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Metal complexes of a novel heterocyclic benzimidazole ligand formed by rearrangementcyclization of the corresponding Schiff base. Electrosynthesis, structural characterization and antimicrobial activity[†]

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The electrochemical oxidation of anodic metals (M = cobalt, nickel, copper, zinc and cadmium) in a solution of the ligand 1H-anthra[1,2-d]imidazol-6,11-dione-2-[2-hydroxyphenyl] [H₂L] afforded homoleptic [ML] compounds. The addition to the electrochemical cell of coligands (L') such as 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) allowed the synthesis, in one step, of heteroleptic [MLL'] compounds. The crystal structures of H₂L (1), [CoL(MeOH)]₂ (2), [CoL(phen)]₂ (3), [NiL(bpy)]₂ (4), [CuL(bpy)] (5), [CuL(phen)] (6) and [CdL(bpy)]₂ (7) have been determined by X-ray diffraction techniques. The crystal structures of 2, 3, 4 and 7 consist of dimeric species in which both metallic atoms are connected through two phenolate bridges in a penta-coordinated (2) or hexa-coordinated (3, 4 and 7) environment. Copper compounds 5 and **6** are monomeric species with the metal in a pentacoordinated $[N_4O]$ environment. In all the compounds, the main interactions responsible for the crystal packing are classic (N-H···O, O-H···N and O-H…O) and non-classic (C-H…O and C-H…N) hydrogen bond interactions, and π interactions $(\pi - \pi - \text{stacking and } C - H \cdots \pi)$. All compounds were also characterized by microanalysis, IR spectroscopy, FAB mass spectrometry and ¹H NMR spectroscopy. Magnetic susceptibility data were measured for 2-4 over the temperature range 2-300 K, and their analysis has revealed the occurrence of intramolecular antiferromagnetic coupling for 2 ($J = -2 \text{ cm}^{-1}$) and ferromagnetic coupling for 3 ($J = 7.8 \text{ cm}^{-1}$) and 4 $(J = 2.8 \text{ cm}^{-1})$ [J being the isotropic magnetic coupling parameter]. The nature of the magnetic coupling in 2-4 is correlated with the magnitude of the M–O_{phenolate}–M angle between the phenolate bridge and the metallic centers [M(n) = Co, Ni]. The *in vitro* antimicrobial properties of the novel ligand and its metal complexes were detected against Gram positive and Gram negative bacteria and fungi. [NiL(bpy)]₂ and all tested Cd(II) complexes were the most active compounds, showing the highest inhibitory effect against bacilli (MIC 1.5–3 μ g mL⁻¹) and Sarcina, Streptococci and Haemophilus influenzae bacterial strains (MIC 12–50 μ g mL⁻¹), while almost no antifungal properties were observed.

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Introduction

The coordination chemistry of dinucleating ligands has been widely investigated. The interest in these ligands arises from

their ability to form dinuclear complexes which are of great importance not only in the development of new catalysts,¹ but also for their use for modelling the chemical environment in many metalloenzymes and metalloproteins that contain two metal ions in their active site.^{2–4} Dinuclear metalloproteins are very common in nature and despite their variety of functions, most of them share important structural characteristics. Regardless of the nature of the metal atoms, in the majority of dinuclear metalloenzymes and metalloproteins the metals are bridged by at least one oxo species (aqua, hydroxido, oxido ligands), derived from exogenous water.⁵ Thus, for example, the di-iron enzyme methane monooxygenase, which selectively oxidises methane to methanol using dioxygen,⁶ and manganese catalase, a dinuclear manganese containing enzyme

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which decomposes hydrogen peroxide,⁷ present an oxo-bridge and a carboxylate bridge between the metal atoms, which is also very common in dinuclear metalloproteins. Examples of di-copper enzymes are tyrosinase,⁸ which uses dioxygen in the hydroxylation of monophenols to o-diphenols and for the twoelectron oxidation of o-diphenols to o-quinones, and cathechol oxidase, which catalyzes the oxidation of catechols to quinones without acting on tyrosine.⁹ Both of them present a dinuclear active site with three hystidine ligands per copper atom and an additional µ-hydroxo bridge between the metal ions.¹⁰ Urease, a dinuclear nickel enzyme which catalyzes the hydrolysis of urea to produce ammonia and carbamate,^{11,12} presents a water bridge and a carboxylate bridge between the two nickel atoms. Similarly, the active site of metalloprotease methionine aminopeptidase contains two cobalt ions bridged by two carboxylate groups from the protein and by a hydroxyl group (or a water molecule).¹³ The same type of water and carboxylate bridges between metal ions can be found in various hydrolytic zincenzymes that mediate the cleavage of amides, phosphates, antibiotics (β -lactams), and other biologically important substrates.12,14

The presence of oxygen-donor bridges between the metal atoms in most natural di-metallic proteins has inspired the production of small-molecule biomimetic dinuclear complexes with bridging oxygen groups, mainly carboxylate¹⁵ and phenoxo^{15c,d,16} bridges, although different bridging N-donors have also been explored.^{15b,17} The phenolate bridge, in particular, with a strong σ - and π -donating oxygen atom, is an excellent bridging group that gives rise to dinuclear complexes with short metal–metal distances, which is important to mimic the behavior of some metalloenzymes, like di-copper catechol oxidase.⁸

Besides their biological interest, the dinuclear complexes with phenolate bridging ligands between paramagnetic metal ions often show interesting magnetic properties. In particular, dinucleating ligands that contain a potentially bridging phenoxo oxygen and nitrogen donor atom sets have been widely used in the synthesis of dinuclear complexes of copper,^{18,19} manganese,²⁰ cobalt,²¹ iron²² and zinc.²¹ As in other hydroxo- and alkoxo-bridged metal complexes, the nature of the magnetic interactions in phenoxo-bridged metal systems is primarily determined by the M–O–M angle and the M···M separation.²³ The understanding of the magnetic properties of such dinuclear species is important in order to explain, for example, the role of these metal ions in living systems.^{4,24}

For these reasons, and as a result of our continuing interest in the chemistry of dinuclear metal complexes, we now report the synthesis of metal(\mathfrak{n}) complexes with the 1*H*-anthra[1,2-*d*] imidazol-6,11-dione-2-[2-hydroxyphenyl] ligand [H₂L], which has the ability to form dinuclear metal species through oxygen atoms as bridges between two metal atoms. Due to the presence in the potential dinucleating ligand of weakly acidic N–H and O–H groups (Scheme 1), the homoleptic complexes were prepared using an electrochemical procedure where the metal is the anode of a cell containing the ligand in solution.²⁵ The



presence in the electrolytic cell of the ligand H_2L and additional coligands, such as 2,2'-bipyridine or 1,10-phenanthroline, allows the synthesis of heteroleptic compounds in one step. This method has been successfully used for the synthesis of metal compounds with other ligands having weak acid groups, such as thiol,^{26,27} NH²⁸ or hydroxyl groups.^{18,29} The new ligand and its corresponding metal complexes were investigated for their antimicrobial properties against some types of Gram positive and Gram negative bacteria, yeasts and mould.

Experimental

General

Cobalt, nickel, copper, zinc and cadmium (Aldrich Chemie) were used as plates (*ca.* 2×2 cm). All other reagents, including solvents, 2,2'-bipyridine, 1,10-phenanthroline, 1,2-diamino-anthraquinone and salicylaldehyde, were commercial products and were used as supplied.

Microanalyses were performed using a PerkinElmer 240B microanalyzer. IR spectra were recorded as KBr mulls on a Bruker IFS-66 V spectrophotometer. The ¹H spectra of the ligand and complexes were recorded on a Bruker WM 350 MHz spectrometer using the DMSO-d₆ solvent. The chemical shifts were recorded against TMS as the internal standard. FAB mass spectra were recorded on a Micromass Autospec instrument, using 3-nitrobenzyl alcohol (3-NBA) as the matrix material. Variable temperature magnetic susceptibility measurements were carried out using microcrystalline samples (20-60 mg) of compounds 2-4, using a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet, operating at 0.1-0.5 T and at temperatures from 300-1.8 K. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants.

Synthesis of 1*H*-anthra[1,2-*d*]imidazole-6,11-dione-2-[2-hydroxyphenyl] (H₂L). The ligand (H₂L) was synthesized by reacting 1,2-diaminoanthraquinone (1.0 g, 2.93 mmol) in absolute ethanol (175 mL) with salicylaldehyde (0.44 mL, 4.10 mmol) using *p*-toluenesulfonic acid (30 mg) as the catalyst (Scheme 2). The reaction mixture was heated to reflux with



constant stirring, changing color from yellow to brown. The water produced during the synthesis process was periodically purged from the Dean-Stark trap. The reaction was followed by thin layer chromatography, using a mixture of hexane/ethyl acetate (5:1) as the eluent, until the complete disappearance of the starting products. Thus, after 12 hours the heating was stopped and the solution was cooled to room temperature. The greenish precipitate formed was filtered, washed with absolute ethanol and diethyl ether and dried under vacuum. Yield: 1.20 g (3.53 mmol, 84%). Suitable crystals for X-ray diffraction were obtained by crystallization of the compound from a 1:1 mixture of MeOH and CH₂Cl₂. Anal. found: C, 73.72; H, 3.59; N, 8.26. Calc. for C₂₁H₁₂N₂O₃ (340.3): C, 74.11, H 3.55, N 8.23. IR (KBr, cm⁻¹): 3354(s); 1666 (s), 1629 (w), 1589(s), 1523(s), 1478(s), 1327(m), 1295(s). ¹H NMR (DMSO-d₆, ppm): 12.8 (s, 1H), 8.4 (s, 1H), 8.2 (s, 2H), 8.1 (s, 2 H), 7.8 (s, 2H), 7.6 (t, 1H), 6.9 (t, 2H), 4.1 (s, 1H). MS (FAB), m/z: 340 [H₂L].

Electrochemical synthesis

The complexes were obtained following an electrochemical procedure.²⁵ The cell consisted of a 100 mL tall-form beaker fitted with a rubber bung through which the electrochemical leads entered. A solution of either the ligand or the ligand/coligand (1,10-phenanthroline or 2,2'-bipyridine) mixture containing about 10 mg of tetraethylammonium perchlorate as a current carrier was electrolyzed using a platinum wire as the cathode and a metal plate suspended from another platinum wire as the sacrificial anode (Caution: perchlorate compounds are potentially explosive and should be handled in small quantities and with great care). Direct current was supplied by using a purpose-built d.c. power supply. Applied voltages of 5-15 volts allowed sufficient current flow for smooth dissolution of the metal. In all cases, hydrogen was evolved at the cathode. The cell can be summarized as $Pt_{(-)}/solvent + H_2L +$ $L'/M_{(+)}$, where H_2L represents the quinone ligand, L' is the additional ligand and M is either Co, Ni, Cu Zn or Cd. After electrolysis, the crystalline solids obtained were filtered, washed with acetonitrile and diethyl ether and dried under vacuum.

Synthesis of [CoL]. Electrolysis of a solution of the ligand (0.0634 g, 0.186 mmol) in acetone (50 cm³) at 12 V and 10 mA for 1 h dissolved 10.7 mg of cobalt from the anode, $E_f =$

0.49 mol F⁻¹. At the end of the experiment, the brown solid obtained was isolated, washed with ether and dried. Yield: 0.0518 g (0.120 mmol, 65%). Crystals of $[CoL(MeOH)]_2$ (2) suitable for X-ray studies were obtained by crystallization of the initial product from MeOH : CH₂Cl₂ (1 : 1). Anal. found: C, 61.25; H, 2.93; N 6.76%. Calc. for C₂₂H₁₄CoN₂O₄ (429.02): C, 61.53; H, 3.29; N, 6.53. IR (KBr, cm⁻¹): 1663(s), 1594(s), 1301(s), 717(s). MS(FAB), *m/z*; 662 [Co₂L₂ - N₂CHPhO], 646 [Co₂L₂ - N₂CHPhO₂], 398 [CoL]. UV-visible (cm⁻¹): 7280, 10 870, 14 900, 17 550.

Synthesis of [CoL(bpy)]. A similar experiment to those described above (8 V, 10 mA, 1 h) with H₂L (0.0634 g, 0.186 mmol) and 2,2'-bipyridine (0.030 g, 0.186 mmol) in acetone (50 cm³) led to the dissolution of 11.4 mg of metal, $E_{\rm f} = 0.52$ mol F⁻¹. The crystals deposited in the cell were isolated, washed with acetonitrile and ether and dried under vacuum. Yield: 0.0981 g (0.161 mmol, 87%). The brown solid was characterised as [CoL(bpy)]·3H₂O. Anal. found: C, 60.77; H, 3.83; N, 8.98%. Calc. for C₃₁H₂₄CoN₄O₆ (607.49): C, 61.29; H, 3.98; N, 9.22. IR (KBr, cm⁻¹): 1651(m), 1324(s), 1292(s), 763(s), 722(w). MS(FAB), *m/z* 1107 [Co₂L₂(bpy)₂], 950 [Co₂L₂(bpy)], 554 [CoL(bpy)], 398 [CoL]. UV-visible (cm⁻¹): 7930, 15 720, 17 420.

Synthesis of [CoL(phen)]. A solution of the ligand (0.0634 g, 0.186 mmol) and 1,10-phenanthroline (0.033 g, 0.186 mmol) in acetone (50 cm³) was electrolyzed at 10 V and 10 mA for 1 h and 10.6 mg of metal was dissolved from the anode, $E_f = 0.48 \text{ mol F}^{-1}$. At the end of the reaction the purpura solid obtained was filtered, washed with acetone and dried under vacuum. Yield: 0.0782 g (0.126 mmol, 73%). Crystals of [CoL(phen)] (3) suitable for X-ray studies were obtained from the mother liquor. Anal. found: C, 68.13; H 3.07; N, 9.30%. Calc. for $C_{33}H_{18}CoN_4O_3$ (577.07): C, 68.62; H, 3.14; N, 9.71%. IR (KBr, cm⁻¹): 1668(s), 1518(s), 1329(s), 1292(s), 841(w), 717 (m). MS(FAB), *m/z* 1155, [Co₂L₂(phen)₂], 975 [Co₂L₂(phen)], 578 [CoL(phen]], 398 [CoL]. UV-visible (cm⁻¹): 7450, 15 650, 17 513.

Synthesis of [NiL]. Electrolysis of a solution of the ligand (0.0634 g, 0.186 mmol) in acetone (40 mL) at 9.2 V and 10 mA for 1 h dissolved 10.2 mg of nickel from the anode, $E_f = 0.47$ mol F⁻¹. At the end of the experiment, the blue solution obtained was concentrated under vacuum and the blue solid obtained was isolated, washed with acetonitrile and ether and dried under vacuum. Yield: 0.0706 g (0.163 mmol, 88%). The red solid was characterised as [NiL]·2H₂O. Anal. found: C, 58.48; H, 3.16; N, 6.07. Calc. for C₂₁H₁₄NiN₂O₅ (432.02): C, 58.33; H, 3.27; N, 6.48; IR (KBr, cm⁻¹): 1665(s), 1558(s), 1294(s), 714(s). MS(FAB), *m/z*; 660[Ni₂L₂ - N₂CHPhO], 644 [Ni₂L₂ - N₂CHPhO₂], 398 [NiL]. UV-visible (cm⁻¹): 9025, 15 530.

Synthesis of [NiL(bpy)]. A solution of the ligand (0.0634 g, 0.186 mmol) and 2,2'-bipyridine (0.030 g, 0.186 mmol) in acetone (50 cm³) was electrolyzed at 11 V and 10 mA for 1 h; 10.3 mg of nickel metal was dissolved from the anode, $E_f = 0.47$ mol F⁻¹. At the end of the experiment, the compound obtained as a solid at the bottom of the cell was isolated, washed with acetone and ether and dried under vacuum. Yield: 0.0954 g (0.167 mmol, 90%). The red solid was characterised as [NiL(bpy)]·H₂O. Anal. found: C, 64.82; H, 3.43; N,

9.57%. Calc. for $C_{31}H_{20}NiN_4O_4$ (571.21): C, 65.17; H, 3.53; N, 9.81%. IR (KBr, cm⁻¹): 1665(s), 1326(s), 1294(s), 754(s), 714(s). MS(FAB), m/z 1107[Ni₂L₂(bpy)₂], 951[Ni₂L₂(bpy)], 553 [NiL(bpy)], 397 [NiL]. UV-visible (cm⁻¹): 8860, 15 800, 20 400. Crystallization of the compound from methanol produced crystals of the methanol solvate suitable for X-ray studies, [NiL(bpy)]₂·2.25(MeOH)·0.5(H₂O) (4).

Synthesis of [NiL(phen)]. A solution of the ligand (0.0634 g, 0.186 mmol) and 1,10-phenanthroline (0.033 g, 0.186 mmol) in a 1:1 mixture of methanol and benzene (40 mL) was electrolysed at 10 mA for 1 h., dissolving 10.7 mg of the metal from the anode, $E_{\rm f}$ = 0.48 mol F⁻¹. At the end of the reaction the violet solid obtained was filtered, washed with acetone and dried under vacuum. Yield: 0.0903 g (0.143 mmol, 77%). The solid was characterised as [NiL(phen)]·3H₂O. Anal. found: C, 62.38; H, 3.68; N, 8.76%. Calc. for C₃₃H₂₄NiN₄O₆ (631.27): C 62.79; H, 3.83; N, 8.88%. IR (KBr, cm⁻¹): 1647(m), 1515(m), 1324(m), 841(m), 717(s). MS(FAB), *m*/z 1155 [Ni₂L₂(phen)₂], 975 [Ni₂L₂(phen)], 577[NiL(phen)], 397 [NiL]. UV-visible (cm⁻¹): 7660, 9025, 15 620, 17 820.

Synthesis of [CuL]. Electrolysis of a solution of the ligand (0.1268 g, 0.373 mmol) in methanol (40 mL) for 1 h at 10 mA dissolved 23.5 mg of copper, $E_{\rm f} = 0.99$ mol F⁻¹. The brown solid formed was filtered, washed with methanol and diethyl ether and dried under vacuum. Yield: 0.126 g (0.30 mmol, 80%). The solid was characterised as [CuL]·H₂O. Anal. found: C, 60.31; H, 3.00; N, 6.94%. Calc. for C₂₁H₁₂CuN₂O₄ (419.88): C, 60.07; H, 2.88; N, 6.67%. IR (KBr, cm⁻¹): 1648(s), 1601(m), 1314(s), 718(s). MS(FAB), *m*/*z* 402 [CuL]. UV-visible (cm⁻¹): 14 900, 16 300.

Synthesis of [CuL(bpy)]. An acetone solution of the ligand (0.1268 g, 0.373 mmol) and 2,2'-bipyridine, (0.0582 g, 0.373 mmol) was electrolysed at 10 mA for 1 hour, dissolving 24.2 mg of metal from the anode, $E_f = 1.02 \text{ mol F}^{-1}$. The brown solid obtained at the end of the reaction was filtered, washed with ether and dried under vacuum. Yield: 0.173 g (0.31 mmol, 83%). The solid was characterised as [CuL(bpy)]. Anal. found: C, 66.40; H, 3.54; N, 9.58%. Calc. for C₃₁H₁₈CuN₄O₃ (558.06): C, 66.72; H, 3.25; N, 10.04%. IR (KBr, cm⁻¹): 1666(s), 1327(m), 1295(s), 770(w), 715(s). MS(FAB), *m/z* 402 [CuL], 341 [L]. UV-visible (cm⁻¹): 15 720, 22 300. Crystals of [CuL(bpy)]-MeOH (5) suitable for X-ray studies were obtained by crystallization from methanol.

Synthesis of [CuL(phen)]. A solution of the ligand (0.1268 g, 0.373 mmol) and phenanthroline (0.0671 g, 0.373 mmol) was electrolysed at 10 mA for 1 hour, dissolving 23.3 mg of metal from the anode, $E_{\rm f} = 0.98$ mol F⁻¹. At the end of the reaction the solid obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.184 g (0.30 mmol, 80%). The red solid was characterised as [CuL(phen)]·2H₂O. Anal. found: C, 64.01; H, 3.48; N, 8.96%. Calc. for C₃₃H₂₂CuN₄O₅ (618.10): C, 64.12; H, 3.59; N, 9.06%. IR (KBr, cm⁻¹): 1648(m), 1516(m), 1330(s), 842(s), 724(s). MS(FAB), *m*/*z* 582 [CuL(phen)], 242 [Cu(phen)]. UV-visible (cm⁻¹): 15 600, 21 000. Red crystals of [CuL(phen)]·(C₃H₆O) (**6**) suitable for X-ray studies were obtained by crystallisation of the product from acetone.

Synthesis of [ZnL]. A solution of the ligand (0.1268 g, 0.373 mmol) in acetonitrile was electrolysed at 10 mA for two hours, dissolving 23.6 mg of the zinc from the anode, $E_{\rm f} = 0.48 \text{ mol F}^{-1}$. At the end of the electrolysis, the solid obtained was recovered, washed with diethyl ether and dried under vacuum. Yield: 0.113 g (0.28 mmol, 75%). The brown solid was characterised as [ZnL]. Anal. found: C, 63.02; H, 2.93; N, 7.06%. Calc. for C₂₁H₁₀ZnN₂O₃ (403.71): C, 62.48; H, 2.50; N, 6.94%. IR (KBr, cm⁻¹): 1667(s), 1590(m), 1327(s), 717(s).

Synthesis of [ZnL(bpy)]. A solution of the ligand (0.1268 g, 0.373 mmol) and 2,2'-bipyridine (0.0582 g, 0.373 mmol) in methanol (40 mL) was electrolysed for 2 hours at 10 mA, dissolving 25.3 mg of metal, $E_{\rm f} = 0.51$ mol F⁻¹. The insoluble solid obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.173 g (0.31 mmol, 80%). The brown solid was characterised as [ZnL(bpy)]. Anal. found: C, 66.34; H, 3.28; N, 9.87%. Calc. for C₃₁H₁₈ZnN₄O₃ (559.89): C, 66.50; H, 3.24; N, 10.01% IR (KBr, cm⁻¹): 1660(s), 1326(m), 1293(s), 755(m), 723(s). MS(FAB), *m/z* 1119 [Zn₂L₂(bpy)₂], 965 [Zn₂L₂(bpy)], 809 [Zn₂L₂], 403 [ZnL].

Synthesis of [ZnL(phen)]. A solution of the ligand (0.1268 g, 0.373 mmol) and 1,10-phenanthroline (0.0671 g, 0.373 mmol) in methanol (40 mL) was electrolysed for 2 hours at 10 mA, dissolving 24.9 mg of zinc, $E_{\rm f} = 0.51$ mol F⁻¹. The insoluble solid obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.176 g (0.28 mmol, 76%). The reddish solid was characterised as [ZnL(phen)]·2H₂O. Anal. found: C, 63.97; H, 3.58; N, 8.94%. Calc. for C₃₃H₂₂ZnN₄O₅ (619.94): C, 63.93; H, 3.58; N, 9.04% IR (KBr, cm⁻¹): 1663(m), 1517(m), 1320(m), 1293(s), 844(m), 722(m). ¹H NMR (DMSO-d₆, ppm): 8.3–6.50 (m, 10H), 8.75 (d, 2H), 8.73 (d, 2H), 8.54 (d, 2H), 8.58 (s, 2H).

Synthesis of [CdL]. A solution of the ligand (0.1268 g, 0.373 mmol) in acetonitrile (40 mL) was electrolysed at 10 mA for 2 h, dissolving 40.7 mg of cadmium from the anode, $E_{\rm f}$ = 0.48 mol F⁻¹. At the end of the experiment, the violet solid deposited at the bottom of the cell was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.146 g (0.32 mmol, 87%). The solid was characterised as [CdL]. Anal. found: C, 55.58; H, 2.50; N, 6.34%. Calc. for C₂₁H₁₀CdN₂O₃ (450.73): C, 55.96; H, 2.24; N, 6.22%. IR (KBr, cm⁻¹): 1667(s), 1590(s), 1327(m), 714(s). ¹H NMR (DMSO-d₆, ppm): 8.3–6.7 (m, 10H).

Synthesis of [CdL(bpy)]. A solution of the ligand (0.1268 g, 0.373 mmol) and 2,2'-bipyridine (0.0582 g, 0.373 mmol) in methanol (40 mL) was electrolysed at 10 mA for 2 h, dissolving 41.1 mg of metal dissolved, $E_f = 0.49 \text{ mol F}^{-1}$. At the end of the experiment, the solid obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.204 g (0.34 mmol, 90%). The brown solid was characterised as [CdL (bpy)]. Anal. found: C, 61.62; H, 3.05; N, 8.95%. Calc. for $C_{31}H_{18}CdN_4O_3$ (606.91): C, 61.35; H, 2.99; N, 9.23% IR (KBr, cm⁻¹): 1665(m), 1324(m), 750(m), 715(s). MS(FAB), *m/z* 607 [CdL(bpy)], 451 [CdL]. Crystals of [CdL(bpy)]_2·3(MeOH) (7) suitable for X-ray studies were obtained by crystallization from methanol.

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Synthesis of [CdL(phen)]. A solution of the ligand (0.1268 g, 0.373 mmol) and 1,10-phenanthroline (0.0671 g, 0.373 mmol) in methanol (40 mL) was electrolysed at 10 mA for 2 h, dissolving 41.3 mg of cadmium, $E_{\rm f} = 0.49$ mol F⁻¹. The solid obtained was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.188 g (0.29 mmol, 80%). The brown solid was characterised as [CdL(phen)]. Anal. found: C, 62.52; H, 2.75; N, 8.46%. Calc. for C₃₃H₁₈CdN₄O₃ (630.93): C, 62.82; H, 2.88; N, 8.88% IR (KBr, cm⁻¹): 1665(m), 1515(m), 1326(m), 1290(m), 850(m), 722(m). ¹H NMR (DMSO-d₆, ppm): 8.2–6.8 (m, 14H), 9.0 (d, 2H), 8.8 (d, 2H). MS(FAB), *m/z* 1262 [Cd₂L₂(phen)₂], 1082 [Cd₂L₂(phen)], 630 [CdL(phen)].

X-Ray crystallography

Intensity data sets for all compounds except 4 were collected at 293 K with the use of a Smart-CCD-1000 Bruker diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) equipped with a graphite monochromator. The omega scans technique was employed to measure the intensities. The intensity data set for 4 was collected at 120 K with the use of a FR591-Kappa-CCD-2000 Bruker-Nonius diffractometer (CuK α radiation, $\lambda = 1.54180$ Å) equipped with a graphite monochromator. The omega and phi scans technique was employed to measure the intensities. No decomposition of the crystals occurred during data collection. The intensities of all data sets were corrected for Lorentz and polarization effects. Absorption effects in all compounds were corrected using the program SADABS.³⁰ The crystal structures of all compounds were solved by direct methods. Crystallographic programs used for structure solution and refinement were those of SHELXL-2014³¹ installed on a PC clone. Scattering factors were those provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in the subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2 , using anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms not involved in classical hydrogen bonding were placed geometrically and refined using a riding model, including free rotation about C-C bonds for methyl groups. For all compounds, hydrogen atoms were refined with Uiso constrained at 1.2 (for nonmethyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. Compound 3 presents two severely disordered molecules of acetone in the voids of the crystal lattice. This solvent was removed using the Squeeze program,32 implemented in Platon.³³ Compound 4 was a very weak diffractor. It was measured with a rotating-anode source diffractometer (CuK α radiation) to theta(max) = 65.14° with 93% completeness (data 98% complete to 58.93°), as it did not give detectable diffraction above that angle. This is reflected in the low precision of the structural parameters. The asymmetric unit of the crystal structure of 4 contains two nickel dimers, three and a half molecules of methanol and a molecule of water. One of the methanol molecules is disordered over two positions. The disorder was handled by introducing split positions for the disordered molecule in the refinement with the respective occupancies (70:30). This structure also contains a very disordered

molecule of methanol per asymmetric unit that was removed using the Squeeze program. The crystal structure of compound 5 contains a disordered molecule of methanol that was removed using the Squeeze program. The asymmetric unit of the crystal structure of 6 contains two copper complexes and two acetone molecules. Compound 7 did not give detectable diffraction above $\theta = 25.35^{\circ}$, which is responsible for the low bond precision. The crystal structure of 7 contains four methanol molecules per asymmetric unit, two of which are disordered over two positions with 55:45 and 65:35 occupancies.

Table S1[†] summarizes pertinent details of the data collection and the structure refinement of the crystal structures of compounds 1–7. Selected bond lengths and angles are listed in Tables S2–S6 of the ESI.[†] The program ORTEP3³⁴ was used to generate all the pictures. CCDC reference numbers: 1584238–1584244.[†]

Antimicrobial activity

The *in vitro* antimicrobial activity assessment of the new compounds was carried out determining their minimum inhibitory concentrations (MICs) against a range of bacteria and fungi by means of the broth two-fold dilution procedure.³⁵ For antibacterial tests, Gram positive *Bacillus megaterium* ATCC 19213, *Bacillus subtilis* ATCC 6633, *Sarcina lutea* ATCC 9341, *Staphylococcus aureus* ATCC 25923, clinical isolates of *Staphylococcus haemolyticus*, *Streptococcus agalactiae* and *Streptococcus faecalis* as well as Gram negative *Escherichia coli* ATCC 8739, *Haemophilus influenzae* ATCC 19418 and *Salmonella typhimurium* ATCC 14028 bacteria were selected. Among fungi, *Candida tropicalis* ATCC 1369 and *Saccharomyces cerevisiae* ATCC 9763 yeasts and *Aspergillus niger* ATCC 6275 mould were used as test microorganisms.

The compounds were dissolved in dimethyl sulfoxide. The solutions were diluted in the media (Haemophilus test medium for Haemophilus influenzae, Mueller Hinton broth for the other bacteria, and Sabouraud liquid medium for fungi) (Oxoid, Basingstoke, UK) in the final concentration range from 200 μ g mL⁻¹ to 0.003 μ g mL⁻¹. In all cases, DMSO never exceeded the amount of 1% v/v and blank tubes containing DMSO were also prepared for each microbial species and used as the control for solvents in the experiments. Aliquots of the bacterial and fungal suspensions were mixed with the chemicals to obtain an inoculum size of 5×10^5 colony forming units per mL and 5×10^3 cells per mL, respectively. Bacteria were then incubated at 37 °C for 24 h and fungi at 30 °C for 48 h. Ampicillin and miconazole were tested under identical conditions to those of antibacterial and antifungal positive references, respectively. In order to determine the minimum inhibitory concentration values (MIC, $\mu g \text{ mL}^{-1}$), the assessment of the lowest concentration of the compound that inhibits visible growth of the tested microorganisms was performed.

The minimum bactericidal concentrations (MBCs) and the minimum fungicidal concentrations (MFCs) were determined by subculturing on fresh sterile medium 100 μ L of culture until each sample remained clear. MBC and MFC values represented the lowest concentration of the compound (μ g mL⁻¹)

showing 99% inhibition after the incubation period of bacteria at 37 °C for 24 hours and of fungi at 30 °C for 48 hours.

Each experiment was performed under sterile conditions and repeated at least three times.

Results and discussion

Synthesis and spectral properties

Paper

The final product of the condensation of 1,2-diaminoanthraquinone and salicylaldehyde in the presence of *p*-toluenesulfonic acid as the catalyst is not the expected Schiff base (represented as HL¹ in Scheme 2), but the ligand 1*H*-anthra[1,2-*d*] imidazol-6,11-dione-2-[2-hydroxyphenyl] (H₂L). The isolation of the ligand H₂L indicates that the reaction involves the formation of the Schiff base (HL¹) in a first step, followed by an intramolecular nucleophilic attack on the iminic carbon atom by the nitrogen atom of the amino group (Scheme 2). The green solid obtained was characterized by elemental analysis, IR and ¹H NMR spectroscopy and mass spectrometry. Crystals of H₂L(1) suitable for X-ray studies were obtained (Fig. 1) by crystallization of the solid from a mixture of dichloromethane and methanol.

The new metal complexes were obtained by electrochemical oxidation of the appropriate metal (cobalt, nickel, copper, zinc or cadmium) in an electrolytic cell containing a solution of the ligand. This method represents a simple alternative to other standard chemical procedures.²⁵ Heteroleptic complexes with 2,2'-bipyridine or 1,10-phenanthroline as co-ligands were also obtained by addition of the corresponding coligand into the cell. In all cases, the elemental analysis shows that the metal ions react with the ligand at a 1:1 molar ratio to afford complexes of the bi-deprotonated ligand (L^{2–}).

The electrochemical efficiency $E_{\rm f}$, defined as the amount of metal dissolved per Faraday of charge, was calculated for all the electrochemical processes. In the case of the Co, Ni, Zn or Cd complexes the values of $E_{\rm f}$ were close to 0.5 mol F⁻¹ (see the Experimental part). These data and the evolution of hydrogen gas from the cathode are consistent with the following reaction scheme:

Cathode:

$$H_2L+2e^- \rightarrow H_2(g)+L^{2-}$$



Fig. 1 Ortep diagram of 1.

Anode:

Overall:

or

$$H_2L + M + L' \rightarrow [MLL'] + H_2(g)$$

 $M \rightarrow M^{2+} + 2 \ e^{-}$

 $H_2L + M \rightarrow [ML] + H_2(g)$

M = Co, Ni, Zn or Cd and L' = bpy or phen.

In the synthesis of the copper complexes, the values obtained for the electrochemical efficiency were always close to 1.0 mol F^{-1} . This fact together with the evolution of hydrogen gas from the cathode shows that 1 oxidation state species are the initial products of the electrochemical process, in agreement with the following reaction scheme: Cathode:

Cathod

Anode:

or

$$2\mathrm{Cu} \rightarrow 2\mathrm{Cu}^+ + 2e^-$$

 $H_2L + 2e^- \rightarrow H_2(g) + L^{2-}$

However, the analytical data show that the final products are compounds in which the copper atom is in π oxidation state. This suggests a subsequent oxidation in solution from Cu(π) to Cu(π) as soon as it is formed. In these cases, the overall reaction can be represented by:

 $Cu+H_2L \rightarrow [CuL]+H_2(g)$

$$Cu + H_2L + L' \rightarrow [CuLL'] + H_2(g)$$

where L' is bpy or phen.

A similar mechanism involving the electrochemical oxidation of Cu to Cu(1) followed by a further oxidation of Cu(1) to Cu(1) was also postulated for other Cu(1) complexes obtained *via* electrochemical oxidation of copper anodes.^{18,29}

The synthesis of [ML] complexes can be readily accomplished in good yields, by the simple one-step electrochemical procedure described above. The IR spectra of these complexes do not show the bands attributed to ν (O–H) and ν (N–H), which appear at 3354 cm⁻¹ in the IR spectra of the free ligand. In addition, the band attributed to ν (C–O), which appears at 1295 cm⁻¹ in the IR spectra of the free ligand, is shifted to higher wavenumbers $(1300-1330 \text{ cm}^{-1})$ in the complexes. These facts show that the amide and phenol protons are lost during the electrochemical synthesis and that the ligand is in the dianionic form in the complexes. The room temperature ¹H NMR spectrum of the cadmium complex only exhibits multiplet resonances in the aromatic region, δ 8.3–6.6 ppm, as the signals attributed to the NH and OH hydrogens, which appear at δ 4.10 and 12.80 ppm, respectively, in the NMR spectrum of the free ligand, are now absent.

The FAB mass spectra of the cobalt, nickel, and copper [ML] compounds show peaks due to the [ML] molecular ions, with the appropriate isotope distribution. In addition, peaks associated with fragments of the dinuclear species $[ML]_2^+$ are also observed in each case (see the Experimental section), which can be taken as an indication of the dimeric structure of these compounds.

The solid state electronic spectrum of the complex [CoL (MeOH)], obtained by crystallization of [CoL] from CH₂Cl₂/ CH₃OH, is consistent with a pentacoordinated environment around the cobalt(π).³⁶ The bands at 7280, 10 870, 14 900 and 17 550 cm⁻¹ are assigned to ${}^{4}A_{2}(F) \rightarrow {}^{4}B_{2}; {}^{4}A_{2}(F) \rightarrow {}^{4}E(F)$, ${}^{4}A_{2}(F) \rightarrow {}^{4}E(P)$ and ${}^{4}A_{2}(F) \rightarrow {}^{4}A_{2}(P)$ transitions in a square pyramidal geometry for the metal.³⁶ However, the spectrum may be interpreted as a trigonal bipyramidal geometry case given that the compound [CoL(MeOH)] has an intermediate structure between both symmetries (vide infra). The diffuse reflectance spectra of [NiL] and [CuL] show two bands at 9025 cm⁻¹ (ν_2) and 15 530 cm⁻¹ (ν_3) for the nickel compound and at 14 900 and 16 300 cm⁻¹ for the copper complex, which can be attributed to the ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(\nu_{2})$ and ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ (ν_3) , transitions, respectively, for a tetrahedral nickel(π) complex and to the ${}^{1}A_{1g}(F) \rightarrow {}^{1}B_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$, transitions for a square planar copper(II) complex.³⁶

The incorporation of additional bidentate ligands into the cell allows the synthesis of heteroleptic complexes of general formula [ML(bpy)] and [ML(phen)], M = Co, Ni, Cu, Zn, and Cd. These complexes show IR bands characteristic of the coordinated L2- ligand and also bands at around 770 and 715 cm^{-1} or at around 1515, 850 and 710 cm^{-1} typical of coordinated 2,2'-bipyridine and 1,10-phenanthroline, respectively. The ¹H NMR spectra of the heteroleptic complexes of zinc and cadmium show, besides the signals attributed to the quinone ligand, the signals due to coordinated 2,2'-bypiridine or 1,10-phenanthroline. In the case of the heteroleptic complexes of cobalt, nickel, zinc and cadmium, the FAB spectra show the peaks corresponding to the dinuclear species $[ML(bpy)]_2^+$ and $[ML(phen)]_2^+$, which are the structures that have been confirmed by X-ray diffraction in many instances (vide supra). In most cases the FAB spectra also show peaks corresponding to the monomeric species and other signals due to fragments formed by the loss of anthraquinone, bipyridine or phenanthroline moieties from the dinuclear species. In the case of the copper heteroleptic compounds, only in the spectrum of the phenanthroline derivative 5 the peak corresponding to the monomeric species at m/z 582 appears, which is the structure that has been confirmed for 5 by X-ray diffraction (vide infra). The mass spectrum of 6 shows the peak corresponding to the ion resulting from the loss of the anthraquinone ligand from the initial complex (m/z = 402) and the peak due to the free ligand, although the peak corresponding to the molecular ion is not observed.

Diffuse reflectance spectra of the heteroleptic complexes of cobalt(II), [CoL(bpy)] and [CoL(phen)], are typical of a d⁷ system in a high-spin octahedral environment. Thus, the complexes present in the UV-visible region three spin-allowed transitions in the ranges 7930–7450, 15720–15650 and 17520–17420 cm⁻¹ which are assigned respectively to the ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(\nu_{1}), {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(\nu_{2})$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{lg}(P)(\nu_{3})$

transitions in a distorted octahedral geometry for the metal. In both cases, the ν_1 band is split probably because of the distortion from the regular symmetry.³⁶ This geometry was confirmed in the case of the complex [CoL(phen)] by X-ray diffraction. The electronic spectra in the solid state of the heteroleptic compounds of $Ni(\pi)$ show bands in the regions 8860–7700, 15 800–15 600, and 17 820–20 400 cm⁻¹. These bands are within the expected range for octahedral Ni²⁺ complexes and can be assigned to the transitions: ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(\nu_{1}), {}^{3}A_{2g} \rightarrow$ ${}^{3}T_{1g}(F)(\nu_{2})$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)(\nu_{3})$, respectively, assuming a distorted octahedral geometry for the complex. The ν_1 band of the phenanthroline derivative (7660, 9025 cm⁻¹) is split probably as a consequence of its distorted octahedral symmetry.³⁶ Diffuse reflectance spectra of the heteroleptic complexes of copper(II) show two broad bands at 15 700 and 22 300 cm^{-1} for (5) and at 15 600 and 21 000 cm^{-1} for (6), which suggests a five-coordinate geometry of these complexes.36

X-ray crystal structure study

The molecular structure of the ligand **1** and the metal complexes **2–6** was determined by single crystal X-ray diffraction analysis.

Description of the crystal structures of 2, 3, 4, 5, 6, and 7

The asymmetric units of the crystal structures of **4** and **6** have two independent molecules. In these cases, only one of the complex molecules will be used for the structural discussion, as they are both very similar.

The cobalt(Π) compounds 2 and 3, the nickel(Π) compound 4 and the cadmium(Π) compound 7 are dimeric molecules with the metal atoms linked by phenoxo bridges (Fig. 2, 3, 4 and 5, respectively). In all dimers, the bridge is slightly asymmetric and the distance between the two metal atoms is high enough to suggest the absence of a binding interaction between them. In the case of the structures that involve transition metals, 2, 3 and 4, the four-membered ring formed by the two metal atoms and the two bridging oxygen atoms is flat, although in the case of the cadmium(Π) complex 7 this ring is bent [dihedral angle: 25.52(12)°].

In all dimers, each dianionic terdentate ligand $(L)^{2-}$ chelates one of the metal atoms through the imidazoline nitrogen atom and the keto and phenolate oxygen atoms, bridging the



Fig. 2 ORTEP diagram of the molecular structure of 2.



Fig. 3 ORTEP diagram of the molecular structure of 3.



Fig. 4 ORTEP diagrams of the molecular structures of 4.



Fig. 5 ORTEP diagrams of the molecular structures of 7.

other metal center through the phenolate oxygen atom. In compounds 2, 4 and 7, each one of the two $(L)^{2-}$ ligands chelates a different metal, giving rise to similar coordination environments for both metal centers. In the case of the cobalt dimer 2, each cobalt atom completes its coordination sphere coordinating a methanol (solvent) molecule, forming five-coordinate coordination entities, [CoO₄N], with an intermediate geometry between a trigonal bipyramid and a square pyramid (trigonality index $\tau = 0.49$).³⁷ In the case of the nickel dimer 4 and of the cadmium dimer 7, each metal atom achieves sixcoordination, [MO₃N₃], by binding an (N, N) chelating 2,2'bipyridine coligand, although the final geometries are very different. In compound 4 (Fig. 4), both nickel atoms show octahedral geometry, which is distorted due to the low value of the N-Ni-N bite angle forced by the chelating 2,2'-bipyridine coligand and the formation of the phenoxo bridge. In compound 7 (Fig. 5), the coordination geometry is different for both cadmium atoms. The values of the twist angles suggest distorted triangular prism geometry for Cd1 and a highly distorted octahedral geometry for Cd2 (see figures and data in the ESI, Fig. S1[†]).

In the case of the cobalt dimer 3, both $(L)^{2-}$ ligands chelate the same metal atom and bridge the other one, which is also bonded to the two chelating phenanthroline coligands (Fig. 3). Thus, the coordination environments for the cobalt atoms are different, [CoO₄N₂] and [CoN₄O₂], with distorted octahedral geometries. The degree of distortion is higher for the one bonded to the two phenanthroline coligands, as the main source of distortion is their small chelation angle, 77.03(9) and 77.14(10)°. These values are similar to those found in other six-coordinated cobalt(II) complexes with chelating phenanthroline ligands.³⁸ The complexes 5 and 6 consist of monomer units in which the copper atom is pentacoordinated to a (O, N, O) terdentate chelating dianionic ligand $(L)^{2-}$ and to a (N, N) chelating neutral coligand; 2,2'-bipyridine for 5 and 1,10-phenanthroline for 6 (Fig. 6). In both cases, the geometry is much closer to a square pyramid than to a trigonal bipyramid, as suggested by the geometric parameter τ (0.08 for 5 and 0.06 for 6),³⁷ with one of the nitrogen atoms of the coligand in the apical position.

The M–O bond distances involving the phenolic oxygen atoms are always shorter than the ones involving the ketonic group (Tables S3–S6†), showing a stronger interaction, as



Fig. 6 ORTEP diagram of the molecular structure of 5 (left) and 6 (right).

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expected. Thus, for example, the Co-O(phenoxo) distances in compound 2, 2.000(2) Å and 2.0850(19) Å, are within the range of 1.886-2.168 Å found in other pentacoordinated cobalt(II) complexes.^{18,39} These Co-O(phenoxo) distances are slightly longer in the octahedral compound 3, 2.0511(19)-2.0990(18) Å, as found for other six-coordinated cobalt(II) complexes with bridging phenoxy groups [2.0323-2.112 Å].40 The weaker Co-O (ketonic) interactions of both complexes are reflected in longer distances, 2.1723(19)-2.1817(19) Å, which are normal compared to similar ligands reported in the literature.⁴¹ In the case of compounds 4 and 7, the values of M-O(ketonic) and M-O(phenolic) distances, M = Ni, Cd, can also be considered normal, as they are similar to those found in other six-coordinated complexes of nickel(π)⁴² and cadmium(π).⁴³ The mononuclear copper complexes follow the same trend, with Cu–O(phenolate) distances typical of pentacoordinate copper(II) complexes,44 and longer Cu-O(ketone) bond distances. However, the Cu-O distances involving ketonic oxygen atoms [2.0622(19) Å in 5 and 2.101(2) Å in 6] are longer than usual, 1.908-1.969 Å.45

The Co–N(imidazole) bond distances of compounds 2 and 3 are very similar [range 1.982(2)–2.010(2) Å] but shorter than those found in related cobalt(II) complexes [2.128–2.163 Å].⁴⁶ This is also observed for the M–N distances of the mononuclear copper complexes 5 and 6, with shorter Cu–N(imidazole) distances than the normal range found in other pentacoordinated copper(II) complexes, 1.953–1.978 Å.⁴⁷ In the case of the six-coordinated dimeric compounds 4 and 7, these M–N distances are similar to those found in similar Ni(II)⁴⁸ or Cd(II)⁴⁹ complexes.

In compound 2, the value of the bond distance that involves the coordinated methanol molecule, Co–O(4): 1.985(2) Å, is shorter than the range found for other pentacoordinated cobalt(π) compounds containing methanol as a ligand [2.056–2.261 Å],⁵⁰ suggesting the presence of a stronger bond compared to the literature compounds.

The M–N distances involving the bipyridine (4, M = Ni; 7, M = Cd) or phenantroline (3, M = Co) coligands of the metal dimers are all normal and similar to those found in related six-coordinated $Co(\pi)$,³⁸ Ni(π),⁵¹ and $Cd(\pi)$ ⁵² complexes. In the case of the mononuclear square pyramidal copper complexes 5 (bpy) and 6 (phen), the Cu–N bond length involving the nitrogen atom on the basal plane [2.024(2) Å for 5 and 2.019(3) Å for 6] is shorter than the one involving the nitrogen atom on the apical position [2.256(2) Å for 5 and 2.271(3) Å for 6]. This behavior has been found in other pentacoordinated copper complexes with 2,2-bipyridine^{53,54} or 1,10-phenanthroline^{54,55} coligands.

Regarding the conformation of the coordinated dianionic ligand $(L)^{2-}$, the formation of the phenoxo bridges in the metal dimers produces a twist of the planar four-fused-ring moiety with respect to the planar phenol moiety, which is more pronounced with increasing coordination number around the metal center. Thus, although these two moieties are almost coplanar in the free ligand [dihedral angle: $4.33(9)^{\circ}$], they twist to $13.55(6)^{\circ}$ in both symmetry equivalent

ligands of the pentacoordinated cobalt dimer 2. In the hexacoordinated dimers 3, 4 and 7 the distortion is higher: $11.48(9)^{\circ}$ and $29.72(7)^{\circ}$ for the asymmetric cobalt dimer 3; $10.12(9)^{\circ}$ and $21.29(8)^{\circ}$ (unit 1) and 14.62(9) and $23.57(9)^{\circ}$ (unit 2) for the nickel dimer 4; and $16.55(19)^{\circ}$ and $25.44(16)^{\circ}$ for the cadmium dimer 7. In the case of the monomer copper compounds 5 and 6, the four-fused-ring moiety and the phenol moiety remain almost coplanar, like in the free ligand $[6.30(23)^{\circ}$ for 5 and $3.21(20)^{\circ}$ (unit 1) and $10.80(84)^{\circ}$ (unit 2) for 6].

In all cases, the C–O distances of the ketone groups of the quinone moiety [range 1.216(7)-1.257(3) Å] have similar values to those found in the free ligand [average value 1.227(3) Å], although the bond distance involving the coordinated oxygen atom is always slightly longer. This fact suggests that the ligand is in its completely oxidized form, as other metal complexes with the ligand in its semiquinone or catecholate forms show C–O distances in the ranges 1.27-1.30 Å and 1.34-1.36 Å, respectively. Thus, the electrochemical process has only involved the deprotonation of the ligand.

A description of the crystal packing of compounds 1–7 is given in the ESI (Fig. S2–S19 and Tables S7–S9†).

Comparison of the crystal structures

The dianionic ligand $(L)^{2-}$ is a (ONO) tridentate chelating ligand. The coordination of $(L)^{2-}$ to a M(II) metal ion is enough to balance its charge but does not produce a coordinatively saturated complex. The dimerization through the formation of a µ-phenoxo bridge increases the coordination number to four. However, the geometry imposed by the planar (ONO) ligand $(L)^{2-}$ implies that the final geometry of the metal in the dimer will be square planar. Incidentally, this is the proposed geometry for the dimeric complex [CuL], as suggested by the diffuse reflectance spectrum (vide supra). In the case of other M(II)ions that do not give stable square planar geometry (Co²⁺, Ni²⁺, Cd^{2+}) the µ-phenoxo dimer has to be stabilized by coordination of other ligands. Coordination of monodentate ligands, like methanol solvent molecules, produces five-coordinate metal centers, as observed for the Co²⁺ ions in the crystal structure of 2. The use of bidentate (N, N) chelating coligands, such as bpy and phen, can complete the six-coordination for the metal atom. The analysis of the molecular structures of 4 and 7 (vide supra) shows that the chelating ligand $(L)^{2-}$ is capable of stabilizing different geometries around the six-coordinated metal atom.

In the case of compound **3**, the use of a phenantroline coligand also produces six-coordinate (octahedral) geometry for both cobalt(II) atoms. However, the final structure is unexpected as it shows asymmetrical environments for the cobalt atoms, $[N_4O_2]$ and $[O_4N_2]$. This is the result of the coordination of both dianionic $(L)^{2-}$ ligands to one cobalt atom, forming a $[Co^{II}(L)_2]^{2-}$ entity, and the coordination of the two phenantroline coligands to the other cobalt atom, forming a $[Co^{II}(phen)_2]^{2+}$ entity. An analysis of the CCDC database (CCDC Version 5.38, November 2016) reveals the rarity of this structure **3**. The search shows that there are only **6** structurally

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characterized Co(II) dimers with two terdentate ligands with a lateral phenoxo group that bridges the cobalt atoms.^{56,57} In all cases, the structures are symmetrical, with a monodentate ligand completing five coordination⁵⁶ as in complex 2 or with two monodentate ligands per cobalt atom, completing six coordination.⁵⁷ In these latter cases described in the literature, the final structures are not as those found in complexes 4 or 7, as the $[Co_2L_2]$ system forms a plane with the monodentate ligands in apical positions. In any case, it is important to stress the symmetrical nature of the related literature complexes. The only related asymmetrical cobalt(II) dimers included in the CCDC database are two examples of complexes of the type [Co(ter-L)₂][CoCl₂], where (ter-L) is a monoanionic terdentate ligand, in which the two terdentate ligands coordinate an octahedral cobalt atom, as in 3, and the phenoxo groups bridge a [CoCl₂] unit, with a tetrahedral cobalt atom.^{58,59} However, in these cases the terdentate ligands are monoanionic and not planar, favoring facial coordination. With dianionic terdentate bridging phenoxo ligands, this type of $\{Co^{II}[(ter-L)]_2\}^{2-}$ unit has only been observed in cobalt(II) trimers of general formula $Co^{II} \{Co^{II} [(ter-L)]_2\}$, in which the central cobalt atom tetrahedrally coordinates the four bridging oxygen atoms, giving rise to symmetrical trimers.^{59,60} However, in these trimers the ligands are not planar and also favor facial coordination.

It is interesting to note that the literature does not present examples of cobalt(II) μ -phenoxo dimers with bidentate coligands, so no cobalt analogs of the nickel dimer 4 or the cadmium dimer 7 are known. In any case, the symmetrical dimer was the expected structure for 3.

In the case of the Cu(II) complexes 5 (bpy) and 6 (phen), the coordination of the dianionic ligand $(L)^{2-}$ and of a (N, N) coligand gives rise to stable five-coordinate mononuclear complexes, so no dimerization is observed.

Magnetic properties

To assess the nature and extent of magnetic exchange between the two cobalt(II) ions in 2 and 3 and between the two nickel(II) ions in 4, variable-temperature (2-300 K) magnetic susceptibility measurements were carried out on powder samples. Fig. 7(a-c) display the $\chi_M T$ product vs. T for 2, 3 and 4 (where $\chi_{\rm M}$ is the magnetic susceptibility per mol of the compound and T is the temperature). The values of $\chi_{\rm M}T$ at 300 K are 4.35, 4.65 and 2.35 cm³ K mol⁻¹ for 2, 3 and 4, respectively. These values are consistent with the expected ones for two uncoupled $cobalt(\pi)$ or $nickel(\pi)$ with some orbital contribution. Upon cooling, the $\chi_M T$ value of 2 is almost constant in the temperature interval 300-150 K, and then decreases more markedly at temperatures below 100 K reaching a value of *ca.* 1.0 cm³ K mol⁻¹ at 2 K. This behavior indicates the occurrence of weak antiferromagnetic coupling between the two cobalt(II) ions in 2. However, no maximum was observed for the $\chi_{\rm M}$ vs. T plot most probably due to very weak magnetic coupling and/or the presence of some paramagnetic impurities. In contrast to 2, the $\chi_M T$ values of 3 gradually increase with decreasing T indicating the occurrence of ferromagnetic exchange interaction. The $\chi_{M}T vs. T$ plot displays a



Fig. 7 Thermal dependence of the product $\chi_M T$ for compounds 2 (a), 3 (b) and 4 (c). The circles represent experimental data and the solid line the fit of the data.

maximum value of 6.89 cm³ K mol⁻¹ at 10 K. The decrease of the $\chi_{\rm M}T$ product below this temperature can be attributed to the occurrence of zero-field splitting (ZFS) and/or intermolecular antiferromagnetic exchange interactions. Similarly to **3**, the $\chi_{\rm M}T$ value for **4** continuously increases to reach a value of 3.44 cm³ K mol⁻¹ at 2 K also indicating the presence of intramolecular ferromagnetic coupling.

High-spin cobalt(π) in regular octahedral surroundings has a ${}^{4}T_{1g}$ ground state. Because of the presence of first-order spin orbit coupling in strict or nearly pure octahedral geometry the

magnetic properties of complexes with T ground terms are often found to show considerable temperature dependence, and interpreting them is difficult.^{2,61} However, when the lowering of the symmetry is strong enough to remove the orbital degeneracy of the ⁴T term only second-order spin orbit coupling is operative and the magnetic properties can be straightforwardly interpreted. This is clearly the situation for 2, which is a centro-symmetric species made up of two five-coordinated cobalt(II) ions defining a geometry half-way between a square planar pyramid and a trigonal bipyramid. Although the cobalt(II) ions are hexacoordinated in 3, the octahedra are distorted enough to eliminate the effects of first-order spin orbit coupling. Thus, the magnetic coupling of 2 and 3 has been satis factorily analyzed for dinuclear species with $S_1 = S_2 = 3/2$ from the isotropic Heisenberg-Dirac-van Vleck (HDVV) spin exchange Hamiltonian $H = -JS_1S_2 + \Sigma_i g_i\beta HS_i$ (*i* = 1,2) where J is the intradimer exchange interaction and S_i is the quantum spin operator.^{62,63} Similarly, the experimental data of 4 were fitted to the $\chi_{\rm M}T$ expression derived from the HDVV Hamiltonian for $S_1 = S_2 = 1$.

A least-squares fit of the data leads to $J = -2 \text{ cm}^{-1}$, g = 2.17and $\rho = 0.08$ (ρ accounts for monomeric paramagnetic impurities)⁶² for 2 and $J = 7.8 \text{ cm}^{-1}$ and g = 2.19 for 3. Although this simple approach is perfectly correct for 3 in the interval 300–12 K, it does not allow simulating the data below 12 K, which essentially reflect the ZFS of the dinuclear states. The best fit between experimental and calculated data was obtained for $J = 2.8 \text{ cm}^{-1}$ and g = 2.14 for 4. The solid lines in Fig. 7(a-c) correspond to the calculated curves using the obtained parameters and show an excellent agreement between the experimental and theoretical $\chi_{\rm M}T$ data.

One important difficulty in making general statements about trends in the magnitude of the coupling constant is the small number of structurally and magnetically characterized µ-phenoxo-bridged dinuclear cobalt(II) complexes.⁶⁴ Furthermore, the combination of the phenoxo bridge with other additional bridges (usually acetato) in the same molecular unit makes this analysis more difficult.65,66 In this respect, as far as we know, the number of µ-phenoxo-dibridged cobalt(II) complexes so far reported is even smaller.^{67–69} The coupling constant in these compounds is commonly rationalized in terms of the Co-Ophenoxo-Co angles and Co--Co intradimer distance.⁶⁵ Additional geometrical factors considering the fold angle along the O-O axis, the solid angle at the oxygen bridge, which affect the s/p character of the hybrid orbitals on the bridging oxygen atom, and electronic effects of the substituents on the phenol ring have been taken into account.⁶⁷ The weak antiferromagnetic J value, -2 cm^{-1} , found for 2 is close to that observed for the complexes $[Co_2L_2Cl_2(CH_3OH)_2]$ (HL = 3-[(furan-2-ylmethylimino)methyl]-2-hydroxy-5-methylbenzaldehyde) $(J = -4.22 \text{ cm}^{-1})^{68}$ and $[Co_2L_2]$ ·H₂O (H₂L = N,N-bis(4,5-dimethyl-2-hydroxybenzyl)-N-(2-pyridylmethyl)amine) $(I = -4.2 \text{ cm}^{-1})$.¹⁹ The three compounds display a similar Co-Ophenolate-Co angle, 100.21°, 99.5° and 100.8°, respectively. A larger antiferromagnetic J value, cm^{-1} , was observed for the related complex -7.5

[Co₂L]·1CH₃CN (H₂L = *N*,*N*-bis(3,4-dimethyl-2-hydroxybenzyl)-*N'*,*N'*-dimethylethylenediamine) ($J = -4.2 \text{ cm}^{-1}$), which shows a Co-O_{phenolate}-Co angle slightly larger (102.04°) than that for 2.¹⁸ In contrast, the ferromagnetic coupling ($J = 7.8 \text{ cm}^{-1}$) observed for complex 3 can be associated with the smaller Co-O_{phenolate}-Co angle of 97.05°. These data are consistent with the critical angle predicted for switching the sign of the coupling constant *J* in phenoxide-bridged compounds which is around 96–98°.^{65,70,71} Given that the average Ni–O–Ni angle is 97.1° for 4, the small positive *J* value obtained for the dinuclear nickel(π) derivative is explained in the same terms as for 3.

Antimicrobial activity

The *in vitro* antimicrobial properties of the novel ligand and its metal complexes were studied targeting the determination of their minimum inhibitory concentration (MIC) against several bacterial and fungal strains. In order to compare the effects, both 2,2'-bipyridine and 1,10-phenanthroline coligands were also included in the evaluation. The results are summarized in Table 1.

The H₂L ligand was completely devoid of antibacterial activity up to the concentration of 200 μ g mL⁻¹. On the other hand, a good inhibition was exhibited by the 1,10-phenanthroline coligand towards both Gram positive and Gram negative tested bacteria (MIC 12–50 μ g mL⁻¹) and, only in higher concentrations, by the other coligand 2,2'-bipyridine against Gram negative *Escherichia coli* and *Heamophilus influenzae* (MIC 100 μ g mL⁻¹) and Gram positive *Bacillus subtilis* (MIC 200 μ g mL⁻¹).

Among the metal complexes, all tested Cd(π) compounds and [NiL(bpy)]₂·2H₂O showed strong antibacterial activity towards Gram positive *Bacillus subtilis*, with MIC values ranging from 1.5 to 3 µg mL⁻¹, and good effectiveness for the Gram negative *Heamophilus influenzae* strain that was inhibited at concentrations of 12–25 µg mL⁻¹. The same microorganisms, as well as *Staphylococcus aureus*, were sensitive also to the Cu(π) complexes [CuL]·H₂O and [CuL(phen)]·2H₂O at 50–100 µg mL⁻¹ and to the Co(π) derivative [CoL(phen)]₂ at 200 µg mL⁻¹. Identical results were detected for [CoL(MeOH)]₂ against both *S. aureus* and *H. influenzae*. The Gram negative *Escherichia coli* strain was resistant to all the tested complexes up to the concentration of 200 µg mL⁻¹.

With regard to the results of antifungal activity, the new compounds had no significant effect on the growth of yeasts and mould under investigation. Only $[NiL(bpy)]_2 \cdot 2H_2O$ and all Cd(II) complexes showed a moderate inhibition of *Saccharomyces cerevisiae* at 100–200 µg mL⁻¹, although both parent coligands were found to be active against all tested fungi at 12–100 µg mL⁻¹.

The Cd complexes and [NiL(bpy)]₂·2H₂O, showing the highest antibacterial properties, were tested against a wide spectrum of other bacteria including Gram positive, such as *Bacillus megaterium* ATCC 19213, *Sarcina lutea* ATCC 9341, clinical isolates of *Staphylococcus haemolyticus*, *Streptococcus agalactiae*, *Streptococcus faecalis* and Gram negative, namely *Salmonella typhimurium* ATCC 14028 (Table 2). Interestingly,

Table 1 Antimicrobial activity, expressed as MIC (µg mL⁻¹) and, in brackets, as MBC (µg mL⁻¹) and MFC (µg mL⁻¹)

Compound	Bacteria ^a		Bacteria ^b		Fungi ^c		
	BS	SA	EC	HI	СТ	SC	AN
H ₂ L (1)	>200	>200	>200	>200	>200	>200	>200
2,2'-Bipyridine	200(>200)	>200	100(>200)	100(>200)	50(200)	25(200)	50(200)
1,10-Phenanthroline	12(100)	25(>200)	12(200)	12(200)	100(200)	12(100)	25(100)
$\left[\text{CoL}(\text{MeOH})\right]_2$ (2)	>200	200(>200)	>200	200(>200)	200(>200)	>200	>200
[CoL(bpy)]·3H ₂ O	>200	>200	>200	>200	>200	>200	>200
$[CoL(phen)]_2$ (3)	200(>200)	200(>200)	>200	200(>200)	>200	>200	>200
[NiL]	>200	>200	>200	>200	>200	>200	>200
$[NiL(bpy)]_2 \cdot 2H_2O(4)$	3(6)	>200	>200	12(100)	>200	>200	>200
[NiL(phen)]·3H ₂ O	>200	>200	>200	>200	>200	200(>200)	>200
CuL H ₂ O	50(100)	50(200)	>200	100(>200)	>200	>200	>200
[CuL(bpy)] (5)	>200	>200	>200	>200	>200	>200	>200
$[CuL(phen)] \cdot 2H_2O(6)$	50(100)	50(100)	>200	100>200	>200	>200	>200
[ZnL]	>200	>200	>200	>200	>200	>200	>200
[ZnL(bpy)]	>200	>200	>200	>200	>200	>200	>200
[ZnL(phen)]·2H ₂ O	>200	>200	>200	>200	>200	>200	>200
[CdL]	3(6)	>200	>200	25(100)	>200	100(>200)	>200
$\left[CdL(bpy)\right]_2(7)$	1.5(6)	>200	>200	12(25)	>200	100(>200)	>200
[CdL(phen)]	3(6)	>200	>200	12(50)	>200	200(>200)	>200
Ampicillin	0.03(0.3)	0.15(0.7)	6(12)	0.07(0.3)	—c	_ ` ´	_
Miconazole	_ ` `	_ ` `	_	_ `	3(25)	12(50)	3(25)

^{*a*} Gram positive bacteria: *Bacillus subtilis* ATCC 6633 (BS) and *Staphylococcus aureus* ATCC 25923 (SA); ^{*b*} Gram negative bacteria: *Escherichia coli* ATCC 8739 (EC) and *Haemophilus influenzae* ATCC 19418 (HI). ^{*c*} Yeasts: *Candida tropicalis* ATCC 1369 (CT) and *Saccharomyces cerevisiae* ATCC 9763 (SC); mould: *Aspergillus niger* ATCC 6275 (AN).

Table 2 Spectrum of the inhibitory activity of the most active compounds, expressed as MIC (μ g mL⁻¹) and, in brackets, as MBC (μ g mL⁻¹) and against several Gram positive and Gram negative bacteria

Compound	Bacteria ^a							
	BM	SL	SH	SAG	SG	ST		
[NiL(bpy)] ₂ ·2H ₂ O (4) [CdL] [CdL(bpy)] ₂ (7) [CdL(phen)] Ampicillin	3(6) 3(6) 1.5(3) 3(6) 0.07(0.15)	25(100) 25(50) 12(25) 50(100) 0.0015(0.007)		$12(25) \\ 12(50) \\ 12(25) \\ 12(25) \\ 0.03(0.07)$	$25(>200) \\ 25(100) \\ 25(50) \\ 50(100) \\ 0.7(6)$	>200 <200 >200 >200 1.5(3)		

^{*a*} Gram positive bacteria: *Bacillus megaterium* ATCC 19213 (BM), *Sarcina lutea* ATCC 9341 (SL), *Staphylococcus haemolyticus* clinical isolate (SH), *Streptococcus agalactiae* clinical isolate (SAG), *Streptococcus faecalis* clinical isolate (SF). ^{*b*} Gram negative bacterium: *Salmonella typhimurium* ATCC 14028 (ST).

these complexes exhibited remarkable activity towards *B. megaterium* at 1.5–3 μ g mL⁻¹ and towards *Sarcina* and both streptococci at 12–50 μ g mL⁻¹, whereas showed low growth inhibition of *S. haemolyticus* and no effect on *S. typhimurium*.

To determine the antimicrobial activity pattern, minimum bactericidal and fungicidal concentrations were detected for the active compounds. The MBC and MFC values reported in Tables 1 and 2 were always higher than the corresponding MICs, suggesting a bacteriostatic and fungistatic behaviour.

Moreover, all tested compounds were demonstrated to be lower antimicrobial agents, when compared to ampicillin and miconazole, positive antibacterial and antifungal controls, respectively (Tables 1 and 2).

Overall, the obtained results revealed that $[CdL(bpy)]_2$ was the best antimicrobial agent among the tested complexes and that Gram positive bacilli were the most sensitive strains to these compounds.

Differential patterns of antimicrobial properties of the ligand and its metal complexes used in this work were observed. Specifically, the ligand and its nickel and zinc homoleptic complexes were devoid of antimicrobial activity. In contrast, the complexation of H_2L with cadmium strongly improved the antimicrobial activity of the ligand against Gram positive *Bacillus subtilis* and Gram negative *Haemophilus influenza* and slightly affected the growth of the yeast *Saccharomyces cerevisiae*. Along the same lines, a moderate increase in the inhibition of bacteria *Staphylococcus aureus* and *Haemophilus influenzae* was promoted by the complexation of H_2L with cobalt and copper metal ions and was also detected for [CuL]·H₂O towards *Bacillus subtilis*.

Collectively, 1,10-phenanthroline heteroleptic complexes were shown to exhibit attenuation and less extensive antimicrobial behavior, compared to the coligand alone, implying that the metal(π)-bond decreases 1,10-phenanthroline antimicrobial properties. Similar observations were made in the case of the cobalt, copper and zinc 2,2'-bipyridine heteroleptic complexes, whereas [NiL(bpy)]₂·2H₂O and [CdL(bpy)]₂ exhibited a remarkable increase of the antibacterial activity of the parent coligand against *Bacillus subtilis* and *Heamophilus influenzae*.

Finally, no differential antimicrobial behavior was noticeable among homoleptic and heteroleptic complexes of each metal, suggesting that the introduction of the coligands into the homoleptic complexes had no great effect, even though coligands themselves were found to be antimicrobial agents. Exceptions were detected for [NiL(bpy)]₂·2H₂O that exhibited an increased strong inhibition of *B. subtilis* and *H. influenzae* when compared to [NiL], and for [CuL(bpy)] that, instead, was completely devoid of the antibacterial activity shown by the homoleptic complex, [CuL]·H₂O.

Conclusions

The one-pot-syntheses of new metal complexes (Co, Ni, Cu, Zn and Cd) containing the novel heterocyclic benzimidazole ligand 1H-anthra[1,2-d]imidazol-6,11-dione-2-[2-hydroxyphenyl] (H₂L) were achieved by using an electrochemical procedure. The homoleptic complexes were obtained by electrolysis of solutions of the ligand H₂L with an appropriate metal anode. The addition of bidentate nitrogen donors such as bpy or phen to the cell solutions containing the ligand H₂L allows the electrosyntheses of the corresponding heteroleptic complexes in only one step with good overall yields. All these complexes were fully characterized by a number of analytical techniques and when possible, by X-ray single-crystal diffraction analysis.

The dianionic phenolate (L^{2-}) , obtained *in situ* by electrochemical reduction of the precursor H₂L, was proven to be an excellent dinucleating ligand. It promotes the formation of dimetallic compounds with both the participation of monodentate coligands (such as donor solvents like methanol or water) and of bidentate chelating coligands (1,10-phenanthroline, 2,2'-bipyridine). The analysis of the crystal structures of some of the final metal dimers revealed that the ligand (L^{2-}) not only promotes the formation of symmetric compounds, but also the formation of unexpected bimetallic compounds with different coordination environments for the metal atoms, as found for the cobalt complex [CoL(phen)]₂. Only in the case of the copper complexes the ligand failed to promote the formation of dinuclear compounds, due to the different coordination preferences of the metal atom. An extensive analysis of the secondary interactions responsible for the crystal packing of these compounds showed that in all cases the four fusedring system of the ligand (L^{2-}) gets involved in π interactions, while the non-coordinated quinone oxygen atom gets involved in C-H-O hydrogen bond interactions.

The magnetic behavior of three reported μ -phenoxo-bridged dinuclear complexes shows the occurrence of intradimer magnetic exchange, which differ in nature. Thus, the estimated

magnetic coupling parameter (*J*) shows the occurrence of antiferromagnetic coupling ($J = -2 \text{ cm}^{-1}$) for 2, and ferromagnetic coupling for 3 ($J = 7.8 \text{ cm}^{-1}$) and 4 ($J = 2.8 \text{ cm}^{-1}$). These values together with the M–O_{phenoxo}–M (M = Ni^{II}, Co^{II}) angles found for the three derivatives are perfectly consistent with magnetostructural correlations recently reported.^{65,71} The *in vitro* antimicrobial properties of the complexes were also studied. Biological studies show that the Cd complexes and [NiL(bpy)]₂·2H₂O exhibit significantly higher antimicrobial selectivity against common Gram-positive bacteria. The antimicrobial behavior among homoleptic and heteroleptic complexes of each metal is not very different, suggesting that the introduction of the coligands into the homoleptic complexes has no effect on the activity of the compounds.

Conflicts of interest

There are no conflicts to declare.

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