

UNUSUAL *cis/trans* ISOMERISM IN OCTAHEDRAL NICKEL(II) COMPLEXES WITH 1,4,8,11-TETRAAZACYCLOTETRADECANE-1,8-BIS(METHYLPHOSPHONIC ACID) AS A LIGAND

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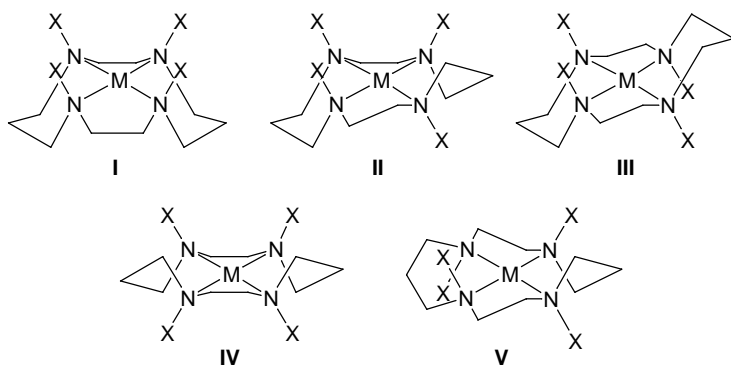
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Dedicated to the memory of Professor Antonín A. Vlček, a teacher, scientist and organiser, for his contribution to development of inorganic chemistry and electrochemistry in Czechoslovakia.

Nickel(II) ion reacts with 1,4,8,11-tetraazacyclotetradecane-1,8-bis(methylphosphonic acid) (H_4L^1) at room temperature with formation of *cis*-[Ni(L¹)]²⁻ complex. The complex was crystallised in several forms in dependence on conditions of isolation (temperature, pH, solvent mixture). Crystal structures of *cis*-O,O-[Ni(H₂L¹)] (1), *cis*-O,O-[Ni(H₂L¹)]·2H₂O (2), *cis*-O,O-[Ni(H₃L¹)]Cl·H₂O (3) and *cis*-O,O-[Ni(H₄L¹)]Cl₂·2H₂O (4) were determined by X-ray diffraction. In all the compounds, Ni²⁺ is in octahedral *cis*-O1,O2-*trans*-N1,N8-*cis*-O1,N4-[Ni(L¹)]²⁻ (hereafter abbreviated as *cis*-O,O-[Ni(L¹)]²⁻) arrangement with V conformation of the cyclam ring. Complexes 3 and 4 exhibit very unusual coordination through the phosphoryl group of double-protonated phosphonate moiety. Tetraethylester of H₄L¹ having only poorly coordinating phosphoryl oxygen atoms also forms nickel(II) complex 5 with *cis* arrangement. Corresponding *trans*-O,O-[Ni(L¹)]²⁻ complex is formed only in strongly acidic medium through conversion of the *cis* complex; it was characterised by X-ray diffraction as dihydrochloride dihydrate, *trans*-O,O-[Ni(H₄L¹)]Cl₂·2H₂O (6). The analogous compound (NH₄)₂(*trans*-O,O-[Ni(L²)]·H₂O (7) is obtained quantitatively by reaction of Ni²⁺ with 4,11-dibenzyl-1,4,8,11-tetraazacyclotetradecane-1,8-bis(methylphosphonic acid) (H₄L²). Formation of this complex 7 in the III cyclam ring conformation is preferred to the *cis* complex due to steric hindrance of bulky benzyl groups in *cis*-[Ni(L²)]²⁻ complex with the V cyclam ring conformation.

Keywords: Azacrown compounds; Cyclam; Phosphonates; Nickel(II) complexes; *cis/trans* Isomerism; Conformation analysis; Crystal structure determination; X-ray diffraction; Macrocylic ligands.

Investigation of Ni^{2+} complexes of cyclam has played a key role in chemistry of macrocyclic complexes. The complexes were thoroughly studied due to their kinetic inertness and presence of an equilibrium between diamagnetic planar complex $[\text{Ni}(\text{cyclam})]^{2+}$ (**III** ring conformation; all possible conformations of the cyclam ring are shown in Chart I) and paramagnetic octahedral complexes, *trans*- $[\text{Ni}(\text{cyclam})\text{X}_2]^{n+}$ (**III** ring conformation) and *cis*- $[\text{Ni}(\text{cyclam})\text{X}_2]^{n+}$ (**V** ring conformation), in aqueous solution^{1,2}. The equilibrium depends on the presence of other ligands, concentration of inert salts, temperature, *etc.* (refs^{1,2}). The *cis* complexes are considered the kinetic product of the reaction of Ni^{2+} and cyclam. Nickel(II) complexes of the cyclam derivatives with coordinating pendants exhibit mostly octahedral arrangement with *trans* isomers occurring more frequently than those with *cis* coordination³. Such *trans*- N_4O_2 configuration (**III** conformation) has been found or proposed in Ni^{2+} complexes of cyclam derivatives with *N*-(2-carbamoyl)ethyl^{2b}, *N*-(hydroxyalkyl)⁴ and acetic⁵ pendants. Examples of the *cis* arrangement (**V** conformation) in Ni^{2+} complexes of such ligands has been observed in *N*-(2-carbamoyl)ethyl², *N*-(2-sulfonatoethyl)⁶ (together with a rare **II** conformation of the cyclam ring due to disorder of one propylene chain) and, very recently, in *N,N'*-bis(2-pyridylmethyl)⁷ derivatives. In continuation of our research on phosphorus acid derivatives of polyazacycles⁸, we synthesised 1,8-bis(phosphonic acid) derivatives of cyclam and investigated their solid state and solution properties⁹. Here we



X = hydrogen or substituent

CHART I

Conformations of cyclam coordinated to metal ions

want to describe the results obtained in a study of Ni^{2+} complexes of two new ligands, H_4L^1 and H_4L^2 (Chart II).

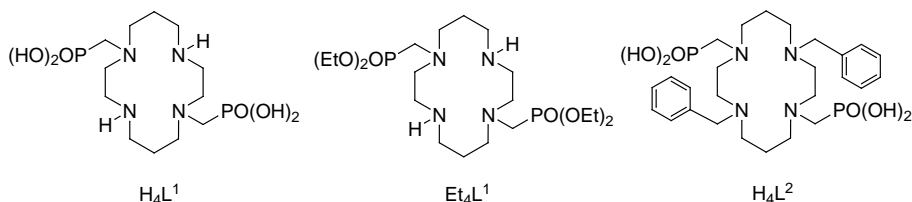


CHART II

EXPERIMENTAL

General

Compounds H_4L^1 , H_4L^2 and Et_4L^2 were prepared by published procedures⁹. Ester Et_4L^1 was synthesized by catalytic hydrogenation of Et_4L^2 (101 kPa H_2 , 10% Pd/C). Amberlite CG50/N1 (weak acid cation exchanger, Rohm & Haas) and other chemicals (Lachema) were used as obtained. Solution UV-VIS spectra of the complexes were measured for 10 mM aqueous solutions on a UV 300 (Pye Unicam) in the 200–1 100 nm range at room temperature (appropriate pH was adjusted using aqueous HCl or NaOH). Diffuse-reflectance UV-VIS spectra of solid samples were recorded on a Perkin–Elmer Lambda 19 in range 250–1 500 nm. Protonation constants were calculated using OPIUM (ref.¹⁰) and the method is described elsewhere⁹.

Crystallography

Single crystals were mounted on glass fibres in random orientation using epoxy glue. A CAD4 diffractometer (Enraf–Nonius) was used for data collection of complexes **1–3** at 293(1) K using graphite monochromatised $\text{MoK}\alpha$ radiation. The lattice parameters of studied compounds **1–3** were determined always from 25 reflections (θ -intervals: **1** 13.0–15.0°; **2** 14.0–15.0°; **3** 13.5–15.0°). The intensities were collected by ω - 2θ scan; three standard reflections were measured always after 1 h (mean variation 3% for **1**, 2.7% for **2**, 2% for **3**). Lorentzian-polarisation corrections were applied to all compounds using program JANA 98 (ref.¹¹). Diffraction data for complexes **4–7** were collected on a KappaCCD diffractometer (Enraf–Nonius) at 293(1) K for **4–6** and at 150(1) K for **7** using graphite monochromatised $\text{MoK}\alpha$ radiation and analysed by HKL DENZO program package¹². Cell parameters were determined from all data by same program package¹². The absorption correction was applied to **7** using program SORTAV (ref.¹³). The structures were solved by the Patterson and Fourier method or by direct methods, and refined by full-matrix least-squares techniques (SIR92, SHELXS86, SHELXL97; refs.^{14,15,16}). The used scattering factors for neutral atoms used were included in program SHELXL97. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were found in all structures on difference maps and refined isotropically. Table I gives pertinent crystallographic data, Table II lists selected bond distances and angles in compounds **1–7**. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication

TABLE I
Experimental data for X-ray diffraction studies of Ni^{2+} complexes of H_3L^1 and H_3L^2

Parameter	cis-O-O- [Ni(H ₂ L ¹)] (1)	cis-O-O- [Ni(H ₂ L ¹)]·2H ₂ O (2)	cis-O-O- [Ni(H ₃ L ¹)]Cl·H ₂ O (3)	cis-O-O- [Ni(H ₄ L ¹)]Cl ₂ ·2H ₂ O (4)	dis-O-O- [Ni(E ₄ L ¹)](ClO ₄) ₂ (5)	trans-O-O- [Ni(H ₂ L ¹)]Cl ₂ ·2H ₂ O (6)	(NH ₄) ₂ (trans-O-O- [Ni(L ¹)]·5H ₂ O) (7)
Formula	C ₁₂ H ₂₈ N ₄ NiO ₈ P ₂	C ₁₂ H ₃₂ N ₄ NiO ₈ P ₂	C ₁₂ H ₃₁ ClN ₄ NiO ₇ P ₂	C ₁₂ H ₃₄ Cl ₂ N ₄ NiO ₈ P ₂	C ₂₀ H ₄₆ Cl ₂ NiO ₁₄ P ₂	C ₁₂ H ₃₄ Cl ₂ N ₄ NiO ₆ P ₂	C ₂₈ H ₆₄ N ₆ NiO ₁₅ P ₂
M	445.0	481.1	499.5	554.0	758.2	554.0	821.5
T, K	293(1)	150(1)	150(1)	293(1)	293(1)	293(1)	150(1)
Crystal dimension, mm	0.55 × 0.48 × 0.12	0.6 × 0.5 × 0.4	0.30 × 0.35 × 0.4	0.65 × 0.55 × 0.4	0.25 × 0.25 × 0.2	0.35 × 0.35 × 0.3	0.5 × 0.4 × 0.45
Shape and colour	plate, pink-violet	rod, sky blue	rod, pink-violet	rod, violet	rod, violet	rod, violet	rod, pale blue
Crystal system	monoclinic	monoclinic	monoclinic	trichlinic	monoclinic	trichlinic	trichlinic
Space group	P2 ₁ /c (No. 14)	C2/c (No. 15)	P2 ₁ /c (No. 14)	P-1 (No. 2)	P2 ₁ /n (No. 14)	P-1 (No. 2)	P-1 (No. 2)
a, Å	15.338(5)	16.719(3)	13.365(2)	9.2570(10)	11.8870(2)	8.772(5)	12.081(6)
b, Å	8.708(5)	8.298(1)	10.410(2)	10.496(2)	15.8050(4)	11.321(5)	12.2635(5)
c, Å	15.235(5)	15.259(2)	15.354(3)	12.689(2)	18.1140(5)	12.158(5)	13.7374(4)
α, °	90	90	90	91.091(10)	90	90.268(5)	93.197(2)
β, °	118.462(5)	116.46(1)	111.19(1)	107.030(9)	96.479(2)	99.897(5)	111.739(2)
γ, °	90	90	90	99.259(9)	90	104.995(5)	96.525(2)
U, Å ³	1.789(1)	1.895.2(5)	1.991.8(6)	1.178.3(3)	3.381.4(1)	1.147(1)	1.867.7(1)
Z	4	4	4	2	4	2	4
D _c , g cm ⁻³	1.652	1.686	1.666	1.561	1.489	1.604	1.461
λ, Å	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
μ, mm ⁻¹	1.301	1.242	1.312	1.230	0.892	1.263	0.678
F(000)	936	1.016	1.048	580	1.592	580	880
θ range of data collection, °	1.51–25.97	2.72–24.96	1.63–24.98	2.98–27.52	3.10–26.41	1.70–25.03	3.03–35.00

TABLE I
(Continued)

Parameter	cis-O,O- [Ni(H ₂ L ¹)] (1)	cis-O,O- [Ni(H ₂ L ¹)]·2H ₂ O (2)	cis-O,O- [Ni(H ₃ L ¹)]Cl·H ₂ O (3)	cis-O,O- [Ni(H ₄ L ¹)]Cl ₂ ·2H ₂ O (4)	cis-O,O- [Ni(Et ₄ L ¹)](ClO ₄) ₂ (5)	trans-O,O- [Ni(H ₄ L ¹)]Cl ₂ ·2H ₂ O (6)	(NH ₄) ₂ (trans-O,O- [Ni(L ¹)]·5H ₂ O) (7)
Index ranges	-18,16; 0,10; 0,18	0,19;9,9; -18,16	-15,14; 0,12	0,12; -13,13; -16,15	0,14; 0,19; -22,22	-10,10; -13,13; -14,14	0,19; -19,18; -18,14
No. of reflections measured	3 634	2 055	3 618	5 402	6 890	7 033	10 487
R _G	0,0162	0,0107	0,0130	0,0173	0,0301	0,0331	0,0473
No. of reflections observed [$I > 2\sigma(I)$]	3 144	1 571	3 288	5 064	5 282	3 467	8 489
No. of independent reflections	3 507	1 655	3 487	5 402	6 890	4 036	10 487
R _{int}	0,0626	0,0238	0,0360	-	-	0,0202	-
Coefficients in weighting scheme ^a	0,0673; 0,6600	0,0374; 3,3965	0,0627; 1,4641	0,0377; 0,8086	0,0913; 2,8593	0,0279; 0,4983	0,0258; 2,2406
Data, restraints parameters	3 507; 0, 339	1 655; 0; 187	3 487; 0; 388	5 402; 0; 399	6 890; 0; 445	4 036; 0; 401	10 487; 2; 710
Goodness-of-fit on F ²	1,057	1,095	1,089	1,048	1,082	1,051	1,020
Final R, R' indices [$I \geq 2\sigma(I)$] ^b	0,0340; 0,0934	0,0242; 0,0669	0,0326; 0,0418	0,0309; 0,0779	0,0638; 0,1651	0,0276; 0,0651	0,0418; 0,1004
Maximum shift, e.s.d.	0,001	0,005	0,021	1,877 (H-atom)	0,050	0,005	0,516 (H-atom)
Largest difference peak and hole, e Å ³	0,804; -1,025	0,261; -0,462	0,807; -0,827	0,696; -0,768	0,696; -0,768	0,268; -0,336	1,273; -1,205

^a $w = 1/(\sigma^2(F_o^2) + (A \cdot P)^3 + B \cdot P)$, where $P = (F_o^2 + 2F_c^2)/3$ (SHELXL97, ref.¹⁹), ^b $R = \Sigma |F_o - F_c|/\Sigma |F_o|$; $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$ (SHELXL97, ref.¹⁹).

TABLE II
Selected bonds (in Å) and angles (in °) in the complexes studied

Parameter	Geometry of the coordination shell of Ni ²⁺								
	1	2	3	4	5	6(A) ^a	6(B) ^a	7(A) ^a	7(B) ^a
Ni-O11	2.084(2)	2.119(1)	2.105(2)	2.100(1)	2.154(3)	2.115(2)	2.110(2)	2.096(1)	2.119(1)
Ni-O21	2.079(2)	^b	2.103(2)	2.130(1)	2.088(3)	^c	^c	^c	^c
Ni-N1	2.110(2)	2.139(2)	2.133(2)	2.101(2)	2.106(3)	2.106(2)	2.102(2)	2.104(1)	2.105(2)
Ni-N4	2.079(2)	2.101(2)	2.090(2)	2.093(2)	2.066(3)	2.061(2)	2.072(2)	2.211(2)	2.196(2)
Ni-N8	2.111(2)	^b	2.117(2)	2.109(2)	2.126(4)	^c	^c	^c	^c
Ni-N11	2.080(2)	^b	2.086(2)	2.078(2)	2.090(4)	^c	^c	^c	^c
O11-N-O21	91.10(7)	86.65(7)	89.43(6)	88.15(6)	86.8(1)	180	180	180	180
O11-Ni-N1	87.80(7)	90.12(6)	87.31(6)	88.04(6)	87.4(1)	86.78(6)	87.11(6)	86.34(5)	86.02(6)
O11-Ni-N4	86.06(7)	93.20(9)	86.91(7)	88.55(6)	86.8(1)	91.50(7)	91.84(7)	91.17(5)	91.37(6)
O11-Ni-N8	90.45(7)	97.01(5)	94.12(6)	91.16(6)	93.3(1)	93.22(6)	92.89(7)	93.66(5)	93.98(6)
O11-Ni-N11	174.51(7)	176.05(5)	176.85(7)	175.84(6)	175.4(1)	88.50(7)	88.16(7)	88.83(5)	88.63(6)
O21-Ni-N1	90.29(7)	^b	92.99(7)	91.10(6)	91.6(1)	^c	^c	^c	^c
O21-Ni-N4	174.79(7)	^b	176.00(7)	175.58(6)	173.2(1)	^c	^c	^c	^c
O21-Ni-N8	87.99(7)	87.44(5)	87.80(7)	88.15(6)	88.2(1)	^c	^c	^c	^c
O21-Ni-N11	85.96(8)	^b	87.65(7)	89.32(6)	89.1(1)	^c	^c	^c	^c
N1-Ni-N4	85.24(8)	85.10(6)	85.23(7)	85.86(7)	85.9(1)	85.93(8)	86.29(7)	86.41(6)	86.92(6)
N1-Ni-N8	177.52(7)	173.90(8)	178.38(7)	178.93(6)	179.2(1)	180	180	180	180
N1-Ni-N11	96.85(8)	90.71(6)	94.03(7)	95.31(7)	94.7(1)	94.07(8)	93.71(7)	93.59(6)	93.08(6)
N4-Ni-N8	96.39(8)	^b	94.07(7)	94.85(7)	94.4(1)	^c	^c	^c	^c
N4-Ni-N11	97.22(8)	93.20(9)	94.04(8)	94.14(7)	97.4(2)	180	180	180	180
N8-Ni-N11	84.82(8)	^b	84.59(7)	84.45(7)	84.6(2)	^c	^c	^c	^c

TABLE II
(Continued)

Parameter	Geometry of the coordination shell of Ni ²⁺								
	1	2	3	4	5	6(A) ^a	6(B) ^a	7(A) ^a	7(B) ^a
P1-O11	1.496(2)	1.506(1)	1.495(2)	1.481(2)	1.470(3)	1.485(2)	1.486(2)	1.536(1)	1.535(1)
P1-O12	1.570(2)	1.568(2)	1.536(2)	1.555(2)	1.554(4)	1.561(2)	1.561(2)	1.527(2)	1.531(1)
P1-O13	1.507(2)	1.512(1)	1.559(2)	1.546(2)	1.565(4)	1.531(2)	1.536(2)	1.518(1)	1.519(2)
P1-C15	1.829(3)	1.830(2)	1.823(3)	1.806(3)	1.805(5)	1.811(3)	1.815(3)	1.842(2)	1.840(2)
O11-P1-O12	112.3(1)	109.04(8)	116.0(1)	116.0(1)	110.0(2)	114.8(1)	114.02(9)	113.29(7)	111.87(8)
O11-P1-O13	115.9(1)	116.77(8)	114.2(1)	111.8(1)	115.0(2)	113.5(1)	115.3(1)	112.58(8)	114.54(8)
O11-P1-C15	107.0(1)	106.11(8)	108.4(1)	107.93(9)	110.2(2)	108.0(1)	108.2(1)	103.55(7)	103.44(8)
O12-P1-O13	105.6(1)	109.16(8)	101.9(1)	109.2(1)	108.6(3)	104.2(1)	103.8(1)	111.42(8)	111.30(8)
O12-P1-C15	107.0(1)	109.06(9)	107.5(1)	106.0(1)	108.8(3)	107.2(1)	108.0(1)	105.12(9)	109.86(8)
O13-P1-C15	108.8(1)	106.45(9)	108.5(1)	109.2(1)	104.0(2)	108.7(1)	107.2(1)	110.29(9)	105.25(8)
Ni-O11-P1	112.22(9)	116.61(7)	115.14(9)	114.60(8)	112.6(2)	116.66(9)	116.21(8)	119.40(7)	119.19(8)
P2-O21	1.503(2)	^b	1.524(2)	1.483(2)	1.478(3)	^c	^c	^c	^c
P2-O22	1.580(2)	^b	1.568(2)	1.554(2)	1.542(2)	^c	^c	^c	^c
P2-O23	1.494(2)	^b	1.503(2)	1.537(1)	1.532(5)	^c	^c	^c	^c
P2-C16	1.831(3)	^b	1.816(2)	1.809(3)	1.787(5)	^c	^c	^c	^c
O21-P2-O22	110.0(1)	^b	110.36(9)	115.17(9)	113.9(3)	^c	^c	^c	^c
O21-P2-O23	117.4(1)	^b	114.73(9)	116.2(1)	116.3(3)	^c	^c	^c	^c
O21-P2-C16	106.3(1)	^b	106.5(1)	107.35(9)	111.5(2)	^c	^c	^c	^c
O22-P2-O23	108.4(1)	^b	111.0(1)	103.0(1)	106.6(4)	^c	^c	^c	^c
O22-P2-C16	104.5(1)	^b	102.0(1)	107.7(1)	104.5(3)	^c	^c	^c	^c
O23-P2-C16	109.5(1)	^b	111.4(1)	107.0(1)	102.8(3)	^c	^c	^c	^c
Ni-O21-P2	114.34(9)	^b	115.35(9)	113.74(8)	113.5(2)	^c	^c	^c	^c

^a Non-equivalent units. ^b Structure with the crystallographic C₂ axis. ^c Structure with the crystallographic inversion centre.

numbers CCDC-154968 (1), CCDC-154969 (2), CCDC-154970 (3), CCDC-154971 (4), CCDC-154972 (5), CCDC-154973 (6) and CCDC-154974 (7). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of *cis*-O,O-[Ni(H₂L¹)] (1) and *cis*-O,O-[Ni(H₂L¹)]·2H₂O (2)

Ligand H₄L¹·4H₂O (0.050 g, 0.11 mmol) and NiCl₂·6H₂O (0.030 g, 0.13 mmol, 1.1 equivalent) were dissolved in 10 ml of water. The solution was heated at reflux for 2 h, cooled and evaporated to dryness in vacuum. The residue was dissolved in water (2 ml) and excess of nickel was removed by chromatography on a weak cation exchange resin (column 1 × 10 cm) by elution with water. The fractions containing the complex were combined and evaporated to dryness in vacuum. Compound **1** was precipitated from saturated aqueous solution with acetone. A violet solid was filtered off, washed with acetone and dried in air. Yield 0.044 g (90%). Single crystals for structure determination were prepared by diffusion of acetone vapours into a concentrated aqueous solution of the complex for two weeks. Compound **2** crystallised from saturated aqueous solution of **1** (0.050 g, 0.077 mmol) by slow evaporation at slightly lowered temperatures (0–15 °C) during two weeks. The large sky-blue crystals of **2** (0.021 g, 40%) were carefully hand-selected from the microcrystalline bulk of **1**. Single crystals for X-ray diffraction studies were cut from the large crystals.

Synthesis of *cis*-O,O-[Ni(H₃L¹)]Cl·H₂O (3)

Ligand H₄L¹·4H₂O (0.036 g, 0.08 mmol) and NiCl₂·6H₂O (0.019 g, 0.084 mmol, 1.05 equivalent) were dissolved in 5 ml of water. The solution was heated at reflux for 2 h and cooled. Violet crystals of **3** crystallised on slow evaporation of water at room temperature during a week. The solid was collected by filtration, washed with acetone and dried in air. Yield 0.018 g (45%). Single crystals suitable for X-ray diffraction studies were picked from the mother liquor, briefly dried on a filter paper, mounted on glass fiber and covered by a mineral oil.

Synthesis of *cis*-O,O-[Ni(H₄L¹)]Cl₂·2H₂O (4) and *trans*-O,O-[Ni(H₄L¹)]Cl₂·2H₂O (6)

Ligand H₄L¹·4H₂O (0.050 g, 0.11 mmol) and NiCl₂·6H₂O (0.030 g, 0.13 mmol, 1.1 equivalent) were dissolved in 10 ml of water. The solution was heated at reflux for 2 h, cooled and evaporated to dryness in vacuum. The residue was dissolved in water (2 ml) and excess of nickel was removed by chromatography on weak cation exchange resin (column 1 × 10 cm) by elution with water. The fractions containing nickel(II) complexes were combined and evaporated to dryness in vacuum. The residue was dissolved in 0.1 M HCl and refluxed for 4 h. The resulting solution was left to crystallise by slow evaporation in air for three weeks. Two kinds of large violet crystals appeared together with some white microcrystalline bulk of hydrochloride of the free ligand. Crystals of **4** and **6** were selected, washed with acetone and dried in air. Crystals of a size suitable for X-ray diffraction studies were cut from the large ones.

Synthesis of *cis*-O,O-[Ni(Et₄L¹)](ClO₄)₂ (5)

Ligand Et₄L¹ (0.035 g, 0.07 mmol) and Ni(ClO₄)₂·6H₂O (0.025 g, 0.07 mmol) were dissolved in 10 ml of EtOH. The solution was heated at reflux overnight and cooled. The solid

crystallising on slow evaporation at room temperature after a week was filtered off and dried in air. Yield 0.049 g (55%). Single crystals were selected from the bulk.

Synthesis of $(\text{NH}_4)_2(\text{trans-O,O}[\text{Ni}(\text{L}^2)])\cdot\text{H}_2\text{O}$ (7)

Ligand $\text{H}_4\text{L}^2\cdot 9\text{H}_2\text{O}$ (0.050 g, 0.068 mmol) and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.023 g, 0.102 mmol, 1.5 equivalent) were dissolved in 5 ml of 5% aqueous ammonia. The solution was heated at reflux with periodic addition of aqueous ammonia for 6 h, cooled and evaporated to dryness in vacuum. The residue was taken into 10 ml of 20% acetic acid, refluxed for 1 h and cooled. The product – a light-blue precipitate – was filtered off and recrystallised by diffusion of acetone vapours into its solution in 5% aqueous ammonia. After two weeks, large light-blue crystals were separated by filtration and dried in air (with loss of some water molecules). Crystals suitable for X-ray analysis were hand-picked from the mother liquor, briefly dried on a filter paper, mounted on glass fibre, covered with Nujol and immediately measured on a diffractometer at low temperature (see Table I).

RESULTS AND DISCUSSION

Synthesis of the Complexes

Ligand H_4L^1 reacts with Ni^{2+} forming $\text{cis-O,O}[\text{Ni}(\text{L}^1)]^{2-}$ complex which can be considered as kinetic product. The reaction is almost quantitative at room temperature. Analogous kinetic products were observed at low temperature with other transition metal cations and the cobalt(III)¹⁷ and copper(II)¹⁸ complexes have also been structurally characterised. The thermodynamically preferred, high-temperature, *trans-O,O* complexes of cobalt(II) (followed by oxidation to cobalt(III))¹⁷ and copper(II)¹⁸ were obtained only after reflux of aqueous solutions of their low-temperature isomers for several hours. Therefore, we tested conversion of $\text{cis-O,O}[\text{Ni}(\text{L}^1)]^{2-}$ to the *trans-O,O* complex by refluxing in water at several pH in the range of 1–10 as the isomerisation kinetics may depend on pH of the solution. In the kinetic measurement on $\text{cis}[\text{Ni}(\text{H}_2\text{O})_2(\text{cyclam})]^{2+}$, it was found¹ that isomerisation to *trans* isomer is the slowest at pH around 3 but the rate is several orders of magnitude higher at pH about 10; the isomerisation is also slightly accelerated under more acidic solutions. Unfortunately, any experiment mentioned, even treatment of the complex in autoclave at 150 °C for a week has not been successful. Thus, the $\text{cis-O,O}[\text{Ni}(\text{L}^1)]^{2-}$ was obtained in several forms 1–4 in dependence on conditions of crystallisation. Compound 2 was found to co-crystallise with 1 only below room temperature and its formation is made possible by a different network of hydrogen bonds (see below) as a consequence of higher hydration of phosphonate group at low temperature. Isolation of compound 3 from slightly acidic so-

lution is a direct proof of an unusual kinetic inertness of the complex to acid-assisted dissociation. To our best knowledge, such behaviour has not been observed for any octahedral nickel(II) complexes. Finally, success in preparation of desired the *trans*-O,O isomer was reached after reflux of *cis*-O,O-[Ni(L¹)]²⁻ in 0.1 M aqueous HCl. The *trans*-O,O isomer was crystallised as dihydrochloride **6** together with additional form of the *cis*-O,O complex **4**. The presence of a free ligand in the mixture indicates that the isomerisation takes place only after partial or whole decomplexation of the ligand. Isolation of dihydrochlorides **4** and **6** is again an indirect proof of high kinetic stability of the complexes prepared. The nickel(II) reacts with cyclam and its alkyl derivatives in low-coordinating solvents with the formation of planar complexes in **III** ring conformation. Therefore, we also tried the reaction of tetraethyl ester of H₄L¹ (Et₄L¹) with nickel(II) perchlorate in ethanol. Unfortunately, the ethoxyphosphoryl group seems to be sufficiently strong donor to form *cis*-O,O complex **5** and thus inhibiting the formation of complex with **III** conformation of the cyclam ring and, therefore, the *trans*-O,O complex **6** cannot be formed after mild hydrolysis of ester groups in **5**.

The other ligand H₄L² introduces the same coordination possibilities; however, two of its ring nitrogen atoms are substituted with bulky benzyl groups. It reacts with Ni²⁺ only at higher pH than H₄L¹ due to its lower complexing ability caused by its lower overall basicity⁹ and its low solubility. A solution of **7** was obtained upon addition of aqueous ammonia (to raise pH) to a suspension of the ligand in aqueous solution of nickel(II) chloride. Compound **7** crystallised on acidification of the reaction mixture. Its recrystallisation from aqueous ammonia produces single crystals suitable for an X-ray diffraction study on slow diffusion of acetone. Complex **7** slowly loses some water molecules on standing in air. In contrast to the complexes of H₄L¹ mentioned above, *trans*-O,O coordination easily arises in complex **7**. To explain the difference, a possible mechanism of formation of the complexes has to be discussed.

Because of protonation of the secondary nitrogen atoms of H₄L¹ in aqueous solution⁹, we assume that preferential formation of *cis*-O,O complexes of H₄L¹ is caused by the presence of the basic phosphonate moiety and, therefore, easy and fast formation of two five-membered, thermodynamically stable Ni-N-C-P-O rings. This was also confirmed by easy formation of the complex with ester Et₄L¹. Consequently, the other two nitrogen atoms are deprotonated and coordinates to the remaining coordination sites. The *cis*-O,O complex formed is kinetically too inert to rearrange to the *trans*-O,O arrangement or, due to its high thermodynamic stability, to dis-

sociate in a slightly acidic solution. Dissociation of some Ni–N bonds can occur only in a strongly acid medium leading to successive inversion on the decoordinated nitrogen atoms and subsequently to rearrangement from **V** to **III** conformation of the cyclam ring with formation of a thermodynamically more stable *trans*-O,O-[Ni(L¹)]²⁻ complex. A similar kinetically preferred complex is formed by the reaction of Cu²⁺ with H₄L¹ at room temperature which isomerises to the thermodynamically preferred *trans* complex at high temperatures; both the copper(II) complexes are highly inert to acid-assisted dissociation and the *trans*-O,O isomer is the most kinetically inert Cu²⁺ complex known so far¹⁸.

In the case of H₄L², protonation of the ring is the same resulting in two protons on the benzylated nitrogen atoms⁹. As above, coordination of phosphonate groups and adjacent nitrogen atoms in *cis*-O,O position requires folding of the cyclam ring into **V** conformation. Such folding with bulky benzyl substituents on the other nitrogen atoms is sterically hindered and the ligand complexes Ni²⁺ after at least partial deprotonation of the nitrogen atoms in **III** conformation not experiencing steric restraint.

Structures of the Complexes

The kinetically blocked *cis*-O,O-[Ni(L¹)]²⁻ octahedral coordination sphere of Ni²⁺ was observed for compounds **1–4** in the solid state. All *cis*-O,O structures contain both enantiomers of the complex in a unit cell. In the compounds, the cyclam ring is present in the **V** conformation common in other *cis* octahedral complexes of cyclam and its derivatives^{1–3,7}.

Structure parameters of **1–4** are listed in Table II and the structures with atom labelling schemes are shown in Figs 1–4. Formulae of both **1** and **2** indicate diprotonation; however, in contrast to **1**, **2** contains two molecules of water. From Table II, it is clear that the hydration results in different Ni–N and Ni–O bond lengths in both the compounds. In the structure of **2**, the molecule of water forms hydrogen bonds O(W)···H41–N4 3.202, O(W)–H(W)···O13 2.832 and O(W)–H(W)···O11 2.969 Å only outwards and thus, weakens the coordination bonds to nickel(II). Therefore, **1** exhibits significantly shorter Ni–O and Ni–N lengths in contrast to **2**. In addition, both the protonated phosphonate groups in **1** are linked by the intramolecular hydrogen bond O22–H···O13 2.649 Å; in **2**, the protonated phosphonic groups are only involved in the network of hydrogen bonds throughout the structure. The bond angles are similar for both the compounds. The structure of **2** results in the more open coordination sphere around Ni²⁺ compared with the structure of **1**. The intermolecular hydro-

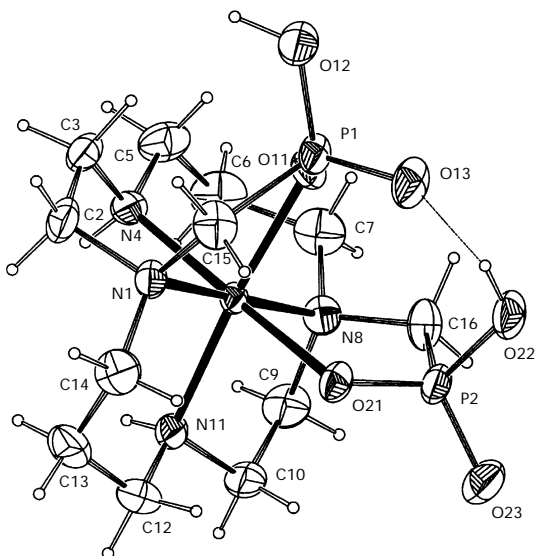


FIG. 1
ORTEP representation of *cis*-O,O-[Ni(H₂L¹)] (1)

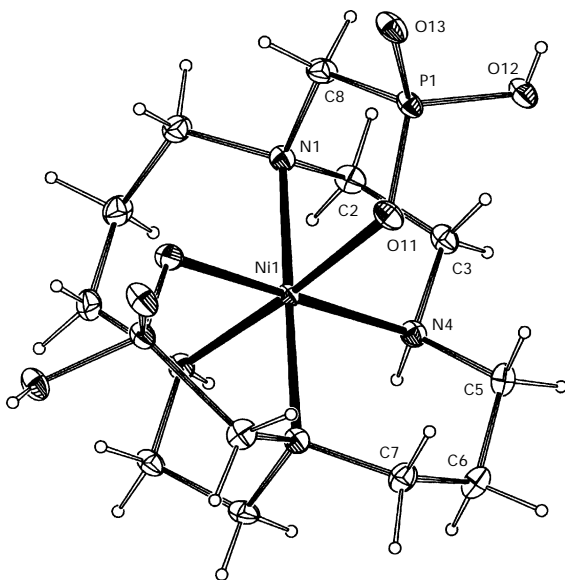


FIG. 2
ORTEP representation of *cis*-O,O-[Ni(H₂L¹)] in 2

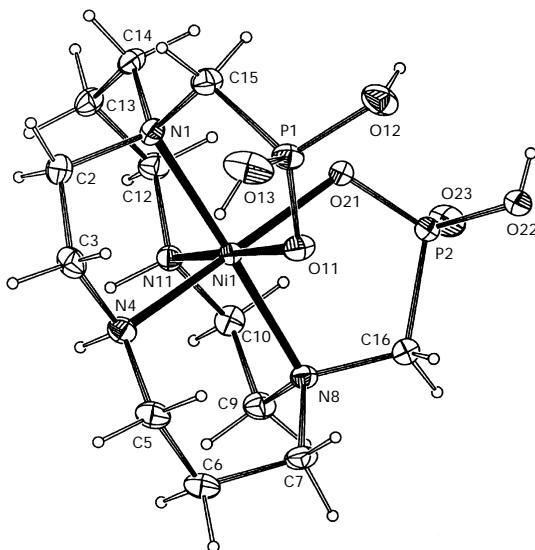


FIG. 3
ORTEP representation of $cis-O,O-[Ni(H_3L^1)]^+$ in **3**

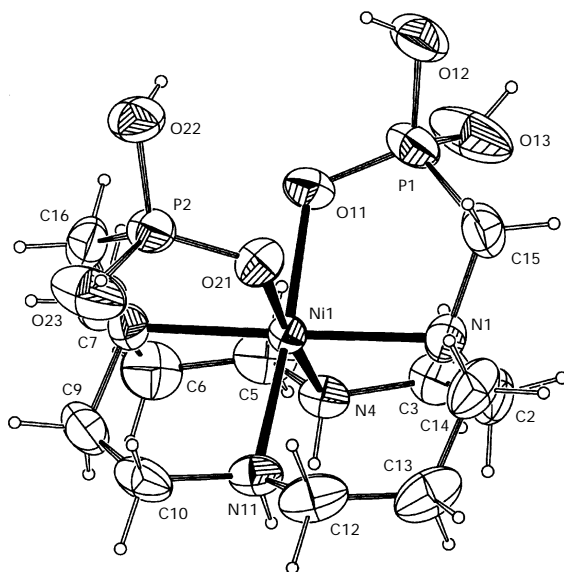


FIG. 4
ORTEP representation of $cis-O,O-[Ni(H_4L^1)]^{2+}$ in **4**

gen bonds O12–H120...O23 (2.504 Å) in **1** link the molecules of complex into indefinite chains similarly to arrays found in crystal structures of *cis*-O,O and *trans*-O,O-[Co(HL¹)] (ref.¹⁷) and *trans*-O,O-[Cu(H₂L¹)] (ref.¹⁸).

Compound **3** is a triprotonated species containing one molecule of water. In spite of hydration the Ni–N lengths are closer to those of **1** than to those of **2** (Table II). A water molecule is involved in hydrogen bond with the double-protonated phosphonate moiety (O13–H130...O(1W) 2.566 Å) and no hydrogen atom of water has a contact to nitrogen or other oxygen atoms of the ligand. They show interactions only with chlorides. The strong hydrogen bond O12–H120...O23 (2.453 Å) links the octahedron to the chain. Both the hydrogen bonds result in lengthening of the N1–Ni bond.

Compound **4** is tetraprotonated species containing two molecules of water. By comparing the bond lengths in the coordination spheres of Ni²⁺ (Table II), we can again see that the parameters of **4** are closer to **1** than to **2**. As in **3**, hydrogen atoms of water are directed only to chloride ions. On the other hand, strong hydrogen bonds are formed between O(1W) and H120–O12 (2.507 Å) and between O(2W) and H230–O23 (2.469 Å). In contrast to the structures of **1** and **3**, the octahedrons in **4** are not linked through hydrogen bonds of phosphonic acid moieties to the chains. The chloride ions are pinched through O12–H120...Cl1 (2.957 Å) and O22–H220...Cl1 hydrogen bonds between two protonated phosphonate moieties.

It seems that protonation does not destabilise the coordination sphere of Ni²⁺ in the structures and the protonated species are stable enough. The positive charge of such species repels additional protons, which could assist in decomplexation reaction(s). Therefore, the species are kinetically stabilised against acid-assisted complex dissociation in acidic solutions.

Tetraethyl ester of H₄L¹ and Ni²⁺ forms complex *cis*-O,O-[Ni(Et₄L¹)](ClO₄)₂ (**5**). The arrangement of the coordination sphere (Fig. 5) is virtually the same as in **1** (see Table II). The perchlorate anion is severely disordered as it is common for the ion due to its spherical symmetry.

Comparison of the structures presented here with *cis* nickel(II) cyclam complexes in literature shows that H₄L¹ is more tightly bonded to Ni²⁺. The Ni–N distances in **1**, **3** and **4** are very close to Ni–N(H) bond lengths in *cis*-[Ni(cyclam)(H₂O)₂]²⁺ (ref.^{1d}) and in the *N*-(2-sulfonatoethyl)cyclam derivative⁶. The distances in **2** are in the same range or shorter than Ni–N(tertiary) bond lengths in *N*-(2-carbamoyl)ethyl^{-2b} or *N*-(2-sulfonatoethyl)cyclam⁶ derivatives. The Ni–O distances are the same as in carboxamides^{2b} (compounds **1**, **3** and **4**) or longer and similar to Ni–OH₂ distances^{1d,6} (compound **2**).

If we consider all possible isomers with *cis* orientation of oxygen atoms, we can deduce the formation of three different isomers: (i) with different *cis/trans* orientation of N1 and N8 atoms bearing pendant arms and (ii) two isomers of the *trans*-N1,N8, with *cis* or *trans* orientation of O1 and N4. All the possibilities are discussed in our previous paper¹⁷. Comparing the possibilities mentioned and the structure found for all the five *cis* complexes studied, it is evident that the isomer found should be described as *cis*-O1,O2-*trans*-N1,N8-*cis*-O1,N4-[Ni(L¹)]²⁻ and it is the same isomer that was observed in *cis*-O,O-[CoL¹]⁻ (ref.¹⁷).

Isomer **6** (Fig. 6) exhibits the *trans*-O,O arrangement of octahedral coordination sphere in [NiL¹]²⁻. The conformation of the cyclam ring corresponds to **III** and demonstrates significantly shortened Ni-N(H) distances (2.061 Å). The bond lengths to the tertiary nitrogen atoms correspond to those found for *cis*-O,O isomers. The Ni-O lengths also fall to the range observed for the *cis* isomers. All protonated phosphonate groups are involved in the intermolecular hydrogen bond network similarly to compound **4**. Water molecules are tightly bonded to the phosphonate moieties (O13-H2...O(2W); 2.496 and 2.505 Å for two independent units).

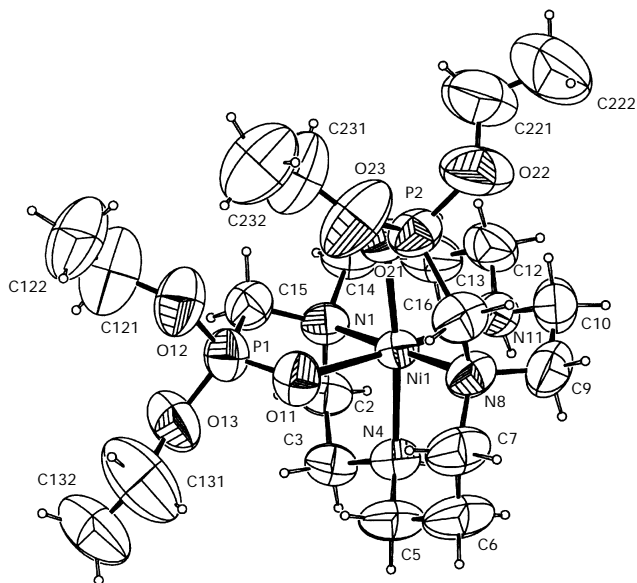


FIG. 5
ORTEP representation of *cis*-O,O-[Ni(Et₄L¹)]²⁺ in **5**

The H_4L^2 and Ni^{2+} form complex **7** which displays *trans*-O,O configuration with the cyclam ring in **III** conformation. The structure consists of two slightly non-equivalent complex moieties in the unit cell; only the complex molecule labelled A will be discussed here. The octahedron (Table II and Fig. 7) should be considered as axially elongated with two benzylated nitrogen atoms placed in the axial positions. Bond lengths in the equatorial plane (Ni1A–O1A 2.096(1) and Ni1A–N1A 2.104(1) Å) are similar to those in the *cis*-O,O complexes above. The axial Ni1A–N4A distance is much longer (2.211(2) Å). Such deformation of coordination octahedron has been observed in *trans* complexes of two ligands with *N*-(2-hydroxyethyl) pendants^{4a,4c} while elongation of Ni–O bonds has been observed in the complex with another 2-hydroxyethyl ligand^{4b} and in the *trans* complex of Ni^{2+} and 1,4,8,11-tetrakis(2-carbamoyl ethyl)-1,4,8,11-tetraazacyclotetradecane^{2b}. Comparison of bond angles around Ni^{2+} shows that complex **4** is the most symmetric of the set of *trans* complexes.

Coordination around phosphorus atoms in all the structures studied is highly distorted from regular tetrahedron. The P–O lengths corresponding to the oxygen atoms which is coordinated to the nickel atom are shorter

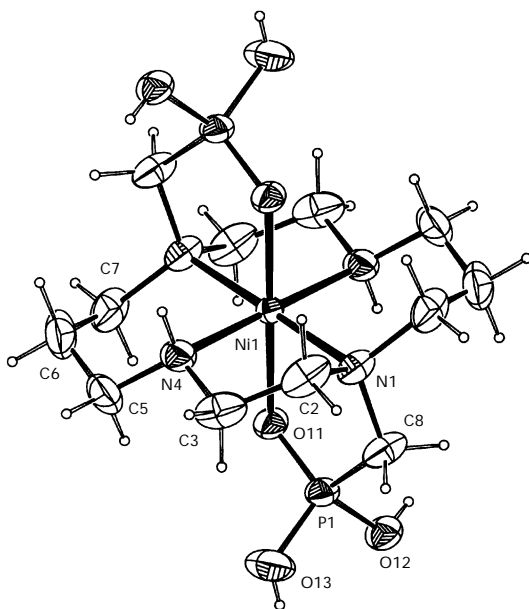


FIG. 6
ORTEP representation of *trans*-O,O-[Ni(H_4L^1)]²⁺ in **6**

than the other P–O bonds in the phosphonic acid moiety (see Table II). From this point of view, we can consider that the phosphoryl oxygen (P=O) participates in the formation of the predominantly covalent Ni–O bond. This can explain easy protonation of the ligand in $[\text{Ni}(\text{L}^1)]^{2-}$ complexes and stability of the multiple-protonated species formed to acid-assisted decomplexation.

Additional Properties

To estimate distribution of the protonated forms in solution, we measured dissociation constants of *cis*-O,O- $[\text{Ni}(\text{L}^1)]^{2-}$ complex (0.1 M KNO_3 , 25 °C). Because of its kinetic inertness in acidic solutions (starting $-\log [\text{H}^+] \approx 1.8$), we were able to determine three constants: $\text{p}K_1 = 1.15$, $\text{p}K_2 = 4.78$ and $\text{p}K_3 = 7.35$. On the basis of the distribution diagram calculated from the dissociation constant values, the fully deprotonated species is present above pH 8.5, the diprotonated species is formed exclusively at pH about 3 and mainly the triprotonated form is found at pH around 0.5.

UV-VIS spectrum of the *trans*-O,O- $[\text{Ni}(\text{L}^1)]^{2-}$ at pH of 9.0 (the complex is almost insoluble at lower pH) exhibits bands at 343 nm (ϵ 13.8 mol⁻¹ dm³ cm⁻¹), 538 (10.4), 630 sh, 747 (8.3) and 975 (15.4) corresponding to typical spectra of six coordinated tetragonally distorted Ni²⁺ complexes, similar to those found for other cyclam derivatives¹⁹. The spectral properties of the *cis*-O,O- $[\text{Ni}(\text{L}^1)]^{2-}$ are different. In the solid state, reflectance spectra showed bands at 310 nm, 430, 660, 800 sh for complex **1** and 350 nm, 455, 700, 810 sh and 990 sh for complex **2**. It confirms the tetragonal distortion

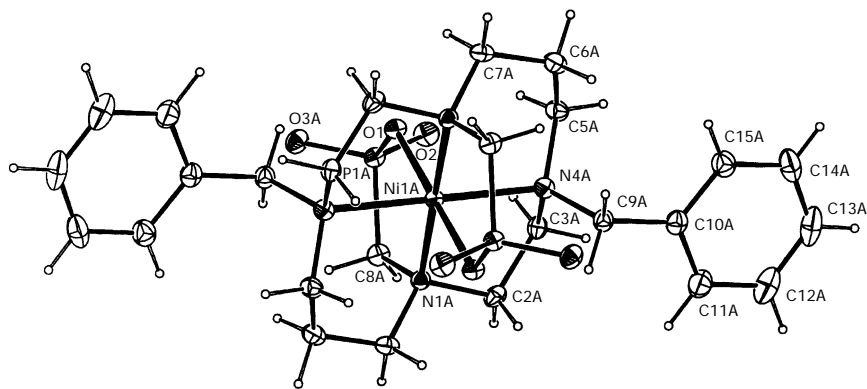


FIG. 7
ORTEP representation of *trans*-O,O- $[\text{Ni}(\text{L}^2)]^{2-}$ in 7

found in their structures. The solution spectra corresponding to the species of *cis*-O,O-[Ni(L¹)]²⁻ with different protonation mentioned above show that, at pH 0.3 and 3.0, they are almost identical with bands at 348 nm (ϵ 15 mol⁻¹ dm³ cm⁻¹ at pH 0.3; 17 at pH 3.0), 560 (12) and 970 (26 at pH 0.3; 33 at pH 3.0) with shoulders at \approx 740, \approx 790 and \approx 890 nm. The spectra at pH 9.1 are slightly altered showing bands at 352 nm (ϵ 16 mol⁻¹ dm³ cm⁻¹), 570 (9) and 970 (28) with shoulders at \approx 740, 795 and \approx 890 nm. Nevertheless, no splitting of the ³T_{1g} (560 nm) term for O_h symmetry to the ³A_{2g} and ³E_g terms expected for D_{4h} was observed in the region of pH. Thus, in contrast to the *trans*-O,O-[Ni(L¹)]²⁻, the *cis*-O,O-[Ni(L¹)]²⁻ exhibits spectral properties corresponding to O_h symmetry in solution.

CONCLUSIONS

We have prepared a series of Ni²⁺ complexes with phosphonate derivatives of cyclam. Existence of different stable protonated forms is consistent with the kinetic stability of H₄L¹ complexes in acid solutions. For the first time, coordination of the phosphoryl group of the protonated phosphonate moiety was confirmed by X-ray crystal structure determination. The protonation seems to protect the atoms in the first coordination sphere against attack of additional protons. Tight binding of water to the phosphonate moieties in the solid state should be probably present in solution as well (as the second-sphere hydration). Such hydration was observed recently in Gd(III) complexes of phosphonate derivatives of 1,4,7,10-tetraazacyclododecane (cyclen) which were proposed as more efficient magnetic resonance imaging (MRI) contrast agents²⁰. A strong influence of hydration on properties of phosphonate complexes is proved by differences between complexes **1** and **2**.

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