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Sybout N. Poelsma[a]; Alastair H. Servante[a]; Francesco P. Fanizzi[a]; Peter M. Maitlis[a]
[a] Department of Chemistry, The University of Sheffield, Sheffield, England

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Discotic metallomesogens: synthesis and properties of square planar metal bis(β-diketonate) complexes

by SYBOUT N. POELSMA, ALASTAIR H. SERVANTE,
FRANCESCO P. FANIZZI and PETER M. MAITLIS*
Department of Chemistry, The University of Sheffield,
Sheffield S3 7HF, England

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Discotic β-diketonate liquid crystals containing palladium(II), and oxovanadium(IV), (V≡O), analogous to known copper complexes (which display discotic lamellar and columnar mesophases), have been prepared and characterized. These are the first enantiotropic discotics containing Pd(II) and among the earliest examples containing VO(IV). The best-behaved Pd(II) complex is $[Pd(DK10,10)_2]$, and it also is probable that the complexes $[Pd(DKn,n)_2]$ ($n = 7$–9) are mesomorphic, however their characterization is difficult due to decomposition in the isotropic phase. The mesophase of $[Pd(DK10^2,10^2)_2]$, which appears below 100°C, is suggested to be an example of the rare N_D phase on the basis of optical microscopy. The complex $[VO(DK8,8)_2]$ is an enantiotropic discotic vanadyl complex; the monotropic behaviour of $[VO(DK10,10)_2]$ was also confirmed. It is suggested that the discotic phase which occurs for $[VO(DK8,8)_2]$ is more organized than that of $[Cu(DK8,8)_2]$.

1. Introduction

(Throughout this paper the abbreviation DKn^a, m^b is used for the β-diketonates 1,3-bis(4-substituted or 3,4-disubstituted phenyl)propane-1,3-diones; n and m indicate the number of carbon atoms in the alkyloxy chains, a and b the number of alkyloxy substituents on the phenyl rings. Thus, $H(DK8^2,8)$ is the β-diketone 1-{3,4-di(*n*-octyloxy)phenyl}-3-(4-*n*-octyloxyphenyl)propane-1,3-dione. H(acK8) indicates 1-(4-*n*-octyloxyphenyl)butane-1,3-dione.)

Metallomesogens, liquid crystals which incorporate metal ions, fall into two broad classes, the calamitic, where the metal atoms are bound to long thin ligands, giving complexes which are long, thin, and rod-like, and the discotic, where the metal is generally coordinated in the centre of a flat disc-like organic ligand system [1]. The ligands play a key role in determining the mesomorphic behaviour, since they usually compose the periphery of the molecule, and hence play a role in controlling the shape. The coordination geometries of the central metals are also important; thus, linear, square planar, square pyramidal, or trigonal bipyramidal lend themselves to forming calamitic or discotic mesomorphs. A current interest is to involve metal ions with partially filled *d*- or *f*-orbitals which can show paramagnetism or ferromagnetism. The introduction of a metal ion, as a centre of high electron density, into the ligand system, will strongly increase the molecular polarizability, which will in turn result in novel and useful properties.

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* Author for correspondence.

The most stable metallomesogens result from the use of chelate ligands, for example β-diketonates. Mesomorphic copper(II) β-diketonate complexes with suitable substituents have for some time been known to give rise to discotic mesophases [2]. More recently it has been shown that calamitic (nematic and smectic A) metallomesogens can also arise from β-diketones with suitable substituents [3]. Such molecules have been the subject of several investigations since they appear to offer entry to the elusive biaxial nematics.

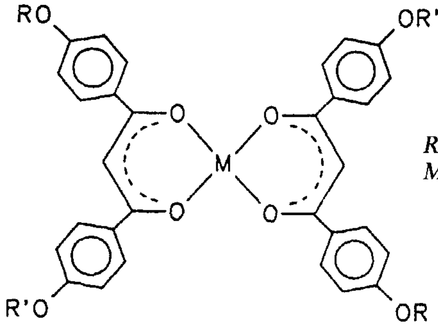
The alkyl-substituted ligands $C_nH_{2n+1}C_6H_4COCH_2COC_6H_4C_mH_{2m+1}$ exhibit smectic E phases when $m+n>17$. It has also been reported [4] that the alkyloxyphenyl-substituted β-diketones $C_nH_{2n+1}OC_6H_4COCH_2COC_6H_4OC_mH_{2m+1}$ show mesophases with narrower ranges than their alkylphenyl analogues, but that the opposite is true for the copper complexes derived from them. The copper complexes of 1,3-bis(4-*n*-alkylphenyl)-β-diketones ($m=n=7$–2; $m=7$, $n=13$), form lamellar discotic phases, where the molecules are organized in columns, while the complexes $[Cu\{(C_nH_{2n+1}OC_6H_4CO)_2CH\}_2]$ ($n=3$–12) are reported to display a discotic lamellar phase D_L, characterized by a tilt of the molecule with respect to the layer and by a random positioning of the molecules within the layer [5].

Copper complexes of β-diketones where each phenyl is substituted 3,4- by two alkyloxy groups have a total of eight chains; they display a hexagonal columnar mesophase D_h [6]. The complexes in which the phenyls were 3,5- rather than 3,4-substituted were not mesogenic. Ohta and co-workers found that copper complexes of 1,3-bis(3,4-di-*n*-alkylphenyl)-β-diketones were also not mesomorphic [7].

By comparison to the copper complexes, few mesomorphic β-diketonate complexes containing other metals have so far been reported. Bulkin *et al.* reported that DSC (differential scanning calorimetry) data indicated potential mesomorphism for bis{1-(4-*n*-octyloxyphenyl)butane-1,3-dionato}palladium [8], but were unable to confirm this optically because the complex darkened on heating. No mesomorphic properties were found for the copper bis{1-(4-*n*-alkylphenyl)butane-1,3-dionate} complexes [3].

However, the palladium complex of 1,3-bis(4-*n*-decylphenyl)-propane-1,3-dione was reported to show a discotic mesophase [9]; the nickel analogues showed no mesomorphism [10], an unsurprising result since they would be expected to have polynuclear octahedral structures. The related oxovanadium complex ($R=R'=-OC_{10}H_{21}$), was recently reported to exhibit a monotropic discotic mesophase over a short temperature range [11].

Thus the rules which govern whether a given β-diketone shape indeed generates discotic metallomesogens are still not clear, and we have therefore synthesized,



$R,R'=C_nH_{2n+1}$, $n=7$–10
$M=$ Cu, Pd, V=O

Figure 1. Metal bis(β-diketonate) complexes.

characterized and investigated the mesomorphic behaviour of a range of metal bis(β-diketonate) complexes, especially of palladium and vanadyl, which have potentially disc-like shapes. Some new β-diketones have also been synthesized.

2. Results and discussion

2.1. *Synthesis and thermal behaviour of the β-diketones*

The disubstituted β-diketone ligands were synthesized by condensing the appropriate 4-alkyloxyacetophenone and ethyl 4-alkyloxybenzoate in the presence of sodium hydride [12]. The 4-alkyloxyacetophenones and the ethyl 4-alkyloxybenzoates were prepared from 4-hydroxyacetophenone and ethyl 4-hydroxybenzoate respectively using the Williamson ether synthesis.

$$R\mathrm{Br} + 4\text{-}\mathrm{HOC_6H_4COMe} \rightarrow 4\text{-}R\mathrm{OC_6H_4COMe}, \quad R = \mathrm{C}_n\mathrm{H}_{2n+1},\ n = 7\text{–}10,$$

$$R'\mathrm{Br} + 4\text{-}\mathrm{HOC_6H_4COOEt} \rightarrow 4\text{-}R'\mathrm{OC_6H_4COOEt}, \quad R' = \mathrm{C}_m\mathrm{H}_{2m+1},\ m = 7\text{–}10,$$

$$4\text{-}R\mathrm{OC_6H_4COMe} + 4\text{-}R'\mathrm{OC_6H_4COOEt} \rightarrow 4\text{-}R\mathrm{OC_6H_4COCH_2COC_6H_4\text{-}4\text{-}OR'} \quad \{\equiv \mathrm{H(DK}m,n)\}.$$

The tri- and tetra-substituted ligands were prepared following the same route using 3,4-dialkyloxyacetophenones and ethyl 3,4-dialkyloxybenzoates. The 3,4-dialkyloxyacetophenones were prepared from catechol by a Williamson alkylation of the hydroxy-groups followed by Friedel–Crafts acylation of the resulting 1,2-dialkyloxybenzenes.

$$2\ R\mathrm{Br} + 1,2\text{-}\mathrm{(HO)_2C_6H_4} \rightarrow 1,2\text{-}(R\mathrm{O})_2\mathrm{C_6H_4}, \quad R = \mathrm{C}_n\mathrm{H}_{2n+1},\ n = 6, 8, 10,$$

$$\mathrm{MeCOCl} + 1,2\text{-}(R\mathrm{O})_2\mathrm{C_6H_4} \rightarrow 3,4\text{-}(R\mathrm{O})_2\mathrm{C_6H_3COMe}, \quad R = \mathrm{C}_n\mathrm{H}_{2n+1},\ n = 6, 8, 10,$$

$$2\ R\mathrm{Br} + 3.4\text{-}\mathrm{(HO)_2C_6H_3COOEt} \rightarrow 3,4\text{-}(R\mathrm{O})_2\mathrm{C_6H_3COOEt}, \quad R = \mathrm{C}_n\mathrm{H}_{2n+1},\ n = 6, 8, 10,$$

$$3,4\text{-}(R\mathrm{O})_2\mathrm{C_6H_3COMe} + 3,4\text{-}(R\mathrm{O})_2\mathrm{C_6H_3COOEt} \rightarrow \{3,4\text{-}(R\mathrm{O})_2\mathrm{C_6H_3CO}\}_2\mathrm{CH_2} \quad \{\equiv \mathrm{H(DK}n^2,n^2)\}.$$

The β-diketones 1-(4-*n*-octyloxyphenyl)butane-1,3-dione, H(acK8) [4], 1,3-di(4-*n*-alkyloxyphenyl)propane-1,3-dione, $n = 7$–10; H(DK7,7)-H(DK10,10) [13] and 1,3-bis{3,4-di(*n*-octyloxy)phenyl}propane-1,3-dione H(DK8^2,8^2) [11] have been described previously. The new β-diketones are the unsymmetric ligands H(DK7,9), H(DK7,10) and H(DK8^2,8) and the tetrasubstituted ligands with 3,4-dialkyloxyphenyl substituents, H(DKn^2,n^2) ($n = 6, 10$).

The β-diketones were studied by DSC and by optical microscopy (see table 1). Our data on compounds H(DK*n*,*n*), $n = 7$–10, showed very similar melting and clearing points to those reported by Ohta [14], although there are some small differences in the enthalpy data. Thus H(DK7,7) is non-mesomorphic, while H(DK8,8), H(DK9,9) and H(K10,10) show mesomorphism. Serranò and co-works recently described the mesophase as a crystalline smectic phase [15], in agreement with the identification of the mesophase of the alkylphenyl-substituted β-diketones as $\mathrm{S_E}$ [6].

Of the the β-diketones synthesized here, H(acK8) is not mesomorphic, as expected, since this ligand only possesses one phenyl-ring, which is generally insufficient to induce mesomorphism. Our data also indicate that H(DK7,9) and H(DK8,8^2) [{1-(3,4-di-*n*-octyloxyphenyl}-3-(4-*n*-octyloxyphenyl)-propane-1,3-dione] do not show mesomorphic behaviour, but that H(DK7,10) shows a monotropic smectic phase. Giroud-Godquin and Ohta and their co-workers found that none of the tetrasubstituted β-diketones H(DKm^2,n^2) $\{(\mathrm{C}_m\mathrm{H}_{2m+1}\mathrm{O})^2\text{–}\mathrm{C_6H_3\text{–}CO\text{–}CH_2\text{–}CO\text{–}C_6H_3}\text{–}(\mathrm{OC}_n\mathrm{H}_{2n+1})^2\}$; with $n = m = 7, 8, 9, 11$; $n = 3$, $m = 11$; $n = 7$, $m = 11$, was mesomorphic

Table 1. Thermal behaviour of the β-diketones.

β-diketone	Transition	Temperature/°C	Enthalpy/kJ mol^{-1}	Range/°C
HDK7,7	C→I	87	48·6	—
HDK8,8	C→M	77	6·7	8
	M→I	85	27·6	
HDK9,9	C→M	69	26·0	21
	M→I	90	42·5	
HDK10,10	C→M	36	2·0	57
	M→I	93	46·5	
HDK7,9	C→I	71	28·8	—
HDK7,10	C→C′	54	4·8	(12)†
	C′→C″	62	7·7	
	C″→I	72	34·8	
	1→(M)	63	14·3	
HacK8	C→I	57	—	—
HDK8,8^2	C→I	71	—	—
HDK6^2,6^2	C→I	72	—	—
HDK8^2,8^2	C→I	80	—	—
HDK10^2,10^2	C→I	76	—	—

†( ) denotes data for a monotropic phase.

[11, 12]. We have found that the ligands of this class, where $n = m = 6, 8$, or 10 did not show any mesomorphic behaviour either. Serrano and co-workers proposed that the increased number of terminal chains on these ligands disrupts the calamitic mesomorphism [15].

2.2. *Synthesis of the diketonate complexes*

The copper(II) bis-(β-diketonate) complexes were synthesized in high yield using the method previously described [8], and were crystallized from a mixture of CH_2Cl_2 and *n*-hexane as fine green needles. The oxovanadium(IV) complexes were prepared by the same method, but from $[VOSO_4].3H_2O$, in the minimum volume of water, diluted with ethanol. They were crystallized from acetone, as green platelets, in yields of 80–90 per cent. The palladium complexes [Pd(β-diketonate)$_2$], made by stirring together palladium chloride, the β-diketone and sodium acetate in absolute ethanol, were crystallized from CH_2Cl_2/*n*-hexane as fine yellow crystals in 50–60 per cent.

2.2.1. *Thermal behaviour of the copper diketonate complexes*

All the complexes were studied by optical microscopy, and the most interesting were also investigated by DSC (see tables 2–4). For the copper complexes [Cu(DK*n*,*n*)$_2$] ($n = 7$–10) and [Cu(DK8^2,8^2)$_2$], our observations agree with those reported by Ohta and co-workers [8, 12]. They all displayed a discotic mesophase, and in general one or more crystal–crystal transitions occurred before the complex melted into the discotic phase. The mesophases were extremely viscous, suggesting that they are highly ordered. This observation was confirmed by the DSC transition enthalpy changes, which showed that a greater enthalpy was associated with the D–I than the C–D transitions.

The new unsymmetric complexes [Cu(DK7,9)$_2$] and [Cu(DK7,10$_2$] did not display mesomorphic behaviour, and their clearing points were in the range observed for the symmetric complexes with similar total chain-lengths. [Cu(acK8)$_2$] was also non-mesomorphic, with a clearing point of 181°C. Thus, on the basis of the information to

Table 2. Thermal behaviour of the copper complexes [Cu(DK*m*,*n*)$_2$].

β-diketonate	Transition	Temperature/°C	Enthalpy/kJ mol^{-1}	Range/°C
DK7,7	$C\to D_L$	93	12·1	89
	$D_L\to I$	182	44·5	
DK8,8	$C\to C'$	26	4·3	92
	$C'\to D_L$	83	11·9	
	$D_L\to I$	175	43·8	
DK9,9	$C\to C'$	35	11·1	90
	$C''\to C''$	54	9·9	
	$C''\to D_L$	81	1·8	
	$D_L\to I$	171	45·5	
DK10,10	$C\to D_L$	37	16·9	132
	$D_L\to I$	169	43·6	
DK7,9	$C\to I$	172	44·2	—
DK7,10	$C\to I$	169	42·5	—
acK8	$C\to I$	181	—	—
DK8^2,8^2	$C\to D_h$	110	—	2
	$D_h\to I$	112		

Table 3. Thermal behaviour of the complexes [VO(DK*m*,*n*)$_2$].

β-diketonate	Transition	Temperature/°C	Enthalpy/kJ mol^{-1}	Range/°C
DK7,7	$C\to I$	150	44·6	—
DK8,8	$C\to I$	174	51·6	55†
	$C'\to D$	114	8·9	
	$D\to I$	169	14·6	
DK9,9	$C\to I$	170	62·6	—
DK10,10	$C\to I$	164	60·9	(4)‡
	$I\to(D)$	141	—	
DK7,9	$C\to I$	168	57·8	—
DK7,10	$C\to I$	164	56·2	—
DK8^2,8^2	$C\to I$	99	—	—

† With respect to the lower meeting crystal form.

‡ ( ) denotes data for a monotropic phase.

Table 4. Thermal behaviour of the palladium complexes.

β-diketonate	Transition	Temperature/°C	Enthalpy/kJ mol^{-1}	Range/°C
DK7,7	$C\to I$	192 (dec)	70·2	—
DK8,8	$C\to I$	175	37·7	—
DK9,9	$C\to I$	171	39·0	—
DK10,10	$C\to I$	168	42·9	
	$C'\to D$	87	8·5	76†
	$D\to I$	163	10·3	
DK7,9	$C\to I$	173	40·1	—
acK8	$C\to I$	243 (dec)	—	—
DK6^2,6^2	$C\to I$	123	—	—
DK8^2,8^2	$C\to I$	105	—	—
DK10^2,10^2	$C\to M$	93	—	4
	$M\to I$	97		

† With respect to the lower meeting crystal form.

hand, loss of symmetry in the copper β-diketonate complexes leads to a loss of mesomorphic behaviour. This is in sharp contrast to the situation in calamitic metallomesogens where a lower symmetry structure does lead to lower temperature C→M transitions and hence to extended mesophase ranges [16, 17].

2.2.2. *Thermal behaviour of the vanadyl diketonate complexes*

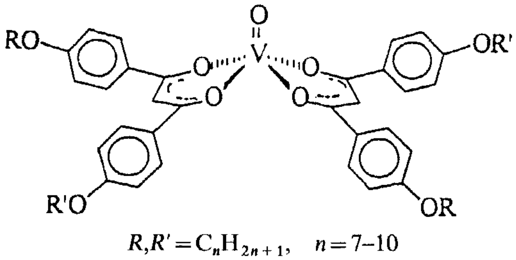
The mesomorphic properties of the vanadyl complexes [VO(β-diketonate)$_2$] (see table 3) were not as pronounced as those of the corresponding copper complexes. Thus, [VO(DK10,10)$_2$] showed a monotropic mesophase over a short temperature range; the phase could only be observed at very low cooling rates, as has already been noted [7].

However, we find that on the first heating of the virgin crystals, the complex [VO(DK8,8)$_2$] showed monotropic behaviour: it melted from the crystals directly into the isotropic liquid, but on cooling a strongly pronounced focal-conic texture was observed, indicating a mesophase. This texture was observed on all the subsequent heatings and coolings of the sample. The focal-conic texture observed by optical microscopy of this sample was different from those complexes. The melting point of [VO(DK8,8)$_2$] was higher than that of [Cu(DK8,8)$_2$], but the clearing point was very similar, resulting in a mesomorphic range of 55°C with respect to the lower melting crystal form. This mesophase could be a hexagonal columnar phase, which would be in agreement with the structure of these oxovanadium complexes, since the V=O bond makes stacking through intermolecular –V–O–V–O– interactions possible. This phenomenon has recently been used to make liquid crystal vanadyl polymers based on salen-type ligand systems [18].

None of the other oxovanadium complexes synthesized was mesomorphic, even though their melting points were similar to those of their copper analogues. [VO(DK7,7)$_2$] displayed a complicated thermal behaviour with several crystal–crystal transitions; however no mesophase could be observed for this complex nor for [VO(DK9,9)$_2$]. The unsymmetric complexes [VO(DK7,9)$_2$] and [VO(DK7,10)$_2$] and the complex [VO(DK8^2,8^2)$_2$] were non-mesomorphic. The last complex did not crystallize on cooling from the isotropic liquid, and supercooled into a glass; as for the analogous copper complex, the melting point was significantly reduced compared to those of the [VO(DKn,n)$_2$].

2.2.3. *Thermal behaviour of the palladium diketonate complexes*

We have made similar observations for the palladium complexes [Pd(DKm,n)$_2$] ($m = n = 7$–9; $m = 7, n = 9$) to those made by Bulkin and co-workers on [Pd(acK8)$_2$] [2]. These complexes decomposed at or near their clearing points, although the extent of decomposition decreased with longer alkyloxy chains in the symmetric complexes. Initial DSC data (see table 4) indicated that these complexes were potentially



$R,R' = C_nH_{2n+1}$, $n = 7$–10

Figure 2. Vanadyl bis(β-diketonate) complexes.

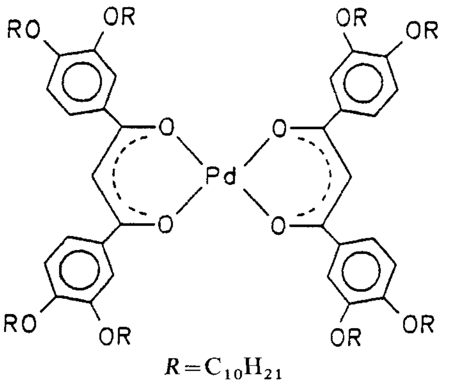


Figure 3. A mesomorphic palladium bis(β-diketonate) complex.

mesomorphic. However, [Pd(DK10,10)$_2$], which showed a very similar behaviour to its homologues with shorter alkyloxy chains, but did not undergo the same extent of decomposition at clearing point, is mesomorphic. It showed a very similar behaviour to [VO(DK8,8)$_2$]; the virgin crystals melted direct to the isotropic liquid, but on subsequent heating of the crystal form obtained on cooling the isotropic liquid (via the mesophase), enantiotropic behaviour was observed. On the basis of optical microscopy, this mesophase has been assigned as a disordered discotic phase. This result for [Pd(DK10,10)$_2$] strongly suggests that the other complexes [Pd(DKn,n)$_2$] (n = 7–9) are also mesomorphic.

The complexes [Pd(DKn^2,n^2)$_2$] (n = 6, 8, 10) containing eight chains did not decompose on clearing, probably due to their significantly reduced transition temperatures compared to their derivatives possessing two or four alkyloxy chains. [Pd(DK6^2,6^2)$_2$] and [Pd(DK8^2,8^2)$_2$] were not mesomorphic, but [Pd(DK10^2,10^2)$_2$] did show a mesophase; it melted at 93°C into a mesophase and cleared at 97°C. This observation was confirmed by DSC. A four-brushed schlieren texture was observed in the mesophase; the texture was very similar to the texture observed for many smectic C phases. However, the structure of the complex, which contains eight decyloxy substituents, makes a calamitic mesophase, such as a smectic C, unlikely. It is possible that the mesophase is an example of the very rare discotic nematic or columnar nematic phase, since these phases also show four-brushed schlieren textures.

3. Conclusion

We have prepared new mesomorphic β-diketonate palladium(II) complexes, such as [Pd(D10,10)$_2$]; it is probable that the complexes [Pd(DKn,n)$_2$] (n = 7–9) are also mesomorphic, but their characterization is difficult due to decomposition in the isotropic phase. The mesophase of [Pd(DK10^2, 10^2)$_2$], which appears below 100°C, is suggested to be an example of the rare N_D phase on the basis of optical microscopy. The vanadyl complex [VO(DK8,8)$_2$] showed enantiotropic mesomorphic behaviour, but only with respect to a lower melting crystal form, and the monotropic behaviour of [VO(DK10,10)$_2$] was also confirmed. Several copper complexes, including [Cu(DKn,n)$_2$] (n = 7–10) and [Cu(DK8^2,8^2)$_2$] display discotic mesophases; however, the unsymmmetric complexes [Cu(DK7,9)$_2$] and [Cu(DK7,10)$_2$] did not show mesomorphism, and [Cu(acK8)$_2$] was also non-mesomorphic. Of the three metals, those of copper form the best mesomorphs; of the β-diketones tried, the best results were obtained using the symmetric ones, H(DKn,n).

4. Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. ^{1}H NMR spectra (250·13 MHz) were recorded on a Bruker AM250 FT spectrometer, using $CDCl_3$ as both solvent and reference. Optical characterization was performed using covered microscope slides on a Zeiss Jenalab POL microscope fitted with crossed polarizers and a Linkam TH600 hot-stage and PR600 integrated temperature controller. Differential scanning calorimetry (DSC) measurements were made using sealed aluminium pans, on a Perkin–Elmer DSC7 instrument, with a TAC7 instrument controller connected to a PE7700 data station using TAS7 software. Temperatures of transitions are quoted from the onset of the transitions in the DSC and were all confirmed microscopically at a heating rate of 1 K min^{-1}; whenever possible

Table 5. Yields and microanalytical data for the β-diketones.

			Found (calculated)	
Number	β-diketone	Yield†/per cent	C/per cent	H/per cent
1a	HDK7,9	65	77·2 (77·4)	9·3 (9·2)
1b	HDK7,10	72	77·1 (77·7)	9·1 (9·4)
1c	HDK8,8^2	6	76·7 (76·9)	9·7 (10·0)
1d	HDK6^2,6^2	22	74·9 (74·9)	9·4 (9·7)
1e	HDK10^2,10^2	11	78·0 (77·8)	10·7 (10·9)

† The yields are overall yields starting from the hydroxyphenyl compounds and therefore include the Williamson ether synthesis, where appropriate Friedel–Crafts acylation, and condensation.

Table 6. Yields and microanalytical data for the copper bis(β-diketonate) complexes.

			Found (calculated)	
Number	β-diketonate	Yield/per cent	C/per cent	H/per cent
2a	acK8	31	67·0 (67·3)	7·7 (67·9)
2b	DK7,9	86	72·8 (72·8)	8·6 (8·4)
2c	DK7,10	55	73·2 (73·1)	8·7 (8·6)

Table 7. Yields and microanalytical data for the vanadyl bis(β-diketonate) complexes.

			Found (calculated)	
Number	β-diketonate	Yield/per cent	C/per cent	H/per cent
3a	DK7	78	71·4 (71·8)	8·1 (8·1)
3b	DK8	80	72·2 (72·6)	8·4 (8·4)
3c	DK9	88	73·3 (73·2)	8·5 (8·7)
3d	DK7,9	90	72·5 (72·5)	8·5 (8·5)
3e	DK7,10	87	72·9 (73·0)	8·6 (8·7)
3f	DK8^2	43	73·1 (73·5)	9·8 (9·8)

Table 8. Yields and microanalytical data for the palladium bis(β-diketonate) complexes.

			Found (calculated)	
Number	β-diketonate	Yield/per cent	C/per cent	H/per cent
4a	DK7	49	69·2 (69·0)	7·7 (7·8)
4b	DK8	60	69·8 (69·9)	8·0 (8·2)
4c	DK9	55	70·3 (70·9)	8·3 (8·1)
4d	DK10	50	70·9 (71·4)	8·4 (8·7)
4e	DK7,9	63	69·2 (69·9)	8·0 (8·2)
4f	acK8	23	62·9 (63·1)	7·0 (7·4)
4g	DK6^2,6^2	16	69·1 (69·2)	8·8 (8·8)
4h	DK8^2,8^2	42	71·1 (71·5)	9·4 (9·6)
4i	DK10^2,10^2	12	72·6 (73·3)	9·8 (10·2)

they were confirmed on the cooling and second heating cycles. There were, in general, no differences in the temperatures when measured in air or in an inert atmosphere.

The β-diketones were prepared by an adaptation of the method of Kopecki and co-workers [13]; a typical preparation is given below. Typical methods are given for the synthesis of each class of metal complex; the commercially available metal salts were used as supplied. The thermal behaviour of the β-diketones is given in table 1, while that of the copper, vanadyl and palladium complexes are collected in tables 2–4. Yields and microanalytical data of the β-diketones are given in table 5, while those of the copper, vanadyl and palladium complexes are in tables 6, 7, and 8 respectively.

4.1. *1,3-disubstituted propane-1,3-diones*

A mixture of ethyl 4-*n*-octyloxybenzoate (5·6 g, 20 mmol) and sodium hydride (5·0 g 50 per cent dispersion in mineral oil, 220 mmol) in dimethoxyethane (80 cm^3) was refluxed for 30 min under nitrogen. A solution of 3,4-di-*n*-octyloxyacetophenone (7·5 g, 20 mmol) in dimethoxyethane (25 cm^3) was added dropwise, and the resulting mixture was refluxed for 6 h. After cooling to 0°C, ice was added carefully until the reaction with the excess of sodium hydride ceased. The mixture was then acidified with aqueous hydrochloric acid (10 per cent v/v, pH = 3). The resulting solution was shaken with ether (2 × 250 cm^3), and the ethereal solution was washed with water (3 × 100 cm^3) and then dried over sodium sulphate. After filtration the ether was removed by rotary evaporation, leaving a yellow solid, which was crystallized from absolute ethanol.

^{1}H NMR: δ 0·86(9 H, m, 3 CH_3); 1·30(30 H, m, 15 CH_2); 1·82(6 H, m, 3 $C\underline{H}_2(CH_2)_5$; 4·03(6 H, m, 3 $C\underline{H}_2O$); 6·70(1 H, s, H_{keto}); 6·88(1 H, d, ^3J(H,H) = 9 Hz, $H(C_6H_3)$); 6·92(2 H, d, ^3J(H,H) = 9 Hz, 2 $H(C_6H_4)$); 7·52(2 H, s, 2 $H(C_6H_3)$); 7·92(2 H, d, ^3J(H,H) = 9 Hz, 2 $H(C_6H_4)$); 17·15(1 H, s, H_{enol}).

4.2. *Bis(β-diketonate)copper(II) complexes*

A solution of $CuCl_2$ (0·054 g, 0·4 mmol) in absolute ethanol (10 cm^3) was added to a solution of H(DK7,9) (385 mg, 0·8 mmol) and KOH (0·045 g, 0·8 mmol) in absolute ethanol (200 cm^3). The solution was stirred for 30 min, during which a green precipitate was formed. The precipitate was filtered off, washed with water (2 × 10 cm^3) and dried *in vacuo*. The product was extracted with $CHCl_3$, and after filtration the solvent was removed. The residue was crystallized from a mixture of CH_2Cl_2 and *n*-hexane giving fine green crystals of the copper bis(β-diketonate) complex.

4.3. *Bis(β-diketonate)oxovanadium complexes*

A solution of [$VOSO_4$].$3H_2O$ (86 mg, 0·4 mmol) in aqueous ethanol (10 cm^3, 80 per cent) was added to a solution of H(DK7,9) (385 mg, 0·8 mmol) in absolute ethanol (200 cm^3). The solution was stirred for 30 min. A green precipitate was formed, which was filtered off, washed with water (2 × 10 cm^{-3}) and dried *in vacuo*. The product was extracted with $CHCl_3$, and after filtration the solvent was removed. The residue was crystallized from acetone giving fine green crystals of the vanadyl bis(β-diketonate) complex.

4.4. *Bis(β-diketonate)palladium complexes*

[$PdCl_2$] (70 mg, 0·4 mmol) was added to a solution of H(DK7,9) (385 mg, 0·8 mmol) and [NaOAc].$3H_2O$ (109 mg, 0·8 mmol) in absolute ethanol (100 cm^3). A grey precipitate was formed on stirring at room temperature for 4 h; this was filtered off and dried *in vacuo*. The crude product was eluted over a column of deactivated alumina (3 per cent water) using CH_2Cl_2, giving a yellow solution. Removal of solvent gave a yellow solid, which was crystallized from CH_2Cl_2/*n*-hexane giving the yellow crystalline palladium complex.

^1H NMR: δ 0·87(6 H, t, $^3J(H,H) = 7$ Hz, 2 CH_3); 1·30(16 H, m, 8 CH_2); 1·45(4 H, m, 2 $C\underline{H}_2(CH_2)_4$); 1·79(4 H, m, 2 $C\underline{H}_2CH_2O$); 4·00(4 H, t, $^3J(H,H) = 7$ Hz, 2 $C\underline{H}_2O$); 6·66(1 H, s, CH); 6·90(4 H, d, $^3J(H,H) = 9$ Hz, 4 H_{ar}); 7·93(4 H, d, $^3J(H,H) = 9$ Hz, 4 H_{ar}).

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References

[1] Giroud-Godquin, A. M., and Maitlis, P. M., 1991, *Angew. Chem. Int. Ed. Engl.*, **30**, 375. Espinet, P., Esteruelas, M. A., Oro, L. A., Serrano, J. L., and Sola, E., 1992, *Coord. Chem. Rev.*, **117**, 215. Hudson, S. A., and Maitlis, P. M., 1993, *Chem. Rev.*, **93**, 861.

[2] Giroud-Godquin, A. M., and Billard, J., 1981, *Molec. Crystals liq. Crystals*, **66**, 147. Ribeiro, A. C., Martins, A. F., and Giroud-Godquin, A. M., 1988, *Molec. Crystals liq. Crystals Lett.*, **5**, 133. Ohta, K., Yokohama, M., Kubayashi, S., and Mikawa, H., 1980, *J. chem. Soc. chem. Commun.*, p. 392.

[3] Thompson, N. J., Gray, G. W., Goodby, J. W., and Toyne, K. J., 1991, *Molec. Crystals. liq. Crystals*, **200**, 109.

[4] Ohta, K., Ishii, A., Muroki, H., Yamamoto, I., and Matsuzaki, K., 1985, *Molec. Crystals liq. Crystals*, **116**, 299.

[5] Sakashita, H., Nitshitani, A., Sumiya, Y., Terauchi, H., Ohta, K., and Yamamoto, I., 1988, *Molec. Crystals liq. Crystals*, **163**, 211.

[6] Giroud-Godquin, A. M., Gauthier, M. M., Sigaud, G., Hardouin, F., and Achard, M. F., 1986, *Molec. Crystals liq. Crystals*, **132**, 35.

[7] Ohta, K., Ema, H., Muroki, H., Yamamoto, I., and Matsuzaki, K., 1987, *Molec. Crystals liq. Crystals*, **147**, 61.

[8] Bulkin, B. J., Rose, R. K., and Santoro, A., 1977, *Molec. Crystals liq. Crystals*, **43**, 53.

[9] Usha, K., Vijayan, K., Sadashiva, B. K., and Rao, P. R., 1990, *Molec. Crystals liq. Crystals*, **185**, 1.

[10] Giroud-Godquin, A. M., and Billard, J., 1983, *Molec. Crystals liq. Crystals*, **97**, 287.

[11] Styring, P., Tantrawong, S., Beattie, D. R., and Goodby, J. W., 1991, *Liq. Crystals*, **10**, 581.

[12] Kopecki, K. R., Nonhebel, D., Morris, G., and Hammond, G. S., 1962, *J. org. Chem.*, **27**, 1036.

[13] Ohta, K., Muroki, H., Hatada, K. I., Yamamoto, I., and Matsuzaki, K., 1985, *Molec. Crystals liq. Crystals*, **130**, 249.

[14] Ohta, K., Muroki, H., Hatada, K. I., Takagi, A., Ema, H., Yamamoto, I., and Matsuzaki, K. K., 1986, *Molec. Crystals liq. Crystals*, **140,** 163.

[15] Barbera, J., Cativiela, C., Serrano, J. L., and Zurbano, M. M., 1992, *Liq. Crystals*, **11,** 887.

[16] Rourke, J. P., Fanizzi, F. P., Bruce, D. W., Dunmur, D. A., and Maitlis, P. M., 1992, *J. chem. Soc. Dalton Trans.*, p. 3009.

[17] Bruce, D. W., Dunmur, D. A., Esteruelas, M. A., Hunt, S. E., le Lagadec, R., Maitlis, P. M., Marsden, J. R., Sola, E., and Stacey, J. M., 1991, *J. mater. Chem.*, **1,** 251.

[18] Serrette, A., Carroll, P. J., and Swager, T. M., 1992, *J. Am. chem. Soc.*, **114,** 1887.