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Complexes of Ni(II) and Pd(II) ions with 15- and 17-membered macrocycles containing O_2N_2 - and O_2N_3 -donors and the crystal structures of Ni(II) and Pd(II) complexes of 2,5-dioxa-13,16,19-triazatricyclo [19.4.0.0^{6,11}]-pentacosa-6,8,10,21,23,25(1)-hexaene

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Abstract

The interactions of O_2N_2 - and O_2N_3 -donor macrocycles with Ni(II) and Pd(II) have been investigated and four new complexes (L^{1a} , L^{2a} , L^2b and L^2c) were synthesized. In rigid 15-membered macrocyclic complex (L^1a), the etheric oxygens are coordinated to the metal ion, while in the more flexible 17-membered macrocyclic complexes $(L^2a, L^2b \text{ and } L^2c)$ the etheric oxygens are not bonded to the metal ions. Comparative FTIR, FAB, TGA, DSC, ¹H- and ¹³C-NMR, elemental analyses, magnetic measurements as well as X-ray structure analysis (on two complexes, L^2a and L^2b) have been used to elucidate the nature of the species formed. The Ni(II) complexes (L^1a and L^2a) were found to be octahedral geometry while the Pd(II) complexes (L^2b and L^2c) were square planar structure. The 1,4,7-triazaheptane macrocyclic fragment in L^2a was co-ordinated to Ni(II) ion in a facial manner as supported by the X-ray structural analysis. Two types of Pd(II) complexes have been isolated with acetate ligand, the more insoluble form contains three water molecules without bonding to Pd(II) ion, the other one has not contained any water molecule as proven by TGA and DSC data. L^2a crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.820(1), b = 8.237(2), c = 17.529(1) \text{ Å}, \beta = 93.17(1)^{\circ}, V = 2280.7(5) \text{ Å}^3, Z = 4 \text{ and } D_x = 1.527 \text{ g cm}^{-3}$. The complex has a distorted octahedral structure, incorporating the three nitrogen donors of the macrocyclic ring, two oxygen atoms of the bidentate and one oxygen atom of the monodentate nitrate ions. $L^{2}b$ crystallizes in the orthorhombic space group P cab with a = 13.791(2), b = 14.620(1), cc = 28.295(2) Å, V = 5705.0(9) Å³, Z = 8 and $D_x = 1.444$ g cm⁻³. The complex contains a mononuclear Pd(II) ion in which there are three water molecules, together with one acetate ion and one acetate ligand bonded to Pd(II). The hydrogen bonds are highly effective between the water molecules, acetate ions and the macroring for stabilizing the molecule as a whole. The coordination around Pd(II) is a distorted square planar. But the close contact of the second O atom of the acetate ligand may cause to a distorted square pyramidal coordination geometry around Pd(II).

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1. Introduction

Macrocyclic multidentate $O_x N_y$ ($x; y = 2, 3, \cdots$) donortype ligands lie at the focal point formed from different fields of research, including the potential transition metal ion selective reagents, coordination complexes and catalysts [1–3]. On the other hand, the transition metal ion recognition with particular metal-ion binding applications are of fundamental importance to broad areas of coordination- and bio-chemistry [4]. A large number of open-chain and macrocyclic multidentate ligand complexes have been investigated extensively, in order to understand their synthetic, thermodynamic and/or structural properties of complex formation [2,5–8]. Our research group have also been investigated the structures of a series of free macrocyclic multidentate $O_x N_y$ donor-type ligands [9–15].

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	Compound	М	X	n
Dibenzo-bis-imino crown ether	L			
	L ²			
Dibenzo-triaza crown ether				
$\begin{array}{c} X \\ 0 \\ HC = N \\ X \\ \end{array} \\ \begin{array}{c} X \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N = CH \\ X \\ \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \\ \end{array} \\ \begin{array}{c} N \\ N \\ N \\ N \\ N \\ \end{array} \\ \begin{array}{c} N \\ \end{array} \\ \begin{array}{c} N \\ N $	L ¹ a	Ni	NO3	2
Dibenzo-bis-imino crown etner complex				
$ \begin{array}{c} X \\ 0 \\ H_2C-NH \\ NH \end{array} \cdot nH_2O $	L ² a	Ni	NO3	
Dibenzo-triaza crown ether complex				
	L ² b	Pd	CH ₃ COO	3
	L ² c	Pd	CH ₃ COO	
Dibenzo-triaza crown ether complex				

Scheme 1.

In this study, the macrocyclic multidentate ligands (L^1 and L^2) [16,17] and their Ni(II) and Pd(II) complexes (L^1a , L^2a-L^2c) have been synthesized (Scheme 1).

The FTIR, ¹H-, ¹³C-NMR and MS spectroscopic data, TGA and DSC results of the newly synthesized products with the crystal structures of complexes (L^2a and L^2b) are reported.

2. Experimental

2.1. Reagents and techniques

Melting points were measured on a Gallenkamp apparatus using a capillary tube ¹H-, ¹³C-, ³¹P-NMR spectra

were obtained on a Bruker DPX FT-NMR (400 MHz) spectrometer (SiMe₄, as internal standard and 85% H₃PO₄ as an external standard). IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs and were reported in cm⁻¹ units. Microanalyses were carried out by the microanalytical service of TÜBİTAK (Turkey), electron impact (EI) and fast atomic bombardment (FAB) spectra were obtained on the PLATFORM II LC-MS and VG-ZAPSPEC spectrometers. Thermogravimetric curves of recently dried samples were recorded using a Du Pont 2050 thermogravimetric analyser (TGA) system. TA Instruments, using ca. 5 mg sample mass and a platinum sample holder. Heating rate of 5 °C min⁻¹ under dry N₂ atmosphere (60 mL min⁻¹) was investigated. DSC curves of samples were recorded on Du Pont 2010 DSC thermal

analyser, TA Instruments, in a covered aluminium sample holder with a central pinhole and a sample mass of ca. 4 mg under a 10 °C min⁻¹ heating rate and 100 cm³ min⁻¹ dynamic air flow. Magnetic moments were determined at 23 °C using a Faraday balance calibrated against Hg[Co(NCS)₄].

2.2. Synthetic procedures

2,5-*Dioxa*-13,17-*diazatricyclo*[17.4.0.0^{6,11}]-*tricosa*-6,8,10,12,17,19,21,23(1)-*octaene*, (**L**¹): Ligand (**L**¹) was prepared according to the literature method [16], ¹H NMR (CDCl₃): δ_{ppm} , 2.32 (m, 2H, N–CH₂–*CH*₂), ³J_{HH} = 5.3 Hz; 3.63 (t, 4H, N–*CH*₂), ³J_{HH} = 5.3 Hz; 4.42 (s, 4H, Ar–O– *CH*₂); 6.98–8.02 (m, 8H, aromatic-H); 8.74 (s, 2H, *H*C=N); ¹³C NMR (CDCl₃): δ_{ppm} , 29.0 (N–CH₂–*C*H₂); 58.2 (N– *C*H₂); 68.2 (Ar–O–*C*H₂); 113.9, 122.2, 126.0, 127.6, 132.2, 159.0 (aromatic-C); 159.2 (H*C*=N).

2,5-Dioxa-13,16,19-triazatricyclo[19.4.0.0^{6,11}]-pentacosa-6,8,10,21,23,25(1)-hexaene, (L²): Ligand (L²) was obtained by the published procedure [17], ¹H NMR (CDCl₃): δ_{ppm} , 2.33 (s, 3H, N–H); 2.73 (t, 4H, N–CH₂– CH₂), ³J_{HH} = 5.0 Hz; 2.85 (t, 4H, N–CH₂), ³J_{HH} = 5.0 Hz; 3.96 (s, 4H, Ar–CH₂–N); 4.54 (s, 4H, Ar–O–CH₂); 7.06– 7.43 (m, 8H, aromatic-H), ¹³C NMR (CDCl₃): δ_{ppm} ; 49.0 (N–CH₂–CH₂); 49.4 (N–CH₂); 51.2 (Ar–CH₂–N); 67.4 (Ar–O–CH₂); 111.3, 121.0, 128.8, 129.1, 131.5, 157.6 (aromatic-C).

{2,5-Dioxa-13,17-diazatricyclo[17.4.0.0^{6,11}]-tricosa-6,8,10,12,17,19,21,23(1)-octaene dinitrato] nickel(II) dihydrate, [Ni(L¹)(NO₃)₂]·2H₂O, (L¹a): To a solution of (L¹) (0.50 g, 1.51 mmol) in butanol (50 ml) was added dropwise a solution of Ni(NO₃)₂·6H₂O (0.44 g, 1.51 mmol) in *n*-butanol (10 ml). The mixture was refluxed for 7 h and then the solvent was removed under reduced pressure. The crude dark blue powder product was crystallized from *n*butanol/H₂O mixture (100:1), yield 0.71 g (89%), 240 °C (decompose), ¹H NMR (DMSO): δ_{ppm} , 2.69 (b, 2H, N– CH₂-CH₂); 3.59 (b, 4H, N–CH₂); 4.54 (b, 4H, Ar–O– CH₂); 7.14–7.98 (b, 8H, aromatic-H); 8.71 (b, 2H, HC=N), ¹³C NMR [D₆–(CH₃)₂CO + D₂O]: δ_{ppm} , 29.1 (N–CH₂– CH₂); 60.2 (N–CH₂); 70.6 (Ar–O–CH₂); 116.9, 124.4, 129.7, 131.0, 140.0, 161.9 (aromatic-C); 164.4 (HC=N).

{2,5-Dioxa-13,16,19-triazatricyclo[19.4.0.0^{6,11}]-pentacosa-6,8,10,21,23,25(1)-hexaene dinitrato} nickel(II), [Ni(L²)(NO₃)₂], (L²a): To a solution of (L²) (0.50 g, 1.47 mmol) in *n*-butanol (35 ml) was added dropwise a solution of Ni(NO₃)₂·6H₂O (0.43 g, 1.47 mmol) in *n*butanol (15 ml). The mixture was refluxed for 7 h, and the solvent was evaporated under reduced pressure. The crude purple powder product was crystallized from *n*butanol/THF/H₂O mixture (70:29:1), yield 0.65 g (85%), 279 °C (decompose), ¹H NMR [D₆-(CH₃)₂CO + D₂O]: δ_{ppm} , 3.32 (b, 4H, N-CH₂-CH₂); 3.41 (b, 4H, N-CH₂); 5.11 (b, 4H, Ar-CH₂-N); 5.49 (b, 4H, Ar-O-CH₂); 7.83– 9.79 (b, 8H, aromatic-H), ¹³C NMR [D₆-(CH₃)₂CO + D₂O]: $δ_{ppm}$, 61.0 (N-CH₂-CH₂); 67.3 (N-CH₂); 72.2 (Ar-CH₂-N); 78.9 (Ar-O-CH₂); 109.4, 118.1, 128.5, 132.6, 141.0, 168.9 (aromatic-C).

{2,5-Dioxa-13,16,19-triazatricyclo[19.4.0.0^{6,11}]-pentacosa-6,8,10,21,23,25(1)-hexaene diacetato} palladium(II). trihydrate, $[Pd(L^2)(CH_3COO)]CH_3COO.3H_2O$, (L²b) and {2,5-Dioxa-13,16,19-triazatricyclo[19.4.0.0^{6,11}]-pentacosa-6,8,10,21,23,25(1)-hexaene diacetato} palladium(II), $[Pd(L^2)(CH_3COO)]CH_3COO, (L^2c)$: To a solution of (L^2) (0.11 g, 0.32 mmol) in dichloromethane (50 ml) was added dropwise a solution of Pd(CH₃COO)₂ (0.07 g, 0.32 mmol) in dichloromethane (30 ml). The mixture was refluxed for 5 h and then cooled and filtered. The residue was dissolved in trichloromethane (30 ml) and set aside for crystallization of $(\mathbf{L}^{2}\mathbf{b})$ at an ambient temperature, yield 0.13 g (33%), m.p. 174 °C, ¹H NMR (CDCl₃): δ_{ppm} , 1.32 (b, 3H, CH₃-C(O)-O), 1.90 (b, 3H, CH₃-C(O)-O); 2.72 (m, 4H, N-CH₂- CH_2); 2.86 (m, 4H, N- CH_2); 3.10 (b, 3H, N-H); 3.68 (m, 2H, Ar-O-CH₂), 3.92 (m, 2H, Ar-O-CH₂); 4.39 (m, 2H, Ar-CH₂-N), 4.82 (m, 2H, Ar-CH₂-N); 6.92-7.41 (b, 8H, aromatic-H), 9.68 (b, 1H, $CH_3-C(O)O \cdots H$), ¹³C NMR (CDCl₃): δ_{ppm}, 22.8, 25.0 (CH₃-C(O)O); 52.1 (N-CH₂-CH₂); 53.2 (N-CH₂); 55.8 (Ar-CH₂-N); 67.3 (Ar-O-CH₂); 111.8, 120.7, 121.7, 131.0, 133.9, 158.6 (aromatic-C); 178.0, 180.1 (CH₃-C(O)O). The mother liquor was evaporated and the residue was redissolved in dichloromethane (25 ml). The mixture was filtered off and set aside for crystallization of $(\mathbf{L}^2 \mathbf{c})$, yield 0.09 g (47%), m.p. 181 °C, ¹H NMR (CDCl₃): δ_{ppm} , 1.28 (b, 3H, CH₃-C(O)-O), 1.85 (b, 3H, CH₃-C(O)-O); 2.71 (m, 4H, N-CH₂-CH₂); 2.87 (m, 4H, N-CH₂); 3.00 (b, 3H, N-H); 3.63 (m, 2H, Ar-O-CH₂), 3.86 (m, 2H, Ar-O-CH₂); 4.34 (m, 2H, Ar-CH₂-N), 4.77 (m, 2H, Ar-CH₂-N); 6.89-7.37 (b, 8H, aromatic-H), 9.51 (b, 1H, CH₃-C(O)O···H), 13 C NMR $(CDCl_3 + CH_2Cl_2): \delta_{ppm}, 22.9, 25.0 (CH_3 - C(O)O); 67.3$ (Ar-O-CH₂); 111.8, 120.7, 121.8, 131.0, 132.0, 158.6 (aromatic-C); 178.0, 180.1 (CH₃-C(O)O).

2.3. Crystallography

The suitable crystals of L^2a and L^2b for X-ray analysis were obtained by recrystallization from n-butanol/THF/H₂O (79:29:1) mixture and trichloromethane, respectively. Experimental data, methods and the procedure used to elucidate the structure and other related parameters are given in Table 1. For L^2a and L^2b , empirical absorption corrections based on a series of psi-scans were applied to the data. The structures of the complexes were solved by direct methods, SHELXS-97 [18]. For L²a, atoms H2 and H3 were located in a difference synthesis and refined isotropically. The remaining H atoms were positioned geometrically at distances of 0.97 Å (CH₂), 0.93 Å (CH) and 0.91 Å (NH) from the parent C and N atoms; a riding model was used during the refinement process. For L^2b , atoms H7', H7", H8', H8", H9', H9", H21 and H31 were located in a difference synthesis and refined isotropically.

Table 1	
Experimental	data

	(L ² a)	$(\mathbf{L}^{2}\mathbf{b})$
Compound	C ₂₀ H ₂₉ N ₅ O ₉ Ni	C ₂₄ H ₃₉ N ₃ O ₉ Pd
Color/shape	Purple/prism	Dark yellow/plate
Formula weight	524.18	619.98
Space group	$P2_1/n$	P cab
Temperature (K)	293	293
Cell constants	a = 15.820(1) Å, $b = 8.237(2)$ Å, $c = 17.529(1)$ Å, $\beta = 93.17(1)^{\circ}$	a = 13.791(2) Å, $b = 14.620(1)$ Å, c = 28.295(2) Å
Cell volume ($Å^3$)	2280.7(5)	5705.0(9)
Formula units/unit cell	4	8
$D_{\rm calc}$ (Mg m ⁻³)	1.527	1.444
$\mu_{\text{calc}} (\text{mm}^{-1})$	0.908	0.703
Diffractometer/scan	Enraf-nonius CAD-4/ ω -2 θ	Enraf-nonius CAD-4/ ω -2 θ
Radiation used, graphite monochromator	Mo K α ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
Maximum crystal dimension (mm ³)	$0.15 \times 0.25 \times 0.35$	$0.15 \times 0.25 \times 0.35$
Standard reflections	3	3
Decay of standard (%)	<1	<1
Reflections measured	3610	5459
$2\theta(\max)(^{\circ})$	26.30	26.29
Range of h, k, l	0 < h < 19, -10 < k < 0, -17 < l < 21	0 < h < 17, -18 < k < 0, -35 < l < 0
Number of reflections with $I > 2\sigma(I)$	2456	3069
Corrections applied	Lorentz-polarization and absorption	Lorentz-polarization and absorption
Computer programs	SHELX-97 [18], ORTEP-3 [19]	SHELX-97 [18], ORTEP-3 [19]
Source of atomic scattering factors	Int. Table for X-ray Cryst. vol. IV, 1976 [20]	Int. Table for X-ray Cryst. vol. IV, 1976 [20]
Structure solution	Direct methods	Direct methods
Treatment of hydrogen atoms	Geometric calculation and difference map	Geometric calculation and difference map
No. of parameters var.	315	361
Weight	$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.7618P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.04\sin\theta/\lambda]$ where $P = 0.33333F_o^2 + 0.66667F_c^2$
GOF	1.096	0.935
$R = \Sigma(F_{\rm o} - F_{\rm c})/\Sigma F_{\rm o} $	0.0396	0.0384
$R_{\rm w} = [\Sigma({\rm w} F_{\rm o} - F_{\rm c})^2 / {\rm w} F_{\rm o} ^2]^{1/2}$	0.1101	0.0982
$(\Delta \rho)_{\rm max} \ (e {\rm \AA}^{-3})$	0.521	0.521
$(\Delta \rho)_{\min} \ (e \mathring{A}^{-3})$	-0.627	-0.338

The remaining H atoms were positioned geometrically at distances of 0.97 Å (CH₂), 0.96 Å (CH₃), 0.93 Å (CH) and 0.91 Å (NH) from the parent C and N atoms; a riding model was used during the refinement process.

3. Result and discussion

3.1. Synthesis and reactions

Dibenzo-bis-imino-crown ether (\mathbf{L}^1) and dibenzo-triaza crown ether (\mathbf{L}^2) have been synthesized from the reaction of 1,4-bis(formylphenyl)-1,4-dioxabutane with 1,3-diaminopropane and 1,3-diamino-3-azapentane, respectively, according to the literature method [16,17]. The syntheses of [Ni(\mathbf{L}^1)X₂] (X = Cl, Br, I, NCS), [Cu(\mathbf{L}^1)](ClO₄)₂, [Cu(\mathbf{L}^1)(X)]ClO₄ (X = Cl, Br, NCS), [Cu(\mathbf{L}^1)](ClO₄)₂, [Cu(\mathbf{L}^1)(X)]ClO₄ (X = Cl, Br, NCS), [Cu(\mathbf{L}^1)(Br)]Y (Y = BF₄, PF₆), [Cd(\mathbf{L}^1)₂](ClO₄)₂·H₂O, [Ni(\mathbf{L}^2)(Cl)]ClO₄, [Ni(\mathbf{L}^2)(NCS)₂]·H₂O, {[Ni(\mathbf{L}^2)(NCS)₂]}₂ and [Cu(\mathbf{L}^2)(X)] ClO₄ (X = Cl, Br) and the crystal structures of some of them have been previously reported in the literature [2,16, 17,21–24]. However, the new Ni(II) complexes (\mathbf{L}^1 **a** and $L^{2}a$) of $(L^{1} \text{ and } L^{2})$ were obtained from the reaction of (L^1) and (L^2) with Ni(NO₃)₂·6H₂O in *n*-butanol, respectively. In the (L^1a) and (L^2a) complexes, two NO₃ ligands are coordinated to Ni(II) ions as monodentate in $(L^{1}a)$ and as monodentate and bidentate in (L^2a) which was supported by X-ray crystallography. These complexes $(L^{1}a \text{ and } L^{2}a)$ have less solubilities in most of the organic solvents, but L¹a is soluble in DMSO and acetone/H₂O mixture and L²a is soluble in acetone/H₂O mixture. The reaction of (L^2) with Pd(CH₃COO)₂ in dichloromethane yield a mixture of complexes $(L^2b \text{ and } L^2c)$. Both complexes (L^2b and L^2c) are suggested to be monomeric structure containing two acetate ions, one of the acetate ion bonded to Pd(II) as a ligand. On the other hand, in (L^2a) , $(L^{2}b)$ and $(L^{2}c)$, the etheric oxygens are not bonded to the metal ions, although; in $(L^{1}a)$, the etheric oxygens are bonded to Ni(II) ion, which are in accordance with the observations reported in the literature [16,22,23,25,26]. The analytical and experimental details of the ligands (L^1 and L^2) and their complexes (L^1a and L^2b-L^2c) are given in Table 2, which are in accordance with the proposed structures.

88

Table 2	
Analytical and experimental details	

Compound	Formula	Color	$\mu_{\rm eff}{}^{\rm a}$ B.M.	Elemental analyses (%) calculated (found)			
				С	Н	N	
L ¹	$C_{19}H_{20}N_2O_2$	_	_	74.00 (74.40)	6.54 (5.79)	9.08(8.69)	
L^2	$C_{20}H_{27}N_3O_2$	_	_	70.35 (70.70)	7.97 (8.00)	12.31 (12.31)	
L ¹ a	$C_{19}H_{24}N_4O_{10}Ni;[NiL^1(NO_3)_2]\cdot 2H_2O$	Dark blue	2.86	43.29 (43.26)	4.59 (3.66)	10.63 (10.36)	
L ² a	$C_{20}H_{27}N_5O_8Ni;[NiL^2(NO_3)_2]$	Purple	3.04	45.83 (46.17)	5.19 (5.77)	13.36 (13.83)	
L ² b	$C_{24}H_{39}N_3O_9Pd;[PdL^2(CH_3COO)]CH_3COO·3H_2O$	Dark yellow	b	46.49 (46.59)	6.34 (6.57)	6.78 (6.57)	
L ² c	$C_{24}H_{33}N_3O_6Pd;[PdL^2(CH_3COO)]CH_3COO$	Brown	b	50.97 (50.49)	5.84 (5.58)	7.43 (7.20)	

^a At 296 K, B.M. = 0.927×10^{-23} A m⁻².

^b Square planar complex.

3.2. Spectroscopic studies

Selected IR data for the ligands $(L^1 \text{ and } L^2)$ and their complexes $(L^{1}a, L^{2}a-L^{2}c)$ are given in Table 3. The free ligand (L^1) and it's mononuclear Ni(II) complex (L^1a) show characteristic imine (C=N) absorption bands at 1632 and 1650 cm⁻¹, respectively. On the other hand, the observations of $\nu(Ar-O)$ and $\nu(C-O-C)$ bands (for L¹ and L² ligands and also for their metal complexes) between 1292-1221 and 1137-1066 cm⁻¹ were the evidences for the existence of etheric groups. In the Ni(II) complexes ($L^{1}a$ and L^2a), two new intense bands are observed at 1344, 830 cm^{-1} (for **L**¹**a**) and 1310, 829 cm⁻¹ (for **L**²**a**), which they can be assigned to the NO_3^- ion stretching bands, which indicate the coordination of the oxygen atom between $NO_3^$ and Ni(II) ions. These absorption bands are comparable with the bands of Ni(NO₃)₂· $6H_2O$ at 1384 and 826 cm⁻¹, values. The IR spectrum of the ligand (L^2) has characteristic peaks indicating three different N-H absorption bands at 3332, 3310 and 3231 cm⁻¹. On the other hand, the IR spectra of the complexes $(\mathbf{L}^2\mathbf{a}-\mathbf{L}^2\mathbf{c})$ contain N–H absorption bands at 3305, 3287, 3261; 3199 and 3192, 3154 cm⁻¹, respectively, which are assigned to the N atoms coordinated to Ni(II) and Pd(II) ions. The observations of the broad absorption bands at 3166 and 3439 cm⁻¹ (for L¹a, L²b) are the evidences for the existence of H₂O molecules.

The ¹H-NMR spectral data of the ligands (L^1 and L^2) and their Ni(II) and Pd(II) metal complexes (L^1a , L^2a-L^2c) are given in experimental section. ¹H-NMR spectra of Ni(II) complexes (L^1a and L^2a) synthesized, show very broad

signals due to the paramagnetism of the Ni(II) ion while, in
the ¹ H-NMR spectra of Pd(II) complexes (L^2b and L^2c), the
signals are very sharp upon to diamagnetism of Pd(II) ion.
The values of Ar- CH_2 -N and N- CH_2 signals for L^2b and
L^2c are in accordance with the values of Zn(II) and Cd(II)
complexes of similar ligands [27]. The azomethine protons
give signals at 8.74 and 8.71 ppm (for L^1 and L_1^1a ,
respectively) as singlets. The peaks of the complex (L^2a)
are considerably shifted toward low-fields with respect to
the peaks of the free ligand (L^2) . The ¹ H-NMR spectra of
the complexes $(\mathbf{L}^2 \mathbf{b} \text{ and } \mathbf{L}^2 \mathbf{c})$ show two different kinds of
CH ₃ COO proton signals at 1.32; 1.90 and 1.28; 1.80 ppm
values, respectively. Besides that, the signals observed at
9.68 and 9.51 ppm (for L^2b and L^2c) indicate the existence
of the $CH_3-C(O)O\cdots H$ hydrogen bonding as supported by
the obtained crystallographic results for L^2b
$[H21(N2) \cdots O3^{1} 2.14(3) \text{ Å and } N2-H21 \cdots O3^{1} 160.2(3.7)^{\circ};$
(i) $x + 0.5, -y, -z + 0.5$].

The ¹³C-NMR spectral data of the ligands (L^1 and L^2) and their complexes (L^1a , L^2a-L^2c) are given in experimental section. As expected, all of the possible carbon peaks are observed in the ¹³C-NMR spectra of the ligands and their complexes, except of L^2c because of overlapping with solvent peaks. The characteristic (C=N) imine carbon peak of L^1a is shifted (ca. 5 ppm) to higher value with respect to the peak of L^1 . On the other hand, the aliphatic carbon signals of L^2a and L^2a are shifted (ca. 2–21 ppm) to higher values with respect to the signals of L^1 and L^2 , respectively. Especially, for L^2a the signals of the CH₂ carbon atoms bonded to the N atoms show higher chemical

Table 3		
Selected	IR	bands

Compound	$\nu_{\rm C=N}$	$\nu_{C-O-C(arom.)}$	$\nu_{C-O-C(aliph.)}$	$\nu_{\rm C-H(aliph.)}$	$\nu_{\rm C=C}$	$ u_{ m N-H} $	$ u_{ m NO3^-}$	$\nu_{\rm CH3COO^-}$	$\nu_{\rm O-H}$
L^1	1632	1290-1232	1110-1069	2941-2829	1600	_	_	_	_
L^2	_	1286-1237	1128-1066	2925-2784	1599	3332; 3310; 3231	_	_	_
L ¹ a	1650	1288-1221	1110-1075	2925-2945	1603	_	1344; 830	_	3166
L ² a	_	1242	1137-1073	2966-2875	1593	3305; 3287; 3261	1310; 829	_	_
L ² b	_	1292-1246	1123-1068	2970-2866	1573	3192; 3154	_	а	3439
L ² c	_	1292-1250	1120-1075	2970-2871	1569	3199	_	а	_

^a Overlapping with C = C stretching bands.

Compound	Fragments ^a (m/z)
(L ¹)	$[L^{1}]^{+}$ (308), $[L^{1}-C_{2}H_{4}]]^{+}$ (280), $[L^{1}-OPhCN]^{+}$ (189), $[L^{\frac{1}{2}}-(OPhCN + C_{2}H_{4})]^{+b}$ (161)
(L^2)	$[L^{2}]^{+}$ (341), $[L^{2}-CH_{5}N]^{+}$ (310), $[L^{2}-C_{2}H_{6}N_{2}]^{+b}$ (283), $[L^{2}-C_{3}H_{8}N_{2}]^{+}$ (267), $[L^{2}-C_{4}H_{10}N_{2}]^{+}$ (253), $[L^{2}-C_{4}H_{11}N_{3}]^{+}$ (238)
$(\mathbf{L}^{1}\mathbf{a})$ [NiL ¹ (NO ₃) ₂]·2H ₂ O	$[NiL^{1}(NO_{3})]^{+b}$ (428), $[NiL^{1}]^{2+}$ (366), $[L^{1}]^{+}$ (308)
$(\mathbf{L}^2 \mathbf{a}) [\operatorname{NiL}^2(\operatorname{NO}_3)_2]$	$[NiL^{2}(NO_{3})]^{+}$ (461), $[NiL^{2}]^{2+b}$ (399), $[{NiL^{2}}-CH_{2}O]^{+}$ (369), $[{NiL^{2}}-CH_{2}O]^{+}$ (355)
$(\mathbf{L}^{2}\mathbf{b})$ [PdL ² (CH ₃ COO)]CH ₃ COO·3H ₂ O	$[PdL^{2}(CH_{3}COO)]^{+}$ (506), $[PdL^{2}]^{2+b}$ (447)
(L ² c) [PdL ² (CH ₃ COO)]CH ₃ COO	$[PdL^{2}(CH_{3}COO)]^{+}$ (506), $[PdL^{2}]^{2+b}$ (447)

Table 4	
EI (for L^1 and L^2) and FAB (for the complexes) mass spectral data	ta

^a Based on the mass of the most abundance isotope.

^b Parent ion peak.

shift values than the other carbon signals, probably due to the coordination of the N atoms to Ni(II) ion. The signals of methyl and carbonyl carbons of CH_3COO were observed at 22.8; 25.0 and 178.0; 180.1 ppm for L^2b and 22.9; 24.9 and 178.0; 181.3 ppm for L^2c , respectively. These data support the results obtained in ¹H-NMR spectra, indicating that one of the acetate ion is bonded to the Pd(II) ion as a ligand while, the other one is non-bonded.

The prominent fragments in the EI and FAB mass spectra of all the compounds are given in Table 4. The molecular ion peaks (M^+) of the free ligands $(L^1 \text{ and } L^2)$ are observed in the EI mass spectra. In the FAB mass spectra of the complexes ($L^{1}a$ and $L^{2}a-L^{2}c$), the molecular ion peaks could not been determined, although the complexes are found to be consistent with the presence of 1:1 (metal to macrocycle) stoichiometries (see Table 4). Both of the complexes $(L^1a \text{ and } L^2a)$ have two nitrate ions. As mentioned before, in $L^{1}a$, two nitrate ions were bonded to the Ni(II) ion as monodentate ligands. On the other hand, in L^2a , one nitrate ion is bonded to the Ni(II) ion as a monodentate ligand, while the other one as bidentate. In each case, $[M(macrocycle)(X)]^+$ and $[M(macrocycle)]^{2+}$ (M: Ni, Pd; X: NO₃, CH₃COO) ion peaks were observed. The FAB mass data are in good agreement with the reported values for nickel(II) thiocyanate complexes of L^2 and other N_3O_2 macrocycles [22]. In nickel thiocyanate complexes, any molecular ion peaks are not observed, but the FAB mass spectra of the monomeric thiocyanate complexes include the [Ni(macrocycle)(NCS)]²⁺and [Ni(macrocycle)]⁺ion peaks.

Both of the Ni(II) complexes ($L^{1}a$ and $L^{2}a$) have magnetic moments which are typical of the Ni(II) ion in the high spin state. On the other hand, Pd(II) complexes ($L^{2}b$ and $L^{2}c$) have not gotten any magnetic moment values due to the their square planar structure (see Table 2 and Fig. 4).

3.3. TGA and DSC

The thermogravimetric (TGA) and differential scanning calorimetric (DSC) curves for the complexes are illustrated

in Figs. 1 and 2, respectively. Mass loss (TGA and calculated), temperature ranges and a description of thermal events observed in the studies are summarised in Table 5. The initial weight loss occurring in the 26-135 °C temperature range for $(L^{1}a)$ and $(L^{2}b)$ is attributed as a loss of the lattice water molecules. The dehydration processes are interpreted by endothermic peaks in DSC curves. DSC curves presented a melting process for $(L^{1}a)$, (L²a), (L²b) and (L²c), at 252, 279, 172 and 179 °C, respectively, followed by decomposition represented by exothermic process for octahedral complexes ($L^{1}a$ and $L^{2}a$) and endothermic process for square planar complexes (L²b and L^2c). All the complexes decomposed completely between 167 and 787 °C. The Ni(II) complexes (L¹a) and (L^2a) decomposed in two steps for (L^1a) and three steps for (L^2a) , resulting in Ni and NiO₂ as the final residue, respectively. On the other hand, the Pd(II) complex (L^2b) also decomposed in three steps, resulting in Pd as the final residue as observed in the Pd(II) complex (L^2c) . The decomposition of PdO in the thermal process $PdO \rightarrow Pd + 1/2O_2$ for (L^2b) is easily distinguished in the TGA curve. The process may be used for obtaining very pure metallic Pd. The presence of metallic Ni and Pd residues for (L^1a) , (L^2b) and (L^2c) indicate the presence of carbonaceous material as decomposition intermediate. Consequently, the order for thermal stability found is $(\mathbf{L}^{2}\mathbf{a}) > (\mathbf{L}^{1}\mathbf{a}) > (\mathbf{L}^{2}\mathbf{b}) > (\mathbf{L}^{2}\mathbf{c})$. It is understood that the octahedral complexes (L^1a) and (L^2a) are more stable than the square planar complexes (L^2b) and (L^2c) .

3.4. Crystal study

Single crystal X-ray structures of the complexes (L^2a and L^2b) are reported to further corroborate the structure assignments. The final coordinates and equivalent isotropic displacement parameters are given in Table 6. The molecular structures with the atom-numbering schemes are shown in Figs. 3 and 4. The molecular packings are shown in Figs. 5 and 6. The packings of the molecules in the unit cells are purely due to dipole–dipole, hydrogen

90



Fig. 2. DSC curves for the complexes $(L^1a \text{ and } L^2a - L^2c)$.

Table 5

Complex		Process	TGA data	DSC Peaks		
			Temperature range (°C)	Mass loss a or residue b (%)		(°C) ²
				TGA	Calculated	
(L ¹ a)	HC = N HC = N H	$\begin{split} & [\text{Ni}(\text{L}^{1})(\text{NO}_{3})_{2}] \cdot 2\text{H}_{2}\text{O} \rightarrow [\text{Ni}(\text{L}^{1})(\text{NO}_{3})_{2}] + 2\text{H}_{2}\text{O} \\ & [\text{Ni}(\text{L}^{1})(\text{NO}_{3})_{2}] \rightarrow [\text{Ni}(\text{B})] + \text{A} + 2(\text{NO} + \text{O}_{2}) \\ & [\text{Ni}(\text{B})] \rightarrow \text{Ni} + \text{B} \end{split}$	78–135 230–248 239–787	6.40 a 44.80 a 10.40 b	6.84 46.39 11.03	132.20 (endo) 252.23 (exo)
(L ² a)	A O Ni H ₂ C-NH HN-CH ₂	$\begin{split} & [\mathrm{Ni}(\mathrm{L}^2)(\mathrm{NO}_3)_2] \rightarrow [\mathrm{Ni}(\mathrm{L}^2)\mathrm{O}_2] + 2\mathrm{NO}_2 \\ & [\mathrm{Ni}(\mathrm{L}^2)\mathrm{O}_2] \rightarrow [\mathrm{Ni}(\mathrm{B})\mathrm{O}_2] + \mathrm{A} \\ & [\mathrm{Ni}(\mathrm{B})\mathrm{O}_2] \rightarrow \mathrm{Ni}\mathrm{O}_2 + \mathrm{B} \end{split}$	265–283 285–423 423–661	20.00 a 12.00 a 17.60 b	17.59 11.02 17.29	279.38 (exo)
(L ² b)	$\begin{array}{c} A \\ 0 \\ C \\ Pd \\ CH_3 \\ H_2C \\ \hline \vdots \\ NH \\ HN \\ HN \\ HN \\ HN \\ HN \\ HN \\ $	$\begin{split} & [PdL^2(AcO)]AcO \cdot 3H_2O \rightarrow [PdL^2(AcO)]AcO + 3H_2O \\ & [PdL^2(AcO)]AcO \rightarrow [Pd(B)O] + A + AcO + Ac \\ & [Pd(B)O] \rightarrow PdO + B \\ & PdO \rightarrow Pd + 1/2O_2 \end{split}$	26-87 170-330 330-467 640-670	9.33 a 54.00 a 15.33 a 16.00 b	8.81 55.79 16.48 17.29	95.66 (endo) 171.45 (endo) 172.16 (endo)
(L ² c)	-	$[PdL^{2}(AcO)]AcO \rightarrow Pd + L^{2} + 2AcO$	167-610	18.58 b	19.17	178.31 (endo) 178.64 (endo)

AcO: CH₃COO; Ac: CH₃CO.

^a Exo: exothermic process; endo: endothermic process.

bonding and van der Waals forces of interaction. The molecules are elongated through the *c*-axes of the unit cells. The bond lengths and angles with some selected torsion angles are given in Tables 7 and 8. The co-ordination geometry of the nickel in $[Ni(L^2)(NO_3)_2]$, (L^2a) is distorted octahedral involving three nitrogen donors of the macrocyclic ring, two oxygen atoms of the bidentate and one oxygen atom of the monodentate nitrate ions. The etheric oxygens are not bound to the nickel, non-co-ordination of the ether oxygens has been previously confirmed for several complexes by X-ray diffraction [16,17,22,23,25,26,28]. The main distortion from octahedral symmetry is arisen with the small bite of the bidentately co-ordinated nitrate ion [Ni-O5 2.197(3) Å]. The angles around the Ni(II) ion in the four- and five-membered chelate rings are as usual, less than the ideal value of 90° [60.0(1), 85.9(1) and 82.8(1)°]. In this structure, the three nitrogens of (L^2) co-ordinate to Ni(II)

ion in a facial configuration. The Ni-N bond lengths vary from 2.047(3) to 2.158(3) Å and hence, fall within the literature range (2.04–2.33 Å) which is typical of nickel to sp³-nitrogen bonds [29]. The nickel to monodentate and bidentate nitrates oxygens bond lengths are in the range 2.096(3)-2.197(3) Å. On the other hand, there are intramolecular hydrogen bonds between etheric oxygen and azanitrogen atoms $[N2 \cdots O1 \quad 2.846(4), \quad O1 \cdots H2(N2)$ 2.370(4) Å, N2-H2···O1 120.3(3.4)°] and also between monodentate nitrate oxygen and aza-nitrogen atoms [N1···O7 2.902(5), O7···H1(N1) 2.178(4) Å, N1-H1···O7 135.9(2)°]. The complex L^2b contains a mononuclear Pd(II) ion in which there are three water molecules and two acetate anions. The one acetate anion in the complex does not act as a ligand but is incorporated into the crystal lattice by hydrogen bonding [N2···O3ⁱ 2.751(6), $H21(N2) \cdots O3^{i} 2.14(3) \text{ Å and } N2 - H21 \cdots O3^{i} 160.2(3.7)^{\circ};$

Table 6 Atomic coordinates and isotropic displacement parameters with e.s.d's in parentheses for $(L^2a \text{ and } L^2b)$

(L ² a)					(L ² b)					
Atom	x	у	Z	U _{iso}	Atom	x	у	z	$U_{\rm iso}$	
Ni	0.77371(3)	0.13941(5)	0.93393(2)	0.03110(19)	Pd1	0.36528(2)	0.02897(2)	0.349818(10)	0.04268(11)	
C1	0.8826(3)	0.3265(4)	1.0357(2)	0.0463(10)	C1	0.6260(3)	0.0426(3)	0.39618(15)	0.0593(12)	
C2	0.7937(3)	0.3631(4)	1.0579(2)	0.0424(10)	C2	0.7197(3)	0.0608(4)	0.38010(17)	0.0774(15)	
C3	0.7357(2)	0.1015(4)	1.1017(2)	0.0383(9)	C3	0.7909(4)	-0.0039(5)	0.38116(18)	0.0861(17)	
C4	0.6966(3)	0.1627(4)	1.1721(2)	0.0372(9)	C4	0.7718(4)	-0.0896(5)	0.39653(18)	0.0886(18)	
C5	0.7401(3)	0.1647(4)	1.2430(2)	0.0489(11)	C5	0.6796(4)	-0.1119(4)	0.41327(18)	0.0751(14)	
C6	0.7020(3)	0.2217(5)	1.3073(2)	0.0589(13)	C6	0.6075(3)	-0.0455(3)	0.41309(15)	0.0583(12)	
C7	0.6209(4)	0.2783(5)	1.3007(2)	0.0620(13)	C7	0.5003(3)	-0.1397(3)	0.45853(16)	0.0663(13)	
C8	0.5752(3)	0.2785(5)	1.2308(2)	0.0521(11)	C8	0.4006(4)	-0.1320(3)	0.47747(16)	0.0638(12)	
C9	0.6130(3)	0.2182(4)	1.1678(2)	0.0390(9)	C9	0.2383(3)	-0.1307(3)	0.44667(16)	0.0557(11)	
C10	0.4942(2)	0.2808(4)	1.0811(2)	0.0422(9)	C10	0.1949(4)	-0.1235(3)	0.49105(17)	0.0722(14)	
C11	0.4678(2)	0.2404(4)	1.0003(2)	0.0425(9)	C11	0.0993(5)	-0.1068(4)	0.4953(2)	0.0826(16)	
C12	0.5240(2)	0.2715(4)	0.8762(2)	0.0322(8)	C12	0.0420(4)	-0.0963(3)	0.4551(2)	0.0842(16)	
C13	0.4574(3)	0.1845(4)	0.8417(2)	0.0426(9)	C13	0.0835(3)	-0.1041(3)	0.41116(17)	0.0643(12)	
C14	0.4540(3)	0.1577(4)	0.7640(2)	0.0491(11)	C14	0.1831(3)	-0.1231(3)	0.40617(16)	0.0545(11)	
C15	0.5152(3)	0.2201(5)	0.7203(2)	0.0496(1	C15	0.2254(3)	-0.1374(3)	0.35845(14)	0.0550(11)	
C16	0.5805(2)	0.3091(4)	0.7553(2)	0.0417(9)	C16	0.2599(3)	-0.0750(3)	0.27960(15)	0.0664(13)	
C17	0.5867(2)	0.3359(4)	0.8330(2)	0.0318(8)	C17	0.3139(3)	0.0000(4)	0.25523(15)	0.0660(12)	
C18	0.6588(2)	0.4356(4)	0.8676(2)	0.0318(8)	C18	0.4615(3)	0.0970(3)	0.26955(14)	0.0572(11)	
C19	0.8119(2)	0.4716(4)	0.8784(2)	0.0382(9)	C19	0.5355(3)	0.1084(3)	0.30803(14)	0.0623(12)	
C20	0.8937(2)	0.3847(5)	0.8968(2)	0.0458(10)	C20	0.5496(3)	0.1151(3)	0.39629(15)	0.0568(11)	
O1	0.57355(16)	0.2029(3)	1.09660(14)	0.0440(6)	C21	0.0550(4)	0.1889(3)	0.21816(17)	0.0671(13)	
O2	0.53149(16)	0.3022(3)	0.95364(14)	0.0413(6)	C22	-0.0020(5)	0.2090(4)	0.17463(18)	0.0935(18)	
O3	0.66695(16)	-0.0023(3)	0.90086(14)	0.0374(6)	C23	0.2445(3)	0.1075(3)	0.42053(17)	0.0595(12)	
O4	0.6621(2)	-0.1491(3)	0.79688(16)	0.0616(9)	C24	0.2123(4)	0.1271(4)	0.47036(17)	0.0818(16)	
O5	0.76715(17)	0.0151(3)	0.82284(15)	0.0469(7)	01	0.3346(2)	-0.1506(2)	0.43977(11)	0.0627(8)	
06	0.81896(18)	-0.0790(3)	0.98198(17)	0.0584(8)	O2	0.5161(2)	-0.0600(2)	0.42990(11)	0.0661(8)	
O7	0.9409(2)	-0.0668(5)	0.9320(2)	0.0911(12)	O3	0.0229(3)	0.1257(3)	0.24382(13)	0.1201(17)	
08	0.9104(2)	-0.2679(3)	1.00595(19)	0.0783(10)	O4	0.1224(3)	0.2379(3)	0.22900(13)	0.0922(12)	
N1	0.88437(19)	0.2630(3)	0.95730(17)	0.0401(7)	O5	0.1965(3)	0.1380(3)	0.38662(14)	0.0881(11)	
N2	0.7377(2)	0.2241(3)	1.03863(17)	0.0336(7)	O6	0.3208(2)	0.05939(19)	0.41675(9)	0.0527(7)	
N3	0.74200(18)	0.3527(3)	0.86684(17)	0.0306(7)	O7	0.0578(5)	0.0516(5)	0.3251(2)	0.1358(19)	
N4	0.6975(2)	-0.0485(3)	0.83902(18)	0.0407(8)	08	0.9078(4)	0.2053(4)	0.3374(3)	0.151(2)	
N5	0.8909(3)	-0.1398(4)	0.9751(2)	0.0572(10)	O9	0.7451(3)	0.2724(3)	0.30169(16)	0.1007(12)	
					N1	0.2475(2)	-0.0523(2)	0.33105(11)	0.0508(8)	
					N2	0.4033(3)	0.0162(3)	0.28223(13)	0.0533(11)	
					N3	0.4828(2)	0.1143(2)	0.35371(12)	0.0499(8)	



Fig. 3. An ORTEP [19] drawing of (L^2a) with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 4. An ORTEP [19] drawing of (L^2b) with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 5. The molecular packing diagram for (L^2a) .

(i) x + 0.5, -y, -z + 0.5]. There are also intramolecular [O8...O9 2.849(8), H9'(O9)...O8 2.22(9) Å, O9–H9'...O8 108.2(5.3)°; O7...N1 3.029(7), H7'(O7)...N1 2.45(9) Å, O7–H7'...N1 130.0(7.2)°; N1...O7 3.029(7), H1(N1)...O7 2.134(6) Å, N1–H1...O7 167.4(3)°] and intermolecular [N3...O8ⁱⁱ 2.871(7), H31(N3)...O8ⁱⁱ 1.94(5) Å, N3– H31...O8ⁱⁱ 156.5(4.1)°; (ii) x - 0.5, -y + 0.5, z; O7...O8ⁱⁱⁱ 3.074(9), H7"(O7)...O8ⁱⁱⁱ 2.31(10) Å, O7– H7"...O8 140.9(7.5)°; (iii) x - 1, y, z; O9...O5^{iv} 2.818(6), H9"(O9)...O5^{iv} 2.20(7) Å, O9–H9"...O5^{iv} 134.4(5.7)°; (iv) x + 0.5, -y + 0.5, z; O8...N3^v 2.871(7), H8"(O8)...N3^v 2.09(15) Å, O8–H8"...N3^v 163.6(5.8)°; (v) x + 0.5, -y + 0.5, *z*] hydrogen bonds between three water molecules and also between the water molecules and the macroring. The macrorings are elongated along the *c*-axis of the unit cell (Fig. 6) and there are cavities between the macroring lines. One of the acetate ion and the three water molecules fill in the cavities by forming the hydrogen bonds. Pd(II) ion is at a distance of -0.1060(3) Å to the best plane of N1, N2, N3, O6 atoms, and the coordination around Pd(II) ion is a distorted square planar (Table 8). Although the Pd(II) ion has four coordination, the close contact of the O5 atom $[Pd \cdots O5 = 3.007(3)$ Å] may cause the Pd(II) ion to have five coordination. The five coordination around Pd(II) can



Fig. 6. The molecular packing diagram for (L^2b) .

Table 8

Table 7 The selected bond lengths (Å) and angles (°) with the torsion angles (°) for $(\mathbf{1}^{2} \mathbf{2})$

The selected bond lengths (Å) and angles (°) with the torsion angles (°)	foi
(L ² b)	

(L⁻a)				(L-D)			
Ni-N1	2.047(3)	C2-C1	1.509(6)	C24-C23	1.505(6)	C20-C1	1.496(6)
Ni-N2	2.072(3)	C17-C18	1.506(4)	Pd1-N2	1.991(4)	O5-C23	1.248(6)
Ni-N3	2.158(3)	C3-C4	1.497(5)	Pd1-O6	2.040(3)	C14-C9	1.380(6)
Ni-O6	2.096(3)	C3-N2	1.499(4)	Pd1-N3	2.048(3)	C14-C15	1.485(6)
Ni-O3	2.108(2)	N1-C1	1.471(5)	Pd1-N1	2.081(3)	C19-C18	1.501(6)
Ni-O5	2.197(3)	O1-C9	1.370(4)	O6-C23	1.270(5)	C1-C6	1.397(6)
O2-C12	1.379(4)	O1-C10	1.423(4)	N3-C19	1.485(5)	O2-C6	1.364(5)
O2-C11	1.426(4)	C4-C9	1.397(5)	N3-C20	1.516(5)	O2-C7	1.435(5)
C11-C10	1.493(5)	O4-N4	1.226(4)	N2-C17	1.469(6)	C7-C8	1.479(7)
C12-C17	1.386(5)	O3-N4	1.269(4)	N2-C18	1.473(6)	C16-C17	1.495(7)
C20-N1	1.473(5)	O5-N4	1.266(4)	N1-C15	1.498(5)	O4-C21	1.213(5)
C20-C19	1.499(5)	O6-N5	1.256(4)	N1-C16	1.503(5)	C21-O3	1.255(5)
N3-C19	1.482(4)	O8-N5	1.218(4)	01-C9	1.373(5)	C21-C22	1.490(7)
N3-C18	1.483(4)	N5-07	1.273(5)	01-C8	1.429(5)		
C2-N2	1.476(4)						
				N2-Pd1-O6	172.34(15)	C9 - C14 - C15	121.8(4)
N1-Ni-N2	85 94(12)	C4-C3-N2	114 1(3)	$N_2 - Pd_1 - N_3$	84 30(15)	$05-C^{23}-06$	124.0(1) 124.9(4)
N1-Ni-06	$94\ 44(12)$	$C_{2}-N_{2}-C_{3}$	113.0(3)	O6-Pd1-N3	93 18(12)	$05 - C^{23} - C^{24}$	1197(4)
N2_Ni_O6	92 15(11)	C2_N2_Ni	105.8(2)	N2_Pd1_N1	84 65(15)	$06-C^{23}-C^{24}$	115.7(1) 115.4(5)
N1_Ni_O3	173 68(11)	C3_N2_Ni	1164(2)	$O6_Pd1_N1$	97 26(12)	N3_C19_C18	107.8(3)
N2-Ni-O3	100.06(11)	$C_{1} = N_{1} = C_{2}^{0}$	116.4(2) 116.0(3)	$N3_Pd1_N1$	168 22(13)	$C_{6}-C_{1}-C_{20}$	107.6(3) 121.6(4)
06-Ni-03	83 44(11)	C1_N1_Nj	107.6(2)	$C^{23} = O6 = Pd1$	116 6(3)	C6 - 02 - C7	121.0(4) 117.7(3)
N1 N; N3	82 70(11)	C_{20} N1 Ni	107.0(2) 108.2(2)	$C_{23} = 00 = 101$	110.0(3) 113.3(3)	N_{2}^{-} C18 C10	117.7(3) 106 4(3)
N2 Ni N3	02.79(11) 08 14(11)	$C_{20} = N_1 = N_1$	100.2(2) 112.3(3)	C19-N3-C20 C10 N3 Pd1	113.3(3) 107.8(3)	$N_2 = C_{10} = C_{19}$	100.4(3) 115 7(3)
$\Omega_{2} = \Omega_{1} = \Omega_{2}$	$160 \ 10(12)$	N1 - C1 - C2 N2 C18 C17	112.3(3) 112.5(2)	C19 = N3 = I d1	107.8(3) 121.0(2)	$01 \ 00 \ 014$	115.7(5) 115.6(4)
$O_2 = N_1 = N_2$	109.10(12)	$N_{3} = C_{10} = C_{17}$	113.3(3)	C_{20} -N3-Ful	121.9(2)	01 - 09 - 014	115.0(4)
N1 NF O5	98.19(10)	$C_{9} = 01 = C_{10}$	119.0(3) 106.1(2)	C17 N2 D41	117.4(4) 107.1(2)	02 - C7 - C8	100.0(4) 107.0(4)
N2 N: 05	114.02(11) 160.02(12)	$C_{1} = C_{10} = C_{11}$	100.1(3)	C17 = N2 = Fu1	107.1(3) 107.6(2)	$C_{17} C_{16} N_{1}$	107.9(4)
N2-NI-03	87 20(11)	$C_{9}-C_{4}-C_{5}$	119.9(3)	C16 - N2 - P01	107.0(3) 100.0(2)	$V_{1}^{-} - C_{10}^{-} - N_{1}^{-}$	110.0(4) 107.2(4)
$O_2 = N_1 = O_2$	67.39(11)	01 - C9 - C4	113.0(3)	C15 N1 D41	109.9(3) 120.1(2)	$N_2 - C_1 - C_{10}$	107.2(4)
N2 N: 05	84 16(10)	$N_{3} = C_{19} = C_{20}$	110.0(3)	CIS-NI-Pul	120.1(2) 106.5(2)	02-00-01	113.0(4) 122.0(5)
$N_{3} = N_{1} = 0.03$	64.10(10) 119.2(2)	N4-05-Ni	95.04(19)	C10-N1-P01	100.3(3)	04 - 021 - 03	125.9(5)
02_011_010	118.3(3)	N4-05-N1	89.0(2)	$C_{9} = 01 = C_{8}$	118.0(3)	04 - 021 - 022	119.8(5)
02-011-010	107.2(3)	N5-06-N1	126.5(3)	CI-C20-N3	114.9(4)	03-021-022	116.0(5)
02-C12-C17	116.3(3)	08-N5-06	120.7(4)				
NI-C20-C19	111.1(3)	08 - N5 - 07	121.5(4)	C19-N3-C20-C1	-48.4(5)	C6-O2-C7-C8	172.1(4)
C19-N3-C18	110.5(3)	06-N5-07	117.7(4)	C20-N3-C19-C18	173.4(3)	C9-O1-C8-C7	-167.9(4)
C19-N3-N1	108.3(2)	04-N4-05	121.3(3)	N3-20-C1-C6	-85.1(5)	02-C7-C8-O1	73.6(4)
C18-N3-N1	123.3(2)	04-N4-03	122.3(3)	C17-N2-C18-C19	168.6(4)	C15-N1-C16-C17	-160.7(4)
N2-C2-C1	110.0(3)	05-N4-03	116.4(3)	N3-C19-C18-N2	-55.4(5)	C18-N2-C17-C16	-170.6(4)
C12-C17-C18	122.5(3)			C9-C14-C15-N1	-101.8(5)	N1-C16-C17-N2	52.6(5)
				C16-N1-C15-C14	-162.6(4)	C7-O2-C6-C1	-164.1(4)
C12-O2-C11-C10	176.2(3)	C12-C17-C18-N3	110.9(4)	C8-O1-C9-C14	161.1(4)	C20-C1-C6-O2	-0.6(6)
C11-O2-C12-C17	179.1(3)	C9-O1-C10-C11	-179.5(3)	C15-C14-C9-O1	1.2(6)		
O2-C12-C17-C18	-0.6(4)	O2-C11-C10-O1	-60.2(4)				
C1-C2-N2-C3	88.7(4)	N2-C3-C4-C9	59.3(4)	the Dd(II) ion is	thorofore	hast described as	a distanted
C4-C3-N2-C2	66.2(4)	C10-O1-C9-C4	-168.9(3)		, mererore,	best described as	a distorted
C19-C20-N1-C1	-77.0(4)	C3-C4-C9-O1	2.7(4)	square pyramid.			
C20-N1-C1-C2	91.1(4)	C18-N3-C19-C20	166.1(3)				
N2-C2-C1-N1	48.5(4)	N1-C20-C19-N3	-48.7(4)				
C19-N3-C18-C17	162.3(3)			Acknowledgeme	nts		
				0			

be described as a distorted square pyramid or trigonal bipyramid. Further information can be obtained by estimating the structural index, τ [30], which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal pyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, where α and β being the two largest angles [β (N2-Pd1-O6) = 172.34(15)° and α (N3-Pd1-N1) = 168.22(13)°] around the central atom. The value of τ is 0.07(14). The co-ordination geometry of

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