Zinc(II) and Co(II) complexes based on bis(*N*-allylbenzimidazol-2-ylmethyl) aniline: synthesis, crystal structures and antioxidative activity

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Bis(*N*-allylbenzimidazol-2-ylmethyl)aniline (L) and its complexes, $[Zn(L)(Cl)_2]$ and $[Co(L)(Cl)_2]$, have been synthesised and the structures of both complexes have been determined. $[Zn(L)(Cl)_2]$ can be described as distorted tetrahedron, while $[Co(L)(Cl)_2]$ has a distorted trigonal bipyramidal geometry. In addition, the complexes were found to possess potent hydroxyl antioxidant activity and be better than standard antioxidants like vitamin C and mannitol. In particular, $[Co(L)(Cl)_2]$ displayed excellent activity towards the superoxide radical.

Keywords: bis(*N*-allylbenzimidazol-2-ylmethyl)aniline, Zn(II) and Co(II) complexes, crystal structure, antioxidative activity

Reactive oxygen species (ROS), such as superoxide anion $O_2^{-\bullet}$, hydrogen peroxide (H_2O_2), and hydroxyl radical $OH^{-\bullet}$, are generated by aerobic cells during normal oxygen metabolism. Cumulative information obtained has proved that the oxidation induced by ROS is involved in the pathogenesis of various diseases, such as lifestyle-related diseases including hypertension and photoaging due to exposure to UV radiation.[1,2] Whereas many superoxide and hydroxyl radicals are produced by the reduction of oxygen in the human body,[3] overproduction of free radicals is considered the main contributor to oxidative stress. Many researchers have been working hard to develop metal complexes in order to achieve efficient antioxidants.[4,5]

Benzimidazole, a typical heterocyclic ligand with nitrogen as the donor atom, is a useful intermediate for the development of molecules of pharmaceutical or biological interest.[6] Benzimidazoles and their derivatives exhibit various remarkable biological activities in such pharmaceuticals as antiulcers,[7] anthelmintics,[8] antivirals,[9] antifungals,[10] and antihistamines,[11] to name just a few.[12–14] Bis-benzimidazoles have potent activity against a number of microorganisms including those that lead to AIDS-related infections.[15] We now describe the synthesis and characterisation of the ligand L (**2**) (Scheme 1) and its transition metal complexes. The antioxidant activities (scavenging effects on $O_2^{-\bullet}$ and $OH^{-\bullet}$) of the ligand and its complexes have also been studied. This information obtained should be helpful in developing new antioxidants.

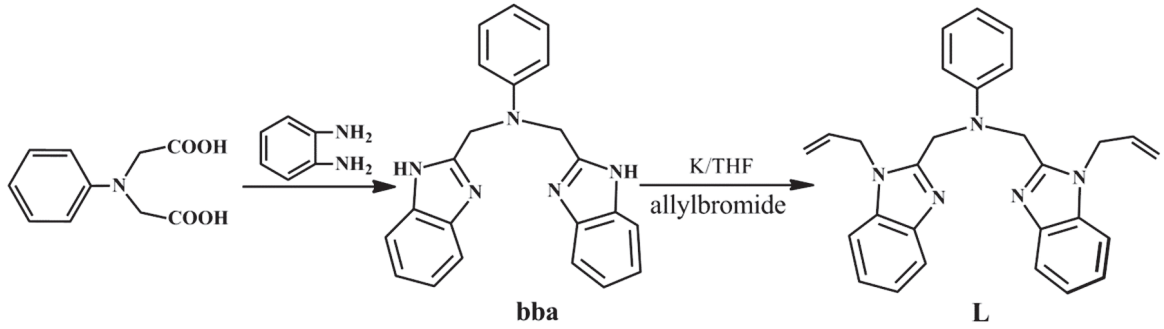
Experimental

All chemicals and solvents were reagent grade and were used without further purification. The C, H and N elemental analyses were determined using a Carlo Erba 1106 elemental analyser. The IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. Electronic spectra were taken on a Lab-Tech UV Bluestar spectrophotometer. The absorbance was measured with a Spectrumlab 722sp spectrophotometer at room temperature. ^1H NMR spectra were recorded on a Varian VR400-MHz spectrometer with TMS as an internal standard. Electrolytic conductance measurements were made with a DDS-307 type conductivity bridge using 3×10^{-3} M solutions in DMF at room temperature.

The synthetic routine of ligand (L) **2** is shown in Scheme 1.

Bis(benzimidazol-2-ylmethyl)aniline (bba) (**1**): The ligand bba was synthesised according to the procedure reported in the literature.[16,17] Yield 75.8%; m.p. 258–259 °C. Anal. calcd for $C_{22}H_{19}N_5$: C, 74.77; H, 5.42; N, 19.82; found: C, 74.79; H, 5.41; N, 19.83%. IR (KBr; ν/cm^{-1}): 744 ν(o-Ar), 1298 ν(C–N), 1445 ν(C=N), 1610 ν(C=C). ^1H NMR (400 MHz, d^6-DMSO): δ 7.2–7.68 (m, 10H, benzimidazole), 6.55–7.10 (m, 5H, Ph), 5.14(s, 4H CH_2). UV-Vis (in DMF), λ_{max} (nm) 277 and 282. Molar conductance: Λ_M (DMF solution, 297 K): 2.69 S·cm^2·mol^{-1}.

Bis(N-allylbenzimidazol-2-ylmethyl)aniline (L) (**2**): Compound **1** (5.3 g, 0.015 mol) was suspended in dry tetrahydrofuran (150 mL) and stirred under reflux with potassium 1.17 g (0.03 mol). The solution was stirred until the potassium disappeared, then allylbromide 3.63 g (0.03 mol) was added. After 1 h, the solvents were concentrated and the resulting powder was washed with distilled water several times to remove KBr. The solid substances were recrystallised with MeOH and a pale-yellow powder bis(*N*-allylbenzimidazol-2-ylmethyl) aniline (**2**) was deposited. Yield 79.7%; m.p. 170–173 °C. Anal. calcd for $C_{28}H_{27}N_5$: C, 77.57; H, 6.28; N, 16.15; found: C, 77.60; H, 6.24; N, 16.16%. IR (KBr; ν/cm^{-1}): 744 ν(o-Ar), 1256 ν(C–N), 1444 ν(C=N), 1600 ν(C=C). ^1H NMR (400 MHz, d_6-DMSO): δ 7.18–8.0 (m, 8H, benzimidazole), 7.18–6.83 (m, 5H, Ph), 4.5–4.87 (s, 4H, CH_2), 4.87–6.0 (m, 10H, allyl). UV-Vis (in DMF), λ_{max} (nm) [ε_{max} (L·mol^{-1}·cm^{-1})]: 278(1.6×10^4), 285(1.52×10^4). Molar conductance: Λ_M (DMF solution): 2.1 S·cm^2·mol^{-1}.



Scheme 1 Synthesis of bba (**1**) and ligand (L) **2**.

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Complex [Zn(L)(Cl)$_2$] (**3**): $ZnCl_2$ (68.15 mg, 0.50 mmol) in EtOH (10 mL) was added to a stirred solution of **2** (216.78 mg, 0.50 mmol) in hot EtOH (10 mL). A white crystalline product formed rapidly. The precipitate was filtered off, washed with EtOH and absolute Et_2O, and dried under reduced pressure. The dried precipitate was dissolved in DMF to form a yellow solution into which Et_2O was allowed to diffuse at room temperature. Crystals suitable for X-ray measurement were obtained after several days. Complex **4** was prepared by a similar procedure as for complex **3**.

Complex **3**: Yield 72%. Anal calcd for $C_{28}H_{27}N_5ZnCl_2$: C, 59.02; H, 4.78; N, 12.29; found: C, 59.14; H, 4.73; N, 12.26%. IR (KBr; ν/cm^{-1}): 758 ν(*o*-Ar), 1264 ν(C–N), 1456 ν(C=N), 1597 ν(C=C). UV-Vis (in DMF), λ_{max} (nm) [ε_{max} (L mol^{-1}·cm^{-1})]: 276(1.47×10^4), 280(1.46×10^4). Molar conductance: Λ_M (DMF solution): 6.67 S·cm^2·mol^{-1}.

Complex **4**: Yield 80%. Anal calcd for $C_{28}H_{27}N_5CoCl_2$: C, 59.69; H, 4.83; N, 12.43; found: C, 59.67; H, 4.85; N, 12.44%. IR (KBr; ν/cm^{-1}): 756 ν(*o*-Ar), 1261 ν(C–N), 1454 ν(C=N), 1597 ν(C=C). UV-Vis (in DMF), λ_{max} (nm) [ε_{max} (L mol^{-1} cm^{-1})]: 275(1.64×10^4), 282(1.49×10^4), 608(347). Molar conductance: Λ_M (DMF solution): 11.3 S·cm^2·mol^{-1}.

Hydroxyl radical scavenging activity

Hydroxyl radicals were generated in aqueous media through the Fenton-type reaction.[18,19] The reaction mixture (3 mL) contained 1.0 mL of 0.10 mmol aqueous safranin, 1 mL of 1.0 mmol aqueous EDTA–Fe(II), 1 mL of 3% aqueous H_2O_2, and a series of quantitative microadditions of solutions of the test compound. A sample without the tested compound was used as the control. The reaction mixtures were incubated at 37 °C for 30 min in a water bath. The absorbance was then measured at 520 nm. The scavenging effect for OH$^\bullet$ was calculated from the following expression:

$$\text{Scavenging effect (\%)} = (A_{sample} - A_{blank})/(A_{control} - A_{blank}) \times 100$$

where A_{sample} is the absorbance of the sample in the presence of the tested compound, A_{blank} is the absorbance of the blank in the absence of the tested compound and $A_{control}$ is the absorbance in the absence of the tested compound and EDTA-Fe(II).[20]

Superoxide radical-scavenging activity

A nonenzymatic system containing 1 mL 9.9×10^{-6} M vitamin B_2, 1 mL 1.38×10^{-4} M nitrotetrazolium blue chloride (NBT), 1 mL 0.03 M methionine (MET) was used to produce the superoxide anion ($O_2^{-\bullet}$), and the scavenging rate of $O_2^{-\bullet}$ under the influence of 0.1–1.0 μM of the test compound was determined by monitoring the reduction in rate of transformation of NBT to monoformazan dye.[21] The solutions of MET, vitamin B_2 and NBT were prepared in 0.02 M phosphate buffer (pH = 7.8) avoiding light. The reactions were monitored at 560 nm with a UV-Vis spectrophotometer, and the rate of absorption change was determined. The percentage inhibition of NBT reduction was calculated using the following equation:[22]

$$\text{percentage inhibition of NBT reduction} = (1 - k'/k) \times 100$$

where k' and k are the slopes of the straight line of absorbance values as a function of time in the presence and absence of SOD mimic compound (SOD is superoxide dismutase), respectively. The IC_{50} values for the complexes were determined by plotting the graph of percentage inhibition of NBT reduction against the concentration of the complex. The concentration of the complex which causes 50% inhibition of NBT reduction is reported as IC_{50}.

X-ray crystallography

Diffraction intensities for complexes **3** and **4** were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 296(2) K. Data reduction and cell refinement were performed using the SMART and SAINT programs. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 of data using SHELXTL software.[23] All H atoms attached to C atoms were fixed geometrically and treated as riding with C–H = 0.93 or 0.97 Å with $U_{iso}(H) = 1.2\,U_{eq}(C)$. Basic crystal data, description of the diffraction experiment, and details of the refinement for complexes **3** and **4** are given in Table 1. Selected bond lengths (Å) and angles (°) are presented in Table 2, respectively.

Results and discussion

The synthetic route to ligand **2** is shown in Scheme 1. The complexes were prepared by reaction of the ligand **2** with $ZnCl_2$ and $CoCl_2$ in ethanol, respectively. All compounds are stable in air. They are soluble in polar aprotic solvents such as DMF, DMSO and MeCN, slightly soluble in water, ethanol, ethyl acetate, and chloroform, and insoluble in Et_2O and petroleum

Table 1 Crystal and structure refinement data for complexes **3** and **4**

Complex	**3**	**4**
Molecular formula	$C_{28}H_{27}N_5ZnCl_2$	$C_{28}H_{27}N_5CoCl_2$
Molecular weight	569.82	563.38
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P2(1)/c*
a/Å	9.4888(10)	8.805(13)
b/Å	10.6798(11)	14.55(2)
c/Å	13.1005(13)	21.00(3)
β/°	96.8020(10)	100.059(17)
V/Å^3	1288.6(2)	2649(7)
Z	2	4
D(calcd)/g·cm^{-3}	1.469	1.412
F (000)	588	1164
Crystal size/mm	0.40×0.38×0.30	0.39×0.38×0.29
θ range for data collection	1.60–25.49	1.71–25.50
h/*k*/*l* (max, min)	–11,11/–12,12/–15,15	–10,10/–16,17/–25,25
Reflections collected	8882	16323
Independent reflections	4677/0.0168	4887/0.0784
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data/restraints/parameters	4677/0/325	4887/7/325
Goodness-of-fit on F^2	1.135	1.001
Final R_1, wR_2 indices [$I>2\sigma(I)$]	0.0274/0.0756	0.0671/0.1852
R_1,wR_2 indices (all data)	0.0313/0.086	0.1061/0.2238
Largest differences peak and hole/eÅ^{-3}	0.258/–0.325	0.695/–0.698

Table 2 Selected bond distances (Å) and angles (°) for complexes **3** and **4**

3			
Zn(1)–N(5)	2.056(2)	Zn(1)–N(3)	2.0646(19)
Zn(1)–Cl(1)	2.2588(7)	Zn(1)–Cl(2)	2.2642(7)
N(5)–Zn(1)–N(3)	109.33(8)	N(5)–Zn(1)–Cl(1)	123.47(6)
N(3)–Zn(1)–Cl(1)	104.46(6)	N(5)–Zn(1)–Cl(2)	102.01(6)
N(3)–Zn(1)–Cl(2)	109.00(6)	Cl(1)–Zn(1)–Cl(2)	108.08(3)
N(5)–Zn(1)–N(1)	67.79(7)	N(3)–Zn(1)–N(1)	68.77(7)
Cl(1)–Zn(1)–N(1)	84.79(4)	Cl(2)–Zn(1)–N(1)	166.91(4)
4			
Co(1)–N(5)	2.041(4)	Co(1)–N(3)	2.080(5)
Co(1)–Cl(2)	2.268(3)	Co(1)–Cl(1)	2.314(3)
Co(1)–N(1)	2.623(5)		
N(5)–Co(1)–N(3)	110.73(17)	N(5)–Co(1)–Cl(2)	122.51(14)
N(3)–Co(1)–Cl(2)	111.77(15)	N(5)–Co(1)–Cl(1)	100.42(15)
N(3)–Co(1)–Cl(1)	105.52(14)	Cl(2)–Co(1)–Cl(1)	103.51(11)
N(5)–Co(1)–N(1)	71.50(16)	N(3)–Co(1)–N(1)	71.56(16)
Cl(2)–Co(1)–N(1)	87.33(12)	Cl(1)–Co(1)–N(1)	168.97(10)

Table 3 IR bonds (cm^{-1}) of compounds

Compounds	$\nu_{(Ar)}$	$\nu_{(C-N)}$	$\nu_{(C=N)}$	$\nu_{(C=C)}$
2	744	1256	1444	1601
3	758	1264	1456	1597
4	756	1261	1454	1597

ether. The elemental analyses show their different compositions and their molar conductivities in DMF solution indicate that they are non-electrolytes.

IR and UV-Vis spectra

The IR spectra data for ligand 2 and its complexes, along with their relative assignments, are given in Table 3. In the free ligand, a strong band is found around 1260 cm^{-1} along with another less strong band around 1450 cm^{-1}. By analogy with the spectrum of imidazole, the former is attributed to ν(C–N), while the other one is ν(C=N).[24,25] One shifts around 10 cm^{-1} and the other at around 5 cm^{-1} in both complexes, which implies direct coordination of both imine nitrogen atoms to metal ions. There are the preferred nitrogen atoms for coordination, as found in other metal complexes with benzimidazoles.[26] This observation agrees with the results determined by X-ray diffraction.

DMF solutions of ligand **2** and its complexes show, as expected, almost identical UV spectra. The UV bands of **2** (278, 285 nm) are only marginally blue-shifted (2–5 nm) in the spectra of the complexes, which is evidence of C=N coordination to the metal centre. These bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ (imidazole) transitions.[27,28]

Crystal structure of complex **3**

The single-crystal X-ray structure of complex **3** with atom labelling is shown in Fig. 1. The selected bond lengths and bond angles are listed in Table 2. The metal atom is coordinated with an N_2Cl_2 ligand set, of which two are N atoms [N(3), N(5)] afforded by the ligand **2**, and the other two are chloride atoms [C1(1), Cl(2)]. The coordination geometry of the zinc(II) may best be described as distorted tetrahedral. Three bonds Zn(1)–N(3), Zn(1)–N(5) and Zn(1)–Cl(1) are formed in the pyramidal bottom plane; the distances are within the range 2.056(2) Å and 2.2588(7) Å. The bond distance between the Zn(1) and the apical Cl(2) is 2.2642(7) Å, and the bond distances between the Zn ion and the basal atoms are [Zn(1)–N(3)=2.0646(19) Å, Zn(1)–N(5)=2.056(2) Å and Zn(1)–Cl(1)=2.2588(7) Å]. Owing to this coordination geometry, an eight-membered ring results, which is connected through the Zn(II) centre and displays an eight-shaped geometry.

As shown in Fig. 2, weak supramolecular π···π and strong C–H···Cl hydrogen-bonding interactions play important roles in the crystal packing modes in the complex.[29] The planes of two benzimidazole rings form π···π stacking interactions (centroid-to-centroid distances: 3.700 Å) along the crystallographic *ac* axis. Such an arrangement can make the crystal structure more stable.

Crystal structure of complex **4**

Complex **4** crystallised in the monoclinic space group P2(1)/c (Fig. 3). The molecular structure consists of a ligand of **2**, two chloride atoms, and one Co(II) atom. The ligand **2** is a terdentate N-donor, and two chloride ion of a monodentate salicylate complete the coordination. The coordination of the Co(II) atom may be best described as distorted trigonal bipyramidal (τ_1=0.77), with approximate *C3* symmetry. The parameter τ is defined as $(\beta-\alpha)/60$ [where β=Cl(1)–Co(1)–N(1), α=N(5)–Co(1)–Cl(2)] and its value varies from 0 (in regular square-based pyramidal) to 1 (in regular trigonal bipyramidal).[30] The axial sites are occupied by N(1) and Cl(1), with Co(1)–N(1)=2.623(5) Å, Co(1)–Cl(1)=2.314(3) Å and Cl(1)–Co(1)–N(1)=168.97(10)°. The trigonal plane is occupied by a ligating N atoms of the benzimidazolyl groups and two chloride atoms, namely atoms N(3)/N(5)/Cl(2). The angles

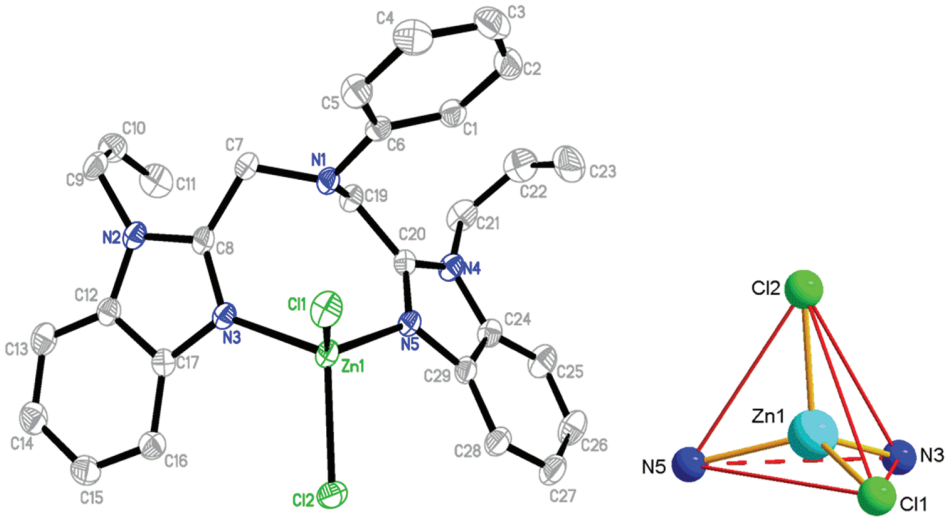

Fig. 1 Molecular structure of complex **3** with hydrogen atoms were omitted for clarity.

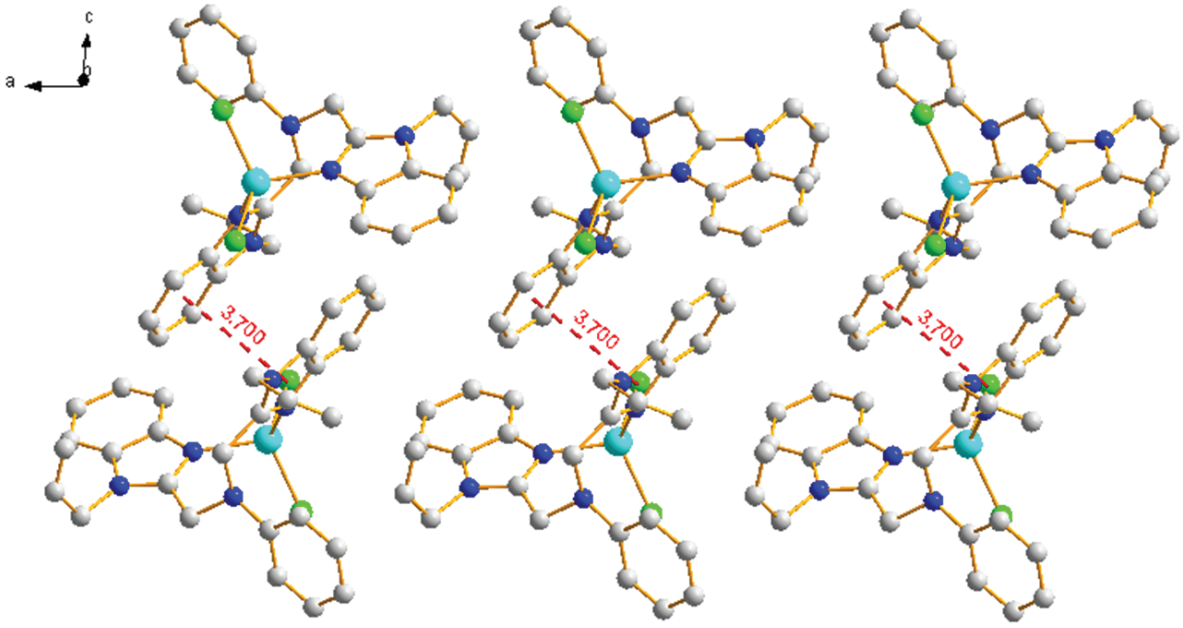

Fig. 2 2-D layer generated by the π···π interactions in the *ac* plane in complex **3** (for clarity, some atoms are omitted).

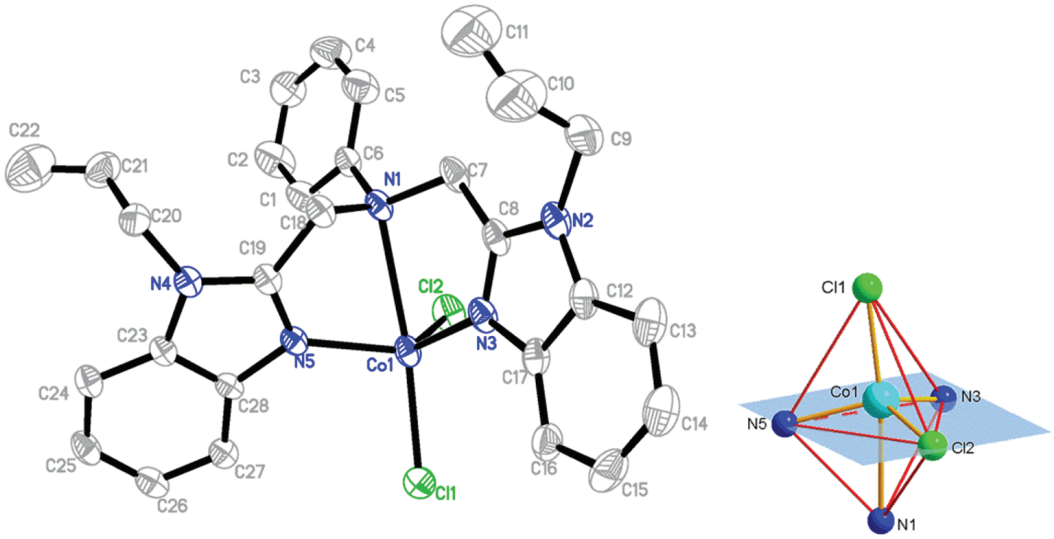

Fig. 3 Molecular structure and atom-numberings of complex **4** with hydrogen atoms omitted for clarity.

N(5)–Co(1)–N(3), N(3)–Co(1)–Cl(2) and N(5)–Co(1)–Cl(2) are 110.73(17)°, 111.77(15)° and 122.51(14)°, respectively. The N(3)–Co(1)–N(1)=71.56(16)°, N(5)–Co(1)–N(1)=71.50(16)° and Cl(2)–Co(1)–N(1)=87.33(12)° angles appear essentially imposed by the stereochemistry of the ligand L and chloride atom.

As one of the important types of supramolecular forces, π···π stacking shows a specific structural requirement for substrate recognition or the arrangement of complicated architectures. In complex **4**, the centroid-to-centroid distance of 3.581 Å between the two nearly parallel planes of the benzimidazole rings indicates weak intramolecular interactions (Fig. 4). The 2D structure was formed through π···π interactions and weak C–H···Cl hydrogen bonding between benzimidazole and chloride anion in adjacent chains.

From the above crystal structures of complexes, we have found that their structural conformations were mainly controlled by the ligand and metal centres, and also influenced by the coordination capabilities of counter anions at the same time. The intramolecular weak interactions also help to assemble the crystal structures into different dimensions.

Antioxidant activities

It is well-documented[6,16] that some transition metal complexes display significant antioxidant activity. Consequently, in this paper, **2** and its complexes were studied for their antioxidant activity by comparing their scavenging effects on $OH^{-\bullet}$ and $O_2^{-\bullet}$.

Hydroxyl radical scavenging activity

We compared the abilities of the present compounds to scavenge hydroxyl radicals with those of the well-known natural antioxidants mannitol and vitamin C, using the same method as reported previously.[18,31] The 50% inhibitory concentration (IC_{50}) values of mannitol and vitamin C are about 9.6×10^{-3} and 8.7×10^{-3} M, respectively. Figure 5 shows the plots of hydroxyl radical scavenging effect (%) for complexes **3** and **4**, and the IC_{50} values of complexes **3** and **4** are 2.92×10^{-5} M and 4.47×10^{-5} M, respectively, but the ligand **2** does not have

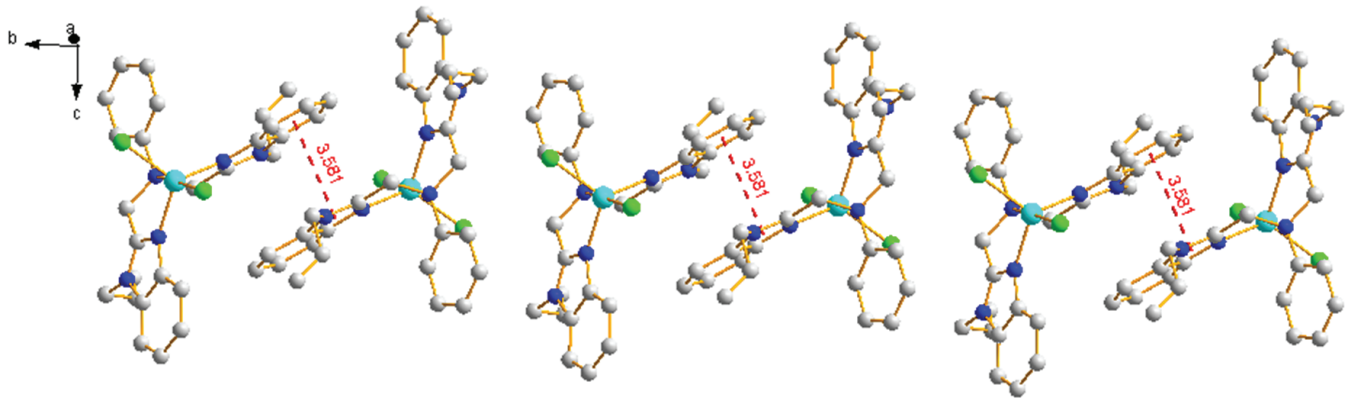

Fig. 4 The $\pi\cdots\pi$ interactions and packing modes in complex **4** (H atoms are omitted).

activity. The result indicates that the binding strength of the two complexes follow the order: **3** > **4**, which imply that the two complexes exhibit better scavenging activity than mannitol and vitamin C. The lower IC_{50} values observed in antioxidant assays demonstrate that the two complexes have a strong potential to be applied as scavengers to eliminate radicals.[32]

Superoxide radical scavenging activity

As another assay of antioxidant activity, superoxide radical ($O_2^{-\bullet}$)-scavenging activity has been investigated.[33,34] As can be seen from Fig. 6, the IC_{50} value of complex **4** is 5.05×10^{-5} M, but complex **3** does not have activity. The result indicates that complex **4** exhibits good superoxide radical-scavenging activity and may be an inhibitor (or a drug) to scavenge superoxide radical ($O_2^{-\bullet}$) in *vivo* which need further investigation.

Conclusions

In summary, the ligand **2** and its complexes **3** and **4** have been synthesised and the structures and geometry of complexes **3** and **4** were analysed through single crystal X-ray diffraction. The complex **3** can be described as distorted tetrahedron. The geometric structure of complex **4** may be treated as distorted trigonal bipyramidal. Furthermore, complexes **3** and **4** were found to possess potent hydroxyl radical scavenging activity and be better than standard antioxidants like vitamin C and mannitol. Furthermore, the complexes possess significant superoxide radical activity. These findings indicate that complexes **3** and **4** have potential practical applications in the development of antioxidants, which warrants further *in vivo* experiments and pharmacological assays.

Crystallographic data for complexes **3** and **4** have been deposited with the Cambridge Crystallographic Data Centre as CCDC1005343 and 1005342, respectively. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel: +44 1223 762910; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

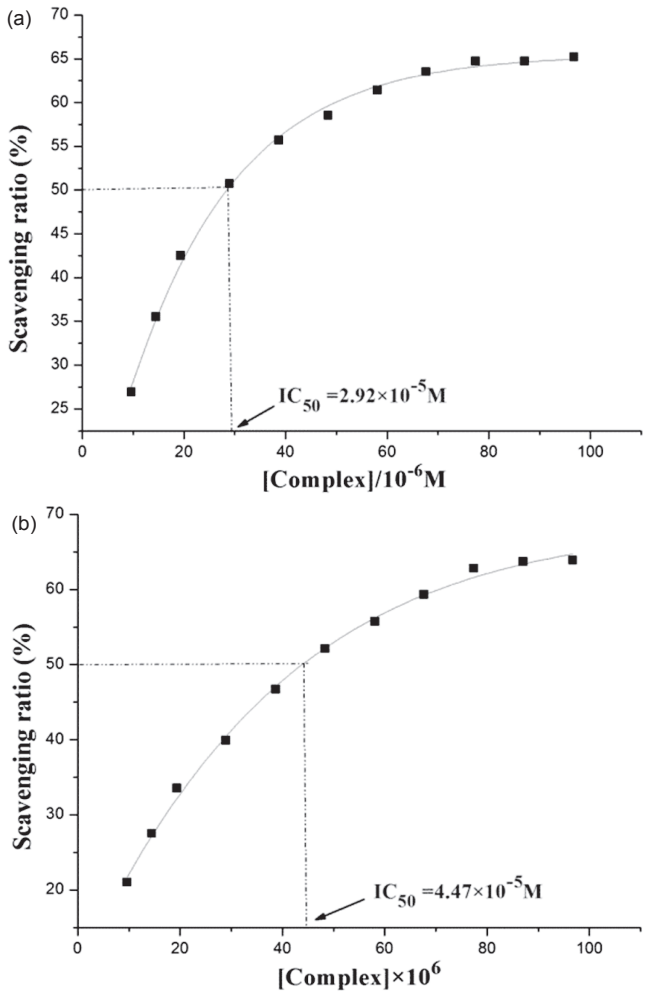

Fig. 5 The inhibitory effect of complex **3** (a) and complex **4** (b) on $OH^{-\bullet}$ radicals; the suppression ratio increases with increasing concentration of the test compounds.

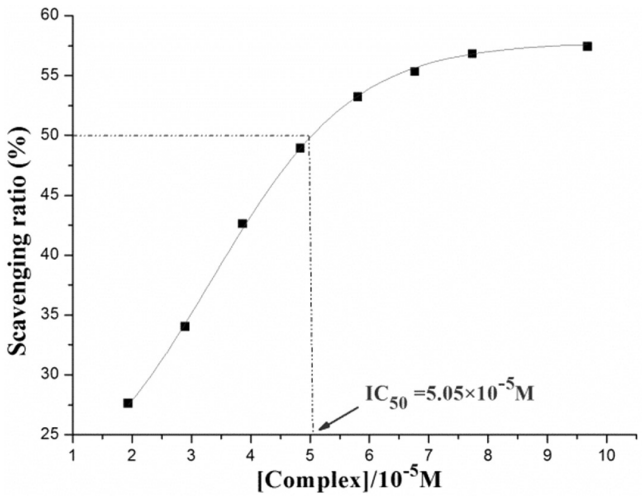

Fig. 6 The superoxide radical scavenging effect (%) for complex **4**.

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