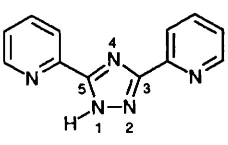
Triazolate-containing Macrocyclic Transition-metal Complexes derived from Bis(3-aminopropyl)amine and 3,5-Diacyl-1,2,4-triazoles

Jose A. Duro,[a] **Jesús M. Ontoria,**[a] **Angela Sastre,**[a] **Wolfram Schäfer**[b] **and Tomás Torres***,[a]
[a] *Departamento de Química (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid, 28049-Madrid, Spain*
[b] *Max-Plank-Institut für Biochemie, 8033-Martinsried bei München, Germany*

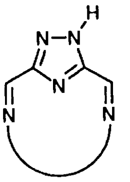
Template 1:1 condensation of 3,5-diacetyl- or 3,5-diformyl-1,2,4-triazole with bis(3-aminopropyl)-amine in the presence of 1 equivalent of LiOH and M(ClO$_4$)$_2$ (M = Ni, Cu, Co or Pb) produces mononuclear tetraaza 14-membered macrocyclic Schiff-base metal(II) complexes [ML]ClO$_4$ {L = 12-hydroxy-2,12-dimethyl- or 12-hydroxy-3,7,11,14,15,16-hexaazabicyclo[11.2.1]hexadeca-2,13,15-trienate}. These compounds are derived from the expected diimino macrocyclic complexes by formal addition of water across one of the azomethine bonds. Reduction of the Schiff-base complexes with sodium tetrahydroborate provides the corresponding saturated tetraaza macrocyclic complexes. Both sets of compounds were identified and studied by liquid secondary ion mass spectrometry.

1,2,4-Triazole derivatives are a class of azole compounds that can bind as either 2,4- or 1,2-bridging nitrogen-donor ligands.[1–3] The 1,2-bridging mode is known to yield polynuclear co-ordination compounds.[1–3] The magnetic properties of dinuclear triazole derivatives containing paramagnetic transition-metal ions have been studied by Haasnoot and co-workers.[1,4] The same authors have recently reported the photophysical and spectroscopic properties of mono- and dinuclear ruthenium complexes with 1,2,4-triazole-containing ligands.[5] The mechanism of exchange interactions between paramagnetic centres bridged by azolate ligands (triazolate, imidazolate) has also been actively investigated by other groups in the last few years.[6–8] The electrochemistry and luminescence properties of mono- and di-nuclear osmium(II) compounds containing 3,5-bis(pyridin-2-yl)-1,2,4-triazole (bpytz) have also been recently studied.[8] It is known[1] that bpytz forms dimeric copper(II) complexes, in which the dinucleating configuration with the pyridine nitrogen atoms directed toward the triazole N^1 and N^2 atoms is more favoured than the terdentate configuration, which would involve co-ordination of N^4, thus resembling an analogue to 2,2′:6′,2″-terpyridine.[1] The incorporation of the diimino 1,2,4-triazole moiety into a rigid macrocyclic configuration, as represented in **I**, constitutes an interesting example in which the system is forced to adopt a N_4 co-ordination mode.[9] On the other hand, the complexing ability of macrocycles of type **I** and other related ligands stems not only from their relatively less flexible and preorganized nature, but also from the readiness of triazole to deprotonate and to form a triazolate anion, which facilitates the metal co-ordination. The capability of the triazole to generate a negative charge is the most important difference between these systems and the related well known diacylpyridine based macrocycles.[10–13]

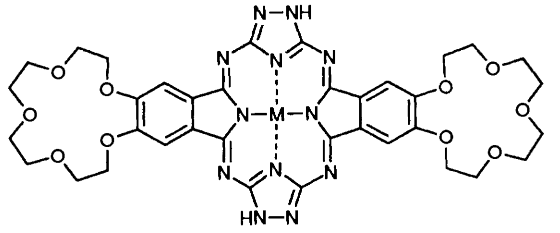
The incorporation of proton ionizable groups into macrocyclic transition-metal receptors has been the focus of a great deal of attention.[14] Since the first report by Pilkington and Robson[15] on phenolic binuclear macrocyclic systems many related examples have been reported.[16,17] For example, almost all the reported model compounds for the active site in dicopper metalloproteins (haemocyanin, tyrosinase) contain dinucleating ligands in which a hydroxide, a phenolate, or an alkoxide group acts as a bridge between the two copper sites.[18] On the other hand, the pyrrolyl moiety has also been introduced as a proton ionizable subunit in binucleating Schiff-base macrocycles.[19]



bpytz



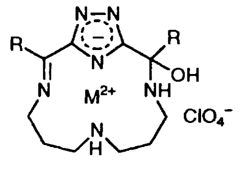
I



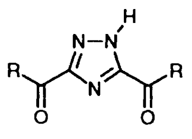
II

Our interest in the synthesis and co-ordination chemistry of 1,2,4-triazole-containing macrocyclic ligands,[9,20–22] especially with regard to their electrical and magnetic properties[20] led us to prepare substituted triazole hemiporphyrazines of type **II**[9,20] as phthalocyanine analogues,[23] in order to study these properties. Now, we have sought to extend our work to [1 + 1] diimine and [2 + 2] tetraimine Schiff-base macrocycles,[11–13,24] containing proton ionizable 1,2,4-triazole subunits.

This paper describes the synthesis and characterization of a family of metal complexes **1**–**5** based on the new polyamine Schiff-base [1 + 1] macrocyclic ligands L^1 (R = Me) or L^2 (R = H). The complexes were prepared by metal-ion promoted template reactions of the corresponding heterocyclic dicarbonyl derivative 3,5-diacetyl- or 3,5-diformyl-1,2,4-triazole[25] and bis(3-aminopropyl)amine. The characterization was carried out by chemical methods, elemental analyses, IR spectra and especially by liquid secondary ion mass spectrometry (LSIMS). This technique has proved to be adequate for the structure elucidation of compounds **1**–**5**.[26]



	M	R
1	Ni	Me
2	Cu	Me
3	Co	Me
4	Pb	Me
5	Ni	H



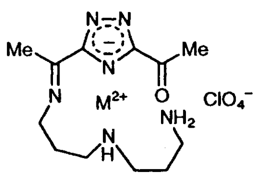
datz (R = Me)
dftz (R = H)

Results and Discussion

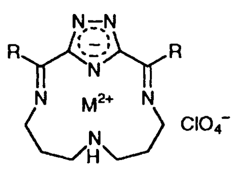
Synthesis of Complexes **1**–**5**.—Direct condensation of 3,5-diacetyl-1,2,4-triazole (datz) with bis(3-aminopropyl)amine in the presence of 1 molar equivalent of lithium hydroxide and metal(II) perchlorate afforded complexes $[ML^1][ClO_4]$ (M = Ni **1**, Cu **2**, Co, **3** or Pb **4**) in moderate to good yields. The microcrystalline compounds had elemental analyses consistent with the formulations given, but crystals suitable for X-ray analysis could not be obtained. The condensation of 3,5-diformyl-1,2,4-triazole (dftz) with bis(3-aminopropyl)amine and nickel perchlorate under the same reaction conditions yielded $[NiL^2][ClO_4]$ **5**. Other metal perchlorates (Cu, Co, Pb) also appeared to form macrocyclic triazolates with dftz (IR data), probably of similar structure to **5**, but these could not be confirmed owing to their low solubility which prevented purification.

Triazole deprotonation also takes place if the condensation reactions are carried out in the absence of lithium hydroxide, but lower yields of the complexes were obtained. No evidence is observed for undeprotonated macrocycles.

The good yield of the [1 + 1] macrocycles obtained and the general absence of [2 + 2] condensation compounds and polymeric side products are probably a consequence of the strong complexation ability of the triazolate component. Formation of an initial monoimino acyltriazolate metal complex **III** would maintain the carbonyl group in the correct orientation for ring closure to give complexes **1**–**5**. The compounds **1**–**5** are derived from the expected complexes **IV** by formal addition of water across one of the azomethine bonds. The presence of the diimino macrocyclic complexes **IV** could not be observed.



III



IV (R = H or Me)

Infrared and ^{1}*H NMR Spectra*.—The infrared spectra of all of the complexes **1**–**5** are similar. The macrocyclic nature of the complexes was confirmed by the absence of the amine ($-NH_2$) and carbonyl vibrations associated with the reactants and the presence of an imine stretch at 1635–1645 cm^{-1}. A band at 3240–3280 cm^{-1} is assigned to the O–H stretch and another one at 1210 cm^{-1} to the C–O vibration of the alcohol. The ν_3 and ν_4 (ClO_4^-) vibrations appear at 1100 and 625 cm^{-1}, respectively and are consistent with ionic perchlorate.

The paramagnetic character in solution of complexes **1**–**5** excludes their study by nuclear magnetic resonance, except for the lead complex **4**, which shows two singlets at δ 2.40 and 2.32 in the ^{1}H NMR spectrum corresponding to the two different methyl groups of the molecule.

Characterisation of Complexes **1**–**5** *by Liquid Secondary Ion Mass Spectrometry* (*LSIMS*).—Compounds **1**–**5** were identified by LSIMS. The spectra showed in all cases a peak corresponding to $(ML)^+$ (L = L^1 or L^2). The mass spectrum for the nickel complex **1** is shown in Fig. 1. A detailed study by LSIMS using different experimental conditions was undertaken in order to confirm the [1 + 1] nature of the complexes. The pseudo-molecular ions $(ML)^+$ showed isotopic distributions corresponding to species containing only one metal atom and so exclude the alternative [2 + 2] formulation. For example, the experimental and theoretical [1 + 1] mass spectra for the lead complex **4**, registered in the mass range corresponding to the pseudo-molecular ion are coincident. The low solubility of complexes **1**–**5** in organic solvents compatible with the employed matrices made it necessary to employ trifluoroacetic acid (tfa) as the co-solvent for the detection of the mass spectra.

A study of Corey–Pauling–Koltun models of complexes **1**–**5** and the use of a simulation program (DTMM) revealed that the size of the macrocyclic cavity is large enough to accommodate Ni^{II}, Cu^{II} or Co^{II} ions. However the larger lead(II) ion is forced to lie outside the cavity. The anionic character of the ligand could be responsible to a great extent for the stability of the complexes. On the other hand, it is remarkable that the flexibility of the organic ligand in complexes **1**–**5**, although low, is higher than that of the corresponding organic ligand of a complex of type **IV**. For complexes **1**–**5** it is possible to obtain a distorted square-planar disposition of the four inner nitrogen atoms of the macrocycle around the metal, which is not possible in complexes of type **IV**. These could be the reasons why complexes **1**–**5** do not lose water to give the initially expected double-iminic macrocyclic systems **IV**. Several examples concerning addition of water, alcohols or amines to iminic double bonds in related macrocyclic systems have been reported.[27]

A LSIMS analysis of the crude reaction mixture, from which compound **4** was isolated in 80% yield, revealed the presence in a low ratio of the corresponding binuclear [2 + 2] macrocyclic complex $[Pb_2L^3][ClO_4]_2$ **6**, although the latter could not be isolated. Compound **6** shows a pseudo-molecular ion at *m*/*z* 942,944,946 which corresponds to the presence of an isotopic cluster relating to a species containing two lead atoms. Such a species was not detected in the mass spectra of the other metal complexes and may be stabilised by the larger lead(II) cations. It is noteworthy that the divalent cation of **6**, $[Pb_2L^3]^{2+}$, has been reduced to a monovalent cation $[Pb_2L^3]^+$ in the LSIMS experiment thus implying the generation of a mixed-valence lead(II)lead(I) complex. Similar reduction processes have been described for related metal macrocyclic complexes.[28]

Electronic Spectra.—The copper(II) complex **2** showed three major absorptions in the electronic spectrum in dimethylformamide (dmf). The two low-energy bands at 720 (sh) and 640 nm have low molar absorption coefficients and are almost certainly due to d–d transitions. The spectral pattern observed is as expected for a distorted octahedral co-ordination of the copper(II) ion. The more intensive higher energy absorption at 270 nm is assigned mainly to intraligand transitions together with charge-transfer transitions.

Compounds **1**, **3** and **5** showed only one low-energy band centred at 540, 480 and 540 nm respectively as well as an intense absorption in the region 250–350 nm.

The low flexibility of the macrocycles in complexes **1**–**5** observed in the molecular models and the almost square-planar disposition of their four nitrogen atoms around the metal ion, as mentioned above, together with the UV/VIS data,[27b,29] infers a basically common octahedral co-ordination for the metal ions in solution, in complexes **1**–**3** and **5**, with solvent occupying the axial sites.

Reduction of Complexes **1**–**3** *and* **5**.—Additional data about the structure of complexes **1**–**5** were obtained by reduc-

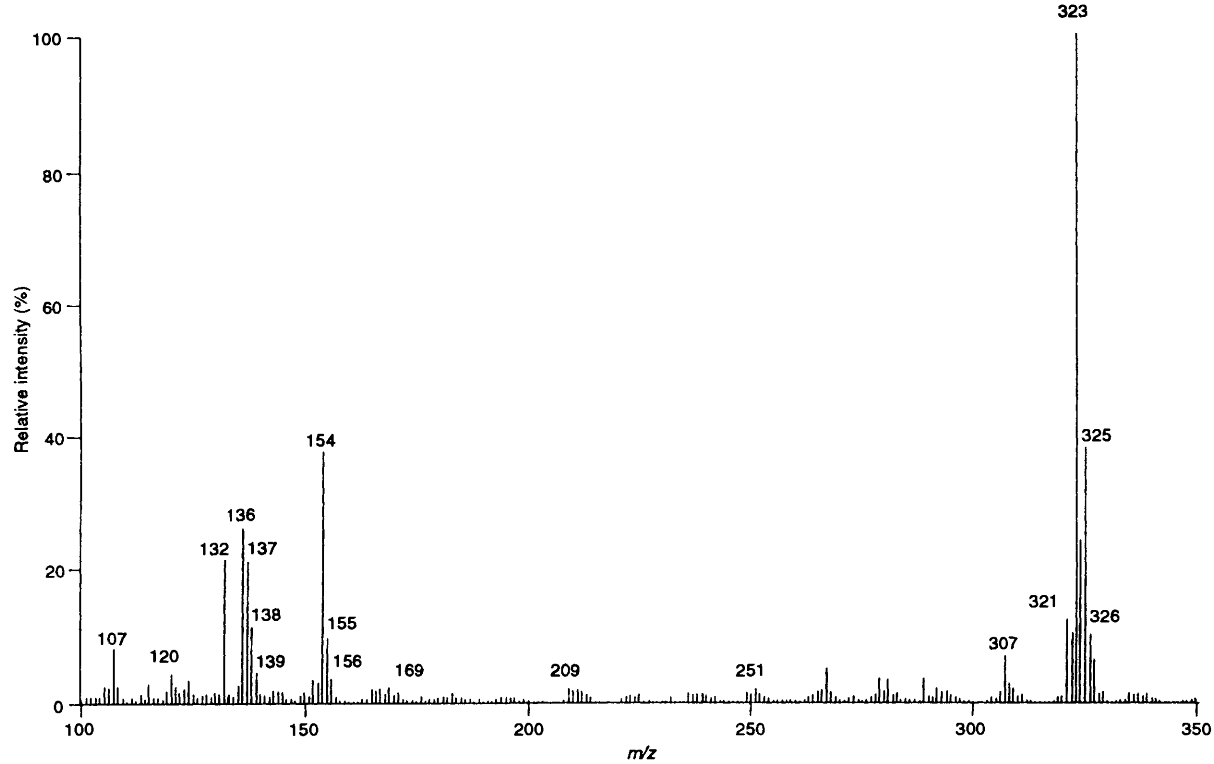
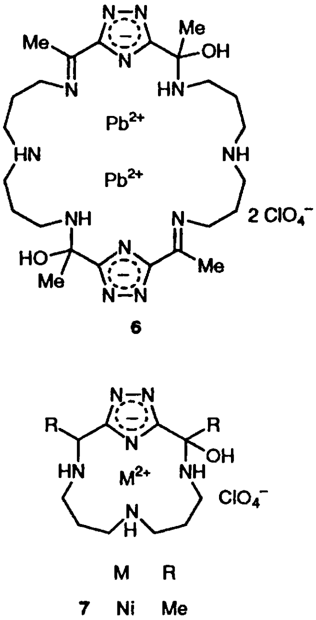


Fig. 1 LSIMS spectrum of [NiL^1][ClO$_4$] **1** in noba–tfa, showing the pseudo-molecular ion (NiL^1)$^+$ at *m*/*z* 323 and 325



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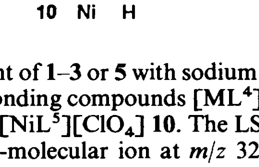

	M	R
7	Ni	Me
8	Cu	Me
9	Co	Me
10	Ni	H

tion. Thus, treatment of **1**–**3** or **5** with sodium tetrahydroborate yielded the corresponding compounds [ML^4][ClO$_4$] (M = Ni **7**, Cu **8** or Co **9**) or [NiL^5][ClO$_4$] **10**. The LSIMS spectrum of **7** showed a pseudo-molecular ion at *m*/*z* 325,327, *i.e.* at two mass units more than its precursor **1**, thus indicating the presence of only one imino group in the latter. The isotopic cluster for this ion also confirms the presence of only one metal atom. The very low solubility of compounds **7**–**10** and/or their instability in trifluoroacetic acid, which induces cleavage of the complexes, avoided their study by LSIMS. The analytical and IR data of the complexes **7**–**10** are in agreement with the proposed structures. The absence of an imine absorption in the IR spectra of these compounds allows the observation of a weak absorption at 1620 cm^{-1} corresponding to the triazolate.

Attempts to obtain the free macrocyclic Schiff-base ligands starting from 3,5-diacetyl- or 3,5-diformyl-1,2,4-triazole and bis(3-aminopropyl)amine in the absence of metal ions under high-dilution conditions were unsuccessful and led to polymeric materials. This fact clearly indicates the importance of the metal ions acting as templates in the reactions described here.

The low solubility of compounds **1**–**5** prevented a comparison of their chemical properties with those of related compounds containing a pyridine moiety.[10–13] For this reason the preparation of soluble analogues of **1**–**5** has recently been undertaken. We are currently exploring the template reaction between 3,5-diacetyl- or 3,5-diformyl-1,2,4-triazole and other amines besides bis(3-aminopropyl)amine. Thus, for example, with smaller amines such as propane-1,3-diamine the corresponding [2 + 2] barium double-iminic Schiff-base complex is obtained. On the other hand, dinuclear transition-metal complexes are obtained by the template reaction of datz or dftz and monoamines.[30]

Experimental

Instrumentation.—The metal complexes were characterised by liquid secondary ion mass spectrometry, IR and NMR spectroscopy and microanalysis (C, H and N). Melting point determinations were performed on a Büchi apparatus. Infrared spectra were recorded on a PU 9716 Philips spectrometer in KBr pellets. Proton NMR spectra were recorded with a Bruker WM-200-SY, 200 MHz spectrometer. UV/VIS spectrophotometric measurements were performed with a Perkin Elmer model Lambda 6 spectrophotometer. The LSIMS measurements were performed with a MAT-900 (Finnigan MAT, GmbH, Bremen) instrument. Elemental analysis were carried out in the Instituto de Química General, Consejo Superior de Investigaciones Cientificas, Madrid.

Materials.—All reagents and chemicals were of highest grade commercial quality and were used without further purification. 3,5-Diformyl-1,2,4-triazole was prepared by the literature method.[25]

3,5-*Diacetyl*-1,2,4-*triazole*.—This compound previously described by us[25] was prepared by modifying an established method. (*S*,*S*)-3,5-Bis(1-hydroxyethyl)-1,2,4-triazole[21] (4.17 g, 30 mmol) was dissolved in 15 mol dm^{-3} H_2SO_4 (70 cm^3). Then CrO_3 (6.60 g, 66 mmol) in the same solvent (50 cm^3) was added. The reaction mixture was left to stir at 70–80 °C for 2 h. The green solution was saturated with NaCl and extracted with methylene chloride (3 × 150 cm^3). The organic extracts were dried with Na_2SO_4 and evaporated to dryness. Recrystallization from toluene afforded the diketone datz as a colourless crystalline solid (3.29 g, 63%), m.p. 135 °C. Spectral data (NMR, IR) were in good agreement with the literature values.[25] High resolution mass spectrum: *m*/*z* 153.052 (M^+), $C_6H_7N_3O_2$ requires 153.057.

General Procedures for the Preparation of Complexes **1**–**5**.—**CAUTION:** Perchlorates of heavy-metal ions with organic ligands are potentially explosive.[31] It is advisable to handle or store only small amounts of these materials and to avoid mixing with concentrated acids. Furthermore, the materials should not be subjected to mechanical or thermal stress.

Method A. A mixture of the dicarbonyl compound datz or dftz (1 mmol), the corresponding metal perchlorate (1 mmol) and lithium hydroxide (1 mmol) in ethanol (15 cm^3) was heated at reflux with stirring for 15 min. Then, bis(3-aminopropyl)-amine (1 mmol) was added and the reaction mixture was heated at reflux and stirred for 1 h. The precipitate was filtered off and dried *in vacuo*. The compounds **1**–**5** were purified as indicated below.

Method B. As for method A but in the absence of lithium hydroxide.

{12-*Hydroxy*-2,12-*dimethyl*-3,7,11,14,15,16-*hexaazabicyclo*-[11.2.1]*hexadeca*-2,13,15-*trienato*}*nickel*(II) *perchlorate* **1**. Compound **1**, isolated as a greenish powder was recrystallized from acetonitrile to give blue crystals [20% (method A), 12% (method B)], m.p. > 300 °C (Found: C, 33.65; H, 4.80; N, 19.50. $C_{12}H_{21}ClN_6NiO_5$ requires C, 34.05; H, 5.00; N, 19.85%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (dmf) 320 (4.0) and 540 (1.8); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3340, 3280 (NH, OH), 1640 (CN imine), 1610 (C=N triazole), 1210 (CO) and 1100, 630 (ClO); mass spectrum [LSIMS 3-nitrobenzyl alcohol (noba)–dmf or –tfa)]: *m*/*z* 323, 325 [(NiL^1)$^+$].

{12-*Hydroxy*-2,12-*dimethyl*-3,7,11,14,15,16-*hexaazabicyclo*-[11.2.1]*hexadeca*-2,13,15-*trienato*}*copper*(II) *perchlorate* **2**. Compound **2** was triturated with methanol at reflux temperature to afford blue crystals [60% (method A), 51% (method B)], m.p. > 300 °C (Found: C, 33.50; H, 4.70; N, 19.45. $C_{12}H_{21}ClCuN_6O_5$ requires C, 33.65; H, 4.95; N, 19.60%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (dmf) 270 (4.2), 640 (2.3) and 720 (sh); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3260, 1645 (CN imine), 1620 (C=N triazole), 1205, 1100 and 630; mass spectrum [LSIMS (noba–tfa): *m*/*z* 328, 330 [(CuL^1)$^+$].

{12-*Hydroxy*-2,12-*dimethyl*-3,7,11,14,15,16-*hexaazabicyclo*-[11.2.1]*hexadeca*-2,13,15-*trienato*}*cobalt*(II) *perchlorate* **3**. Compound **3** was triturated with methanol at reflux temperature to afford a reddish brown solid [92% (method A), 70% (method B)], m.p. > 300 °C (Found: C, 32.25; H, 5.00; N, 18.90. $C_{12}H_{21}ClCoN_6O_5 \cdot H_2O$ requires C, 32.65; H, 5.25; N, 19.00%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (dmf) 270 (3.9) and 480 (2.2); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3420, 3260, 1635 (C=N), 1100 and 630; mass spectrum [LSIMS (noba–dimethyl sulfoxide or –dmf)]: *m*/*z* 324 [(CoL^1)$^+$].

{12-*Hydroxy*-2,12-*dimethyl*-3,7,11,14,15,16-*hexaazabicyclo*-[11.2.1]*hexadeca*-2,13,15-*trienato*}*lead*(II) *perchlorate* **4**. Compound **4** was triturated successively with butanol and ethanol at reflux temperature to give a pale yellow solid [77% (method A)], m.p. > 300 °C (Found: C, 25.40; H, 3.55; N, 14.55. $C_{12}H_{21}ClN_6O_5Pb$ requires C, 25.20; H, 3.70; N, 14.70%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3250, 1640 (C=N), 1100 and 630; δ_H{[$^2H_7$]dmf} 1.4–2.4 (4 H, m, $CH_2CH_2CH_2$), 2.32 and 2.40 (3 H and 3 H, 2 × s, CH_3), 2.7–3.4 (6 H, m, CH_2NH) and 3.3–4.2 (2 H, m, $CH_2CH_2N{=}C$); mass spectrum [LSIMS (noba–tfa)]: *m*/*z* 471, 472, 473 [(PbL^1)$^+$]. LSIMS analysis of the crude reaction material showed the presence of the corresponding [2 + 2] dinuclear lead complex **6**; mass spectrum [FAB (noba–tfa)]: *m*/*z* 942, 944, 946 [(Pb$_2$L^3)$^+$] and 924, 926, 928 [(Pb$_2$L^3–H$_2$O)$^+$]. Similar results were obtained using lead thiocyanate as the starting material instead of lead perchlorate, the more soluble complex [PbL^1]SCN being formed.

{12-*Hydroxy*-3,7,11,14,15,16-*hexaazabicyclo*[11.2.1]*hexadeca*-2,13,15-*trienato*}*nickel*(II) *perchlorate* **5**. Nickel perchlorate hexahydrate was used. Compound **5** was triturated successively with butanol and ethanol at reflux temperature to give a pale greenish powder [65% (method A), 58% (method B)], m.p. > 300 °C (Found: C, 30.15; H, 4.55; N, 20.85. $C_{10}H_{17}ClN_6NiO_5$ requires C, 30.35; H, 4.35; N, 21.25%); λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (dmf) 300 (4.0) and 540 (1.9); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3320, 3240 (NH, OH), 1640 (CN imine), 1610 (C=N triazole) and 1100, 630 (ClO); mass spectrum [LSIMS (noba–tfa)]: *m*/*z* 295, 297 [(NiL^2)$^+$].

Reduction of Compounds **1**–**3** *and* **5**.—*Preparation of* {2-*Hydroxy*-2,12-*dimethyl*- or 2-*hydroxy*-3,7,11,14,15,16-*hexaazabicyclo*[11.2.1]*hexadeca*-13,15-*dienato*}*metal*(II) *Perchlorates* **7**–**10**.—A mixture of the corresponding metal complex **1**–**3** or **5** (1 mmol) and sodium tetrahydroborate (2 mmol) in ethanol (10 cm^3) was heated at reflux temperature with stirring for 1 h. The precipitate was filtered off and triturated successively with butanol and ethanol at reflux temperature and finally dried in vacuum. LSIMS measurements were performed only for **7** (nickel complex) because of partial to total decomposition of complexes **7**–**10** in trifluoroacetic acid which was required as solvent in the LSIMS experiments, due to their high insolubility.

Complex **14**. Greyish powder (63%), m.p. > 300 °C (Found: C, 33.85; H, 5.45; N, 19.75. $C_{12}H_{23}ClN_6NiO_5$ requires C, 33.65; H, 5.60; N, 19.25%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3300, 1620 (C=N triazole), 1210, 1100 and 630; mass spectrum [LSIMS (noba–tfa)]: *m*/*z* 325, 327 [(NiL^4)$^+$].

Complex **8**. Green powder (55%), m.p. > 300 °C (Found: C, 33.50; H, 5.40; N, 19.55. $C_{12}H_{23}ClCuN_6O_5$ requires C, 34.30; H, 5.20; N, 19.00%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3260, 1625 (C=N triazole), 1100 and 630.

Complex **9**. Brown powder (78%), m.p. > 300 °C (Found: C, 33.85; H, 4.95; N, 19.75. $C_{12}H_{23}ClCoN_6O_5$ requires C, 33.45; H, 5.35; N, 19.50%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1625 (C=N triazole), 1100 and 630.

Complex **10**. Greenish powder (50%), m.p. > 300 °C (Found: C, 30.35; H, 4.35; N, 21.25. $C_{10}H_{19}ClN_6NiO_5$ requires C, 29.70; H, 4.85; N, 20.85%); $\tilde{\nu}_{max}$/cm^{-1} (KBr) 3420, 3280, 1620 (C=N triazole), 1100 and 630.

Acknowledgements

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