

# Co-ordination chemistry of 1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane (L) with nickel(II), copper(II) and palladium(II) †

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1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane (L) has been synthesized and its co-ordination chemistry with nickel(II), copper(II) and palladium(II) investigated. The reaction of L with  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in a chloroform–ethanol mixture affords orange, diamagnetic  $[\text{NiL}][\text{ClO}_4]_2$  **1** which consists of the square-planar dication  $[\text{NiL}]^{2+}$  in the solid state and in weakly or non-co-ordinating solvents (nitromethane, acetone). In co-ordinating solvents (acetonitrile, pyridine, dimethylformamide) or in the presence of co-ordinating anions ( $\text{NCS}^-$ ) blue solutions of **1** are obtained from which blue, paramagnetic species were isolated as crystalline materials:  $[\text{NiL}(\text{NCS})_2]$  **2** and  $[\text{NiL}(\text{MeCN})_2][\text{ClO}_4]_2 \cdot 1.5 \text{ MeCN}$  **3**. Complex **2** was shown by X-ray crystallography to consist of neutral, octahedral  $[\text{NiL}(\text{NCS})_2]$ . Using  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  as starting material both square-planar, orange  $[\text{NiL}][\text{NO}_3]_2$  **4a** and blue, octahedral  $[\text{NiL}(\text{NO}_3)_2]$  **4b** containing two monodentate  $\text{NO}_3^-$  ligands were isolated. Reaction of L with  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in  $\text{CHCl}_3$ –EtOH produced blue crystals of square-planar  $[\text{CuL}][\text{ClO}_4]_2$  **5** and five-co-ordinate  $[\text{CuL}(\text{H}_2\text{O})][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$  **7**, respectively. Recrystallization of **5** from MeCN produced blue crystals of  $[\text{CuL}][\text{ClO}_4]_2 \cdot 2\text{MeCN}$  **6**. Palladium(II) acetate reacts with L in  $\text{CHCl}_3$ –EtOH affording orange-brown crystals of  $[\text{PdL}][\text{ClO}_4]_2$  **8**. The crystal structures of **1**, **2**, **5**, **7** and **8** have been determined by X-ray crystallography. In the solid state the ligand is always equatorially co-ordinated in a transoid fashion where one of the two  $\text{M}-\text{N}_{\text{amine}}-\text{C}-\text{C}-\text{C}-\text{N}_{\text{aniline}}$  chelate rings adopts a boat and the other a twist-boat conformation. This has been corroborated by solid-state  $^{13}\text{C}$  cross-polarization magic angle spinning NMR spectroscopy of **1** and **8**.

The co-ordination chemistry of aniline has in the past received comparatively little attention.<sup>1</sup> This is probably due to the fact that the metal-to-nitrogen bond is in general weak; the phenyl group renders the amine nitrogen a relatively weak  $\sigma$  donor. On the other hand, its monodeprotonated anilide form has been shown readily to form bridges between two metals.<sup>2</sup> Anilides are, in principle, strong  $\sigma$ - and  $\pi$ -donor ligands. We have recently shown that the inherent instability of the aniline-to-metal bond may be overcome by attaching this functionality to a macrocyclic aza backbone. Thus 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane binds strongly to divalent transition-metal ions.<sup>3,4</sup> Exploiting the same principle, some open-chain polyamine ligands which contain terminal aniline residues have been reported previously.<sup>5</sup>

In this paper we report the synthesis of an analogous tetradentate compound, namely 1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane (L), and investigate its co-ordination chemistry with nickel(II), copper(II) and palladium(II). The two tertiary amine donor atoms of the piperazine moiety provide only a small bite angle and the  $\text{N}_{\text{amine}}-\text{M}-\text{N}_{\text{amine}}$  bond angle is expected to be significantly smaller than  $90^\circ$ . They are in fact in the range  $69$ – $77^\circ$  in the complexes reported here. The steric rigidity of the co-ordinated piperazine unit is enforced by the presence of two ethylene bridges between the amine nitrogen donors.<sup>6</sup>

## Experimental

### Materials and methods

All chemicals were obtained from commercial sources in the

highest-purity grade available. Infrared spectra were recorded on a Perkin-Elmer FT IR 1720X spectrometer as KBr discs, electronic spectra on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer in the range  $200$ – $1500 \text{ nm}$  and X-band ESR spectra on a Bruker 200 ESR spectrometer at  $9.4266 \text{ GHz}$  microwave frequency. Magnetic moments were determined from temperature-dependent ( $77$ – $298 \text{ K}$ ) magnetic susceptibility measurements by using the Faraday method. Corrections for the underlying diamagnetism were carried out with Pascal's constants. Solid-state  $^{13}\text{C}$  cross polarization magic angle spinning (CP MAS) NMR spectra were measured on a Bruker MSL-300 spectrometer equipped with a CP MAS double-bearing probe and a Bruker BV-1000 temperature-control unit. Zirconia rotors ( $7 \text{ mm}$  outside diameter) completely or partially filled under argon were spun at spin rates of  $4 \text{ kHz}$ . Adamantane was used as external standard.

### Preparation of L

To a solution of 1,4-diazacyclohexane (piperazine) ( $3.45 \text{ g}$ ,  $0.04 \text{ mol}$ ) in toluene ( $80 \text{ cm}^3$ ) was added 2-nitrobenzyl bromide ( $17.3 \text{ g}$ ,  $0.08 \text{ mol}$ ) and KOH ( $4.98 \text{ g}$ ,  $0.09 \text{ mol}$ ). The reaction mixture was stirred at  $60^\circ\text{C}$  for  $5 \text{ h}$ . The then orange solution was cooled ( $20^\circ\text{C}$ ), filtered and dried over  $\text{MgSO}_4$ . After removal of the solvent by rotary evaporation a yellow powder of 1,4-bis(*o*-nitrobenzyl)-1,4-diazacyclohexane was obtained in  $98\%$  yield.  $80 \text{ MHz } ^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$   $2.4$  (s,  $8 \text{ H}$ ,  $\text{CH}_2\text{CH}_2$ ),  $3.75$  (s,  $4 \text{ H}$ , benzyl), and  $7.2$ – $7.9$  (m,  $8 \text{ H}$ , aromatic protons). This material ( $13.97 \text{ g}$ ,  $0.03 \text{ mol}$ ) was dissolved in ethanol ( $200 \text{ cm}^3$ ) and graphite catalyst ( $3.0 \text{ g}$ ) added. The solution was purged with argon and oxygen-free hydrazine hydrate ( $31.4 \text{ g}$ ,  $0.063 \text{ mol}$ ) added. The resulting mixture was heated to reflux for  $12 \text{ h}$  under an argon blanketing atmosphere. The still hot solution was filtered and the residue extracted with  $\text{CHCl}_3$ . Upon

† Non-SI unit employed:  $\mu_{\text{B}} \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$ .

cooling to 20 °C, colourless crystals grew from the filtrate and were filtered off. The ethanol and chloroform solutions were combined and the solvents removed by rotary evaporation. A colourless to yellow powder of 1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane was obtained (yield 10.2 g, 88%), m.p. 192.3 °C. 80 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.4 (s, 8 H,  $\text{CH}_2\text{CH}_2$ ), 3.5 (s, 4 H, benzyl), 4.6 (s, br, 4 H,  $\text{NH}_2$ ) and 6.5–7.2 (m, 8 H, aromatic protons). UV/VIS (MeCN):  $\lambda = 290$  ( $\epsilon = 5200$ ) and 241 nm ( $5180 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ). IR(KBr):  $\nu_{\text{asym}}(\text{NH}_2)$  3440  $\text{cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{NH}_2)$  3264. Mass spectrum:  $m/z$  296 ( $M^+$ ) (Found: C, 72.7; H, 8.9; N, 19.1. Calc. for  $\text{C}_{18}\text{H}_{24}\text{N}_4$ : C, 72.9; H, 8.5; N, 19.1%).

### Preparation of complexes

**[NiL][ClO<sub>4</sub>]<sub>2</sub> 1.** To a solution of 1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane (L) (0.25 g, 0.8 mmol) in chloroform (15  $\text{cm}^3$ ) was added a solution of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.29 g, 0.8 mmol) in ethanol (15  $\text{cm}^3$ ). The orange solution was heated to reflux for 30 min during which time an orange, microcrystalline precipitate formed which was filtered off and washed with ethanol and diethyl ether (yield 0.31 g, 70%). Single crystals for X-ray crystallography were obtained from the remaining solution upon slow evaporation of the solvent (Found: C, 38.7; H, 4.3; N, 10.0;  $\text{ClO}_4$ , 10.2. Calc. for  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_4\text{NiO}_8$ : C, 39.0; H, 4.4; N, 10.1;  $\text{ClO}_4$ , 10.6%).

**[NiL(NCS)<sub>2</sub>] 2.** To a solution of complex 1 (0.20 g, 0.36 mmol) in nitromethane (15  $\text{cm}^3$ ) was added a solution of NaSCN (0.058 g, 0.72 mmol) in ethanol (5  $\text{cm}^3$ ). A change from orange to blue was observed. Within 1 d large blue crystals precipitated at ambient temperature which were filtered off (yield, 0.15 g, 90% (Found: C, 51.1; H, 5.3; N, 18.0. Calc. for  $\text{C}_{20}\text{H}_{24}\text{N}_6\text{NiS}_2$ : C, 51.0; H, 5.1; N, 17.8%).

**[NiL(NCMe)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub>·1.5MeCN 3.** A blue solution of complex 1 (0.25 g, 0.45 mmol) in acetonitrile (20  $\text{cm}^3$ ) was allowed to stand in an open vessel. Upon slow evaporation of the solvent blue crystals were obtained which were filtered off (yield 0.22 g, 70%) (Found: C, 42.9; H, 5.0; N, 14.9; Ni, 7.9. Calc. for  $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{N}_6\text{NiO}_8 \cdot 1.5\text{CH}_3\text{CN}$ : C, 43.1; H, 5.0; N, 15.1; Ni, 8.4%).

**[NiL][NO<sub>3</sub>]<sub>2</sub> (orange) 4a and [NiL(NO<sub>3</sub>)<sub>2</sub>] (blue) 4b.** To a solution of L (0.25 g, 0.80 mmol) in  $\text{CHCl}_3$  (15  $\text{cm}^3$ ) was added a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.20 g, 0.80 mmol) in ethanol (15  $\text{cm}^3$ ). The reaction mixture immediately became yellow. From such solutions orange-red crystals precipitated at room temperature in approximately two out of three experiments. In the other instances blue crystals or a mixture of both forms were obtained. We have not found decisive, experimentally controllable parameters to enforce the precipitation of either the pure orange or blue form in a predictable fashion. Orange and blue crystals were separated manually under a microscope. The yields were in the range 60–70%. Both forms have identical elemental analyses (Found: C, 45.4; H, 5.3; N, 17.5; Ni, 11.5. Calc. for  $\text{C}_{18}\text{H}_{24}\text{N}_6\text{NiO}_6$ : C, 45.1; H, 5.1; N, 17.5; Ni, 12.2%).

**[CuL][ClO<sub>4</sub>]<sub>2</sub> 5.** To a solution of L (0.25 g, 0.8 mmol) in  $\text{CHCl}_3$  (15  $\text{cm}^3$ ) was added a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.30 g, 0.8 mmol) in ethanol (15  $\text{cm}^3$ ). Within 2 d at room temperature in an open vessel violet crystals precipitated which were filtered off (yield 0.36 g, 80%) (Found: C, 38.9; H, 4.0; N, 9.9. Calc. for  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_4\text{CuO}_8$ : C, 38.7; H, 4.3; N, 10.0%).

**[CuL][ClO<sub>4</sub>]<sub>2</sub>·2MeCN 6.** From a solution of complex 5 (0.25 g, 0.45 mmol) in acetonitrile (20  $\text{cm}^3$ ) at room temperature blue crystals were obtained upon slow evaporation of the solvent

(yield 0.20 g, 68%) (Found: C, 41.2; H, 4.8; N, 13.5. Calc. for  $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{N}_6\text{CuO}_8$ : C, 41.2; H, 4.7; N, 13.1%).

**[CuL(H<sub>2</sub>O)][NO<sub>3</sub>]<sub>2</sub>·H<sub>2</sub>O 7.** Blue-black crystals of this material were obtained by using the same experimental conditions described for the preparation of 5 but with  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.21 g, 0.8 mmol) instead of copper perchlorate (yield 0.33 g, 80%) (Found: C, 44.7; H, 5.1; N, 17.4. Calc. for  $\text{C}_{18}\text{H}_{28}\text{CuN}_6\text{O}_8$ : C, 44.7; H, 5.0; N, 17.4%).

**[PdL][ClO<sub>4</sub>]<sub>2</sub> 8.** To a solution of L (0.30 g, 1.0 mmol) in chloroform (15  $\text{cm}^3$ ) was added a solution of palladium(II) acetate (0.23 g, 1.0 mmol) dissolved in ethanol (15  $\text{cm}^3$ ). After stirring for 1 h at room temperature a clear, red-brown solution was obtained from which, upon addition of three drops of 60%  $\text{HClO}_4$ , brown crystals of complex 8 precipitated within 2 d (yield 0.41 g, 67%) (Found: C, 35.7; H, 4.2; N, 8.9. Calc. for  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_8\text{Pd}$ : C, 35.9; H, 4.0; N, 9.3%).

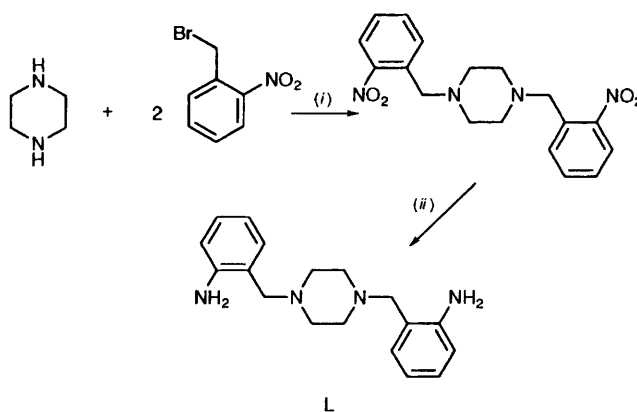
### Crystallography

Table 4 summarizes the relevant data for the crystal structure determinations. Final atom coordinates are given in Tables 5–9 for complexes 1, 2, 5, 7 and 8, respectively. Intensity data were corrected for Lorentz-polarization and absorption effects in the usual manner. The structures were solved by conventional Patterson and Fourier-difference methods by using the SHELXTL PLUS program package.<sup>7</sup> The function minimized during full-matrix least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w = \sigma^{-2}(F)$ . Neutral atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 8. The positions of the hydrogen atoms of the aromatic, methylene and aniline groups were calculated and included with fixed isotropic thermal parameters ( $U = 0.080 \text{ \AA}^2$ ). The positions of hydrogen atoms of the water molecules in 7 were located in the final Fourier-difference map and were also included. One of the nitrate groups [N(11)] was found to be slightly disordered. The disorder was successfully modelled by a split-atom model for oxygen atoms O(11) and O(13) (occupancy factor 0.8) and by O(17) and O(18) with an occupancy factor of 0.2, respectively. All other atoms were refined with anisotropic thermal parameters.

Complete atomic coordinates, thermal parameters and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

### Results and Discussion

The synthetic route to 1,4-bis(*o*-aminobenzyl)-1,4-diazacyclohexane (L) is shown in Scheme 1. Reaction of piperazine with 2 equivalents of 2-nitrobenzyl bromide in toluene over KOH yields 1,4-bis(*o*-nitrobenzyl)-1,4-diazacyclohexane. The



**Scheme 1** Reaction conditions: (i) toluene–KOH; (ii) ethanol,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , graphite catalyst

nitro groups are readily converted into amine groups by reduction with hydrazine hydrate in ethanol using graphite powder as efficient catalyst.<sup>9</sup>

### Preparation of complexes

From a chloroform–ethanol mixture of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and **L** (1:1) at elevated temperatures an orange precipitate of  $[\text{NiL}][\text{ClO}_4]_2$  **1** was obtained in ca. 70% yield. The material may be recrystallized from weakly or non-co-ordinating solvents such as nitromethane or acetone. Complex **1** is diamagnetic. A colour change of a solution of **1** in nitromethane was observed upon addition of co-ordinating anions such as  $\text{NaNCS}$  dissolved in ethanol; the orange-yellow solution became deep blue. Blue crystals of paramagnetic  $[\text{NiL}(\text{NCS})_2]$  **2** precipitated from such a solution within 1 d. In the infrared spectrum of **2** (KBr disc) one sharp, very strong band at  $2072\text{ cm}^{-1}$  is assigned to the stretching mode  $\nu(\text{CN})$  of N-co-ordinated thiocyanate. A temperature-independent magnetic moment of  $3.0\ \mu_{\text{B}}$  (80–298 K) for **2** is typical for two unpaired electrons of  $\text{Ni}^{2+}$  ( $d^8$ ) in an octahedral ligand environment and, consequently, **2** is formulated as the neutral complex *trans*- $[\text{NiL}(\text{NCS})_2]$ . Solutions of **1** in co-ordinating solvents like pyridine, acetonitrile or dimethylformamide are also blue and from the acetonitrile solution blue, paramagnetic crystals of  $[\text{NiL}(\text{NCMe})_2][\text{ClO}_4]_2 \cdot 1.5\text{MeCN}$  **3** were obtained. In the infrared spectrum three  $\nu(\text{CN})$  stretching modes at 2303, 2275 and  $2251\text{ cm}^{-1}$  are observed where the former is assigned to N-co-ordinated acetonitrile and the last two to acetonitrile molecules of solvation. The magnetic moment of  $3.0\ \mu_{\text{B}}$  of **3** is again typical for an octahedral nickel(II) complex.

When in the above synthesis of complex **1** the salt  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was used instead of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  under otherwise identical reaction conditions the crystalline product obtained was in most cases orange  $[\text{NiL}][\text{NO}_3]_2$  **4a** but in some cases blue crystals of identical composition  $[\text{NiL}(\text{NO}_3)_2]$  **4b** precipitated and in other instances both forms precipitated simultaneously. Orange and blue crystals were separated manually under a microscope. Although the chemical composition of crystals of orange **4a** and of blue **4b** is identical, the infrared spectra of the two species are quite different. For **4a** a very intense absorption maximum in the range  $1410\text{--}1300\text{ cm}^{-1}$  which is split into approximately four components is assigned to the  $\nu(\text{NO})$  stretching mode of unco-ordinated nitrate anions ( $1395\text{ cm}^{-1}$ ). The observed splitting is probably due to the differing site symmetry of the  $\text{NO}_3^-$  groups in crystalline **4a**. Thus diamagnetic, orange **4a** contains the square-planar dication  $[\text{NiL}]^{2+}$  and unco-ordinated  $\text{NO}_3^-$  anions. In contrast, in the infrared spectrum of blue **4b** two intense, sharp  $\nu(\text{NO})$  stretching modes at  $1418$  and  $1305\text{ cm}^{-1}$  are observed which are assigned to  $\nu_{\text{asym}}(\text{NO})$  and  $\nu_{\text{sym}}(\text{NO})$  stretching frequencies of co-ordinated, monodentate  $\text{NO}_3^-$  groups. Complex **4b** is paramagnetic ( $3.0\ \mu_{\text{B}}$ ) and is therefore considered to consist of the octahedral neutral species *trans*- $[\text{NiL}(\text{NO}_3)_2]$ .

The reaction of **L** and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in ethanol–chloroform (1:1) produced within 2 d blue-violet crystals of  $[\text{CuL}][\text{ClO}_4]_2$  **5**. The temperature-independent magnetic moment of  $1.74\ \mu_{\text{B}}$  is typical for  $\text{Cu}^{\text{II}}$  ( $d^9$ ) with one unpaired electron. Fig. 1 shows the X-band ESR-spectrum of a solid sample of **5** at 50 K. The rhombic signal was successfully simulated with  $g_1 = 2.033$ ,  $g_2 = 2.084$  and  $g_3 = 2.190$  and hyperfine coupling constants  $A_x$ ,  $A_y \leq 10^{-3}\text{ cm}^{-1}$  and  $A_z = 177 \times 10^{-4}\text{ cm}^{-1}$ . According to Hathaway's analysis<sup>10</sup> a spectrum like this indicates axially elongated octahedral or square-planar symmetry with a  $d_{x^2-y^2}$  ground state. Complex **5** is isostructural with **1** and consists of square-planar  $[\text{CuL}]^{2+}$  dications and unco-ordinated  $\text{ClO}_4^-$  anions. Recrystallization of **5** from acetonitrile solution produces blue-violet crystals of composition  $[\text{CuL}][\text{ClO}_4]_2 \cdot 2\text{MeCN}$  **6**. In the infrared spectrum two  $\nu(\text{CN})$  stretching frequencies at  $2290\text{vw}$  and

$2232\text{vw cm}^{-1}$  are observed which may be assigned to unco-ordinated rather than co-ordinated acetonitrile molecules of crystallization. This notion is supported by the observation that the crystals lose their acetonitrile molecules upon standing for 2 d in an open vessel at ambient temperature. The infrared spectrum of the resulting solid material is identical with that of **5**. On the other hand, it is also conceivable that one or both acetonitrile molecules are axially, weakly co-ordinated in the solid state forming thereby the species  $[\text{CuL}(\text{NCMe})]^{2+}$  or  $[\text{CuL}(\text{NCMe})_2]^{2+}$ .

When the ligand **L** reacts with  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in a chloroform–ethanol mixture at room temperature blue-black crystals of  $[\text{CuL}(\text{H}_2\text{O})][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$  **7** are obtained in 80% yield. From a single-crystal X-ray diffraction study (see below) it is established that **7** consists of the dication  $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ , unco-ordinated nitrate anions and water molecules of crystallization. Thus, in contrast to orange **4a** and blue **4b**, a five-co-ordinate copper(II) ion containing a tetradentate **L** and an apical, co-ordinated water molecule is formed by using the same reaction conditions. Consequently, in the infrared spectrum of **7** only the  $\nu(\text{NO})$  stretching frequencies of two crystallographically distinct, unco-ordinated nitrate anions are observed at  $1385$  and  $1344\text{ cm}^{-1}$ .

Finally, the reaction of **L** with palladium(II) acetate in a chloroform–ethanol mixture at room temperature affords upon addition of 60%  $\text{HClO}_4$  brown crystals of  $[\text{PdL}][\text{ClO}_4]_2$  **8**. Complex **8** is isostructural with **1** and **5** and contains the diamagnetic, square-planar dication  $[\text{PdL}]^{2+}$ .

Table 1 summarizes the observed  $\nu(\text{N-H})$  stretching frequencies of complexes **1–8**. From these data an interesting trend appears to emerge. All new compounds have two co-ordinated aniline  $\text{NH}_2$  groups in *cis* position relative to each other and in all cases at least *three*  $\nu(\text{N-H})$  frequencies are observed. This is an indication that the two  $\text{NH}_2$  groups are inequivalent in the solid state each giving rise to a  $\nu_{\text{asym}}(\text{N-H})$

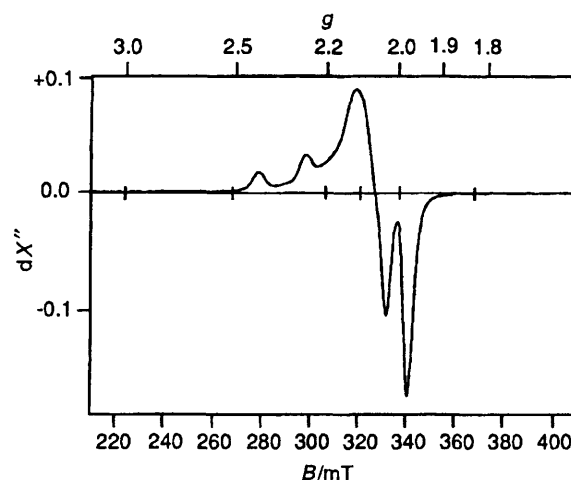


Fig. 1 X-Band ESR spectrum of complex **5** in acetone at 50 K (microwave frequency  $9.4266\text{ GHz}$ ,  $dX''/dB = 200\ \mu\text{W}$ ,  $40\text{ dB}$ )

Table 1 Stretching frequencies  $\nu(\text{NH})$  of co-ordinated aniline groups of **L**

Complex	$\tilde{\nu}(\text{NH})/\text{cm}^{-1}$	Polyhedron
<b>1</b>	3266, 3204, 3127	Square planar
<b>4a</b>	3143, $\approx 3054$ (sh), 2992	Square planar
<b>5</b>	3295, 3213, 3141	Square planar
<b>6</b>	3273, 3224, 3142	Square planar
<b>8</b>	3253, 3214, 3130	Square planar
<b>7</b>	3220, 3127	Square-base pyramidal
<b>2</b>	3311, 3242, 3146	Octahedral
<b>3</b>	3309, 3268, 3158	Octahedral
<b>4b</b>	3315, 3291, 3258, 3240	Octahedral



and a  $\nu_{\text{sym}}(\text{N-H})$  stretching mode (two of which are overlapping). In the unco-ordinated L the two  $\text{NH}_2$  groups are equivalent and display  $\nu_{\text{asym}}(\text{N-H})$  at  $3440\text{ cm}^{-1}$  and  $\nu_{\text{sym}}(\text{N-H})$  at  $3264\text{ cm}^{-1}$ . Upon co-ordination of the aniline groups in a square-planar fashion these frequencies are shifted to lower energy (1, 4a, 5, 6, 8), whereas for the five-co-ordinate species 7 and even more pronounced for octahedral complexes 2, 3, 4b these frequencies are observed at higher energies but still somewhat lower than for the unco-ordinated L. Thus the metal-to-aniline bond strength appears to decrease with increasing co-ordination number at the respective metal ion to which L is co-ordinated. This observation is fully corroborated by the crystal structure determinations discussed in the next section.

### Crystal structures

Table 2 gives selected bond distances and angles and Figs. 2–6 show the structures of the co-ordination compounds in crystals of 1, 2, 5, 7 and 8, respectively.

The co-ordinated piperazine structural unit of the ligand L forms two five-membered chelate rings  $\text{M-N-C-C-N}$  which in

analogy to metal-bound ethylenediamine (en) can adopt a  $\lambda$  or  $\delta$  conformation. This leads, in principle, to a situation where the co-ordinated piperazine moiety adopts either  $(\lambda, \lambda)$  or  $(\delta, \delta)$  conformation (enantiomeric forms) or a 'meso'  $(\lambda, \delta)$  conformation which is clearly energetically unfavourable due to a higher strain energy. This is schematically shown in Fig. 7 (bottom). Consequently, in all the determined crystal structures the co-ordinated piperazine units adopt the  $(\lambda, \lambda)$  or  $(\delta, \delta)$  conformation. Since all the complexes crystallize in the centrosymmetric space group  $P2_1/n$  (no. 14) both forms are present in equal amounts (racemate). In addition, complexes of L form two six-membered chelate rings by co-ordination of the pendant aniline groups:

$\text{M-N}_{\text{amine}}-\text{C}-\text{C}-\text{C}-\text{N}_{\text{aniline}}$ . In a previous study<sup>3,4</sup> we have shown that in complexes containing the hexadentate ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane these six-membered chelates can adopt either a boat or a twist-boat conformation (Fig. 7, middle) which in solution are in a

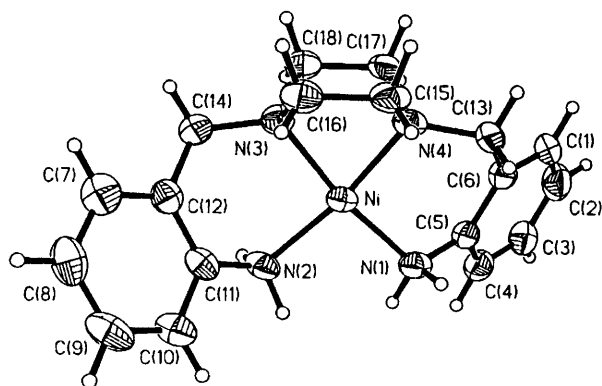


Fig. 2 Structure of the dication  $[\text{NiL}]^{2+}$  in crystals of complex 1

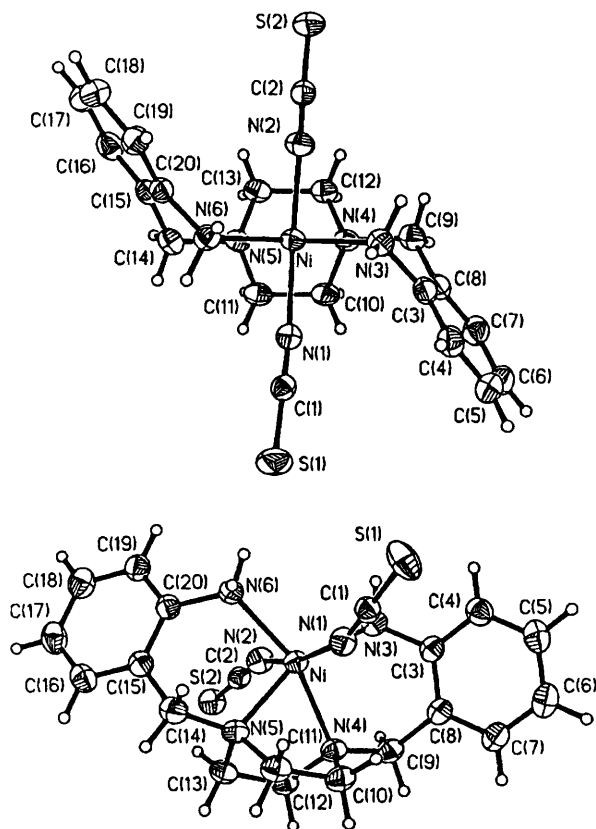


Fig. 3 Two views of the crystal structure of the neutral complex 2

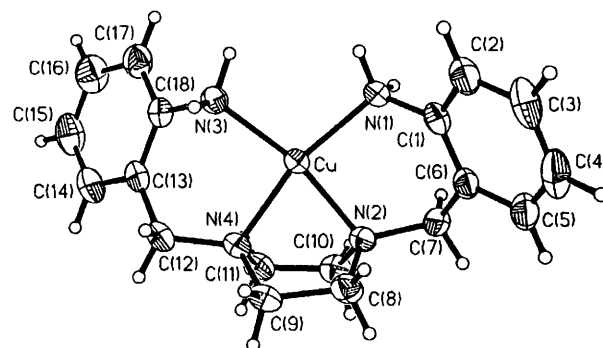


Fig. 4 Structure of the dication  $[\text{CuL}]^{2+}$  in crystals of complex 5

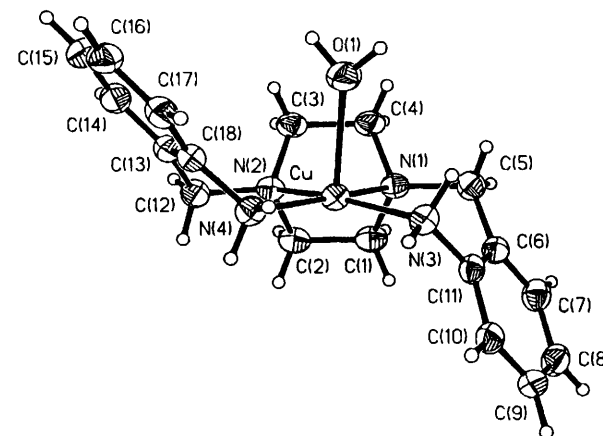


Fig. 5 Structure of the dication  $[\text{CuL}(\text{H}_2\text{O})]^{2+}$  in crystals of complex 7

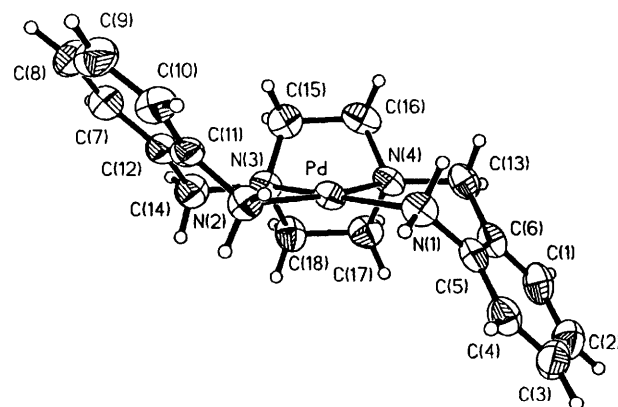
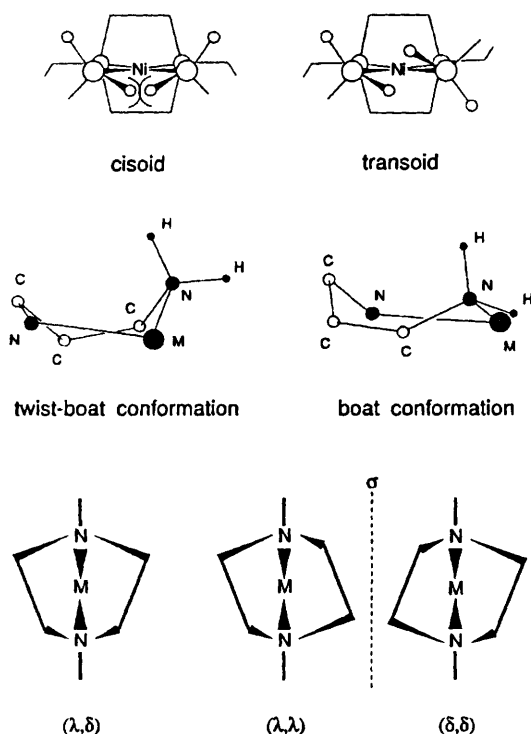


Fig. 6 Structure of the dication  $[\text{PdL}]^{2+}$  in crystals of complex 8



**Fig. 7** Schematic representation of the possible stereochemical arrangements of co-ordinated L. Top: transoid and cisoid configuration of equatorially bound L. Middle: two conformations of the six-membered chelate rings  $M-N_{\text{amine}}-C-C-C-N_{\text{aniline}}$ . Bottom: conformations of the five-membered chelate rings  $M-N_{\text{amine}}-C-C-N_{\text{amine}}$ .

dynamic equilibrium. Furthermore, Fig. 7 (top) shows that in principle the aniline structural units of the equatorially bound ligand L can be arranged in a cisoid or transoid fashion relative to each other. Space-filling models clearly show that the cisoid mode is energetically unfavourable due to steric congestion of the protons of the two *cis*-coordinated  $NH_2$  groups. This co-ordination mode would enforce considerable strain in the piperazine entity. Consequently, the cisoid co-ordination mode has not been observed in the present crystal structures only the transoid.

Complexes **1**, **5** and **8** are isostructural; they contain a square-planar nickel(II), copper(II) and palladium(II) ion, respectively, co-ordinated to a tetradentate ligand L and unco-ordinated perchlorate ions. The dications do not lie on a crystallographic symmetry element but have molecular  $C_1$  symmetry. This is due to the fact that one of the six-membered chelate rings has a boat whereas the other has a twist-boat conformation. Thus these two chelates are *chemically inequivalent*. Note that if both rings had the same conformation the molecules would possess  $C_2$  symmetry which is clearly not the case. In full agreement with this is the observation of three  $\nu(N-H)$  stretching modes in the infrared spectra (a  $\nu_{\text{sym}}$  and a  $\nu_{\text{asym}}$  mode for each  $NH_2$  group of which two coincide) and the solid-state  $^{13}C$  CP MAS NMR spectra of **1** and **8** (see below). It is also noted that the  $ClO_4^-$  anions do not form strong  $O \cdots H-N$  hydrogen-bonding contacts to the co-ordinated amine groups.

The average  $M-N_{\text{piperazine}}$  and  $M-N_{\text{aniline}}$  bonds are within experimental error equidistant in complexes **1** and **5** but slightly different at 2.012 and 2.059 Å, respectively, in **8**.

The average Ni–N distance at 1.922 Å in complex **1** is quite typical for square-planar  $NiN_4$  complexes<sup>11</sup> and is shorter by 0.094 Å than the corresponding Cu–N distance in **5**, and by 0.114 Å than the averaged Pd–N distance in **8**. These differences clearly reflect the differences of ionic radii between square-planar  $Ni^{2+}$  (0.63) and  $Cu^{2+}$  (0.71) or  $Pd^{2+}$  ions (0.78 Å).<sup>12</sup>

Crystals of complex **2** consist of octahedral neutral molecules

of  $[NiL(NCS)_2]$  which contain ligand L in the equatorial plane and two N-bound NCS anions in the axial positions. Thus the nickel(II) ion is six-co-ordinate. The average Ni– $N_{\text{eq}}$  bond distance at 2.141 Å is longer by 0.219 Å than in square-planar **1**, which reflects the increase in ionic radius of six-co-ordinate *vs.* square-planar  $Ni^{2+}$  ions (the difference is 0.20 Å<sup>12</sup>). Despite this difference, the configuration of the  $NiL$  fragment in **2** is the same as in **1**; one six-membered chelate ring adopts a boat whereas the other has a twist-boat conformation and both are in transoid relative to each other.

Interestingly, the axial Ni– $N_{\text{NCS}}$  bonds are shorter by 0.08 Å than the equatorial Ni– $N_{\text{amine}}$  bonds. The average Ni–N–CS bond angle is 158° which is intermediate between 162.8 and 171.3° observed in  $[Ni(\text{deen})_2(NCS)_2]$ <sup>13</sup> (deen = *N,N*-diethylethylenediamine) and 140° in  $[Ni(\text{en})_2(NCS)_2]$ .<sup>14</sup> The trans-axial bond angle  $N_{\text{NCS}}-Ni-N_{\text{NCS}}$  is 166.6°; the two  $NCS^-$  ligands are slightly bent away by 6.7° from the axis perpendicular with respect to the equatorial plane of the four amine nitrogen atoms of L. This is probably due to the steric requirements of the methylene groups of the piperazine moiety.

Deeth and Gerloch<sup>15</sup> have analysed the d–d spectra of *trans*- $[Ni(NCS)_2N_4]$  complexes within the cellular ligand-field model and show that it is not necessary to consider the  $NCS^-$  ligand as a  $\pi$  donor<sup>16</sup> in *trans*- $[Ni(NH_3)_4(NCS)_2]$  but as a  $\pi$  acceptor in *trans*- $[Ni(\text{en})_2(NCS)_2]$ . In particular, there is no simple correlation between the Ni– $N_{\text{NCS}}$  bond length and the Ni–N–CS bond angle  $\alpha$  considering approximately 10 crystal structure determinations of *trans*- $[Ni(NCS)_2N_4]$  complexes, where  $N_4$  represents a pure amine-type  $\sigma$  donor.

Crystals of complex **7** consist of the five-co-ordinate dication  $[CuL(H_2O)]^{2+}$  and unco-ordinated nitrate anions and water molecules of crystallization. The geometry of the co-ordination polyhedron is square-based pyramidal where the ligand L occupies four equatorial positions and a water molecule is in the apical position. It is instructive to compare the metrical details of the  $CuL^{2+}$  fragment in **7** with those of the square-planar dication  $[CuL]^{2+}$  in **5**. In **5** the Cu– $N_{\text{piperazine}}$  and Cu– $N_{\text{aniline}}$  bonds are equidistant within experimental error at 2.016 Å whereas in **7** these bond lengths are significantly different: Cu– $N_{\text{piperazine}}$  2.028 and Cu– $N_{\text{aniline}}$  2.006 Å (average 2.017 Å). The Cu–O bond is weak at 2.348(2) Å. In contrast to **1** and **2** the increase in the co-ordination number from four to five in **5** and **7** does not lead to an increase in the Cu–N bond lengths. One of the oxygen atoms [O(16)] of a nitrate anion points toward the vacant sixth co-ordination site of the  $[CuL(H_2O)]^{2+}$  cation; the Cu  $\cdots$  O(16) interaction at 2.834(3) Å is considered to be essentially non-bonding. The co-ordinated water molecule in **7** forms a weak O–H  $\cdots$  O hydrogen bond to a water molecule of crystallization [O(1)  $\cdots$  O(2) 2.826(3) Å] which in turn is hydrogen bonded to an oxygen atom of a  $NO_3^-$  group [O(2)  $\cdots$  O(13) 2.795(3) Å] and to a second  $NO_3^-$  group [O(2)  $\cdots$  O(12) 2.807(3) Å].

### Solution behaviour of complexes **1**, **4a**, **4b** and **5**

Table 3 summarizes the electronic spectral data and effective magnetic moments of the complexes. The solid-state reflectance spectrum of orange, diamagnetic **1** exhibits two maxima at 457 and 288 nm. The former is assigned to a d–d transition ( $^1A_{1g} \longrightarrow ^1A_{2g}$  in  $D_{4h}$  symmetry) and the latter is a  $\pi \longrightarrow \pi^*$  transition of the aniline moiety of the ligand L. Solutions of **1** in the non-co-ordinating solvents nitromethane and acetone are yellow and display the d–d transition in the visible at 466 ( $\epsilon = 210$ ) and 463 nm (211 dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>), respectively. This is typical for square-planar nickel(II) complexes such as  $[Ni(\text{cyclam})]^{2+}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) [463 nm(116 dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>)] and complexes containing open-chain tetramine ligands.<sup>17</sup>

Upon addition of acetonitrile to the above  $MeNO_2$  solution of complex **1** a change to blue is observed with increasing

**Table 2** Selected bond distances (Å) and angles (°)**Complex 1**

Ni–N(1)	1.928(5)	Ni–N(4)	1.920(6)	N(3)–C(14)	1.474(9)	N(3)–C(18)	1.504(9)
Ni–N(2)	1.916(6)	N(1)–C(5)	1.451(9)	N(4)–C(13)	1.487(9)	N(4)–C(15)	1.490(8)
Ni–N(3)	1.925(5)	N(2)–C(11)	1.457(9)	N(3)–C(16)	1.509(8)	N(4)–C(17)	1.489(8)
N(1)–Ni–N(2)	94.8(2)	Ni–N(3)–C(16)	101.1(4)	Ni–N(2)–C(11)	115.8(4)	N(3)–Ni–N(4)	77.2(2)
N(1)–Ni–N(4)	94.6(2)	N(1)–Ni–N(3)	171.1(3)	Ni–N(4)–C(13)	118.2(4)	Ni–N(3)–C(14)	119.8(4)
Ni–N(1)–C(5)	114.6(4)	N(2)–Ni–N(4)	169.6(2)	N(2)–Ni–N(3)	93.6(2)	Ni–N(4)–C(15)	101.6(4)

**Complex 2**

Ni–N(1)	2.066(2)	Ni–N(6)	2.129(3)	C(2)–S(2)	1.631(3)	N(4)–C(12)	1.484(3)
Ni–N(2)	2.049(2)	C(10)–C(11)	1.545(4)	N(3)–C(3)	1.446(4)	N(5)–C(11)	1.480(4)
Ni–N(3)	2.151(2)	N(1)–C(1)	1.161(3)	N(4)–C(9)	1.477(4)	N(5)–C(13)	1.482(3)
Ni–N(4)	2.144(3)	C(1)–S(1)	1.625(3)	C(12)–C(13)	1.550(4)	N(5)–C(14)	1.484(4)
Ni–N(5)	2.139(2)	N(2)–C(2)	1.160(3)	N(4)–C(10)	1.482(4)	N(6)–C(20)	1.443(3)
N(1)–Ni–N(2)	166.6(1)	Ni–N(4)–C(10)	102.1(2)	N(2)–Ni–N(6)	89.4(1)	Ni–N(1)–C(1)	159.1(3)
N(1)–Ni–N(3)	85.5(1)	Ni–N(5)–C(13)	105.7(2)	Ni–N(3)–C(3)	112.7(2)	N(1)–C(1)–S(1)	178.9(3)
N(2)–Ni–N(3)	85.6(1)	N(1)–Ni–N(5)	95.0(1)	Ni–N(4)–C(12)	106.2(2)	Ni–N(2)–C(2)	157.9(3)
N(1)–Ni–N(4)	98.0(1)	N(2)–Ni–N(5)	97.0(1)	Ni–N(5)–C(14)	116.8(2)	Ni–N(4)–C(9)	116.2(2)
N(2)–Ni–N(4)	91.9(1)	N(3)–Ni–N(5)	158.9(1)	N(3)–Ni–N(6)	111.7(1)	Ni–N(5)–C(11)	103.1(2)
N(3)–Ni–N(4)	89.3(1)	N(4)–Ni–N(5)	69.8(1)	N(4)–Ni–N(6)	159.1(1)	Ni–N(6)–C(20)	112.8(2)
N(2)–C(2)–S(2)	178.7(3)	N(1)–Ni–N(6)	84.6(1)	N(5)–Ni–N(6)	89.3(1)		

**Complex 5**

Cu–N(1)	2.018(3)	Cu–N(4)	2.029(3)	N(2)–C(8)	1.487(5)	N(4)–C(9)	1.485(5)
Cu–N(2)	2.022(3)	N(1)–C(1)	1.457(5)	N(2)–C(10)	1.488(5)	N(4)–C(11)	1.491(5)
Cu–N(3)	1.993(3)	N(2)–C(7)	1.484(5)	N(3)–C(18)	1.470(5)	N(4)–C(12)	1.493(5)
N(1)–Cu–N(2)	92.3(1)	Cu–N(4)–C(11)	101.6(2)	Cu–N(1)–C(1)	113.4(2)	Cu–N(2)–C(10)	105.0(2)
N(1)–Cu–N(3)	100.9(1)	N(2)–Cu–N(4)	73.7(1)	Cu–N(2)–C(7)	116.4(2)	Cu–N(3)–C(18)	113.7(2)
N(2)–Cu–N(3)	166.5(1)	N(3)–Cu–N(4)	92.9(1)	Cu–N(2)–C(8)	100.6(2)	Cu–N(4)–C(9)	104.5(2)
N(1)–Cu–N(4)	165.3(1)						

**Complex 7**

Cu–N(1)	2.025(3)	Cu–O(1)	2.348(2)	N(1)–C(5)	1.496(4)	N(3)–C(11)	1.446(4)
Cu–N(2)	2.032(2)	N(1)–C(1)	1.487(4)	N(2)–C(2)	1.493(4)	N(4)–C(18)	1.449(4)
Cu–N(3)	2.009(2)	N(1)–C(4)	1.488(4)	N(2)–C(12)	1.484(4)	N(2)–C(3)	1.482(3)
Cu–N(4)	2.002(3)						
N(1)–Cu–N(2)	73.5(1)	N(1)–Cu–N(4)	166.6(1)	N(1)–Cu–O(1)	96.2(1)	N(4)–Cu–O(1)	88.1(1)
N(1)–Cu–N(3)	92.5(1)	N(2)–Cu–N(4)	93.2(1)	N(2)–Cu–O(1)	101.4(1)	Cu–N(3)–C(11)	112.2(2)
N(2)–Cu–N(3)	163.5(1)	N(3)–Cu–N(4)	100.3(1)	N(3)–Cu–O(1)	88.4(1)	Cu–N(4)–C(18)	113.1(2)

**Complex 8**

Pd–N(1)	2.060(5)	Pd–N(4)	2.018(6)	N(3)–C(14)	1.468(10)	N(4)–C(13)	1.485(9)
Pd–N(2)	2.058(6)	N(1)–C(5)	1.454(9)	N(3)–C(15)	1.470(8)	N(4)–C(16)	1.514(8)
Pd–N(3)	2.006(5)	N(2)–C(11)	1.442(9)	N(3)–C(18)	1.481(9)	N(4)–C(17)	1.480(9)
N(1)–Pd–N(2)	98.3(2)	N(2)–Pd–N(3)	93.9(2)	N(2)–Pd–N(4)	167.6(2)	N(3)–Pd–N(4)	74.2(2)
N(1)–Pd–N(3)	167.6(2)	N(1)–Pd–N(4)	93.7(2)				

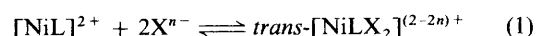
**Table 3** Electronic spectral data and magnetic moments of the complexes

Complex	Solvent	$\lambda_{\max}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	$\mu_{\text{eff}}(81-298 \text{ K})/\mu_{\text{B}}$
<b>1</b>	Acetone	463 (211)	Diamagnetic
<b>2</b>	Dimethylformamide	1106 (11), 720 (sh), 664 (9), 397 (22)	3.0
<b>3</b>	Acetonitrile	874 (30), 798 (24), 664 (11), 550 (11), 332 (107), 246 (6800)	3.0
<b>4a</b>	Solid	444, 292	Diamagnetic
<b>4b</b>		n.m.	3.0
<b>5</b>	Nitromethane	550 (260), 371 (2000)	1.74
	Solid	550, 373, 317, 217	
<b>6</b>	Acetonitrile	571 (240), 357 (1900), 308 (5500), 270 (4900)	1.75
<b>7</b>	Water	568 (240), 356 (1800), 305 (5600), 269 (4900)	1.74
<b>8</b>	Acetonitrile	300 (sh), 251 (9600)	Diamagnetic

n.m. = Not measured.

concentration of MeCN. In the absorption spectrum of **1** in MeCN four maxima of low intensity are observed in the visible region. This is typical for tetragonally distorted octahedral nickel(II) complexes. The intense band of square-planar **1** at 466 nm is absent and the lowest-energy band at 874 nm

is asymmetric indicating the presence of more than one transition.<sup>18</sup> These experiments clearly show that equilibrium (1) exists in solution<sup>19</sup> where X represents a co-ordinating

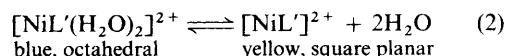


solvent molecule or an anion. The electronic spectrum of a yellow solution of **1** in nitromethane clearly shows that only the square-planar  $[\text{NiL}]^{2+}$  species is present. This spectrum is temperature-independent in the range 5–60 °C and identical with the reflectance spectrum of **1**. No indication of the formation of octahedral nickel(II) complexes containing either co-ordinated nitromethane or perchlorate anions or water molecules of adventitiously present  $\text{H}_2\text{O}$  was detected. Thus  $\text{ClO}_4^-$  does not bind to  $[\text{NiL}]^{2+}$  under these conditions.

The situation changes dramatically when equimolar amounts of pure orange **4a** or pure blue **4b** were dissolved in nitromethane. Both spectra are identical (Fig. 8) and show the presence of orange, square-planar  $[\text{NiL}]^{2+}$  and of the blue, octahedral form which is presumably  $[\text{NiL}(\text{ONO}_2)_2]$ . The absorption maximum at 466 nm is due to the square-planar  $[\text{NiL}]^{2+}$  species whereas the band at 915 nm (not shown)

corresponds to an octahedral  $[\text{NiLX}_2]$  species. The intensity ratio between these two bands is (i) temperature dependent and (ii) dependent on the ionic strength of the solution. Thus, addition of  $\text{NaClO}_4$ , which does not bind co-ordinatively to  $[\text{NiL}]^{2+}$ , to such a solution induces an increase in the  $[\text{NiL}]^{2+}$  species and a decrease in  $[\text{NiL}(\text{ONO}_2)_2]$ , i.e. the band at 466 nm increases whereas that at 915 nm decreases. Since the molar absorption coefficient of  $[\text{NiL}]^{2+}$  at 466 nm is known ( $210 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and that of  $[\text{NiLX}_2]^{2+}$  is smaller than  $\approx 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  the equilibrium constant  $K$  of equilibrium (1) [ $K = \epsilon_{\text{obs}}/(\epsilon_{\text{yellow}} - \epsilon_{\text{obs}})$ ] can be calculated.

Fig. 8 shows the temperature dependence of the absorption spectrum of **4a** (or **4b**) in nitromethane and the inset shows a linear plot of  $\ln K$  versus  $1/T$  from which values for  $\Delta H^\circ$  and  $\Delta S^\circ$  were determined to be  $12.1 \text{ kJ mol}^{-1}$  and  $26.7 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. These thermodynamic data may be compared with those reported for equilibrium (2) where  $\text{L}'$  represents the



macrocyclic ligands cyclam<sup>20</sup> and isocyclam (1,4,7,11-tetraazacyclotetradecane)<sup>17b</sup> and some open-chain tetramines.<sup>21–23</sup> The ligand in  $[\text{NiL}]^{2+}$  behaves very similarly with respect to stabilization of the octahedral form  $[\text{NiLX}_2]$  to the open-chain tetramines *N,N'*-bis(2-aminoethyl)propane-1,3-diamine and *N,N'*-bis(2-aminoethyl)ethane-1,2-diamine. The data for the macrocyclic systems with cyclam and isocyclam are quite different. This effect has been interpreted by Sabatini and Fabbrizzi.<sup>17b</sup> Equilibria as formulated in equations (1) or (2) were detected in the solid state by Lifschitz *et al.*<sup>23</sup> in 1939 for yellow  $[\text{Ni}(\text{en})_2]\text{X}_2$  salts and their corresponding neutral blue  $[\text{Ni}(\text{en})_2\text{X}_2]$  species.

The electronic spectrum of square-planar  $[\text{CuL}]^{2+}$  **5** has been measured in the solid state and in nitromethane solution (Table 3). Since the d–d transition at 550 nm remains unaffected, it is concluded that nitromethane is a non-co-ordinating solvent and the square-planar  $[\text{CuL}]^{2+}$  dications of **5** persist in such a solution. In contrast, in acetonitrile solution a shift of 21 nm to 571 nm is observed. This is an indication that at least one MeCN molecule is co-ordinated. Similar behaviour is observed when **5** is dissolved in water. A shift of the d–d transition to 568 nm is observed which may indicate the formation of five-co-ordinate  $[\text{CuL}(\text{H}_2\text{O})]^{2+}$  as is present in crystals of **7**.

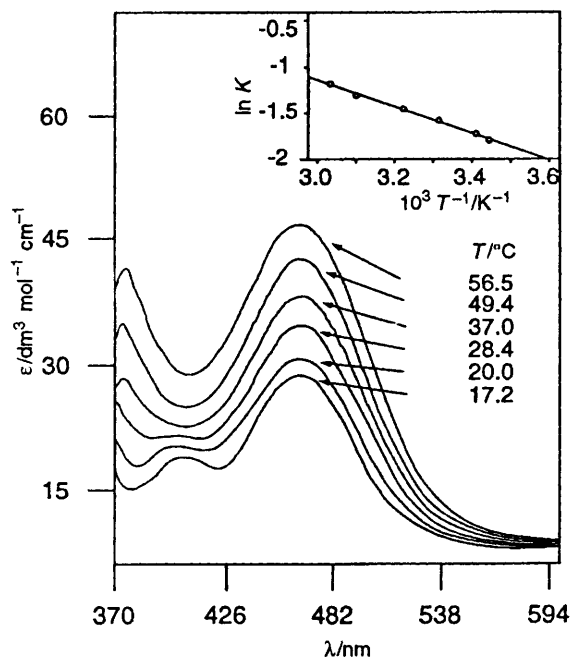


Fig. 8 Temperature dependence of the electronic spectrum of complexes **4a**, **4b** in nitromethane. The inset shows the temperature dependence of equilibrium (1)

Table 4 Crystal data and data collection parameters for the complexes

	<b>1</b>	<b>2</b>	<b>5</b>	<b>7</b>	<b>8</b>
Molecular formula	$\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_4\text{NiO}_8$	$\text{C}_{20}\text{H}_{24}\text{N}_6\text{NiS}_2$	$\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{CuN}_4\text{O}_8$	$\text{C}_{18}\text{H}_{28}\text{CuN}_6\text{O}_8$	$\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_8\text{Pd}$
<i>M</i>	554.0	471.3	558.9	520.0	601.7
Crystal size/mm	$0.4 \times 0.5 \times 0.6$	$0.35 \times 0.4 \times 0.8$	$0.3 \times 0.4 \times 0.6$	$0.5 \times 0.6 \times 0.9$	$0.4 \times 0.7 \times 0.8$
<i>a</i> /Å	9.709(4)	10.387(2)	8.478(2)	9.745(2)	9.671(3)
<i>b</i> /Å	17.161(6)	14.491(4)	10.521(3)	17.833(3)	17.162(4)
<i>c</i> /Å	14.064(5)	14.808(4)	25.060(6)	13.025(3)	14.239(4)
$\beta/^\circ$	104.51(3)	106.65(2)	90.10(2)	102.20(2)	104.50(2)
<i>U</i> /Å <sup>3</sup>	2268.6	2135.4	2235.3	2212.4	2288.0
<i>D<sub>c</sub></i> /g cm <sup>−3</sup>	1.62	1.47	1.66	1.56	1.75
<i>F</i> (000)	1144	984	1148	1084	1216
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	1.15	1.12	1.27	1.04	1.10
2 $\theta$ range/ $^\circ$	3–52.5	3–54	3–54	3–57.5	3–60
Reflections measured	5024	4856	5395	6222	5350
Observed reflections	3415	3702	3645	4437	4800
Least-squares parameters	299	263	299	307	299
<i>R</i>	0.068	0.036	0.047	0.042	0.064
<i>R'</i>	0.066	0.035	0.044	0.038	0.059

Details in common:  $T = 298 \text{ K}$ ; Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ Å}$ ); absorption correction, empirical  $\psi$  scans;  $Z = 4$ ;  $\omega$  scans;  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ ;  $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ; monoclinic, space group  $P2_1/n$  (no. 14), Syntex R3 diffractometer; criterion for observed reflections  $I \geq 2.5\sigma(I)$ .



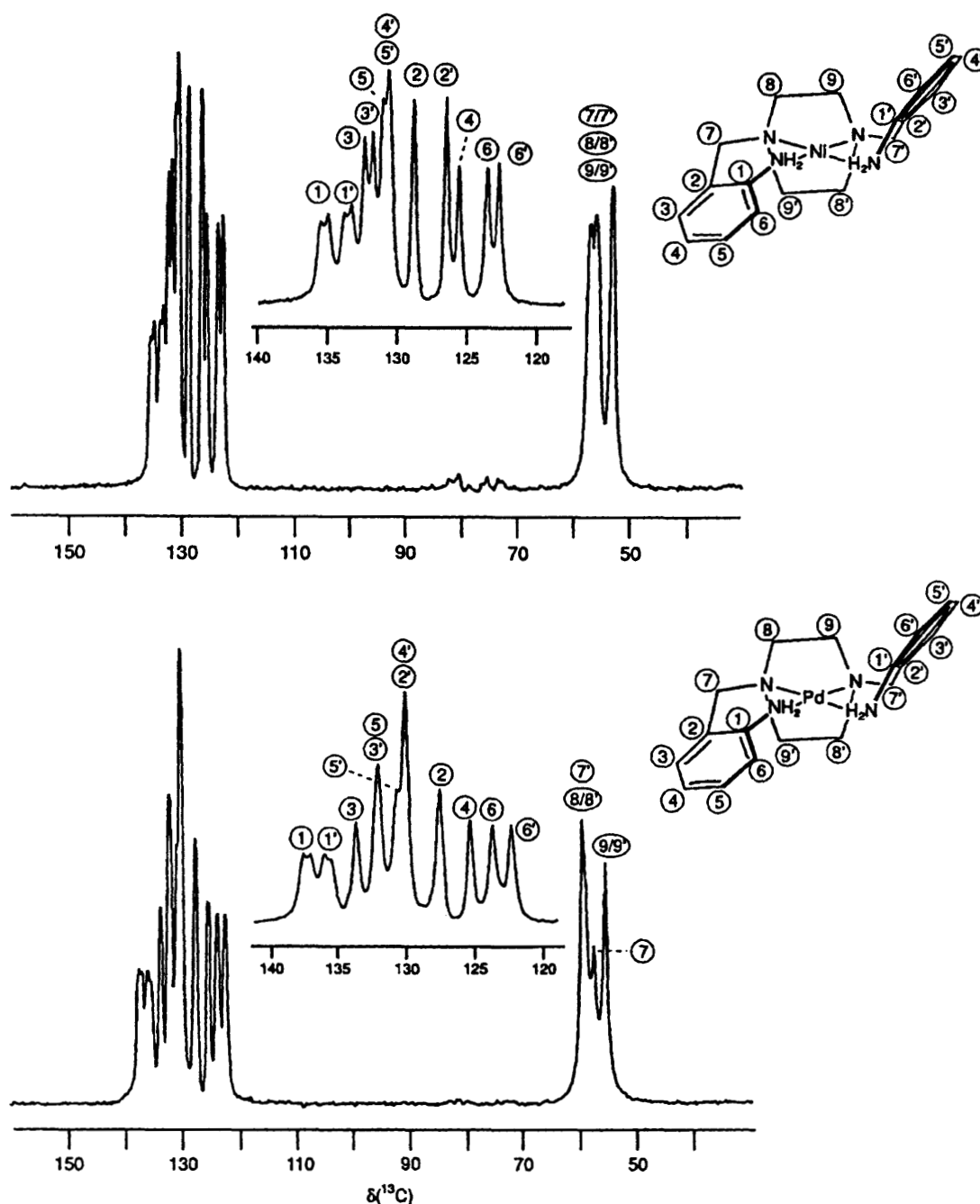


Fig. 9 Carbon-13 CP MAS NMR spectra of solid samples of complexes **1** (top) and **8** (bottom). The primed indices for carbon atoms indicate a given atom in the first or second chelate ring irrespective of its actual conformation

### $^{13}\text{C}$ CP MAS NMR spectra of complexes **1** and **8**

Fig. 9 displays the solid state  $^{13}\text{C}$  CP MAS NMR spectra of complexes **1** and **8**. Since each of the two dications possesses  $C_1$  symmetry, the respective two six-membered chelate rings are chemically inequivalent and each carbon atom is expected to show a resonance at a different value of the chemical shift  $\delta$ . Thus a total of 18 resonances (12 aromatic C, two benzylic C, and four ethylene atoms) are, in principle, observable. On the other hand, for a  $C_2$  symmetric dication only nine such signals are expected. Clearly, more than nine signals are detectable in the solid-state spectra shown in Fig. 9. The aromatic carbon resonances of solid **1** and **8** are observed in the region  $\delta$  120–140 whereas the benzyl and ethylene carbon atoms resonate in the range  $\delta$  50–65.

The differences in chemical shift  $\delta$  are not large enough fully to resolve all expected 18 resonances. Nevertheless, it is possible

to obtain definitive evidence for  $C_1$  symmetry of complexes **1** and **8** in the solid state. Non-quaternary suppression spectra (not shown) revealed two groups of signals for quaternary C atoms at  $\delta$  133–138 and at 126–129 for both **1** and **8**. The first group consists of two well resolved doublets for  $C^1$  and  $C^{1'}$ . The observed splitting is due to quadrupole interactions with the adjacent  $^{14}\text{N}$  atoms. The second group of signals at  $\delta \approx 127$  displays two well resolved lines of equal intensity for  $C^2$  and  $C^{2'}$  of **1** and **8**.

The splitting patterns of the signals of the protonated aromatic carbon atoms ( $C^{3-6}$  and  $C^{3'-6'}$ ) of complexes **1** and **8** are indicative of and fully consistent with the presence of two chemically inequivalent disubstituted aromatic rings, respectively. For **1** eleven aromatic carbon signals (one of which has twice the intensity of the others) and for **8** ten such signals (two of which have twice the intensity of the others) have been observed. For **1** three methylene carbon



**Table 5** Atomic coordinates ( $\times 10^4$ ) for complex **1**

Atom	x	y	z
Ni	2 403(1)	1 850(1)	2 017(1)
N(1)	1 886(6)	2 935(3)	2 010(4)
N(2)	3 290(6)	1 941(3)	949(4)
N(3)	2 702(6)	741(3)	2 138(4)
N(4)	1 737(6)	1 599(3)	3 156(3)
C(1)	−1 243(9)	2 879(4)	3 066(5)
C(2)	−2 183(9)	3 348(5)	2 452(6)
C(3)	−1 818(8)	3 695(4)	1 658(6)
C(4)	−467(8)	3 562(4)	1 514(5)
C(5)	486(7)	3 080(4)	2 163(5)
C(6)	110(8)	2 733(4)	2 968(5)
C(7)	5 835(8)	281(5)	1 319(5)
C(8)	7 037(8)	637(5)	1 143(6)
C(9)	7 038(8)	1 424(5)	961(6)
C(10)	5 813(8)	1 853(5)	916(5)
C(11)	4 595(7)	1 495(4)	1 045(5)
C(12)	4 603(7)	700(4)	1 272(5)
C(13)	1 170(8)	2 241(4)	3 658(5)
C(14)	3 281(8)	320(4)	1 410(5)
C(15)	3 015(8)	1 219(4)	3 799(5)
C(16)	3 634(8)	683(4)	3 170(5)
C(17)	633(8)	990(4)	2 808(5)
C(18)	1 245(7)	438(4)	2 130(6)
Cl(1)	7 024(3)	5 944(1)	26(2)
O(11)	6 965(20)	5 254(5)	84(11)
O(12)	8 231(11)	6 291(10)	27(8)
O(13)	6 189(15)	6 195(10)	−767(13)
O(14)	6 674(21)	6 141(11)	696(13)
Cl(2)	−91(2)	1 593(1)	9 236(2)
O(21)	−114(8)	2 164(5)	8 452(5)
O(22)	−1 399(7)	1 224(4)	8 921(5)
O(23)	5(6)	2 016(4)	10 108(4)
O(24)	1 106(6)	1 119(4)	9 303(4)

**Table 6** Atomic coordinates ( $\times 10^4$ ) for complex **2**

Atom	x	y	z
Ni	996(1)	452(1)	2265(1)
N(1)	−661(2)	−323(2)	1572(2)
C(1)	−1426(3)	−705(2)	959(2)
S(1)	−2477(1)	−1240(1)	90(1)
N(2)	2628(2)	1313(2)	2639(2)
C(2)	3505(3)	1730(2)	3132(2)
S(2)	4719(1)	2316(1)	3843(1)
N(3)	−5(2)	1574(2)	1391(2)
N(4)	258(2)	961(2)	3383(2)
N(5)	1600(2)	−443(2)	3461(2)
N(6)	2044(2)	−407(2)	1547(2)
C(3)	−1374(3)	1698(2)	1419(2)
C(4)	−2429(3)	1657(2)	601(2)
C(5)	−3745(3)	1725(2)	629(3)
C(6)	−4008(3)	1847(2)	1486(3)
C(7)	−2949(3)	1894(2)	2310(2)
C(8)	−1626(3)	1813(2)	2293(2)
C(9)	−491(3)	1840(2)	3200(2)
C(10)	−552(3)	172(2)	3550(2)
C(11)	308(3)	−709(2)	3622(2)
C(12)	1443(3)	1029(2)	4226(2)
C(13)	2312(3)	152(2)	4262(2)
C(14)	2410(3)	−1263(2)	3371(2)
C(15)	3582(3)	−1006(2)	3013(2)
C(16)	4900(3)	−1153(2)	3568(2)
C(17)	5985(3)	−960(2)	3241(2)
C(18)	5777(3)	−602(2)	2339(2)
C(19)	4478(3)	−430(2)	1783(2)
C(20)	3386(3)	−631(2)	2113(2)

signals of equal intensity (2:2:2) are observed whereas for **8** four such signals with an intensity ratio of 2:1:1:2 are observed. Thus, the solid-state NMR spectra of **1** and **8** are in excellent agreement with the crystallographically determined asymmetric structures of the dications in **1** and **2**.

**Table 7** Atomic coordinates ( $\times 10^4$ ) for complex **5**

Atom	x	y	z
Cu	6 096(1)	9 855(1)	1 272(1)
N(1)	3 798(3)	9 413(3)	1 171(1)
N(2)	6 358(4)	8 555(3)	1 860(1)
N(3)	6 389(4)	11 153(3)	702(1)
N(4)	8 418(3)	9 858(3)	1 468(1)
C(1)	3 498(5)	8 049(4)	1 162(2)
C(2)	2 712(5)	7 512(5)	726(2)
C(3)	2 507(6)	6 211(5)	705(2)
C(4)	3 076(6)	5 463(5)	1 116(2)
C(5)	3 835(5)	5 992(4)	1 542(2)
C(6)	4 055(5)	7 301(4)	1 574(2)
C(7)	4 905(5)	7 891(4)	2 037(2)
C(8)	7 540(5)	7 691(4)	1 614(2)
C(9)	8 912(5)	8 509(4)	1 416(2)
C(10)	7 161(5)	9 249(4)	2 301(2)
C(11)	8 358(5)	10 163(4)	2 049(1)
C(12)	9 465(5)	10 736(4)	1 163(2)
C(13)	8 771(5)	12 066(4)	1 116(2)
C(14)	9 620(5)	13 123(4)	1 290(2)
C(15)	9 017(6)	14 328(5)	1 213(2)
C(16)	7 585(7)	14 501(5)	968(2)
C(17)	6 715(6)	13 461(4)	799(2)
C(18)	7 320(5)	12 259(4)	873(2)
Cl(1)	2 417(1)	1 762(1)	45(1)
O(11)	1 094(6)	2 453(6)	−98(2)
O(12)	3 570(5)	1 763(4)	−363(2)
O(13)	3 014(4)	2 162(4)	548(1)
O(14)	1 957(6)	474(4)	113(2)
Cl(2)	3 894(1)	11 858(1)	2 210(1)
O(21)	2 596(4)	11 076(3)	2 073(1)
O(22)	4 439(5)	11 435(4)	2 721(1)
O(23)	5 152(4)	11 678(3)	1 839(1)
O(24)	3 460(5)	13 121(3)	2 256(2)

**Table 8** Atomic coordinates ( $\times 10^4$ ) for complex **7**

Atom	x	y	z
Cu	1427(1)	1411(1)	2761(1)
N(1)	2335(3)	1121(1)	1555(2)
N(2)	1445(2)	272(1)	2716(2)
N(3)	1921(2)	2498(1)	2657(2)
N(4)	558(3)	1439(1)	4022(2)
C(1)	3519(3)	625(2)	2049(2)
C(2)	2952(3)	80(2)	2779(2)
C(3)	683(3)	107(2)	1629(2)
C(4)	1245(3)	648(2)	884(2)
C(5)	2794(3)	1757(2)	958(2)
C(6)	3786(3)	2258(2)	1700(2)
C(7)	5165(3)	2353(2)	1600(3)
C(8)	6105(3)	2762(2)	2332(3)
C(9)	5662(3)	3083(2)	3172(2)
C(10)	4293(3)	3002(2)	3282(2)
C(11)	3352(3)	2600(2)	2542(2)
C(12)	868(3)	−126(2)	3533(2)
C(13)	−519(3)	195(2)	3657(2)
C(14)	−1697(3)	−255(2)	3532(2)
C(15)	−2978(3)	21(2)	3673(3)
C(16)	−3078(3)	765(2)	3945(3)
C(17)	−1908(3)	1226(2)	4067(2)
C(18)	−641(3)	944(2)	3932(2)
N(11)	−5085(4)	1333(2)	−1117(3)
O(11)	−5589(4)	1960(2)	−1276(3)
O(12)	−5741(4)	799(2)	−945(3)
O(13)	−3783(4)	1255(2)	−996(3)
N(12)	−922(3)	3277(2)	207(2)
O(14)	−1868(3)	2895(2)	450(2)
O(15)	306(3)	3189(2)	658(2)
O(16)	−1251(2)	3728(1)	−525(2)
O(1)	−799(2)	1677(1)	1725(2)
O(2)	−2814(3)	563(2)	948(2)
O(17)	−4119(20)	1667(9)	−704(12)
O(18)	−5493(25)	1434(14)	−1969(19)

**Table 9** Atomic coordinates ( $\times 10^4$ ) for complex **8**

Atom	x	y	z
Pd	2363(1)	1840(1)	1943(1)
Cl(1)	2971(3)	4048(1)	−48(2)
Cl(2)	−158(2)	1589(2)	−785(2)
O(11)	3257(18)	4580(10)	440(14)
O(12)	3912(11)	3479(5)	179(9)
O(13)	1706(10)	3871(9)	19(7)
O(14)	3031(16)	4302(11)	−822(12)
O(21)	−1482(7)	1287(4)	−1175(5)
O(22)	−36(10)	2126(7)	−1576(7)
O(23)	991(7)	1111(4)	−681(5)
O(24)	−112(7)	2068(4)	14(4)
N(1)	1799(6)	2996(3)	1953(4)
N(2)	3294(5)	1877(3)	793(3)
N(3)	2658(6)	688(3)	2142(4)
N(4)	1658(6)	1576(3)	3124(3)
C(1)	−1339(8)	2829(4)	2984(5)
C(2)	−2309(9)	3273(5)	2371(6)
C(3)	−1960(8)	3656(4)	1609(5)
C(4)	−605(8)	3562(4)	1485(5)
C(5)	383(7)	3097(4)	2114(4)
C(6)	24(8)	2723(4)	2877(4)
C(7)	5802(8)	200(5)	1351(5)
C(8)	7020(8)	524(5)	1165(5)
C(9)	7014(9)	1283(6)	912(5)
C(10)	5802(8)	1733(5)	807(5)
C(11)	4571(7)	1409(4)	956(4)
C(12)	4554(7)	644(4)	1238(5)
C(13)	1070(8)	2226(4)	3594(4)
C(14)	3248(8)	260(4)	1438(5)
C(15)	3572(8)	640(4)	3135(5)
C(16)	2946(8)	1184(4)	3780(5)
C(17)	587(7)	956(4)	2783(5)
C(18)	1223(8)	398(4)	2161(5)

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