New β-Diketones with Oligoether Side-chains and their Complexes with Barium and Copper. Crystal and Molecular Structure of Bis(1-phenyl-7,10-dioxaundecane-1,3-dionato)copper(II) at 150 K†

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A range of new β-diketones of formula $RC(O)CH_2C(O)(CH_2)_3(OCH_2CH_2)_nOMe$ ($n = 1$, R = Me, Ph, $2,4,6\text{-}Me_3C_6H_2$ or Bu^t; $n = 2$, R = Me) has been prepared and spectroscopically characterised. Complexes of these β-diketones with barium(II) and with copper(II) ($n = 1$, R = Me or Ph) have been prepared and are shown to be involatile because the polyether chain binds to a different metal atom from that to which the β-diketonate function is bound, thus forming polymers. The complex $[Cu\{PhC(O)CHC(O)(CH_2)_3O(CH_2)_2OMe\}_2]$ crystallises in the space group $P2_1/c$ with $a = 9.109(9)$, $b = 11.189(8)$, $c = 14.453(6)$ Å, $\beta = 103.64(9)°$ and $Z = 2$. The structure was refined to $R = 0.065$, using 990 independent reflections. The copper atoms exhibit Jahn–Teller distorted six-co-ordinate geometry with the oxygen atoms of two bidentate β-diketonates occupying the equatorial positions (Cu–O 1.92 Å) and two terminal oxygen atoms from the polyether chains of different neighbouring molecules occupying the axial sites (Cu ··· O 3.065 Å).

Owing to the wide interest generated by high T_c superconductors such as $YBa_2Cu_3O_{7-x}$, there is considerable activity in the development of volatile compounds of all of the elements contained in the superconductors so that they can be deposited by chemical vapour deposition (CVD) techniques.[1,2] Several such compounds are available for yttrium and copper, but barium has proved a more difficult element to volatilise on account of its ability to expand its co-ordination number up to at least 10 whilst retaining its valency of two.[1]

The only compounds of barium that can be repeatedly sublimed at 1 atm (*ca.* 10^5 Pa) without decomposition are $[Ba(tdfnd)_2]$ (Htdfnd = 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione)[3,4] and the adduct of this compound with tetraglyme (2,5,8,11,14-pentaoxapentadecane).[5] The adduct melts at 70 °C and can be used repeatedly as a liquid CVD precursor at a pot temperature of 80 °C. Both compounds have been shown to provide reproducible growth of BaF_2,[5,6] which can be converted into BaO on annealing in an atmosphere containing steam. Superconducting layers of $YBa_2Cu_3O_{7-x}$ have been grown using both precursors.[5,6] The main disadvantage to using these materials is the initial growth of BaF_2 and it is highly desirable to develop volatile barium compounds which do not contain fluorine. The most successful precursor of this kind that has been used to date is $[Ba(tmhd)_2]$ (Htmhd = 2,2,6,6-tetramethylheptane-3,5-dione),[7] but this compound, which may be present as the partially hydrolysed pentamer, $[Ba_5(tmhd)_9(OH)(H_2O)_3]$[8a] or as the tetramer $[\{Ba(tmhd)_2\}_4]$,[9] decomposes as it sublimes. The lifetime of this precursor and its volatility can be enhanced if Htmhd,[10] amines,[11] or ethers[12] are added to the carrier gas during the growth process.

Tetraglyme adducts of a variety of fluorinated β-diketonates of barium show enhanced stability and volatility over their uncomplexed analogues,[13–15] but again BaF_2 is formed. Drake *et al.*[16] have reported the synthesis of the tetraglyme adduct of $[Ba(tmhd)_2]$ which is monomeric in the solid state. Simultaneous thermal analysis (STA) of this adduct shows that it can be sublimed essentially without decomposition, although dissociation of the tetraglyme precedes the sublimation and a residue of ≈6% was attributed to carbonaceous products arising from its decomposition. This means that this adduct is not a suitable CVD precursor for repeated use so we have synthesised new β-diketones in which the polyether group is incorporated into a side chain. Barium and copper complexes of these β-diketones have been prepared and their lack of volatility is attributed to inter-, rather than intra-molecular binding of the polyether side chains.

Results and Discussion

Synthesis and Properties of $[Ba(tmhd)_2]$*-tetraglyme.*—Reaction with tetraglyme ($C_{10}H_{22}O_5$) of the product obtained from $BaBr_2 \cdot 2H_2O$ and Htmhd in aqueous ethanol produces a white crystalline solid of formula $[Ba(tmhd)_2] \cdot C_{10}H_{22}O_5$ despite the fact that the intermediate is probably $[Ba_5(tmhd)_9(OH)(H_2O)_3]$.[8a,‡] The tetraglyme adduct is identical in every way to that prepared by Drake *et al.*[16] from $[\{Ba(OEt)_2(EtOH)_4\}_n]$, except that our sample leaves a residue of only *ca.* 4% after the STA analysis. This suggests that the residue observed by Drake *et al.*[16] may arise from impurities $[Ba(OH)_2?]$ rather than carbonaceous decomposition products. Nevertheless, macroscopic sublimation experiments confirm that tetraglyme is transported into the collecting vessel and no barium-containing species sublimes. This suggests that, in the STA experiment, monomeric $[Ba(tmhd)_2]$ is produced from the adduct *via* loss of tetraglyme and that this sublimes before it has a chance to oligomerise (the heating rate is rapid, 20 °C min^{-1}, the sample size is small and the distance over which it is transported is short). By contrast, in the macroscopic experi-

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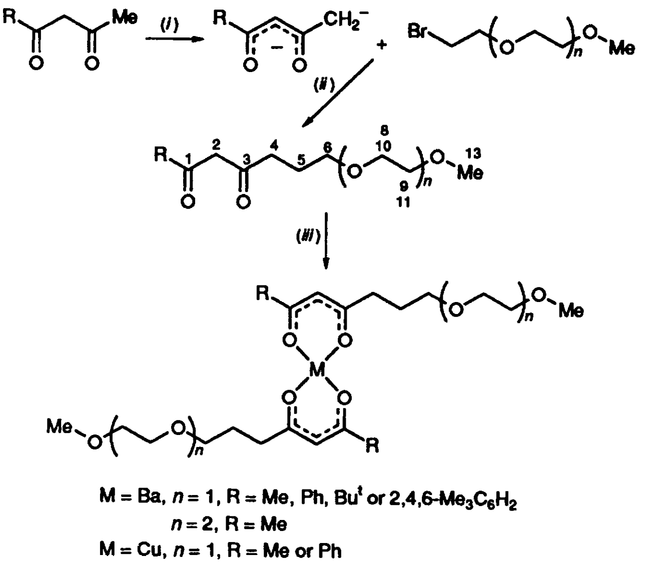
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: Torr ≈ 133 Pa.

‡ *Note added at proof.* A recent report[8b] suggests that this reaction may also give $[Ba_6(tmhd)_{12}(H_2O)_{13}]$.

ment, the sample size is larger and the sublimate must pass over a large distance so that, either in the solid sample or in the atmosphere above it, there is the opportunity for $[Ba(tmhd)_2]$ to oligomerise and form less-volatile tetramers.

In view of the ease with which tetraglyme dissociates from $[Ba(tmhd)_2]{\cdot}C_{10}H_{22}O_5$ we sought to synthesise β-diketonate compounds in which polyethers are bound to the barium, but from which the ether either could not dissociate or, if it did dissociate, could not escape. In order for this to be the case we reasoned that it would be necessary to bind the polyether chain to the β-diketonate. Rees[17] has adopted a somewhat similar strategy using the β-diketonate $Bu^tC(O)CHC(O)(CH_2)_3OMe$ and has proposed that this leads to monomeric products, although they do not show high volatility or stability during sublimation. During the course of this work Marks and co-workers[18,19] attempted a similar strategy using β-ketoimines in which the nitrogen bears a polyether side chain. These compounds do give structurally characterised monomeric barium compounds but they decompose on heating and cannot be sublimed intact.



Scheme 1 Synthesis of β-diketones with polyether side-chains and their complexes. (*i*) $NaNH_2$–NH_3(l); (*ii*) NH_3(l); (*iii*) BaH_2, toluene or $Cu(NO_3)_2$, ethanol, NH_3(qq)

Synthesis of β*-Diketones with Oligoether Side-chains.*—The general strategy is shown in Scheme 1. A β-diketone bearing at least one methyl group was treated with 2 molar equivalents of sodium amide in ammonia, prepared *in situ* by addition of sodium to liquid ammonia in the presence of catalytic quantities of iron(III) nitrate. The doubly deprotonated β-diketone was then treated with 1 molar equivalent of the bromide of a polyether to give, after work-up, the desired β-diketone in moderate yield. A similar method has been reported for the synthesis of $MeC(O)CH_2C(O)(CH_2)_3CO_2H$.[20] The liquid products were fully characterised by microanalysis, ^1H and ^{13}C NMR and IR spectroscopy (see Tables 1–3). All of the β-diketones exist with their keto and enol forms in equilibrium at room temperature and resonances from both forms are recorded in Tables 1 and 2. The most distinctive feature of the ^1H NMR spectra is the quintet near δ 1.9 arising from the hydrogens on the C atom β to the β-diketone (C^5 in the numbering scheme, see Scheme 1). In some cases, *e.g.* for R = Me, the keto and enol forms have this signal superimposed, whereas for others, *e.g.* for R = $2,4,6-Me_3C_6H_2$, the keto and enol C^5 hydrogen atoms have different chemical shifts and the signal appears as a septet from two overlapping triplets of triplets. All of the compounds are obtained in a pure state as evidenced by the lack of signals in the ^1H or ^{13}C NMR spectra apart from those attributable to the keto and enol forms of the β-diketones. In general, all the compounds give parent ions in the mass spectrometer as well as extensive fragmentation patterns.

Preparation of Metal Complexes.—Reactions of new β-diketones with $BaBr_2{\cdot}2H_2O$ in aqueous ethanol in the presence of sodium hydroxide produce white solids which appear to contain water (IR evidence) and which are insoluble in all common organic solvents as well as in water. These white solids, which are also involatile, have not been characterised further.

An alternative method for the production of Lewis-base adducts of barium β-diketonates involves the interaction of BaH_2 with the β-diketone in dry toluene.[21] Although no reaction occurs in the absence of added Lewis bases, in their presence BaH_2 dissolves smoothly to give the Lewis-base adduct of the β-diketonate. We have attempted this strategy for the synthesis of complexes of barium with the new β-diketones,

Table 1 Proton NMR data for new β-diketones[a] and their barium complexes[b]

				δ								
n	R		E (%)	H^2	H^4	H^5	H^6	H^8	H^9	H^{13}	OH	*R*
Free diketones												
1	Me	K		*c*	2.63	1.91	3.52	3.58	3.57	3.41		2.27
		E	76	5.54	2.39	1.91	3.52	3.58	3.57	3.40	15.55	2.07
1	Bu^t	K		*c*	2.60	1.85	3.52	3.60	3.56	3.34		1.10
		E	71	5.54	2.34	1.85	3.52	3.60	3.56	3.33	15.71	1.10
1	Ph	K		4.04	2.85	1.88	3.46	3.49	3.47	3.33		7.3–7.9
		E	92	6.14	2.65	1.93	3.46	3.49	3.47	3.32	16.15	
1	$2,4,6-Me_3C_6H_2$	K		*c*	2.53	1.74	3.25	3.25	3.25	3.07		1.91,2.02,6.29
		E	46	5.15	2.22	1.76	3.25	3.25	3.25	3.06	15.65	
2	Me[d]	K		*c*	2.61	1.90	3.52	3.56	3.57	3.42		2.27
		E	62	5.54	2.38	1.90	3.52	3.56	3.57	3.40	15.47	2.09
Barium complexes												
1	Me			5.14	2.12	1.82	3.41–3.60					1.82
1	Bu^t			5.38	2.20	1.85	3.38–3.55					1.10
1	Ph			5.83	2.20	1.78	3.23–3.36					7.2–7.8
1	$2,4,6-Me_3C_6H_2$			5.11	2.60	1.80	3.40–3.51					2.23, 6.75
2	Me			5.25	2.24	1.90	3.34–3.60					0.9

[a] δ in ppm to high field of internal $SiMe_4$; K = keto, E = enol; ratio, *R*, obtained from integration of H^4 resonances, J_{HH} = 7 Hz for H^4 (t), H^5 (qnt) and H^{8-11} (t). [b] All resonances are broad. [c] Masked by resonances from H^8 and H^9. [d] H^{10}, δ 3.56 (K + E), H_{11}, δ 3.57 (K + E).

Table 2 Carbon-13 NMR data for new β-diketonates[a] and their barium complexes

			δ								
n	R		C^1	C^2	C^3	C^4	C^5	C^6	C^8	C^9	C^{13}
Free diketones											
1	Me	K	204.60	57.83	203.10	40.44	25.43	70.02	71.92	70.24	59.03
		E	194.14	99.85	190.70	34.92	23.52	70.02	71.92	70.24	59.03
1	Bu^t	K	199.67	51.38	200.86	35.43	25.51	70.28	71.89	70.01	58.98
		E	195.41	95.15	196.71	32.35	23.50	70.28	71.89	70.01	58.98
1	Ph	K	196.77	53.71	204.50	40.08	25.55	70.21	71.90	69.93	58.98
		E	182.90	96.18	194.00	35.86	23.58	70.21	71.90	69.93	58.98
1	2,4,6-$Me_3C_6H_2$	K	197.43	51.17	210.42	36.02	25.30	70.08	71.93	70.28	59.03
		E	187.07	102.34	197.43	36.02	23.39	70.01	71.93	70.18	59.03
2	Me[b]	K	204.01	57.89	194.16	40.47	25.49	70.13	71.96	70.62	59.04
		E	194.16	99.90	190.81	34.94	23.58	70.13	71.96	70.62	59.04
Barium complexes											
1	Me		194.30	99.94	189.00	37.81	26.47	69.45	71.79	71.12	58.92
1	Bu^t		198.32	93.15	190.54	39.88	25.68	69.02	71.27	70.55	58.35
1	Ph		182.61	95.78	192.97	38.34	26.74	69.23	71.51	70.95	58.79
1	2,4,6-$Me_3C_6H_2$		179.15	101.07	191.60	38.35	27.76	70.09	72.37	71.19	59.84
2	Me[c]		192.86	99.20	189.88	38.71	26.08	69.85	71.88	70.72	58.94

[a] δ in ppm to high field of $SiMe_4$; K = keto, E = enol. [b] C^{10} δ 70.56 (K + E), C^{11} δ 70.20 (K + E). [c] C^{10} δ 70.53, C^{11} δ 70.41.

Table 3 Infrared data (cm^{-1}) for new β-diketones and their complexes

n	R	ν(O–H)[a]	ν(C=O)[b]	ν(C=C)[c]	ν(M–O)[d]
Free diketones					
1	Me	3490	1723, 1706	1619	
1	Bu^t	3444	1727, 1699w	1607	
1	Ph	3503	1710, 1670w	1603	
1	2,4,6-$Me_3C_6H_2$	3370	1699	1613	
2	Me	3533	1717	1619	
Barium complexes					
1	Me	3465	1607	1510	460
1	Bu^t	3420	1597	1510	460s
1	Ph	3375	1569	1501	407m
1	2,4,6-$Me_3C_6H_2$	—	1590	1507	452
2	Me	3410	1603	1510	452
Copper complexes					
1	Me	—	1574	1523	476
1	Ph	—	1590	1510	448

[a] All w(br); for barium complexes vw(br). [b] All s unless otherwise indicated. [c] All s. [d] All w unless otherwise indicated.

but because the co-ordinating Lewis base is directly attached to the β-diketone it is not necessary to add other Lewis bases.

On reaction with the β-diketones in dry toluene, BaH_2 dissolves smoothly to give yellow solutions containing small amounts of insoluble impurities from the BaH_2. From the solution, products can be obtained which are soluble in *e.g.* toluene and other organic solvents. Most of these compounds are liquids and it has proved very difficult to remove the last traces of the parent β-diketones (as evidenced by a weak broad feature in the IR spectrum and a weak resonance near δ 16 both from the enol form of the β-diketone). Nevertheless, microanalysis suggests that the complexes are of the form $[BaL_2]$ (L = β-diketonate) and their solubility suggests that, in solution, they may be monomeric. The NMR spectra, although broader than for the free β-diketones, show that the latter have remained intact during the synthesis.

Unfortunately, simultaneous thermal analysis and sublimation studies show that these compounds are not volatile and decompose extensively on heating. The STA traces are complicated with many small features exhibiting weight losses, whilst the condensates obtained after attempted sublimation of $[Ba\{RC(O)CHC(O)(CH_2)_3OCH_2CH_2OMe\}_2]$ (R = Ph or Me) contain RC(O)Me and $MeOCH_2CH_2O(CH_2)_3C(O)Me$ suggesting that substantial degradation of the ligands has occurred. These observations suggest that the complexes, although possibly monomeric in solution, undergo changes when freed from solvent to give involatile polymeric products. This possibility is confirmed by observations on related copper complexes.

Complexes analysing as $[CuL_2]$ (L = β-diketonate) can be isolated as blue or turquoise crystalline solids from reactions of $RC(O)CH_2C(O)(CH_2)_3O(CH_2)_2OMe$ (R = Me or Ph) with hydrated copper nitrate in aqueous ethanol containing aqueous ammonia. From a comparison of their visible spectra with those in the literature[22] it seems probable that these complexes are five- or six-co-ordinate, although correlations for copper(II) are not very reliable since the ranges of λ_{max} overlap for four-, five- and six-co-ordination.[23] The solubility properties of the complexes in cyclohexane are interesting. Thus, the compound with R = Me shows very little solubility at room temperature but up to 1 g can dissolve in 50 cm^3 at the boiling point. In addition, solutions of the compound with R = Me in cyclohexane are blue (characteristic of six-co-ordinate copper) at room temperature but become green (square-planar copper) on heating to 50 °C. Solutions in dimethylformamide start off blue but become green on standing even at room temperature. The large variation in solubility with temperature and the thermochromism probably suggest that these complexes are polymeric in the solid state, but dissociate to monomers in solution at higher temperature. We have, therefore, determined the crystal structure of $[Cu\{PhC(O)CHC(O)(CH_2)_3O(CH_2)_2OMe\}_2]$.

Crystal and Molecular Structure of Bis(1-*phenyl*-7,10-*dioxaundecane*-1,3-*dionato*)*copper*(II).—The structure of $[Cu\{PhC(O)CHC(O)(CH_2)_3O(CH_2)_2OMe\}_2]$ is shown in Figs. 1 and 2 with bond lengths and angles in Table 4. It reveals that, in the solid state, the complex is polymeric with each copper atom surrounded by six oxygen atoms. Two β-diketonate ligands are bound in a bidentate manner to each copper atom to give a distorted square-planar arrangement, whilst the two axial co-ordination sites are taken up by the terminal oxygen atoms of the polyether chain from a β-diketonate attached to the neighbouring copper atom. The Cu–O distances for the β-diketonate O atoms are *ca.* 1.92 Å, similar to the shorter ones (1.919 Å) found in $[Cu(acac)_2]$ (acac = pentane-2,4-dionate)[24] or $[Cu\{Bu^tC(O)CHC(O)(CH_2)_3OMe\}_2]$ (1.92 Å),[17] whilst those to the other two oxygen atoms are 3.065 Å. These distances, which are on the borderline of those found for bonding interactions, are similar to those found in *e.g.* $[Cu\{Bu^tC(O)CHC(O)(CH_2)_3OMe\}_2]$ (2.987 Å)[17] and reflect the Jahn–Teller distortion expected for the d^9 Cu^{2+} ion. They are, however, much larger than would be expected for genuinely six-co-ordinate complexes with 4 + 2 co-ordination (generally < 2.8 Å). The length of these axial Cu–O bonds suggests a weak interaction and is consistent with the breakdown of the complex to give monomers in solution under mild conditions.

The polyether chains of the scorpion-tail adopt a planar zigzag arrangement which is parallel with the plane of the β-diketonate moiety but displaced from it because the C(12)–C(13) bond is out of the plane and there appears to be no tendency towards chelation. Models suggest that co-ordination to the same metal atom of the oxygen δ to the co-ordinated carbonyl would induce substantial strain, whilst co-ordination of more remote O atoms would provide little chelate stabilisation. β-Ketoimine compounds derivatised with similar polyether side-chains on the nitrogen do show co-ordination to the same barium atom of the O atom γ and ζ to N but more remote O atoms remain unco-ordinated.[18,19]

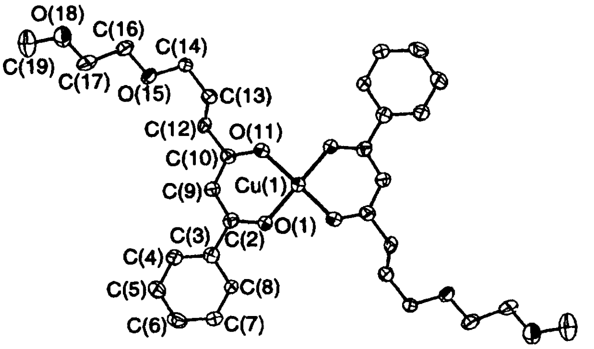


Fig. 1 Molecular structure and numbering scheme for $[Cu\{PhC(O)CHC(O)(CH_2)_3OCH_2CH_2OMe\}_2]$

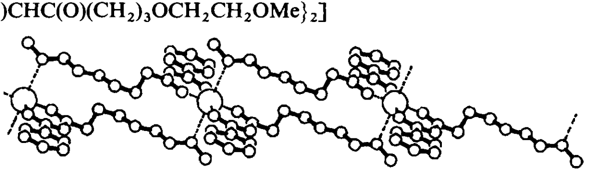


Fig. 2 Side view of a molecule of $[Cu\{PhC(O)CHC(O)(CH_2)_3OCH_2CH_2OMe\}_2]$ showing the long-range intermolecular Cu···O interaction

The low tendency of the β-diketonates to bind the polyether side-chain and the β-diketonate to the same metal atom presumably means that the barium complexes, like those of copper, are polymeric rather than monomeric and hence explains their comparative involatility. It also calls into question the nature of $[Ba\{MeC(O)CHC(O)(CH_2)_3OMe\}_2]$ which has been claimed to be monomeric but which does not readily sublime.[17]

Conclusion

We have confirmed that $[Ba(tmhd)_2]\cdot C_{10}H_{22}O_5$ can be sublimed *in vacuo* under STA conditions but is not suitable as a CVD precursor because the tetraglyme readily dissociates. We have synthesised a range of β-diketones with polyether side-chains and co-ordinated them in their anionic form to barium(II) and copper(II). In the isolated state, intermolecular bridging is favoured over intramolecular chelation so that the final products decompose well below their sublimation temperatures. The complexes probably dissociate to monomers or low oligomers in *e.g.* hydrocarbon solvents.

Experimental

Microanalyses were by the University of St. Andrews Materials Analysis Service. The NMR spectra were recorded on a Brüker Associates AM300 or a Varian Associates Gemini 200 MHz spectrometer operating in the Fourier-transform mode with, for ^{13}C, broad-band proton decoupling; UV spectra were recorded on a Philips UV/VIS spectrometer, infrared spectra on a Perkin-Elmer 1710 FTIR spectrometer and STA measurements under nitrogen on a Stanton Redcroft STA1000 analyser with a heating rate of 20 °C min^{-1}. All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-line and catheter-tubing techniques, unless otherwise stated. Toluene and light petroleum b.p. (40–60 °C) were dried by refluxing over

Table 4 Bond lengths (Å) and angles (°) for $[Cu\{PhC(O)CHC(O)(CH_2)_3OCH_2CH_2OMe\}_2]$

Cu(1)–O(1)	1.919(4)	C(9)–C(10)	1.412(8)
Cu(1)–O(11)	1.923(4)	C(10)–O(11)	1.285(7)
O(1)–C(2)	1.287(6)	C(10)–C(12)	1.514(7)
C(2)–C(9)	1.396(8)	C(12)–C(13)	1.504(8)
C(2)–C(3)	1.510(8)	C(13)–C(14)	1.510(7)
C(3)–C(4)	1.397(8)	C(14)–O(15)	1.442(6)
C(3)–C(8)	1.419(7)	O(15)–C(16)	1.408(6)
C(4)–C(5)	1.391(9)	C(16)–C(17)	1.532(9)
C(5)–C(6)	1.400(9)	C(17)–O(18)	1.373(7)
C(6)–C(7)	1.398(8)	C(18)–C(19)	1.406(8)
C(7)–C(8)	1.387(8)	O(18)···Cu(1^{II})	3.065(7)
O(1)–Cu(1)–O(11^{I})	85.9(2)	C(7)–C(8)–C(3)	120.5(5)
O(1)–Cu(1)–O(11)	94.1(2)	C(2)–C(9)–C(10)	124.9(6)
O(1)–Cu(1)–O(18^{III})	95.0(2)	O(11)–C(10)–C(9)	124.2(5)
O(11)–Cu(1)–O(18^{III})	83.4(2)	O(11)–C(10)–C(12)	116.5(5)
O(1)–C(2)–C(9)	125.3(5)	C(9)–C(10)–C(12)	119.3(5)
C(2)–O(1)–Cu(1)	125.3(4)	C(10)–O(11)–Cu(1)	126.1(4)
O(1)–C(2)–C(3)	114.3(5)	C(13)–C(12)–C(10)	113.2(5)
C(9)–C(2)–C(3)	120.4(5)	C(12)–C(13)–C(14)	114.3(5)
C(4)–C(3)–C(8)	118.0(5)	O(15)–C(14)–C(13)	109.1(4)
C(4)–C(3)–C(2)	123.0(5)	C(16)–O(15)–C(14)	112.9(4)
C(8)–C(3)–C(2)	119.0(5)	C(15)–C(16)–C(17)	108.6(5)
C(5)–C(4)–C(3)	121.9(6)	O(18)–C(17)–C(16)	110.3(5)
C(4)–C(5)–C(6)	118.9(6)	C(17)–O(18)–C(19)	115.6(6)
C(7)–C(6)–C(5)	120.5(6)	C(17)–O(18)–Cu(1^{II})	102.3(5)
C(8)–C(7)–C(6)	120.0(5)	C(19)–O(18)–Cu(1^{II})	100.0(4)

Symmetry transformations used to generate equivalent atoms: I $-x + 1, -y, -z$; II $x, y + 1, z$; III $x, y - 1, z$.

sodium diphenylketyl. Ammonia was redistilled immediately before use. Barium hydride was weighed into a degassed flask in a dry-box and sealed before transferring to the Schlenk line. The compounds BaH_2 (Aldrich), $BaBr_2\cdot 2H_2O$ (Fisons), tetraglyme, Htmhd, $Me[O(CH_2)_2]_2Br$, $Me[O(CH_2)_2]_3OH$, $MeC(O)CH_2C(O)R$ (R = Me or Ph) and PBr_3 (all Aldrich) were all reagent grade and used as received; $MeC(O)CH_2C(O)R$ (R = Bu^t[25] or 2,4,6-$Me_3C_6H_2$[26]) and $Me[O(CH_2)_2]_3Br$[27] were prepared by standard literature methods.

$[Ba(tmhd)_2]\cdot C_{10}H_{22}O_5$.—The compound Htmhd (1.84 g, 0.01 mol) was dissolved in aqueous ethanol (20 cm^3, 50%) and treated with sodium hydroxide (0.40 g, 0.01 mol) dissolved in aqueous ethanol (30 cm^3, 50%). To this stirred solution was added $BaBr_2\cdot 2H_2O$ (1.67 g, 0.005 mol) dissolved in aqueous ethanol (25 cm^3, 50%). The solution was stirred for 1 h and then reduced to 66% of its volume under vacuum. Water (30 cm^3) was then added to ensure precipitation of all of the product. The precipitate of '$[Ba(tmhd)_2]$' was then collected and dried *in vacuo*. This material (5.03 g, 0.01 mol) was suspended in dry toluene (60 cm^3) and to the stirred suspension was added tetraglyme (2.22 g, 0.01 mol) dropwise over 15 min. The slightly turbid solution was then filtered and the toluene removed *in vacuo*. The residue appeared to be slightly moist after removal of solvent, a fact we attribute to the presence of unreacted tetraglyme. The solid was then dissolved in warm, dry light petroleum (25 cm^3) and placed in a refrigerator at 5 °C for recrystallisation. A good crop of clear crystals up to 3 mm in length was produced (Found: C, 52.4; H, 8.3. $C_{36}H_{60}BaO_9$ requires C, 52.9; H, 9.0%). Spectroscopically, the sample was identical to that reported by Drake *et al.*[16]

8,11-*Dioxadodecane*-2,4-*dione*.—Sodium (3.77 g, 0.164 mol) cut into small lumps was added to liquid ammonia (400 cm^3) containing iron(III) nitrate (40 mg) to give a grey suspension. Pentane-2,4-dione (9.96 g, 0.1 mol) in diethyl ether (30 cm^3) was added dropwise at 78 °C. After refluxing for 1 h, $MeO(CH_2)_2O(CH_2)_2Br$ (15.8 g, 0.08 mol) in diethyl ether (30 cm^3) was added to give a pale orange solution. The resulting mixture was stirred for 4 h before the ammonia was allowed to evaporate and the resulting cream suspension heated to 40 °C for 5 min. It was then cooled in ice–water for 15 min and treated with a few chips of ice followed by ice (40 g) and concentrated HCl (30 cm^3). The layers were separated and the aqueous solution was extracted with diethyl ether (3 × 100 cm^3). The ether extracts were combined, dried over magnesium sulfate and evaporated to give a brown oil. This was fractionally distilled *in vacuo* to give the product as a colourless oil (b.p. 113–114 °C, 10 Torr). Yield 13.2 g, 55% (Found: C, 58.5; H, 8.35. $C_{10}H_{18}O_4$ requires C, 59.4; H, 9.0%). The following compounds were similarly prepared: 1-phenyl-7,10-dioxaundecane-1,3-dione from Na (3.24 g, 0.14 mol), $PhC(O)CH_2C(O)Me$ (10.7 g, 0.066 mol) and $MeO(CH_2)_2O(CH_2)_2Br$ (11.3 g, 0.061 mol), b.p. 166–168 °C (3.5 Torr), yield 10.50 g (64.5%) (Found: C, 68.3; H, 8.2; $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.6%); 1-(2,4,6-trimethylphenyl)-7,10-dioxaundecane-1,3-dione from Na (2.3 g, 0.1 mol), 2,4,6-$Me_3C_6H_2C(O)CH_2C(O)Me$ (9.26 g, 0.045 mol) and $MeO(CH_2)_2O(CH_2)_2Br$ (8.3 g, 0.045 mol), yield 2.89 g (20.8%) (Found: C, 71.0; H, 8.9. $C_{18}H_{26}O_4$ requires C, 70.6; H, 8.6%); 2,2-dimethyl-9,12-dioxatridecane-3,5-dione from Na (1.58 g, 0.069 mol), $Bu^tC(O)CH_2C(O)Me$ (4.1 g, 0.029 mol) and $MeO(CH_2)_2O(CH_2)_2Br$ (6.2 g, 0.034 mol), b.p. 143–145 °C (10 Torr), yield 4.20 g (59.1%) (Found: C, 63.7; H, 10.4. $C_{13}H_{24}O_4$ requires C, 63.9; H, 9.9%); 8,11,14-trioxapentadecane-2,4-dione from Na (1.7 g, 0.07 mol), pentane-2,4-dione (2.9 g, 0.029 mol) and $Me[O(CH_2)_2]_3Br$ (5.7 g, 0.025 mol), b.p. 139–141 °C (3.5 Torr), yield 4.44 g (62.2%) (Found: C, 59.2; H, 9.5. $C_{12}H_{22}O_5$ requires C, 58.5; H, 9.0%).

Bis(8,11-*dioxadodecane*-2,4-*dionato*)*barium*(II).—8,11-Dioxadodecane-2,4-dione (2.2 g, 0.01 mol) was added to a suspension of BaH_2 (0.71 g, 0.005 mol) in toluene (30 cm^3). On stirring for 16 h the BaH_2 dissolved with evolution of H_2. The resulting solution was filtered several times to remove insoluble impurities and evaporated to dryness. The resulting orange oil was dissolved in CH_2Cl_2 (10 cm^3) and decanted into light petroleum (150 cm^3). The orange solution was evaporated to 30 cm^3 and residual petroleum was decanted from the orange oil formed. The oil was then washed with light petroleum (5 × 10 cm^3) and dried *in vacuo*. Yield 1.17 g, 44% (Found: C, 42.5; H, 6.1. $C_{20}H_{34}BaO_8$ requires C, 44.4; H, 6.3%). The following compounds were similarly prepared from the corresponding β-diketones: bis(1-phenyl-7,10-dioxaundecane-1,3-dionato)barium(II), yield 5.1 g, (81.3%) (Found: C, 55.2; H, 6.0. $C_{30}H_{38}BaO_8$ requires C, 54.3; H, 5.8%); bis[1-(2,4,6-trimethylphenyl)-7,10-dioxaundecane-1,3-dionato]barium(II), yield 0.52 g (74.3%) (Found: C, 59.8; H, 7.2. $C_{36}H_{50}BaO_8$ requires C, 57.8; H, 6.7%); bis(2,2-dimethyl-9,12-dioxatridecane-3,5-dionato)barium(II), yield 2.08 g (81.1%) (Found: C, 49.7; H, 8.2. $C_{26}H_{46}BaO_8$ requires C, 50.0; H, 7.4%); and bis(8,11,14-trioxapentadecane-2,4-dionato)barium(II), yield 0.851 g (72%).

Bis(8,11-*dioxadodecane*-2,4-*dionato*)*copper*(II).—The compound $MeO(CH_2)_2O(CH_2)_3C(O)CH_2C(O)Me$ (2.0 g, 0.008 mol) in ethanol (20 cm^3, 95%) was treated with copper(II) nitrate (1.3 g, 0.005 mol) in water (20 cm^3) in air. A green solution with a cloudy white precipitate formed. Upon addition of ammonia (13 cm^3, 5 mol dm^{-3}, aqueous) a blue precipitate formed. The blue suspension was extracted with diethyl ether (3 × 50 cm^3) and, after drying over $MgSO_4$, the ether was evaporated to leave a blue residue which was recrystallised from the minimum amount of diethyl ether and dried *in vacuo* at 180 °C. Yield 0.83 g, 35.8% (Found: C, 51.8; H, 7.3. $C_{20}H_{34}CuO_8$ requires C, 51.6; H, 7.4%). Bis(1-phenyl-7,10-dioxaundecane-1,3-dionato)copper(II) was prepared similarly from $MeO(CH_2)_2O(CH_2)_3C(O)CH_2C(O)Ph$. Yield 1.65 g (74.4%) (Found: C, 61.1; H, 6.5. $C_{30}H_{38}CuO_8$ requires C, 61.1; H, 6.5%).

Crystallography.—Green platelet crystals were obtained by the slow evaporation of a solution of $[Cu\{PhC(O)CHC(O)(CH_2)_3O(CH_2)_2OMe\}_2]$ in dimethyl sulfoxide. After 4 d sharply defined crystals suitable for X-ray crystallographic studies were produced. Twinning occurred in 50% of them. They were air and moisture stable.

After preliminary photographs, the unit cell was refined and intensity data collected at 150 K from a crystal 0.5 × 0.3 × 0.3 mm, mounted in an oil drop, using the FAST/MADNESS system on an Enraf-Nonius CAD4 diffractometer fitted with an area detector. Data were collected for $2.3 > 2\theta > 26.8°$, covering the ranges $-10 \geqslant h \geqslant 9$, $-13 \geqslant k \geqslant 8$, $-16 \geqslant l \geqslant 14$. 4841 Reflections collected gave 2587 unique reflections but the crystal showed high mosaicity and only 990 reflections (38%) had $I > 4\sigma(I)$. Absorption corrections were not applied. The structure was solved by direct methods (SHELXS 86),[28] which revealed all the non-hydrogen atoms with the Cu atom on a centre of inversion (Wyckoff position 2b). The structure was refined using the SHELXL 93 package.[29] Atomic scattering factors were taken from ref. 30. In the final refinement anisotropic atomic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed on calculated positions (riding model) with isotropic atomic displacement parameters refined for groups of atoms. The terminal OCH_3 group is markedly anisotropic but there is no evidence of disorder at this temperature. At convergence the traditional *R* factor (based on *F*) for 183 refined parameters was 0.0648 for 990 reflections with $I > 4\sigma(I)$ and 0.1246 for all unique data. The weighted *R* factors, using $w = 1/[\sigma^2(F^2) + (0.100P)^2]$, where $P = 0.333\,33(F^2 + 2F_c^2]$, were 0.154 and 0.221 respectively. The goodness of fit, *S*,

Table 5 Atomic coordinates ($\times 10^4$) for [Cu{PhC(O)CHC(O)$(CH_2)_3OCH_2CH_2OMe\}_2$]

Atom	*x*	*y*	*z*
Cu(1)	5000	0	0
O(1)	3348(5)	236(3)	−1086(3)
C(2)	2528(6)	1184(5)	−1257(4)
C(3)	1379(6)	1168(5)	−2200(4)
C(4)	497(8)	2160(6)	−2563(4)
C(5)	−566(9)	2121(6)	−3429(4)
C(6)	−747(7)	1058(6)	−3954(4)
C(7)	163(7)	67(5)	−3630(4)
C(8)	1219(7)	118(5)	−2765(4)
C(9)	2629(7)	2165(5)	−649(4)
C(10)	3696(7)	2288(5)	229(4)
O(11)	4711(5)	1506(3)	573(3)
C(12)	3638(6)	3382(5)	836(4)
C(13)	5132(7)	4015(5)	1136(4)
C(14)	5093(7)	5130(5)	1718(4)
O(15)	4037(4)	5967(3)	1166(3)
C(16)	4026(8)	7074(5)	1626(4)
C(17)	2819(9)	7871(6)	1003(5)
O(18)	3035(6)	9041(4)	1288(4)
C(19)	1768(9)	9791(6)	1008(7)

was 0.554. Molecular graphics were prepared using PLATON 92[31] and 93.[32]

Bond lengths and angles are collected in Table 4 with atomic coordinates in Table 5.

Crystal data. $C_{30}H_{38}CuO_8$, $M_r = 590.14$, monoclinic, space group $P2_1/c$, $a = 9.109(9)$, $b = 11.189(8)$, $c = 14.453(6)$ Å, $\beta = 103.64(9)°$, $U = 1432(2)$ Å^3, $Z = 2$, $D_c = 1.369$ Mg m^{-3}, λ(Mo-Kα) = 0.710 69 Å, $\mu = 0.812$ mm^{-1}, $F(000) = 622$, $T = 150(2)$ K. Maximum and minimum residual electron densities were 0.86 and -0.29 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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