opposing effects on the ^{113}Cd shielding tensor are shown by the principal components of +285, +137 and −10 p.p.m. In the absence of single-crystal ^{113}Cd NMR data we cannot know with certainty the direction of these components but the crystal structure permits us to make some reasonable guesses. A thiourea S might contribute +300 p.p.m., a water O atom 0 p.p.m., a bipyridine N +9 p.p.m. and a sulfate O −100 p.p.m. (Honkonen, Marchetti & Ellis, 1986). A component of the chemical shift tensor reflects the contribution to the chemical shift of chemical species in the plane normal to this component. Therefore, the direction of the +285 component should be parallel to or make only a small angle with the O—Cd—O line. The other two components are more difficult to locate with the meagre information presently available but they must be approximately in the CdN_2OS plane. Hopefully, in the future as more of the present type of data become available, more specific interpretations of the chemical shift tensor can be made.

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Structure of (2,4-Dinitrophenolato)(triethanolamine)lithium Monohydrate*

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Abstract. $[Li(C_6H_3N_2O_5)\{N(CH_2CH_2OH)_3\}].H_2O$, $M_r = 357\cdot2$, monoclinic, $C2/c$, $a = 25\cdot731\ (5)$, $b = 6\cdot426\ (4)$, $c = 21\cdot831\ (5)$ Å, $\beta = 112\cdot81\ (4)°$, $V = 3327\cdot40$ Å^3, $Z = 8$, $D_x = 1\cdot426$, D_m (by flotation) $= 1\cdot372$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 1\cdot22$ cm^{-1}, $F(000) = 1504$, room temperature, $R = 0\cdot053$ for 1273 observed reflections. Lithium is five-coordinated to the four heteroatoms of triethanolamine

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* Triethanolamine is 2,2′,2″-nitrilotriethanol.

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(tea) and to the oxygen of the water molecule in a trigonal bipyramidal geometry. Dinitrophenolate (dnp) is not coordinated to Li but its phenolic O atom is hydrogen-bonded to the water molecule and to the (OH) groups of the tea moiety.

Introduction. With a chelating nitrophenolate [2,4-dinitrophenolate (dnp) or 2,4,6-trinitrophenolate (pic)] as a charge neutralizer and triethanolamine (tea) as a ligand, structural results have been reported for the complexes $Ba(dnp)_2(tea)_2$ (Kanters, Smeets, Venkatsubramanian & Poonia, 1984) and $Ba(pic)_2(tea)_2$ (Kanters, de Koster, Schouten, Venkatsubramanian & Poonia, 1985). Here we present the coordinating preferences of a smaller cation, Li, in the system $Li(dnp)(tea).H_2O$.

Experimental. The complex was synthesized by a 1:1 reaction of Li(dnp) and tea in 2-propanol using 1·0 m*M* of Li(dnp) for 5 ml of the synthesis medium. Deep yellow crystals (m.p. 436–443 K) were grown by slow evaporation of the reaction medium at room temperature. Intensity data (crystal size 0·10 × 0·16 × 0·32 mm) collected with an indigenously fabricated computer-controlled four-circle diffractometer (Padmanabhan *et al.*, 1979), Zr-filtered Mo *K*α radiation, ω–2θ step scan, 2107 unique reflections recorded in the range $8 \leq 2\theta \leq 50°$, 1273 with $I \geq 2{\cdot}5\sigma(I)$ considered observed, index range *h* −25→23, *k* 0→7 and *l* 0→24, corrections applied for Lp and absorption, maximum and minimum values of absorption 0·982 and 0·962 respectively. Unit-cell parameters obtained from least-squares fit of 2θ values of 25 reflections measured on the diffractometer. Two check reflections monitored through data collection showed only random variations. Structure was solved by using the automatic centrosymmetric direct method of the program *SHELX*76 (Sheldrick, 1976). All the hydrogen atoms were located from difference maps; structure refinement by least squares based on *F* values using anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms, $R = 0{\cdot}053$, $wR = 0{\cdot}064$ with $w = k/[\sigma^2(F_o) + g(F_o)^2]$ where *k* and *g* refined to 1·2419 and 0·00122 respectively; $(\Delta/\sigma)_{max} = 0{\cdot}14$; $\Delta\rho$ in the final difference map −0·2 to 0·3 e Å^{-3}, C—H distances in the range 0·859 (4)–1·081 (8) Å; O—H distances 0·749 (4)–0·992 (5) Å, programs *SHELX*76 (Sheldrick 1976), *PLUTO* (Motherwell & Clegg, 1978); computer NORSK DATA. Atomic scattering factors those of *SHELX*76.

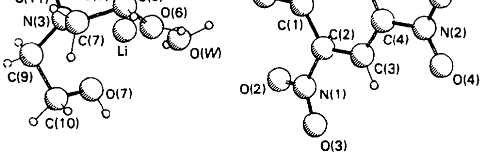

Fig. 1. General view of the molecule.

Table 1. *Final positional parameters and equivalent isotropic temperature factors* (Å² × 10³) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
Li	0·5757 (3)	0·1074 (12)	0·5869 (3)	46 (9)
C(1)	0·6248 (2)	0·6990 (7)	0·4504 (2)	41 (5)
C(2)	0·6430 (2)	0·6035 (8)	0·4041 (2)	45 (6)
C(3)	0·6856 (2)	0·6848 (8)	0·3894 (2)	49 (6)
C(4)	0·7111 (2)	0·8624 (9)	0·4191 (2)	50 (6)
C(5)	0·6961 (2)	0·9632 (8)	0·4656 (2)	58 (7)
C(6)	0·6548 (2)	0·8818 (8)	0·4810 (2)	55 (6)
O(1)	0·5857 (1)	0·6281 (5)	0·4664 (1)	50 (4)
N(1)	0·6165 (2)	0·4165 (7)	0·3690 (2)	60 (6)
O(2)	0·5696 (2)	0·3752 (8)	0·3639 (2)	118 (8)
O(3)	0·6415 (2)	0·3085 (7)	0·3451 (2)	107 (7)
N(2)	0·7553 (2)	0·9507 (8)	0·4026 (2)	66 (6)
O(4)	0·7662 (1)	0·8668 (8)	0·3595 (2)	90 (6)
O(5)	0·7795 (2)	1·1062 (7)	0·4322 (2)	93 (5)
N(3)	0·5996 (2)	−0·0282 (6)	0·6869 (2)	45 (4)
C(7)	0·6597 (2)	−0·0098 (8)	0·7194 (2)	64 (7)
C(8)	0·6805 (2)	0·1820 (9)	0·6972 (2)	74 (7)
O(6)	0·6565 (1)	0·1852 (5)	0·6282 (2)	64 (4)
C(9)	0·5810 (2)	−0·2450 (7)	0·6750 (2)	56 (6)
C(10)	0·5899 (2)	−0·3320 (7)	0·6172 (2)	54 (6)
O(7)	0·5628 (1)	−0·1967 (4)	0·5628 (1)	47 (3)
C(11)	0·5695 (2)	0·0915 (9)	0·7188 (2)	66 (7)
C(12)	0·5125 (2)	0·1488 (9)	0·6717 (2)	68 (8)
O(8)	0·5172 (1)	0·2336 (5)	0·6155 (2)	59 (4)
O(*W*)	0·5550 (1)	0·2332 (5)	0·5007 (1)	56 (4)

$*U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/[3(1-\cos^2\beta)]$.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Li—O(6)	1·983 (8)	N(2)—O(5)	1·221 (6)
Li—O(7)	2·018 (8)	C(4)—C(5)	1·379 (8)
Li—O(8)	2·011 (9)	C(5)—C(6)	1·339 (8)
Li—N(3)	2·206 (8)	C(6)—C(1)	1·423 (7)
Li—O(*W*)	1·924 (8)	N(3)—C(7)	1·433 (6)
C(1)—O(1)	1·270 (6)	C(7)—C(8)	1·498 (8)
C(1)—C(2)	1·410 (7)	C(8)—O(6)	1·390 (6)
C(2)—N(1)	1·447 (6)	N(3)—C(9)	1·463 (6)
N(1)—O(2)	1·196 (8)	C(9)—C(10)	1·477 (8)
N(1)—O(3)	1·194 (8)	C(10)—O(7)	1·417 (5)
C(2)—C(3)	1·361 (8)	N(3)—C(11)	1·447 (7)
C(3)—C(4)	1·351 (7)	C(11)—C(12)	1·476 (6)
C(4)—N(2)	1·436 (8)	C(12)—O(8)	1·389 (7)
N(2)—O(4)	1·209 (7)		

O(1)—C(1)—C(2)	124·1 (4)	C(5)—C(6)—C(1)	123·0 (5)
C(1)—C(2)—N(1)	121·4 (5)	C(6)—C(1)—O(1)	120·8 (5)
C(2)—N(1)—O(2)	119·0 (5)	C(6)—C(1)—C(2)	115·1 (5)
C(2)—N(1)—O(3)	119·3 (5)	N(3)—C(7)—C(8)	111·1 (4)
O(2)—N(1)—O(3)	121·6 (5)	C(7)—C(8)—O(6)	107·4 (4)
N(1)—C(2)—C(3)	116·9 (5)	N(3)—C(9)—C(10)	111·4 (4)
C(2)—C(3)—C(4)	119·8 (5)	C(9)—C(10)—O(7)	107·2 (4)
C(3)—C(4)—N(2)	119·8 (5)	N(3)—C(11)—C(12)	111·7 (4)
C(4)—N(2)—O(4)	117·7 (4)	C(11)—C(12)—O(8)	108·1 (4)
C(4)—N(2)—O(5)	118·7 (5)	C(7)—N(3)—C(9)	112·4 (4)
O(4)—N(2)—O(5)	123·5 (6)	C(7)—N(3)—C(11)	113·2 (4)
N(2)—C(4)—C(5)	118·3 (5)	C(9)—N(3)—C(11)	113·1 (4)
C(4)—C(5)—C(6)	118·5 (5)		
O(6)—Li—O(7)	113·6 (4)	O(8)—Li—N(3)	78·9 (3)
O(6)—Li—O(8)	122·4 (4)	O(6)—Li—O(*W*)	100·5 (4)
O(7)—Li—O(8)	113·9 (4)	O(7)—Li—O(*W*)	101·4 (4)
O(6)—Li—N(3)	79·0 (3)	O(8)—Li—O(*W*)	100·3 (3)
O(7)—Li—N(3)	80·2 (3)	O(*W*)—Li—N(3)	178·4 (4)

Discussion. The molecular structure of the title compound is shown in Fig. 1; the final coordinates, bond distances and angles are given in Tables 1 and 2.* The Li atom is five-coordinated by an oxygen atom of a water molecule, the three O atoms and the N atom of tea. The coordination geometry is trigonal bipyramidal. The O atom of the water molecule and the N atom of tea occupy the axial positions, while the three O atoms of tea make up the equatorial belt (Fig. 2). There is some distortion from ideal bipyramidal geometry as a result of the restricted bite of the O—C—C—N section of the ligand and also the deviation of the Li atom by 0·371 (6) Å from the equatorial plane. The distances between Li and the four heteroatoms of tea are in the range 1·983 (8)–2·206 (8) Å while the Li—O(*W*) distance, 1·924 (8) Å, is shorter. The angles subtended at Li by neighbouring equatorial atoms deviate from the ideal value of 120° for a trigonal bipyramid [113·6 (4)–122·4 (4)°], but the interaxial angle is close to 180° [178·4 (4)°] and the equatorial–Li–axial angle also deviates from 90° [79·0 (3)–101·4 (4)°]. It is interesting to note that the dnp anion does not take part in Li coordination. Its phenolic O atom is hydrogen-bonded to the water molecule [O(1)···O(*W*)]. The other water hydrogen in turn bonds an OH group of tea [O(W)···O(7)] (see Table 4). Thus these hydrogen bonds stabilize the structure as a whole. The bond lengths and angles of the phenyl ring agree with those reported in a number of *o*-nitrophenolate-containing complexes (Hughes, 1975; Bush & Truter, 1971; Krogh Anderson & Krogh Anderson, 1975; Hough, 1976) and show common features such as the larger C—C bond lengths and smaller C—C—C angles at the phenolic site and the larger twist of the *o*-nitro group [22·3 (4)°] than the *p*-nitro group [3·3 (4)°] with respect to the plane of the aromatic ring (Kanters *et al.*, 1984). The benzene ring is reasonably planar, σ_{plane} defined as $[\sum_i d_i^2/(N-3)]^{1/2}$ being 0·011 (5) Å. The tea ligand is in an extended conformation with approximately planar C—N—C—C fragments and terminal OH groups in *gauche* conformation with respect to the C—N bonds. The N—C—C—O torsion angles [49·1 (4)–54·1 (5)°] (Table 3) are in the range 46·8 (4)—67·4 (4)° reported in the literature (Voegele, Thierry & Weiss, 1974; Kanters *et al.*, 1984). The bond distances and angles of tea are consistent with those reported earlier. The molecular packing is shown in Fig. 3. Table 4 shows that the phenolic O atom accepts three hydrogen bonds, one from the water molecule and two from OH groups of tea, whose third OH group is bonded to an O atom of the *p*-nitro group of dnp.

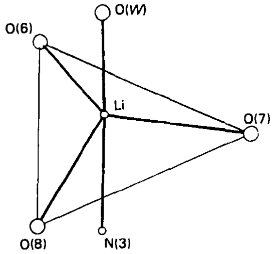

Fig. 2. Lithium coordination.

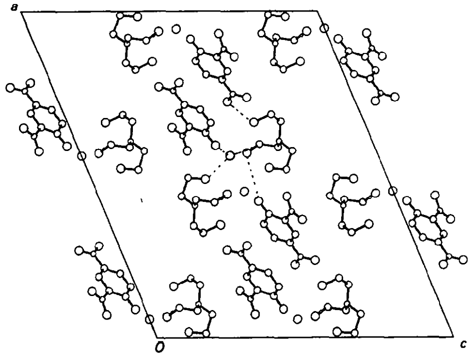

Fig. 3. Molecular packing viewed down *b* axis. Broken lines indicate hydrogen bonds.

Table 3. *Torsion angles* (°)

N(3)—C(7)—C(8)—O(6)	−49·1 (4)	C(7)—C(8)—O(6)—O(6)H	−160·5 (4)
N(3)—C(9)—C(10)—O(7)	−54·1 (5)	C(9)—C(10)—O(7)—O(7)H	170·0 (5)
N(3)—C(11)—C(12)—O(8)	−49·2 (5)	C(11)—C(12)—O(8)—O(8)H	−165·5 (4)

Table 4. *Possible hydrogen-bond distances* (Å) *and angles* (°)

O—H···O	O···O	O···H	H···O	O—H···O	Symmetry code of acceptor atom
O(*W*)—H···O(1)	2·844 (5)	0·992 (5)	1·853 (4)	175·9 (5)	x,y,z
O(*W*)—H′···O(7)	2·813 (5)	0·749 (4)	2·133 (5)	151·2 (5)	$1-x, -y, 1-z$
O(6)—H···O (5)	2·817 (5)	0·885 (5)	1·968 (5)	160·2 (5)	$\frac{3}{2}-x, \frac{3}{2}-y, 1-z$
O(7)—H···O (1)	2·646 (7)	0·836 (5)	1·823 (5)	167·8 (4)	$x, y-1, z$
O(8)—H···O (1)	2·707 (7)	0·843 (4)	1·884 (5)	165·2 (6)	$1-x, 1-y, 1-z$

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43731 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of (2,2′-Bipyridyl)(4-hydroxy-L-prolinato)palladium(II) Chloride Dihydrate

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Abstract. $[Pd(C_{10}H_8N_2)(C_5H_8NO_3)]Cl.2H_2O$, $M_r = 464{\cdot}2$, m.p. = 458 K, triclinic, $P1$, $a = 11{\cdot}100\ (3)$, $b = 13{\cdot}139\ (4)$, $c = 6{\cdot}887\ (4)$ Å, $\alpha = 105{\cdot}80\ (3)$, $\beta = 103{\cdot}50\ (3)$, $\lambda = 106{\cdot}63\ (3)°$, $V = 871{\cdot}64$ Å^3, $Z = 2$, $D_x = 1{\cdot}769$, D_m(by flotation) = $1{\cdot}777$ g cm^{-3}, λ(Mo $K\alpha$) = $0{\cdot}7107$ Å, Zr filter, $\mu = 12{\cdot}34$ cm^{-1}, $F(000) = 468$, room temperature, $R = 0{\cdot}053$, $wR = 0{\cdot}068$ for 1844 observed reflections. The two N atoms of bipyridyl and the imino N atom and carboxyl O atom of hydroxyproline give distorted square-planar coordination around palladium. Average Pd—O = 1·988 (10), Pd—N = 2·028 (11) Å. The proline rings are in the envelope conformation. The N atoms of the bipyridyl ring have bite angles of 80·9 (4) and 80·5 (4)° at palladium. The pyridine rings are twisted about the 2,2′ bond because of chelation strain. The two molecules are stacked along the c axis and linked with weak hydrogen bonds through the water molecules.

Introduction. In continuation of our work on the structural aspects of palladium(II) complexes, we report the structure of the title compound, a mixed-ligand chelate. A literature survey shows that very little work has been done on the synthesis and structural aspects of mixed-ligand palladium(II) amino-acid complexes (Nakayama, Komorita & Shimura, 1984).

Experimental. The complex was synthesized as follows:

(i) $K_2PdCl_4 + 2,2'\text{-bipyridyl} \overset{CH_3OH}{\rightarrow} Pd(bpy)Cl_2 + 2KCl$;

(ii) $Pd(bpy)Cl_2 + \text{4-hydroxyprol} + NaHCO_3 \overset{H_2O}{\rightarrow}$
$[Pd(bpy)(hyd.prol)]^+ Cl^- + NaCl + H_2O + CO_2\uparrow$.

Pale yellow crystals of the complex were prepared by repeated recrystallization from water. Intensity data for 1891 reflections (crystal size 0·47 × 0·30 × 1·10 mm) were collected on an indigenously fabricated computer-controlled four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation in the range $6 < 2\theta < 55°$ with ω–2θ step scan width of 1·8° with 33 steps deg^{-1} and 1·0 s step^{-1}. Data corrected for Lp and absorption effects (max. and min. values of the absorption coefficients are 0·697 and 0·570 respectively). Unit-cell parameters were obtained from a least-squares fit of the 2θ values of 25 reflections measured on the diffractometer in the range $5 < \theta < 12°$. Two standard reflections measured for every 100 reflections showed no significant change during the data collection process. The Pd atoms were located from a Patterson map. As expected, space group $P1$ with two molecules in the asymmetric unit presented some difficulties in its structure solution, because of false symmetry in the electron density maps (Stout & Jensen, 1968). However, the structure was solved by delineating chemically meaningful non-hydrogen atoms from a series of Fourier and difference Fourier maps. The non-hydrogen atoms were refined with anisotropic temperature factors. H atoms were fixed at calculated positions and two cycles of refinement with fixed isotropic temperature factors (0·05 Å^2) showed no significant changes in their parameters. The x,y,z coordinates for Pd were fixed to define the origin while the absolute configuration was established from the configuration of the amino acid. The scattering factor for palladium with corrections for dispersion effects was taken from *International Tables for X-ray*

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