ORIGINAL ARTICLE

Liquid–liquid extraction studies with 4,4′-biphenylene-spaced bis-β-diketones

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Abstract 4,4′-biphenylene spaced lipophilic bis-β-diketone ligands of the type 4,4′-bis(RC(O)CH$_2$C(O))C$_{12}$H$_8$ (R = Pr, Ph, hexyl, octyl, nonyl) have been prepared and used for the liquid–liquid extraction of d-block metal ions. These ligands are expected to interact with divalent metal ions to form charge-neutral trinuclear metallocycles of type [M$_3$(**L^3**)$_3$(solvent)] as has been demonstrated with the previously reported derivative of H$_2$**L^3** (R = ^{t}Bu), the X-ray structure of which is reported. Liquid–liquid extraction studies were performed in a two-phase water/chloroform system employing a radiotracer technique for cobalt(II) and zinc(II). These experiments involved the systematic variation of ligand, metal and 4-ethylpyridine concentrations to probe the stoichiometries of the species extracted. Synergistic extraction was observed when 4-ethylpyridine was present with the ligand in the organic phase. Competitive extraction studies demonstrated the ligands are highly selective for copper(II) over cobalt(II), nickel(II), zinc(II) and cadmium(II).

Dedicated to Mrs Fay Lindoy on the occasion of Len's 75th birthday.

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Introduction

The rich array of interesting metal ion coordination chemistry of the versatile β-diketone chelating group has now been studied for well more than a century [1–6]. There has been significant recent interest in the metallo-supramolecular chemistry of these systems [7–11] particularly where more than one β-diketone group have been incorporated into extended ligand structures [12–50]. In part motivated by the above studies, we [19, 51–60], and others [61–65], have recently employed a series of bis-β-diketone ligands of type H$_2$**L^1**, H$_2$**L^2**, H$_2$**L^3** and H$_2$**L^4** and their derivatives[66] to form discrete charge-neutral materials upon interaction with suitable metal ions such as cobalt(II), nickel(II), copper(II), zinc(II), iron(III) and gallium(III).

H₂**L**¹

H₂**L**²

H₂**L**³

H₂**L**⁴
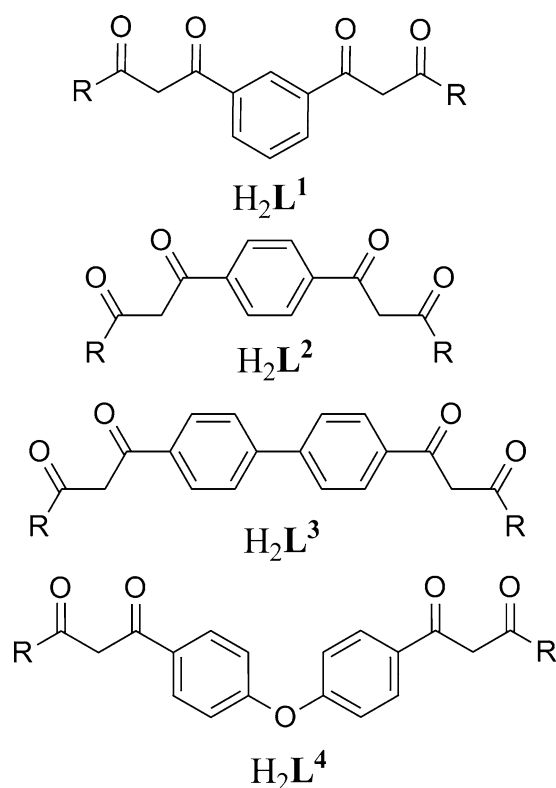
R = Me, Et, Pr, ^{t}Bu, Ph, hexyl, octyl, nonyl

The well-defined coordination vectors of the doubly deprotonated forms of H₂**L**$^{1–4}$ lead to the formation of a variety of multinuclear species. For example, with divalent metal ions these include both planar dinuclear metallocycles of type [M₂(**L**¹)₂(solvent)] [52, 54, 55, 57], as well as planar triangular molecules of type [M₃(**L**$^{2–3}$)₃(solvent)] [51, 53, 56, 58]. With trivalent metal ions dinuclear triple helical complexes of type [M₂(**L**¹)₃] [52, 55] and [M₂(**L**⁴)₃], tetrahedra of type [M₄(**L**$^{2–3}$)₆] [51, 56, 60] and the unprecedented [M₈(**L**⁴)₁₂] universal 3-ravel motif result [59].

[M₂(**L**¹)₂]

[M₃(**L**²)₃]

[M₃(**L**³)₃]
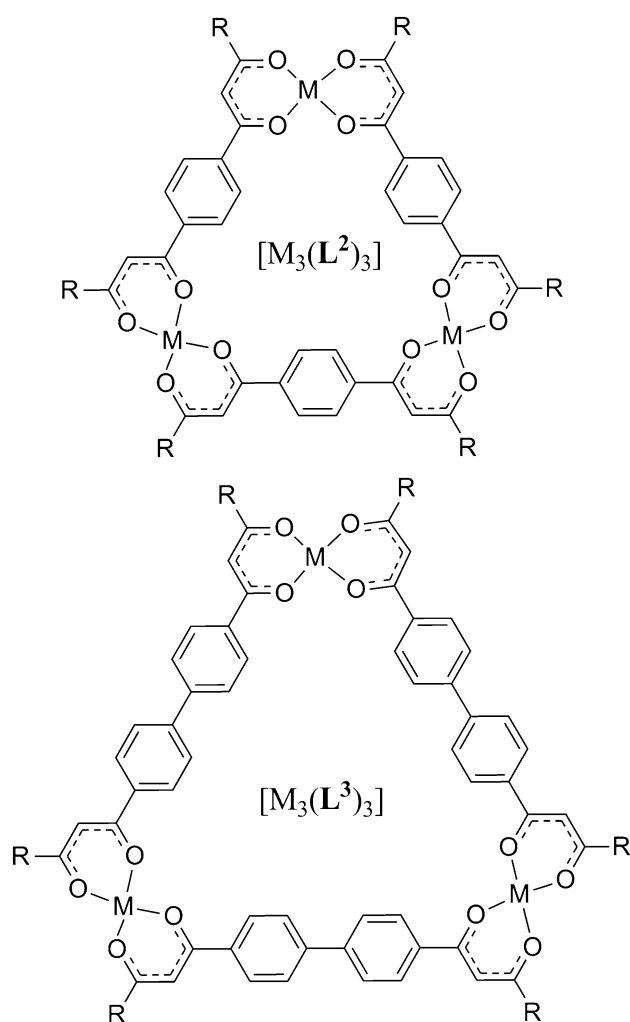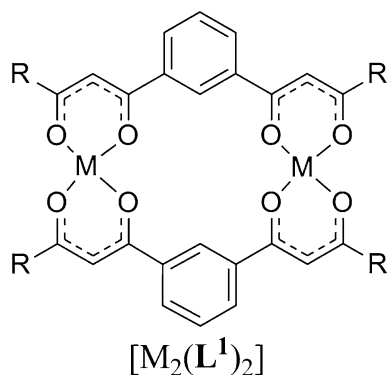
R = Me, Et, Pr, ^{t}Bu, Ph, hexyl, octyl, nonyl

In previous investigations it has been demonstrated that the metal centres in the copper(II) complexes of **L**$^{1–3}$ ([Cu₂(**L**¹)₂], [Cu₃(**L**²)₃] and [Cu₃(**L**³)₃]) are either coordinatively unsaturated or are weakly bound by axial solvent molecules which can be readily displaced by the reaction of an ancillary nitrogen donor ligand such as pyridine. This allows for the essentially planar metallocycles to be employed as essentially planar platform-like building blocks for the facile formation of extended discrete multinuclear architectures and one-, two- and three-dimensional metal–organic framework materials, when reacted with appropriate di- (or higher) functional heterocyclic nitrogen ligands.

In extensions of these studies we investigated the liquid–liquid extraction behaviour of H₂**L**¹ and H₂**L**² and noted both a strong synergistic effect in the extraction of cobalt(II) and zinc(II) when ethylpyridine (EtPy) was added to the bis-β-diketone ligand in the organic phase and strong

competitive discrimination in extraction in favour of copper(II) over cobalt(II), nickel(II) zinc(II) and cadmium(II). Further to those reports, herein we present the synthesis of four new expanded ligands of type H_2L^3 (R = Pr, hexyl, octyl, nonyl) and the liquid–liquid extraction properties of this class of ligands including the two previously reported ligands (R = ^tBu, Ph) [58, 60, 67].

Experimental

All reagents and solvents were purchased from commercial sources and used without further purification. THF was pre-dried over sodium wire before use. NMR spectra were recorded on Bruker Avance DPX200, DPX300 or DPX400 spectrometers; δ^H values are relative to Me_4Si at 0 ppm. Low resolution electrospray ionisation mass spectra (ESI–MS) were obtained on a Finnigan LCQ-8 spectrometer. FTIR (KBr) spectra were collected using a Bio-Rad FTS-40 spectrometer. Microanalyses were carried out by the Microanalytical Laboratories at the University of Otago, NZ.

Ligand synthesis

Ligand H_2L^3 (R = ^tBu) was prepared as previously reported [58, 60]. Ligands H_2L^3 (R = Pr, Ph, hexyl, octyl, nonyl) were prepared via an adaptation of that procedure.

Sodium hydride (5.0 g, 0.21 mol) was added to a mixture of dimethyl biphenyl-4,4′-dicarboxylate (6.76 g, 0.025 mol) and pentan-2-one (4.3 g, 0.05 mol) (R = Pr), or acetophenone (6 g, 0.05 mol) (R = Ph), or 2-octanone (6.4 g, 0.05 mol) (R = hexyl), or 2-decanone (7.8 g, 0.05 mol) (R = octyl), or 2-undecanone (8.5 g, 0.05 mol) (R = nonyl) in dry tetrahydrofuran (100 mL) at 0 °C. The mixture was stirred for 2 h at this temperature and then for 2 h at 26 °C over which time the mixture turned yellow. The reaction solution was quenched with ice water (100 mL) and then acidified to pH 4 using 1 M hydrochloric acid; two phases formed. The organic phase (tetrahydrofuran) was separated from the aqueous phase. The aqueous phase was washed twice with chloroform (100 mL), the organic phases were combined and the solvent was removed under reduced pressure to yield the crude product. This was recrystallised from ethanol.

1,1′-(4,4′-Biphenylene)-bis-hexane-1,3-dione, H_2L^3(R = Pr)

Yield 5.21 g (55%), yellow plates.
^{1}H-NMR δ (200 MHz CDCl$_3$): 16.68 (broad s, enol, 2H), 7.99 (d, aromatic, 4H), 7.72 (d, aromatic, 4H), 6.35 (s, –CH– enol, 2H), 2.37(t, –CH$_2$–, 4H), 1.65 (qu, –CH$_2$–, 4H), 0.94 ppm (t, –CH$_3$, 6H). (ESI–MS): m/z 379 [M + H]$^+$. FTIR (KBr): 2963(br), 1617(vbr), 1270, 825, 786 cm^{-1}. Found: C, 76.07; H, 6.76%. Calc. for C$_{24}$H$_{26}$O$_4$: C, 76.17; H, 6.93%.

1,1′-(4,4′-Biphenylene)-bis-3-phenylpropane-1,3-dione, H_2L^3(R = Ph)

Yield 7.25 g (65%), yellow plates.
^{1}H NMR δ(200 MHz CDCl$_3$): 16.50 (broad s, enol, 2H),), 7.99 (d, aromatic, 4H), 7.72 (d, aromatic, 4H), 7.63 (m, –Ph, 10H), 6.35 (s, –CH– enol, 2H). (ESI–MS): m/z 447 [M + H]$^+$. FTIR (KBr): 3010(br), 1560(vbr), 1113, 840, 761 cm^{-1}. Found: C, 78.54; H, 5.31%. Calc. for C$_{30}$H$_{22}$O$_4$·0.75(CH$_3$OH): C, 78.48; H, 5.36%.

1,1′-(4,4′-Biphenylene)-bis-nonane-1,3-dione, H_2L^3 (R = hexyl)

Yield 8.66 g (75%), yellow plates.
^{1}H-NMR δ (200 MHz CDCl$_3$): 16.10 (broad s, enol, 2H), 7.99 (d, aromatic, 4H), 7.72 (d, aromatic, 4H), 6.35 (s, –CH– enol, 2H), 2.45 (br m, –CH$_2$–, 4H), 1.70 (br m, –CH$_2$–, 4H), 1.34 (br m, –CH$_2$–, 12H), 0.90 ppm (br m, –CH$_3$, 6H). (ESI–MS): m/z 463 [M + H]$^+$. FTIR (KBr): 2952(br), 1635(vbr), 1322, 1134, 1078, 804, 778 cm^{-1}. Found: C, 78.10; H, 8.22%. Calc. for C$_{30}$H$_{38}$O$_4$: C, 77.89; H, 8.28%.

1,1′-(4,4′-Biphenylene)-bis-undecane-1,3-dione, H_2L^3 (R = octyl)

Yield 8.03 g (62%), yellow plates.
^{1}H NMR δ(200 MHz CDCl$_3$): 16.07 (broad s, enol, 2H), 7.99 (d, aromatic, 4H), 7.72 (d, aromatic, 4H), 6.32 (s, –CH– enol, 2H), 2.44 (br m, –CH$_2$–, 4H), 1.70 (br m, –CH$_2$–, 4H), 1.34 (br m, –CH$_2$–, 20H), 0.89 ppm (br m, –CH$_3$, 6H).) (ESI–MS): m/z 519 [M + H]$^+$. FTIR (KBr): 2932(br), 1616(vbr), 1271, 1137, 1081, 802, 778, 720 cm^{-1}. Found: C, 78.91; H, 8.80%. Calc. for C$_{34}$H$_{46}$O$_4$: C, 78.71; H, 8.94%.

1,1′-(4,4′-Biphenylene)-bis-dodecane-1,3-dione, H_2L^3 (R = nonyl)

Yield 8.19 g (60%), yellow plates.
^{1}H-NMR δ (200 MHz CDCl$_3$): 16.30 (broad s, enol, 2H), 7.99 (d, aromatic, 4H), 7.72 (d, aromatic, 4H), 6.33 (s, –CH– enol, 2H), 2.46 (br m, –CH$_2$–, 4H), 1.71(br m, –CH$_2$–, 4H), 1.33 (br m, –CH$_2$–, 24H), 0.88 ppm (br m, –CH$_3$, 6H). (ESI–MS): m/z 547 [M + H]$^+$. FTIR (KBr): 2928(br), 1635(vbr), 1322, 1081, 786 cm^{-1}. Found: C, 78.84; H, 8.95%. Calc. for C$_{36}$H$_{50}$O$_4$: C, 79.07; H, 9.22%.

Liquid–liquid extraction experiments

Liquid–liquid extraction experiments were performed at 24 ± 1 °C in microcentrifuge tubes (2 mL) with a phase ratio $V_{(org)}$:$V_{(aq)}$ of 1:1 (500 μL each). The aqueous phase contained the metal perchlorate (normally 1×10^{-4} M, except where variable concentration experiments were employed), and a selected buffer. The zwitterionic buffer systems, TAPS/NaOH, HEPES/NaOH and MES/NaOH, were used (depending on the chosen pH) to maintain the pH in this phase; as a precaution, the pH of this phase was checked before and after each experiment. A majority of the experiments were carried out at pH 8.7 using the TAPS/NaOH system. The chloroform organic phase contained a known concentration of a H_2L^3 ligand (normally 1×10^{-3} M, except where variable concentration experiments were employed) and in some experiments also 4-ethylpyridine (normally 2×10^{-3} M except where variable concentration experiments were conducted). All solvent extraction experiments involved the mechanical shaking of the two-phase system until equilibrium had been established. The overall error for individual extractions is estimated to be approximately $\pm 5\%$.

In the case of the single metal ion experiments a shaking time of three hours was used for the cobalt(II) experiments and 30 min for the zinc(II) experiments. At the end of these times, the phases were separated, centrifuged and then duplicate 100 μL samples of the aqueous and organic phases were removed for analysis. The concentration of the cobalt or zinc was measured in both phases radiometrically using ^{60}Co and ^{65}Zn radioisotopes (ROTOP Pharmaka) by means of a NaI (TI) scintillation counter (Cobra II/Canberra-Packard) [68, 69].

The competitive (multi-metal) extraction experiments employed a shaking time of 24 h. For these experiments the depletion of the metal ion concentrations in the aqueous phase was measured using an ICP-MS (ELAN 9000/Perkin Elmer) spectrometer.

Three sets of variable concentration experiments were also undertaken. Ligand dependence studies were performed in which the concentration of H_2L^3 (R = ^{t}Bu, nonyl) was varied from 5×10^{-4} to 1.5×10^{-3} M while the zinc(II) concentration was maintained at 1×10^{-4} M. Similar experiments were carried out in the presence of 4-ethylpyridine (2×10^{-3} M) for both cobalt(II) and zinc(II). In each case $\log D_M$ was plotted against $\log [H_2L^3]_{org}$ and the slope determined.

4-Ethylpyridine dependence studies were also carried out. These involved varying the 4-ethylpyridine concentration from 2×10^{-4} to 2×10^{-3} M while maintaining the metal ion concentration at 1×10^{-4} M and the ligand concentration at 1×10^{-3} M. Log D_M was then plotted against $\log [4\text{-ethylpyridine}]_{org}$ and the slope determined.

A series of experiments were also performed in which the metal ion concentration was varied from 1×10^{-4} to 5×10^{-3} M at pH 8.7 (TAPS/NaOH), both in the absence and presence of 4-ethylpyridine (2×10^{-3} M), while maintaining the ligand concentration at 1×10^{-3} M. From the observed maximum metal loading of the organic phase, the stoichiometry of the extracted complex can be deduced [70].

Multi-metal competitive extraction experiments were also performed using an equimolar mixture of the following metal ions in the aqueous phase: cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) at pH 7.8 in the absence of 4-ethylpyridine in the organic phase or at pH 7.4 (HEPES/NaOH buffer) in its presence. The aqueous phase contained each of the above metal perchlorate salts at a concentration of 1×10^{-4} M and the organic phase (chloroform) contained a 1×10^{-3} M concentration of H_2L^3 and in the second set of experiments also 4-ethylpyridine at 2×10^{-3} M.

X-ray structure determination

Data for H_2L^3 (R = ^{t}Bu) were collected on a NoniusKappa CCD employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å) with φ and ω scans to approximately 56°2θ at 293(2) K. Data collections were undertaken with COLLECT, [71] cell refinement with Dirax/lsq [72], data reduction with EvalCCD [73]. Subsequent computations were carried out using the WinGX-32 graphical user interface [74]. The Structure were solved by direct methods using SIR97 [75]. A Multi-scan empirical absorption correction was applied to data sets using the program SADABS [76]. Data were refined and extended with SHELXL-97 [77]. All non-hydrogen atoms were refined anisotropically. Oxygen-bound hydrogen atoms were first located in the difference Fourier map before refinement. Carbon and oxygen-bound hydrogen atoms were included in idealised positions and refined using a riding model.

Formula $C_{26}H_{30}O_4$, M 406.50, monoclinic, space group $P2_1/c(\#14)$, a 18.792(1), b 5.7140(2), c 10.551(1) Å, β 102.721(3), V 1105.13(13) Å^3, D_c 1.222 g cm^{-3}, Z 2, crystal size 0.43 by 0.41 by 0.12 mm, colour colourless, habit plate, temperature 293(2) K, λ(MoKα) 0.71073 Å, μ(MoKα) 0.081 mm^{-1}, T(SADABS)$_{min,max}$ 0.9660, 0.9903, $2\theta_{max}$ 50.82, hkl range -22 22, -6 6, -12 12, N 13064, N_{ind} 2025(R_{merge} 0.0375), N_{obs} 1424 (I > 2σ(I)), N_{var} 141, residuals * $R1(F)$ 0.0415, $wR2(F^2)$ 0.1118, GoF(all) 1.034, $\Delta\rho_{min,max}$ -0.190, 0.155 e$^-$ Å^{-3}.

$^*R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = \left(\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2\right)^{1/2}$ all reflections

$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.2224P]$ where $P = (F_o^2 + 2F_c^2)/3$

Results and Discussion

Ligand synthesis and X-ray structure of H$_2$L^3 (R = ^{t}Bu)

Ligands of type H$_2$L^3 were synthesised in good yields by employing a Claisen condensation from bis-methyl ester and 2-ketone starting materials in the presence of sodium hydride following an adaptation of literature procedures for related compounds [21, 51, 52, 58, 60, 67, 78–80]. The broad peak present above 16 ppm integrating to two protons in each of the ^{1}H NMR spectra of the H$_2$L^3 (R = Pr, ^{t}Bu, Ph, hexyl, octyl, nonyl) ligands indicated that these compounds exist almost entirely in their bis-enol tautomeric form in deuterochloroform solution. This is supported by the presence of a sharp singlet at ∼6.3 ppm which corresponds to Hγ. The solid state infrared spectra also suggest the presence of hydrogen bonded hydroxy and carbonyl groups (peaks at ∼1600 cm^{-1} and ∼3000 cm^{-1}) [81]; intramolecular hydrogen bonding in the enol form of β-diketone fragments stabilises them with respect to their keto tautomers [82]. These observations are consistent with those made for ligands of type H$_2$L^1, H$_2$L^2 and H$_2$L^4. [44, 51, 52, 55, 56, 59, 63, 64] In contrast to these systems, numerous simple β-diketones [83] and a number of bis- and tris-β-diketone ligands have been reported in which the β-diketone groups have been shown to exist as a mixture of both keto and enol forms in solution [41, 42, 45, 46]. In the solid state, however, a number of tris-β-diketone ligands have been shown by X-ray crystallography to exist either exclusively in their tris-diketo [46] or tris-enol [47] forms, while at least in one case, a bis-β-diketone ligand has been shown to occur in a mixed form (one diketo group and one enol/keto arrangement) in the solid state [45]. Crystal structures of H$_2$L$^{1−2}$ on the other hand, suggest that they are present exclusively in the enol form in the solid state [52, 56, 63].

In this context it was of interest to confirm what configuration the present ligands of type H$_2$L^3 adopt in the solid state. Small colourless plate-like crystals of H$_2$L^3 (R = ^{t}Bu) were grown from the slow evaporation of a tetrahydrofuran solution and the structure was determined (Fig. 1). Like the structure of H$_2$L^2 (R = ^{t}Bu) previously reported [56], this structure contains crystallographic inversion symmetry such that half the molecule lies within the asymmetric unit. The structure reveals that, as occurs in solution, the bis-enol form exists in the crystalline phase with the enol hydrogens disordered over two positions and exist with 50% occupancy on both (adjacent) oxygens. The expected intramolecular hydrogen bonds are present between each pair of adjacent oxygen atoms (O(1)⋯O(2) = 2.4636(15) Å; O(1)–H(1)–(O2) angle 150.6°).

The ligand exists in its idealised *trans* configuration with the two β-diketone fragments orientated such that their chelation vectors aligned approximately 180° with respect to each other. The molecule is essentially planar, reflecting the sp^2 hybridisation of the ligand backbone and the presence of weak CH(phenylene) to oxygen interactions (C(9)H⋯O(2) = 2.4 Å). There are a variety of weak edge-to-face π–π interactions present in the lattice between the biphenylene units in adjacent molecules. These are reflected by CH–C distances of ∼3.0 Å. These interactions may contribute to reducing the electron withdrawing effects of the phenyl rings and assist the delocalisation of the enol hydrogen bond.

Liquid–liquid extraction studies

Simple β-diketones have been previously employed as extractants in a variety of liquid–liquid extraction experiments including mineral processing applications [85, 86], however, there appear to be no reports of the use of bis-β-diketone ligands of the present type for similar studies, despite them being known for some time [78], their relative ease of synthesis in good yields and low cost starting materials. We recently reported that both the 1,3- and 1,4-phenylene bridged ligands of type H$_2$L^1 and H$_2$L^2

Fig. 1 ORTEP [84] representation of the structure of H$_2$L^3 (R = ^{t}Bu) shown with 50% probability ellipsoids. Only one enol hydrogen position shown. Symmetry code for generating equivalent atoms: −x, 1 − y, −z
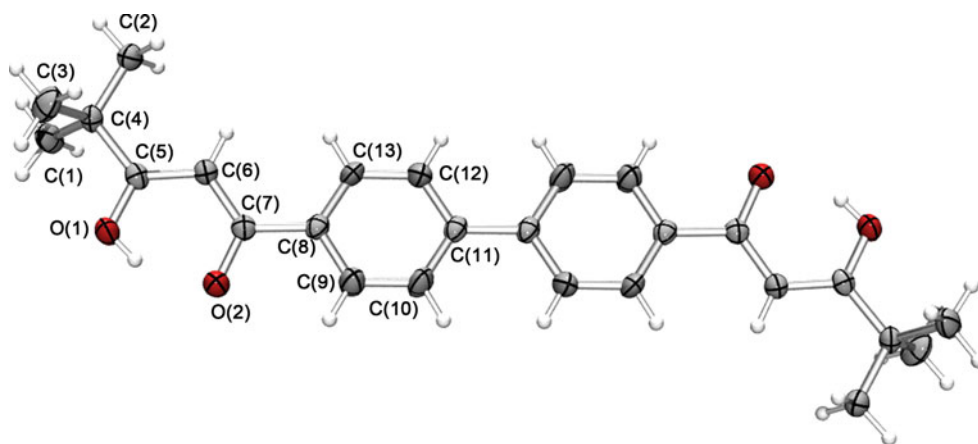
synergistically extract a variety of metal ions in the presence of 4-ethylpyridine (EtPy) and displayed a strong preference for the selection of copper(II) in competitive extractions [55, 56, 87]. It was therefore of interest to explore the liquid–liquid extraction behaviour of the expanded 4,4′-biphenylene ligands of type H_2L^3.

Extraction experiments at constant metal and ligand concentration

The extraction behaviour of H_2L^3 (R = Pr, Ph, ^tBu, hexyl, octyl and nonyl) was studied using the previously described radiotracer technique [68, 69] employing cobalt(II) and zinc(II). Extraction experiments were performed in parallel both in the absence and presence of 4-ethylpyridine; the results are summarised in Fig. 2. 4-Ethylpyridine was used as it is both more lipophilic and less water soluble than pyridine. At pH 8.7 in the absence of 4-ethylpyridine, cobalt(II) extraction is insignificant (≤1%) for the ligand series, while extraction is more pronounced for zinc(II) (ranging from 2 to 31%). As expected, the more lipophilic ligand derivatives clearly give rise to enhanced extraction.

Repeating the experiments with the addition of two equivalents of 4-ethylpyridine relative to H_2L^3 (2 × 10^{-3} M) the extraction of cobalt(II) slightly increased to 8% in the case of H_2L^3 (R = nonyl) and also increased from 31 to 51% for zinc(II) with H_2L^3 (R = nonyl). The time required to reach equilibrium in the case of cobalt(II) was also approximately halved (from three to one and a half hours) and the synergistic effect is more pronounced for the nonyl derivative, especially in the case of cobalt(II). Parallel

'control' experiments in the absence H_2L^3 but at the same concentration of 4-ethylpyridine were performed; under these conditions metal extraction was negligible at ≤1%.

Both in the presence and absence of 4-ethylpyridine, these systems show no significant extraction of metal below approximately pH 6 and thus the extracted metal may be stripped by pH adjustment of the aqueous phase to below this pH.

Clearly the enhancement of extraction in the presence of 4-ethylpyridine is significant for both zinc(II) and cobalt(II) for H_2L^3 (R = hexyl, octyl, nonyl); however, under identical experimental conditions more pronounced increases in extraction were observed for H_2L^{1-2}. In the case of H_2L^1 (R = nonyl) an increase from 12 to 70% was observed for cobalt(II) while the increase for zinc was 53 to 85% [55] and in the case of H_2L^2 (R = nonyl) the increase in extraction was from 2 to 26% for cobalt(II) and from 35 to 61% for zinc(II) [56].

H_2L^3 dependence studies

The stoichiometries of the extracted species were analysed by undertaking the extraction of cobalt(II) and zinc(II) (at 1 × 10^{-4} M) under variable H_2L^3 (R = nonyl) concentration in the presence of a fixed concentration (2 × 10^{-3} M) of 4-ethylpyridine as well as in its absence. For the extractions involving zinc(II) and H_2L^3 (R = ^tBu, hexyl, octyl, nonyl) in all cases the concentration of the H_2L^3 was varied from 5 × 10^{-4} to 1.5 × 10^{-3} M (namely, it was always in excess relative to the metal ion concentration in an attempt to approximate constant ionic strength
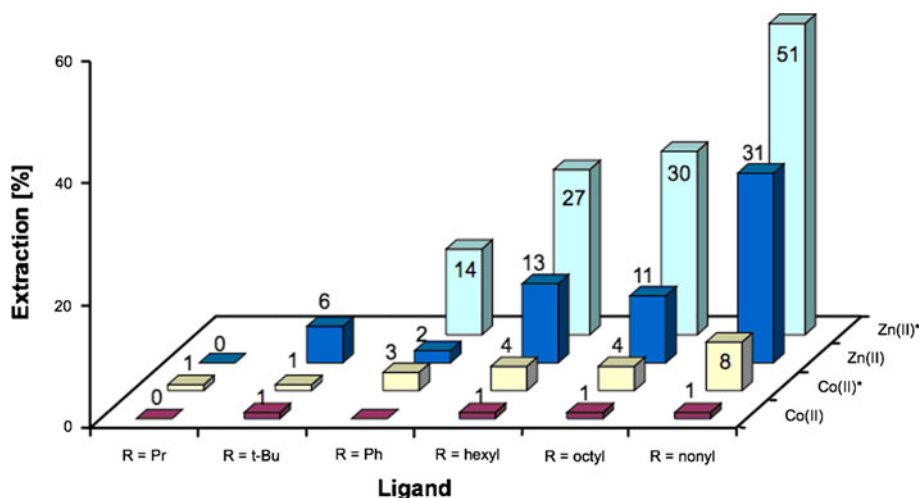

Fig. 2 Percentage of metal ion extracted from the aqueous into the organic phase by H_2L^3 (R = Pr, ^tBu, Ph, hexyl, octyl and nonyl), and on the addition of 4-ethylpyridine (*). [M(ClO$_4$)$_2$] = 1 × 10^{-4} M, pH 8.7 (TAPS/NaOH buffer); [H_2L^3] = 1 × 10^{-3} M, [4-ethylpyridine] = 2 × 10^{-3} M in CHCl$_3$ (*); shaking time 30 min for zinc(II), 3 h for cobalt(II) or 1.5 h (when 4-ethylpyridine was added);

T = 24 ± 1 °C. Attempts to obtain data for zinc(II) with H_2L^3 (R = Pr and Ph) in the presence of 4-ethylpyridine were unsuccessful due to precipitation at the respective aqueous/organic interfaces. Values of less than 1% have high uncertainty and may lie within experimental error of zero

Table 1 Gradients of the plots obtained for the variable H_2L^3 and 4-ethylpyridine (EtPy) (water–chloroform) studies

Experiment	H_2L^3 Ligand	Slope		
		Zn(II)/H_2L^3	Zn(II)/H_2L^3 + EtPy	Co(II)/H_2L^3 + EtPy
H_2L^3 dependence	R = t-Bu	1.7	N/A	N/A
	R = hexyl	2.0	N/A	N/A
	R = octyl	2.0	N/A	N/A
	R = nonyl	1.9	1.7	2.0
4-ethylpyridine dependence	R = nonyl	N/A	0.7	0.8

conditions) [69]. The negligible extraction observed for cobalt(II) in the absence of 4-ethylpyridine (Fig. 2) across all H_2L^3 ligands prevented investigation of this system over the above concentration range.

For each of the above experiments, log D_M (D_M = $[M^{n+}]_{(org)}/[M^{n+}]_{(aq)}$) was plotted against log $[H_2L^3]$. Provided a 'simple' equilibrium is involved, the slope of this plot gives the stoichiometry (n) of the extracted species directly since log D_M = n log$[L]_{org}$ + K_{ex} (where K_{ex} is the extraction constant) [69, 88, 89]. The results for both cobalt(II) and zinc(II) with H_2L^3 at pH 8.7 in both the absence and presence of 4-ethylpyridine show that linear relationships occur between log D_M and the log $[H_2L^3]$ in each case. For the present ligand series, slopes that range from 1.7 to 2.0 were obtained (Table 1), suggesting that, like H_2L^2, but unlike H_2L^1 (in which a mixture of products was observed to form), predominantly 1:2 (M:L) species are extracted under the conditions employed.

4-Ethylpyridine dependence studies

These involved variation of the 4-ethylpyridine concentration over the range 2×10^{-4}–2×10^{-3} M while the other concentrations were held constant. In the case of H_2L^3 (R = nonyl) with both cobalt(II) and zinc(II), a metal: 4-ethylpyridine ratio of approximately 0.8 was obtained (Table 1). This suggests that, under the conditions employed, the predominant species extracted has one 4-ethylpyridine coordinated per metal centre.

Variable metal concentration studies

A further procedure for probing the stoichiometry of the extracted species has been undertaken as part of the present study. This method is based on a defined complex being generated in the organic phase under 'saturation' conditions—corresponding to a constant ligand concentration in the presence of excess metal ion [70]. H_2L^3 (R = nonyl) at a concentration of 1×10^{-3} M was employed in the chloroform phase. In the case of zinc the [metal]/[ligand] ratio of the extracted species was probed by incrementally increasing the zinc concentration in the aqueous phase

from 1×10^{-4} to 5×10^{-3} M (at pH 8.7) while the degree of zinc extracted into the chloroform phase was monitored. The inflection in the corresponding plot obtained from this experiment provides an indication of the maximum zinc to ligand ratio for complex formation. The conditions employed for these studies are thus somewhat different to those used for the extraction experiments discussed above.

The results for the variable metal concentration studies are summarised in Table 2 and show that, like the studies for the H_2L^1 and H_2L^2 ligand series under the conditions employed, an equimolar ratio (metal:ligand = 1:1) is indicated for zinc(II) in the absence of added 4-ethylpyridine. This ratio is comparable to that present in the X-ray crystal structure of $[Co_3(L^3)_3Py_6]\cdot5.55Py\cdot0.6H_2O$ (R = ^tBu) [58] and suggests that the structures in solution may be of a similar type ($[M_3(L^3)_3]$) under the experimental conditions employed.

Further variable metal concentration loading experiments were undertaken in which the solution stoichiometries of the cobalt(II) and zinc(II) systems with H_2L^3 (R = nonyl) were probed under similar conditions, but this time in the presence of a fixed concentration of 4-ethylpyridine of 2×10^{-3} M. The presence of 4-ethylpyridine causes a major change in the species being extracted, leading to ratios that approximate the formation of ML_2 (M = Co, Zn) derivatives. From these experiments, two types of extracted complexes of the H_2L^3 ligand series can be proposed to form under the saturation conditions discussed above. As in the case of the H_2L^2 series, in the absence of 4-ethylpyridine only a 1:1 (metal:ligand) complex (most likely of type $[M_3(L^3)_3]$) occurs while in the presence of 4-ethylpyridine the dominant complex in each

Table 2 Maximum metal:ligand ratios for the organic phases obtained from loading experiments involving a fixed concentration of H_2L^3 (R = nonyl) and varying metal ion concentration

Ligand H_2L^3	Metal: ligand ratio		
	Zn(II)/ H_2L^3	Zn(II)/ H_2L^3 + EtPy	Co(II)/ H_2L^3 + EtPy
R = nonyl	1.0	0.6	0.6

case corresponds to a 1:2 (metal:ligand) species (most likely of type [M(**L**^{3})$_2$(EtPy)]). These results are in general accord with those obtained in the ligand dependence studies where, under different conditions, it is likely that 1:2 (metal:ligand) species exist in both the presence and absence of added 4-ethylpyridine.

Summary of extracted complex species

As might be expected, the results of the solvent extraction experiments for H$_2$**L**^{3} parallel those obtained with H$_2$**L**^{2} in which two complex species were formed in the respective organic phases [56], with the mix of species depending on the conditions employed. In the absence of 4-ethylpyridine with an excess of H$_2$**L**^{3} ligand a 1:2 (metal:ligand) complex forms, while in the presence of excess metal ion, complexes of stoichiometry 1:1 (3:3) (metal:ligand) are postulated to occur. In the presence of 4-ethylpyridine a 1:2:1 (metal:ligand: 4-ethylpyridine) complex appears to be the dominant (perhaps only) extracted species in all cases. These conclusions are illustrated graphically in Scheme 1.
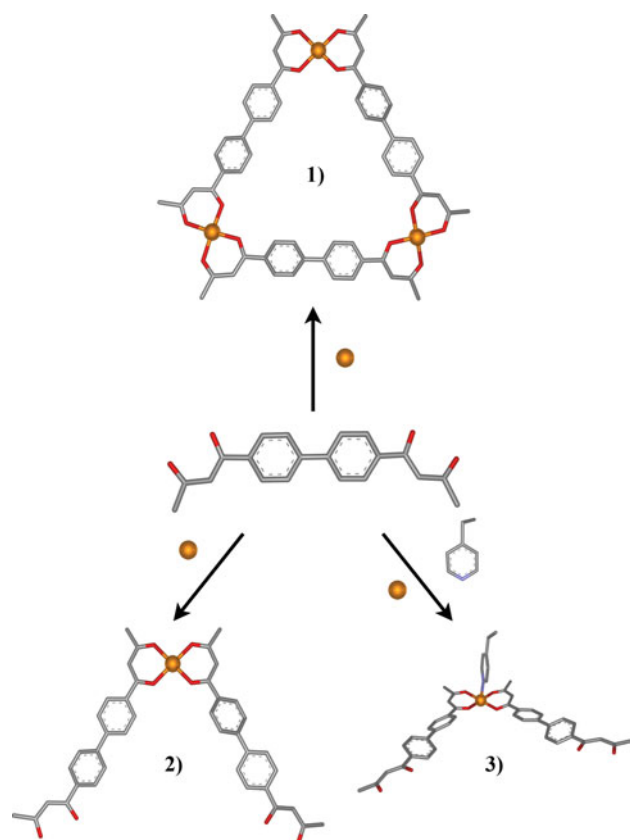
Scheme 1 Proposed complex species formed in the liquid–liquid extraction studies with H$_2$**L**^{3}: (1) with excess metal in the aqueous phase (in the absence of EtPy); (2) with excess of ligand in the organic phase (in the absence of EtPy); (3) in presence of EtPy under conditions used for either (1) or (2) being employed

Competitive extractions

In order to explore the metal ion selectivities of these ligands, competitive extraction experiments were carried out at pH 7.4 (HEPES/NaOH) in the absence of 4-ethylpyridine for the ligands H$_2$**L**^{3} (R = ^{t}Bu, hexyl, octyl and nonyl). Equal concentrations of five different divalent transition metal perchlorate salts (cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), each 1×10^{-4} M) were added to the aqueous phase and H$_2$**L**^{3} (R = ^{t}Bu, hexyl, octyl or nonyl) at 1×10^{-3} M were added to the organic phase. The phases were combined and shaken for 24 h before the metal ion concentrations were determined by ICP-MS. A marked selectivity for copper(II) over the other four divalent transition metal ions present was obtained (Fig. 3). Within experimental error, nearly quantitative (>95%) extraction of copper ion occurred in each case, with practically no extraction occurring for the remaining four metals.

Similar competitive extraction experiments were carried out in the presence of 4-ethylpyridine (2×10^{-3} M) at pH 7.4 but otherwise the conditions were identical to those used in the above studies. The results again show a high selectivity for copper(II) (100% extraction), while the extraction of the other metal ions is negligible ($\leq$4%) (Fig. 3). For each of the systems investigated, the selectivity for copper(II) is most pronounced in the present case compared to the results obtained with H$_2$**L**$^{1-2}$ [55, 56, 87]. These results are in broad accord with the synergistic effects discussed earlier for the radiotracer studies involving zinc(II) and cobalt(II).
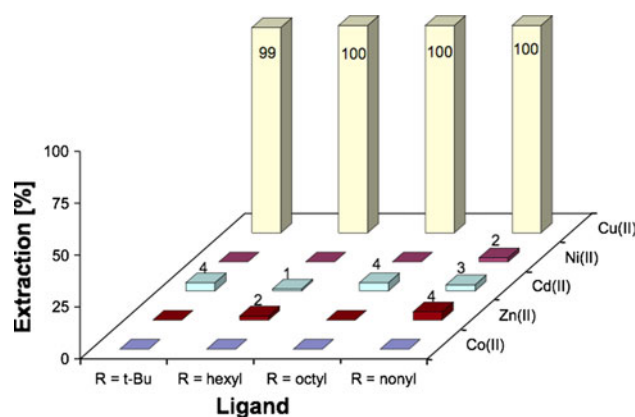

Fig. 3 Percentage of cadmium(II), cobalt(II), nickel(II), zinc(II) and copper(II) competitively extracted from the aqueous into the organic phase with H$_2$**L**^{3}(R = ^{t}Bu, hexyl, octyl and nonyl) in the presence of 4-ethylpyridine. [M(ClO$_4$)$_2$] = 1×10^{-4} M, pH 7.4. (HEPES/NaOH buffer); [H$_2$**L**^{3}] = 1×10^{-3} M, [4-ethylpyridine] = 2×10^{-3} M in CHCl$_3$; shaking time 24 h; T = 24 ± 1 °C. Metal content of the organic phase was determined directly using ICP-MS

Concluding Remarks

We present the synthesis of four new lipophilic 4,4′-biphenylene spaced bis-β-diketone ligands of type H_2L^3. The crystal structure of H_2L^3 (R = ^{t}Bu) displays a similar arrangement in the crystalline phase to H_2L^2 (R = ^{t}Bu). Liquid–liquid extraction studies employing H_2L^3 (R = Pr, ^{t}Bu, Ph, hexyl, octyl, nonyl) have been undertaken with, in general, the results paralleling those obtained for the related 1,3- and 1,4-phenylene spaced ligands H_2L^1 and H_2L^2 [55, 56, 87]. Collectively, they show that the stoichiometries of the extracted species depend on the relative concentrations of metal and ligand species present as well as their lipophilicities; higher levels of extraction were observed by the more lipophilic ligands. Interestingly, synergistic extraction was observed on addition of 4-ethylpyridine to the respective ligand/metal ion systems. Competitive metal extraction studies indicated a clear selectivity for copper(II) extraction when equal concentrations of cobalt(II), nickel(II), zinc(II) and cadmium(II) were also present in the aqueous phase.

Supplementary material

Crystallographic data H_2L^3 (R = ^{t}Bu) has been deposited with CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and is identified by deposition number CCDC 813650. Copies of this information can be obtained free of charge on request by e-mail at deposit@ccdc.cam.ac.uk or at http://www.ccdc.cam.ac.uk.

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