Inorg. Chem. **1995,** *34,* 6449−6455 **6449**

Divalent Transition Metal Complexes [LM^{II}](ClO_4)$_2$ (M = Mn, Fe, Co, Ni, Cu, Pd) of the Hexadentate Ligand 1,4,7-Tris(*o*-aminobenzyl)-1,4,7-triazacyclononane (L)

Oliver Schlager,[1a] Karl Wieghardt,*,[1a] and Bernhard Nuber[1b]

Max-Planck-Institut für Strahlenchemie, D-45470 Mülheim, Germany, and
Anorganisch-Chemisches Institut der Universität, D-69120 Heidelberg, Germany

Received June 7, 1995[⊗]

Reaction of the hexadentate ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane (L) in ethanol with perchlorate salts of divalent transition metal ions, $M^{II}(ClO_4)_2\cdot 6H_2O$, affords crystalline salts [ML](ClO_4)$_2$ (M: Mn, **1**; Fe, **2**; Co, **3**; Cu, **5**). The nickel complex **4** crystallizes as the monohydrate, [NiL](ClO_4)$_2\cdot H_2O$. The reaction of L with $Pd(CH_3CO_2)_2$ in ethanol gives red-brown crystals of [PdL](ClO_4)$_2\cdot H_2O$, **6**, after addition of $HClO_4$. The crystal structures of [NiL](ClO_4)(BPh_4)(C_3H_6O)$_2$, **5**, and **6** have been determined by single-crystal X-ray crystallography. [NiL](ClO_4)(BPh_4)(C_3H_6O)$_2$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 10.991(3)$ Å, $b = 13.817(6)$ Å, $c = 19.314(7)$ Å, $\alpha = 77.19(3)°$, $\beta = 77.99(2)°$, and $\gamma = 72.80(3)°$. The nickel ion is six-coordinate with a distorted octahedral NiN_6 polyhedron; the cation possesses C_3 symmetry. Complex **5** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 9.393(5)$ Å, $b = 17.16(1)$ Å, $c = 18.99(1)$ Å, and $\beta = 92.70(5)°$. The copper ion (d^9) is five-coordinate with a square-based pyramidal CuN_5 polyhedron; it contains one uncoordinated pendant *o*-aminobenzyl arm. A similar structure is adopted by the palladium(II) ion (d^8) in **6**; it crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 10.895(2)$ Å, $b = 18.578(4)$ Å, $c = 15.541(3)$ Å, and $\beta = 93.41(2)°$. X-ray powder diffraction data for **1**−**3** show that these salts are isostructural with the complex [ZnL](ClO_4)$_2$, for which it has been shown previously that the zinc ion is in a distorted trigonal prismatic environment of six nitrogen donor atoms. Two of the six-membered aniline chelate rings adopt a boat whereas the third has a twist-boat conformation. The symmetry of the dications in **1**−**3** is therefore also C_1.

Introduction

In the previous paper[2] we have shown that the new hexadentate ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane forms stable complexes [ML](ClO_4)$_2\cdot xH_2O$ with Zn^{2+} ($x = 0$), Cd^{2+} ($x = 0.5$), and Hg^{2+} ($x = 0.5$). From X-ray structure determinations it was shown that the ligand is in all cases hexadentate and that the MN_6 polyhedron is best described as trigonal prismatic. Interestingly, the dications possess C_1 symmetry in the solid state but in solution dynamic behavior has been observed. In the C_1 species two of the six-membered chelate rings $\overline{M-N_{amine}-CH_2-C{=}C-N_{aniline}}$ adopt a boat whereas the third of these chelates has a twist-boat conformation. Here we will use the descriptors Λ or Δ for the configuration of the MN_6 polyhedron, λ'/δ' for the boat and λ''/δ'' for the twist-boat conformation of the pendent arm chelates, and λ/δ for the conformation of the five-membered chelate rings of the 1,4,7-triazacyclononane backbone. Figure 1 shows schematically the structures of and the descriptors for a C_1- and a C_3-symmetric species.

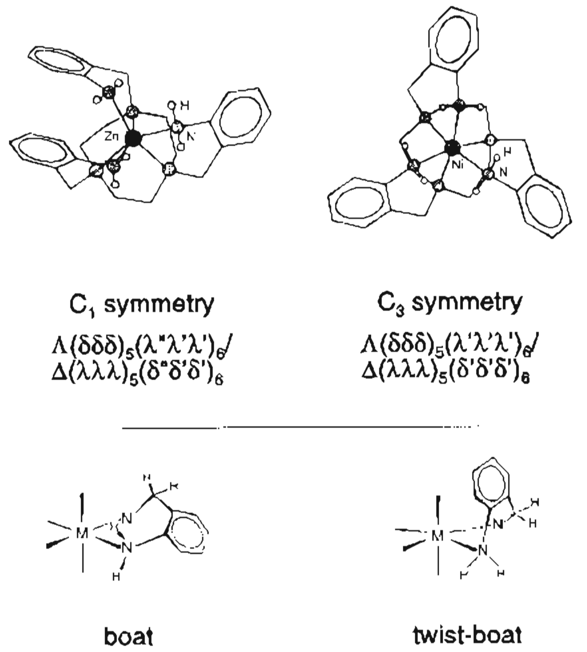


Figure 1. Schematic representation of the structures of the dications [ZnL]$^{2+}$ and [NiL]$^{2+}$ and descriptors for the conformation of the six-membered chelate rings.

The geometry of the distorted trigonal prismatic MN_6 coordination polyhedra in the zinc, cadmium, and mercury complexes is governed by the steric requirements of the ligand L only since electronic factors such as ligand field stabilization energy are absent (d^{10} electronic configuration). Here we report the effect of an increasing electronic preference for octahedral vs trigonal prismatic coordination on the stereochemistry of dicationic species [$M^{II}L$]$^{2+}$. The d^n configuration of the central metal ion is changed stepwise on going from Mn(II) (d^5 high spin) to Fe(II) (d^6 hs), Co(II) (d^7 hs), Ni(II) (d^8 hs), and, finally, Cu(II) (d^9) and Pd(II) (d^8 ls). As we will show, the last two metal ions prefer five- over six-coordination of the ligand L.

Experimental Section

The ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane (L) has been prepared as described previously.[2] All other chemicals were obtained from commercial sources and used as received.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) (a) Max-Planck-Institut für Strahlenchemie. (b) Universität Heidelberg.

(2) Schlager, O.; Wieghardt, K.; Grondey, H.; Rufińska, A.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 6440.

0020-1669/95/1334-6449$09.00/0

Table 1. Crystallographic Data for $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, **5**, and **6**

	$[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$	**5**	**6**
empirical formula	$C_{57}H_{62}N_6O_6ClBNi$	$C_{27}H_{36}N_6Cl_2O_8Cu$	$C_{27}H_{38}N_6Cl_2O_9Pd$
fw	1032.11	707.07	767.95
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	10.991(3)	9.393(5)	10.895(2)
b, Å	13.817(6)	17.16(1)	18.578(4)
c, Å	19.314(7)	18.99(1)	15.541(3)
α, deg	77.19(3)		
β, deg	77.99(2)	92.70(5)	93.41(2)
γ, deg	72.80(3)		
V, Å^3	2700.0(9)	3057.5(12)	3140.1(12)
Z	2	4	4
ρ(calcd), g cm^{-3}	1.27	1.54	1.62
temp, °C	22	22	22
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
abs coeff, mm^{-1}	0.46	0.95	0.81
min/max transm coeff	0.87/1.00	0.92/1.00	0.88/1.00
R^a	0.080	0.077	0.047
$R_w{}^b$	0.067	0.065	0.044

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2\}^{1/2}$.

Preparation of Complexes. $[Mn^{II}L](ClO_4)_2$, 1. A solution of $Mn(ClO_4)_2\cdot 6H_2O$ (0.18 g; 0.50 mmol) and the ligand L (0.22 g; 0.50 mmol) in ethanol (25 mL) under an argon atmosphere was heated to reflux for 30 min. Upon cooling of the solution to 20 °C, colorless microcrystals precipitated, which were collected by filtration, washed with ethanol and ether, and air-dried. Yield: 0.23 g (65%). Anal. Calcd for $C_{27}H_{36}N_6Cl_2O_8Mn$: C, 46.4; H, 5.2; N, 12.0; ClO_4, 28.5. Found: C, 45.9; H, 5.1; N, 11.6; ClO_4, 28.3.

$[Fe^{II}L](ClO_4)_2$, 2. This complex was prepared as described above for **1** by using $Fe(ClO_4)_2\cdot 6H_2O$ (0.50 mmol) as starting material. Product: pale green microcrystalline, air-sensitive compound. Yield: 0.20 g (57%). Anal. Calcd for $C_{27}H_{36}N_6Cl_2O_8Fe$: C, 46.4; H, 5.2; N, 12.0; Fe, 8.0. Found: C, 46.4; H, 5.3; N, 12.4; Fe, 7.7.

$[Co^{II}L](ClO_4)_2$, 3. This complex was prepared as described above for **1** by using $Co(ClO_4)_2\cdot 6H_2O$ (0.50 mmol) as starting material. Product: brick-red microcrystalline compound. Yield: 0.26 g (74%). Anal. Calcd for $C_{27}H_{36}N_6Cl_2O_8Co$: C, 46.2; H, 5.2; N, 12.0. Found: C, 46.0; H, 5.2; N, 12.3.

$[Ni^{II}L](ClO_4)_2\cdot H_2O$, 4. This complex was prepared as described above for **1** by using $Ni(ClO_4)_2\cdot 6H_2O$ as starting material. Red-brown microcrystals precipitated within 2 d at ambient temperature from the reaction mixture to which two drops of concentrated $HClO_4$ had been added. Yield: 0.19 g (53%). Anal. Calcd for $C_{27}H_{38}N_6Cl_2O_9Ni$: C, 45.0; H, 5.3; N, 11.7; Ni, 8.2. Found: C, 45.1; H, 5.3; N, 10.9; Ni, 7.9.

$[Cu^{II}L](ClO_4)_2$, 5. To a solution of L (0.22 g; 0.50 mmol) in methanol (10 mL) was added a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.19 g, 0.50 mmol) in ethanol (20 mL). Two drops of 60% $HClO_4$ were added. From the clear deep-green solution a green precipitate formed within 2 d at ambient temperature. Single crystals suitable for X-ray crystallography were grown by recrystallization from a saturated acetonitrile solution. Yield: 0.17 g (48%). Anal. Calcd for $C_{27}H_{36}N_6Cl_2O_8Cu$: C, 45.9; H, 5.1; N, 11.9; ClO_4, 28.1. Found: C, 54.4; H, 5.3; N, 11.5; ClO_4, 24.8.

$[Pd^{II}L](ClO_4)_2\cdot H_2O$, 6. To a solution of L (0.22 g; 0.50 mmol) in ethanol (30 mL) was added $Pd(CH_3CO_2)_2$ (0.11 g; 0.50 mmol). The solution was stirred at ambient temperature until the $Pd(ac)_2$ was completely dissolved. Two drops of 60% $HClO_4$ were then added, which initiated the precipitation of a brownish, shiny material, which was carefully filtered off. From the clear orange-brown solution complex **6** crystallized within 3 d as brown microcrystals. Single crystals for X-ray crystallography were obtained by recrystallization of **6** from an acetonitrile solution. Yield: 0.15 g (38%). Anal. Calcd for $C_{27}H_{38}N_6Cl_2O_9Pd$: C, 42.2; H, 5.0; N, 10.9. Found: C, 43.2; H, 5.3; N, 10.9.

X-ray Crystallography. Intensities and lattice parameters of a blue needle-shaped crystal of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, a deep-blue parallelepiped of **5**, and a red-brown, translucent, irregular-shaped crystal of **6** were measured on a Syntex R3 ($[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, **6**) or an AED II (Siemens) (**5**) diffractometer at ambient temperature by using monochromated Mo Kα radiation. Crystal parameters and details of the data collection and refinement are summarized in Table 1 (for full details see the Supporting Information). Complexes **5** and **6** crystallize in the monoclinic space group No. 14 and were refined in the nonstandard setting $P2_1/n$. Empirical absorption corrections were carried out in each case. The structures were solved by direct methods for the nickel complex and by conventional Patterson and difference Fourier methods for **5** and **6**. The Siemens program package SHELXTL-PLUS was used throughout.[3] The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F)$. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 4. The positions of hydrogen atoms were placed at calculated positions with isotropic thermal parameters. One of the perchlorate anions in **5** was found to be disordered; it rotates around the axis Cl2–O24. Therefore, oxygen atoms O21, O22, and O23 were refined with isotropic thermal parameters only. Overall, the quality of the crystals of **5** was not very good. Intensities of reflections decreased rapidly with increasing 2θ values. Hydrogen atoms at N6 were not located and were not included in the refinement. Tables 2–4 give atom coordinates for $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, **5**, and **6**, respectively.

X-ray diffraction data for powdered samples of $[ZnL](ClO_4)_2$ and **1**–**4** were measured on the Stoe powder diffraction system (Stadi P) by using monochromated (germanium single crystal) Cu Kα radiation (λ = 1.540 589 Å) and a stationary linear positional sensitive detector. The smoothed background was subtracted from the spectra in Figure 6. The calculated powder diffraction pattern for $[ZnL](ClO_4)_2$ was obtained by using the previously published single-crystal diffraction data.[2]

Physical Measurements. Infrared spectra were recorded in the 4000–400 cm^{-1} range as KBr disks on a Perkin-Elmer FT IR 1720 X spectrometer. UV–vis spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic susceptibility data were obtained by using the Faraday method. Data are corrected for underlying diamagnetism by use of tabulated Pascal's constants.

Results

Synthesis and Characterization of Complexes. The reaction of the ligand L with divalent transition metal perchlorate salts, $M^{II}(ClO_4)_2\cdot 6H_2O$, in ethanol under anaerobic conditions produced microcryrstalline solid products of the composition $[M^{II}L](ClO_4)_2$ (M: Mn, **1**; Fe, **2**; Co, **3**; Cu, **5**). The corresponding nickel(II) complex crystallizes as the monohydrate $[NiL](ClO_4)_2\cdot H_2O$, **4**. Slow crystallization of a sample of **4** in

---

(3) Full-matrix least-squares structure refinement program package SHELXTL-PLUS: G. M. Sheldrick, Universität Göttingen.

(4) *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$

atom	*x*	*y*	*z*	*U*(eq)[a]	atom	*x*	*y*	*z*	*U*(eq)[a]
Ni1	89(1)	1940(1)	2664(1)	45(1)	O12	8202(7)	142(6)	5679(3)	146(5)
N1	−324(6)	1974(5)	1632(3)	53(3)	O13	8815(11)	−690(7)	4691(5)	214(7)
N2	301(6)	3437(4)	2220(3)	56(3)	O14	6734(7)	311(9)	4990(4)	223(7)
N3	2023(5)	1471(4)	2177(3)	48(3)	B1	2064(8)	2429(6)	−1258(4)	44(4)
N4	344(5)	2190(4)	3717(3)	50(3)	C31	3129(4)	3567(4)	−2421(3)	61(4)
N5	172(5)	333(4)	3159(3)	45(2)	C32	3261	3995	−3149	84(5)
N6	−1998(5)	2261(4)	3077(3)	54(3)	C33	2501	3846	−3591	84(5)
C1	−354(7)	3028(6)	1191(4)	72(4)	C34	1608	3269	−3304	74(4)
C2	−568(8)	3836(6)	1668(4)	70(4)	C35	1475	2841	−2576	60(4)
C3	1666(7)	3366(6)	1880(4)	62(4)	C36	2236	2990	−2134	46(3)
C4	2555(7)	2354(6)	2161(4)	60(4)	C37	3224(4)	630(4)	−1711(2)	52(3)
C5	2063(7)	1310(6)	1424(3)	63(4)	C38	3848	−417	−1594	58(4)
C6	769(7)	1180(6)	1328(3)	63(4)	C39	4213	−896	−926	57(4)
C7	−1558(7)	1708(6)	1660(4)	63(4)	C40	3955	−328	−374	54(4)
C8	−154(7)	4152(5)	2751(4)	64(4)	C41	3332	719	−490	54(4)
C9	2785(6)	518(5)	2600(3)	54(4)	C42	2966	1198	−1159	44(3)
C10	−2719(8)	2534(6)	1901(4)	56(4)	C43	1637(3)	3855(4)	−422(2)	42(3)
C11	−3594(9)	3082(7)	1439(4)	72(4)	C44	2053	4464	−82	52(3)
C12	−4639(9)	3876(7)	1641(6)	92(6)	C45	3368	4317	−92	61(4)
C13	−4789(9)	4146(7)	2301(6)	89(5)	C46	4266	3560	−440	71(4)
C14	−3921(8)	3602(6)	2775(4)	70(4)	C47	3849	2951	−780	62(4)
C15	−2900(7)	2818(6)	2579(4)	55(4)	C48	2534	3098	−770	44(3)
C16	1013(7)	2936(6)	3740(4)	55(4)	C49	206(4)	1493(3)	−637(2)	52(3)
C17	1915(8)	2715(6)	4195(4)	71(4)	C50	−1080	1474	−420	67(4)
C18	2543(9)	3438(9)	4218(5)	94(6)	C51	−2061	2371	−552	66(4)
C19	2295(10)	4380(8)	3786(6)	103(6)	C52	−1755	3286	−901	58(4)
C20	1388(9)	4619(7)	3331(5)	87(5)	C53	−469	3305	−1117	53(3)
C21	755(8)	3917(6)	3287(4)	60(4)	C54	512	2409	−985	45(3)
C22	2401(7)	−426(6)	2591(4)	49(4)	O1	7383(5)	224(4)	3230(3)	74(3)
C23	3292(8)	−1252(7)	2307(4)	67(4)	C61	5209(8)	996(7)	3664(4)	96(5)
C24	2933(9)	−2111(7)	2250(5)	84(5)	C62	6361(9)	96(7)	3545(4)	68(5)
C25	1676(9)	−2158(7)	2479(5)	83(5)	C63	6130(9)	−917(7)	3801(5)	121(6)
C26	785(7)	−1348(7)	2768(4)	64(4)	O2	2386(7)	6590(5)	5663(3)	102(3)
C27	1130(7)	−485(6)	2839(3)	49(4)	C64	1672(13)	6993(9)	4574(6)	193(10)
Cl1	7955(3)	293(2)	5002(1)	99(1)	C65	2673(14)	6731(9)	5035(7)	126(7)
O11	8393(6)	1035(4)	4505(3)	112(4)	C66	3923(14)	6721(13)	4677(8)	391(21)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

acetone in the presence of an equimolar amount of sodium tetraphenylborate gave brown single crystals of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$ which were suitable for single-crystal X-ray crystallography. Reaction of palladium(II) acetate and the ligand L in ethanol afforded brown crystals of $[PdL](ClO_4)_2 \cdot H_2O$, **6**.

Electronic spectral and magnetic data of the new complexes **1**–**6** are summarized in Table 5. The effective magnetic moments at room temperature are characteristic of a d^5 high-spin electronic configuration for the manganese complex **1**, a d^6 high-spin configuration for the iron(II) species **2**, and a high-spin d^7 configuration for **3**. Complex **4** exhibits a spin-only value of two unpaired electrons, which is characteristic of octahedral nickel(II), and **5** has a magnetic moment typically found for Cu(II) (d^9). In contrast, **6** is diamagnetic (d^8). The UV–vis spectra of **1**–**4** are also quite characteristic for divalent high-spin transition metal ions in a six-coordinate ligand environment. Two intense charge transfer bands in the near-UV are due to $\pi \rightarrow \pi^*$ transitions of the coordinated aniline pendant arms of the ligand.

In solution, **1**–**3** are quite sensitive to oxygen. These oxidation products will be described in detail in a subsequent paper.

The infrared spectra of solid samples of complexes **1**–**4** (KBr disks) in the region 3500–3100 cm^{-1} proved to be quite informative. Figure 2 displays the spectra. We have included the spectrum of $[ZnL](ClO_4)_2$, for which we have previously reported the crystal structure and shown that the dication $[ZnL]^{2+}$ possesses C_1 symmetry with a twist-boat and two boat conformations of the six-membered chelate rings. This inequivalency of the coordinated aniline groups is clearly reflected in the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ stretching frequencies in the infrared. For the $[ZnL]^{2+}$ species, as well as for **1**–**3**, two $\nu_{as}(NH_2)$ modes in the range 3300–3350 cm^{-1} and two $\nu_s(NH_2)$ modes in the region 3300–3200 cm^{-1} are observed. In contrast, complex **4** and $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$ display only one $\nu_{as}(NH_2)$ at 3303 cm^{-1} and one $\nu_s(NH_2)$ stretching frequency at 3247 cm^{-1}. In the spectrum of **4** the water molecule of crystallization gives rise to a broad ν(OH) stretching frequency at 3484 cm^{-1} which is absent in the spectrum of the mixed perchlorate/tetraphenylborate salt. These results clearly point to stereochemical differences of the dications in **1**–**3** (C_1 symmetry) on the one hand and **4** (C_3 symmetry) on the other hand.

The infrared spectra of **5** and **6** are very similar in the region 3700–3100 cm^{-1}. Two weak, sharp ν(NH) frequencies at 3399 and 3338 cm^{-1} are due to an uncoordinated NH_2 group in **5** whereas the coordinated aniline groups display these modes at 3282 and 3219 cm^{-1}. Clearly, **5** and **6** do not contain CuN_6 or PdN_6 but contain square-base pyramidal MN_5 polyhedra (see below).

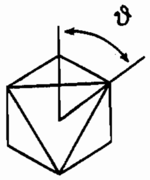
X-ray Crystallography. In Table 6 selected bond lengths and angles of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, **5**, and **6** are summarized. Figures 3–5 show the structures of the dications $[NiL]^{2+}$, $[CuL]^{2+}$, and $[PdL]^{2+}$, respectively. Crystals of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$ consists of the dication $[NiL]^{2+}$, a perchlorate and a tetraphenylborate anion, and two acetone molecules of crystallization. The nickel(II) ion is in a distorted octahedral environment composed of three aliphatic and three aromatic amine nitrogen donor atoms. The twist angle ϑ,

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**

atom	*x*	*y*	*z*	*U*(eq)[a]
Cu1	885(1)	217(1)	2566(1)	37(1)
N1	1993(10)	−52(5)	1699(5)	52(4)
N2	1673(10)	−823(5)	2980(5)	50(4)
N3	−801(11)	−565(5)	2043(5)	56(4)
N4	878(9)	1361(4)	2322(4)	46(4)
N5	208(8)	531(4)	3533(4)	42(3)
N6	−2345(10)	1306(6)	2468(5)	79(5)
C1	2916(13)	−730(7)	1862(7)	82(6)
C2	3082(13)	−863(7)	2652(6)	75(6)
C3	731(14)	−1491(6)	2750(6)	67(6)
C4	−771(14)	−1256(6)	2544(7)	73(6)
C5	−252(13)	−783(7)	1376(6)	69(6)
C6	842(12)	−232(7)	1119(5)	55(5)
C7	2952(11)	609(7)	1504(6)	57(5)
C8	1860(12)	−814(6)	3781(6)	58(5)
C9	−2365(12)	−316(7)	1986(6)	68(6)
C10	2129(11)	1315(7)	1212(6)	45(4)
C11	2363(13)	1602(7)	554(6)	60(5)
C12	1553(13)	2204(7)	275(6)	57(5)
C13	542(12)	2533(7)	668(6)	59(5)
C14	309(12)	2260(6)	1338(6)	55(5)
C15	1103(11)	1660(6)	1620(6)	39(4)
C16	439(12)	−723(7)	4106(6)	46(5)
C17	−115(14)	−1295(7)	4515(6)	58(5)
C18	−1459(15)	−1231(7)	4780(6)	67(6)
C19	−2263(13)	−586(7)	4626(6)	62(5)
C20	−1711(12)	15(6)	4220(5)	50(5)
C21	−381(12)	−65(6)	3966(5)	40(4)
C22	−2702(11)	354(7)	1508(6)	46(4)
C23	−3175(12)	219(8)	805(6)	64(5)
C24	−3571(13)	804(8)	362(7)	66(6)
C25	−3521(13)	1534(8)	613(8)	77(7)
C26	−3138(14)	1713(8)	1291(9)	90(7)
C27	−2735(12)	1114(7)	1781(7)	57(5)
Cl1	512(3)	7291(2)	6356(2)	48(1)
O11	−958(10)	7535(5)	6321(5)	105(5)
O12	841(9)	7087(4)	7056(4)	77(4)
O13	661(9)	6651(4)	5914(4)	80(4)
O14	1341(10)	7910(5)	6147(5)	102(5)
Cl2	566(4)	6341(3)	1441(2)	86(2)
O21	−444(17)	5735(9)	1635(8)	221(7)
O22	480(15)	6861(9)	1937(8)	205(7)
O23	140(20)	6526(11)	856(11)	295(11)
O24	1899(9)	6025(6)	1444(7)	146(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

defined as follows,between the aliphatic and aniline nitrogen



atoms is 50°, which is to be compared with 13.6° for the distorted trigonal prism of the ZnN_6 polyhedron in [ZnL]-$(ClO_4)_2$.[2] The $[NiL]^{2+}$ dication does not possess crystallographic symmetry, but its molecular symmetry is C_3. The five-membered $\overline{\mathrm{Ni{-}N{-}C{-}C{-}N}}$ chelate rings of the coordinated 1,4,7-triazacyclononane backbone adopt a $(\lambda\lambda\lambda)_5$ or $(\delta\delta\delta)_5$ conformation whereas all three six-membered chelate rings of the pendant arms adopt a boat conformation $(\lambda'\lambda'\lambda')_6$ or $(\delta'\delta'\delta')_6$ and, finally, the NiN_6 octahedron has a Λ or Δ configuration. Thus the two enantiomeric forms $\Lambda(\delta\delta\delta)_5(\lambda'\lambda'\lambda')_6$ and $\Delta(\lambda\lambda\lambda)_5(\delta'\delta'\delta')_6$ (Figure 1) are present in equal amounts in the unit cell.

The average $Ni-N_{amine}$ bond length at 2.12 Å is significantly shorter than the $Ni-N_{aniline}$ distance at 2.21 Å. This is again in contrast to the corresponding $[ZnL](ClO_4)_2$ complex, where all six Zn−N distances are equidistant at 2.23 Å. The $Ni-N_{amine}$ distance is typical for nickel(II) complexes containing ligands with a 1,4,7-triazacyclononane backbone. In $[NiL^1(CH_3CN)](BPh_4)_2$ (L^1 = 1,4-bis(pyrazolyl-1-ylmethyl)-1,4,7-triazacyclononane), this bond length was found at 2.07 Å,[5] and in $[Ni_2(maptacn)_2(\mu\text{-}Cl)_2](ClO_4)_2$ (maptacn = 1-(3-aminopropyl)-1,4,7-triazacyclononane), a $Ni-N_{amine}$ bond distance of 2.10 Å has been reported.[6] The $Ni-N_{aniline}$ distances may be compared with those in $[Ni(DApPz)_2(H_2O)_2]Cl_2 \cdot H_2O$ and $[Ni(DApPz)_2(NCS)_2] \cdot H_2O$ (DApPz = 3,5-dimethyl-1-(*o*-aminophenyl)pyrazole) at 2.15 Å, which is 0.06 Å shorter than in $[NiL]^{2+}$.[7]

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **6**

atom	*x*	*y*	*z*	*U*(eq)[a]
Pd1	2165(1)	2383(1)	3561(1)	42(1)
N1	2145(4)	1975(3)	5237(3)	48(2)
N2	1454(5)	1355(3)	3462(3)	51(2)
N3	427(4)	2659(3)	3878(3)	46(2)
N4	3836(4)	2077(3)	3098(3)	56(2)
N5	2761(4)	3434(2)	3502(3)	47(2)
N6	4851(5)	2850(3)	4919(3)	69(2)
C1	2241(6)	1202(3)	5043(4)	57(2)
C2	1397(6)	940(3)	4313(4)	60(3)
C3	202(6)	1506(3)	3065(4)	61(3)
C4	−435(5)	2042(3)	3611(4)	60(3)
C5	396(5)	2813(3)	4829(3)	48(2)
C6	873(6)	2196(3)	5411(4)	54(2)
C7	3039(6)	2166(3)	5952(4)	56(3)
C8	2140(6)	917(3)	2845(4)	57(2)
C9	23(5)	3312(3)	3355(4)	52(2)
C10	3308(6)	2956(3)	5995(4)	49(2)
C11	2688(6)	3413(4)	6537(4)	63(3)
C12	2927(7)	4145(4)	6580(5)	75(3)
C13	3833(8)	4424(4)	6101(5)	89(4)
C14	4479(7)	3993(4)	5584(4)	72(3)
C15	4227(6)	3261(4)	5508(4)	55(2)
C16	5446(6)	1237(4)	3653(4)	67(3)
C17	5837(8)	546(4)	3857(5)	88(4)
C18	5065(8)	−22(4)	3700(5)	87(4)
C19	3882(8)	96(4)	3373(4)	72(3)
C20	3453(6)	778(3)	3166(4)	53(2)
C21	4261(6)	1345(3)	3301(4)	53(2)
C22	711(6)	3990(3)	3611(3)	48(2)
C23	17(6)	4602(4)	3770(4)	60(3)
C24	572(7)	5246(4)	3999(4)	63(3)
C25	1850(7)	5295(4)	4099(4)	61(3)
C26	2544(6)	4694(3)	3932(4)	52(2)
C27	1981(5)	4055(3)	3691(3)	40(2)
Cl1	−2542(2)	1992(1)	6106(1)	71(1)
O11	−2459(5)	1800(3)	5241(3)	112(3)
O12	−3734(5)	1853(3)	6361(3)	109(3)
O13	−2229(6)	2718(3)	6227(3)	123(3)
O14	−1722(5)	1581(3)	6640(3)	109(3)
Cl2	1440(2)	1403(1)	−1825(1)	70(1)
O21	2026(5)	1334(3)	−986(3)	104(3)
O22	2131(4)	1002(3)	−2412(3)	82(2)
O23	1343(6)	2125(3)	−2087(4)	116(3)
O24	222(4)	1122(3)	−1813(3)	106(3)
O10	137(9)	394(5)	6430(6)	228(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The copper(II) ion in $[CuL](ClO_4)_2$, **5**, is coordinated to three aliphatic amine nitrogen atoms of the 1,4,7-triazacyclononane backbone of L and two aniline nitrogen donors of two of the

---

(5) de Martino Norante, G.; Di Vaira, M.; Mani, F.; Mazzi, S.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1992**, 361.

(6) Fortier, D. G.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1991**, 101.

(7) Saha, N.; Saha, A.; Chaudhuri, S.; Mak, T. C. W.; Banerjee, T.; Roychaudhury, C. *Polyhedron* **1992**, *11*, 2341.

(8) Wieghardt, K.; Schöffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877.

Table 5. Spectroscopic and Magnetic Data for the Complexes

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})^a	μ_{eff}(298 K), μ_B
1	233 (9.4 × 10^3), 270 (2.15 × 10^3)	5.9
2	716 (7)	5.2
3	228 (3.6 × 10^3), 270 (sh), 497 (22), 620 (sh), 1056 (9)	4.8
4	240 (11.3 × 10^3), 270 (sh), 918 (23)	3.0
5	244 (sh), 291 (6.0 × 10^3), 363 (2.4 × 10^3), 605 (276), 885 (70)	1.9
6	240 (24.5 × 10^3), 280 (14.3 × 10^3), 340 (4.4 × 10^3), 430 (2.6 × 10^3)	diamagnetic

^{a} Solvent: CH_3CN.

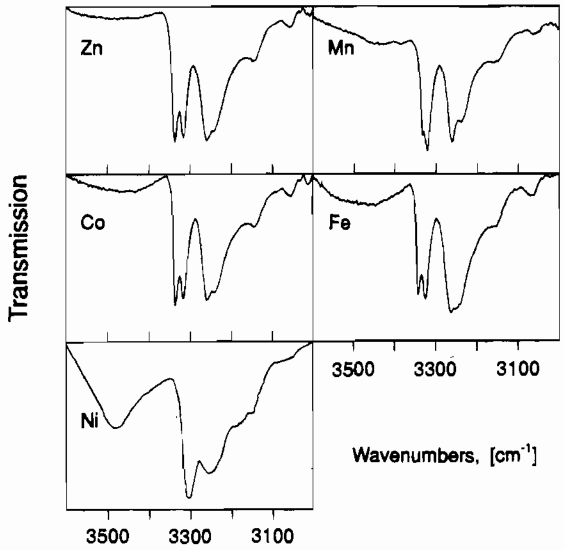


Figure 2. Infrared spectra of $[ML](ClO_4)_2$ (M = Zn, Mn, Co, Fe, Ni) in the $\nu(NH_2)$ region (KBr disks).

pendant arms where the third is not bound to the metal and is dangling. The CuN_5 polyhedron is best described as square-base pyramidal with two Cu$-$N$_{amine}$ and two equidistant Cu$-$N$_{aniline}$ bonds in equatorial positions at 2.04 Å and an apical Cu$-$N$_{amine}$ distance at 2.268(10) Å. The vacant sixth coordination site is occupied by an oxygen atom O24 of one of the ClO_4^- counteranions (Cu$-$O24 3.070(10) Å). The same oxygen atom forms a weak hydrogen bonding contact to the coordinated aniline group N5 (N5$-$H···O24 2.845(12) Å).

The structure of the dication of **6** is very similar to that of **5**. Thus the geometry of the PdN_5 polyhedron is also square-base pyramidal, but in contrast to that **5**, in the apical Pd$-$N$_{amine}$ bond is significantly longer at 2.714(6) Å. Interestingly, in the analogous complex $[(tptacn)Pd](ClO_4)_2$, where tptacn represents 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, a shorter apical Pd$-$N$_{amine}$ bond length of 2.580(3) Å has been observed whereas the basal Pd$-$N$_{amine}$ distances are within experimental error the same (2.06 Å) in both **5** and $[(tptacn)Pd](ClO_4)_2$. Note that the latter distances have also been found in other square planar Pd(II) complexes with coordinated 1,4,7-triazacyclononane ligands.[9] One of the perchlorate anions is also weakly hydrogen bonded to a coordinated aniline group (N5$-$H···O24 2.876(7) Å), and a water molecule of crystallization also forms a weak O$-$H···O contact to this anion (O10$-$H···O24 2.961(8) Å).

Table 6. Selected Bond Distances (Å) and Angles (deg) for $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, **5**, and **6**

	$[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$		
Ni1$-$N1	2.121(6)	N4$-$C16	1.445(12)
Ni1$-$N2	2.118(6)	N5$-$C27	1.451(8)
Ni1$-$N3	2.109(5)	N6$-$C15	1.455(10)
Ni1$-$N4	2.223(6)	N1$-$Ni1$-$N2	83.8(3)
Ni1$-$N5	2.197(5)	N2$-$Ni1$-$N3	83.8(2)
Ni1$-$N6	2.211(5)	N2$-$Ni1$-$N4	88.2(2)
N1$-$Ni1$-$N5	101.0(2)	N1$-$Ni1$-$N3	83.9(2)
N3$-$Ni1$-$N5	89.4(2)	N1$-$Ni1$-$N4	170.1(2)
N1$-$Ni1$-$N6	89.2(2)	N3$-$Ni1$-$N4	101.0(2)
N3$-$Ni1$-$N6	170.7(3)	N2$-$Ni1$-$N5	171.2(2)
N5$-$Ni1$-$N6	85.9(2)	N4$-$Ni1$-$N5	87.7(2)
N4$-$Ni1$-$N6	86.8(2)	N2$-$Ni1$-$N6	101.6(2)
	Complex **5**		
Cu1$-$N1	2.041(9)	N4$-$C15	1.453(13)
Cu1$-$N2	2.073(9)	N5$-$C21	1.439(13)
Cu1$-$N3	2.268(10)	N6$-$C27	1.379(16)
Cu1$-$N4	2.017(8)	N1$-$Cu1$-$N2	85.7(4)
Cu1$-$N5	2.044(8)	N1$-$Cu1$-$N3	83.4(4)
N2$-$Cu1$-$N3	83.5(3)	N1$-$Cu1$-$N4	91.8(3)
N2$-$Cu1$-$N4	157.3(3)	N3$-$Cu1$-$N4	118.7(3)
N1$-$Cu1$-$N5	167.5(3)	N2$-$Cu1$-$N5	90.4(3)
N3$-$Cu1$-$N5	108.0(3)	N4$-$Cu1$-$N5	87.3(3)
	Complex **6**		
Pd1$-$N1	2.714(7)	N4$-$C21	1.464(8)
Pd1$-$N2	2.064(5)	N5$-$C27	1.473(7)
Pd1$-$N3	2.049(5)	N6$-$C15	1.400(9)
Pd1$-$N4	2.077(5)	N2$-$Pd1$-$N3	84.3(2)
Pd1$-$N5	2.061(5)	N2$-$Pd1$-$N4	93.1(2)
N3$-$Pd1$-$N4	173.4(2)	N2$-$Pd1$-$N5	172.4(2)
N3$-$Pd1$-$N5	94.1(2)	N4$-$Pd1$-$N5	87.7(2)
N1$-$Pd1$-$N2	77.8(2)	N1$-$Pd1$-$N3	77.2(2)
N1$-$Pd1$-$N4	108.2(2)	N1$-$Pd1$-$N5	109.1(2)

Complexes **5** and **6** allow a comparison of the C$-$NH$_2$ bond lengths in coordinated and uncoordinated aniline groups. The C$-$N distance of the uncoordinated pendant arm is 1.400(9) Å in **6** and 1.38(2) Å in **5** whereas the average C$-$N bond length of coordinated aniline groups is 1.473 Å in **5** and 1.468 Å in **6**.

Figure 6 shows the powder X-ray diffraction pattern of polycrystalline samples of $[ZnL](ClO_4)_2$ and **1**$-$**4**. In addition the pattern for $[ZnL](ClO_4)_2$ has been calculated by using the data obtained from the single-crystal X-ray structure determination reported in the previous paper.[2] Both the calculated and the experimental spectra agree within experimental error. Inspection of the data shown in Figure 6 immediately reveals that complexes **1**$-$**3** and $[ZnL](ClO_4)_2$ are isostructural whereas the nickel complex **4** crystallizes in a different space group. This together with the infrared spectral data given above implies that the dications $[MnL]^{2+}$, $[FeL]^{2+}$, $[CoL]^{2+}$, and $[ZnL]^{2+}$ have the same C_1-symmetric structure with two six-membered pendant arm chelate rings adopting a boat and the third with a twist-boat conformation (Figure 1). Most importantly, it also suggests that the MN_6 polyhedron in these dications is distorted trigonal prismatic rather than octahedral as in $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$ and—probably—in $[NiL](ClO_4)_2$, **4**.

Discussion

The crystal structure determinations of $[ZnL](ClO_4)_2$[2] and of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$ have established that the ligand 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane is coordinated in a hexadentate fashion to the divalent metal ions zinc (d^{10}) and nickel (d^8). From an X-ray powder diffraction study, it is concluded that the same is true for the corresponding manganese (d^5 hs), iron (d^6 hs), and cobalt (d^7 hs) complexes since they

---

(9) $[Pd(tacn)_2](PF_6)_2$ (tacn = 1,4,7-triazacyclononane): Hunter, G.; McAuley, A.; Whitcombe, T. W. *Inorg. Chem.* **1988**, *27*, 2634. $[Pd(tacn)(tacnH)](PF_6)_2(NO_3)\cdot H_2O$: Blake, A. J.; Gordon, L. M.; Holder, A. J.; Hyde, T. I.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1452. $[Pd(tacnH)_2](ClO_4)_4$: Margulis, T. N.; Zompa, L. J.; *Inorg. Chim. Acta* **1992**, *201*, 61. $[Pd(Me_3[9]aneN_3)(NCMe)_2](PF_6)_2$ ($Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane): Blake, A. J.; Holder, A. J.; Roberts, Y. V.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1993**, 260.

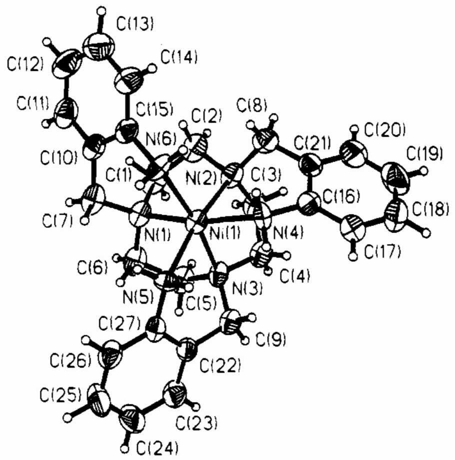


Figure 3. Structure of the dication in crystals of $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$.

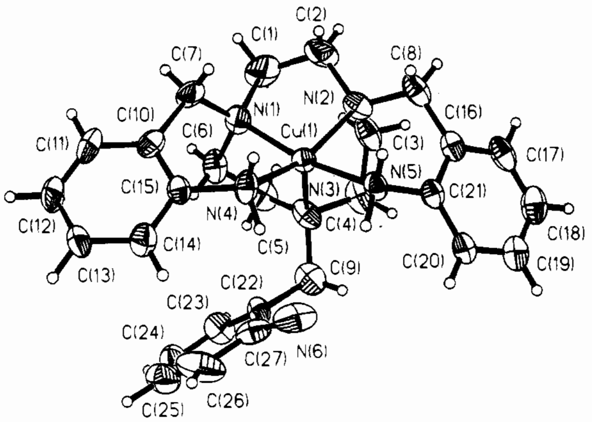


Figure 4. Structure of the dication in crystals of $[CuL](ClO_4)_2$, **5**.

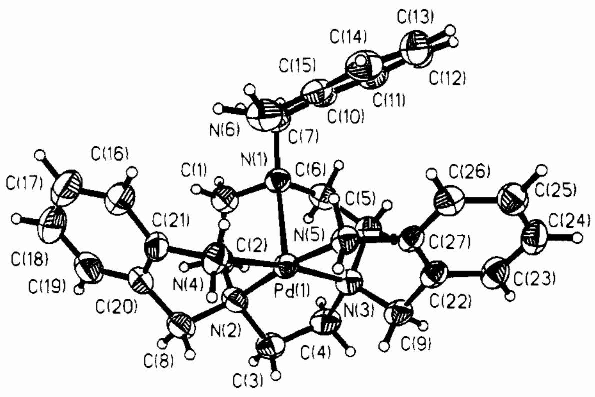


Figure 5. Structure of the dication in crystals of $[PdL](ClO_4)_2\cdot H_2O$, **6**.

crystallize in the same space group as $[ZnL](ClO_4)_2$[2] with very similar unit cell parameters.

Transition metal ions lacking ligand field stabilization energy with d^5 hs and d^{10} electronic configurations adopt a slightly distorted trigonal prismatic MN_6 polyhedra. In these cases, two of the six-membered pendant arm chelate rings adopt a boat and the third a twist-boat conformation, leading to the enantiomers $\Lambda(\delta\delta\delta)_5(\lambda'\lambda'\lambda'')_6/\Delta(\lambda\lambda\lambda)_5(\delta'\delta'\delta'')_6$ with C_1 symmetry. On the other hand, a distorted octahedral MN_6 polyhedron is favored for nickel(II), yielding a C_3-symmetric pair of enantiomers Λ-$(\delta\delta\delta)_5(\lambda'\lambda'\lambda')_6/\Delta(\lambda\lambda\lambda)_5(\delta'\delta'\delta')_6$. The reason for this preference of an octahedral over a trigonal prismatic coordination is electronic in origin. Analyses of Wentworth et al.[10] and Hoffmann et al.[11] have shown that for a d^8 electronic configuration an octahedral coordination is more stable than a trigonal prismatic one by $-6.8D_q$. This difference in energy decreases to $-3.4D_q$ for a d^7 hs configuration and is zero for a d^6 hs configuration. Consequently, in $[CoL](ClO_4)_2$ and $[FeL](ClO_4)_2$ the steric requirements of the ligand dominate and the trigonal prismatic MN_6 polyhedron is the preferred one.

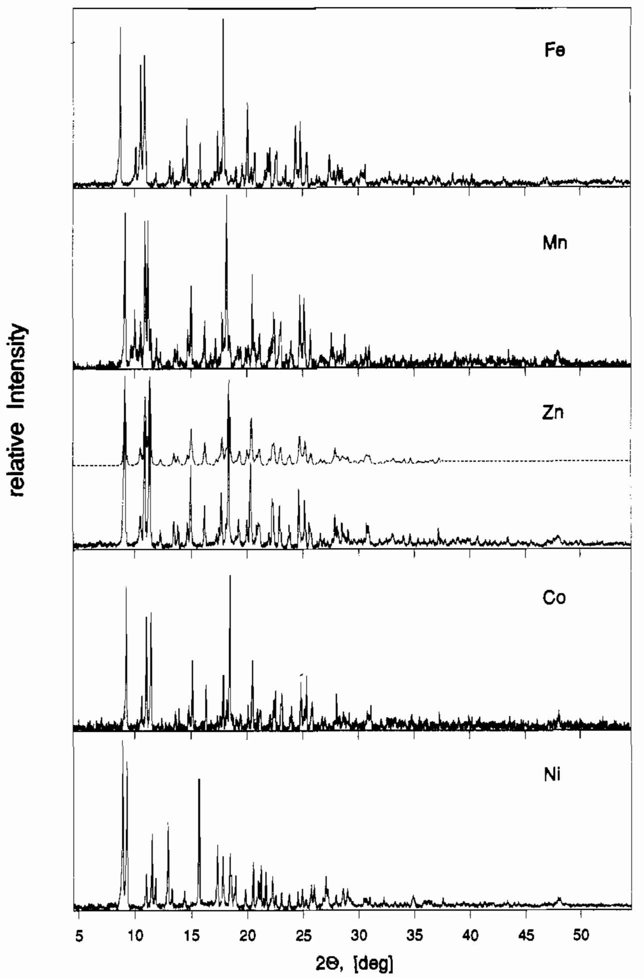


Figure 6. X-ray powder diffraction pattern of $[ML](ClO_4)_2$ (M = Fe, Mn, Zn, Co) and of $[NiL](ClO_4)_2\cdot H_2O$ (Cu Kα radiation). The dotted line represents a calculated spectrum based on single-crystal diffraction data from ref 2.

In $[CuL](ClO_4)_2$ and $[PdL](ClO_4)_2$ the copper(II) (d^9) and palladium(II) ions (d^8 ls) are only five-coordinate with a square-base pyramidal MN_5 polyhedron. Superficially, the dications in both species have quite similar structures, but the apical $M-N_{amine}$ distances differ significantly. This bond is long in palladium(II) complexes (2.714 Å in $[PdL](ClO_4)_2$, 2.580(3) Å in $[(tptacn)Pd](ClO_4)_2$, and 2.523(8) Å in $[Pd(Me_3[9]aneN_3)(NCCH_3)_2](PF_6)_2$) but short in copper(II) complexes (2.268 Å in $[CuL](ClO_4)_2$ and 2.344 Å in $[Cu(Htatp)]$[12] (H_3tatp is 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane).

It is noteworthy that in all complexes referred to above the apical amine nitrogen donor atom stems from a coordinated 1,4,7-triazacyclononane backbone. In spite of this, the apical $M-N_{amine}$ bonds vary considerably whereas the corresponding two equatorial $M-N_{amine}$ bonds are nearly invariant. Hoffmann and Rossi[13] have provided a theoretical model for this observa-

---

(10) (a) Gillum, W. O.; Huffmann, J. C.; Streib, W. E.; Wentworth, R. A. D. *J. Chem. Soc., Chem. Commun.* **1969**, 843. (b) Gillum, W. O.; Wentworth, R. A. D.; Childers, R. F. *Inorg. Chem.* **1970**, *9*, 1825.

(11) Hoffmann, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 2484.

(12) Auerbach, U.; Eckert, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1990**, *29*, 938.

tion. They have shown that the d_{z^2} and the $d_{x^2-y^2}$ orbitals become less antibonding upon decreasing the $N_{basal}-M-N_{basal}$ angle ϑ from 180° in a regular square-base pyramid to 120°, whereas at the same time the d_{xz}, d_{yz} orbital energy increases and d_{xy} is unaffected. The basal angles ϑ in the above palladium(II) complexes $[PdL](ClO_4)_2$ and $[Pd(tptacn)](ClO_4)_2$ are 172.4°/173.4° (average 172.9°) and 163.3°/168.8° (average 166°), respectively. Thus the d_{z^2} orbital is less antibonding in the latter than in the former and the $Pd-N_{apical}$ bond is expected to be shorter, in agreement with the experiment. The same explanation holds for the two complexes $[CuL](ClO_4)_2$ and [Cu(Htatp)], where the average basal angles are 162.4 and 165°, respectively. Again the complex with the larger basal angle ϑ [Cu(Htatp)] has the longer $Cu-N_{apical}$ bond.

In the analysis of the bonding in square-base pyramidal complexes by Hoffmann and Rossi,[13] the effect of pure σ-donor ligands only on the apical bond length as a function of the basal angle ϑ has been considered. It is interesting to compare the present structural details of $[PdL]^{2+}$ and $[Pd(tptacn)]^{2+}$ with those reported recently by Schröder et al. for purple $[Pd(Me_3\text{-}[9]aneN_3)(NCCH_3)_2]^{2+}$,[9] which contains a square-base pyramidal PdN_5 polyhedron composed of a coordinated 1,4,7-trimethyl-1,4,7-triazacyclononane σ-donor and two basal acetonitrile ligands (π-acceptor). The apical $Pd-N_{amine}$ bond is here the shortest of the series at 2.523(8) Å, but the basal angle, $N_{amine}-Pd-N_{CH_3CN}$, is the *largest* at 177.0(3)°. The basal $Pd-N_{CH_3CN}$ bonds are short at 2.016(6) Å whereas the basal $Pd-N_{amine}$ bonds at 2.037(7) Å are the same as in $[PdL]^{2+}$ or $[Pd(tptacn)]^{2+}$. According to the above analysis, Schröder's complex should show the longest apical Pd−N bond, which is clearly not the case. It is at present not quite clear what the effect is of π-acceptor ligands bound in the basal plane on the apical Pd−N bond, but it obviously strengthens the σ-bonding interaction between the filled d_{z^2} orbital and the σ orbital of the apical ligand.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Supporting Information Available: Listings of the full details of the structure determinations, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for $[NiL](ClO_4)(BPh_4)(C_3H_6O)_2$, $[CuL](ClO_4)_2$ (**5**), and $[PdL](ClO_4)_2\cdot H_2O$ (**6**) (28 pages). Ordering information is given on any current masthead page.

IC950711B

---

[13] Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.