

Crystal and Molecular Structures of some Binuclear Complexes of Cobalt(II) and Nickel(II) Acetylacetonates with Pyridines and Piperidine and a Refinement of the Crystal and Molecular Structure of Hexakis(acetylacetonato)trinickel(II) †

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The crystal and molecular structures of the binuclear complexes $[M_2(py)(acac)_4]$ [$M = Ni^{II}$, (1), $M = Co^{II}$, (2); $py = pyridine$, $acac = acetylacetonate$] and $[Ni_2(pip)_2(acac)_4]$ (3; $pip = piperidine$) have been determined by single-crystal X-ray methods. Complexes (1) and (2) are isostructural in the monoclinic space group $P2_1/c$, $Z = 4$, with cell dimensions $a = 16.859(12)$, $b = 10.873(11)$, $c = 17.010(15)$ Å, $\beta = 112.97(7)^\circ$; and $a = 17.039(12)$, $b = 10.904(11)$, $c = 17.106(12)$ Å, $\beta = 113.55(8)^\circ$ respectively. The structures have been refined to $R = 0.077$ for (1) and 0.062 for (2) using 1 664 and 2 791 observed diffractometer intensities respectively. Compound (3) is triclinic, space group $P\bar{1}$, with $a = 9.637(5)$, $b = 9.052(5)$, $c = 11.414(7)$ Å, $\alpha = 73.54(8)$, $\beta = 113.90(9)$, $\gamma = 103.37(8)^\circ$, and $Z = 1$. R has refined to 0.077 for 1 180 observed data. The metal atoms are octahedrally co-ordinated in all three compounds. In the pyridine complexes, three oxygen atoms from chelating acetylacetonate ligands form monoatomic bridges between the two metal atoms so that the metal atom co-ordination polyhedra share a triangular face. The Ni–Ni and Co–Co separations in (1) and (2) are $2.891(3)$ and $2.966(5)$ Å whilst the Ni–O–Ni and Co–O–Co bridge angles average 87.8 and 88.2° respectively. Each M–O–M bridge is unsymmetrical and there are trigonal distortions in the metal co-ordination octahedra. Molecules of (3) are centrosymmetric and comprise two O–O edge-shared octahedra. The Ni–Ni separation is 3.240 Å. The structure of $[Ni_3(acac)_6]$, (4), has been redetermined and refined to $R = 0.0787$ using 980 data and gives an average Ni–Ni separation of $2.856(7)$ Å and an average Ni–O–Ni bridge angle of 85.6° . There are marked trigonal distortions of the NiO_6 octahedra and the Ni–O (bridging) distances vary considerably from $1.98(2)$ to $2.31(2)$ Å.

THE tendency of β -diketonates of bivalent $3d$ transition elements to polymerise has received much study¹ since the discovery² that bis(acetylacetonato)nickel(II) is trimeric in the solid state. The β -diketonates and their polynuclear adducts with unidentate ligands form a group of complexes in which it is possible to study the effects of systematic variations in metal, diketonate, or ligand on structures and physical properties, particularly magnetic behaviour. We have prepared a number of dimeric complexes of the types $[M_2LX_4]$ and $[M_2L_2X_4]$ where L is a unidentate ligand and X is a diketonate ion. This paper reports the determination of the crystal and molecular structures of some of these compounds. We have also refined the structure of $[Ni_3(acac)_6]$ previously determined from photographic data² in an attempt to obtain improved molecular geometry parameters. The following paper³ describes the preparations and spectral and magnetic properties of our compounds.

EXPERIMENTAL

Compounds (1), $[Ni_2(py)(acac)_4]$, and (2), $[Co_2(py)(acac)_4]$, were prepared by an adaptation of Fackler's method³ and crystals were obtained from light petroleum (b.p. 100 – $120^\circ C$) ($py = pyridine$, $acac = acetylacetonate$). Compound (3), $[Ni_2(pip)_2(acac)_4]$, was prepared³ by the reaction of nickel(II) acetylacetonate with piperidine (pip) in benzene and crystals grown by allowing a warm solution of the complex in benzene to absorb vapour from light petroleum (b.p. 80 – $100^\circ C$) in a vacuum desiccator. A crystal of compound (4), $[Ni_3(acac)_6]$, was grown by vacuum sublimation. All specimens used for X-ray work were sealed in Lindemann capillaries.

† *ad, ik*-Bis(μ -pentane-2,4-dionato- μ -O,O')-*eh, fg*-bis(μ_3 -pentane-2,4-dionato- μ -O, μ -O')-*bc, jl*-bis(pentane-2,4-dionato)trinickel(II).

For compounds (1)–(4), preliminary crystal data were obtained from oscillation and Weissenberg photographs and accurate values for all compounds from diffractometer measurements. For compounds (1), (2), and (4), these data and intensity measurements were obtained using a Nonius CAD4 diffractometer in a manner described in detail in ref. 4. For compound (3) a manual diffractometer was used as described in ref. 5. The crystal data and details of intensity measurements are given in Table 1. The structures of compounds (1)–(3) were solved *via* the heavy-atom method and all structures refined by full-matrix least squares. A common feature in crystals of all these compounds was a tendency to show large mosaic spreads in the exploratory ω scans (many crystals were examined in a fruitless search for better quality specimens) and a general weakness in diffraction power. Accordingly, many data were lost through the $I/\sigma(I)$ rejection test and it was subsequently possible to refine only some of the atoms anisotropically in each case. Details of the refinement processes are given in Table 1. All calculations were performed on the University of London CDC 6600/7600 computers using the X-RAY program system⁶ and SHELX.⁷ Scattering factors for neutral atoms were taken from ref. 8. Lists of the final atomic positional parameters, with estimated standard deviations in parentheses, for compounds (1)–(4) are given in Tables 2–5. Observed and calculated structure factors and tables of thermal parameters have been deposited as Supplementary Publication No. SUP 23175 (33 pp.). ‡

RESULTS AND DISCUSSION

$[Ni_3(acac)_6]$, (4).—Detailed interpretation of our magnetochemical results³ on dimeric diketonate complexes

‡ For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1
Crystallographic data

(a) Crystal data	(1)	(2)	(3)	(4)
Compound				
Formula	$C_{25}H_{33}NNi_2O_8$	$C_{25}H_{33}Co_2NO_8$	$C_{30}H_{43}N_2Ni_2O_8$	$C_{30}H_{43}Ni_3O_{12}$
<i>M</i>	592.97	593.19	682.15	770.80
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
<i>a</i> /Å	16.859(12)	17.039(12)	9.637(5)	23.252(14)
<i>b</i> /Å	10.873(11)	10.904(11)	9.052(5)	9.616(10)
<i>c</i> /Å	17.010(15)	17.106(12)	11.414(7)	15.624(12)
α /°	90.0	90.0	73.54(8)	90.0
β /°	112.97(7)	113.55(8)	113.90(9)	90.0
γ /°	90.0	90.0	103.37(8)	90.0
<i>U</i> /Å ³	2 870.8	2 913.5	841.3	3 493.4
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Pca</i> 2
<i>Z</i>	4	4	1	4
<i>D_c</i> /g cm ⁻³	1.44	1.43	1.35	1.46
<i>F</i> (000)	1 240	1 232	362	1 608
<i>X</i> radiation, λ/Å	Cu- <i>K</i> α , 1.541 78	Mo- <i>K</i> α , 0.710 69	Cu- <i>K</i> α , 1.541 78	Cu- <i>K</i> α , 1.541 78
μ /cm ⁻¹	18.37	11.18	16.3	9.62
(b) Data collection				
$\theta_{\min.}$: $\theta_{\max.}$ /°	3.0, 60.0	1.5, 25.0	2.0, 55.0	3.0, 60.0
Scan type	ω -2 θ	ω -2 θ	Stationary	ω
Total unique data	4 256	5 129	1 409	2 162
σ cut-off	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 2\sigma(F_o)$	$F_o > 3\sigma(F_o)$
Total observed data	1 664	2 791	1 180	980
(c) Refinement details				
No of parameters	202	207	190	195
Weighting scheme	Unit weights	Unit weights	Unit weights	$w = 1/[\sigma^2(F_o) + 0.012(F_o)^2]$
<i>R</i> = ($\Sigma \Delta F /\Sigma F_o $)	0.077	0.0615	0.077	0.0787
<i>R'</i> = [$\Sigma w \Delta F ^2/\Sigma w F_o ^2$] ^{1/2}				0.0857

TABLE 2
Atomic fractional co-ordinates ($\times 10^4$) for
[Ni₂(py)(acac)₄], (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ni(1)	3 147(2)	2 149(4)	254(2)
Ni(2)	1 699(2)	3 619(3)	208(2)
N(1)	1 794(11)	4 776(15)	1 209(10)
O(11)	4 336(9)	2 330(14)	1 099(9)
O(12)	3 505(8)	2 074(14)	-740(9)
O(21)	2 532(8)	2 311(12)	1 062(8)
O(22)	3 185(10)	304(13)	396(11)
O(31)	577(8)	2 903(13)	106(9)
O(32)	1 796(8)	2 304(12)	-600(8)
O(41)	1 116(8)	4 886(14)	-682(9)
O(42)	2 863(8)	4 053(12)	231(10)
C(1)	2 553(14)	5 050(21)	1 802(14)
C(2)	2 664(17)	5 763(25)	2 523(17)
C(3)	1 918(16)	6 170(24)	2 576(16)
C(4)	1 140(16)	5 930(22)	2 005(15)
C(5)	1 060(15)	5 180(22)	1 282(15)
C(11)	5 009(15)	2 013(22)	972(15)
C(12)	5 833(16)	2 000(26)	1 697(17)
C(13)	4 971(15)	1 689(20)	156(15)
C(14)	4 282(14)	1 774(20)	-589(14)
C(15)	4 370(16)	1 467(25)	-1 443(15)
C(21)	2 378(13)	1 402(23)	1 463(13)
C(22)	1 880(14)	1 747(20)	2 030(14)
C(23)	2 609(13)	196(22)	1 457(14)
C(24)	2 991(14)	-316(22)	912(15)
C(25)	3 155(16)	-1 652(22)	964(16)
C(31)	172(13)	2 071(22)	-370(14)
C(32)	-688(14)	1 719(22)	-365(15)
C(33)	448(14)	1 364(23)	-932(14)
C(34)	1 240(13)	1 519(22)	-992(13)
C(35)	1 460(15)	607(23)	-1 558(15)
C(41)	1 518(13)	5 744(20)	-919(14)
C(42)	973(14)	6 673(21)	-1 499(14)
C(43)	2 418(13)	5 814(20)	-656(13)
C(44)	3 023(13)	5 015(22)	-176(14)
C(45)	3 980(13)	5 162(22)	12(14)

TABLE 3
Atomic fractional co-ordinates ($\times 10^4$) for
[Co₂(py)(acac)₄], (2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Co(1)	3 171(1)	2 189(1)	262(1)
Co(2)	1 672(1)	3 651(1)	179(1)
N(1)	1 739(5)	4 776(6)	1 213(4)
O(11)	4 393(4)	2 416(7)	1 091(4)
O(12)	3 531(4)	2 071(7)	-713(4)
O(21)	2 541(4)	2 307(6)	1 054(4)
O(22)	3 208(4)	310(6)	415(4)
O(31)	541(4)	2 897(6)	39(4)
O(32)	1 777(4)	2 320(6)	-644(4)
O(41)	1 137(4)	5 012(6)	-686(4)
O(42)	2 838(4)	4 114(6)	194(4)
C(1)	2 510(7)	5 098(10)	1 800(6)
C(2)	2 592(8)	5 811(11)	2 513(7)
C(3)	1 858(8)	6 140(11)	2 585(8)
C(4)	1 076(8)	5 838(11)	2 012(7)
C(5)	1 036(6)	5 132(10)	1 315(6)
C(11)	5 023(7)	2 050(10)	932(6)
C(12)	5 878(7)	2 056(12)	1 687(8)
C(13)	4 987(7)	1 688(9)	152(6)
C(14)	4 278(6)	1 743(9)	-613(6)
C(15)	4 381(8)	1 405(12)	-1 429(7)
C(21)	2 369(5)	1 422(9)	1 462(5)
C(22)	1 862(6)	1 786(9)	1 979(6)
C(23)	2 610(6)	235(9)	1 451(6)
C(24)	2 996(6)	-269(9)	935(6)
C(25)	3 152(7)	-1 632(10)	981(7)
C(31)	161(6)	2 024(9)	-446(6)
C(32)	-693(7)	1 696(11)	-440(7)
C(33)	459(6)	1 352(10)	-962(6)
C(34)	1 237(6)	1 489(9)	-1 015(5)
C(35)	1 486(7)	606(11)	-1 556(7)
C(41)	1 539(6)	5 833(9)	-890(6)
C(42)	995(7)	6 817(11)	-1 474(7)
C(43)	2 416(6)	5 876(9)	-646(6)
C(44)	3 017(6)	5 047(9)	-162(6)
C(45)	3 938(7)	5 186(11)	-19(7)

TABLE 4
Atomic fractional co-ordinates ($\times 10^4$) for
[Ni₃(pip)₂(acac)₄], (3)

Atom	x	y	z
Ni(1)	-181(2)	-244(2)	6 398(2)
O(1)	-1 405(10)	-1 983(10)	7 340(8)
O(2)	852(9)	1 442(10)	5 098(7)
O(3)	-2 157(9)	856(10)	5 442(8)
O(4)	464(10)	826(10)	7 914(7)
N(1)	2 001(11)	-1 224(11)	7 227(9)
C(1)	1 890(16)	-2 795(14)	8 117(14)
C(2)	3 441(16)	-3 499(15)	8 629(14)
C(3)	4 823(16)	-2 429(16)	9 405(14)
C(4)	4 938(15)	-836(16)	8 454(14)
C(5)	3 361(15)	-130(15)	7 920(13)
C(6)	-2 896(17)	-4 370(15)	7 908(14)
C(7)	-2 098(15)	-3 278(16)	7 012(13)
C(8)	-2 117(15)	-3 724(15)	5 907(14)
C(9)	1 497(15)	2 906(14)	5 036(13)
C(10)	1 580(18)	3 629(14)	6 102(13)
C(11)	-4 321(15)	2 092(16)	5 142(14)
C(12)	-2 716(16)	1 544(15)	5 997(15)
C(13)	-1 966(17)	1 833(15)	7 261(14)
C(14)	-470(19)	1 533(15)	8 096(14)
C(15)	234(17)	2 103(17)	9 371(13)

TABLE 5
Atomic fractional co-ordinates ($\times 10^4$) for
[Ni₃(acac)₆], (4)

Atom	x	y	z
Ni(1)	351(2)	2 540(5)	1 032(6)
Ni(2)	1 209(2)	1 235(5)	0
Ni(3)	2 060(2)	-253(5)	-978(6)
O(1)	368(7)	1 466(19)	-226(14)
O(2)	1 179(9)	-698(20)	-432(16)
O(3)	2 045(9)	861(21)	251(16)
O(4)	1 190(8)	3 209(18)	350(14)
O(5)	933(9)	986(21)	1 264(16)
O(6)	1 585(9)	1 539(21)	-1 194(17)
O(7)	-154(9)	4 043(21)	566(17)
O(8)	515(9)	3 591(25)	2 107(19)
O(9)	2 451(10)	-1 907(21)	-514(16)
O(10)	1 940(8)	-1 102(21)	-2 084(16)
O(11)	-302(9)	1 416(22)	1 480(17)
O(12)	2 758(9)	695(24)	-1 384(18)
C(16)	267(14)	4 691(33)	2 293(27)
C(2)	759(11)	-1 261(28)	-769(19)
C(26)	2 184(13)	-2 256(31)	-2 377(26)
C(22)	762(13)	-159(34)	1 616(25)
C(30)	2 539(17)	-3 065(38)	-1 875(31)
C(5)	205(14)	-770(31)	-875(26)
C(21)	-232(16)	235(42)	1 817(29)
C(23)	-815(15)	-437(36)	2 105(28)
C(27)	2 663(15)	-2 878(37)	-979(33)
C(17)	-289(12)	5 096(30)	972(27)
C(29)	3 059(17)	-3 918(44)	-519(33)
C(4)	837(15)	-2 657(37)	-1 288(26)
C(6)	2 378(17)	1 683(38)	648(30)
C(1)	27(15)	563(34)	-576(26)
C(20)	-119(16)	5 421(38)	1 797(29)
C(12)	1 775(19)	2 780(44)	-1 511(33)
C(3)	-611(14)	941(35)	-505(26)
C(25)	244(14)	-546(34)	2 002(29)
C(24)	1 328(14)	-1 131(38)	1 777(26)
C(28)	2 039(19)	-2 610(47)	-3 274(38)
C(15)	2 326(24)	2 747(55)	-1 826(44)
C(10)	2 195(23)	2 953(57)	900(39)
C(14)	1 409(22)	3 776(56)	-1 723(39)
C(8)	2 930(26)	1 311(63)	919(45)
C(18)	394(16)	5 278(40)	3 215(31)
C(11)	2 849(20)	1 837(52)	-1 540(36)
C(9)	1 490(18)	5 344(42)	860(32)
C(7)	1 642(21)	3 783(53)	714(38)
C(13)	3 478(17)	2 242(37)	-1 739(29)
C(19)	-715(14)	6 028(34)	513(27)

requires accurate bond lengths and angles for the molecules, especially in the metal co-ordination sphere. In addition, comparison of these data with those of the parent diketonates was also considered to be useful. In view of the limited accuracy of the earlier structure determination² of [Ni₃(acac)₆], we considered it worthwhile to re-examine this structure.

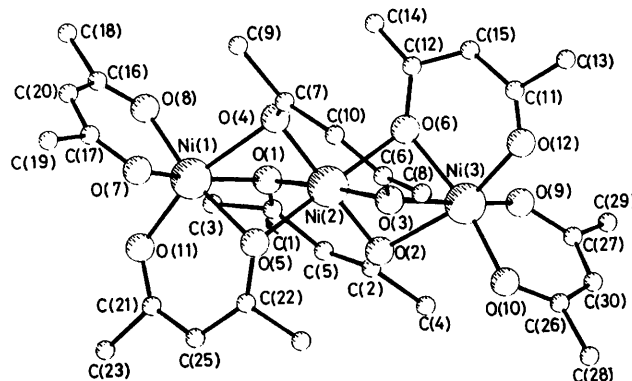


FIGURE 1 Molecular structure of [Ni₃(acac)₆]

A diagram of the trimeric molecule is shown in Figure 1, the atom-labelling scheme shown being that of Bullen *et al.*² Selected bond lengths and angles are given in Table 6 for the Ni and O atoms. Although our new analysis is still not as reliable as we would have liked, the precision in the Ni-O bond length determination is significantly improved and shows that the differences in Ni-O bond lengths, previously attributed to different

TABLE 6
Selected bond lengths and angles for
[Ni₃(acac)₆], (4)

(a) Bond lengths (Å)			
Ni(2)-Ni(1)	2.856(7)	O(3)-Ni(2)	2.017(23)
O(1)-Ni(1)	2.221(23)	O(4)-Ni(2)	1.976(20)
O(4)-Ni(1)	2.314(21)	O(5)-Ni(2)	2.090(27)
O(5)-Ni(1)	2.049(23)	O(6)-Ni(2)	2.082(28)
O(7)-Ni(1)	1.999(23)	O(2)-Ni(3)	2.259(23)
O(8)-Ni(1)	1.997(30)	O(3)-Ni(3)	2.199(26)
O(11)-Ni(1)	1.991(23)	O(6)-Ni(3)	2.074(23)
Ni(3)-Ni(2)	2.881(10)	O(9)-Ni(3)	1.971(24)
O(1)-Ni(2)	1.999(19)	O(10)-Ni(3)	1.930(26)
O(2)-Ni(2)	1.979(21)	O(12)-Ni(3)	1.967(25)
(b) Bond angles (°)			
O(4)-Ni(1)-O(1)	73.0(8)	O(5)-Ni(2)-O(3)	95.3(10)
O(5)-Ni(1)-O(1)	78.8(9)	O(5)-Ni(2)-O(4)	80.9(9)
O(5)-Ni(1)-O(4)	74.2(8)	O(6)-Ni(2)-O(1)	103.7(10)
O(7)-Ni(1)-O(1)	91.4(10)	O(6)-Ni(2)-O(2)	80.9(10)
O(7)-Ni(1)-O(4)	97.3(9)	O(6)-Ni(2)-O(3)	78.1(10)
O(8)-Ni(1)-O(4)	94.9(9)	O(6)-Ni(2)-O(4)	97.0(9)
O(8)-Ni(1)-O(5)	95.4(10)	O(3)-Ni(3)-O(2)	75.5(9)
O(8)-Ni(1)-O(7)	93.0(11)	O(6)-Ni(3)-O(2)	74.8(9)
O(11)-Ni(1)-O(1)	94.1(10)	O(6)-Ni(3)-O(3)	74.3(10)
O(11)-Ni(1)-O(5)	92.6(9)	O(9)-Ni(3)-O(2)	97.3(10)
O(11)-Ni(1)-O(7)	94.2(10)	O(9)-Ni(3)-O(3)	94.5(10)
O(11)-Ni(1)-O(8)	97.1(11)	O(10)-Ni(3)-O(2)	97.3(9)
O(2)-Ni(2)-O(1)	90.6(9)	O(10)-Ni(3)-O(6)	97.4(10)
O(3)-Ni(2)-O(2)	86.1(10)	O(10)-Ni(3)-O(9)	93.2(10)
O(4)-Ni(2)-O(1)	85.5(9)	O(12)-Ni(3)-O(3)	93.9(11)
O(4)-Ni(2)-O(3)	97.9(9)	O(12)-Ni(3)-O(6)	90.0(10)
O(5)-Ni(2)-O(1)	83.1(9)	O(12)-Ni(3)-O(9)	96.4(10)
O(5)-Ni(2)-O(2)	101.8(10)	O(12)-Ni(3)-O(10)	91.5(11)

hybridisation at bridging and non-bridging oxygen atoms, follow a rather more complicated pattern.

First of all we note that all terminal (*i.e.* non-bridging) oxygen atoms do indeed form short Ni-O bonds, with a range of 1.93(3)–2.00(3) Å. However, although on average the bridging Ni-O bonds are longer, some of the bridges are quite asymmetric. In particular, the bonds between Ni(2) and O(1), O(2), O(3), and O(4), which all lie in a plane and constitute two chelating acac groups, are as short [1.98–2.02(2) Å] as the terminal bonds, whilst the bonds from these oxygen atoms to the outer nickels are quite long, 2.20–2.31(1) Å. The other two bridges, involving O(5) and O(6), are less distorted although there is an indication that the two bonds to Ni(2) are slightly longer [2.08, 2.09(3) Å] than those to Ni(1) and Ni(3) [2.05, 2.07(2) Å]. Thus, there is an indication that the central nickel atom is showing a slight tendency to adopt a square-planar geometry. Whilst this distortion may not be very serious in terms of the gross electronic and magnetochemical properties, the stereochemical result may be very significant, since the longest bonds are probably the most reactive and breaking these may be the first step to the formation of bi- or mono-nuclear complexes on reaction with donor ligands. It is also worth noting that, in general, the acac ligands are fairly symmetrical in the chelating mode, *i.e.* where a bridging atom gives two different O-Ni distances the shorter one is to the Ni atom which is chelated by the ligand to which the bridge atom belongs.

The inequalities in bond lengths are accompanied by variations in bond angles at the nickel atoms from the ideal angle of 90° for octahedral co-ordination. A marked trigonal distortion is introduced, so that for the terminal nickel atoms the ONiO angles within the bridging face average 75.2° and those on the opposite face average 94.2°. There is also a trigonal distortion to the co-ordination of the central nickel atom, the ONiO angles within the bridging faces averaging 82.4°. Trigonal distortions of this type were also found⁹ in [Co₃-(EtO)₂P(O)CHC(O)Me₆], where the OCoO angles subtended by the bridging faces are 77° at all three cobalt atoms, while the opposite outside face gives an average OCoO angle of 92.5°.

There are very few other linear trinuclear complexes whose structures have been found to include octahedrally co-ordinated metal ions sharing a face. In [Co₃(OH₂)(acac)₆], trigonal distortions to angles of 75.3 and 78.5° were found,¹⁰ but this molecule contains one bridge by a face and one by an edge. In [Co₃(quin)₂(O₂CPh)₆] (quin = quinoline) only the central cobalt atom is octahedrally co-ordinated, with all the OCoO angles close to 90°, but in that molecule pairs of cobalt atoms are linked by one bridging oxygen atom and three O-C-O bridges.¹¹

[Ni₂(py)(acac)₄], (1).—Our structure analysis of this complex confirms Fackler's suggestion¹ that this molecule contains two octahedrally co-ordinated nickel atoms with the octahedra sharing a triangular face. Figure 2 shows the molecular structure and atom-labelling

scheme. Selected bond lengths and angles are given in Table 7.

One acetylacetonate ligand chelates Ni(1) and is not

TABLE 7
Selected bond lengths and angles for
[M₂(py)(acac)₄], (1) and (2)

	M = Ni (1)	M = Co(2)
(a) Bond lengths (Å)		
M(1)–M(2)	2.891(3)	2.966(5)
M(1)–O(11)	1.968(17)	2.011(8)
M(1)–O(12)	2.008(14)	1.998(8)
M(1)–O(21)	2.026(13)	2.041(7)
M(1)–O(22)	2.018(17)	2.063(9)
M(1)–O(32)	2.177(16)	2.263(8)
M(1)–O(42)	2.122(16)	2.165(8)
M(2)–N(1)	2.072(18)	2.118(9)
M(2)–O(21)	2.124(16)	2.194(8)
M(2)–O(31)	1.990(14)	2.020(8)
M(2)–O(32)	2.034(15)	2.079(8)
M(2)–O(41)	1.999(17)	2.035(8)
M(2)–O(42)	2.004(14)	2.040(8)
(b) Bond angles (°)		
O(12)–M(1)–O(11)	93.7(7)	91.2(3)
O(21)–M(1)–O(11)	98.1(7)	101.2(3)
O(22)–M(1)–O(11)	92.1(8)	93.6(4)
O(22)–M(1)–O(12)	93.1(7)	92.2(4)
O(22)–M(1)–O(21)	90.4(7)	88.6(3)
O(32)–M(1)–O(12)	91.2(6)	91.2(3)
O(32)–M(1)–O(21)	76.5(6)	76.3(3)
O(32)–M(1)–O(22)	97.6(7)	96.9(4)
O(42)–M(1)–O(11)	94.2(7)	95.4(4)
O(42)–M(1)–O(12)	99.4(7)	100.3(4)
O(42)–M(1)–O(21)	75.9(6)	77.2(3)
O(42)–M(1)–O(32)	75.1(6)	73.8(3)
O(21)–M(2)–N(1)	91.5(7)	91.2(3)
O(31)–M(2)–N(1)	94.3(7)	93.7(4)
O(31)–M(2)–O(21)	98.6(6)	99.3(3)
O(32)–M(2)–O(21)	77.6(6)	77.2(3)
O(32)–M(2)–O(31)	89.5(6)	88.4(3)
O(41)–M(2)–N(1)	93.5(7)	92.5(4)
O(41)–M(2)–O(31)	92.0(7)	94.7(4)
O(41)–M(2)–O(32)	96.8(6)	98.8(3)
O(42)–M(2)–N(1)	94.6(7)	96.8(3)
O(42)–M(2)–O(21)	76.3(6)	76.6(3)
O(42)–M(2)–O(32)	80.9(6)	80.5(3)
O(42)–M(2)–O(41)	92.3(7)	88.9(3)

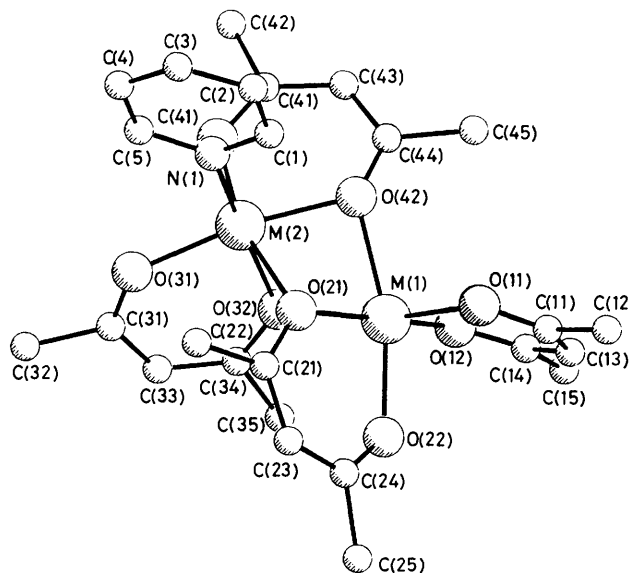


FIGURE 2 Molecular structure of [M₂(acac)₄(py)],
M = Ni or Co

involved in bridging; another chelates Ni(1) and shares one oxygen atom, O(21), with Ni(2), and the other two chelate Ni(2) and share one oxygen atom each, O(32) and O(42), with Ni(1). The pyridine molecule is bonded to Ni(2). Thus, Ni(1) is co-ordinated by six oxygen atoms, and Ni(2) by one nitrogen and five oxygen atoms. The structure of the complex can be considered as being derived from that of $[\text{Ni}_3(\text{acac})_6]$ by replacing one $\text{Ni}(\text{acac})_2$ unit by the pyridine molecule.

The variation in Ni-O bond lengths is very interesting, particularly in comparison with those in compound (4). For the one chelating-only acac ligand, the two Ni-O(11), O(12) distances are equal and short, very similar to those in similar ligands in (4). The remaining acac ligands are all chelating/bridging and show the same features as in compound (4), that is the chelation gives rise to almost equal, short Ni-O bonds with the bridging atom giving a

TABLE 8
Selected bond lengths and angles for
 $[\text{Ni}_2(\text{pip})_2(\text{acac})_4]$, (3)

(a) Bond lengths (Å)			
O(1)-Ni(1)	2.040(11)	O(3)-Ni(1)	2.050(10)
O(2)-Ni(1)	2.160(10)	O(4)-Ni(1)	2.033(10)
O(2')-Ni(1)	2.287(10)	N(1)-Ni(1)	2.156(11)
Ni(1)-Ni(1')	3.240(7)		
(b) Bond angles (°)			
O(3)-Ni(1)-O(1)	89.1(4)	N(1)-Ni(1)-O(2)	85.8(4)
O(3)-Ni(1)-O(2)	87.4(4)	N(1)-Ni(1)-O(4)	92.1(5)
O(4)-Ni(1)-O(1)	87.5(4)	O(2')-Ni(1)-O(1)	90.1(4)
O(4)-Ni(1)-O(2)	101.9(4)	O(2')-Ni(1)-O(2)	80.5(4)
O(4)-Ni(1)-O(3)	90.2(5)	O(2')-Ni(1)-O(3)	91.0(4)
N(1)-Ni(1)-O(1)	97.4(5)	O(2')-Ni(1)-N(1)	87.0(3)
Ni(1)-O(2)-Ni(1')	99.5(9)		

longer bond to the next nickel atom. Each metal atom carries four short and two long Ni-O bonds but the former do not lie in a plane. Nevertheless, it is possible to identify the way in which the bridge system can be cleaved to form one $\text{Ni}(\text{acac})_2$ monomer unit and a $[\text{Ni}(\text{py})(\text{acac})_2]$ adduct *via* breakage of the Ni(1)-O(42), Ni(1)-O(32), and Ni(2)-O(21) bonds.

The other bond lengths are like those encountered for comparable molecules. The Ni-Ni distance of 2.891 Å is slightly longer than in $[\text{Ni}_3(\text{acac})_6]$. The trigonal distortion found in $[\text{Ni}_3(\text{acac})_6]$ occurs also in $[\text{Ni}_2(\text{py})(\text{acac})_4]$. The ONiO angles subtended at the nickel atoms by the bridging face have an average value of 77°, while the angles at the opposite face average 93°.

$[\text{Co}_2(\text{py})(\text{acac})_4]$, (2).—This complex is isomorphous and isostructural with (1). Selected bond lengths are shown in Table 7, along with those of (1).

The Co-Co distance of 2.966 Å is identical to that found¹⁰ in the face-sharing part of $[\text{Co}_3(\text{OH}_2)(\text{acac})_6]$ but is shorter than the corresponding distance (3.19 Å) in $[\text{Co}_4(\text{acac})_8]$ ¹² and considerably shorter than the Co-Co distances in the edge-sharing parts of these molecules (3.283 and 3.57 Å respectively), and much shorter also than the Co-Co distances in the edge-shared dimers $[\text{Co}_2\{\text{N}(\text{C}_6\text{H}_{11})\text{H}_2\}_2(\text{acac})_4]$ (3.332 Å, ref. 13) and $[\text{Co}_2(\text{OH}_2)_2(\text{acac})_4]$ (3.33 Å, ref. 14).

Similar inequalities in the Co-O bond lengths in the

Co_2O_3 bridging unit were found here as were described for $[\text{Ni}_2(\text{py})(\text{acac})_4]$. The other bond lengths and angles in the molecule are normal with the exception of the Co-N distance of 2.118 Å.⁹ This is shorter than the length of 2.187 Å found¹⁵ for $[\text{Co}(\text{py})_2(\text{acac})_2]$ which was itself considered shorter than expected.

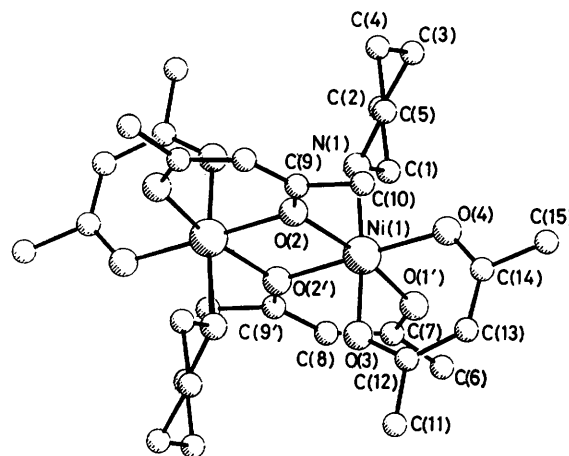
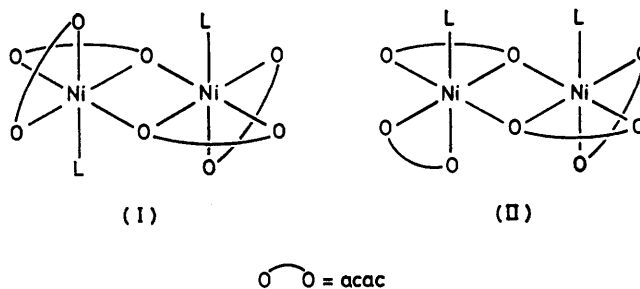


FIGURE 3 Molecular structure of $[\text{Ni}_2(\text{pip})_2(\text{acac})_4]$

$[\text{Ni}_2(\text{pip})_2(\text{acac})_4]$, (3).—This molecule is shown to be a centrosymmetric dimer, comprising two edge shared (O-O) NiO_5N octahedra. A diagram of the structure is shown in Figure 3; selected bond lengths and angles are given in Table 8. Two of the four acetylacetonates are bonded to one nickel atom only; the other two chelate one nickel atom but have one of their oxygen atoms also bonded to the other nickel atom. The bridging unit is similar to that found for $[\text{Co}_2\{\text{N}(\text{C}_6\text{H}_{11})\text{H}_2\}_2(\text{acac})_4]$,¹³



$[\text{Co}_2(\text{OH}_2)_2(\text{acac})_4]$,¹⁴ and $[\text{Mn}_2\{\text{N}(\text{C}_3\text{H}_5)\text{H}_2\}_2(\text{acac})_4]$.¹⁶ The piperidine ligand adopts the chair conformation.

One feature of the dimeric $[\text{Ni}_2(\text{pip})_2(\text{acac})_4]$ has also been noted for $[\text{Co}_2\{\text{N}(\text{C}_6\text{H}_{11})\text{H}_2\}_2(\text{acac})_4]$,¹³ namely the possibility of π bonding within the Ni_2O_2 bridging unit. Although many isomers could be designed for this stoichiometry, π bonding may occur only when the chelate ring which contains the bridging oxygen atoms lies in the same plane as the Ni_2O_2 ring. Two structures, (I) and (II), allow this. Structure (I) is the one reported here, but (II) might give greater steric repulsions and has yet to be found in an $[\text{M}_2\text{L}_2(\text{acac})_4]$ complex.

The nickel-nickel separation in this structure is natur-

ally much greater here than in the face-shared dimer. In another edge-shared octahedral nickel(II) dimer, bis-(1,5-diphenylpentane-1,3,5-trionato)tetrakis(pyridine)dinickel(II), the Ni-Ni separation was found¹⁷ to be 3.166 Å, quite close to our value of 3.240 Å.

Again there is some inequality in the Ni-O bond lengths, the bonds to bridging oxygen atoms being of length 2.156 Å and those to other oxygen atoms averaging 2.043 Å. The other bond lengths and angles are comparable to those found in related molecules and require no special comment.

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