Synthesis, Magnetic and Mass Spectrometric Studies on Dinuclear Complexes based on Schiff-base Triazolic Ligands

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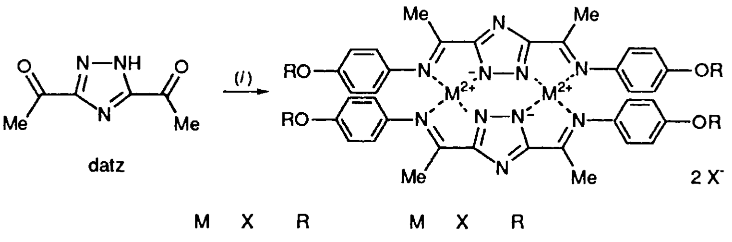
A series of dinuclear complexes of Ni^{II}, Co^{II} and Cu^{II} have been prepared by template 1:2 condensation of 3,5-diacetyl-1,2,4-triazole and the corresponding aniline in the presence of 1 equivalent of lithium hydroxide and the corresponding metal(II) salt. The dinuclear nature of the nickel and cobalt compounds have been demonstrated by FAB mass spectrometry and magnetic measurements, which indicate the presence of antiferromagnetic exchange interactions.

Metal complexes containing two or more metal centres in close proximity have been the subject of intensive studies from the standpoint of their electrochemical properties[1] and especially in the field of magnetochemistry, in the understanding of the phenomenon of exchange interactions.[2] Moreover, the incorporation of proton-ionizable groups into transition-metal dinuclear receptors as models of metalloproteins,[3] to provide for example phenoxide-bridging donor groups, has also received great attention.[4,5] Due to the good co-ordination capabilities of 1,2,4-triazole, a large number of interesting di- and poly-nuclear complexes of copper, nickel, ruthenium, osmium and iridium containing this moiety have been synthesized and studied in recent years.[6-9]

Recently, we reported[10] the synthesis and characterization of a family of metal complexes based on proton-ionizable Schiff-base triazolic macrocyclic ligands.[11] The present paper deals with two series of isostructural nickel(II) and cobalt(II) compounds **1**–**11** containing a tetradentate dinucleating anionic triazolic ligand (Scheme 1) and the related copper(II) complexes **12** and **13** (Scheme 2). The synthesis and spectroscopic characterization, and the magnetic properties of some of these complexes will be described. In particular, the dinuclear nature of the complexes is unequivocally established by fast atom bombardment mass spectrometry (FAB-MS) and magnetic measurements, which was not possible by other techniques, and the fragmentation behaviour of the complexes is rationalized.

Results and Discussion

Synthesis and Spectroscopic Studies.—Condensation of 3,5-diacetyl-1,2,4-triazole (datz)[10,12] with 2 molar equivalents of the corresponding aniline in the presence of 1 equivalent each of lithium hydroxide and the corresponding nickel(II) or cobalt(II) salt afforded complexes **1**–**11** in moderate to good yield (Scheme 1). The infrared spectra of all the metal complexes are similar, showing the presence of an imine stretch at *ca.* 1610 cm^{-1}. Proton and ^{13}C NMR spectra could not be obtained probably due to the paramagnetic character in solution of the metal complexes. The electronic spectra show very intense bands in the UV region for all complexes which have been assigned to $\pi \longrightarrow \pi^*$ transitions located on the ligands. The compounds gave correct elemental analysis, but crystals suitable for X-ray analysis could not be obtained. The FAB-MS data and the magnetic measurements described below confirmed the proposed structures. Copper complexes isostructural to the former ones could not be obtained using *p*-methoxyaniline and copper(II) salts because of oxidation of the amine under the reaction conditions. The use of a less

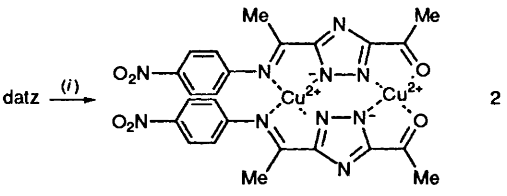


	M	X	R		M	X	R
1	Ni	Cl	Me	**7**	Co	Cl	Me
2	Ni	Cl	Et	**8**	Co	Br	Me
3	Ni	Br	Me	**9**	Co	BF_4	Me
4	Ni	BF_4	Me	**10**	Co	NO_3	Me
5	Ni	NO_3	Me	**11**	Co	ClO_4	Me
6	Ni	ClO_4	Me				

Scheme 1 (*i*) $H_2NC_6H_4OR$-*p*, MX_2, LiOH, EtOH

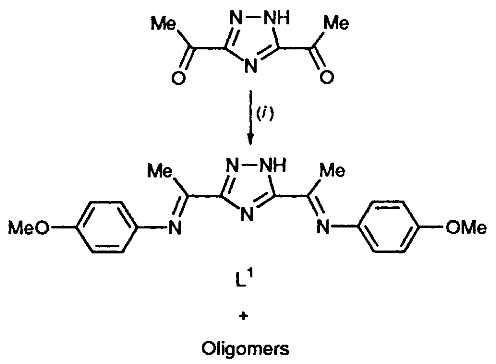
oxidizable amine, such as *p*-nitroaniline, lead to copper complexes with only two iminic moieties of probable structures **12** and **13** (Scheme 2). The lower reactivity of the *p*-nitroaniline and the insolubility of the compounds should be responsible for the formation of these complexes. The IR spectra of both show an intense band at 1680 cm^{-1} assigned to the carbonyl stretches. Analytical and FAB-MS data are also in agreement with the proposed structure.

A non-template procedure to synthesize the free [2 + 1] Schiff base by reaction of datz with an excess of *p*-methoxyaniline (Scheme 3) was not straightforward and gave only a moderate yield of this product mixed with different oligomers formed by condensation of several diacyltriazole and *p*-methoxyaniline units. The ligand L^1 could not be isolated but it was identified in the crude reaction mixture by ^{1}H and ^{13}C NMR spectroscopy and FAB-MS. Attempts to demetallate the metal complexes **1** and **7** in acidic media to regenerate the free ligand L^1 were unsuccessful probably due to the lability of the iminic double bonds.



X
12 Cl
13 BF$_4$

Scheme 2 (*i*) H$_2$NC$_6$H$_4$NO$_2$-*p*, CuX$_2$, LiOH, EtOH

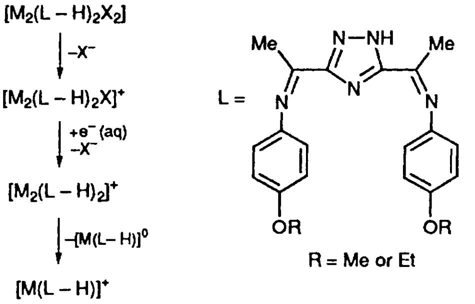


Scheme 3 (*i*) H$_2$NC$_6$H$_4$OMe-*p*, 4 Å molecular sieves

Characterization of the Dinuclear Nickel and Cobalt Complexes **1–11** *by Fast Atom Bombardment Mass Spectrometry.*—There has been a great deal of interest in the last few years in using new mass spectrometric techniques for the characterization of transition-metal complexes.[13] Fast atom bombardment mass spectrometry (FAB-MS) and liquid secondary ion mass spectrometry (LSIMS) have produced significant results. Although several studies on organometallic and co-ordination compounds using these methods have been reported,[10,13,14] only a few examples on bi- and poly-metallic derivatives are known.[15]

We have now undertaken a study by FAB-MS in order to characterize the binuclear metal complexes. Table 1 summarizes the data obtained for compounds **1–11** [M$_2$(L − H)$_2$X$_2$]. The spectra are interpreted using the low-mass isotopic peak for each isotopic cluster. Scheme 4 rationalizes the general fragmentation behaviour.

Thus, removal of one counter ion from the compound [M$_2$(L − H)$_2$X$_2$] produces [M$_2$(L − H)$_2$X]$^+$ cations. Subsequent matrix-assisted one-electron reduction of these ions with loss of the second anion produces singly-charged species [M$_2$(L − H)$_2$]$^+$ which are the most intense ions in the spectra. On the other hand, the cleavage of these ions into two parts may rationalize the production of monometallic fragments [M(L − H)]$^+$. All dinuclear complexes **1–11** show the same fragmentation pattern. Similar fragmentation behaviour has been observed in other metal complexes.[13,14]



Scheme 4 The LSIMS-induced fragmentation of dinuclear metal complexes **1–11**

Table 1 The FAB-MS fragmentation of dinuclear metal complexes [M$_2$(L − H)$_2$X$_2$] **1–11**[a]

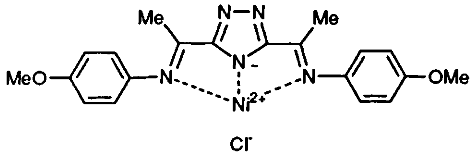
	Mass (m/z) (intensity)[b]										
Ion	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
	876	932	—	—	—	940	878	922	—	—	942
	(12)	(14)				(26)	(13)	(21)			(10)
[M$_2$(L − H)$_2$X]$^+$	875	931	919	—	—	939	877	921	877	—	941
	(27)	(32)	(20)			(30)	(23)	(36)	(11)		(32)
	841	897	841	841	841	841	843	843	843	843	843
	(66)	(64)	(62)	(31)	(62)	(88)	(50)	(20)	(42)	(48)	(69)
[M$_2$(L − H)$_2$]$^+$	840	896	840	840	840	840	842	842	842	842	842
	(100)	(100)	(100)	(47)	(31)	(100)	(100)	(100)	(90)	(100)	(100)
	735	777	735	735	735	735	737	737	737	737	737
	(8)	(5)	(12)	(100)	(100)	(26)	(29)	(10)	(100)	(21)	(23)
	—	—	630	630	630	630	—	—	631	631	—
			(5)	(26)	(31)	(13)			(38)	(6)	
	421	421	421	421	421	421	422	422	422	422	422
	(28)	(10)	(19)	(41)	(42)	(40)	(42)	(30)	(55)	(10)	(22)
[M(L − H)]$^+$	420	420	420	420	420	420	421	421	421	421	421
	(18)	(18)	(12)	(28)	(25)	(50)	(65)	(49)	(66)	(36)	(54)

[a] Glycerol matrix, solvent dmso. [b] Non-isotopically corrected.

The nickel and cobalt series **1**–**6** and **7**–**11**, respectively, allow the study of the influence of the counter ion on the fragmentation. $[M_2(L - H)_2]^+$ is presumed to be generated from the ion $[M_2(L - H)_2X]^+$ as described above. The ratio of the intensities of these two ions, $[M_2(L - H)_2]^+ : [M_2(L - H)_2X]^+$, should represent a measure of the facility in splitting an anion from complexes with the same cation. From the data of Table 1 it is possible to establish a series $NO_3 > BF_4 > Cl \geqslant Br \geqslant ClO_4$ which is in good agreement with the decreasing basicity of these anions. This anion effect had been already observed in other transition-metal complexes.[14]

In order to demonstrate that the peaks observed in the spectra genuinely correspond to dinuclear species and are not 'artefacts' produced by dimerization of mononuclear species taking into account the relatively high concentration of the complexes in the matrix, a cross experiment using nickel compounds **1** and **2** was undertaken.

With the purpose of discriminating between structures **1** and **14**, and **2** and **15** an equimolecular mixture of **1** and **2** was studied by FAB-MS using different experimental conditions. If the genuine structures for these compounds were **1** and **2**, as proposed, the spectrum of the mixture should be exactly the sum of the individual spectra of **1** and **2** (Table 1). On the contrary, if the structures for both compounds were **14** and **15** respectively, which would associate by dimerization in the matrix, besides the peaks corresponding to **1** $\{[M_2(L - H)_2X]^+$ at *m/z* 875 and base peak $[M_2(L - H)_2]^+$ at *m/z* 840$\}$ and **2** (*m/z* 931 and 896, respectively), new peaks of the mixed product **16** (at *m/z* 903 and 868) should appear in the spectrum. When the experiment is carried out under standard conditions using glycerol as matrix and dimethyl sulfoxide (dmso) as solvent, a mixture of compounds **1**, **2** and **16** are observed, apparently indicating the monomeric nature of the complexes. However, to avoid the possibility of a cleavage of **1** and **2** by means of dmso in the FAB-MS conditions, making possible ligand interchange to give **16**, measurements were also carried out using *m*-nitrobenzyl alcohol (noba) as matrix and methanol as solvent. Under these conditions only peaks corresponding to **1** and **2** were observed, thus indicating clearly the dinuclear nature of the complexes studied here. In agreement with this fact, the intensity ratio of the most characteristic ions of **1** and **2** is the same at different concentrations.



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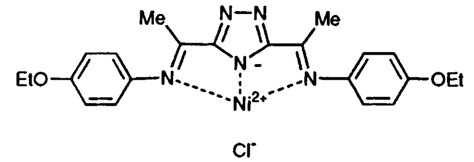

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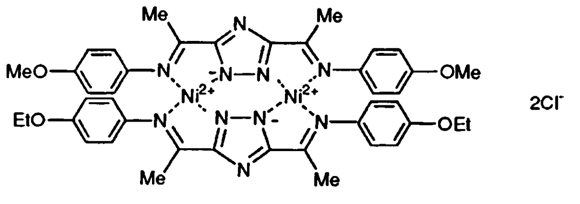

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The stability of compounds **1** and **2** in the presence of dmso under the FAB-MS conditions depends also upon the matrix employed. Thus ligand interchange between the complexes to afford **16** takes place much more readily in glycerol than in *m*-nitrobenzyl alcohol matrix. The low solubility of many of the complexes in noba precluded the detection of their spectra in this matrix. For this reason the mass spectra of **1**–**11** (Table 1) were measured using glycerol–dmso. The complexes also undergo demetallation during the experiments either in glycerol or noba matrices to give the free ligands to a greater or lesser extent, especially in the mixed glycerol–dmso matrix. The demetallation process is more pronounced at lower concentrations of the substrates.

Magnetic Measurements of Nickel and Cobalt Complexes.—The dinuclear nature of the nickel(II) and cobalt(II) complexes is confirmed by magnetic susceptibility data (4.2–300 K) which show antiferromagnetic behaviour at low temperatures in agreement with the presence of exchange-coupled metal ions. Figs. 1 and 2 show the magnetic curves for the chloride salts of these complexes (compounds **1** and **7**).

In the nickel compound **1**, the value at room temperature of the product of the molar magnetic susceptibility χ and the temperature T is 2.2 cm^3 K mol^{-1}, which is about the value

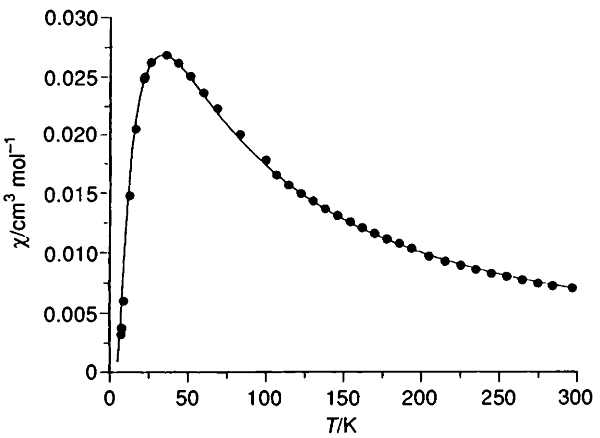


Fig. 1 Magnetic susceptibility χ *versus* temperature for the nickel compound **1**. The solid line is the best fit to a $S = 1$ Heisenberg dinuclear species ($J = -33$ cm^{-1}, $g = 2.12$)

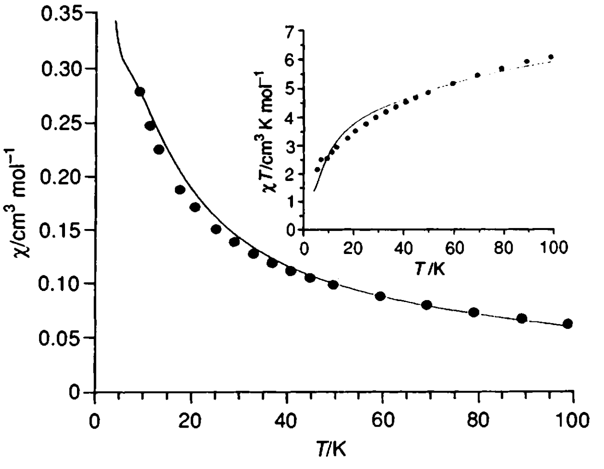
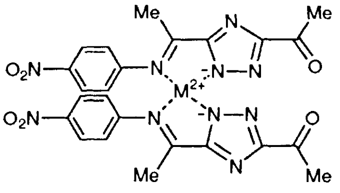


Fig. 2 Magnetic susceptibility χ *versus* temperature for the cobalt compound **7**. The solid line is the best fit from the Lines approach for a cobalt(II) dinuclear species ($J = -4.3$ cm^{-1}, $\lambda = -145$ cm^{-1}, $k = 0.67$); a plot of χT *versus* T is given in the inset

expected for a pair of uncoupled octahedrally co-ordinated nickel(II) ions with a $^3A_2$ ground state. As the temperature is lowered, χT shows a continuous decrease which indicates the presence of antiferromagnetic Ni $\cdots$ Ni exchange interactions. This is confirmed by the χ *vs.* T plot, which displays a maximum in χ at *ca.* 30 K (Fig. 1). These magnetic data can be satisfactorily fitted to the theoretical expression for the magnetic susceptibility of a $S = 1$ Heisenberg dimer.[16] The resulting parameters are $J = -33$ cm^{-1} and $g = 2.12$ (for the exchange Hamiltonian $-JS_1 \cdot S_2$).

In the cobalt compound **7** an antiferromagnetic behaviour is also observed with χT decreasing from 6.1 cm^3 K mol^{-1} at 100 K to 2.1 cm^3 K mol^{-1} at 4.2 K (inset of Fig. 2). In this case, however, the magnetic susceptibility shows a continuous increase upon cooling, which suggests the presence of small amounts of magnetically isolated cobalt(II) ions. Owing to the orbital degeneracy exhibited by octahedral Co^{II} ($^4T_1$ ground state), the usual Heisenberg exchange-coupling scheme is no longer appropriate to analyse the magnetic behaviour of exchange-coupled cobalt(II) compounds, and models including orbital effects are required.[17] The simplest approach takes advantage of the fact that in distorted octahedral sites the $^4T_1$ ground state of Co^{II} splits into six Kramers doublets in such a way that the lowest Kramers doublet is very anisotropic being separated in energy from the excited ones by more than 100 cm^{-1}. In fact, in the present case powder EPR measurements at 4 K show an axial spectrum with g components of $g_{\parallel} = 2.16$ and $g_{\perp} = 5.1$ which is typical of a CoN$_4$X$_2$ octahedral chromophore.[18] Since at $T < 20$–30 K only the ground Kramers doublet will be appreciably populated, the low-temperature magnetic behaviour of exchange-coupled cobalt complexes can be described from a model that assumes an effective (anisotropic) exchange interaction between fictitious spins $S = \frac{1}{2}$. This approach is restricted to those cobalt systems exhibiting very weak exchange interactions, since for these systems the low-temperature data are sufficient to obtain information on the splitting in the ground spin levels caused by the exchange interaction. However, for intermediate and strong exchange interactions such information is too limited and the effects of the upper levels need to be considered and the only available approach is the so-called Lines' theory of cobalt(II) cluster complexes.[19] This theory assumes that the cobalt cluster contains equivalent and undistorted octahedral cobalt sites which are coupled by isotropic exchange. In this theory the exchange interactions in the excited single-ion levels are included as a molecular field, and therefore, it is expected to be appropriate over the entire temperature range.

We attempted to fit the magnetic susceptibility data through the Lines approach for complex **7**. The corresponding equations are given in ref. 20 and the calculated curves are compared with the experimental data in Fig. 2. We observe that this approach reproduces in a satisfactory manner the experimental data from the following set of parameters: $J = -4.3$ cm^{-1}, $\lambda = -145$ cm^{-1}, $k = 0.67$, $p = 0.08$, where J is the exchange interaction, λ the spin–orbit coupling ($\lambda_o \approx -180$ cm^{-1} in the free Co^{2+} ion), k the orbital reduction factor, and p the amount of $S = \frac{3}{2}$ paramagnetic impurity. It is interesting to comment on the values of the resulting parameters, since they are expected to be strongly correlated. Thus, while the ratio $\lambda:\lambda_o = 0.8:1$ is in the expected range, the covalency effects reflected in the orbital reduction factor k seem to be overestimated. This may be related to the limitations of the Lines approach which assumes undistorted octahedral sites. In fact, for isolated cobalt(II) complexes it has been shown that a distortion parameter exerts a similar influence on the effective magnetic moment μ_{eff} (proportional to the square root of χT) to that of a decrease of k, so leading to a reduction in μ_{eff} at high temperatures. With respect to the validity of J, it is to be noticed that this parameter is strongly correlated with λ. Both parameters exert similar effects in the low-temperature region, so that the resulting antiferromagnetic J value can only be taken as approximate.



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Spectroscopic and Magnetic Characterization of the Copper Compounds **12** *and* **13**.—Compounds **12** and **13** were also identified by FAB-MS. In both cases an intensive isotopic cluster at m/z 670, 672 was observed. These peaks can be assigned to an ion, obtained by removal of the two counter ions, in which only two iminic moieties are present. This result suggests a partial condensation of the *p*-nitroaniline with datz, giving rise to the structures proposed in Scheme 2.

The magnetic behaviour of these compounds show a continuous decrease of χT upon cooling and a tendency to a plateau below 10 K. This result may indicate that besides the dinuclear Cu $\cdots$ Cu unit indicated in Scheme 2, the compounds contain mononuclear copper species. A tentative fit of the experimental data to a mixture of mono- plus di-nuclear copper species indicates that the samples contain similar amounts of both components. The exchange coupling in the dinuclear species is around -10 cm^{-1}. The mononuclear species could not be isolated and its nature has not been established but could correspond to complex **17**, taking into account the lower complexing ability of the carbonyl subunits in comparison with that of the imine functions.

Experimental

Instrumentation.—Melting-point determinations were performed on a Büchi melting-point apparatus. Infrared spectra were recorded on a PU 9716 Philips spectrometer in KBr pellets. UV/VIS spectrophotometric measurements were performed with a Perkin-Elmer Model Lambda 6 instrument. Elemental analyses were carried out in the Servicio Interdepartamental de Investigación (SIDI), Universidad Autónoma de Madrid. The LSIMS spectra were measured with a HSQ30-BEQQ system and a MAT900 instrument (Finnigan MAT, Bremen), both equipped with a caesium gun from AMD Intectra GmbH, Harpstedt and from Finnigan, respectively. To analyse the isotopic clusters, 20–50 spectra of a limited mass range were sampled, averaged and then corrected. The samples were dissolved in dmso and mixed on the probe with glycerol (1 : 1 v/v); the concentration was in the range of 15–100 nmol for each measurement.

Variable-temperature magnetic susceptibility measurements were carried out in the range 4.2–300 K with a fully automated AZTEC DSM8 pendulum-type susceptometer equipped with a TBT continuous-flow crysostat. The EPR spectra at 4 K were recorded with a Bruker ER 200D spectrometer equipped with a continuous-flow cryostat.

General Procedure for the Preparation of Metal Complexes **1**–**13**.—A mixture of datz (1 mmol), *p*-methoxy-, *p*-ethoxy- or *p*-nitro-aniline (2 mmol), the corresponding metal salt (1 mmol) and lithium hydroxide (1 mmol) in ethanol (10 cm^3) was heated at reflux with stirring for 3 h. After cooling to room temperature, the precipitate was filtered off and dried *in vacuo*. For soluble complexes the volume of the filtered solution was reduced by evaporation. The compounds were purified as indicated below.

Complex **1**. Recrystallized from ethanol–diethyl ether, green crystals, yield 24%, m.p. > 300 °C (Found: C, 49.05; H, 4.70; Cl, 7.00; N, 14.15; Ni, 12.25. Calc. for $C_{40}H_{40}Cl_2N_{10}Ni_2O_4{\cdot}3H_2O$: C, 49.65; H, 4.80; Cl, 7.35; N, 14.50; Ni, 12.15%). UV/VIS: λ_{max}/nm (log ε) [dimethylformamide (dmf)] 278 (4.46), 315 (sh) and 350 (sh). IR (KBr): ν_{max}/cm^{-1} 1605 [C=N-(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 875, 877, 879 $[C_{40}H_{40}ClN_{10}Ni_2O_4]^+$..

Complex **2**. Recrystallized from ethanol–diethyl ether, green crystals, yield 44%, m.p. > 300 °C (Found: C, 51.35; H, 5.05; Cl, 6.80; N, 13.40; Ni, 11.70. Calc. for $C_{44}H_{48}Cl_2N_{10}Ni_2O_4{\cdot}3H_2O$: C, 51.65; H, 5.30; Cl, 6.95; N, 13.70; Ni, 11.45%). UV/VIS: λ_{max}/nm (log ε) (dmf) 278 (4.5) and 338 (sh). IR (KBr): ν_{max}/cm^{-1} 1605 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 931, 933, 935 $[C_{44}H_{48}ClN_{10}Ni_2O_4]^+$.

Complex **3**. Triturated with methanol, brown-green powder, yield 46%, m.p. > 300 °C (Found: C, 46.15; H, 4.00; Br, 15.70; N, 14.30; Ni, 11.10. Calc. for $C_{40}H_{40}Br_2N_{10}Ni_2O_4{\cdot}2H_2O$: C, 46.30; H, 4.25; Br, 15.40; N, 13.50; Ni, 11.30%). UV/VIS: λ_{max}/nm (log ε) (dmf) 268 (4.47) and 312 (sh). IR (KBr): ν_{max}/cm^{-1} 1605 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 919, 921, 923 $[C_{40}H_{40}BrN_{10}Ni_2O_4]^+$.

Complex **4**. Recrystallized from ethanol–diethyl ether, yellow-green powder, yield 47%, m.p. > 300 °C (Found: C, 45.05; H, 4.95; N, 12.80; Ni, 10.90. Calc. for $C_{40}H_{40}B_2F_8N_{10}Ni_2O_4{\cdot}3H_2O$: C, 44.90; H, 4.35; N, 13.10; Ni, 11.00%). UV/VIS: λ_{max}/nm (log ε) (dmf) 275 (4.61) and 316 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 840, 842 $[C_{40}H_{40}N_{10}Ni_2O_4]^+$.

Complex **5**. Triturated with ethanol, yellow-green powder, yield 32%, m.p. > 300 °C (Found: C, 48.55; H, 4.40; N, 16.10; Ni, 11.40. Calc. for $C_{40}H_{40}N_{12}Ni_2O_{10}{\cdot}2H_2O$: C, 47.95; H, 4.40; N, 16.75; Ni, 11.70%). UV/VIS: λ_{max}/nm (log ε) (dmf) 268 (4.57) and 316 (sh). IR (KBr): ν_{max}/cm^{-1} 1605 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 840, 842 $[C_{40}H_{40}N_{10}Ni_2O_4]^+$.

Complex **6**. Triturated with methanol, green powder, yield 59%, m.p. > 300 °C (Found: C, 43.25; H, 4.95; Cl, 6.65; N, 12.90; Ni, 10.65. Calc. for $C_{40}H_{40}Cl_2N_{10}Ni_2O_{12}{\cdot}3H_2O$: C, 43.85; H, 4.25; Cl, 7.35; N, 12.80; Ni, 10.70%). UV/VIS: λ_{max}/nm (log ε) (dmf) 276 (4.66). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (noba–dmso): *m*/*z* 939, 941, 943 $[C_{40}H_{40}ClN_{10}Ni_2O_8]^+$.

Complex **7**. Triturated with toluene, brown powder, yield 16%, m.p. > 300 °C (Found: C, 48.70; H, 3.90; Cl, 8.30; Co, 11.70; N, 13.50. Calc. for $C_{40}H_{40}Cl_2Co_2N_{10}O_4{\cdot}3H_2O$: C, 49.65; H, 4.80; Cl, 6.45; Co, 12.20; N, 14.45%). UV/VIS: λ_{max}/nm (log ε) (dmf) 268 (4.59) and 342 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 877, 879 $[C_{40}H_{40}N_{10}ClCo_2O_4]^+$.

Complex **8**. Recrystallized from ethanol–diethyl ether, brown powder, yield 38%, m.p. > 300 °C (Found: C, 45.65; H, 4.60; Br, 15.05; Co, 10.70; N, 12.95. Calc. for $C_{40}H_{40}Br_2Co_2N_{10}O_4{\cdot}3H_2O$: C, 45.45; H, 4.40; Br, 15.15; Co, 11.15; N, 13.25%). UV/VIS: λ_{max}/nm (log ε) (dmf) 272 (4.49) and 334 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 921, 923 $[C_{40}H_{40}BrCo_2N_{10}O_4]^+$.

Complex **9**. Recrystallized from ethanol–diethyl ether, orange powder, yield 16%, m.p. > 300 °C (Found: C, 42.80; H, 3.95; Co, 10.35; N, 13.45. Calc. for $C_{40}H_{40}B_2Co_2F_8N_{10}O_4{\cdot}5H_2O$: C, 43.45; H, 4.55; Co, 10.65; N, 12.55%). UV/VIS: λ_{max}/nm (log ε) (dmf) 272 (4.53) and 325 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 877 $[C_{40}H_{40}BCo_2F_4N_{10}O_4]^+$.

Complex **10**. Triturated with ethanol, orange powder, yield 70%, m.p. > 300 °C (Found: C, 46.55; H, 3.85; Co, 11.00; N, 16.55. Calc. for $C_{40}H_{40}Co_2N_{12}O_{10}{\cdot}3H_2O$: C, 47.05; H, 4.55; Co, 11.55; N, 16.45%). UV/VIS: λ_{max}/nm (log ε) (dmf) 275 (4.60) and 328 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N-(imine)]. FAB-MS (glycerol–dmso): *m*/*z* 842 $[C_{40}H_{40}Co_2N_{10}O_4]^+$.

Complex **11**. Recrystallized from acetonitrile–water, orange powder, yield 24%, m.p. > 300 °C (Found: C, 43.65; H, 4.60; Cl, 5.50; Co, 10.40; N, 12.50. Calc. for $C_{40}H_{40}Cl_2Co_2N_{10}O_{12}{\cdot}3H_2O$: C, 43.85; H, 4.25; Cl, 6.45; Co, 10.75; N, 12.80%). UV/VIS: λ_{max}/nm (log ε) (dmf) 277 (4.62) and 336 (sh). IR (KBr): ν_{max}/cm^{-1} 1610 [C=N(imine)]. FAB-MS (glycerol–dmf): *m*/*z* 941, 943 $[C_{40}H_{40}ClCo_2N_{10}O_8]^+$.

Complex **12**. Triturated with ethanol, green powder, yield 27%, m.p. > 300 °C (Found: C, 36.55; H, 3.30; Cl, 9.05; Cu, 16.25; N, 17.25. Calc. for $C_{24}H_{20}Cl_2Cu_2N_{10}O_6{\cdot}3H_2O$: C, 36.20; H, 3.30; Cl, 8.90; Cu, 15.95; N, 17.60%). UV/VIS: λ_{max}/nm (log ε) (dmf) 266 (4.48), 304 (4.47), 346 (sh) and 382 (sh). IR (KBr): ν_{max}/cm^{-1} 1680 (C=O), 1620 [C=N(imine)] and 1355 (NO_2). FAB-MS (glycerol–dmso): *m*/*z* 670, 672 $[C_{24}H_{20}Cu_2N_{10}O_6]^+$.

Complex **13**. Triturated with ethanol, green powder, yield 26%, m.p. > 300 °C (Found: C, 31.25; H, 2.60; Cu, 14.75; N, 16.05. Calc. for $C_{24}H_{20}B_2Cu_2F_8N_{10}O_6{\cdot}3H_2O$: C, 32.05; H, 2.90; Cu, 14.15; N, 15.60%). UV/VIS: λ_{max}/nm (log ε) (dmf) 275 (4.48) and 382 (4.10). IR (KBr): ν_{max}/cm^{-1} 1680 (C=O), 1620 [C=N(imine)] and 1355 (NO_2). FAB-MS (glycerol–dmso): *m*/*z* 670, 672 $[C_{24}H_{20}Cu_2N_{10}O_6]^+$.

Ligand L^1. 3,5-Diacetyl-1,2,4-triazole (0.3 g, 1.96 mmol) and *p*-methoxyaniline (0.73 g, 5.88 mmol) were dissolved in dry dichloromethane (8 cm^3), and then 4 Å molecular sieves (1 g) were added. The mixture was stirred at room temperature for 24 h. After centrifugation the solvent was removed under reduced pressure and the oily residue was induced to solidify with dry diethyl ether to afford 0.29 g of a yellow solid which was identified by ^{1}H NMR spectroscopy as a mixture of several products, the major product being the [2 + 1] Schiff base L^1. Compound L^1 could not be purified by column chromatography. Estimated yield: (by ^{1}H NMR) 55%. IR (KBr): ν_{max}/cm^{-1} 1600 [C=N(imine)]. FAB-MS (noba–dmso): *m*/*z* 364 $[C_{18}H_{13}N_5O_2]^+$. NMR $[(CD_3)_2SO]$: ^{1}H (200 MHz), δ 6.90 (AA′BB′, aromatic), 3.75 (s, OCH_3) and 2.29 (s, CH_3); ^{13}C (50 MHz), δ 156.3 (CN), 142.5, 121.4, 114.4 (aromatic), 55.4 (OCH_3) and 17.4 (CH_3).

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