

## Complexes of Bis(2,4-pentanedionato)nickel(II) and -cobalt(II) with Triphenylarsine Oxide.

### Crystal and Molecular Structures of Bis[ $\mu$ -(2,4-pentanedionato-0:0,0')]-bis(2,4-pentanedionato-0,0')[ $\mu$ -(triphenylarsine oxide-0:0)] dinickel(II) and -dicobalt(II), $[M(C_5H_7O_2)_2]_2 \cdot Ph_3AsO$ (M = Ni, Co)

J. H. BINKS, G. J. DORWARD\*, R. A. HOWIE and G. P. McQUILLAN\*\*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB9 2UE, U.K.

Received September 30, 1980

The reaction of  $Ni(acac)_2 \cdot 2H_2O$  ( $acac = 2,4$ -pentanedionate,  $C_5H_7O_2^-$ ) with  $Ph_3AsO$  in ethanol yields the 2:1 complex  $[Ni(acac)_2]_2 \cdot Ph_3AsO$  as the only product. Similar reactions with  $Co(acac)_2 \cdot 2H_2O$  yield mainly  $Co(acac)_2 \cdot 2Ph_3AsO$  with a small amount of  $[Co(acac)_2]_2 \cdot Ph_3AsO$ . The 2:1 complexes  $[M(acac)_2]_2 \cdot Ph_3AsO$  are binuclear, isomorphous (space group  $P2_1/a$ ,  $Z = 4$ ) with three  $M-O-M$  bridges. One bridging oxygen atom belongs to the arsine oxide ligand; the other two come from pentanedionate ligands. The complex molecules are asymmetric. The orientation of the arsine oxide ligand, with the  $As-O$  bond bent sharply away from the bridging  $M-O-M$  plane (where  $O$  is the arsine oxide oxygen atom) suggests a strongly stereochemically active lone pair on the oxygen atom.

#### Introduction

The reactions of bis(2,4-pentanedionato)nickel(II), or the corresponding cobalt(II) compound, with ligands containing nitrogen or oxygen as the donor atom usually lead to the formation of mononuclear octahedral complexes,  $M(acac)_2L_2$  (M = Ni, Co;  $acac = 2,4$ -pentanedionate,  $C_5H_7O_2^-$ ; L = ligand) as the final, stable, isolable products [1–12]. Under anhydrous conditions, the initially trimeric  $[Ni(acac)_2]_3$  [13] or tetrameric  $[Co(acac)_2]_4$  [14] break down in a series of steps, and in some cases intermediate binuclear or trinuclear complexes can be isolated [7–11].

The reaction of diaquobis(2,4-pentanedionato)nickel(II),  $Ni(acac)_2 \cdot 2H_2O$ , with triphenylarsine oxide gives the 2:1 complex,  $[Ni(acac)_2]_2 \cdot Ph_3AsO$ , in good yield, as the only product. The correspond-

ing reaction with  $Co(acac)_2 \cdot 2H_2O$  yields a mixture of products from which crystals of  $[Co(acac)_2]_2 \cdot Ph_3AsO$  can be separated. No definitive structural data appear to be available for complexes with 2:1 metal pentanedionate:ligand stoichiometry, and in systems with amine ligands there has been some dispute as to their existence [11]. In view of their general interest, and because of their rather unexpected formation from the mononuclear hydrated starting materials, we have carried out X-ray crystal structure determinations for the triphenylarsine oxide complexes. Preliminary data for  $[Ni(acac)_2]_2 \cdot Ph_3AsO$  have been published [15].

#### Experimental

##### $[Ni(acac)_2]_2 \cdot Ph_3AsO$

Solutions of  $Ni(acac)_2 \cdot 2H_2O$  (14.7 g, 0.05 mol) and  $Ph_3AsO$  (16.1 g, 0.05 mol) in the minimum quantities of ethanol were mixed and boiled with vigorous stirring. The pale green complex crystallised on cooling. Similar reactions in benzene or toluene yielded a poorly crystallised product but well-formed crystals were obtained from benzene diluted with an equal volume of petroleum ether. *Anal.* Found: Ni, 14.1; C, 54.9; H, 5.2; As, 9.1%. Calcd. for  $C_{38}H_{43}O_9Ni_2As$ : Ni, 14.0; C, 54.6; H, 5.2; As, 9.0%. M.p. 206–209 °C (dec.) Yield 50–60%.

##### Cobalt Complexes

The reaction of equimolar hot ethanolic solutions of  $Co(acac)_2 \cdot 2H_2O$  and  $Ph_3AsO$  yielded, on cooling and standing overnight, copious quantities of a pale pink microcrystalline solid mixed with a few (<1%) larger deep red-pink slightly distorted octahedral crystals. These larger crystals were separated manually and were found to correspond analytically to  $[Co(acac)_2]_2 \cdot Ph_3AsO$ . (*Anal.* Found: C, 54.3; H, 4.9%. Calcd. for  $C_{38}H_{43}O_9Co_2As$ : C, 54.6; H,

\*Deceased.

\*\*Author to whom correspondence should be addressed.

TABLE I. Crystal Data (e.s.d. in last significant figure).

	[Ni(acac) <sub>2</sub> ] <sub>2</sub> ·Ph <sub>3</sub> AsO	[Co(acac) <sub>2</sub> ] <sub>2</sub> ·Ph <sub>3</sub> AsO
	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>a</i>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i>	18.12(2) Å	18.64(2) Å
<i>b</i>	12.04(1)	12.28(1)
<i>c</i>	18.98(2)	19.15(2)
β	117.5(1)°	118.1(1)°
μ	3673 Å <sup>3</sup>	3867.5
MW	836.1	836.5
<i>D</i> <sub>obs</sub> (flotation)	1.50 g cm <sup>-3</sup>	1.43 g cm <sup>-3</sup>
<i>D</i> <sub>calc</sub>	1.51 g cm <sup>-3</sup>	1.44 g cm <sup>-3</sup>
<i>Z</i>	4	4

5.2%). Preliminary X-ray powder diffraction measurements, confirmed by the subsequent single-crystal analysis (see below) indicated the complex to be isomorphous with [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO.

The pale pink product remaining after removal of the 2:1 complex appeared to consist predominantly of the 1:2 complex Co(acac)<sub>2</sub>·2Ph<sub>3</sub>AsO (Found, *e.g.*: C, 62.5; H, 4.8%. Calcd. for C<sub>56</sub>H<sub>58</sub>O<sub>10</sub>As<sub>2</sub>Co: C, 61.3; H, 5.2%).

#### Physical measurements

X-ray powder diffraction data were obtained using a Phillips PW 1051 powder diffractometer, magnetic data with a Newport Instruments Ltd variable temperature Guoy balance, and IR and UV-visible spectra with Perkin-Elmer 457 and Unicam SP 700 spectrophotometers.

#### Structure Determinations

##### Crystal Data

The complexes [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO and [Co(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO were obtained as octahedral crystals distorted by elongation along one axis. The distortion is rather more developed in the nickel than in the cobalt complex. Space-group and preliminary unit-cell data were obtained from rotation and Weissenberg photographs (Cu/Kα radiation, λ = 1.5406 Å); the final unit-cell parameters listed in Table I were obtained by refinement of the single-crystal diffraction data. The crystals are monoclinic, space group *P*2<sub>1</sub>/*a*, with four [M(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO formula units in the unit cell.

##### [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO

##### Data collection

Intensity data were obtained for a crystal mounted about the unique axis *b* using a Hilger and Watts

Model Y190 automatic linear diffractometer with balanced filters and Mo/Kα radiation (λ = 0.7107 Å). Reflections were measured over a half-sphere of the reciprocal lattice, averaging values for equivalent positions. Four estimates were made of each measured intensity with an ω scan of 3°. Data were collected for the layers, (h, 0–10, l).

A few reflections which gave poor agreement in opposite quadrants were discarded, and those for which *I* < 3σ(*I*) were rejected as unobserved. A total of 926 independent reflections, corrected for Lorentz and polarisation effects, remained for use in the structure determination.

##### Structure determination

The arsenic and nickel atom positions were identified from an initial three-dimensional Patterson function, and subsequent Fourier syntheses phased on these atoms located all of the carbon and oxygen atoms. Five cycles of block-diagonal least-squares refinement with all atoms isotropic, followed by five cycles with the nickel and arsenic atoms anisotropic, reduced the conventional *R*-value from 0.13 to 0.066 [16]. At this point the shifts in the atom positions were all < 0.1 e.s.d. and no significant features appeared on a difference map. Anisotropic refinement of the carbon and oxygen atom positions was not possible with the number of structure amplitudes available. Removal of fourteen reflections for which Δ*F* > 0.3*F*<sub>c</sub> and further refinement using the 912 remaining reflections led to a final *R*-value of 0.059.

The calculated atomic positional parameters are listed in Table II. Full details of observed and calculated structure factors and thermal vibrational parameters are included in the supplementary tables\*.

\*Supplementary tables detailed in the text are available on request from the Editor or the authors.

TABLE II. [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO. Final Positional Parameters<sup>a</sup> (e.s.d. in last significant figure).

	x/a	y/b	z/c
Ni(1)	0.0124(2)	0.1440(2)	0.2578(2)
Ni(2)	-0.1040(2)	-0.0177(2)	0.2565(2)
As(1)	0.0706(2)	-0.1276(2)	0.2720(1)
O(1)	0.0251(8)	-0.0325(10)	0.2958(9)
C(1)	0.187(2)	-0.092(2)	0.326(1)
C(2)	0.238(2)	-0.163(2)	0.313(2)
C(3)	0.324(2)	-0.1482(2)	0.360(2)
C(4)	0.350(2)	-0.050(2)	0.407(2)
C(5)	0.296(2)	0.016(2)	0.419(2)
C(6)	0.209(1)	-0.014(2)	0.374(1)
C(7)	0.038(2)	-0.148(2)	0.162(1)
C(8)	-0.029(2)	-0.225(2)	0.116(2)
C(9)	-0.048(2)	-0.241(2)	0.032(2)
C(10)	-0.006(2)	-0.189(2)	0.003(1)
C(11)	0.054(1)	-0.119(2)	0.045(1)
C(12)	0.079(1)	-0.093(2)	0.130(2)
C(13)	0.062(1)	-0.262(2)	0.318(1)
C(14)	0.081(2)	-0.359(2)	0.281(2)
C(15)	0.070(2)	-0.461(2)	0.319(2)
C(16)	0.049(2)	-0.458(2)	0.378(2)
C(17)	0.036(1)	-0.362(2)	0.407(2)
C(18)	0.033(1)	-0.261(2)	0.367(1)
O(2)	0.0977(8)	0.2098(10)	0.3575(9)
O(3)	0.0911(8)	0.1356(9)	0.2137(8)
C(19)	0.212(1)	0.316(2)	0.444(2)
C(20)	0.162(1)	0.258(2)	0.361(1)
C(21)	0.190(1)	0.255(2)	0.307(1)
C(22)	0.156(1)	0.190(2)	0.243(1)
C(23)	0.212(2)	0.175(2)	0.198(2)
O(4)	-0.0282(9)	0.2898(11)	0.2055(10)
O(5)	-0.0800(8)	0.0679(10)	0.1666(9)
C(24)	-0.103(2)	0.422(2)	0.110(2)
C(25)	-0.085(1)	0.307(2)	0.140(2)
C(26)	-0.139(2)	0.223(2)	0.086(2)
C(27)	-0.134(1)	0.113(2)	0.104(1)
C(28)	-0.198(2)	0.030(3)	0.043(2)
O(6)	-0.1065(2)	-0.0738(10)	0.3533(9)
O(7)	-0.0703(9)	0.1318(10)	0.3040(9)
C(29)	-0.133(2)	-0.079(2)	0.463(2)
C(30)	-0.103(1)	-0.011(2)	0.408(1)
C(31)	-0.099(1)	0.098(2)	0.411(2)
C(32)	-0.073(1)	0.165(2)	0.368(1)
C(33)	-0.059(1)	0.281(2)	0.380(1)
O(8)	-0.2230(8)	0.0229(11)	0.2066(9)
O(9)	-0.1263(9)	-0.1616(11)	0.2100(9)
C(34)	-0.367(2)	0.000(2)	0.136(2)
C(35)	-0.283(1)	-0.048(2)	0.166(2)
C(36)	-0.270(1)	-0.154(2)	0.154(1)
C(37)	-0.197(2)	-0.203(2)	0.176(2)
C(38)	-0.199(2)	-0.327(2)	0.156(2)

<sup>a</sup>Numbering system is indicated in Fig. 2.TABLE III. [Co(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO. Final Positional Parameters<sup>a</sup> (e.s.d. in last significant figure).

	x/a	y/b	z/c
Co(1)	0.0150(1)	0.1452(2)	0.2596(1)
Co(2)	-0.1018(1)	-0.0198(2)	0.2584(1)
As(1)	0.0732(1)	-0.1285(1)	0.2723(1)
O(1)	0.0270(4)	-0.0314(6)	0.2962(5)
C(1)	0.1893(7)	-0.0952(11)	0.3268(7)
C(2)	0.2410(8)	-0.1685(13)	0.3171(8)
C(3)	0.3239(8)	-0.1488(14)	0.3598(9)
C(4)	0.3525(9)	-0.0536(13)	0.4100(9)
C(5)	0.2957(9)	0.0136(12)	0.4183(9)
C(6)	0.2117(8)	-0.0084(10)	0.3768(7)
C(7)	0.0397(7)	-0.1449(11)	0.1616(7)
C(8)	-0.0229(10)	-0.2185(14)	0.1211(9)
C(9)	-0.0477(10)	-0.2348(16)	0.0376(10)
C(10)	-0.0063(9)	-0.1839(15)	0.0042(9)
C(11)	0.0563(9)	-0.1109(13)	0.0482(9)
C(12)	0.0801(9)	-0.0917(12)	0.1293(8)
C(13)	0.0602(8)	-0.2662(11)	0.3125(7)
C(14)	0.0792(11)	-0.3596(14)	0.2830(10)
C(15)	0.0715(12)	-0.4631(14)	0.3149(11)
C(16)	0.0488(10)	-0.4600(15)	0.3761(10)
C(17)	0.0329(8)	-0.3656(15)	0.4039(9)
C(18)	0.0366(8)	-0.2664(12)	0.3697(8)
O(2)	0.1007(5)	0.2141(7)	0.3596(5)
O(3)	0.0960(5)	0.1345(7)	0.2174(5)
C(19)	0.2170(9)	0.3154(14)	0.4477(9)
C(20)	0.1651(8)	0.2600(12)	0.3664(8)
C(21)	0.1948(8)	0.2598(12)	0.3118(8)
C(22)	0.1604(8)	0.1906(11)	0.2424(8)
C(23)	0.2118(9)	0.1847(15)	0.1987(9)
O(4)	-0.0276(5)	0.2927(8)	0.2048(5)
O(5)	-0.0815(5)	0.0694(7)	0.1699(5)
C(24)	-0.0974(11)	0.4260(14)	0.1048(11)
C(25)	-0.0862(9)	0.3060(13)	0.1352(9)
C(26)	-0.1389(9)	0.2211(12)	0.0847(9)
C(27)	-0.1345(8)	0.1125(13)	0.1040(8)
C(28)	-0.1966(10)	0.0329(15)	0.0461(9)
O(6)	-0.1040(5)	-0.0730(7)	0.3585(5)
O(7)	-0.0647(5)	0.1266(7)	0.3092(5)
C(29)	-0.1296(10)	-0.0691(14)	0.4690(9)
C(30)	-0.1074(8)	-0.0136(13)	0.4090(7)
C(31)	-0.0946(9)	0.1023(12)	0.4177(9)
C(32)	-0.0715(7)	0.1634(11)	0.3678(8)
C(33)	-0.0539(9)	0.2831(11)	0.3863(9)
O(8)	-0.2227(6)	0.0196(8)	0.2050(5)
O(9)	-0.1267(5)	-0.1663(7)	0.2099(5)
C(34)	-0.3650(9)	0.0010(15)	0.1381(10)
C(35)	-0.2807(9)	-0.0498(12)	0.1682(8)
C(36)	-0.2719(8)	-0.1598(12)	0.1571(8)
C(37)	-0.1972(8)	-0.2107(12)	0.1772(8)
C(38)	-0.1970(10)	-0.3334(13)	0.1598(10)

<sup>a</sup>Numbering system is indicated in Fig. 2.

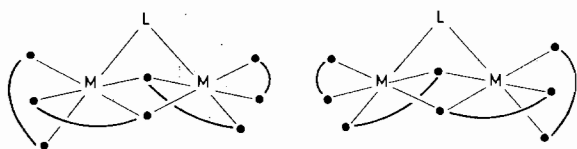


Fig. 1. Enantiomers of  $[M(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$ . ( $M = \text{Ni}, \text{Co}$ ,  $L = \text{Ph}_3\text{AsO}$ ).

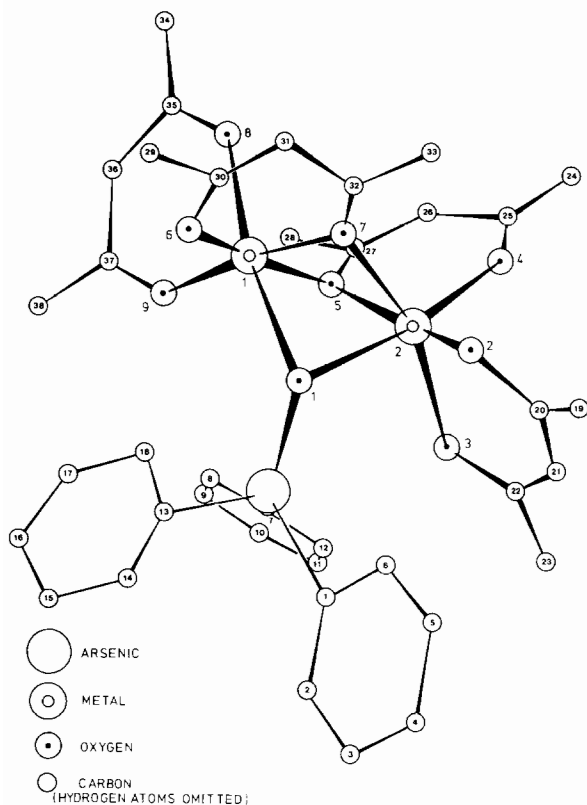


Fig. 2.  $[M(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$  projected onto the plane containing the  $M_1$ ,  $M_2$  and  $\text{As}$  atoms.

### $[\text{Co}(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$

#### Data collection

The X-ray intensity data were collected by courtesy of Dr. R. C. G. Killean, using the University of St. Andrews Siemens AED four-circle diffractometer with  $\text{Mo}/K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The general data collection strategy has been described by Killean [17] and Grant [18]. After elimination of reflections with  $I < 3\sigma(I)$ , 1372 independent observed reflections, corrected for Lorentz and polarisation effects, were available for use in the structure determination.

#### Structure determination

An initial structure-factor calculation, using the final positional parameters obtained for  $[\text{Ni}(\text{acac})_2]_2 \cdot$

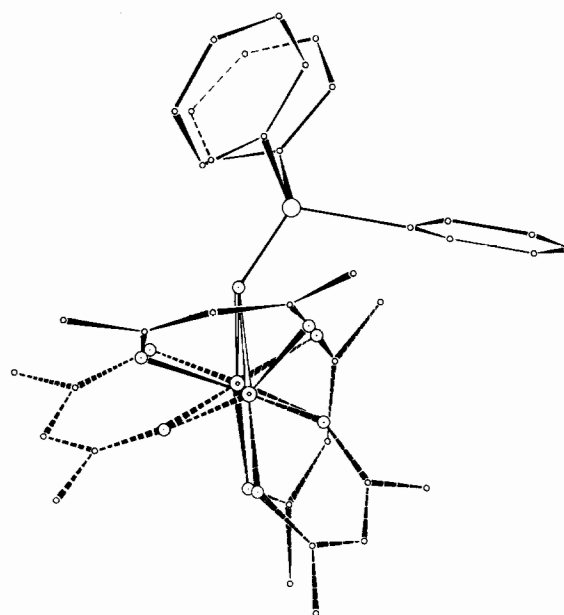


Fig. 3.  $[M(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$  viewed along the  $M_1-M_2$  axis, illustrating tilted orientation of  $\text{Ph}_3\text{AsO}$  ligand.

$\text{Ph}_3\text{AsO}$ , yielded an  $R$ -value of 0.13. After five cycles of block-diagonal least-squares refinement, with all atoms isotropic, the  $R$ -value fell to 0.054. At this point six reflections for which  $\Delta F > 0.3 F_c$  were eliminated and five further least-squares cycles, with all atoms refining anisotropically gave a final  $R$ -value of 0.0395. (inclusion of the 6 poor-quality reflections raises this to 0.0417). Shifts in the atomic parameters did not exceed 0.25 esd, and a difference map was featureless. The positional parameters are listed in Table III, and full data are included in the supplementary tables\*.

### Description of Structure

The nickel and cobalt complexes  $[M(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$  are fully isostructural: the diagrams in Figs. 1–3 apply to both complexes. The structure determination for the cobalt complex was based on a substantially greater number of observed reflections than that for the nickel complex, and refined to a lower final  $R$ -value; in general, the e.s.d.s in the lighter atom positions in the cobalt complex are about half those for corresponding atoms in the nickel complex (Tables II, III). Bond length and angle data are given in detail for  $[\text{Co}(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$

\*Supplementary tables detailed in the text are available on request from the Editor or the authors.

TABLE IV. [Co(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO. Bond Lengths (Å) (e.s.d. in last significant figure).

Co(1)–O(1)	2.26(1)	Co(2)–O(1)	2.16(1)
Co(1)–O(5)	2.03(1)	Co(2)–O(5)	2.20(1)
Co(1)–O(7)	2.12(1)	Co(2)–O(7)	2.00(1)
Co(1)–O(2)	2.01(1)	Co(2)–O(6)	2.04(1)
Co(1)–O(3)	2.02(1)	Co(2)–O(8)	2.05(1)
Co(1)–O(4)	2.05(1)	Co(2)–O(9)	1.98(1)

*Ph<sub>3</sub>AsO*

As(1)–O(1)	1.66(1)	As(1)–C(7)	1.92(1)
As(1)–C(1)	1.95(1)	As(1)–C(13)	1.92(1)
C(1)–C(2)	1.39(2)	C(4)–C(5)	1.41(2)
C(2)–C(3)	1.39(2)	C(5)–C(6)	1.41(2)
C(3)–C(4)	1.45(2)	C(6)–C(1)	1.36(2)
C(7)–C(8)	1.39(2)	C(10)–C(11)	1.40(2)
C(8)–C(9)	1.45(2)	C(11)–C(12)	1.42(2)
C(9)–C(10)	1.36(3)	C(12)–C(7)	1.35(2)
C(13)–C(14)	1.40(2)	C(16)–C(17)	1.37(3)
C(14)–C(15)	1.45(3)	C(17)–C(18)	1.40(2)
C(15)–C(16)	1.42(3)	C(18)–C(13)	1.36(2)

*Pentanedionate ligands*

O(2)–C(20)	1.28(2)	O(4)–C(25)	1.27(2)
C(19)–C(20)	1.55(2)	C(24)–C(25)	1.56(2)
C(20)–C(21)	1.39(2)	C(25)–C(26)	1.45(2)
C(21)–C(22)	1.45(2)	C(26)–C(27)	1.38(2)
C(22)–C(23)	1.54(2)	C(27)–C(28)	1.52(2)
O(3)–C(22)	1.27(2)	O(5)–C(27)	1.29(2)
O(6)–C(30)	1.24(2)	O(8)–C(35)	1.29(2)
C(29)–C(30)	1.55(2)	C(34)–C(35)	1.53(3)
C(30)–C(31)	1.44(2)	C(35)–C(36)	1.39(2)
C(31)–C(32)	1.43(2)	C(36)–C(37)	1.41(2)
C(32)–C(33)	1.51(2)	C(37)–C(38)	1.54(2)
O(7)–C(32)	1.27(2)	O(9)–C(37)	1.28(2)
Co(1)–Co(2)	2.966(3)		

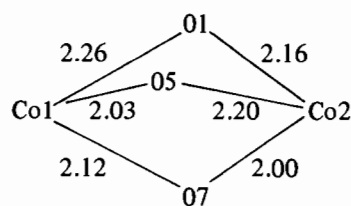


Fig. 4. M–O–M bond lengths (Å).

in Tables IV and V and for the immediate nickel environment in [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO in Table VI. Comprehensive data for both complexes are included in the supplementary tables\*. Except where stated, specific bond lengths and angles mentioned in the following discussion refer to the cobalt complex.

The complexes are binuclear, with three bridging oxygen atoms. The metal atoms are octahedrally coordinated and the structure consists in essence of two MO<sub>6</sub> octahedra sharing a common face. The triphenylarsine oxide oxygen atom (O1) occupies the apical position in the shared face and the other two shared oxygen atoms are provided by two pentanedionate ligands from opposite sides of the molecule. The orientations of the bridging and non-bridging ligands in the two 'halves' of the molecule are not symmetry-related and the molecule as a whole is asymmetric (Fig. 1).

The individual MO<sub>6</sub> octahedra are appreciably distorted, the angles subtended at the metal atoms

\*Supplementary tables detailed in the text are available on request from the Editor or the authors.

TABLE V. [Co(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO. Selected Bond Angles (°) (e.s.d. in last significant figure).

O(1)–Co(1)–O(2)	100.9(3)	O(1)–Co(2)–O(5)	74.0(3)
O(1)–Co(1)–O(3)	94.5(3)	O(1)–Co(2)–O(6)	100.0(4)
O(1)–Co(1)–O(4)	164.3(4)	O(1)–Co(2)–O(7)	79.7(3)
O(1)–Co(1)–O(5)	75.0(3)	O(1)–Co(2)–O(8)	166.2(4)
O(1)–Co(1)–O(7)	75.2(3)	O(1)–Co(2)–O(9)	94.4(4)
O(2)–Co(1)–O(3)	90.0(3)	O(5)–Co(2)–O(6)	166.1(4)
O(2)–Co(1)–O(4)	93.3(4)	O(5)–Co(2)–O(7)	77.4(4)
O(2)–Co(1)–O(5)	170.0(4)	O(5)–Co(2)–O(8)	92.6(4)
O(2)–Co(1)–O(7)	91.7(4)	O(5)–Co(2)–O(9)	100.3(4)
O(3)–Co(1)–O(4)	92.0(4)	O(6)–Co(2)–O(7)	89.2(4)
O(3)–Co(1)–O(5)	99.3(4)	O(6)–Co(2)–O(8)	92.3(4)
O(3)–Co(1)–O(7)	169.7(4)	O(6)–Co(2)–O(9)	92.6(4)
O(4)–Co(1)–O(5)	89.8(4)	O(7)–Co(2)–O(8)	94.4(4)
O(4)–Co(1)–O(7)	98.0(4)	O(7)–Co(2)–O(9)	174.0(4)
O(5)–Co(1)–O(7)	78.5(4)	O(8)–Co(2)–O(9)	91.2(4)
Co(1)–O(1)–Co(2)	84.3(3)	O(1)–As(1)–C(1)	106.9(5)
Co(1)–O(5)–Co(2)	89.0(4)	O(1)–As(1)–C(7)	116.1(5)
Co(1)–O(7)–Co(2)	91.9(4)	O(1)–As(1)–C(13)	110.0(5)
Co(1)–O(1)–As(1)	126.4(5)	Co(2)–O(1)–As(1)	126.5(5)

TABLE VI.  $[\text{Ni}(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$ . Selected Bond Lengths and Angles (e.s.d. in last significant figure).

<i>Bond Lengths (Å)</i>			
Ni(1)–O(1)	2.28(1)	Ni(2)–O(1)	2.11(2)
Ni(1)–O(5)	2.00(2)	Ni(2)–O(5)	2.22(2)
Ni(1)–O(7)	2.06(2)	Ni(2)–O(7)	2.03(1)
Ni(1)–O(2)	1.98(2)	Ni(2)–O(6)	1.98(2)
Ni(1)–O(3)	1.96(2)	Ni(2)–O(8)	1.98(2)
Ni(1)–O(4)	2.03(1)	Ni(2)–O(9)	1.95(2)
As(1)–O(1)	1.62(1)	As(1)–C(7)	1.90(2)
As(1)–C(1)	1.92(2)	As(1)–C(13)	1.92(2)
	Ni(1)–Ni(2)		2.901(4)
<i>Bond Angles (°)</i>			
O(1)–Ni(1)–O(5)	75.2(6)	O(1)–Ni(2)–O(5)	74.6(6)
O(1)–Ni(1)–O(7)	77.5(6)	O(1)–Ni(2)–O(7)	83.3(6)
O(5)–Ni(1)–O(7)	81.5(6)	O(5)–Ni(2)–O(7)	72.3(6)
Ni(1)–O(1)–Ni(2)	82.6(5)	O(1)–As(1)–C(1)	104.9(9)
Ni(1)–O(5)–Ni(2)	86.7(6)	O(1)–As(1)–C(7)	117.6(9)
Ni(1)–O(7)–Ni(2)	90.3(6)	O(1)–As(1)–C(13)	110.4(9)
Ni(1)–O(1)–As(1)	123.9(8)	Ni(2)–O(1)–As(1)	126.1(9)

by the bridging oxygen atoms all being less than  $80^\circ$ . Angles involving only the terminal oxygen atoms are all very close to  $90^\circ$ . The three M–O–M bridges are slightly asymmetric, with O1 and O7 displaced towards M2 and O5 towards M1 (Fig. 4). The immediate metal environment is very similar to that of the terminal Ni or Co atoms in  $[\text{Ni}(\text{acac})_2]_3$  or  $[\text{Co}(\text{acac})_2]_4$  [13, 14].

The  $\text{Ph}_3\text{AsO}$  ligand is tilted sharply away from the M1–O1–M2 bridge, so that the arsenic atom is displaced by 0.99 Å from the plane defined by these three atoms (Fig. 3). Within the ligand, the OAsC bond angles vary from  $106^\circ$  to  $116^\circ$ , and the As–O bond does not coincide with the notional  $\text{AsC}_3$  threefold axis. The three CAsC angles are all equal, within the experimental limits, but the phenyl rings are not equivalently oriented (dihedral angles C(1–6)/C(2–12),  $66^\circ$ ; C(1–6)/C(13–18),  $42^\circ$ ; C(7–12)/C(13–18)  $124^\circ$ ) and the  $\text{Ph}_3\text{As}$  grouping has no overall symmetry.

Three of the four pentanedionate ligands are planar, within the experimental limits\* but in the fourth (Table VII) the carbon atoms C19 and C21 are displaced by 0.17 and 0.11 Å, respectively, from the calculated best plane. Similar deviations occur in the corresponding ligand in the nickel complex\*. While it is possible that this is merely an artefact

TABLE VII.  $[\text{Co}(\text{acac})_2]_2 \cdot \text{Ph}_3\text{AsO}$ . Deviation of Pentanedionate Ligand C<sub>19</sub>–C<sub>23</sub> from Calculated Best Plane.

Atom	Deviation (Å)
O(2)	–0.012
O(3)	–0.039
C(19)	–0.112
C(20)	+0.049
C(21)	+0.170
C(22)	–0.033
C(23)	–0.090
Equation of plane $-0.3050x + 0.8246y - 0.4765z = -0.2998$	

of the structure determination, the pentanedionate ligand in question [C(19–23)] approaches the phenyl groups of the arsine oxide ligand more closely than do the other three. (The closest intramolecular non bonded distances are C12–O3 and C8–O9, 3.19 Å, and C6–C22, 3.35 Å). The distortion in the ligand, if it is real, and the minor asymmetries in the  $\text{Ph}_3\text{AsO}$  ligand, are probably caused by this intramolecular crowding.

## Discussion

These two ligand-bridged complexes appear to be the only examples of their type to have been identified

\*Supplementary tables detailed in the text are available on request from the Editor or the authors.

ed. In the binuclear and trinuclear hydrates, [Co(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [9] and [Co(acac)<sub>2</sub>]<sub>3</sub>·H<sub>2</sub>O [10], obtained by the addition of appropriate quantities of water to anhydrous [Co(acac)<sub>2</sub>]<sub>4</sub> all of the bridging positions are occupied by pentanedionate oxygen atoms and the water molecules are terminally bound. Similar structures, with terminally bound pyridine ligands, are proposed for the 2:1 complexes [M(acac)<sub>2</sub>]<sub>2</sub>·py [8].

The reactions leading to the formation of the arsine oxide complexes are essentially associative in nature, starting from the mononuclear dihydrates M(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, and are thus not directly comparable with the degradation reactions used to prepare the oligomeric hydrate and amine complexes from the anhydrous parent compounds [8–10]. So far, we have failed to obtain [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO from the reaction of Ph<sub>3</sub>AsO with [Ni(acac)<sub>2</sub>]<sub>3</sub> under anhydrous conditions.

Triphenylarsine oxide does not characteristically act as a bridging ligand, and the only other Ph<sub>3</sub>AsO-bridged complex we are aware of is the dimer [HgCl<sub>2</sub>·Ph<sub>3</sub>AsO]<sub>2</sub> [19]. Other molecules with oxygen donor atoms, notably heterocyclic amine N-oxides, will much more readily adopt a bridging role [20–23], but the reactions of anhydrous or hydrated nickel(II) or cobalt(II) pentanedionate with pyridine N-oxide, quinoline N-oxide or their substituted derivatives appear to yield the mononuclear octahedral 1:2 complexes as the only isolable products, with no analogues of the arsine oxide bridged compounds [4, 12]. In the M(acac)<sub>2</sub>-Ph<sub>3</sub>AsO systems the formation of a simple *trans* [M(acac)<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>2</sub>] complex would present no steric problems and the separation of the rather crowded 2:1 binuclear complexes is thus particularly surprising, especially in the nickel system where the 2:1 complex, under the conditions of our experiments, is the exclusive product. A much more detailed understanding of the mechanisms of the dehydration and association processes occurring in the preparative reactions is clearly desirable.

The sharply tilted orientation of the arsine oxide ligand relative to the M1–O1–M2 plane is not dictated by any obvious steric requirement, and indeed the intramolecular non-bonded contacts discussed in the preceding Section would be reduced if the M1–O1–M2 bridge and the As–O bond were more nearly coplanar. The structure thus appears to imply a strongly stereochemically active lone pair on the bridging arsine oxide oxygen atom, and is consistent with a representation of the ligand as Ph<sub>3</sub>As<sup>+</sup>–O<sup>–</sup>. The bridging arsine oxide ligands in [HgCl<sub>2</sub>·Ph<sub>3</sub>AsO]<sub>2</sub> are similarly, although less spectacularly, tilted, with the arsenic atom displaced by 0.54 Å from the Hg–O–Hg plane, compared with 0.99 Å for the arsenic atom from the Co1–O1–Co2 plane in [Co(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO [19]. In the mercury complex,

the arsine oxides are the only bridging ligands and the Hg–O–Hg angle is 101°. In the cobalt and nickel complexes, the geometry is influenced by the requirements of the bridging pentanedionate oxygen atoms and the angle at the bridging arsine oxide oxygen is reduced to 84° (Co1–O1–Co2). To accommodate this angle, the ligand is tilted more sharply than in the mercury complex.

The nickel complex [Ni(acac)<sub>2</sub>]<sub>2</sub>·Ph<sub>3</sub>AsO has a typical octahedral nickel visible absorption spectrum [ $\lambda_{\text{max}}$ : 9000 (11.6), 15700 (11.0) cm<sup>-1</sup>, in dichloromethane, molar absorbances in parentheses] and magnetic moment ( $\mu_{\text{eff}}$  = 3.16 BM at 300 K). The complex obeys the Curie-Weiss Law between 90–410 K, with an extrapolated Weiss constant of 6°. Deviations from Curie-Weiss behaviour are likely at very low temperatures: the Ni–Ni distance across the molecule (2.901 Å) is very similar to those in anhydrous [Ni(acac)<sub>2</sub>]<sub>3</sub> (2.882, 2.896 Å), in which the Ni atoms are ferromagnetically coupled below 10 K [25].

In the IR spectra the As–O stretch occurs at 842 cm<sup>-1</sup> in both complexes, compared with 810 cm<sup>-1</sup> in [HgCl<sub>2</sub>·Ph<sub>3</sub>AsO]<sub>2</sub> [26]. The As–O bond lengths are the same, within the experimental limits, in all three complexes. Arsenic–oxygen stretching vibrations in complexes containing terminal Ph<sub>3</sub>AsO ligands occur, roughly, in the range 880–835 cm<sup>-1</sup> [26]: clearly, the As–O stretching frequency cannot be used to distinguish between bridging and terminally bound ligands. In the metal–oxygen stretching frequency region (400–450 cm<sup>-1</sup> [27]) strong, very broad absorptions appear at about 430 cm<sup>-1</sup>, consistent with the rather distorted NiO<sub>6</sub> and CoO<sub>6</sub> environments. In Co(acac)<sub>2</sub>·2Ph<sub>3</sub>AsO, for which a much more regular CoO<sub>6</sub> environment is to be expected, especially if we assume a *trans*-Ph<sub>3</sub>AsO geometry, the Co–O stretch appears as a single strong sharp peak at 415 cm<sup>-1</sup>.

### Acknowledgements

We thank Dr. R. Killean and Dr. P. Grant for data-collection facilities for the cobalt complex, and the Carnegie Trust for a maintenance grant for the late Dr. G. J. Dorward.

### References

- (a) J. P. Fackler, *Prog. Inorg. Chem.*, **7**, 361 (1966);  
(b) J. P. Fackler, *Adv. in Chem.*, **62**, 580, (1966);  
(c) R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal  $\beta$ -diketonates and Allied Derivatives', Academic Press, New York (1978).
- C. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).
- H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **17**, 1481 (1964).
- A. G. Patrick, M.Sc. Thesis, Aberdeen University (1970).

- 5 J. M. Haigh, N. P. Slabbert and D. A. Thornton, *J. Mol. Structure*, **7**, 199 (1971).
- 6 J. T. Hashagen and J. P. Fackler, *J. Am. Chem. Soc.*, **87**, 2821 (1965).
- 7 J. P. Fackler, *Inorg. Chem.*, **2**, 266 (1963).
- 8 J. P. Fackler, *J. Am. Chem. Soc.*, **84**, 24 (1962).
- 9 F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **5**, 423 (1966).
- 10 F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **90**, 38 (1968).
- 11 R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).
- 12 R. W. Kluibler and W. de W. Horrocks, Jr., *J. Am. Chem. Soc.*, **87**, 5350 (1965).
- 13 G. J. Bullen, R. Mason and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
- 14 F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965).
- 15 J. H. Binks, G. J. Dorward, L. S. Dent Glasser, R. A. Howie and G. P. McQuillan, *Inorg. Chim. Acta*, **22**, L17 (1977).
- 16 Crystallographic programmes were those of F. R. Ahmed, S. R. Hall, M. E. Pippy and C. P. Huber, (1966), modified by R. A. Howie, J. S. Knowles and H. F. W. Taylor.
- 17 R. C. G. Killean, *Acta Cryst.*, **29A**, 216 (1973).
- 18 D. F. Grant, *Acta Cryst.*, **29A**, 217 (1973).
- 19 C. I. Branden, *Arkiv Kemi*, **22**, 485 (1964).
- 20 G. Sawitzki and H. G. von Schnering, *Chem. Ber.*, **107**, 3266 (1974).
- 21 R. J. Williams, W. H. Watson and A. C. Larson, *Acta Cryst.*, **31B**, 2362 (1975).
- 22 E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **15**, 348 (1976).
- 23 W. H. Watson, *Inorg. Chem.*, **8**, 1879 (1969).
- 24 G. B. Aitken and G. P. McQuillan, *Inorg. Chim. Acta*, **15**, 221 (1975).
- 25 A. P. Ginsberg, R. L. Martin and R. P. Sherwood, *Inorg. Chem.*, **7**, 932 (1968).
- 26 D. J. Phillips and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 1806 (1961).
- 27 M. Mikami, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).