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Monomer−Trimer Isomerism in 3-Substituted Pentane-2,4-dione Derivatives of Nickel(II)

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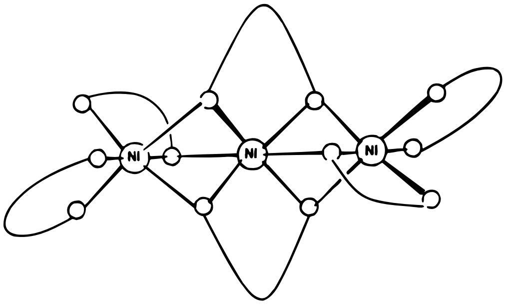
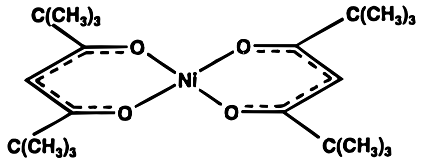
Bis(η^3-allyl)nickel reacts with pentane-2,4-dione derivatives having alkenyl substituents in the 3-position to give Ni(3-R-pentane-2,4-dionato)$_2$ compounds which have been shown by X-ray diffraction and NMR spectroscopy to be monomeric [R = 5-hexenyl, $C_{22}H_{34}NiO_4$, $a = 13.718(3)$ Å, $b = 4.962(1)$ Å, $c = 16.643(3)$ Å, $\beta = 92.46(3)°$, space group $P2_1/n$, $Z = 2$; R = 7-octenyl, $C_{26}H_{42}NiO_4$, $a = 4.8449(5)$ Å, $b = 8.3202(8)$ Å, $c = 16.792(1)$ Å, $\alpha = 89.480(4)°$, $\beta = 88.240(4)°$, $\gamma = 77.30(1)°$; R = 9-decenyl, $C_{30}H_{50}NiO_4$, $a = 4.8067(2)$ Å, $b = 8.2809(3)$ Å, $c = 19.4014(7)$ Å, $\alpha = 90.974(4)°$, $\beta = 91.907(4)°$, $\gamma = 102.495(4)°$, space group $P\bar{1}$, $Z = 1$; R = methyl, $C_{12}H_{18}NiO_4$, $a = 4.9447(4)$ Å, $b = 8.0649(7)$ Å, $c = 9.0633(6)$ Å, $\alpha = 109.377(6)°$, $\beta = 93.706(7)°$, $\gamma = 106.283(7)°$, space group $P\bar{1}$, $Z = 1$; R = phenylethano, $C_{26}H_{30}NiO_4$, $a = 12.792(1)$ Å, $b = 6.503(1)$ Å, $c = 14.933(1)$ Å, $\beta = 109.025(7)°$, space group $P2_1/n$, $Z = 2$] in the crystal and in solution at room temperature. No inter- or intramolecular interaction of the alkenyl substituent with the 16e metal atom is observed. The corresponding Ni compounds containing the 3-phenyl-substituted dione have been shown to adopt both monomeric [$C_{22}H_{22}NiO_4$, $a = 10.2261(5)$ Å, $b = 6.6439(3)$ Å, $c = 13.7862(7)$ Å, $\beta = 93.677(6)°$, space group $P2_1/n$, $Z = 2$] and trimeric [$(C_{22}H_{22}NiO_4)_3$, $a = 10.5917(7)$ Å, $b = 12.3092(8)$ Å, $c = 12.5926(5)$ Å, $\alpha = 103.937(4)°$, $\beta = 96.388(3)°$, $\gamma = 96.227(5)°$, space group $P\bar{1}$, $Z = 1$] forms in the crystal while the compound formed by *tert*-butyl acetoacetate [$(C_{16}H_{26}NiO_6)_3$, $a = 9.713(1)$ Å, $b = 17.550(1)$ Å, $c = 17.391(1)$ Å, $\beta = 100.272(5)°$, space group $P2_1/n$, $Z = 2$] is a trimer in which the central Ni atom interacts solely with bridging acetyl groups. The crystal structure of 3-phenyl-2,4-pentanedione [$C_{11}H_{12}O_2$, $a = 19.2961(6)$ Å, $b = 6.8561(2)$ Å, $c = 7.5935(2)$ Å, space group $Pnma$, $Z = 4$] has also been determined.

Introduction

It has been known for at least 35 years that the substitution of the methyl groups in the trimer [Ni(acac)$_2$]$_3$ (shown schematically as **1**) by sterically more demanding groups leads to the formation of a monomeric species containing square-planar Ni(II),[1−4] and this has been confirmed in the crystal for the *tert*-butyl-substituted derivative (**2**) by X-ray diffraction.[5]

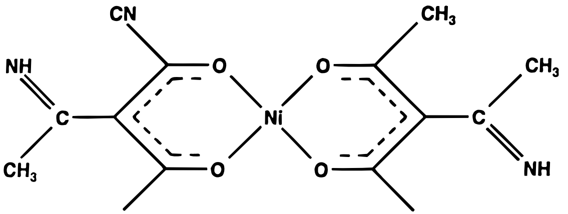


1



2

As part of our investigation of the catalytic and stoichiometric reactions of diketones and diesters containing unsaturated substituents with transition metals,[6] we have had occasion to prepare a number of pentane-2,4-dione derivatives having alkenyl substituents in the 3-position. The products of the reaction of these with nickel(II) are also monomeric. The surprising paucity of structural information for nickel compounds having substituents in the 3-position (the only crystal structure determination we are aware of is that of **3**, which is the product of the reaction between **1** and cyanogen)[7] prompts us to report our results and the structure of six additional examples.



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Experimental Section

General Techniques. Infrared spectra (KBr pellets) have been recorded on a Nicolet MagnaIR 750 spectrophotometer in the range of 4000−400 cm^{-1}. Mass spectra have been recorded on a Finigan MAT 8200 using an EI method with a 70 eV ionization energy. NMR spectra have been recorded on a Bruker apparatus with 200 MHz in toluene using TMS as an internal standard. DEPT technique has been used to

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Table 1. Analytical Data for the Bis(3-R-pentane-2,4-dionato)nickel Compounds (**4**−**11**)

		anal. calcd (found) %			
compd (R)	reactn time	Ni	C	H	MS/M$^+$ (T °C)
4 ($C_4H_8CH{:}CH_2$)	48 h	13.95 (14.04)	62.75 (62.56)	8.08 (8.12)	420 (90)
5 ($C_6H_{12}CH{:}CH_2$)	48 h	12.30 (12.10)	65.41 (64.15)	8.81 (8.56)	476 (120)
6 ($C_8H_{16}CH{:}CH_2$)	24 h	11.00 (11.18)	65.75 (67.55)	9.45 (9.35)	532 (150)
7 ($C_{12}H_{24}CH{:}CH_2$)	24 h	9.09 (10.00)	70.69 (71.21)	10.31 (9.75)	664 (180)
8 ($CH_2CH{:}CHCH{:}CH_2$)	7 d	15.18 (15.32)	62.06 (61.38)	6.21 (6.86)	388 (120)
9 (Me)	7 d	20.60 (20.61)	50.58 (49.29)	6.34 (5.96)	284 (80)
10 (Ph)	12 h	14.35 (15.02)	64.87 (64.11)	5.42 (5.60)	408 (40)
11 (C_2H_4Ph)	12 h	12.61 (13.12)	67.12 (66.45)	6.51 (6.22)	464 (140)

assign unknown peaks in the ^{13}C-NMR spectra. The general experimental conditions have been described earlier.[6]

Bis(η^3-allyl)nickel was prepared by literature methods.[8] The 3-substituted 2,4-diones were prepared in high yield by reacting acetylacetone with potassium *tert*-butylate and the appropriate organic halide.[9]

Bis(3-R-pentane-2,4-dionato)nickel(II) Complexes (4−9, 11). The compounds have all been prepared by reacting bis(η^3-allyl)nickel with 2 equiv of the 3-substituted 2,4-pentanedione in pentane or THF at room temperature. A typical example is described below, and analytical data are collected together in Table 1. The reaction is accompanied by partial decomposition of the bis(η^3-allyl)nickel, and the yields never exceed 50%. A parent peak is observed for all of the compounds in the mass spectra.

Bis[3-(5-hexenyl)pentane-2,4-dionato]nickel (4). A solution of bis(η^3-allyl)nickel in THF (8.9 mmol in 66 mL THF) was cooled to −78 °C, and 3-(5-hexenyl)pentane-2,4-dione (3.86 g, 21.2 mmol) was added. The reaction mixture was stirred at room temperature for 48 h to give a brown solution which was filtered and concentrated to 70 mL. Pentane (30 mL) was added, and the compound precipitated as a pink/red solid and was dried under high vacuum. Yield: 1.28 g (34% theory). The compound (yield ca. 30%) was also the product of an analogous reaction with bis(cyclo-1,5-octadiene)nickel. The diamagnetic nature of the compound has been confirmed by a solid state ^{13}C-NMR spectrum.

^{13}C-NMR (solid state CP/MAS): δ 186.91/185.44 (C2/C4), 138.14 (C10), 117.59 (C11), 112.70 (C3), 36.66/34.37/32.35/34.05 (C6/C7/C8/C9), 24.64/24.23 (C1/C5). For numbering scheme, see Figure 1a.[10]

Bis(3-phenylpentane-2,4-dionato)nickel (10). This compound was prepared as described above from bis(η^3-allyl)nickel and 3-phenyl-2,4-pentanedione in pentane. However, since evaporation of the reaction mixture led to the formation of a brown oil which could not be purified, this was dissolved in ethanol and the green ethanol adduct was isolated. Heating in pentane overnight led to the formation of pink crystals of **10** as well as green crystals, which were isolated and identified by X-ray crystallography as the trimer [Ni(3-Phacac)$_2$]$_3$ (**12**) (see Figure 4a).

Bis(*tert*-butyl acetoacetato)nickel Trimer (13). A solution of bis(η^3-allyl)nickel in THF (10.49 mmol in 50 mL THF) was cooled to −78 °C, and *tert*-butyl acetoacetate (3.65 g, 24.0 mmol) was added. The yellow solution was slowly warmed to room temperature and stirred overnight to give a green suspension. The reaction mixture was evaporated to dryness and the residue extracted with THF (50 mL). The solution was filtered, treated with pentane (10 mL), and cooled to −78 °C to give the compound as bright green needles, which were washed with pentane/THF (1:1) and dried under high vacuum. Yield: 2.57 g (66% theory). Anal. Calcd for $C_{48}H_{78}O_{18}Ni_3$: C, 51.5; H, 7.0; Ni, 15.7. Found: C, 51.7; H, 6.6; Ni, 15.9. MS (FAB, 140 °C): *m/e* 1116 (M_3^+), 959, 744 (M_2^+), 587, 372 (M^+), 316, 260. Magnetic susceptibility: 4.9 μ_B. Crystal structure: see Figure 4b and Table 8.

X-Ray Crystallography. Details of the crystal data and refinement for the compounds studied are given in Table 2. The atomic coordinates have been deposited with the other Supporting Information. Crystals were sealed in glass capillaries under argon, and intensity data collection was carried out using an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Cu Kα radiation by a coupled $\omega-2\theta$ scan technique with the speed varying from 1.0 to 10.0°/min, depending on a standard deviation to intensity ratio of a preliminary 10°/min scan. The time taken to measure the background was half that taken to measure the peak. A Ni filter was placed in front of the detector if the peak count was greater than 50 000 counts/s.

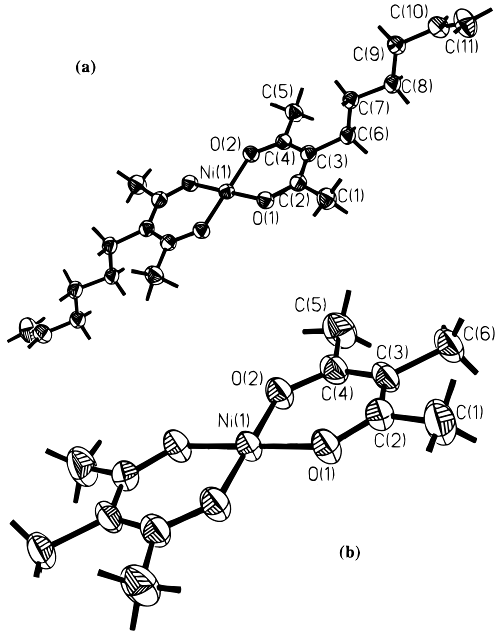

Figure 1. Molecular structures of (a) bis[3-(5-hexenyl)pentane-2,4-dionato]nickel (**4**) (30% probability level) and (b) bis(3-methylpentane-2,4-dionato)nickel (**9**) (50% probability level) with numbering scheme.

Unit cell parameters were determined by the least-squares technique from 25 reflections; data reduction was by DATAP.[11] Because of the low absorption coefficients, absorption corrections have not been applied. All structures were solved by direct methods using SHELXS-86[12] and refined by full-matrix, least-squares on all F_o^2 using SHELXL-93.[13] Real and imaginary parts of the atomic scattering factors have been taken from the literature.[14] All non-hydrogen atoms were refined anisotropically. For **10** (R = Ph) and **11** (R = C_2H_4Ph), all hydrogen atoms were found in the difference Fourier maps and refined isotropically. For **9** (R = Me), the hydrogen atoms were constrained to an idealized tetrahedral and the isotropic thermal parameters were refined. The two trans hydrogen atoms for **4**, **5**, and **6** (R = $(CH_2)_nCH{:}CH_2$, n = 4, 6, 8) attached to the terminal double bond were not localized and were included in the subsequent cycles in the idealized positions. The remaining hydrogen atoms were included without constraint. The

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(9) See, for example: Martin, D. F.; Fernelius, W. C; Shamma, M. *J. Am. Chem. Soc.* **1959**, *81*, 130.

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(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol 4, p 99.

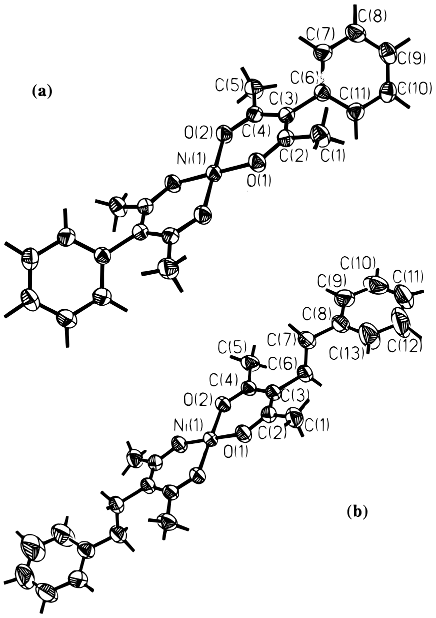


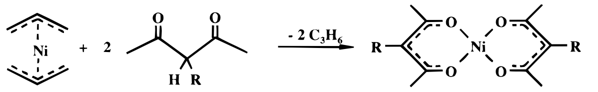
Figure 2. Molecular structures of (a) bis(3-phenylpentane-2,4-dionato)nickel (**10**) and (b) bis(3-phenylethanopentane-2,4-dionato)nickel (**11**) with numbering scheme (50% probability level).

disordered hydrogen atoms for 3-phenylpentane-2,4-dione were calculated. H(10) was refined isotropically without constraint, and all other hydrogen atoms were assigned an idealized ($U_H = 1.3U_C$) geometry.

The correct choice of space group was confirmed by the subsequent refinements. Attempts to refine **9** in the noncentrosymmetric space group *Pna*2_1 (No. 33) did not resolve the rotational disorder of the phenyl groups.

Results and Discussion

The 3-substituted pentane-2,4-dionate derivatives **4**−**8** have been prepared by reacting bis(η^3-allyl)nickel [or (cod)$_2$Ni] with the appropriate alkenyl- or alkadienyl-substituted diketone in pentane at room temperature.



4–**7**, R=$(CH_2)_nCH{:}CH_2$ (n=4, 6, 8, 12)
8, R=$CH_2CH{:}CHCH{:}CH_2$

In addition, we have used the same method to prepare the derivatives in which R = Me (**9**), Ph (**10**), and C_2H_4Ph (**11**). **9**[15] and **10**[3,16] are known compounds and have been suggested to be in equilibrium in solution with a trimeric structure related to **1** while UV evidence has been presented which indicates that monomers are formed upon vaporization of the trimers.[3d] The 3-phenyl-substituted derivative **10** proved difficult to crystallize and was isolated by reacting the impure product with ethanol, isolating the green ethanol adduct, and removing the ethanol by refluxing in pentane. During the workup, we also managed to isolate crystals of the green trimer, and the structure of this compound is discussed below. Compounds **4**−**11** are red to pink and stable at room temperature. They dissolve readily in ethanol to give octahedral adducts, whose structures and reactions will be discussed in a further publication along with the magnetic behavior: the compounds are diamagnetic in toluene at room temperature and, upon cooling, form green, paramagnetic solutions, from which the red monomer is precipitated at low temperature.[17]

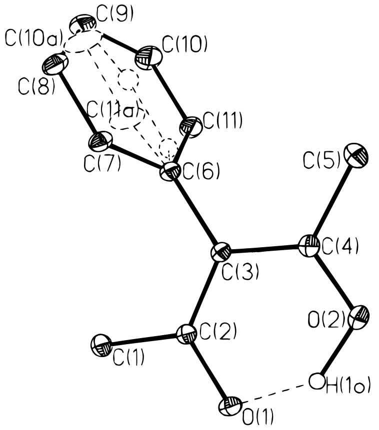


Figure 3. Molecular structure of 3-phenyl-2,4-pentanedione with numbering scheme. The atoms C(7), C(8), C(10), and C(11) are disordered in two positions (a) (50% probability level).

Representative preparative details for compounds **4**−**11** have been included in the Experimental Section, and analytical data are summarized in Table 1. The reaction with bis(η^3-allyl)nickel occurs in a stepwise manner, and although we have not isolated the intermediate (η^3-allyl)Ni(diketonate) species, these have been identified in the mass spectra. We had anticipated that, in suitable cases, the terminal double bond in **4**−**8** might interact with the metal atom; however, no evidence for either inter- or intramolecular interaction has been found either in the crystal or in solution.

The crystal structures of **4**−**6** [R = $(CH_2)_nCH{:}CH_2$, *n* = 4, 6, 8] and **9**−**11** (R = Me, Ph, C_2H_4Ph) have been determined by X-ray diffraction. Selected structural data are listed in Tables 3 and 4, and the molecular structures of **4**, **9**, **10**, and **11** are shown in Figures 1 and 2 along with the numbering scheme. The structures of **5** and **6** are very similar to that of **4** and have been included in the Supporting Information.

The compounds are all monomeric, and there are no intermolecular interactions to neighboring molecules. The nickel atoms in **4**−**6**, **9**, and **11** lie in a strictly square-planar environment, and the deviation of the non-hydrogen atoms of the 2,4-diketonate fragment out of the molecular plane does not exceed 0.1 Å. The H atoms have been refined, and one H atom of each 2,4-Me group lies in the molecular plane.

In contrast to the other five examples, the 2,4-diketonate fragments in the 3-phenyl-substituted derivative (**10**) are not planar: the O1/Ni/O2 and C2/C3/C4 planes generate an angle of 4.3(2)°. Furthermore, the central C atom (C3) and the phenyl atom C6 lie 0.113(1) Å and 0.350(5) Å, respectively, out of, and on the same side of, the NiO_4 plane. The phenyl group is twisted by ca. 69° out of the molecular plane, while C3−C6 is significantly shorter than in the other examples (Table 3). In order to assess the significance of these observations, we undertook the crystal structure of the parent diketone, 3-phenyl-2,4-pentanedione, and the molecular structure of this compound is shown in Figure 3 and selected structural data in Table 5.

In the crystal the molecule adopts the enol form with all non-hydrogen atoms located in the plane of either the phenyl or enol groups. The phenyl group takes up two identical positions with respect to a mirror plane through the enol group and is twisted by 77.2° out of this plane. The enolic H atom is bonded asymmetrically to the oxygen atoms [O1−H/O2−H, 1.45(6)/

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(15) Addison, A. W.; Graddon, D. P. *Aust. J. Chem.* **1968**, *21*, 2003.

(16) Graddon, D. P.; Heng, K. B. *Aust. J. Chem.* **1972**, *25*, 2247.

(17) Polyakov, V. R. To be submitted for publication.

Table 2. Crystal and Structure Refinement Details[a]

compd	**4**	**5**	**6**
empirical formula	$C_{22}H_{34}NiO_4$	$C_{26}H_{42}NiO_4$	$C_{30}H_{50}NiO_4$
fw	421.20	477.31	533.41
T (K)	293(2)	293(2)	293(2)
wavelength (Å)	1.541 78	1.541 78	1.541 78
color	pink	pink	pink
cryst syst	monoclinic	triclinic	triclinic
space group (no.)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
θ range for cell determination	16.14−31.48	18.7−44.6	18.755−33.9
unit cell dimens			
a, *b*, *c* (Å)	13.718(3), 4.962(1), 16.643(3)	4.8449(5), 8.3202(8), 16.792(1)	4.8067(2), 8.2809(3), 19.4014(7)
α, β, γ (deg)	90, 92.46(3), 90	89.480(4), 88.240(4), 77.30(1)	90.974(4), 91.907(4), 102.495(4)
V (Å^3)	1131.8(4)	660.0(1)	753.31(5)
Z	2	1	1
ρ_{calcd} (Mg/mm^3)	1.236	1.201	1.176
abs coeff (mm^{-1})	1.409	1.264	1.156
F(000)	452	258	290
cryst size, mm	0.70 × 0.14 × 0.11	0.56 × 0.07 × 0.07	0.22 × 0.10 × 0.05
θ range	4.09−75.01	2.63−74.96	2.28−74.93
index ranges	$-17 \le h \le 17$, $0 \le k \le 6$, $0 \le l \le 20$	$-5 \le h \le 6$, $-10 \le k \le 10$, $0 \le l \le 21$	$-6 \le h \le 5$, $-10 \le k \le 10$, $0 \le l \le 24$
rflns collected	2707	2736	3118
indep rflns	2332 [*R*(int) = 0.01]	2651 [*R*(int) = 0.002]	3031 [*R*(int) = 0.003]
obsd data/restrictions/params	1924/4/185	2417/1/215	2848/0/253
GOF, *S*	1.061	1.153	1.070
final R1, $_w$R2 [$I > 2\sigma(I)$]	0.0532, 0.1487	0.0524, 0.1504	0.0447, 0.1292
R1, $_w$R2 (all data)	0.0619, 0.1574	0.0564, 0.1538	0.0465, 0.1309
(Fourier map) max, min (e/Å^{-3})	0.692, −0.586	0.588, −0.561	0.481, −0.496
extinction coeff, ϵ	0.016(2)		
compd	**9**	**10**	**11**
empirical formula	$C_{12}H_{18}NiO_4$	$C_{22}H_{22}NiO_4$	$C_{26}H_{30}NiO_4$
fw	284.97	409.11	465.21
T (K)	293(2)	293(2)	293(2)
wavelength (Å)	1.54178	1.541 78	1.541 78
color	pink	pink	pink
cryst syst	triclinic	monoclinic	monoclinic
space group (no.)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)
θ range for cell determination	18.2−45.9	27.65−49.05	24.4−46.7
unit cell dimens			
a, *b*, *c* (Å)	4.9447(4), 8.0649(7), 9.0633(6)	10.2261(5), 6.6439(3), 13.7862(7)	12.792(1), 6.503(1), 14.933(1)
α, β, γ (deg)	109.377(6), 93.706(7), 106.283(7)	90, 93.677(6), 90	90, 109.025(7), 90
V (Å^3)	322.28(4)	934.72(8)	1174.4(2)
Z	1	2	2
ρ_{calcd} (Mg/mm^3)	1.468	1.454	1.316
abs coeff (mm^{-1})	2.193	1.705	1.419
F(000)	150	428	492
cryst size (mm)	0.53 × 0.25 × 0.03	0.37 × 0.22 × 0.21	0.56 × 0.32 × 0.18
θ range	5.25−74.83	4.33−74.91	3.13−74.82
index ranges	$-5 \le h \le 6$, $-10 \le k \le 9$, $0 \le l \le 11$	$-12 \le h \le 12$, $-7 \le k \le 8$, $0 \le l \le 17$	$-16 \le h \le 15$, $0 \le k \le 7$, $0 \le l \le 18$
rflns collected	1389	3758	2426
indep rflns	1311 [*R*(int) = 0.0134]	1921 [*R*(int) = 0.0165]	2342 [*R*(int) = 0.0176]
obsd data/restrictions/params	1280/0/92	1848/0/169	2143/0/203
GOF, *S*	1.226	1.037	1.046
final R1, $_w$R2 [$I > 2\sigma(I)$]	0.0625, 0.2124	0.0339, 0.0968	0.0401, 0.1140
R1, $_w$R2 (all data)	0.0632, 0.2127	0.0353, 0.0982	0.0428, 0.1159
(Fourier map) max, min (e/Å^{-3})	0.746, −0.520	0.307, −0.498	0.316, −0.403
extinction coeff, ϵ	0.029(6)		
compd	MeCOC(Ph):C(Me)OH	**12**	**13**
empirical formula	$C_{11}H_{12}O_2$	$[C_{16}H_{26}NiO_6]_3$	$[C_{22}H_{22}NiO_4]_3$
fw	176.21	373.08	409.11
T (K)	293(2)	293(2)	293(2)
wavelength (Å)	1.541 78	1.541 78	1.541 78
color	colorless	green	green
cryst syst	orthorhombic	monoclinic	triclinic
space group (no.)	Pnma (62)	$P2_1/c$ (14)	$P\bar{1}$ (2)
θ range for cell determination	23.95−31.45	12.9−27.1	18.9−44.4
unit cell dimens			
a, *b*, *c* (Å)	19.2961(6), 6.8561(2), 7.5935(2)	9.713(1), 17.550(1), 17.391(1)	10.5917(7), 12.3092(8), 12.5926(5)
α, β, γ (deg)	90, 90, 90	90, 100.272(5), 90	103.937(4), 96.388(3), 96.227(5)
V (Å^3)	1004.59(5)	2917.0(4)	1567.9(2)
Z	4	2	1
ρ_{calcd} (Mg/mm^3)	1.165	1.274	1.300
abs coeff (mm^{-1})	0.639	1.654	1.525
F(000)	376	1188	642

Table 2 (Continued)

cryst size (mm)	0.56 × 0.46 × 0.21	0.74 × 0.22 × 0.11	0.30 × 0.20 × 0.19
θ range	4.58−74.93	3.61−74.95	3.65−75.05
index ranges	$-24 \le h \le 24$, $0 \le k \le 8$, $-9 \le l \le 9$	$-11 \le h \le 11$, $0 \le k \le 21$, $0 \le l \le 21$	$-13 \le h \le 99$, $-15 \le k \le 99$, $0 \le l \le 99$
rflns collected	3417	5972	6778
indep rflns	1125 [R(int) = 0.0417]	5790 [R(int) = 0.0126]	6472 [R(int) = 0.0173]
obsd data/restrictions/params	981/0/86	4635/0/469	5437/0/499
GOF, S	1.154	0.991	1.045
final R1, $_w$R2 [$I > 2\sigma(I)$]	0.0708, 0.2317	0.0360, 0.0867	0.0383, 0.1075
R1, $_w$R2 (all data)	0.0756, 0.2381	0.0491, 0.0919	0.0463, 0.1110
(Fourier map) max, min (e/Å^{-3})	0.412, −0.200	0.217, −0.323	0.289, −0.388
extinction coeff, ϵ	0.011(3)		

[a] $R(\text{int}) = \sum|F_o^2 - F_o^2\,(\text{mean})|/\sum|F_o^2|$; $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $_wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$; $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; where F_o = observed structure factors, F_c = calculated structure factors, w = weighting scheme (see instructions to SHELXL-93), n = number of elections, p = total number of parameters refined. Corrections for extinction used the expression $F_c^{\text{new}} = kF_c[1 + 0.001\epsilon F_c^2\lambda^3/\sin(2\theta)]^{-0.25}$.

Table 3. Selected Bond Distances (Å) for Compounds **4**−**6** and **9**−**11**[a]

	4 (R = $C_4H_8CH{:}CH_2$)	**5** (R = $C_6H_{12}CH{:}CH_2$)	**6** (R = $C_8H_{16}CH{:}CH_2$)	**9** (R = Me)	**10** (R = Ph)	**11** (R = C_2H_4Ph)
Ni−O(1)	1.830(2)	1.830(2)	1.8326(13)	1.829(4)	1.8329(11)	1.8251(14)
Ni−O(2)	1.837(2)	1.831(2)	1.8318(12)	1.834(3)	1.8389(11)	1.8327(12)
O(1)−C(2)	1.285(3)	1.291(3)	1.286(2)	1.287(6)	1.277(2)	1.279(2)
O(2)−C(4)	1.281(3)	1.290(3)	1.289(2)	1.289(6)	1.283(2)	1.285(2)
C(2)−C(1)	1.505(4)	1.490(4)	1.498(3)	1.500(8)	1.503(2)	1.500(3)
C(4)−C(5)	1.505(4)	1.504(3)	1.499(3)	1.505(7)	1.509(2)	1.504(3)
C(3)−C(6)	1.514(4)	1.531(3)	1.528(2)	1.514(7)	1.502(2)	1.521(3)
C(6)−C(7)	1.524(4)	1.527(3)	1.526(2)		1.388(2)	1.532(3)
C(7)−C(8)	1.519(4)	1.518(3)	1.522(2)		1.387(2)	1.504(3)
C(8)−C(9)	1.519(4)	1.521(3)	1.519(3)		1.387(2)	1.368(3)
C(9)−C(10)	1.497(5)	1.512(4)	1.520(3)		1.383(3)	1.396(4)
C(10)−C(11)	1.236(7)	1.523(4)	1.520(3)		1.385(2)	1.352(6)
C(11)−C(6)					1.393(2)	
C(11)−C(12)		1.492(4)	1.520(3)			1.338(7)
C(12)−C(13)		1.226(4)	1.518(3)			1.378(5)
C(13)−C(8)						1.376(4)
C(13)−C(14)			1.502(4)			
C(14)−C(15)			1.227(4)			

[a] See figures for numbering scheme.

Table 4. Selected Bond Angles (deg) for Compounds **4**−**6** and **9**−**11**[a]

	4 (R = $C_4H_8CH{:}CH_2$)	**5** (R = $C_6H_{12}CH{:}CH_2$)	**6** (R = $C_8H_{16}CH{:}CH_2$)	**9** (R = Me)	**10** (R = Ph)	**11** (R = C_2H_4Ph)
O(1)−Ni−O(2)	93.81(8)	94.17(7)	94.19(5)	94.1(2)	93.63(5)	93.65(5)
O(1)−Ni−O(2*)	86.19(8)	85.83(7)	85.81(5)	85.9(2)	86.37(3)	86.35(5)
O(1)−Ni−O(1*)	180.0	180.0	180.0	180.0	180.0	180.0
Ni−O(1)−C(2)	127.1(2)	127.5(2)	127.27(12)	127.3(4)	127.53(1)	127.30(13)
O(1)−C(2)−C(3)	125.9(2)	124.5(2)	125.2(2)	125.7(5)	124.97(14)	125.1(2)
C(2)−C(3)−C(4)	120.3(2)	121.4(2)	120.8(2)	120.0(4)	120.16(13)	120.1(2)
C(3)−C(4)−O(2)	125.4(2)	125.3(2)	125.3(2)	126.0(5)	125.46(13)	125.2(2)
C(4)−O(2)−Ni(1)	127.4(2)	127.1(2)	127.21(12)	126.8(4)	126.85(10)	127.08(12)
O(1)−C(2)−C(1)	112.6(3)	113.2(2)	112.8(2)	113.3(5)	114.10(14)	112.8(2)
C(1)−C(2)−C(3)	121.5(3)	122.3(2)	121.9(2)	120.9(5)	120.91(14)	122.1(2)
O(2)−C(4)−C(5)	113.1(2)	112.3(2)	112.9(2)	113.3(5)	113.18(14)	112.4(2)
C(5)−C(4)−C(3)	121.4(3)	122.3(2)	121.9(2)	120.6(5)	121.36(14)	122.4(2)
C(2)−C(3)−C(6)	119.6(3)	118.7(2)	119.4(2)	120.2(5)	119.34(14)	120.0(2)
C(4)−C(3)−C(6)	120.1(3)	119.9(2)	119.8(2)	119.8(5)	120.50(13)	119.9(2)

[a] See figures for numbering scheme.

1.14(6) Å]. The crystal structures of eight 3-aryl-substituted 2,4-pentanedione derivatives have been published,[18−22] and all are found to exist in the enol form. A significant difference in these structures is the angle of twist adopted by the aryl ring with respect to the enol plane, which varies from 88.6° (practically orthogonal) to 65° (Table 6).

Although it is tempting to relate the angle of twist to the electronic influence of the ring substituents, the lack of any correlation with C3−C6 (Table 4) suggests that this is probably the result of a combination of steric interference between the ortho H atoms and the pentanedionate Me groups and crystal-packing forces.

The formation of bis(3-phenylpentane-2,4-dionato)nickel (**10**) (see above) was accompanied by the deposition of a small amount of a green crystalline compound, which we initially suspected to be the ethanol adduct but which was shown by X-ray diffraction to actually be the trimer [Ni(3-Phacac)$_2$]$_3$ (**12**)

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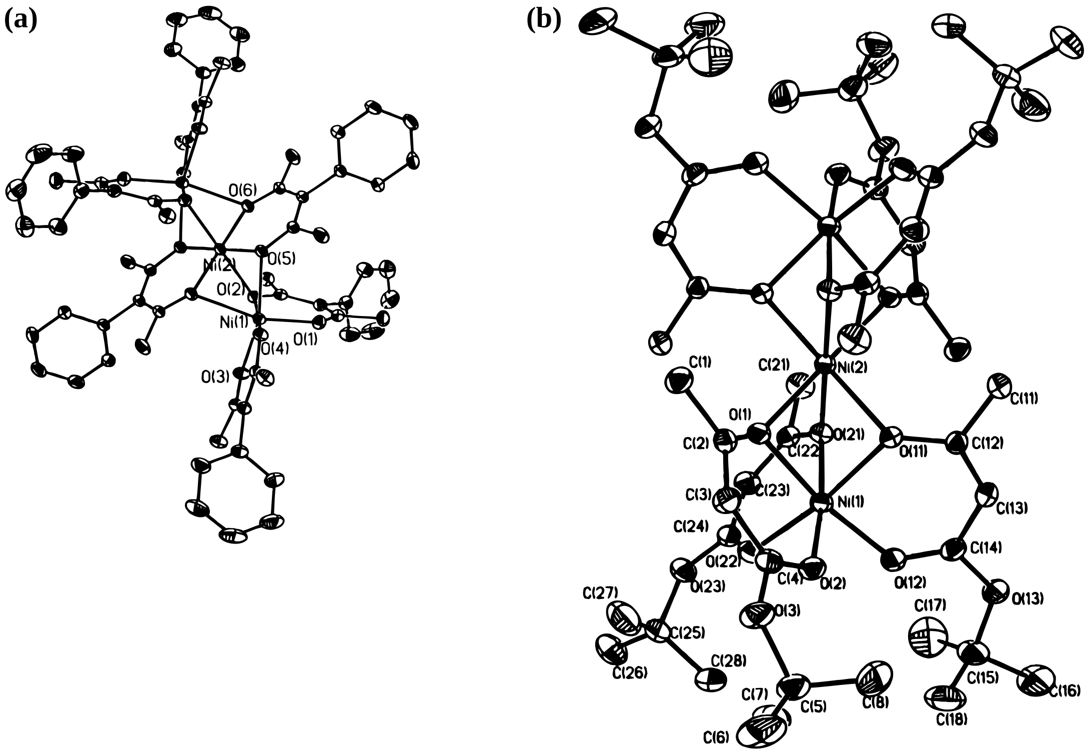

Figure 4. Molecular structures of (a) $[Ni(3\text{-phenylpentane-2,4-dionato})_2]_3$ (**12**) [Ni(1)···Ni(2) = 2.854 Å] and (b) [Ni(*tert*-butyl acetoacetato)$_2$]$_3$ (**13**) [Ni(1)···Ni(2) = 2.777 Å]. H atoms were omitted for clarity (25% probability level).

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 3-Phenyl-2,4-pentanedione[a]

O(1)−C(2)	1.287(3)	C(3)−C(6)	1.502(3)
O(2)−C(4)	1.284(3)	C−C(Ph)	1.39[b]
C(2)−C(1)	1.491(4)	O(1)−H	1.45(6)
C(4)−C(5)	1.488(4)	O(2)−H	1.14(6)
O(1)−C(2)−C(3)	121.8(2)	O(2)−C(4)−C(5)	116.1(3)
C(2)−C(3)−C(4)	118.5(2)	C(5)−C(4)−C(3)	122.5(3)
C(3)−C(4)−O(2)	121.4(3)	C(2)−C(3)−C(6)	121.3(2)
O(1)−C(2)−C(1)	115.2(2)	C(4)−C(3)−C(6)	120.2(2)
C(1)−C(2)−C(3)	123.0(3)		

[a] See Figure 3 for numbering scheme. [b] Assigned.

Table 6. Selected Structural Data for 3-Ar-2,4-pentanedione Derivatives

Ar	C3−C6 (Å)[a]	angle (deg)	ref
4-PhOC$_6$H$_4$	1.487(4)	65.0	22
4-O$_2$NC$_6$H$_4$	1.495(5)	67.3	22
4-PhC$_6$H$_4$	1.494(4)	73.1	21
Ph	1.502(3)	77.2	this work
2,4-(MeO)$_2$C$_6$H$_3$	1.480(5)	78.3	19
4-*i*-PrC$_6$H$_4$	1.484(7)	82.3	22
3,4,5-Me$_3$C$_6$H$_2$	1.487(3)	85	18
4-MeOC$_6$H$_4$	1.499(4)	88.9	20

[a] See Figure 3.

and as such is the only example of a trimer with 3-substituted diketonato groups whose crystal structure has been determined. The molecular structure is shown in Figure 4a, and selected data are listed in Table 7. It has, however, been pointed out that the UV spectra of the bis(3-chloropentane-2,4-dionato)nickel species suggest that this species is also trimeric in solution.[3d] The structure is related to that of [Ni(acac)$_2$]$_3$:[23−25] two molecules of the organic ligand are bonded in a chelating manner to each of the three metal atoms while both oxygen atoms of the inner organic ligands and one of the oxygen atoms of the outer organic ligand form bridges to the neighboring nickel atoms. As has been noted previously for [Ni(acac)$_2$]$_3$, it is difficult to interpret the differences in the Ni−O bond for the 3-phenyl-substituted derivative. In general, the bond to a nonbridging O atom is shorter than to a bridging O atom, e.g., Ni(2)−O(5) 1.970(1) Å, Ni(1)−O(5) 2.219(1) Å, Ni(1)−O(1) 1.971(2) Å, Ni(1)−O(2) 1.999(1) Å, Ni(2)−O(2) 2.099(1) Å. The central Ni atom adopts a symmetrical octahedral geometry with slightly elongated axial Ni−O bonds, O(2)−Ni(2)−O(2*) 180°, O(5)−Ni(2)−O(6) 92.70(5)°, whereas the terminal Ni atom shows considerable distortion, O(5)−Ni(1)−O(3) 162.99(6)°, O(2)−Ni(1)−O(4) 171.90(6)°. The three independent phenyl groups adopt positions in which the two terminal rings are almost perpendicular to the Ni−dione plane, 88.7(1)° and 89.2(1)°, and the central ring adopts an angle of 81.8(1)°.

In addition, we have prepared bis(*tert*-butyl acetoacetato)nickel(II) (**13**) by reacting the keto ester with bis(η^3-allyl)nickel. The compound is paramagnetic (4.9 μ_B), and the molecular

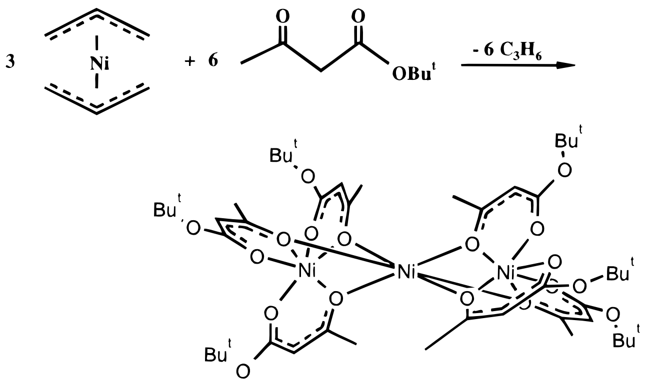

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Table 7. Selected Bond Distances (Å) and Angles (deg) for [Ni(3-phenylpentane-2,4-dionato)$_2$]$_3$ (**12**)[a]

Ni(1)−Ni(2)	2.8543(4)	Ni(1)−O(1)	1.971(2)	O(6)−C(44)	1.283(2)	C(2)−C(3)	1.421(3)
Ni(1)−O(2)	1.9991(13)	Ni(1)−O(3)	1.9516(14)	C(3)−C(4)	1.391(3)	C(22)−C(23)	1.406(3)
Ni(1)−O(4)	1.9463(13)	Ni(1)−O(5)	2.2189(13)	C(23)−C(24)	1.410(3)	C(42)−C(43)	1.401(3)
Ni(1)−O(6)*	2.3632(14)	Ni(2)−O(6)*	1.9751(13)	C(43)−C(44)	1.414(3)	C(1)−C(2)	1.514(3)
Ni(2)−O(2)	2.0987(13)	Ni(2)−O(5)	1.9695(12)	C(4)−C(5)	1.501(3)	C(21)−C(22)	1.513(3)
Ni(2)−O(6)	1.9751(13)	O(1)−C(2)	1.258(3)	C(24)−C(25)	1.513(3)	C(41)−C(42)	1.501(3)
O(2)−C(4)	1.292(2)	O(3)−C(22)	1.264(2)	C(44)−C(45)	1.502(3)	C(3)−C(6)	1.505(3)
O(4)−C(24)	1.268(2)	O(5)−C(42)	1.286(2)	C(23)−C(26)	1.495(3)	C(43)−C(46)	1.504(3)

O(1)−Ni(1)−O(2)	89.27(6)	O(3)−Ni(1)−O(4)	91.73(6)	N(1)−O(3)−C(22)	126.75(13)	Ni(1)−O(4)−C(24)	126.26(12)
O(5)−Ni(1)−O(6)*	72.83(5)	O(5)−Ni(2)−O(6)	92.70(5)	O(3)−C(22)−C(23)	125.6(2)	O(4)−C(24)−C(23)	125.9(2)
O(5)−Ni(2)−O(6)*	87.30(5)	O(5)−Ni(2)−O(2)	81.32(5)	C(22)−C(23)−C(24)	122.9(2)	Ni(2)−O(5)−C(42)	125.91(12)
O(2)−Ni(2)−O(6)*	81.28(5)	Ni(1)−O(1)−C(2)	128.20(14)	Ni(2)−O(6)−C(44)	125.44(13)	O(5)−C(42)−C(43)	125.2(2)
Ni(1)−O(2)−C(4)	127.87(12)	O(1)−C(2)−C(3)	125.8(2)	O(6)−C(44)−C(43)	125.4(2)	C(42)−C(43)−C(44)	125.2(2)
O(2)−C(4)−C(3)	124.3(2)	C(2)−C(3)−C(4)	123.5(2)				

[a] See figures for numbering scheme.

Table 8. Selected Bond Distances (Å) and Angles (deg) for [Ni(*tert*-butyl acetoacetato)$_2$]$_3$ (**13**)[a]

Ni(1)−Ni(2)	2.772 (3)	Ni(1)−O(1)	2.0336(13)	C(3)−C(4)	1.419(3)	C(1)−C(2)	1.501(3)
Ni(1)−O(2)	2.0189(14)	O(1)−C(2)	1.301(2)	O(3)−C(4)	1.340(2)	O(3)−C(5)	1.479(3)
O(2)−C(4)	1.237(3)	C(2)−C(3)	1.360(3)				

O(1)−Ni(1)−O(2)	91.68(6)	O(1)−Ni(2)−O(11)	78.12(5)	C(2)−C(3)−C(4)	127.0(2)	C(4)−O(3)−C(5)	122.1(2)
O(1)−Ni(2)−O(11)*	101.88(5)	O(1)−Ni(2)−O(1)*	180	Ni(1)−O(1)−Ni(2)	85.07(5)	O(1)−Ni(1)−O(12)	170.99(6)
Ni(1)−O(1)−C(2)	124.79(12)	Ni(1)−O(2)−C(4)	123.85(13)	O(2)−Ni(1)−O(21)	172.42(6)		
O(1)−C(2)−C(3)	124.5(2)	O(2)−C(4)−C(3)	127.4(2)				

[a] See figures for numbering scheme.

structure is shown in Figure 4b. Selected structural data are listed in Table 8. The three *tert*-butyl acetoacetato groups are practically identical, and the data listed are for only one. The compound is trimeric with a linear arrangement of the three Ni atoms. In contrast to [Ni(acac)$_2$]$_3$ and [Ni(3-phenylpentane-2,4-dionato)$_2$]$_3$, the organic ligand bonds in a chelate manner exclusively to the terminal Ni atoms with the six *tert*-butoxy groups located on the periphery of the molecule. The central Ni atom is bonded to six bridging acetyl groups. This arrangement of the organic ligand probably has a steric origin and minimizes congestion at the central atom.

Conclusions

Our results suggest that, in the presence of electron-donating substituents in the 3-position of the pentane-2,4-dionato group, monomer formation is preferred, whereas in the presence of the electron-withdrawing phenyl group, both monomeric and trimeric species are possible.

Supporting Information Available: X-ray crystallographic files in CIF format for $C_{11}H_{12}O_2$ and compounds **4**, **5**, **6**, **9**, **12**, and **13** are available on the Internet only. Access information is given on any current masthead page.

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