molecules

Synthesis and Characterization of the Complexes of Pentane-2,4-dione with Nickel(II) and Cobalt(III): [Ni(acac)$_2$]·0.5CH$_3$OH and [Co(acac)$_2$NO$_3$]·2H$_2$O (acac = Pentane-2,4-dione)

Yang Qu [1,2], Hai-Liang Zhu [1,2,*], Zhong-Lu You [1,2] and Min-Yu Tan [2,*]

[1] Department of Chemistry, Fuyang Normal College, Fuyang Anhui 236041, P.R.China

[2] Department of Chemistry, Lanzhou University, Lanzhou 730000, P.R.China

[*] Authors to whom correspondence should be addressed; e-mail: hailiang_zhu@fync.edu.cn;
   tangyu@lzu.edu.cn

Abstract: Two mononuclear complexes, [Ni(acac)$_2$]·0.5CH$_3$OH (**1**) and [Co(acac)$_2$NO$_3$]·2H$_2$O (**2**) (acac = pentane-2,4-dione), have been synthesized and characterized by single crystal X-ray analysis. Complex **1** crystallizes in the monoclinic space group P2$_1$/c with a = 9.295(4), b = 11.450(5), c = 12.974(6) Å, V = 1379.1(11) Å^3, β = 92.854(7), and Z = 4. Complex **2** crystallizes in the triclinic space group *P(-1)* with a = 8.153(9), b = 9.925(11), c = 10.355(12), V = 746.3(15) Å^3, α = 70.530(16), β = 71.154(15), γ = 80.698(16) and Z = 2. Complex **1** has a one-dimensional chain-like structure, which is extended by weak hydrogen contacts, while complex **2** shows a three–dimensional network structure.

Keywords: Pentane-2,4-dione, crystal structure, cobalt(III) complex, nickel(II) complex

Introduction

The d-transition metal - β-diketone compounds were used extensively as starting materials in the early days of metallocene chemistry [1]. Currently complexes containing the pentanedionato ligand have been the focus of much investigation as electroluminescent materials [2-3], presumably due to their ease of preparation, high stability and high volatility in comparison to other chelate complexes [5-6]. The pentanedionato ligand possesses a rather complicated coordination behavior toward redox-active and inactive transition metal ions because it can exist in various protonated forms [7]. Studies

on the structures of pentanedionato complexes and the characterization are becoming of more and more interest to chemists and biochemists [8-9]. Herein we present two new complexes, [Ni(acac)$_2$]$_2$·0.5CH$_3$OH (**1**) and [Co(acac)$_2$NO$_3$]·2H$_2$O (**2**), and describe their syntheses and crystal structures.

Results and Discussion

2,4-Pentanedionato complexes of cobalt were usually obtained adventitiously from the attempted preparation of cobalt(II)-Schiff bases, presumably due to Co(II) redox-activity. It is usually difficult to produce single crystals of these kinds of compounds, but we have found that large crystals of these two complexes can be readily obtained using the hydrothermal method. Both complexes are soluble in common polar organic solvents, such as DMSO, DMF, EtOH, MeCN and Me$_2$CO, but poorly soluble in water and MeOH.

Table 1 Crystallographic and experimental data for complexes **1** and **2**

Complexes	1	2
Formula	C$_{11}$H$_{18}$NiO$_5$	C$_{10}$CoH$_{18}$O$_9$
FW	288.96	355.18
Crystal shape/color	Yellow	brown-red
Crystal size/ mm	0.30 x 0.24 x 0.20 mm	0.42 x 0.37 x 0.31 mm
T/K	293K	298 K
Crystal system	Monoclinic	Triclinic
Space group	*P2(1)*	*P(-1)*
a/Å	9.254(4)	8.153(9)
b/Å	11.450(5)	9.925(11)
c/Å	12.974(6)	10.355(12)
α/°	90.00	70.530(16)
β/°	92.854(7)	71.154(15)
γ/°	90.00	80.698(16)
U/Å^3	1379.1(11)	746.3(15)
μ/mm^{-1}(Mo-Kα)	1.413	1.192
Dx/g cm^{-3}	1.392	1.581
Reflections/parameters	2434/173	2546/204
Independent reflections (R$_{int}$)	1203 (0.0478)	2024 (0.0163)
F(000)	608	368
Goodness of fit on F^2	0.957	0.984
R$_1$, wR$_2$ [$I \geq 2\sigma(I)$][a]	0.0554, 0.1469	0.0520, 0.1384
R$_1$, wR$_2$ (all data)[a]	0.1135, 0.1670	0.0645, 0.1480

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(Fo2)2]1/2$,
$w = [\sigma^2(F_o)^2+(0.0838((F_o)^2+2F_c^2)/3)^2]+0.0242((F_o)^2+2F_c^2)/3]^{-1}$ for **1**
$w = [\sigma^2(F_o)^2+(0.099((F_o)^2+2F_c^2)/3)^2]^{-1}$ for **2**

Table 2. Selected bond (Å) distances and angles (^{o})

	1		**2**
Ni(1)-O(1)	1.865(5)	Co(1)-O(1)	1.888(4)
Ni(1)-O(2)	1.858(4)	Co(1)-O(2)	1.876(4)
Ni(2)-O(3)	1.861(5)	Co(1)-O(3)	1.894(4)
Ni(1)-O(4)	1.855(5)	Co(1)-O(4)	1.908(4)
O(2)-Ni(1)-O(2A)	180.000(1)	Co(1)-O(5)	1.928(3)
O(2)-Ni(1)-O(1)	90.5(2)	Co(1)-O(6)	1.958(3)
O(2A)-Ni(1)-O(1)	89.5(2)	O(2)-Co(1)-O(1)	89.57(17)
O(2)-Ni(1)-O(1A)	89.5(2)	O(2)-Co(1)-O(3)	92.62(16)
O(2A)-Ni(1)-O(1A)	90.5(2)	O(1)-Co(1)-O(3)	89.21(16)
O(1)-Ni(1)-O(1A)	180.000(1)	O(2)-Co(1)-O(4)	89.99(17)
O(4A)-Ni(2)-O(4)	180.000(1)	O(1)-Co(1)-O(4)	178.30(14)
O(4A)-Ni(2)-O(3A)	90.2(2)	O(3)-Co(1)-O(4)	89.17(16)
O(4)-Ni(2)-O(3)	89.8(2)	O(2)-Co(1)-O(5)	97.61(4)
O(4A)-Ni(2)-O(3)	89.8(2)	O(1)-Co(1)-O(5)	91.51(15)
O(4)-Ni(2)-O(3)	90.2(2)	O(3)-Co(1)-O(5)	169.76(13)
O(3A)-Ni(2)-O(3)	180.000(1)	O(4)-Co(1)-O(5)	90.17(15)
O(2)-Ni(1)-O(2A)	180.000(1)	O(2)-Co(1)-O(6)	165.34(14)
O(2)-Ni(1)-O(1)	90.5(2)	O(1)-Co(1)-O(6)	89.54(16)
O(2A)-Ni(1)-O(1)	89.5(2)	O(3)-Co(1)-O(6)	102.00(14)
O(2)-Ni(1)-O(1A)	89.5(2)	O(4)-Co(1)-O(6)	91.30(15)
O(2A)-Ni(1)-O(1A)	90.5(2)	O(5)-Co(1)-O(6)	67.80(12)
		O(2)-Co(1)-N(1)	131.70(15)
		O(1)-Co(1)-N(1)	90.30(16)
		O(3)-Co(1)-N(1)	135.68(15)
		O(4)-Co(1)-N(1)	91.21(16)
		O(5)-Co(1)-N(1)	34.12(13)

Table 3. Hydrogen-bonding geometry (Å) for complexes **1** and **2**

Complexes	D-H···A	D-H	H···A	D···A	D-H···A
1	O5-H1···O1	0.878	2.23	3.072	161
2	O8-H12··· O6	0.882	2.47	3.189	139
2	O9-H13···O7	0.884	1.94	2.794	161

*Structural Descriptions of Ni(acac)]₂·0.5CH₃OH (**1**) and [Co(acac)₂NO₃]·2H₂O (**2**).*

The crystallography data reveal that complexes **1** and **2** have similar mononuclear molecular structures, as shown in Figures 1 and 3, respectively. The mononuclear nickel(II) complex **1** consists of a nickel atom, two pentane-2,4-dione anions and one uncoordinated molecule of CH_3OH. The molecular structure is thus essentially the same as that reported for this complex by Zhou [9], but without coordinated water. The central nickel(II) atom is united by four oxygen donors of two di-chelating pentane-2,4-dione anions. The NiO_4 core involving the central atom is a well-defined plane. The O(2A)-Ni(1)-O(2) and O(1A)-Ni(1)-O(1) angles are 180°. The bond lengths in the coordination square of the Ni atom are normal. The average Ni-O bond distance, 1.880(5) Å, is in good agreement with the corresponding square in the Ni-O distance reported in reference [1] (1.890 Å). Weak hydrogen contacts of 3.072(7) Å between the oxygen of the pentane-2,4-dione anions and the oxygen of the methanol molecule link the discrete monomers along the *b*-axis into a one-dimensional chain.

Figure 1. Molecular structure of [Ni(acac)₂]₂·0.5CH₃OH (**1**) at 30% probability displacement.
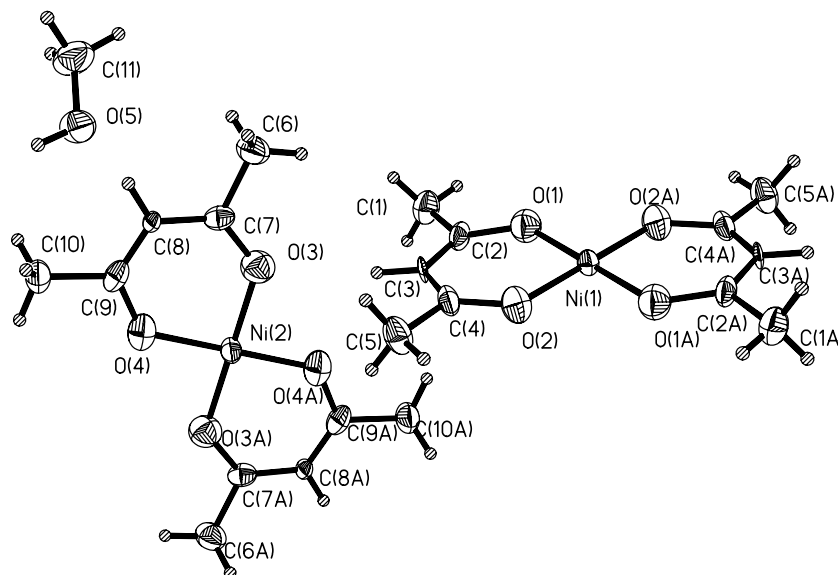
Compound **2** is a mononulear cobalt complex. The average Co-O bond distance of 1.909(4) Å is in good agreement with the corresponding Co-O distance reported in the literature (average 1.919(3) Å, [9]). In reference [8] the Co atom is described as being located on a centre of symmetry and consequently the two chelate rings are coplanar. The cobalt oxygen bond length is 1.917(3) Å. There are weak hydrogen contacts of 3.072(7) Å between the oxygen atoms from the ligands. The central Co atom has a slightly distorted octahedral coordination geometry and is hexacoordinated by four oxygen donors, two of which are from a di-chelating pentane-2,4-dione anion and the other two from a di-chelating nitrate anion. The three diagonal angles in the Co octahedrons are 169.76°, 165.34° and 178.3°, respectively. The O-H···O hydrogen bonds link the symmetry related molecules to form a network (Figures 2, 4 and Table 3).

Figure 2. The crystal packing for [Ni(acac)₂]₂·0.5CH₃OH (**1**) viewed along *a*-axis, showing intermolecular O-H···O hydrogen bonds as dashed lines.
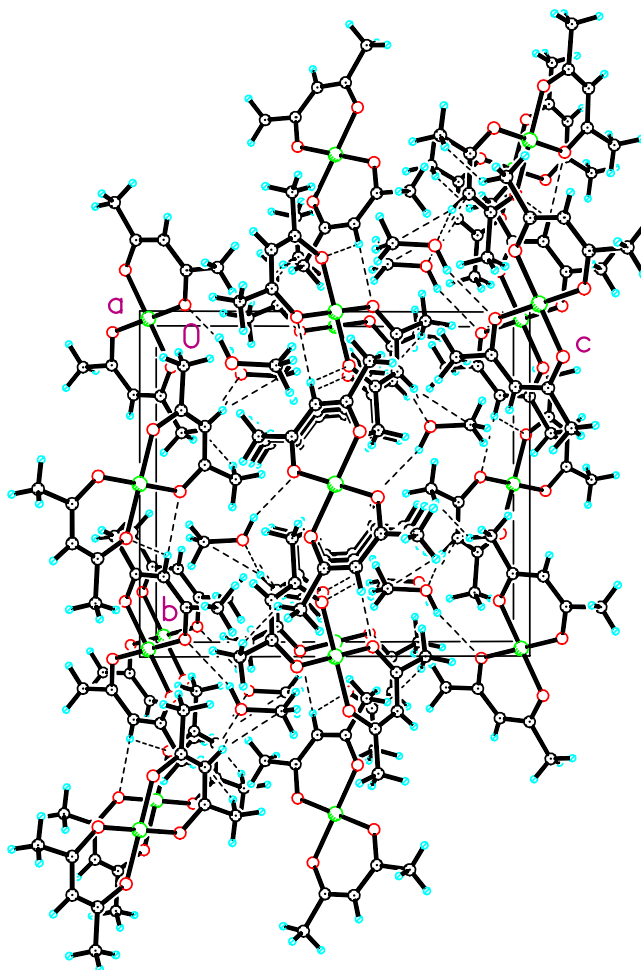
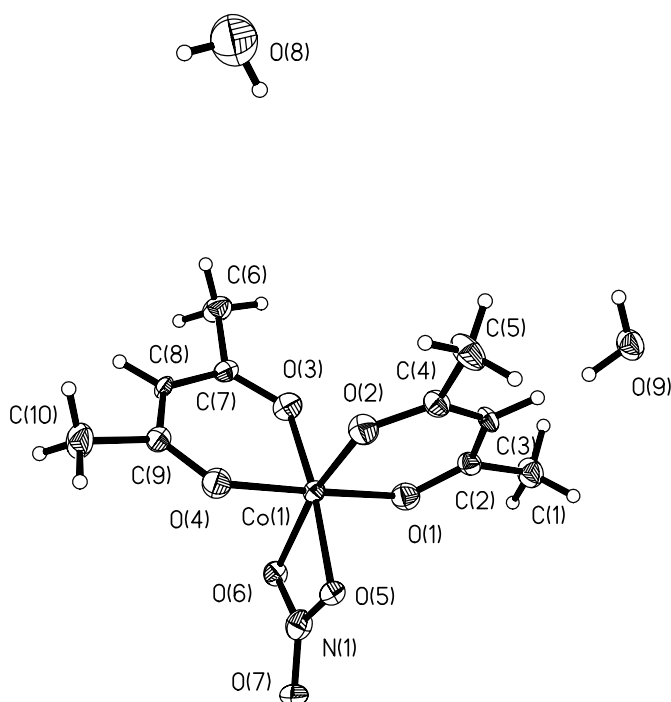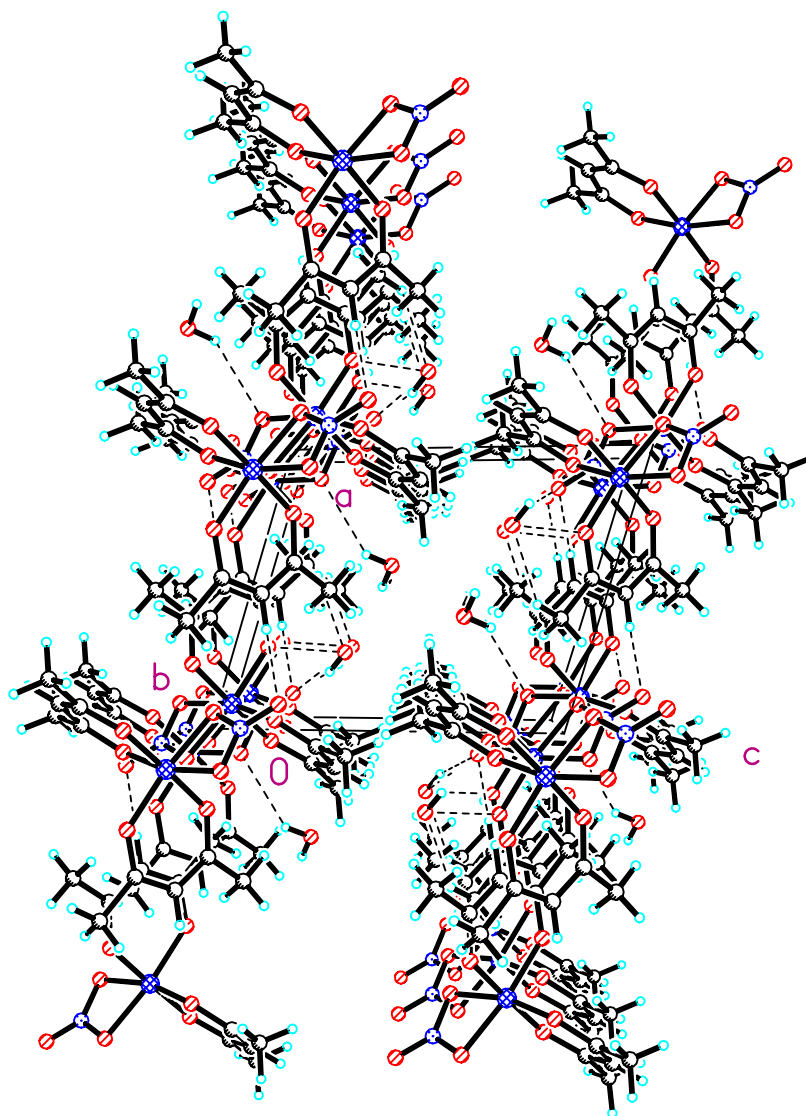**Figure 3.** Molecular structure of [Co(acac)₂NO₃]·2H₂O (**2**) at 30% probability displacement.

Figure 4. The crystal packing for **2** viewed along the *b*-axis, showing intermolecular O-H···O hydrogen bonds as dashed lines.

Experimental

General

Pentane-2,4-dione, $NiClO_4 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were available commercially and were used without further purification.

Synthesis of [Ni(acac)$_2$]·0.5 CH$_3$OH (**1**)

A methanol solution (5mL) of $NiClO_4 \cdot 6H_2O$ (1 mmol, 366 mg) was added to an ethanol solution (5 mL) of pentane-2,4-dione (1 mmol, 100 mg). The reaction mixture was stirred for 20 minutes and poured into a Teflon vessel until 30% of its volume was filled. The vessel was then placed in a stainless steel tank, which was heated at 150°C under autogenous pressure for 24 h. After the autoclave was depressurized and cooled, yellow crystals were formed in the solution. These crystals were

separated by filtration, washed twice with aqueous alcohol solution and dried over $CaCl_2$. Yield, 0.22 g (75%). Calculated for $C_{11}H_{18}NiO_5$ (FW 288.96): C, 45.83; H, 6.14. Found C, 45.72; H, 6.28. Decomposition point: 170°C.

*Synthesis of [Co(acac)₂NO₃]·2H₂O (**2**)*

An ethanol solution (5mL) of $Co(NO_3)_2$·$6H_2O$ (1 mmol, 291 mg) was added to an ethanol solution (5mL) of pentane-2,4-dione (1 mmol, 100 mg). The reaction mixture was stirred for 20 minutes and poured into a Teflon vessel until 30% of its volume was filled. The vessel was then placed in a stainless steel tank, which was heated at 130°C under autogenous pressure for 24 h. After the autoclave was depressurizedcooled and , brown-red crystals were formed in the solution. These crystals were separated by filtration, washed twice with aqueous alcohol solution and dried over $CaCl_2$. Yield: 0.291 g (82%). Calculated for $C_{10}CoH_{18}NO_9$ (FW 355.18): C, 33.81; H, 5.11; N, 3.94%. Found: C, 33.76; H, 5.18; N3.87%. Decomposition point: 160.0 °C.

Data collection, Crystal Structure Determination and Refinement

A yellow crystal of **1** (approximate dimensions of 0.30 x 0.24 x 0.20 mm) and a brown-red crystal of **2** (approximate dimensions of 0.42 x 0.37 x 0.31 mm) were mounted on a CCD area detector equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 293 K for **1** and 298 K for **2** using the ω/2θ scan mode. A total of 2434 reflections for **1** and 2546 reflections for **2** were collected in the range of $2.19° < \theta < 25.02°$ for **1** and $2.64° < \theta < 25.02°$ for **2**, of which 1231 for **1** and 2024 for **2** were unique. The data sets were corrected for Lorentz - polarization effects, and a MULTI-SCANE absorption correction was applied (T_{min} = 0.6766 and T_{max} = 0.7654 for **1**; T_{min} = 0.6344 and T_{max} = 0.7088 for **2**). The structures were solved by direct methods. The remaining non-hydrogen atoms were located by use of successive difference Fourier maps and full-matrix least-squares refinement. All standard deviations (esds) (except the esd in the dihedral angle between two least-square planes) were estimated using the full covariance matrix. The cell esds were taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they were defined by crystal symmetry. An approximate (isotropic) treatment of cell esds was used for estimating esds involving least square planes. The weighted R-factor (Rw) and goodness of fit (S) are based on F^2, conventional R-factors are based on F, with F set to zero for negative F^2. The threshold expression of $I > 2\sigma(I)$ is used only for calculating R-factors (gt) etc., and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. The final R_1 ($R_1 = \Sigma||F_o| - |F_c||/\Sigma||F_o|$) value for **1** was 0.0554 for 173 parameters and 1231 observed reflections ($I > 2\sigma(I)$); and the final R_1 for **2** was 0.0520 for 204 parameters and 522 observed reflections ($I > 2\sigma(I)$). All calculations were carried on a Bruker SMART computer using the SHELXS and SHELXL programs and published scattering factors. Crystallographic data for the complexes reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 233227 for complex **1** and CCDC 233226 for complex **2**; these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

1. Smith, M. E.; Andersen, R. A. Me$_5$C$_5$Ni(acac): A Monomeric, Paramagnetic, 18-Electron, Spin-Equilibrium Molecule. *J. Am. Chem. Soc.* **1996**, *118*, 11119-11128.
2. Silvana, C. N., Kulbinder, K. B., Paul J. T., John T. W. Synthesis and physical and structural characterization of Ag(I) complexes supported by non-fluorinated β-diketonate and related ancillary ligands. *Polyhedron* **2002**, *21*, 1289-1297.
3. Zhu, W.G.; Qing, J.; Lu, Z.Y.; Wei, X.Q.; Xie, M.G.; Novel binuclear uropium β-diketone chelate used as red emitter in organic electroluminescent device. *Thin Solid Films* **2000**, *363*, 167-169.
4. Song, D.T.; Liu, S.F.; Wang, R.Y.; Wang, S.N. Syntheses and structures of new blue luminescent B(III) and Al(III) complexes: BPh$_2$(acac-azain) and Al(CH$_3$)(acac-azain)$_2$, acac-azain=1-N-7-azaindolyl-1,3-butanedionato. *J. Organomet. Chem.* **2001**, *631*, 175–180.
5. Mehrotra, R.C.; Bohra, R.; Gaur, D.P. *Metal-Diketonates and Allied Derivatives*; Academic Press: New York, **1978**.
6. Sievers, R.E., Eisentraut, K.J., Springer Jr., C.S. In *Lanthanide/Actinide Chemistry*, Gould, R.F. (Ed.); American Chemical Society: Washington, DC, **1967**; Chapter 11.
7. Alexander, D. G.., Alexander, P. S., Marina, I. S. Common and less-common coordination modes of the typical chelating and heteroaromatic ligands. *Coord. Chem. Rev.* **1998**, 17331–77.
8. Burgess, J., Fawcett, J., Russell, D. R., Gilani, S. R. Monomeric bis(2,4-pentanedionato)cobalt(II). *Acta Cryst.* **2000**. C56, 649-650.
9. Zhou, X. F., Han, A. J., Chu, D.B., Huang, Z. X., Electrochemical synthesis and a redetermination of Ni(acac)$_2$(H$_2$O)$_2$·H$_2$O. *Acta Cryst.* **2001**, *E57*, 506-508.

Sample Availability: Available from the authors.