New Dinuclear Transition Metal Complexes with the \([M_2(\mu-dhbq)]^{n+}\) Core and 2-(2’-Pyridyl)quinoxaline (L) as a Terminal Ligand: Preparation and Characterization (dhbq\(^{2-}\) = the Dianion of 2,5-Dihydroxy-1,4-benzoquinone; \(M = \text{Ag}^{1+}, \text{Mn}^{11}, \text{Co}^{11}, \text{Ni}^{11}, \text{Cu}^{11}, \text{Ru}^{11}, \text{Pd}^{11}, \text{Rh}^{11}, \text{Fe}^{III}; n = 0, 2, 4\))

Sahar I. Mostafa\(^a\), Spyros P. Perlepes\(^b\), and Nick Hadjiliadis\(^c\)

\(^a\) Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt
\(^b\) Department of Chemistry, University of Patras, 265 00 Patras, Greece
\(^c\) Laboratory of Inorganic and General Chemistry, Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece

Reprint requests to Prof. Dr. N. Hadjiliadis. E-mail: nhadjil@cc.uoi.gr

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2,5-Dihydroxy–1,4-benzoquinonate(−2) Complexes, Dinuclear Complexes, 2-(2’-Pyridyl)quinoxaline Complexes

Synthetic procedures are described that allow access to the new complexes \([\text{Mn}_2(\text{dhbq})\text{L}_2(\text{H}_2\text{O})_4]\) (1), \([\text{Fe}^{\text{III}}(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_4]\) (2), \([\text{Co}_2(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_2]\) (3), \([\text{Ni}_2(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_2]\) (4), \([\text{Cu}_2(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_2]\) (5), \([\text{Ru}_2(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2]\) (6), \([\text{Rh}_2(\text{dhbq})\text{Cl}_2\text{L}_2(\text{H}_2\text{O})_2\text{Cl}_2\text{H}_2\text{O}]\) (7), \([\text{Pd}_2(\text{dhbq})\text{L}_2\text{Cl}_2\text{H}_2\text{O}]\) (8) and \([\text{Ag}_2(\text{dhbq})\text{L}_2]\) (9), where dhbq\(^{2-}\) is the dianion of 2,5-dihydroxy-1,4-benzoquinone and L is the biheteroaromatic ligand 2-(2’-pyridyl)quinoxaline. The new complexes were characterized by elemental analyses and by a variety of physical and spectroscopic techniques. Dinuclear structures are assigned for the complexes in the solid state. The two metal ions are bridged by the bischelating dhbq\(^{2-}\) ion, while L behaves as a bidentate chelate with the 2’-pyridyl nitrogen and the nearest quinoxaline nitrogen atom as the ligand atoms. The metal ion coordination geometries are octahedral, tetrahedral or square planar.

Introduction

Catecholate and benzoquinone complexes of transition metals are of general interest in the investigation of ligand-centered redox processes, in magnetochemistry, and as models for metallo-biochemical processes as diverse as microbial ion transport, dioxygenase activity and electron transfer in bacterial photosynthesis [1,2]. More specifically, 2,5-dihydroxy–1,4-benzoquinone (H\(_2\)dhbq) and its 3,6-disubstituted derivatives, such as chloranilic acid (H\(_2\)ca), have been used to prepare dinuclear complexes [3–11] and one-, two- or three-dimensional coordination polymers [12–24] with interesting optical, electronic, magnetic, ion- or molecule-exchange, absorption, and catalytic properties. Since dihydroxybenzoquinonates have several resonance forms (Fig. 1), several coordination modes are possible (Fig. 2). In the \(p\)-quinone form I dhbq\(^{2-}\) and ca\(^{2-}\) act as chelating ligands using the 1,2- and 4,5-oxygen atoms and forming bridges between two metal centres (IV) [3–18, 20–24]. The \(o\)-quinone form II is less...
Fig. 2. Coordination modes of dhbq\textsuperscript{2−} and ca\textsuperscript{2−} established by single-crystal X-ray crystallography.

common and appears mainly in some mononuclear complexes (V) [2, 25–37]. The bis(carbanion) form III has been found in complexes of metal ions with a remarkable affinity for sp\textsuperscript{3}-hybridised carbon atoms [36, 38, 39], such as Pd(II) and Pt(II) (VI). Examples in which the metal centres are \pi-bonded to the dihydroxybenzoquinonate ligands (VII, VIII) are also known [5, 40, 41]. Moreover, dhbq\textsuperscript{2−} and ca\textsuperscript{2−} are potential “ion-innocent” bridging ligands and can in principle bind to two metal ions in two additional oxidation states (Fig. 3) as radical trianions (IX) and as tetraanions (X); both forms were found in dinuclear complexes of triplositive transition metals [42, 43]; the radical trianion also exists in (Bu\textsubscript{4}N)\textsubscript{2} [Mo\textsubscript{4}O\textsubscript{10}(ca)\textsubscript{2}] as a \mu\textsubscript{4} ligand [2].

The coordination chemistry of 2-(2’-pyridyl)quinoxaline (L) is another area of interest [44–55], as it has become apparent that this chemistry is rich in structural types, reactivity characteristics and ligand coordination modes. Ligand L, which can potentially combine the chelating properties of 2,2’-bipyridine [56] and the bridging behaviour of quinoxaline [57], belongs to a family of heteroaromatic ligands whose coordination chemistry is important in understanding electron transfer processes, mixed-valence complexes, excited-state acid-base properties of inorganic systems and magnetic exchange interactions [58–62].

Fig. 3. The “non-innocent” character of dhbq\textsuperscript{2−} (X = H) and ca\textsuperscript{2−} (X = Cl) [see text for details].
Results and Discussion

The Experimental Part lists nine new complexes. The elemental analyses of the isolated compounds agree with the assigned formulae. The formation of some representative complexes can be summarized in eq. (1)–(3):

\[
2\text{CoCl}_2\cdot 6\text{H}_2\text{O} + \text{H}_2\text{dhbq} + 2\text{L} \rightarrow 2\text{HC1} + 10\text{H}_2\text{O} + \text{Co}_2\text{(dhbq)Cl}_2\text{L}_2(\text{H}_2\text{O})_2\ (1)
\]

\[
2[\text{PdCl}_2\text{L}] + \text{H}_2\text{dhbq} + 2\text{KOH} + 3\text{H}_2\text{O} \rightarrow [\text{Pd}_2(\text{dhbq})\text{L}_2]\text{Cl}_25\text{H}_2\text{O} + 2\text{KCl} + \text{H}_2\text{O} - \text{Me}_0\text{H} - \text{Me}_2\text{CO} \ (2)
\]

\[
2\text{AgNO}_3 + \text{H}_2\text{dhbq} + 2\text{L} \rightarrow 2\text{HNO}_3 + \text{Ag}_2(\text{dhbq})\text{L}_2 + \text{H}_2\text{O} - \text{Me}_0\text{H} \ (3)
\]

Complexes 1–5, 7 and 9 were prepared by the reactions of the appropriate metal salts with half an equivalent of dhbq and one equivalent of L in H$_2$O-MeOH. The liberation of hydrogen ions during complex formation was established by conductometric titrations [63] of 1:1 metal salt-L solutions ($10^{-3}$ M) in EtOH with a solution of H$_2$dhbq (5 $\times$ $10^{-3}$ M) in the same solvent. Complex [Ru$_2$(dhbq)L$_2$(H$_2$O)$_4$](ClO$_4$)$_2$ (6) was prepared by the reaction of [RuL$_2$(H$_2$O)$_2$]$^{2+}$, formed in situ from cis-[RuCl$_2$L$_2$] [53] and a slight excess of AgNO$_3$, with half an equivalent of dhbq in the presence of Et$_3$N and ClO$_4^-$ in H$_2$O-MeOH under reflux. Complex [Pd$_2$(dhbq)L$_2$]Cl$_2$5H$_2$O (8) was obtained by the reaction of cis-[PdCl$_2$L] [51] with half an equivalent of H$_2$dhbq and one equivalent of KOH in H$_2$O-MeOH-Me$_2$CO.

Complexes 1–9 seem to be the only products from the 2:1:2 ratio of metal ion: H$_2$dhbq:L in the reaction mixtures. A point of synthetic interest is the fact that the sequence of reagent addition in all procedures is not critical. The complexes are microcrystalline or powder-like, stable in the normal laboratory atmosphere and soluble in warm MeOH, DMF and DMSO, but to varying extents. We had hoped to structurally characterize one of the complexes by single-crystal X-ray crystallography, but were thwarted on numerous occasions by very small crystal dimensions or twinning problems. Thus, the characterization of the complexes was based on physical and spectroscopic techniques.

The molar conductivity ($\Lambda_M$) values of 3, 4, 5 and 9 in DMF (2–6 S cm$^2$ mol$^{-1}$) are in accord with these complexes being formulated as non-electrolytes [64]. The $\Lambda_M$ values (assuming a dimer formulation) of 1, 6, 7 and 8 at 25 °C indicate that these complexes are 1:2 electrolytes [64] in DMF ($\Lambda_M = 164$–189 S cm$^2$ mol$^{-1}$), supporting the conclusion that the perchlorates and chlorides in 1, 6, and 2, and two chlorides in 7, do not participate in coordination. The very high $\Lambda_M$ value of complex 2 in DMF (323 S cm$^2$ mol$^{-1}$ assuming a dimer formulation) indicates that this compound can be formulated as an 1:4 electrolyte [64]; thus, all nitrate groups are ionic in solution.

The thermal decomposition of the representative complexes 7 and 9 was studied using thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) techniques under nitrogen. The data for 7 show one-step, first weight loss of 3.6% between 83 and 130 °C, which corresponds almost exactly to the release of two mmol of H$_2$O per mmol of complex (calcd. 3.7%); the relatively low temperature of water loss shows that these H$_2$O molecules are crystal lattice held [65]. A clear plateau is not reached above 130 °C, because a new strongly endothermic decomposition occurs between 130 and 200 °C, as revealed by a very distinct inflection in the TG curve; this second weight loss is attributed [65, 66] to the release of the two coordinated H$_2$O molecules (calcd. 3.7, found 3.6%). The absence of a plateau above 130 °C indicates that the lattice H$_2$O molecules are essential for the stabilization of the crystal structure. The thermally stable anhydrous Rh$_2$(dhbq)Cl$_4$L$_2$ material further decomposes in the 316–481 °C range and finally transforms into Rh$_3$O$_7$, above 615 °C (calcd. 26.1, found for the residue 26.3%). The data for 9 show only one endothermic weight loss between 253 and 432 °C attributable to the release of two L molecules (calcd. 53.9, found 53.8%), followed by the formation of Ag$_2$O at ~580 °C (calcd. 30.2, found for the residue 29.3%). The thermally stable intermediates at 481–615 °C (7) and 432–580 °C (9), isolated by the temperature-arrest technique [51], were found to contain only dhbq$^{2-}$, as expected (IR and $^1$H NMR evidence).

IR assignments are given in the Experimental Part. In the ν(OH)$_{\text{water}}$ region, the spectra of 1–7 show one relatively strong and sharp band at
~3450 cm\(^{-1}\), assignable to coordinated water [67]. The presence of \(\text{H}_2\text{O}\) molecules in the coordination spheres of these complexes is further confirmed by the appearance of the rocking mode of the aquo ligand at \(-840\) cm\(^{-1}\) [68]. The spectra of 2 and 7 exhibit, in addition to the band of coordinated water, a medium broad absorption covering the whole range 3350–3000 cm\(^{-1}\); this is apparently due to the simultaneous presence of crystal and coordinated water in these complexes [67]. The spectrum of 8 shows only the broad, low-frequency band, indicative of the presence of exclusively lattice water. Dehydration of complex 7 at 83–200 °C (see above) causes the disappearance of the water O-H stretching bands confirming their origin.

The IR spectra of all the complexes below 1650 cm\(^{-1}\) are complicated due to the simultaneous presence of two different organic ligands. The spectra are similar to those of the complexes in which \(L\) behaves as a bidentate chelate [44–49, 51–53]. The characteristic in-plane and out-of-plane 2'-pyridyl ring deformation bands, which appear at 620 and 401 cm\(^{-1}\), respectively, in free \(L\), are shifted to higher frequencies in the complexes indicating the involvement of the pyridyl nitrogen atoms \([N(1')], \text{see formula of } L\) in coordination [69]. The \(-950\) cm\(^{-1}\) region is viewed as the key to differentiate between monodentate terminal and bidentate bridging coordination of the quinoxaline ring [70, 71]. The spectrum of free \(L\) shows a strong band at 960 cm\(^{-1}\). The appearance of a single, sharp band at 965–975 cm\(^{-1}\) in the spectra of 1–9, \(i.e.\) the fact that this band does not split on complexation, is characteristic of the monodentate quinoxaline coordination [70].

The IR spectra of 1–9 exhibit a very strong band at 1520–1538 cm\(^{-1}\) and a medium-intensity one at 1370–1380 cm\(^{-1}\); both bands are assigned to carbon-oxygen stretching vibrations [5, 12, 42, 72, 73]. Their frequencies are consistent with a C-O bond order of 1.5, agree with \(D_{2h}\) symmetry for the dhbq\(^{2-}\) ligand, and suggest the bis-chelating bridging coordination mode IV (Fig. 2) [5, 12, 42, 72–74]. The C=O stretch in free H\(\text{H}_2\text{dbhq}\) is at 1640 cm\(^{-1}\) [72]. The non-appearance of carbonyl stretching bands above 1600 cm\(^{-1}\), which would be associated with localized C=O groups [3], is in accord with the absence of the form \(V\) from the solid-state structures [5].

The spectra of 1 and 6 exhibit a very strong band at \(-1100\) and a medium band at \(-625\) cm\(^{-1}\) due to the \(v_3(F_2)\) and \(v_4(F_2)\) modes of the uncoordinated \(\text{ClO}_4^-\), respectively [75]. The broad character of the band at \(-1100\) cm\(^{-1}\) indicates the involvement of the \(\text{ClO}_4^-\) ion in hydrogen bonding. The iron-(III) complex 2 shows a very strong band at 1388 cm\(^{-1}\) assignable to the \(v_3(E')\) mode of the ionic \((D_{3h})\) nitrate group [75]; the characteristic bands of coordinated nitrate groups \((C_x, C_{2y})\) were not observed, indicating that all the nitrate groups are counterions.

The region of the free ligands’ spectra between 500 and 150 cm\(^{-1}\) contains several weak bands. This would indicate that some of the other bands observed in this region are assignable to \(v(M-N), v(M-O)\) and \(v(M-\text{Cl})\) vibrations [75]. A detailed study, however, of the far-IR spectra of the metal complexes fails to give clearcut assignments. The strong bands at 269, 249, 321 and 300 cm\(^{-1}\) in the far-IR spectra of 3, 4, 5 and 7, respectively, arise from the terminal M-Cl stretching vibration in an octahedral environment [75–78]. It is quite clear that the frequency of the \(v(M-\text{Cl})\) band rules out the possibility of bridging chloro ligands [75].

Complexes 6–9 are diamagnetic, as expected. The room-temperature effective magnetic moments \((\mu_{\text{eff}})\) for complexes 1, 2, 3, 4 and 5 are 4.15, 4.13, 2.81, 2.10 and 1.41 B. M. per metal ion, respectively. These values are smaller than the corresponding spin-only, high-spin values, indicating antiferromagnetic exchange interactions. It is well-known that the \(\mu_{\text{eff}}\)-dhbq\(^{2-}\) ligand leads to antiferromagnetic exchange interactions between paramagnetic metal centres [3, 72, 79].

The electronic spectra of the complexes in DMSO in the 350–800 nm region contain intense bands due to ligand-to-metal charge transfer (LMCT) transitions [73, 74] and weaker bands assigned to d-d transitions. The spin- and Laporte-forbidden d-d transitions of the \(t_{3g}e_{g}^{2}\) manganese(II) complex 1 are very weak and could hardly be observed even in concentrated solutions; a band at 530 nm may be assigned to the \(6A_{1g} \rightarrow 4T_{1g}\) \((^4G)\) transition [80] under \(O_{h}\) symmetry. Because of the greater oxidising power of iron(III) relative to manganese(II), LMCT bands obscure the very low intensity d-d absorptions in 2; in the visible region, one weaker band is apparent, which is similar in position to the \(6A_{1g} \rightarrow 4T_{2g}\) transition.
in other high-spin, octahedral Fe(III) complexes [80]. The d-d spectra of 3, 4, 6 and 7 can be assigned to transitions in octahedral ligand fields under $O_h$ symmetry [80]. Assignments are as follows ($\lambda$, nm):

For 3: 620, $^4T_{1g} \rightarrow ^4A_{2g}$; 500, $^4T_{1g} \rightarrow ^4T_{1g}(P)$.

For 4: 635, $^3A_{2g} \rightarrow ^3T_{1g}$; 390, $^3A_{2g} \rightarrow ^3T_{1g}(P)$.

For 6: 525, $^1A_{1g} \rightarrow ^1T_{1g}$. For 7: 590, $^1A_{1g} \rightarrow ^3T_{2g}$; 495, $^1A_{1g} \rightarrow ^1T_{1g}$.

The d-d spectrum of 5 consists of a featureless band at 530 nm. The spectrum of 8 is typical of a square planar environment around palladium(II) with O- and N-donors; the band at 410 nm may be assigned to the $^1A_{1g} \rightarrow ^1A_{2g}$ transition under $D_{4h}$ symmetry [80]. The ligand field parameters of 3 (10 $D_q = 8600$ cm$^{-1}$, $B = 907$ cm$^{-1}$) and 4 (10 $D_q = 9800$ cm$^{-1}$, $B = 800$ cm$^{-1}$) are within the ranges found for other high-spin, octahedral Co(II) and Ni(II) complexes with NO-donor sets [80].

The $^1H$ NMR assignments for the diamagnetic complexes 6–9 in d$_6$-DM SO presented in the Experimental Part are based on studies of coordinated dhbq$^{2-}$ [5, 10, 36, 43] and L [46, 47, 49–51, 53], and on two-dimensional COSY experiments. The two protons of the bridging dhbq$^{2-}$ ligand appear as a singlet at $\delta = 4.9–5.2$. This signal is shifted to higher fields with the free protonated ligand H$_2$dhbq ($\delta = 5.81$ in d$_6$-DM SO) and appears at almost the same $\delta$ value as for other complexes [5, 10] containing bis-chelating bridging dhbq$^{2-}$. A detailed NMR comparison of the complexes with the uncoordinated (free) ligand L can not be made because single-crystal X-ray crystallography has shown [46] that free L has a trans conformation, i.e. the pyridine nitrogen and the nearest quinoxaline nitrogen are located on the opposite side of the carbon-carbon bond which connects the pyridine and quinoxaline rings (this conformation is most probably retained in solution); the reverse has been observed on chelation [45–52, 54]. However, the electron density on the 2'-pyridyl ring of L diminishes upon coordination to Ru(II), Rh(III), Pd(II) and Ag(I), inducing a downfield shift [81,82] of $\delta$ H(6') [see formula of L], which appears at $\delta = 9.35$ in the complexes versus $\delta = 8.94$ in free L. The downfield shift observed for H(3) [ $\delta = 10.0$ in free L versus $\delta = 10.1$ in the complexes] is rather small (~0.1 ppm), indicating that the N(4) atom of the quinoxaline ring remains uncoordinated; a larger downfield shift would be expected if coordination had occurred. The slight (0.1 ppm) and moderate (~0.25 ppm) downfield shift of H(3) and H(3') resonances, respectively, may be explained [81] by the fact that these protons lie close to each other (stERIC effect) in the complexes (see proposed structures in Fig. 4), as opposed to the structure of free L.

Concluding Comments

The M/dhbq$^{2-}$/L general reaction system fulfilled its promise as a source of interesting complexes. From the overall study presented above, it is concluded that complexes 1–9 all have di-nuclear structures. The dhbq$^{2-}$ ligand displays the more common “innocent” p-quinone form and bridges the two metal centres acting as a tetradentate, bis-chelating bridging ligand (IV, Fig. 2), through the four oxygen atoms. One molecule occupies two coordination sites at each metal ion; L behaves as a bidentate chelating ligand, the ligated atoms being the 2'-pyridyl nitrogen and the nearest quinoxaline nitrogen atom. Two terminal H$_2$O molecules in the cationic complexes 1, 2 and 6, or one H$_2$O molecule and one terminal chloro ligand in 3–5 and 7, complete the octahedral coordination at each metal centre; these two monodentate ligands are most probably in trans positions. A square planar stereochemistry is assigned for the Pd$^{II}$ atoms in the cationic complex 8, while the most plausible coordination geometries around the Ag$^{+}$ atoms in the neutral dimer 9 is a distorted tetrahedral one. The proposed schematic structures for the representative complexes 3–5, 7 and 8 are shown in Fig. 4.

The coordination chemistry of dhbq$^{2-}$ and ca$^{2-}$ is currently under intense investigation in our groups. In the hope of obtaining robust framework solids with potential zeolite-like applications, e.g. in catalysis, we are investigating the coordination polymers formed by connecting ligands that can simultaneously chelate and bridge in a variety of geometrical ways; two of the simplest such ligands are the dianions dhbq$^{2-}$ and ca$^{2-}$. These ligands can be regarded as the chelating equivalents of simple linear two-connectors such as cyanide, pyrazine or 4,4'-bipyridine, which have proved to be prolific generators of infinite networks [83]. An attractive feature of these “bis-bidentate” linear two-connectors is that associated octahedral metal
centres then effectively become trigonal centres giving in principle access to a range of rare three-connected three-dimensional (3D) nets. Work also is in progress on M/dhbq$_2$ or ca$_2$/L$'$ systems, where L$'$s are neutral bis-mono-dentate, bridging aromatic heterocycles, which seem to lead to interesting polymers.

**Experimental Part**

All manipulations were performed under aerobic conditions using starting materials (Merek) and solvents as received. L [44], cis-[PdCl$_2$L] [51] and cis-[RuCl$_2$] [53] were synthesized as described earlier. Elemental analyses (C, H, N) were conducted by the University of Ioannina, Greece, Microanalytical Service. For chloride determination, samples of the complexes were decomposed in 2 N HNO$_3$; the chloride content was determined potentiometrically with a standard 0.1 M AgNO$_3$ solution, using a Corning-Eel mode 12 potentiometer with calomel and sulphide-selective electrodes. Conductivity measurements were carried out at room temperature with a YSI model 32 bridge and a cell of standard design. TG, DTG and DTA data (20–800 °C) were obtained on Shimadzu TGA–50 thermogravimetric analyzer in a dinitrogen gas flow using a–Al$_2$O$_3$ as reference; sample weights of 5–10 mg and a heating rate of 10 °C min$^{-1}$ were used. IR spectra were recorded on a Mattson 5000 FTIR spectrometer with samples prepared as KBr pellets. Far-IR spectra were recorded on a Bruker IFS 113v FT spectrometer with samples prepared as polyethylene pellets. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey balance standardized with HgCo(NCS)$_4$; the molar susceptibilities were corrected for the core diamagnetism of the constituent atoms using Pascal’s constants. Solution electronic spectra (350–800 nm) were recorded on a Unicam UV–2–100 instrument. $^1$H NMR spectra were recorded on Varian Gemini (Laser Centre, Cairo University, Egypt) and Bruker Avance DPX spectrometers. Chemical shifts, quoted on the δ scale and referenced versus external TMS or the protio impurity of the solvents employed, are assigned below according to the atomic labeling scheme of dhbq$^{2–}$ (Fig. 1) and L.

\[
[Mn_2(dhbq) L_2(H_2O)_4](ClO_4)_2 \quad (1)
\]

A stirred solution of MnCl$_2$·4H$_2$O (0.099 g, 0.50 mmol) in H$_2$O (2 ml) was added dropwise to a solution of L (0.104 g, 0.50 mmol) in MeOH (25 ml). A yellow homogeneous solution was obtained, and to this was added a solution of H$_2$dhbq (0.035 g, 0.25 mmol) in MeOH (10 ml). To the new red solution obtained was added a solution of NaClO$_4$ (0.122 g, 1.00 mmol) in H$_2$O (5 ml). The resultant yellowish red solid was collected by filtration, washed with H$_2$O, MeOH and Et$_2$O, and dried in air. The yield was ~65%. Conductivity data (DMF, 10$^{-3}$ M, 25 °C): $\lambda_M = 166$ S cm$^{-2}$ mol$^{-1}$. Magnetic data (24 °C): $\mu_{\text{eff}} = 4.15(3)$ $\mu_B$/Mn$^{II}$ atom. – UV/vis (DMSO): $\lambda_{\text{max}}$ = 530 nm. – IR (KBr pellet): $\nu$ = 3440 $\nu$(OH), 1530, 1375 $\nu$(CO), 1095 $\nu_3$(F$_2$) perchlorate, 970 [quinoxaline ring], 627 $\nu_4$(F$_2$) perchlorate cm$^{-1}$. – C$_{32}$H$_{78}$N$_{6}O$_{16}Cl$_2$Mn$_2$ (933.44): calcd C 41.17, H 3.03, N, 9.00; found C 41.77, H 2.94, N 9.04.

\[
[Fe_2(dhbq) L_2(H_2O)_4](NO_3)_4 \cdot 6H_2O \quad (2)
\]

A stirred solution of Fe(NO$_3$)$_3$·9H$_2$O (0.202 g, 0.50 mmol) in H$_2$O (2 ml) was added dropwise to a solution of L (0.104 g, 0.50 mmol) in MeOH (22 ml). A red-brown homogeneous solution was obtained, and to this was added a solution of H$_2$dhbq (0.035 g, 0.25 mmol) in MeOH (10 ml). Upon the addition of H$_2$dhbq a brown solid was precipitated. Stirring was continued for a further 30 min. The precipitate was filtered off, washed...
with H2O, MeOH and Et2O, and dried in air. The yield was ~50%. Conductivity data (DMF, 10−3 M, 25 °C): \( \Lambda_M = 323 \text{ S cm}^{-2} \text{ mol}^{-1} \). Magnetic data (22 °C): \( \mu_{\text{eff}} = 4.13(3) \mu_B / \text{Fe}^{II} \) atom. - UV/vis (DMSO): \( \lambda_{\text{max}} = 385 \text{ (LMCT), 530 (d-d) nm} \). - IR (KBr pellet): \( \nu = 3440, 3350-3050 \ \text{[v(OH)], 1535, 1375 \ [v(CO)], 1388 \ [v_3(E_{\text{nitrate})}, 975 \ [\text{quinoxaline ring}] \ cm^{-1} \). - C32H40N10O96Fe2 (1092.52): calcd C 35.18, H 3.70, N 12.79.

(3)

A stirred pink solution of CoCl2·6H2O (0.119 g, 0.50 mmol) in H2O (2–3 ml) was added dropwise to a solution of L (0.104 g, 0.50 mmol) in MeOH (25 ml). A royal blue homogeneous solution was obtained, and to this was added a solution of H2dhbq (0.035 g, 0.25 mmol) in MeOH (10 ml). A noticeable colour change from blue to pink occurred and, after a few minutes stirring, a fine pink microcrystalline precipitate was deposited. The solid was collected by filtration, washed with a little cold H2O, MeOH and Et2O and dried in air. The yield was ~60%. Conductivity data (DMF, 10−3 M, 25 °C): \( \Lambda_M = 4 \text{ S cm}^{-2} \text{ mol}^{-1} \). Magnetic data (20 °C): \( \mu_{\text{eff}} = 2.81(3) \mu_B / \text{Co}^{II} \) atom. - UV/vis (DMSO): \( \lambda_{\text{max}} = 500, 620 \text{ (d-d) nm} \). - IR (KBr pellet): \( \nu = 3435 \ \text{[v(OH)], 1538, 1374 \ [v(CO)], 970 \ [\text{quinoxaline ring}] \ cm^{-1} \). - Far-IR (polyethylene pellet): 269 \ [\nu(\text{CO}-\text{Cl})], cm−1.

(4)

Using NiCl2·6H2O and following exactly the same procedure as that described for the corresponding cobalt(II) complex, a greenish brown microcrystalline material was isolated. The yield was ~65%. Conductivity data (DMF, 10−3 M, 25 °C): \( \Lambda_M = 3 \text{ S cm}^{-2} \text{ mol}^{-1} \). Magnetic data (21 °C): \( \mu_{\text{eff}} = 2.10(3) \mu_B / \text{Ni}^{II} \) atom. - UV/vis (DMSO): \( \lambda_{\text{max}} = 390, 635 \text{ (d-d) nm} \). - IR (KBr pellet): \( \nu = 3440 \ \text{[v(OH)], 1535, 1370 \ [v(CO)], 970 \ [\text{quinoxaline ring}] \ cm^{-1} \). - Far-IR (polyethylene pellet): 249 \ [\nu(\text{Ni-Cl})], cm−1. - C32H24N606Cl2Co2 (777.38): calcd C 49.75, H 3.12, N 10.81, Cl 9.12; found C 49.75, H 2.93, N 10.92, Cl 9.00.

(5)

Using CuCl2·2H2O and following exactly the same procedure as that described for the corresponding cobalt(II) and nickel(II) complexes, a brown solid was isolated. The yield was ~70%.

(6)

A solution of cis-[RuCl2(dhbq)] (0.293 g, 0.50 mmol) in H2O (10 ml) was treated with an excess of AgNO3 (0.238 g, 1.40 mmol) under reflux for 1 h. The precipitate of AgCl was removed by filtration and to the filtrate was added a solution of H2dhbq (0.035 g, 0.25 mmol) and Et3N (1 ml) in MeOH (10 ml). The homogeneous solution obtained was refluxed for 1 h, and to this was added a solution of NaClO4 (0.122 g, 1.00 mmol) in H2O (5 ml) to yield a brown solution. This solution was then concentrated in vacuo and the resulting brown solid was collected by filtration, washed with MeOH and Et2O, and dried in vacuo. The yield was ~45%. Conductivity data (DMF 10−3 M, 95 °C): \( \Lambda_M = 189 \text{ S cm}^{-2} \text{ mol}^{-1} \). UV/vis (DMSO): 525 (d-d) nm. - IR (KBr pellet): \( \nu = 3465 \ [v(OH)], 1525, 1375 \ [v(CO)], 1100 \ [v_2(F_2)\text{perchlorate)}], 975 \ [\text{quinoxaline ring}], 625 \ [v_4(F_2)\text{perchlorate}] \ cm^{-1}. - 1^1\text{H NMR (400.1 MHz, d_6-DMSO):} \delta = 10.09 \ [s, 1 \ H, H(3)], 9.33 \ [d, 1 \ H, H(6')], 8.91 \ [d, 1 \ H, H(3')], 8.39 \ [d, 1 \ H, H(8)], 8.32 \ [d, 1 \ H, H(5)], 8.25 \ [t, 1 \ H, H(4)], 8.16 \ [t, 1 \ H, H(7)], 8.05 \ [t, 1 \ H, H(6)], 7.82 \ [t, 1 \ H, H(5')], 4.97 \ [s, 1 \ H, H(3,6)\text{dhbq}^2], 2.14 \ [s, \text{H}_2O], - C_{32}H_{28}N_{6}O_{16}Cl_2Ru_2 (1025.70): calcd C 37.47, H 2.76, N 8.19; found C 37.88, H 2.82, N 8.28.

(7)

Using RhCl3·3H2O and following exactly the same procedure as that described for the cobalt(II) complex 3, a purple material was isolated. The yield was ~70%. Conductivity data (DMF, 10−3 M, 25 °C): \( \Lambda_M = 189 \text{ S cm}^{-2} \text{ mol}^{-1} \). - UV/vis (DMSO): \( \lambda_{\text{max}} = 495, 590 \text{ (d-d) nm} \). - IR (KBr pellet): \( \nu = 3435, 3300–3000 \ [v(OH)], 1520, 1380 \ [v(CO)], 976 \ [\text{quinoxaline ring}] \ cm^{-1}. - 1^1\text{H NMR (200 MHz, d_6-DMSO):} \delta = 10.14 \ [s, 1 \ H, H(3)], 9.34 \ [d, 1 \ H, H(6')], 8.89 \ [d, 1 \ H, H(3')], 8.34 \ [m, 2 \ H, H(5,8)], 8.25 \ [t, 1 \ H, H(4)], 8.17 \ [t, 1 \ H, H(7)], 8.08 \ [t, 1 \ H, H(6)], 7.80 \ [t, 1 \ H, H(5')], 5.20 \ [s, 1 \ H, H(3,6)\text{dhbq}^2], - 3.70 \ [s, \text{H}_2O], 2.05 \ [s, \text{H}_2O], - C_{32}H_{28}N_{6}O_{16}Cl_2Rh_2 (972.26): calcd C
39.53, H 2.91, N, 8.64, Cl 14.58; found C 39.13, H 2.67, N 9.18, Cl 7.44.

\[ \text{Pd}^2(dhbq)_2]Cl_25H_2O \ (8) \]

A stirred yellow solution of \textit{cis}-\([\text{PdCl}_2L]_2\) (0.192 g, 0.50 mmol) in \text{Me}_2CO (20 ml) was added dropwise to a solution of \text{H}_2dhbq (0.035 g, 0.25 mmol) and KOH (0.028 g, 0.50 mmol) in \text{MeOH}/\text{H}_2O (2:1 v/v, 15 ml). The brown solution soon began to deposit a light brown powder. The reaction mixture was stirred at room temperature for 3 h. The product was isolated by filtration, washed with MeOH and Et₂O, and dried in vacuo. The yield was ~35%. Conductivity data (DMF, 10⁻³ M, 25 °C): \(\lambda_{\text{M}} = 178 \ \text{S cm}^2 \ \text{mol}^{-1}\). UV/vis (DMSO): \(\lambda_{\text{max}} = 410 \ (d-d) \ \text{nm}\). IR (KBr pellet): \(\nu = 3350-3300 \ [\nu(\text{OH})], 1520, 1380 \ [\nu(\text{CO})], 970 \ [\text{quinoxaline ring}] \ \text{cm}^{-1}\). \(\delta = 10.12 \ [s, 1 \ H, H(3)], 9.30 \ [d, 1 \ H, H(6')], 8.94 \ [d, 1 \ H, H(5')], 8.23 \ [t, 1 \ H, H(4')], 8.15 \ [t, 1 \ H, H(7)], 8.08 \ [t, 1 \ H, H(6)], 7.80 \ [t, 1 \ H, H(5')], 5.10 \ [s, 1 \ H, H(3,6)dhbq^2-] \). \text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_9\text{Cl}_2\text{Pd}_2 \ (926.49): \text{calcd} C 41.48, H 3.27, Cl 7.44.

\[ \text{Ag}^2(dhbq)_2]L_2 \ (9) \]

Using AgNO₃ and following the same procedure as that described for the cobalt(II) complex 3, a red-brown solid was isolated; the product was kept in the dark. The yield was ~50%. Conductivity data (DMF, 10⁻³ M, 25 °C): \(\lambda_{\text{M}} = 2 \ \text{S cm}^2 \ \text{mol}^{-1}\). IR (KBr pellet): \(\nu = 1525, 1370 \ [\nu(\text{CO})], 970 \ [\text{quinoxaline ring}] \ \text{cm}^{-1}\). \(\delta = 10.12 \ [s, 1 \ H, H(3)], 9.30 \ [d, 1 \ H, H(6')], 8.90 \ [d, 1 \ H, H(3')], 8.36 \ [mt, 2 \ H, H(5,8)], 8.26 \ [t, 1 \ H, H(4')], 8.17 \ [t, 1 \ H, H(7)], 8.07 \ [t, 1 \ H, H(6)], 7.79 \ [t, 1 \ H, H(5')], 4.91 \ [s, 1 \ H, H(3,6)dhbq^2-] \). \text{C}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Ag}_2 \ (768.32): \text{calcd} C 50.02, H 2.63, N 10.94; found C 50.05, H 2.67, N 10.51.