Synthetic, structural, electrochemical and solvent extraction studies of neutral trinuclear Co(II), Ni(II), Cu(II) and Zn(II) metallocycles and tetrahedral tetrannuclear Fe(III) species incorporating 1,4-aryl-linked bis-β-diketonato ligands†‡§

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Uncharged complexes, formulated as trimeric metallocycles of type [M(tL1)(Py)n] (where M = cobalt(ii), nickel(ii) and zinc(ii) and L1 is the doubly deprotonated form of a 1,4-phenylene linked bis-β-diketonato ligand of type 1,4-bis(RC(O)O)CH2C(O)R′ (R = t-Bu)) have been synthesised, adding to related, previously reported complexes of these metals with L1 (R = Ph) and copper(ii) with L1 (R = Me, Et, Pr, t-Bu, Ph). New lipophilic ligand derivatives with R = hexyl, octyl or nonyl were also prepared for use in solvent extraction experiments. The X-ray structures of H2L1 (R = t-Bu) and of its trinuclear (triangular) nickel(ii) complex [Ni2(L1)(Py)n]·3.5Py (R = t-Bu) are also presented.

Electrochemical studies of H2L1, [Co(L1)(Py)n], [Ni2(L1)(Py)n], [Cu2(L1)(Py)n], [Zn2(L1)(Py)n] and [Fe2(L1)n] (all with R = t-Bu) show that oxidative processes for the complexes are predominantly irreversible, but several examples of quasireversible behaviour also occur and support the assignment of an anodic process, seen between +1.0 and +1.6 V, as involving metal-centred oxidations. The reduction behaviour for the respective metal complexes is not simple, being irreversible in most cases. Solvent extraction studies (water/chloroform) involving the systematic variation of the metal, bis-β-diketone and heterocyclic base concentrations have been performed for cobalt(ii) and zinc(ii) using a radiotracer technique in order to probe the stoichiometries of the respective extracted species. Significant extraction synergism was observed when 4-ethylpyridine was also present with the bis-β-diketone ligand in the chloroform phase. Competitive extraction studies demonstrated a clear uptake preference for copper(ii) over cobalt(ii), nickel(ii), zinc(ii) and cadmium(ii).

Introduction

The metal coordination chemistry of β-diketone ligands has now been investigated for over 100 years1 and it has been well demonstrated that these versatile ligands give rise to a diverse range of interesting metal coordination behaviour.2 More recently, there has also been increasing interest in the metallo-supramolecular structural aspects of such systems.3 In a parallel development, several groups have extended the chemistry of such systems by incorporating more than one β-diketone motif,4–12 or a related malonate motif,13 into extended ligand structures before investigating their metal ion chemistry. For example, we14–19 and others20,21 have recently reported the use of a series of bis-β-diketone ligands of types H2L1 and H2L2 for the construction of a variety of new metallo-supramolecular arrays. The largely rigid sp2 hybridised backbone of the doubly deprotonated forms of these ligands results in particular defined geometries, which when combined with metal ions such as cobalt(ii), nickel(ii), copper(ii), zinc(ii) iron(iii), and gallium(iii) produce a variety of discrete and extended neutral metallo-species. For example, with copper(ii) these include neutral dinuclear species of type M1L2(solvent)15,17 as well as neutral trinuclear (triangular) species of type M1L2(solvent)14,16 with trivalent ions dinuclear triple helical complexes of type M1L218,19,22 and tetrahedral-shaped species of type M1L3 are obtained.24 In a recent extension of these studies we reported25 aspects of structural, electrochemical and liquid–liquid extraction behaviour involving cobalt(ii), nickel(ii), copper(ii), zinc(ii) and iron(iii) complexes incorporating ligands of type H2L2. In particular, we observed marked synergism in the extraction of cobalt(ii) and zinc(ii) when 4-ethylpyridine (EtPy) was added as a co-extractant to the bis-β-diketone in the organic phase.
In our prior studies it was demonstrated that neutral species of stoichiometry Cu₃L₁(solvent), containing triangular planar Cu₃L₁ units, can be used for the formation of extended multi-nuclear architectures by reaction with difunctional heterocyclic nitrogen ligands that include pyrazine, dabc and 4,4'-bipyridine. In contrast to the situation for copper, the metal ion chemistry of H₂L₁ with other divalent metals has received less attention, although two triangular cobalt(II) and nickel(II) derivatives and a polymeric zinc(II) complex derived from H₂L₁ (with R = Ph) have been reported. It is also noted that related triangular complexes incorporating difunctional, non-β-diketone ligand derivatives of a range of metals are also known.

In an extension of our prior studies of copper(II) and iron(III) complexes of H₂L₁ derivatives, we now report an investigation of new species incorporating cobalt(II), nickel(II) and zinc(II) derived from this ligand type; these products also incorporate pyridine (Py) as a co-ligand. Aspects of the synthesis, electrochemistry and liquid–liquid extraction properties of these systems are now presented.

**Experimental**

NMR spectra were recorded on Bruker Avance DPX200, DPX300 or DPX400 spectrometers. 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. UV-Vis spectra were recorded on a Cary 1E spectrophotometer in the solid state (all reported peaks are broad). Tetrahydrofuran was pre-dried over sodium wire before use. Ligands of type H₂L₁ (R = hexyl, octyl and nonyl) were prepared using the previously reported method [Cu₃(L₁)₃] and [Fe₄(L₁)₆]

**General preparation of H₂L₁ (R = hexyl, octyl and nonyl)**

Sodium amide (5.0 g, 0.13 mol) was added to a mixture of dimethyl terephthalate (5.00 g, 0.025 mol) and 2-octanone (for H₂L₁; R = hexyl) (6.4 g, 0.05 mol) or 2-decanone (for H₂L₁; R = octyl) (7.8 g, 0.05 mol) or 2-undecanone (for H₂L₁; R = nonyl) (8.5 g, 0.05 mol) in dry tetrahydrofuran (100 ml) at 0°C. The reaction 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 was quenched with ice water (100 ml) and then acidified to pH 4 using 1 M hydrochloric acid; two phases formed. The organic (tetrahydrofuran) phase 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 which was recrystallised from ethanol. Yields and characterisation details for each product are given below.

1.1'-{(1,4-Phenylene)-bis-nonane-1,3-dione, H₂L₁ (R = hexyl). Yld 6.85 g (70%), pale yellow platelets. 'H-NMR δ (200 MHz CDCl₃): 16.23 (br s, enol, 2H), 7.95 (s, aromatic, 4H), 6.24 (s, –CH – enol, 2H), 2.45 (br m, –CH₂, 4H), 1.70 (br m, –CH₃, 6H). (ESI-MS): m/z 387 (M + H)⁺, 385 (M – H)⁻. FTIR (KBr) (major peaks only): 3000 (br), 1601 (vbr), 1559, 1290, 858, 775 cm⁻¹. Found: C, 73.48; H, 9.55%. Calc. for C₂₄H₃₄O₄: C, 75.98; H, 9.56%.

1.1'-{(1,4-Phenylene)-bis-dodecane-1,3-dione, H₂L₁ (R = octyl). Yld 8.48 g (75%), pale yellow platelets. 'H-NMR δ (200 MHz CDCl₃): 16.02 (br s, enol, 2H), 7.96 (s, aromatic, 4H), 6.20 (s, –CH – enol, 2H), 2.46 (br m, –CH₂, 4H), 1.71 (br m, –CH₃, 4H), 1.33 (br m, –CH₂, 2H), 0.88 ppm (br m, –CH₃, 6H). (ESI-MS): m/z 443 (M + H)⁺, 469 (M + Na)⁺, 441 (M – H)⁻. FTIR (KBr) (major peaks only): 3000 (br), 1598 (vbr), 1507, 1102, 781 cm⁻¹. Found: C, 78.12; H, 8.90%. Calc. for C₃₈H₄₆O₄: C, 79.86; H, 9.56%.

1.1'-{(1,4-Phenylene)-bis-undecane-1,3-dione, H₂L₁ (R = nonyl). Yld 165 mg (79%), orange microcrystalline powder. 'H-NMR δ (200 MHz CDCl₃): 16.02 (br s, enol, 2H), 7.96 (s, aromatic, 4H), 6.30 (s, –CH – enol, 2H), 2.46 (br m, –CH₂, 4H), 1.71 (br m, –CH₃, 4H), 1.33 (br m, –CH₂, 2H), 0.90 ppm (br m, –CH₃, 6H). (ESI-MS): m/z 471 (M + H)⁺, 497 (M – H)⁻. FTIR (KBr) (major peaks only): 3000 (br), 1598 (vbr), 1507, 1102, 781 cm⁻¹. Found: C, 74.77; H, 8.90%. Calc. for C₃₉H₄₈O₄: C, 75.98; H, 9.56%.

**Synthesis of [Co₃(L₁)₃(Py)] (R = t-Bu), [Ni₃(L₁)₃(Py)] (R = t-Bu), [Zn₃(L₁)₃(Py)] (R = t-Bu)**

H₂L₁ (R = t-Bu) (0.4 mmol) in dry tetrahydrofuran (40 ml) was added to Na₂CO₃ (1.0 g, ~0.01 mol) suspended in dry tetrahydrofuran (10 ml). This mixture was stirred for 1 h before the appropriate metal(III) chloride (0.4 mmol) in tetrahydrofuran (40 ml) and pyridine (0.8 mmol) were added dropwise. The mixture was stirred at 40°C for 16 h. The resulting solution was filtered and the volume of the filtrate was then reduced to a small volume in a rotary evaporator to yield the solid complex as a microcrystalline product which was isolated and washed with ether.

[Co₃(L₁)₃(Py)]²⁺·H₂O (R = t-Bu). Yield 174 mg (79%), orange microcrystalline powder. Found: C, 65.37; H, 6.24; N, 4.92%. Calc. for C₉₀H₁₀₂N₆Co₃O₁₂·H₂O: C, 65.31; H, 6.34; N, 5.08%. UV-Vis (solid state): 350, 375, 415, 460, 560 nm.

[Ni₃(L₁)₃(Py)]²⁺·Py·4THF (R = t-Bu). Yield 149 mg (56%), green microcrystalline powder. Found: C, 66.53; H, 6.79; N, 4.53%. Calc. for C₉₀H₁₀₂Ni₃O₁₂·Py·4THF·0.125CHCl₃·0.125EtOH: C, 66.61; H, 7.00; N, 4.90%. UV-Vis (solid state): 360, 410, 560 nm. Crystals used for the X-ray study were obtained by dissolving this product in pyridine and letting the solution stand (see later).

[Zn₃(L₁)₃(Py)]²⁺·Py·4THF (R = t-Bu). Yield 165 mg (75%), colourless microcrystalline powder. Found: C, 65.40; H, 6.42; N, 5.16%. Calc. for C₉₀H₁₀₂Ni₃O₁₂·Zn·0.125CH₃CO₂H·0.125H₂O·0.125EtOH·0.125CHCl₃·0.125EtOH: C, 65.43; H, 6.23; N, 5.09%. 'H-NMR δ (200 MHz, DMSO-d₆, 300 K): 8.61 (m, Py, 4H), 7.96 (s, aromatic, 4H), 7.88 (m, Py, 2H), 7.39 (m, Py, 4H), 6.24 (s, –CH – enol, 2H), 1.94 (s, CH₃, 18H). UV-Vis (solid state): 359, 415 nm.

**Electrochemical studies**

The electrochemistry of H₂L₁ (R = t-Bu), along with its trinuclear neutral complexes, [M₃(L₁)₃(Py)]⁺ (M = Co, Ni, Zn),
[Cu(L1)3] and [Fe(L1)3], was investigated in acetonitrile or an acetonitrile/tetrahydrofuran mixture. Cyclic voltammetry studies were performed using a conventional three-electrode configuration with R compensation and a BAS Model 100B electrochemical system, operated by a computer using the BAS100W software. The working electrodes were glassy carbon (GCE) or platinum discs, polished with alumina. The reference electrode was Ag/AgCl and was separated from the working and Pt wire auxiliary electrodes in a glass sleeve fitted with a Vycor frit. Solutions were made up in HPLC-grade acetonitrile or acetonitrile–tetrahydrofuran (usually 1 : 1) and were 0.05–0.1 M in (Et3N)(ClO4); they were purged with argon gas. Complex concentrations in the millimolar range were used throughout. Unless otherwise stated, results discussed below refer to behaviour at the GCE.

Solvent extraction studies

Liquid–liquid extraction experiments were performed at 24 ± 1 °C in microcentrifuge tubes (2 ml) with a phase ratio \( V_{\text{org}} : V_{\text{aq}} \) 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 H2L1 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 ±5%.

In the case of the single metal ion experiments a shaking time of 3 h was used for the cobalt(II) experiments and 30 min for the zinc(II) experiments. At the end of these times, the phases radiometrically using 60Co and 65Zn radioisotopes (ROTOP Pharmaka) by means of a NaI (TI) scintillation counter (Cobra II/Canberra-Packard) were first located in the difference Fourier map before refinement.

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 H2L1 (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 [H2L1]org and the slope determined.

4-Ethylpyridine dependence studies were also carried out. These involved varying the 4-ethylpyridine concentration from 2 × 10^{-4} M 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-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} M 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.

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 H2L1 and in the second set of experiments also 4-ethylpyridine at 2 × 10^{-3} M.

X-Ray structural determinations

Data for H2L1 (R = t-Bu) were collected with \( ω \) scans to approximately 56° 20 using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å) at 150(2) K. Data integration and reduction were undertaken with SAIN'T and XPREP. Data for [Ni(L1)3(Py)6]·3.5Py (R = t-Bu) were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with \( ω \) and \( ψ \) scans to approximately 44° 20 at 100(2) K. Subsequent computations were carried out using the WinGX-32 graphical user interface. Structures were solved by direct methods using SIR97. Multi-scan empirical absorption corrections were applied to the data set using the program SADABS. Data were refined and extended with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen-bound hydrogen atoms were first located in the difference Fourier map before refinement.

Crystal and structure refinement data for H2L1 (R = t-Bu) and [Ni(L1)3(Py)6]·3.5Py (R = t-Bu) are summarised below and an ORTEP depiction of the structure of H2L1 (R = t-Bu) is provided in Fig. 1, schematic representations of [Ni(L1)3(Py)6]·3.5Py (R = t-Bu) are provided in Fig. 2 and Fig. 3. Tables of selected bond lengths and angles are given in the ESI.²

\[
H_2L_1 \quad (R = t-Bu) \quad \text{Formula: } C_{30}H_{44}O_4, \quad M = 330.41, \quad \text{orthohombic, space group } Pbc a (\#61), \quad a = 10.232(3), \quad b = 10.158(3), \quad c = 17.738(5) \text{ Å, } V = 1843.8(9) \text{ Å}^3, \quad D_r = 1.190 \text{ g cm}^{-3}, \quad Z = 4, \quad \text{crystal size 0.600 by 0.370 by 0.032 mm, colour colourless, habit plate, temperature } 150(2) \text{ K, } \lambda (\text{MoKα}) = 0.71073 \text{ Å, } \mu (\text{MoKα}) = 0.082 \text{ mm}^{-1}, \quad T(\text{SADABS})_{\text{max}} = 0.864765, \quad 1.000000, \quad 20_{\text{max}} = 56.58, \quad hkl \text{ range } -13 \text{ to } 13, \quad -13 \text{ to } 13, \quad -22 \text{ to } 22, \quad N = 16191, \quad N_{\text{calc}} = 2229, \quad (R\text{merge} = 0.0612),
\]
the solid ligands are in keeping with the presence of hydrogen bonding in the enol forms of the \( \text{H}_2\text{L}^1 \) ligand. The existence of a sharp singlet in each spectrum at \( \sim 6.2 \text{ ppm} \) in the \( \text{H}_2\text{L}^1 \) (R = t-Bu) hydrogen atoms located on the oxygens of the hydrogens were located on the oxygens closest to the phenylene ring in \( \text{H}_2\text{L}^1 \) (R = Ph) in which each hydrogen was partially located on each \( \beta \)-diketone oxygen atom (with 50% occupancy). In the present structure the expected ‘enolic’ intramolecular hydrogen bonds are present between each pair of adjacent oxygen atoms \( (\text{O}(1) - \text{O}(2) \text{ distance } 2.479 (2) \text{ Å}; \text{O}(1) - \text{H}(13) - \text{O}(2) \text{ angle } 154 (2)^\circ) \). Analysis of the crystal packing shows the presence of a number of close CH(phenylene)–O interactions within the lattice \( (\text{H}(9) - \text{O}(2), 2.6 \text{ Å}; \text{CH}(t-Bu) - \text{O}(\text{H}(6), 2.6 \text{ Å}; \text{CH}(\text{H}(9)) - \text{O}(3A) - \text{O}(2), 2.6 \text{ Å}) \), giving rise to an infinite sheet-like motif.

\[ \text{Fig. 1 ORTEP}^{33} \text{ representation of the X-ray crystal structure of } \text{H}_2\text{L}^1 \text{ (R = t-Bu) shown with } 50\% \text{ probability ellipsoids. The molecule occupies a crystallographic 2-fold cell (symmetry code: } 1 - x, -y, 1 - z). \]

Claisen condensations were employed to synthesise the ligands of type \( \text{H}_2\text{L}^1 \) in good yield using an adaptation of literature procedures.\(^{5,13,14,16} \) The \(^1\text{H} \) NMR spectra of deuterochloroform solutions of the respective ligands of type \( \text{H}_2\text{L}^1 \) with \( R = \text{Pr}, \text{t-Bu, Ph, hexyl, octyl, nonyl} \) in each case indicated that these species exist almost entirely in their (bis) enol tautomeric forms, shown by the presence of a broad resonance at \( \sim 16.2 \text{ ppm} \) (enol protons), integrating to two protons, in the respective spectra. The existence of a sharp singlet in each spectrum at \( \sim 6.2 \text{ ppm} \) (due to \( \text{H}_2\text{L}^1 \)) integrating to two protons, is also in harmony with this assignment. In the solid state, the infrared spectra of the solid ligands are in keeping with the presence of hydrogen bonded hydroxy and carbonyl groups (absorptions at \( \sim 3000 \) and \( \sim 1600 \text{ cm}^{-1} \), respectively,\(^{36} \) the occurrence of \( \text{O} - \text{H} \cdots \text{O} \) hydrogen bonding in the enol forms of the \( \beta \)-diketone fragments has been proposed to confer added stability on such a structure with respect to its corresponding (bis) keto form.\(^{35} \) Nevertheless, it is noted that a number of bis- and tris-\( \beta \)-diketone ligands have been reported recently in which the \( \beta \)-diketone groups exist as a mixture of both keto and enol forms in solution\(^{37,38,39} \)—an observation also made for simple \( \beta \)-diketones some considerable time ago.\(^{40} \) We have previously reported the X-ray structure of \( \text{H}_2\text{L}^1 \) (R = t-Bu) in which it was shown that this ligand exists exclusively in its (bis) enol form both in solution and in the crystalline state.\(^{31} \) Similar results have also been reported for the \( \text{H}_2\text{L}^1 \) (R = Ph) ligand\(^{32} \) and a ligand related to \( \text{H}_2\text{L}^1 \) incorporating a resorcinol spacer.\(^{16} \)

In view of the above it was of interest to confirm what configuration the present ligands of type \( \text{H}_2\text{L} \) adopt in the solid state with respect to possible enol/keto tautomerism as well as to determine the relative orientations of the \( \beta \)-diketone fragments with respect to each other. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a diethyl ether solution of \( \text{H}_2\text{L}^1 \) (R = t-Bu). The X-ray structure (Fig. 1) reveals that the \( \beta \)-diketone fragments are essentially in the same plane as the central phenylene core, reflecting the presence of the sp\(^2\) conjugated backbone and perhaps aided by weak C(phenylene)–O interactions present in this arrangement. The two \( \beta \)-diketone fragments are orientated with their coordination vectors aligned approximately \( 180^\circ \) with respect to each other. The \( \beta \)-diketone groups exist in their enol form, with the enol hydrogen atoms located on the oxygens \( (\text{O}(1)) \) furthest from the central phenylene ring; this contrasts with the solid state structure of the \( \text{H}_2\text{L}^2 \) (R = t-Bu) isomer in which the hydrogens were located on the oxygens closest to the phenylene ring and \( \text{H}_2\text{L}^1 \) (R = Ph) in which each hydrogen was partially located on each \( \beta \)-diketone oxygen atom (with 50% occupancy).\(^{37} \) In the present structure the expected ‘enolic’ intramolecular hydrogen bonds are present between each pair of adjacent oxygen atoms \( (\text{O}(1) - \text{O}(2) \text{ distance } 2.479 (2) \text{ Å}; \text{O}(1) - \text{H}(13) - \text{O}(2) \text{ angle } 154 (2)^\circ) \). Analysis of the crystal packing shows the presence of a number of close CH(phenylene)–O interactions within the lattice \( (\text{H}(9) - \text{O}(2), 2.6 \text{ Å}; \text{CH}(t-Bu) - \text{O}(\text{H}(6), 2.6 \text{ Å}; \text{CH}(\text{H}(9)) - \text{O}(3A) \cdots \text{O}(2), 2.6 \text{ Å}) \), giving rise to an infinite sheet-like motif.

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ligand metal complexes of deprotonated \( H_2L^1 \) (\( R = \text{Ph} \)) but is analogous to that used by us for the synthesis of corresponding triangular (trinuclear) copper(II) complexes incorporating deprotonated \( H_2L^1 \) ligands\(^{14,17} \) and dinuclear cobalt(II), nickel(II) and zinc(II) complexes containing deprotonated \( H_2L^2 \) ligands.\(^{19} \) The following new derivatives were isolated in the present study: \([\text{Co}_3(L^1)_3(\text{Py})_6\cdot\text{H}_2\text{O} \ (R = \text{t-Bu}), [\text{Ni}_3(L^1)_3(\text{Py})_6\cdot\text{Py} \cdot 4\text{THF} \ (R = \text{t-Bu}) \text{ and } [\text{Zn}_3(L^1)_3(\text{Py})_6 \ (R = \text{t-Bu}) ; all contain } M : L : \text{Py ratios of } 1:1:2 \text{ and were formulated as trinuclear by analogy with the corresponding triangular copper(II) species of } L^1 \ (R = \text{Me}, \text{Pr})^{14} \text{ and the analogous cobalt(II) and nickel(II) complexes of this ligand type (with } R = \text{Ph}),^{20} \text{ all of which have been characterised by single crystal X-ray structures. In this context it is noted that } [\text{Zn}_3(L^1)_3(\text{Py})_6 \ (R = \text{t-Bu}) \text{ yields a symmetric } ^1H \text{ NMR spectrum confirming ligand equivalence in DMSO-}d_6 \text{ solution.}

The X-ray structure of the above nickel(II) complex recrystallised from pyridine, \([\text{Ni}_3(L^1)_3(\text{Py})_6\cdot3.5\text{Py} \ (R = \text{t-Bu}), \text{ confirms its triangular nature and shows that each nickel centre adopts a tetragonally distorted octahedral arrangement (mean Ni–O lengths, 2.020 Å; mean Ni–N lengths, 2.108 Å) with the pyridine ligands occupying axial sites (Fig. 2); the structure is generally similar to the corresponding structure reported by Soldatov (with } R = \text{Ph}),^{20,21} \text{ It is noted that recrystallisation of the present complex resulted in very small needle-like crystals that rapidly decay out of pyridine. Despite rapid handling at dry-ice temperature, the diffraction qualities of the crystals were not ideal. Even though long exposure times were used and a comparatively high powered laboratory X-ray source (5 kW from a rotating anode) was employed, only reflections to } \sim 1.0 \text{ Å resolution could be recorded.}

Fig. 2 A schematic representation of the X-ray structure of \([\text{Ni}_3(L^1)_3\cdot(\text{Py})_6\cdot3.5\text{Py} \ (R = \text{t-Bu}), \text{ hydrogen atoms, solvent molecules and regions of disorder are not shown for clarity.}

The structure shows the presence of disordered pyridine solvent molecules in the lattice. As can be seen in Fig. 2, the triangular structure is somewhat distorted from an ideal equilateral triangle, with Ni–Ni distances ranging from 10.56 Å to 10.77 Å. The N–Ni–N axes through each of the metal centres are also significantly distorted from the ideal perpendicular to the average plane of the triangle. This is in part due to the presence of strong offset face-to-face π–π stacking between the coordinated pyridyl ligands in adjacent molecules. This results in an infinite one-dimensional ‘prismatic’ arrangement (Fig. 3) with triangles stacking above one another along the \( \alpha \)-axis. The above extended packing motif results in the formation of a number of voids within the structure. There are pyridine solvent molecules present between each of the columns and also encapsulated within the channels formed by the stacked prisms (Fig. 3). Each of these pyridine solvent molecules is involved in both edge-to-face and offset face-to-face π–π interactions with other pyridine molecules (both coordinated and uncoordinated) and with the phenylene rings of the \( L^1 \) ligands.

Electrochemical studies

The electrochemistry of \( H_2L^1 \) (\( R = \text{t-Bu}) \), both protonated and deprotonated, along with the present trinuclear neutral complexes, \([\text{M}_3(L^1)_3(\text{Py})_6] \ (M = \text{Co, Ni, Zn}), \text{ has been investigated in acetonitrile or acetonitrile/tetrahydrofuran. Additionally, a comparative investigation of the previously reported}^{14,17} \text{ complexes } [\text{Cu}_3(L^1)_3] \text{ and } [\text{Fe}_4(L^1)_6] \ (\text{both with } R = \text{t-Bu}) \text{ was also undertaken. The results for these ligand and complexes species are summarised in Table 1. Since the paramagnetic iron(III), cobalt(II), nickel(II) and copper(II) centres in the respective complexes are almost certainly sufficiently separated not to be significantly magnetically coupled,}^{14,17,19} \text{ M}^{n+} \text{M}^{n+1+} \text{ or } \text{M}^{n+} \text{M}^{n-1+} \text{ intermediate systems where the metals ‘share’ the higher or lower oxidation state effectively equally are not expected to occur. Instead, oxidation or reduction at one metal centre is anticipated to occur initially, thereby affecting the redox behaviour of the other metal centres. As a consequence the latter metal centres are expected to be oxidised or reduced at a somewhat different observed...}
potential, provided the integrity of the complex is maintained to a reasonable extent. However, if fragmentation and dissociation occur rapidly following the first single electron reduction, release of the remaining metal ions may lead to a significant alteration of their redox properties, to the point where these other centres either immediately undergo redox processes or become redox inert in the electrochemical window under examination. Complex electrochemical behaviour is hence likely to result from such sequential processes. As for our previous studies involving the related dinuclear complexes of H2L2 (R = t-Bu),29 the present studies were in part undertaken to probe the validity of the above postulates.

**Free ligand.** H2L1 (R = t-Bu) exhibits no oxidation processes before +2 V (versus Ag/AgCl), and shows only an irreversible process, presumably ligand oxidation, near the system limit of +2.2 V in acetonitrile. The reduction behaviour in acetonitrile is more complex, displaying reductions that are shifted anodically compared with those for H2L2 (R = t-Bu),29 with waves at +1.33 and −1.50 V. Even at 100 mV s−1 scan rate, a broad ill-defined backwave at −1.45 V, with another at −1.33 V observed at higher speed. These reduction processes are affected (at both glassy carbon and platinum working electrodes) by strong adsorption spikes coincident with the positions of the cathodic and anodic waves near −1.3 V. This suggests that the anodic wave, whose peak current varies linearly with respect to increasing scan rate, corresponds predominantly to a desorption phenomenon and not to an electron transfer process. The observed behaviour does not change significantly with working electrode, dilution or addition of other aprotic solvents (such as tetrahydrofuran). In particular, deprotonation of the ligand through addition of sodium methoxide causes a clear cathodic shift in the oxidation behaviour, with a poorly resolved shoulder appearing at −1.52 V as occurs for the protonated ligand. The observed shifts presumably reflect both the influence of deprotonation and the effect of weak coordination to the introduced sodium cation. Cyclic voltammograms for H2L1 (R = t-Bu) together with those for [Co2(L1)2(Py)n] (R = t-Bu), [Ni2(L1)2(Py)n] (R = t-Bu) and [Zn2(L1)2(Py)n] (R = t-Bu) are given as Fig. S1 in the ESI.8

**[Zn3(L1)3(Py)6] (R = t-Bu).** Because zinc(II) is not electroactive, any observed redox processes must originate in the ligand framework, albeit influenced by the coordinated metal ion. The zinc(II) complex displays an irreversible oxidation process at +1.43 V. This amounts to a cathodic shift of −0.6 V as a result of complexation, although of course, the character of the ligand has changed from neutral to dianionic. At a GCE, the major reduction wave lies at −1.61 V, with a broad ill-defined following wave at −2.0 V, and pre-waves at −1.16 and −1.31 V, as well as a backwave at −1.45 V that appears from wave shape and size/scan rate profile to be a desorption process. The presence and position of pre-waves between −1.2 and −1.5 V vary both with scan rate and with successive scans, leaving a single consistent reduction process at Epa −1.75 V for 10 V s−1 scan rate, although backwaves on the anodic sweep occur at −1.33 and −1.13 V. Adsorption and desorption phenomena clearly complicate the voltammograms, but are less obtrusive than similar affects that occur for the free ligand. The reduction process is shifted ∼0.3 V cathodically on complexation (compared to the free ligand), so that, overall, both oxidation and reduction processes display cathodic shifts as a consequence of deprotonation and complexation.

**Table 1** Oxidation and reduction processes (Epa or Epa, V versus Ag/AgCl)* observed for complexes of L1

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidations</strong></td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>∼+2.1 (irrev.)</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>+1.43 (irrev.)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>+1.37 (irrev.), +1.55 (sh, irrev.)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>+1.29 (irrev.)</td>
</tr>
<tr>
<td>Co(II)</td>
<td>+1.31 (irrev.)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>+1.36 (irrev.)</td>
</tr>
<tr>
<td><strong>Reductions</strong></td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>−1.33 (irrev.), −1.50 (irrev.)</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>−1.61 (irrev.)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>−1.19 (irrev.), −2.06 (sh, irrev.)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>−1.84 (irrev.), −2.12 (irrev.)</td>
</tr>
<tr>
<td>Co(II)</td>
<td>−1.64 (quasirev.; ΔE 230 mV)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>−0.65 (irrev.), −1.48 (irrev.), −1.77 (irrev.)</td>
</tr>
</tbody>
</table>

* Glassy carbon electrode; 0.1 M tetraethylammonium perchlorate in acetonitrile or mixed acetonitrile/tetrahydrofuran solvent. Pre-waves at −1.16, −1.31 V; some reversible character at high scan rates. Additional backwave at −0.25 V, indicative of competing dissociation.
Liquid–liquid extraction studies

Simple β-diketones have long been used as extractants in numerous liquid–liquid extraction studies (including, for example, for mineral processing applications). In contrast, there appears, however, to be no report of the use of bis-β-diketone ligands of the present type for similar studies even though individual examples of the latter have also been known for a considerable time. Nevertheless we have recently demonstrated that 1,3-phenylene bridged ligands of type H₂L₁ give rise to significant synergistic metal extraction behaviour in the presence of added 4-ethylpyridine. In this context, it was of interest to explore the comparative behaviour of similar ligands of type H₂L₁ given the difference in the directions of the coordination vectors in these two ligand types.

Studies at constant metal and ligand concentration. The extraction of cobalt(II) and zinc(II) using the H₂L₁ ligands with R = Pr, Ph, t-Bu, hexyl, octyl and nonyl was performed using the previously described radiotracer technique. Parallel sets of extractions were carried out both in the absence and presence of 4-ethylpyridine and the results are summarised in Fig. 4. At pH 8.7 in the absence of 4-ethylpyridine, cobalt(II) extraction is negligible (1 to 2%) for each member of the above ligand series, while the range towards zinc(II) is ~2 to 35%. As expected, the more lipophilic ligand derivatives give rise to enhanced extraction.

The above experiments were repeated with 4-ethylpyridine (2 × 10⁻³ M) added to the organic phase but under otherwise identical experimental conditions; the results are also summarised in Fig. 4. On addition of two equivalents (relative to H₂L₁) of 4-ethylpyridine, the extraction of cobalt(II) was markedly enhanced (from ~2 to 26%) in the case of H₂L₁ (R = nonyl) and also enhanced from 35 to 61% for zinc(II) with this ligand. Further, the time for equilibrium to be reached in the case of cobalt(II) was also approximately halved (from 3 to 1.5 h). Parallel 'control' experiments in the absence H₂L₁ but at the same concentration of 4-ethylpyridine were performed; under these conditions metal extraction was negligible at ≤1%. Overall, it is noted that synergism is more pronounced for the nonyl derivative, especially in the case of cobalt(II).

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

Clearly the enhancement of extraction in the presence of 4-ethylpyridine is substantial for both zinc(II) and cobalt(II) for H₂L₁ (R = nonyl). It is of interest to compare the results for
**H₂L² (R = nonyl)** under identical experimental conditions: this ligand gave an increase of 12 to 70% for cobalt(II) while the increase for zinc was 53 to 85%.²⁴

**H₂L¹ (R = nonyl)** dependence studies. The stoichiometries of the extracted species were analysed by undertaking the extraction of cobalt(II) and zinc(II) (at a fixed concentration of 1 × 10⁻⁴ M) under variable H₂L¹ (R = nonyl) concentration in the presence of a fixed concentration (2 × 10⁻⁴ M) of 4-ethylpyridine as well as in its absence. For the extractions involving zinc(II) and H₂L¹ (R = t-Bu, hexyl, octyl, nonyl) in all cases the concentration of the H₂L¹ 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 conditions).²⁵ The negligible extraction observed for cobalt(II) in the absence of 4-ethylpyridine (Fig. 4) across all H₂L¹ 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 \([H_{2}L]^{-}\). Provided a ‘simple’ equilibrium is involved, the slope of this plot gives the stoichiometry (\(n\)) of the extracted species directly since log \(D_M\) = \(n \log[L]_{org} + K\) (where \(K\) is a constant).²⁶ The results for both cobalt(II) and zinc(II) with H₂L¹ 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 of the ligand concentration in each case. For the present ligand series, slopes that range from 1.8 to 2.1 were obtained (Table 2), suggesting that predominately 1 : 2 (M : L) species (unlike H₂L², for which case a mixture of species was postulated to form) are extracted under the conditions employed.

**4-Ethylpyridine dependence studies.** These involved variation of the 4-ethylpyridine concentration over the range 2 × 10⁻⁴ M to 2 × 10⁻³ M while the other concentrations were held constant. In the case of H₂L¹ (R = nonyl) with both zinc(II) and cobalt(II), a metal : 4-ethylpyridine ratio of approximately 0.8 was obtained (Table 2). This suggests that, under the conditions employed, the predominant species extracted approximates 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.²⁶ H₂L¹ (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 M 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 are summarised in Table 3. Under the conditions employed, an equimolar ratio (metal : ligand = 1 : 1) is indicated for zinc(II) in the absence of added 4-ethylpyridine. This 1 : 1 ratio is comparable to that present in the complexes formulated as \([M_{3}L_{1}Py_{6}]^{17}\) (M = Ni, Co or Zn; R = t-Bu) (and confirmed for nickel by X-ray diffraction) synthesised in the present study and also those reported for the complexes of H₂L¹ with R = Ph which, as mentioned previously, were shown to be M₃L₆ triangles when cobalt(II) and nickel(II) were employed (while zinc(II) yielded a polymeric species in the solid state).

Further variable metal concentration loading experiments were undertaken in which the solution stoichiometries of the cobalt(II) and zinc(II) systems with H₂L¹ (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 ML₆ (M = Co, Zn) derivatives. From these experiments, two types of extracted complexes can be proposed to form under the saturation conditions discussed above. In the absence of 4-ethylpyridine only a species with a M : L ratio of 1 : 1 is predicted (most likely of type \(Zn_{3}(L^{1}_{3})\)) while in the presence of 4-ethylpyridine the dominant complex appears to be a 1 : 2 (M : L) species where M = Zn or Co (most likely of type \([M(L^{1}_{3})(4-ethylpyridine)]\)). These latter results appear not inconsistent with those obtained from the ligand

### Table 2

<table>
<thead>
<tr>
<th>Run</th>
<th>Ligand</th>
<th>Slopes (Zn(II),H₂L¹)</th>
<th>(Zn(II),H₂L¹) + EtPy</th>
<th>(Co(II),H₂L¹) + EtPy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L¹ dependence</td>
<td>R = t-Bu</td>
<td>1.8</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>R = Hexyl</td>
<td>2.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>R = Octyl</td>
<td>2.1</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>R = Nonyl</td>
<td>2.0</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>4-Ethylpyridine dependence</td>
<td>R = Nonyl</td>
<td>N/A</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Metal : ligand ratio</th>
<th>(Zn(II),H₂L¹)</th>
<th>(Zn(II),H₂L¹) + EtPy</th>
<th>(Co(II),H₂L¹) + EtPy</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Nonyl</td>
<td>1.0</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>
dependence studies where under conditions of ligand excess 1 : 2 (M : L) species were proposed to occur in both the presence and absence of added 4-ethylpyridine.

**Summary of complex species extracted.** Overall, on the basis of the solvent extraction experiments three complex species may be proposed to form in the respective organic phases (Scheme 1), with the particular species generated depending on the conditions employed. In the absence of 4-ethylpyridine both 1 : 1 and 1 : 2 (M : L) metal to ligand ratios were indicated, with the 1 : 1 species dominating under higher metal (zinc) concentrations. For the case where the ligand is in clear excess with respect to the metal ion (cobalt or zinc), the formation of the corresponding 1 : 2 (M : L) complex is proposed. In the presence of 4-ethylpyridine a 1 : 2 : 1 (M : L : EtPy) complex is proposed to be the dominant extracted species in both the cobalt and zinc cases.

**Competitive extractions.** In order to probe the potential metal ion selectivities of these ligands, competitive extraction experiments were carried out at pH 7.8 (HEPES/NaOH) in the absence of 4-ethylpyridine for the ligands H2L1 (R = t-Bu, hexyl, octyl or nonyl). Equal concentrations of five different divalent transition metal perchlorate salts (cobalt(ii), nickel(ii), copper(ii), zinc(ii), cadmium(ii), each 1 × 10⁻³ M) were added to the aqueous phase and H2L1 (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. Selectivity for copper(ii) over the other four divalent transition metal ions present was obtained. Within experimental error, quantitative (100%) extraction of copper ion occurred in each case, with zero 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. As above, the results show effectively quantitative extraction of copper(ii) across all ligand derivatives. In contrast, extraction of cobalt(ii), nickel(ii), zinc(ii) and cadmium(ii) was found to be zero (within experimental error) in all cases apart from nickel(ii) with H2L1 (R = nonyl). In this case 63% extraction of nickel(ii) was observed. Thus, the additional presence of 4-ethylpyridine in this experiment results in a marked synergistic enhancement of the extraction of nickel(ii) (from ~0 to 63%) under the conditions employed.

**Concluding remarks**

In the present study we present the synthesis of three new lipophilic ligands of the 1,4-phenylene-linked, bis-β-diketone category (H2L1) as well as new solid complexes of cobalt(ii), nickel(ii) and zinc(ii) of H2L1 with R = t-Bu. Electrochemical and liquid–liquid extraction studies for individual systems have been undertaken with, in general, the results paralleling those reported previously for the related complexes of the 1,3-phenylene-linked ligands of type H2L1.59

It is clear that the present compounds are associated with a rich electrochemistry; while many of the observed processes for the complexes appear to be ligand centred, the occurrence of peaks removed from the expected positions for normal ligand processes is in accord with dominantly metal-centred behaviour also occurring. While the metal centres in the tri- and tetrameric systems appear sufficiently separate to prevent significant metal coupling, the distances are still of such a magnitude for a given metal centre to feel the effect of neighbouring ‘spectator’ metal ions. As a consequence processes at different potentials might be expected but these were not able to be definitively assigned because of interfering adsorption/desorption processes and complications due to the presence of an electroactive ligand.

The solvent extraction studies collectively show that the stoichiometries of the extracted species clearly depend on both the relative concentrations of the metal and ligand species as well as on their respective natures. As expected, enhanced metal extraction efficiencies in general occur for the more lipophilic ligand derivatives. An interesting feature of the results obtained is the substantial extraction synergism obtained on addition of 4-ethylpyridine to the respective lipophilic ligand/metal ion systems. As also found for related H2L1 systems, competitive metal ion studies indicate a clear preference for copper(ii) extraction when equal concentrations of cobalt(ii), nickel(ii), zinc(ii) and cadmium(ii) were also present in the corresponding aqueous phase.

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References


