals of **III**, **IV** and phen as by-products.

2.2 Physical techniques

¹H NMR spectra in d₆-acetone with TMS as an internal standard were recorded using a Bruker AVANCE-400 (400 MHz) spectrometer. FT-IR spectra in the 4000-650 cm⁻¹ range were measured

on a Perkin-Elmer Spectrum One FTIR spectrometer in the Frustrated Total Internal Reflection mode. TG curves were recorded on a Q-1500D Derivatograph (in air and N₂ atmosphere) with a 10°/min heating rate. The C, H and N contents were determined by conventional elemental analysis. Powder XRD data were collected using an Enraf-Nonius FR-552 Guinier-Johanson camera and STOE Stadi P diffractometer (curved Ge monochromator, Cu-K α_1 radiation, $\lambda = 1.54056$ Å) at room temperature.

Single crystal X-ray diffraction data were collected on Bruker SMART 1000 and Oxford X-Calibur 2 diffractometers with CCD area detectors (the data were corrected for absorption by SADABS [24] and ABSPACK [25]) and STOE IPDS with an imaging plate (without absorption correction) using Mo K_{α} radiation ($\lambda = 0.71073$ Å, graphite monochromator). The crystal structures were solved by direct methods and refined anisotropically for all non-H atoms with the full-matrix F^2 least-squares technique (SHELXTL PLUS) [26]. Hydrogen atoms of water molecules were found in the difference Fourier synthesis; other H atoms were placed in geometrically calculated positions. All hydrogen atoms were refined in a riding mode. Details of the data collection and refinement parameters are summarized in Table 1.

2.3. Theoretical simulation

Quantum chemical calculations of the molecular geometries and ligand-to-metal bonding energies were carried out in a framework of the Density Functional Theory (B3LYP) with the 6-31G(d) basis set on all atoms in the Firefly 7.1.g package [27]. All geometry optimizations were performed without any symmetry constrains in the C₁ point group symmetry. The optimized molecular geometries were checked by Hessian calculations. The system energy change values (ΔE) due to addition reactions (A+B = C) were calculated as:

 $\Delta E = E_{\rm C} - E_{\rm A} - E_{\rm B} - E_{\rm BSSE},$

where E_{BSSE} is the basis set superposition error, calculated by the Boys and Bernardi approach [28].

	Ι	II	IV	VI
Formula	$K_2C_{10}H_{14}O_4 \cdot (H_2O)$	$C_{22}H_{24}K_2N_2O_5$	$C_{18}H_{29}Na_3O_7$	$\overline{C_{22}H_{22}N_2Na_2O_4}$
Formula weight	294.42	474.63	426.38	424.40
Diffractometer	SMART 1000	SMART 1000	STOE IPDS	$X calibur^{TM} 2$
Data collection method	$\phi\text{-}$ and $\omega\text{-}$ scans	φ - and ω - scans	φ-scan	ϕ - and ω - scans
Temperature (K)	120	120	100	106
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P \overline{1}$	$P 2_1/n$	$P 2_1/n$	C 2/c
a (Å)	7.352(3)	12.917(4)	10.4897(5)	11.6645(8)
<i>b</i> (Å)	8.750(4)	7.2201(16)	12.4028(4)	16.7097(11)
<i>c</i> (Å)	10.696(5)	25.181(6)	17.4433(9)	22.3126(14)
α (°)	87.875(9)	90	90	90
β (°)	87.262(8)	103.166(5)	94.795(4)	95.432(6)
γ (°)	88.631(8)	90	90	90
V (Å ³)	686.6(5)	2286.8(10)	2261.46(17)	4329.4(5)
Z	2	4	4	8
Color, habit	Colorless, needle	Colorless, plate	Colorless, block	Colorless, plate
Crystal dimensions (mm)	$0.60\times0.10\times0.05$	$0.20\times0.10\times0.04$	$0.60 \times 0.30 \times 0.30$	$0.50 \times 0.20 \times 0.1$
$D_{calc} (g \text{ cm}^{-3})$	1.424	1.379	1.252	1.302
$\mu (\text{mm}^{-1})$	0.70	0.45	0.14	0.12
Unique reflections (R _{int})	3184 (0.068)	5494 (0.066)	6095 (0.089)	5019 (0.117)
Observed reflections $[I > 2\sigma(I)]$	2124	3299	4489	2035
Parameters	158	286	271	275
$R_I[I > 2\sigma(I)], \omega R_2$	0.068, 0.166	0.075, 0.175	0.054, 0.111	0.043, 0.076
Goodness-of-fit on F ²	1.08	1.06	1.09	0.71
Absorption correction	SADABS	SADABS	none	ABSPACK
T _{min} , T _{max}	0.680, 0.966	0.916, 0.982	-	0.946, 0.986
. ? 2.	-0.70.072	-0.49, 0.72	-0.26, 0.39	-0.24, 0.23

Table 1. Crystal and refinement data for the structures $[K_2(acac)_2(H_2O)]_{\infty}$ (I), $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (II), $[Na_3(acac)_3({}^{i}PrOH)]_{\infty}$ (IV) and $[Na_2(acac)_2(phen)]_{\infty}$ (VI).

3. Results and discussion

3.1. Synthesis

The synthesis of alkaline β -diketonates is a rather common interjacent stage for the preparation of 3d- and 4f-metal β -diketonates [29]. In this case, sodium and potassium β -diketonates were synthesized in situ from alkalis and β -diketone in aqua-alcohol solution. The solid compounds obtained via this reaction were the hydrated sodium and potassium β -diketonates [15-16].

To isolate the anhydrous alkaline metal β -diketonates, we used another known method of synthesis, performing the reaction in dried solvents and using MO^tBu instead of MOH (M = Na, K). The syntheses of compounds I-VI were performed by the reaction of MO^tBu, Hacac and phen (for II and VI) in dried solvents – *iso*-propanol, benzene or pyridine - in air or under Ar atmosphere. The composition of the obtained compounds was confirmed by CHN analysis, IR and ¹H NMR spectroscopy. The identity of powder samples and single crystals was proved by a comparison of powder XRD patterns with theoretical ones calculated from single crystal data.

The reaction between MO^IBu and Hacac in air resulted in the formation of hydrated compounds, $K_2(acac)_2(H_2O)$ (I) and Na(acac)(H₂O) (III), in spite of using dried solvents. The large ionic radii and unsaturated coordination sphere of alkaline elements lead to the formation of mixed-ligand complexes, even with traces of water. The addition of the bidenate ancillary ligand phenanthroline does not prevent the coordination of water molecules: in case of potassium, $K_2(acac)_2(phen)(H_2O)$ (II) was obtained, while for sodium, the mixed-ligand complex with phen was not formed and only III was isolated. The syntheses using Schlenk techniques in dry Ar atmosphere leads to the formation of the anhydrous complexes Na₃(acac)₃(ⁱPrOH) (IV) and Na₃(acac)₃(Py) (V), but Na₂(acac)₂(phen) (VI) was not isolated by conventional methods, even under dry Ar. Only slow crystallization in an evacuated sealed tube allowed us to obtain several small single crystals of VI. In order to understand the origins of the differences in the synthesis and composition of II and VI one should consider the X-ray structures and quantum chemical simulations.

3.2. X-ray crystal structures

The 1D polymer structures of **I-VI** have chain (**I**, **III**) or ribbon (**II**, **IV-VI**) motifs with additional bridging and chelating functions of acac ligands (tetra- or hexadentate). For convenience, the description of the structures can be represented as consisting of formal binuclear building blocks, $[M_2(acac)_2]$. Four types of $[M_2(acac)_2]$ building blocks can be found in the structures of **I-VI**, which differ by their metal-oxygen cores (A-D blocks, Fig. 1).

The A-block has a nearly square {M₂O₂} metal-oxygen core (Fig. 1). Each acac⁻ ligand forms

one chelate cycle only with one M cation, and coordinates to the other M as a bridging ligand.

In the *B*-block four oxygen atoms of two acac⁻ ligands in the equatorial plane and two apical M atoms form a distorted octahedral metal-oxygen core $\{M_2O_4\}$ (Fig. 1). Each M cation takes part in two chelate cycles with both bi-chelating acac⁻ ligands.

The *C*-block has a distorted square or tetrahedral metal-oxygen core $\{M_2O_2\}$ (Fig. 1). In the *C*-block two M-atoms have different coordination environments. Two acac⁻ ligands coordinate to M^1 as chelating ligands, while the same acac⁻ ligands coordinate to M^2 only as bridging ligands.

The *D*-block has a trigonal bipyramidal metal-oxygen core (Fig. 1). Like in the A-block, each acac⁻ ligand formes one chelate cycle only with one M cation and coordinates to the other M as a bridging ligand. Additionally, a donor ligand μ_2 -L bridges to the M atoms.

Thus, the descriptions of structures **I-VI** go two ways: (i) the coordination environment of the alkaline ions and (ii) the building block types and their arrangement in the polymeric structure.



Fig. 1. The geometry of the A-D binuclear building blocks in the structures I-VI. Blue dash lines show the metal-oxygen core of the blocks. The arrows show the additional interactions with neighboring building blocks or terminal ligands. M = Na, K; L - O donor atom (H_2O , acac, ⁱPrOH) or N donor atom (Py, phen).

3.2.1 $[K_2(acac)_2(H_2O)]_{\infty}$ (**I**) and $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (**II**)

The crystal structure of **I** at room temperature ($\mathbf{I}_{\mathbf{R}}$) with low accuracy ($\sigma(\mathbf{C}-\mathbf{C}) = 0.03$ Å) was reported by Shibata et al. in 1975 [16]. Here, we present the results of a modern low temperature diffraction experiment ($\mathbf{I}_{\mathbf{L}}$). The structures $\mathbf{I}_{\mathbf{R}}$ and $\mathbf{I}_{\mathbf{L}}$ were found to be identical, so the thermally induced phase transition reported previously for structurally flexible coordination compounds of alkaline-earth β -diketonates [30] was not observed for **I**.

The asymmetric unit cell of I consists of two seven-fold coordinated potassium cations (K1

and K2), two acetylacetonate-anions (μ_4 -O1-C1-C2-C3- μ_2 -O2 and μ_4 -O3-C6-C7-C8- μ_2 -O4) and a water molecule (μ_2 -O1w) (Fig. 2). The H₂O molecules form a framework of hydrogen bonds with acac-anions of neighboring chains, resulting in their association into sheets parallel to the (001) plane.



Fig. 2. A fragment of the polymeric $[K_2(acac)_2(H_2O)]_{\infty}$ chain in **I**. Empty lines show the acac ligands, dashed lines show H-bonds. H-atoms are partially omitted for clarity. Symmetry codes: (i) -x, -y+2, -z; (ii) -x+1, -y+2, -z; (iii) x, -y+1, z.

The K1 and K2 cations have similar coordination environments, formed by four oxygen atoms $(O1^{i} - O4^{i} \text{ or } O1 - O4 \text{ respectively})$ of two chelate-bridging acac-anions, two bridging oxygen atoms (O1, O3 or O1ⁱⁱ, O3ⁱⁱ) of two other acac⁻ ligands and a bridging water molecule (O1w or O1wⁱⁱ) (Fig. 2). The average K-O distance in I is equal to 2.85(11) Å, and only the K1-O1 and K2-O3 distances (3.007(3) and 3.044(3) Å respectively) are significantly longer due to enhanced bridging functions of μ_4 -O1 and μ_4 -O3 (Table S1). Therefore, the coordination number of K1 and K2 is 6+1.

The polymeric chain in I can be represented as a combination of edge- and corner-sharing *B*and *D*- formal building blocks (Fig. 3). The *B*-block $[K_2(acac)_2]$ contains a distorted octahedral metal-oxygen core {K1ⁱK2O1O2O3O4}. Neighboring *B*-blocks are connected via bridging K1–O3, K2ⁱⁱ–O3, K1–O1, K2ⁱⁱ–O1 and K1–O1w, K2–O1wⁱⁱ interactions forming a trigonal bipyramidal {K1K2ⁱⁱO1O3O1w} *D*-block metal-oxygen core.



Fig. 3. Metal-oxygen framework and building blocks in the polymeric chain $[K_2(acac)_2(H_2O)]_{\infty}(I)$.

In the asymmetric unit cell of **II** there are two potassium cations (K1 and K2) in different coordination environments, two acac- anions (O1-C1-C2-C3-O2 and O3-C6-C7-C8-O4), phen (N1-C15-C16-N2) and a water molecule (H_2O1w). The seven-coordinated K1 is surrounded by four Oatoms of two chelating acac⁻ anions (μ_2 -O1, μ_3 -O2 and μ_3 -O3, μ_2 -O4), two bridging atoms (O2¹ and $O3^{i}$) of two other acac⁻ anions and μ_2 -O1wⁱⁱ of water (Fig.4). Therefore, the coordination environment of K1 is similar to that in I, while the average K-Oacac distance, 2.77 Å, is slightly shorter than in I (2.85 Å, Table 2).

		II						9	9	9	5	5	9
Bond distances (Å)						1							
K1—O1	2.856(3)					The A							The the at
K1—O2	2.691(3)							€\$_\$\$\$\$ \$					
K1—O3	2.731(3)												
K1—O4	2.862(3)				(C)					N1 K2 K2			
K1—O2 ⁱ	2.680(3)		9										
K1—O3 ⁱ	2.693(3)												
K1—O1w ⁱⁱ	2.984(3)												
K2—O1	2.970(3)												
K2—O2	2.749(3)						-30			30 100			
K2—O3	2.742(3)												
K2—O4	2.918(3)												
K2—O1w ⁱⁱⁱ	2.866(4)												
K2—N1	2.880(4)												
K2—N2	2.856(4)									Clar,	je)	CB4	jeto
Hydrogen bond ge	eometry (Å	l, °)		1	Fig. 4.	Fig. 4. A frag	Fig. 4. A fragment	Fig. 4. A fragment of	Fig. 4. A fragment of the p	Fig. 4. A fragment of the polyme	Fig. 4. A fragment of the polymeric r	Fig. 4. A fragment of the polymeric rible	Fig. 4. A fragment of the polymeric ribbo
	D···A	D−H···A		[[K ₂ (acac) show the	$[K_2(acac)_2(phen)]$	$[K_2(acac)_2(phen)(H_2C)]$	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$ in $[K_2(acac)_2(phen)(H_2O)]_{\infty}$	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$ in II . En show the acac ligands dashed line	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$ in II . Empty show the acac ligands dashed lines sho	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$ in II . Empty li	$[K_2(acac)_2(phen)(H_2O)]_{\infty}$ in II . Empty line show the acac ligands dashed lines show H
O1w-H1wa…O1	2.782(4)	152		ł	bonds. H	bonds. H-atoms	bonds. H-atoms are p	bonds. H-atoms are partie	bonds. H-atoms are partially or	bonds. H-atoms are partially omitted	bonds. H-atoms are partially omitted for c	bonds. H-atoms are partially omitted for clar	bonds. H-atoms are partially omitted for clarit
O1w-H1wb…O4	2.779(4)	138		S	Symmetry	Symmetry codes.	Symmetry codes: (i) -	Symmetry codes: (i) $-x+1$	Symmetry codes: (i) $-x+1/2$, y-	Symmetry codes: (i) $-x+1/2$, $y-1/2$, -	Symmetry codes: (i) $-x+1/2$, $y-1/2$, $-z+1/2$	Symmetry codes: (i) $-x+1/2$, $y-1/2$, $-z+1/2$;	Symmetry codes: (i) $-x+1/2$, $y-1/2$, $-z+1/2$; (i)

Table 2. Selected geometrical parameters in II.

O1w-H1wb····O4 2.779(4) 138

Symmetry codes: (i) -x+1/2, y-1/2, -z+1/2; (ii) -x+1/2, y+1/2, -x+1/2, y+1/2, -z+1/2; (iii) x, y+1, z. -z+1/2; (iii) x, y+1, z.

The coordination environment of K2 with CN=7 (Fig. 4) is formed by four O-atoms of two chelating acac⁻ anions (μ_2 -O1, μ_3 -O2 and μ_3 -O3, μ_2 -O4), a chelating phen ligand (N1 and N2) and a bridging water (μ_2 -O1wⁱⁱⁱ). The average K-N_{phen} distance (2.868 Å) is close to that observed for

hexacoordinated (2.871 Å in K(thd)(phen)₂ [31]) and heptacoordinated (2.834 Å in $K_2(Piv)_2(phen)(H_2O)$ [32]) potassium atoms and is in good agreement with typical values of K-N_{phen} distances in other known potassium complexes with phen [33].

The ribbons in **II** can be represented as a combination of the same *B*- and *D*- formal building blocks (Fig. 5). In contrast to **I**, these blocks share faces and vertices. The *B*-block consists of K1, K2 and two acac⁻ anions and has a distorted octahedral metal-oxygen core {K1K2O1O2O3O4}. Connection of K1ⁱⁱ and μ_2 -O1wⁱⁱⁱ to the {K2O2O3} triangular face of the *B*-block leads to the formation of the trigonal-bipyramidal metal-oxygen core of the *D*-block.



Fig. 5. Metal-oxygen framework and building blocks in the polymeric ribbon $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (**II**).

The neighboring ribbons contact each other through alternating face-to-face π - π stacked phen ligands (the inter-planar distance is 3.48 Å, the molecular centroids separation is 3.87 Å). The water molecule and O atoms of the acac⁻ anions form two intra-ribbon H-bonds (d(O1w-H1wa-O1) = 2.782(4) Å, d (O1w-H2wa-O4) = 2.779(4) Å) in contrast to **I** which has only inter-ribbon H-bonds.

3.2.2. $[Na(acac)(H_2O)]_{\infty}$ (III), $[Na_3(acac)_3(^iPrOH)]_{\infty}$ (IV) and $[Na_2(acac)_2(phen)]_{\infty}$ (VI)

Although the structure of **III** was reported earlier [15], we discuss it here using our formal building block approach. The distorted octahedral coordination environment of the Na atom in **III** consists of one bidentate-chelating acac⁻, two bridging acac⁻ and two bridging water molecules (Fig. 6). The chains in **III** can be represented as corner-shared *D*-blocks.



Fig. 6. The fragment of the polymeric chain $[Na(acac)(H_2O)]_{\infty}$ (**III**) and formal building blocks. Symmetry codes: (i) -x, y+1/2, -z+1/2; (ii) -x, y-1/2, -z+1/2.

In the structure of **IV**, the asymmetric unit cell contains three pentacoordinated Na cations in distorted square-pyramidal coordination environments, three acetylacetonate-anions (O1-C2-C3-C4-O2, O3-C7-C8-C9-O4, O5-C12-C13-C14-O6) and one *iso*-propanol molecule (O7-C16-C17(C18)). To confirm the square-pyramidal coordination geometry around the Na cation we have calculated the geometric parameter $\tau = (\beta - \alpha)/60$. The α and β values are the two largest basal angles in the polyhedra. Thus, $\tau = 0$ corresponds to an ideal square-pyramid, while $\tau = 1$ corresponds to an ideal trigonal bipyramid [34]. The coordination environment of Na1 consists of four oxygen atoms of two chelating acac ligands (μ_3 -O1, μ_3 -O2 and μ_2 -O3, μ_2 -O4) in the basal plane and an apical O7 atom of *iso*-propanol ($\tau = 0.14$). The Na1 atom is displaced by 0.97 Å from the basal plane (Fig. 7a).



Fig. 7. Structure of $[Na_3(acac)_3({}^{l}PrOH)]_{\infty}$ (**IV**): a) fragment of the polymeric ribbon; b) metaloxygen framework and building blocks. Empty lines show the acac ligands. H-atoms are omitted for clarity. Symmetry codes:(i) -x+1, -y+1, -z; (ii) x, y+1, z; (iii) -x+1, -y+2, -z.

The Na2 and Na3 atoms are coordinated by oxygen atoms of acac ligands only (Fig. 7a). The Na2 atom connects to two oxygen atoms (μ_3 -O1ⁱ and μ_3 -O2ⁱ) of a bi-chelating acac ligand and two bridging oxygen atoms (μ_3 -O2 and μ_2 -O5) in the basal plane and one apical μ_2 -O4 ($\tau = 0.15$). The Na3 atom is coordinated by two oxygen atoms (μ_2 -O5ⁱ and μ_2 -O6ⁱ) of a chelating acac ligand and two bridging oxygen atoms (μ_3 -O1 and μ_2 -O6ⁱⁱ) in the basal plane and one apical μ_2 -O3 ($\tau = 0.20$). The Na2 and Na3 atoms are located at 0.44 and 0.47 Å from the basal plane of the square pyramid, respectively. Therefore, the fashion of the chelating acac ligand coordination is the main difference in the coordination environments of Na2 and Na3. Bonding of one acac (μ_3 -O1 and μ_3 -O2) as a bi-chelating ligand leads to an increase of the Na1-O1 and Na1-O2 distances compared with Na1-O4 and Na1-O3 (Table 3).

	e	1
	IV	V
Bond distances	(Å)	
Na1—O1	2.3642(13)	3.354(2)
Na1—O2	2.3125(13)	2.307(2)
Na1—O3	2.2641(14)	2.229(2)
Na1—O4	2.2936(14)	2.302(2)
Na1—O7(N1)	2.3238(15)	2.423(2)
Na2—O2	2.2877(13)	2.311(2)
Na2—O4	2.3026(14)	2.332(2)
Na2—O5	2.2662(14)	2.286(2)
Na2—O1 ⁱ	2.4661(14)	2.481(2)
Na2—O2 ⁱ	2.4330(14)	2.447(2)
Na3—O1	2.3790(13)	2.336(2)
Na3—O3	2.3307(13)	2.305(2)
Na3—O5 ⁱ	2.3026(13)	2.314(2)
Na3—O6 ⁱ	2.3172(13)	2.291(2)
Na3—O6 ⁱⁱ	2.3272(13)	2.321(2)

Table 3. Selected geometrical parameters in IV and V [17].

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) *x*, *y*+1, *z*.

The ribbons in **IV** can be represented as the central chain of corner-shared A-blocks and pairs of corner-shared C-blocks alternating on both sides of the central chain (Fig. 7b). The metal-oxygen cores of the A-blocks are {Na2O2Na2ⁱO2ⁱ}, {Na2ⁱO1Na3O5ⁱ} and {Na3O6ⁱNa3ⁱⁱⁱO6ⁱⁱ}. The cores of the C-blocks are {Na1O1Na3O3} and {Na1O2Na2O4}.

So, on going from structure III to IV, the replacement of H₂O by ⁱPrOH occurs, followed by

decreasing the metal to neutral ligand molar ratio from 1:1 to 3:1 and rearrangement of the chains into ribbons in the crystal structures.

In the case of the replacement of ¹PrOH by Py (i.e. going from **IV** to **V**) neither the metal to neutral ligand molar ratio nor the ribbon structure changes. The corresponding bond lengths in structures **IV** and **V** are very close, the difference is less than 0.04 Å (Table 3). Meanwhile, the packing of ribbons in **IV** and **V** differ significantly (Fig. S1). The planes on neighboring ribbons in **IV** are parallel to each other, while in **V** these planes form a herring-bone motif in the *ab* projection (with a dihedral angle of 73.16°).

The asymmetric unit cell in the mixed-ligand complex VI contains two sodium cations in different coordination environments, two acac anions (O1-C2-C3-C4-O2 and O3-C7-C8-C9-O4), and a phen ligand. The sodium to neutral bidentate phen ligand molar ratio is equal to 2:1. The Na1 atom, in a nearly octahedral environment (Fig. 8a), is coordinated by chelating acac (μ_2 -O1 and μ_2 -O2), chelating phen (N1 and μ_2 -N2) and two bridging acac⁻ ligands (μ_2 -O1ⁱ and μ_2 -O3). The Na2 atpm, in a distorted square-pyramidal coordination environment (Fig. 8a), connects to a chelating acac ligand (μ_2 -O3 and μ_2 -O4ⁱⁱ), bridging acac⁻ ligands (μ_2 -O4) and an apical μ_2 -N2 of a phen ligand ($\tau = 0.18$).



Fig. 8. Structure of $[Na_2(acac)_2(phen)]_{\infty}$ (**VI**): a) fragment of the polymeric ribbon; b) metaloxygen framework and building blocks. Empty lines show the acac ligands. H-atoms are omitted for clarity. Symmetry codes:(i) -x+1, y, -z+1/2; (ii) -x+3/2, -y+1/2, -z+1.

The Na1-N1 distance, 2.48 Å (Table 4), is typical for the Na-N_{phen} bond length (2.45-2.49 Å [35]), while the bridging Na1-N2 and Na2-N2 bonds, 2.70-2.81 Å, are significantly longer and exceed the sum of the ionic radii (2.48 Å) by 0.22-0.33 Å, and thus correspond to weak interactions. Thus, the CN is 5+1 for Na1 and 4+1 for Na2.

Polymer ribbons along the [101] direction are formed due to μ_2 -bridging oxygen atoms of acac ligands and μ_2 -N2 atoms of phen ligands. These ribbons could be described as corner-shared alternating A- and D- building blocks (Fig. 8b). The atoms Na1, Na1ⁱ, O1 and O1ⁱ form the distorted square metal-oxygen core of the A-block. Atoms Na1, Na2, O2, O3 and N2 form the trigonal bipyramidal core of the D-block.

Table 4	I. Selected geon
	VI
Bond distance	es (Å)
Na1—O1	2.3199(16)
Na1—O3	2.3286(17)
Na1— $O1^i$	2.3328(15)
Na1—O2	2.3493(16)
Na1—N1	2.4809(19)
Na1—N2	2.8118(18)
Na2—O2	2.2195(16)
Na2—O4	2.2531(16)
Na2—O4 ⁱⁱ	2.2631(15)
Na2—O3	2.2854(15)
Na2—N2	2.702(2)
Symmetry	codes: (i) $-x+1$, y, $-z+$

In the crystal structure of VI the ribbons interact with each other due to edge-to-face stacking of alternating phen ligands with the chelating rings of two acac ligands (the molecular centroids separations are 5.10 and 4.97 Å, and the dihedral angles are 87 and 60°). The phen ligands of neighboring ribbons are parallel to each other (with an inter-planar distance of 3.417 Å), but with a lateral displacement of 6.14 Å. While the two neighboring phen ligands in one ribbon are also parallel (inter-planar distance 3.28(5) Å), their centroids are shifted by 7.69 Å. Thus, there are no face-to-face stacking interactions between two phen molecules.

Consequently, for four sodium polymers (III-VI) the A-, C- and D-blocks were observed. These blocks are in different pairwise combinations in structures **IV-VI**. At the same time, for the

potassium polymers only B- and D-blocks were observed in both structures I and II.

3.3. Theoretical study of mixed ligand complex formation

Theoretical simulations of the binuclear molecules $[M_2(acac)_2]$ as molecular analogues of *A-D* building blocks were carried out to understand the structural isomerism of these building blocks, to compare their energies and to reveal the most stable ones. The geometries of the four isomers of the $[M_2(acac)_2]$ molecules were optimized (Fig. 9). These calculated isomers, α -, β -, γ - and δ - $[M_2(acac)_2]$, have the same metal-oxygen core as in the building blocks *A*-, *B*-, *C*- and *D*- respectively, Fig. 1. The only difference was made in the *D*- and δ - pair; namely, in the simulated molecule δ - $[M_2(acac)_2]$ the trigonal bipyramidal core was constructed only by acac-ligands (one bichelating and one chelate-bridging), while in the *D*-block, the core included a donor atom of the L ligand (Fig. 1).



Fig. 9. Geometry of the simulated $[M_2(acac)_2]$ isomers (M = Na and K). Dashed lines complete the polyhedron of the metal-oxygen core. H-atoms are omitted for clarity.

	<i>x</i> 0)2] 01	oens in the stre				
Simulated [M ₂ (acac) ₂] molecules			Experimental [M ₂ (acac) ₂] blocks			
Molecule	$CN^{1)}$	$< d_{M-O} >^{2)}, Å$	E _{rel} ³⁾ , kJ/mol	Fragment	CN ¹⁾	$< d_{M-O} >^{2)}, Å$
			M = Na			
	2.2			A-block (IV, V)	5, 5	2.35(7)
α -[Na ₂ (acac) ₂]	3, 3	2.197	0	A-block (VI)	5, 5	2.31(6)
β -[Na ₂ (acac) ₂]	4, 4	2.345	+47.7	-		-
γ -[Na ₂ (acac) ₂]	4, 2	2.222	+37.6	C-block (IV, V)	5, 5	2.32(4)
S [N]- ()]	4 2			D-block (III)	6,6	2.38(5)
$0-[\ln a_2(acac)_2]$	4, 3	2.268	+12.2	D-block (VI)	5, 5	2.30(6)

Table 5. Selected parameters of the simulated isomers of the $[M_2(acac)_2]$ molecules and binuclear building $[M_2(acac)_2]$ blocks in the structures **I-VI**

			M = K			
α -[K ₂ (acac) ₂]	3, 3	2.578	+11.3	-		-
$\beta_{-}[K_{a}(acac)_{a}]$	1 1	2 (01	4.7	B-block (I)	6+1,6+1	2.82(11)
p-[K2(dede)2]	4, 4	2.691	+4.7	B-block (II)	6,7	2.79(12)
γ -[K ₂ (acac) ₂]	4, 2	2.602	+35.7	-		-
δ [K (2000)]	1 2			D-block (I)	6+1,6+1	2.85(10)
0-[K2(acac)2]	4, 3	2.636	0	D-block (II)	6,7	2.81(10)

M = K

1) Coordination number of two M-atoms in $[M_2(acac)_2]$

2) Average intra-block M-O distance

3) Energy of $[M_2(acac)_2]$ isomer relative to the most stable one (with $E_{rel} = 0$)

The stabilities and relative energies of the different $[M_2(acac)_2]$ isomers depend mainly on two competitive factors - the strength of the M-O interactions and their number. The average M-O distance ($<d_{M-O}>$) and coordination number (CN) corresponding to these two factors are listed in Table 5. For $[Na_2(acac)_2]$, the strength of the M-O interactions is the dominant factor; α - $[Na_2(acac)_2]$, with the shortest $<d_{M-O}>$, is the most stable isomer. While for $[K_2(acac)_2]$, with larger K cations, the CN factor becomes more important. Indeed, the CN values for the most stable δ and β isomers, with very close relative energies, are higher than for the α and γ isomers, in spite of weaker M-O interactions (Table 5).

The M-O distances in the α - δ isomers of the M₂(acac)₂ molecules are slightly shorter (by 0.03-0.13 Å for M = Na and by 0.13-0.21 Å for M = K) than in the corresponding *A-D* blocks of the crystal structures. This is due to a lower CN of M in the simulated [M₂(acac)₂] molecules than in the building blocks *A-D*.

Note, the energy difference between all isomers does not exceed 40 kJ/mol, which is comparable to the energy of the H-bonds and intermolecular interactions. This explains the presence of all types of building blocks, except the most unstable ones, in structures **I-VI**.

The formation of dimeric $[M_2(acac)_2]$ molecules was also considered as the first stage of polymerization. This process competes with the formation of mononuclear mixed-ligand complexes, [M(acac)L].

The formation of the most stable binuclear molecules $[M_2(acac)_2]$ was simulated and the system energy change ΔE was calculated:

2 Na(acac) = α -[Na₂(acac)₂], ΔE = -143 kJ/mol (1)

2 K(acac) = δ -[K₂(acac)₂], Δ E = -111 kJ/mol (2)

The theoretical simulations of mixed-ligand complexes were carried out for the isolated

molecules [Na(acac)(phen)] and [K(acac)(phen)]. As a result, the optimized molecules have a planar geometry. In [M(acac)(phen)], the phen and acac ligands act as chelating ligands and CN = 4 (Fig. 10). The weak attractive interaction between the aromatic hydrogen atom and oxygen atom of acac lead to broken axial symmetry and bond length differences in the M-N1/M-N2 and M-O1/M-O2 pairs (Table 6).



Fig. 10. Geometry of the simulated M(acac)(phen) molecule (M = Na and K).

The calculated ΔE values for reactions (3) and (4) show that the formation of mixed ligand complexes is energetically favorable, but the formation of $[M_2(acac)_2]$ dimers leads to lower energies (reactions (1) and (2)). This agrees with the experimental results from the syntheses and X-ray structure analyses. Indeed, the addition of the phen ligand to polymeric chains of hydrates I and III leads to mixed-ligand complexes II and VI, which retain the polymeric structure.

Distance	M = Na	M = K
M-01	2.170	2.518
M-O2	2.199	2.554
M-N1	2.516	2.995
M-N2	2.401	2.805

Table 6. Selected distances (Å) in the simulated [M(acac)(phen)] molecules

The phen binding ΔE value for M = K is smaller due to the larger ionic radius and lower positive charge surface density. A similar tendency was observed in [36] according to quantum chemical calculations of the interaction of the M⁺ cation (M = Li, Na, K) with the neutral phen ligand. The absolute ΔE values reported in [36] (-254 and -172 kJ/mol for Na and K respectively)

seem to be significantly overestimated due to the small basis set used for the calculations and the absence of an anion in the model to compensate the positive charge of the central atom.

The calculated M-N distances (Table 6) are close to those observed in structures II and VI. The M-O distances in both modelled [M(acac)(phen)] and $[M_2(acac)_2]$ molecules are rather close, but are shorter than the experimental M-O distances in the polymeric structures I-VI.

3.4. Thermal behavior

Thermal analyses in air and N_2 were carried out for the three compounds I, II and III. The anhydrous complexes IV-VI are unstable in air and rapidly lose ⁱPrOH, Py and phen respectively, with the formation of III.

The TG curve of **I** in N₂ shows the complete elimination of H₂O at 90-130 °C (exp. weight loss 6%, calc. 6%) with the formation of anhydrous "K(acac)", which is stable in the range 130-220 °C. In air, the first stage of weight loss (24%) occurs at 95-250 °C and corresponds to elimination of H₂O accompanied by partial decomposition. The total weight loss of **I** in air at 800 °C (55%) corresponds to the formation of K₂CO₃ (calc. weight loss 53%).

For III, in both atmospheres, the first stage of weight loss corresponds to complete elimination of H₂O (70-110 °C, exp. 13%, calc. 13%), followed by the formation of anhydrous "Na(acac)", which is stable in the range 110-170 °C. The total weight loss at 600 °C in air corresponds to the formation of Na₂CO₃ (exp. 64%, calc. 62%).

Heating of **II** in both atmospheres leads to the complete elimination of coordinated H₂O at 90-155 °C (exp. 4%, calc. 4%), followed by elimination of phen at 163-295 °C (exp. 39%, calc. 38%), which overlaps with the range of the thermal stability of "K(acac)". Similarly to **I**, the total weight loss of **II** in air at 800 °C (70%) corresponds to the formation of K₂CO₃ (calc. weight loss 71%).

4. Conclusions

A comprehensive overview of the results of the synthesis and crystal structures for $[K_2(acac)_2(H_2O)]_{\infty}$ (I), $[K_2(acac)_2(phen)(H_2O)]_{\infty}$ (II), $[Na(acac)(H_2O)]_{\infty}$ (III), $[Na_3(acac)_3(^iPrOH)]_{\infty}$ (IV), $[Na_3(acac)_3(Py)]_{\infty}$ (V) and $[Na_2(acac)_2(phen)]_{\infty}$ (VI) allowed us to reveal key factors of the M(acac) (M = Na and K) reactions with ancillary neutral ligands (H₂O, ⁱPrOH, Py and phen). The compounds I-VI have one-dimentional polymeric structures. The chains or ribbons can be represented as a combination of corner-, edge- or face-shared formal binuclear $[M_2(acac)_2]$ building blocks of four types (*A-D*). A theoretical simulation of the molecular analogs of these blocks showed that the stability of the blocks changed in the row A > D >> C > B (M = Na) or $D \approx B > A >> C$ (M = K). In spite of the structural flexibility of alkaline metal coordination compounds, these building blocks were found to be rather rigid units. These four types of formal blocks appear not only in the

polymeric acetylacetonates **I-VI** but also in oligomeric structures of sodium and potassium hexafluoroacetylacetonates, which will be reported later.

In general, one could expect that the formation of mixed-ligand complexes results in an increasing CN of the central atom accompanied by transformation of the polymeric structure into structures of lower nuclearity. Indeed, such transformations are widely used to decrease the nuclearity of various metal acetylacetonates. However, for polymeric alkaline metal acetylacetonates, this rule does not work. The coordination of additional neutral donor ligands to polymeric chains of acetylacetonates retains the polymeric motif, but changes the types of blocks in some cases. It is noteworthy that the formation of mixed ligand complexes of M(acac) does not necessarily lead to an increase in CN (e.g. CN = 6 in **III**, but in **VI** CN = 5 and 6).

Appendix A. Supplementary data.

CCDC 904026 (I), 904027 (IV), 904028 (II) and 904029 (VI) contain the supplementary obtained free be of charge crystallographic data. These data can 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. Supplementary data associated with this article can be found in the online version.

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Six mixed ligand acetylacetonates of Na and K with H₂O, 1,10-phenanthroline, iso-propanol and pyridine were synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, ¹H NMR and FTIR spectroscopy. All the compounds have one-dimensional polymeric structures described as a combination of formal binuclear building blocks, $[M_2(acac)_2]$, of four types. Acceleration

