ChemComm

A heterodinuclear macrocyclic complex containing both nickel(II) and palladium(II) ions

Przemysław Starynowicz and Jerzy Lisowski*

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland.
E-mail: jurekl@wchuwr.chem.uni.wroc.pl

Received (in Cambridge, UK) 4th Febuary 1999, Accepted 16th March 1999

The first heterodinuclear macrocyclic Schiff base complex containing both first- and second row transition metal ions, $[NiPdL](ClO_4)_2{\cdot}3MeCN$ has been synthesised and characterised by spectroscopic methods; the X-ray structure of this complex and its mononuclear precursor are reported.

The first macrocyclic dinuclear complexes $[M_2L]^{2+}$ {where H_2L is the macrocyclic Schiff base ligand (Fig. 1) 11,23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.1^{19,13}]hexacosa-2,7,9,11,13(26),14,19,21(25),22,24-decaene-25,26-diol and $M^1 = M^2 = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} ord Zn^{2+}} were synthesised in a direct template 2+2 condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminopropane by Robson and Pilkington[1] and by Okawa and Kida[2] in a stepwise synthesis. More recently, the first examples of homodinuclear complexes of the ligand L^{2-} with second- and third-row transition metal ions have been reported.[3]

Apart from homodinuclear complexes, the analogous heterodinuclear ($M^1 \neq M^2$) complexes have also been synthesised in stepwise syntheses starting from non-cyclic precursors.[4] This synthetic strategy often utilises the difference in the coordination preferences of the two metal ions by using two different diamine fragments in the left and right side of the macrocyclic system. Both homo- and hetero-dinuclear complexes of L^{2-} and related ligands have proved to be very useful in studying magnetic coupling phenomena, mimicking bimetalic metalloenzymes, investigating mixed-valence systems *etc.*,[4–6]

Here, we report the synthesis, spectroscopic characterisation and X-ray crystal structure of the mixed nickel(II)–palladium(II) complex $[NiPdL](ClO_4)_2{\cdot}3MeCN$. To the best of our knowledge this is the first example of a heterodinuclear macrocyclic complex containing both first- and second-row transition metal ions. We present also the X-ray crystal structure of the mononuclear complex $[Ni(H_2L](ClO_4)_2{\cdot}2MeOH$[1] which is the precursor in the synthesis of the mixed $Ni^{II}Pd^{II}$ complex and other heterodinuclear complexes.[7]

The starting complex $[Ni(H_2L)](ClO_4)_2{\cdot}H_2O$ was obtained as described in ref. 1. $[NiPdL](ClO_4)_2{\cdot}3MeCN$† was obtained by reacting $[NiH_2L](ClO_4)_2{\cdot}H_2O$ with palladium(II) acetate in acetonitrile, in a similar fashion to related heterodinuclear complexes containing two first row metal ions[7]. This synthetic strategy is remarkably simple compared to the stepwise syntheses of related heterodinuclear macrocyclic complexes. Moreover, our attempts to obtain the $[NiPdL]^{2+}$ complex in alternative stepwise syntheses starting from the non-cyclic *N,N′*-propylenebis(3-formyl-5-methylsalicylideneaminato)-nickel(II) or -palladium(II) complexes, although while leading to the desired heterodinuclear systems as judged from spectroscopic data, have not yielded pure products so far.

^1H NMR and electrospray MS spectra confirm the heterodinuclear nature of the obtained complex and show that no scrambling of metal ions takes place during the synthesis. The ESMS of $[NiPdL](ClO_4)_2{\cdot}3MeCN$ shows signals with a maximum at *m/z* 667.3 corresponding to $[NiPdL](ClO_4)^+$ and at *m/z* 282.9 corresponding to $[NiPdL]^{2+}$. The large isotropic shifts observed for the ^1H NMR spectra of $[NiPdL](ClO_4)_2{\cdot}3MeCN$ in D_2O or CD_3OD solutions are in accord with the presence of high-spin Ni^{II}. The signal assignment was based on the intensity, expected shift values, linewidth analysis and comparison with the spectra[7] of $[Ni(H_2L)](ClO_4)_2{\cdot}H_2O$ and $[Ni_2L]Cl_2{\cdot}2H_2O$. Protons **a**, **b**, **d**, **e**, **h** and **i** resonate at δ −6.17, 119.2, 9.77, 3.06, 6.32 and 2.75, respectively (see Fig. 1 for labelling scheme). The signals at δ 24.34 and 11.55 correspond to positions **f** and **g** or *vice versa*, while the signal of proton **c**, expected in the region δ 250–450 region, is too broad to be

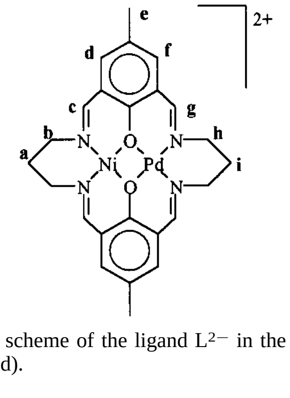

Fig. 1 The labelling scheme of the ligand L^{2-} in the $[NiPdL]^{2+}$ complex (axial ligands omitted).

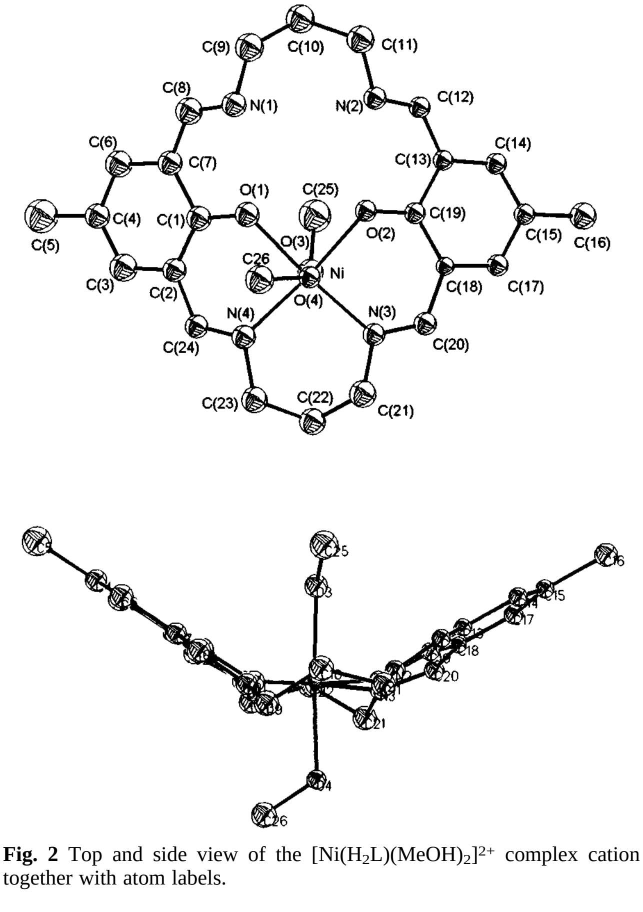

Fig. 2 Top and side view of the $[Ni(H_2L)(MeOH)_2]^{2+}$ complex cation together with atom labels.

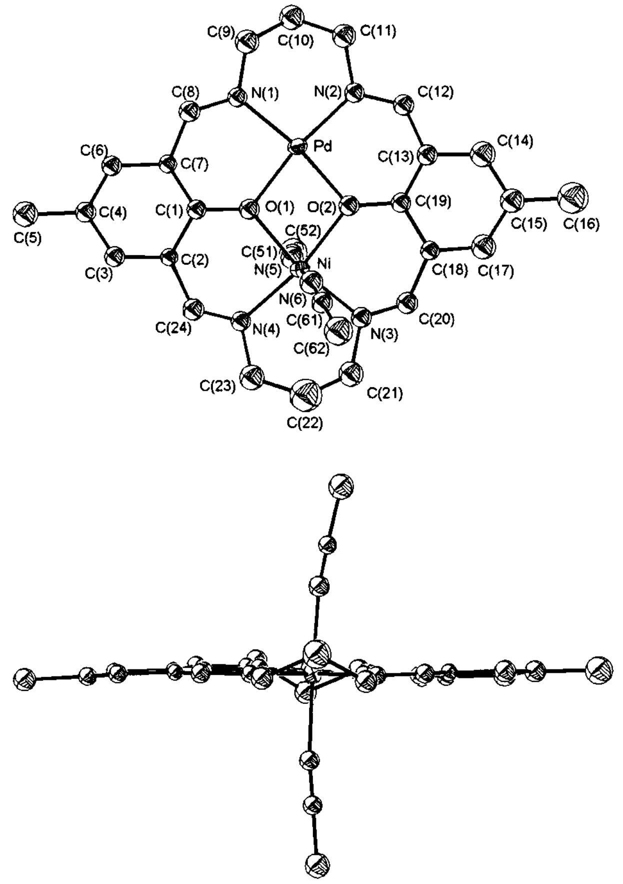

Fig. 3 Top and side view of the $[NiPdL(MeCN)_2]^{2+}$ complex cation together with atom labels.

detected. As expected, the protons that are three or four bonds away from the paramagnetic Ni^{II} ion exhibit relatively large isotropic shifts. On the other hand the protons that belong to the methyl group and the Pd^{II}-complexed side of the ligand experience smaller isotropic shifts due to less effective spin delocalisation.

Crystals of $[Ni(H_2L)](ClO_4)_2·2MeOH$ were obtained by diffusion of diethyl ether into methanol solution of $[Ni(H_2L)](ClO_4)_2·H_2O$ and crystals of $[NiPdL](ClO_4)_2·3MeCN$ were grown from acetonitrile.‡ The complex cation in $[Ni(H_2L)](ClO_4)_2·2MeOH$ (Fig. 2) is composed of the macrocyclic ligand bonded to Ni^{II} with four of its ligating atoms [two O and two N atoms; Ni–O(1) 2.013(11), Ni–N(3) 2.017(13), Ni–O(2) 2.022(10), Ni–N(4) 2.040(13) Å]. The two remaining coordination sites of Ni^{II} are occupied by two methanol molecules [Ni–O(4) 2.101(10), Ni–O(3) 2.156(11) Å], leading to a slightly distorted octahedron around the metal ion. In $[NiPdL](ClO_4)_2·3MeCN$ the macrocyclic ligand binds two metal ions, Ni^{II} and Pd^{II} (Fig. 3). Both phenyl oxygen atoms, unlike in the case of $[Ni(H_2L)](ClO_4)_2·2MeOH$, are deprotonated. The octahedral coordination of Ni^{II} cation is completed by two acetonitrile molecules [Ni–N(4) 2.002(15), Ni–N(3) 2.003(14), Ni–O(2) 2.035(12), Ni–O(1) 2.037(11), Ni–N(5) 2.09(2), Ni–N(6) 2.10(2) Å], whereas the Pd^{II}) environment forms a slightly distorted square [Pd-N(1) 1.990(14), Pd-O(2) 1.997(11), Pd-N(2) 2.000(13), Pd-O(1) 2.012(11) Å]. The presence of Pd^{II} changes the overall conformation of the macrocycle. In $[NiPdL](ClO_4)_2·3MeCN$ the ligand adopts a planar conformation similar to that observed in other crystallographically characterised $[M_2L]^{n+}$ complexes.[3a,6] The angle between two flat fragments of the ligand [C(1)C(2)C(3)C(4)C(5)C(6)C(7)C(8)C(24)O(1)N(1)N(4) and C(12)C(13)C(14)C(15)C(16)C(17)C(18)C(19)C(20)O(2)N(2)-N(3)] is 177.4°. In contrast, in $Ni(H_2L)](ClO_4)_2·2MeH$ (Fig. 3) the ligand is considerably bent with the above mentioned planes forming the angle of 115.9°. However, this bending of the ligand is not as profound as that observed in the completely bent conformation of the protonated free ligand[3a] (phenyl rings almost parallel).

In principle, the unique combination of macrocyclic environment and different reactivities of the first- and second-row metal complexes may lead to new catalytic systems. Presently we are investigating the catalytic properties of $[NiPdL](ClO_4)_2·3MeCN$ and related complexes.

This work was supported by KBN grant 3 T09A 071 12.

Notes and references

† The complex has been characterised by elemental analysis, IR and UV-VIS spectroscopy

‡ *Crystal data:* the crystals chosen for the data collection were placed in Lindemann glass capillaries and then mounted on a Kuma KM4 diffractometer. The intensities of three standards were monitored every 100 reflections. During measurement both crystals partially decomposed. The final loss of intensity was 57% for $[NiPdL](ClO_4)_2·3MeCN$ and 79% for $[Ni(H_2L)](ClO_4)_2·2MeOH$. The structures were solved using Patterson methods with SHELXS-86, and then refined with SHELXL-93. The C-bonded hydrogen atoms were placed in geometrically calculated positions. As both crystals were poor scatterers, and the data/parameters ratios were unfavourable, the anisotropic thermal vibration parameters were applied to metal and chlorine atoms only, the other atoms being refined isotropically. The temperature factors for H atoms were set as 1.2 times the factors of the C atoms to which the relevant H atoms were bonded. For $[NiPdL](ClO_4)_2·3MeCN$ it was found that the oxygen atoms of the perchlorate anions and a part of the solvent (acetonitrile) molecules were disordered. The respective site occupation factors were assumed to be 0.5. a)

_$[Ni(H_2L)](ClO_4)_2·2MeOH$: $C_{26}H_{36}Cl_2N_4NiO_{12}$, M = 726.20, triclinic, $P\bar{1}$, a = 9.789(2), b = 11.737(2), c = 14.795(3) Å, α = 92.05(3), β = 99.19(3), γ = 107.00(3)°, V = 1598.6(5) Å^3, Z = 2, T = 293(2) K, μ = 0.840 mm^{-1}, number of reflections measured = 2270, number of observed reflections [$I \geqslant 3\sigma(I)$] = 1466, $R(F)$ = 0.0707, $R_w(F^2)$ = 0.1352.

$[NiPdL](ClO_4)_2·3MeCN$: $C_{30}H_{35}Cl_2N_7NiO_{10}Pd$, M = 889.66, monoclinic, $P2_1/c$, a = 16.627(3), b = 19.701(4), c = 10.951(2) Å, β = 91.35(3)°, V = 3586.2(12) Å^3, Z = 4, T = 293(2) K, μ = 1.239 mm^{-1}, number of reflections measured = 3308, number of reflections observed [$I \geqslant 3\sigma(I)$] = 1837, $R(F)$ = 0.0673, $R_w(F^2)$ = 0.1243.

CCDC 182/1198. See http://www.rsc.org/suppdata/cc/1999/769/ for crystallographic files in .cif format.

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Communication 9/00969H