Geometry and Bonding of Nitro- and Azido-groups in Palladium(II) Four-co-ordinate Complexes containing Terdentate Ligands

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The crystal structures of the following palladium(II) complexes: (I) $[NO_2Pd(dien)]NO_3$, (II) $[NO_2Pd(Et_4dien)]NO_3$, and (III) $[N_3Pd(Et_4dien)]NO_3$ (dien = diethylenetriamine) have been determined by Patterson and Fourier methods. Crystal data are: (I), monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.627(7)$, $b = 7.617(6)$, $c = 17{\cdot}380(9)$ Å, $\beta = 133.77(5)°$; (II), orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 21.825(9)$, $b = 10.977(7)$, $c = 8.233(6)$ Å; (III), orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 20.167(9)$, $b = 11.262(6)$, $c = 8.644(6)$ Å. Anisotropic least-squares refinement reduced R to 0.034 (I), 0.052 (II), and 0.059 (III). The co-ordination geometry of the nitro-group is determined by the bulkiness of the terdentate ligand in such a way that NO_2^- is nearly parallel to the donor-atom plane in (I) and nearly normal to it in (II). A π contribution in the Pd–NO_2 and Pd–N_3 bonds seems to be excluded on the basis of structural parameters.

THE stereochemical behaviour of terdentate ligands such as diethylenetriamine (dien) and 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) in first-row transition-metal complexes has been well established both in solution and in the solid state.[1] Comparatively few data are available for the second- and third-row transition-metal complexes,[2,3] especially for four-co-ordinate compounds.[2] A structure study of the properties of these ligands is of particular interest in complexes containing co-ordinated small ions such as NO_2^-, N_3^-, and SCN^-. In fact, few crystallographic studies of azido- and nitro-complexes have been reported and the bonding mode of the N_3^- and NO_2^- ions is still in question, particularly the possibility of π-bonding contributions.[4-8]

In order to obtain further insight into the bonding mode

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[1] R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.* 1972, **11**, 3044, and refs. therein.

[2] M. Cusumano, G. Guglielmo, V. Ricevuto, R. Romeo, and M. Trozzi, *Atti Accad. Peloritana Pericolanti*, 1974, **LIV**, 89, and refs. therein.

[3] R. F. Ziolo, R. M. Shelby, R. H. Stanford, jun., and H. B. Gray, *Cryst. Struct. Comm.*, 1974, **3**, 469.

[4] L. F. Druding and F. D. Sancilio, *Acta Cryst.*, 1974, **B30**, 2386, and refs. therein.

[5] Z. Dori and R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247.

[6] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1962, **1**, 1, and refs. therein.

[7] J. L. Burmeister, R. L. Hassel, K. A. Johnson, and J. C. Lim, *Inorg. Chim. Acta*, 1974, **9**, 23, and refs. therein.

[8] J. L. Burmeister and R. C. Timmer, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1973.

of such ligands and the stereochemistry of Pd^{II} complexes with terdentate ligands, we have undertaken a structural study of a series of $[XPd(dien)]NO_3$ and $[XPd(Et_4dien)]NO_3$ compounds ($X = NO_2^-$, N_3^-, and SCN^-). We report here the crystal structure results of the nitrate of the nitro- and azido-derivatives ($X = NO_2^-$ and N_3^-) with the ligands dien and Et_4dien. A preliminary report has appeared.[9]

EXPERIMENTAL

Crystal Data.—(*a*) $[NO_2Pd(N_3C_4H_{13})]NO_3$, (I). M = 317.6, Monoclinic, a = 11.627(7), b = 7.617(6), c = 17.380(9) Å, β = 133.77(5)°, U = 1 111.5 Å^3, D_m = 1.89, Z = 4, D_c = 1.90. μ(Mo-K_α) = 16.54 cm^{-1}, μR = 0.15. Space group $P2_1/c$.

(*b*) $[NO_2Pd(N_3C_{12}H_{29})]NO_3{\cdot}H_2O$, (II). M = 447.9, Orthorhombic, a = 21.825(9), b = 10.977(7), c = 8.233(6) Å, U = 1 972.4 Å^3, D_m = 1.48, Z = 4, D_c = 1.51. μ(Mo-K_α) = 9.55 cm^{-1}, μR = 0.06. Space group $P2_12_12_1$.

(*c*) $[N_3Pd(N_3C_{12}H_{29})]NO_3{\cdot}\frac{1}{2}H_2O$, (III). M = 434.9, Orthorhombic, a = 20.167(9), b = 11.262(6), c = 8.644(6) Å, U = 1 963.2 Å^3, D_m = 1.48, Z = 4, D_c = 1.47. μ(Mo-K_α) = 9.54 cm^{-1}, μR = 0.08. Space group $P2_12_12_1$.

TABLE 1

(*a*) Atomic positional parameters of non-hydrogen atoms (× 10^4) for (II) with estimated standard deviations in parentheses

	x	*y*	*z*
Pd	1 098(1)	2 038(1)	204(2)
O(1)	−120(7)	2 822(19)	−502(29)
O(2)	−75(7)	1 797(22)	1 606(24)
N(1)	167(7)	2 258(13)	409(23)
N(2)	1 306(7)	3 649(15)	1 419(19)
N(3)	1 999(5)	1 791(11)	67(21)
N(4)	1 034(6)	294(11)	−825(18)
C(1)	2 012(8)	3 763(16)	1 321(24)
C(2)	2 293(10)	2 505(21)	1 406(27)
C(3)	2 118(8)	488(17)	17(36)
C(4)	1 661(9)	−71(16)	−1 259(25)
C(5)	644(8)	200(19)	−2 321(26)
C(6)	760(14)	1 156(24)	−3 569(30)
C(7)	789(11)	−523(17)	520(26)
C(8)	690(10)	−1 841(17)	−13(37)
C(9)	1 083(11)	4 771(17)	691(21)
C(10)	1 030(9)	4 839(16)	−1 183(23)
C(11)	1 149(9)	3 474(19)	3 196(20)
C(12)	1 252(9)	4 601(20)	4 311(23)
N(5)	2 606(7)	2 843(15)	6 204(20)
O(3)	2 779(9)	3 243(17)	4 934(21)
O(4)	2 736(12)	3 243(21)	7 502(23)
O(5)	2 260(11)	1 995(21)	6 172(29)
O(6)	3 629(8)	1 713(19)	−626(29)

(*b*) Co-ordinates (× 10^3) of hydrogen atoms, numbered according to the atom to which they are bonded

	x	*y*	*z*
H(N3)	214	215	−109
H1(C1)	215	414	7
H2(C1)	220	438	220
H1(C2)	277	256	138
H2(C2)	214	216	261
H1(C3)	259	30	−31
H2(C3)	202	11	121
H1(C4)	178	29	−249
H2(C4)	171	−105	−130
H1(C5)	69	−69	−288
H2(C5)	14	26	−192
H1(C7)	34	−14	99
H2(C7)	110	−52	159
H1(C9)	141	549	105
H2(C9)	64	496	124
H1(C11)	144	272	369
H2(C11)	68	319	333

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer (Mo-K_α). Visual comparison of the diffraction patterns showed the crystals of (II) and (III) to be isomorphous.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation to $2\theta_{max.}$ 50° for (I), (II), and (III). Reflections having $I_0 < 3\sigma(I_0)$ were rejected and the remainder corrected for Lorentz-polarization factors. A total of 1 351 reflections for (I), 1 087 for (II), and 1 332 for (III) were used in the subsequent calculations. No absorption correction was applied.

Structure Determination and Refinement.—The three structures were solved by conventional Patterson and Fourier methods. The final anisotropic refinement, including the contribution of hydrogen atoms (set at B 4.0 Å^2) held constant, gave R 0.034 for (I). The introduction of non-methyl hydrogen atoms [set at B 5.0 Å^2 for both (II) and (III)] and of a water molecule [with an occupancy factor of 1.0 for (II) and 0.5 for (III)] detected in three-dimensional difference-Fourier maps led to a final value of the conventional R factor of 0.052 for (II) and 0.059 for (III).

TABLE 2

(*a*) Atomic positional parameters (× 10^4) of non-hydrogen atoms for (I), with estimated standard deviations in parentheses

	x	*y*	*z*
Pd	1 868(0)	974(1)	2 440(0)
O(1)	578(6)	−2 327(7)	2 315(4)
O(2)	2 760(5)	−1 788(8)	3 873(4)
N(1)	1 746(5)	−1 351(8)	2 949(4)
N(2)	−498(5)	1 057(8)	1 078(4)
N(3)	2 004(5)	3 332(7)	1 942(3)
N(4)	4 196(6)	1 486(8)	3 787(4)
C(1)	−761(7)	2 576(10)	439(5)
C(2)	353(7)	4 071(9)	1 190(5)
C(3)	3 271(7)	4 381(10)	2 907(5)
C(4)	4 715(7)	3 165(11)	3 629(5)
N(5)	3 165(6)	2 628(9)	561(4)
O(3)	2 286(5)	1 706(9)	551(4)
O(4)	3 506(6)	2 204(10)	68(4)
O(5)	3 666(7)	4 016(8)	1 092(5)

(*b*) Co-ordinates (× 10^3) of hydrogen atoms, numbered according to the atom to which they are bonded

	x	*y*	*z*
H1(N2)	−111	12	48
H2(N2)	−117	146	121
H(N3)	230	290	140
H1(N4)	443	186	446
H2(N4)	513	71	404
H1(C1)	−49	219	−4
H2(C1)	−199	301	−11
H1(C2)	26	516	73
H2(C2)	4	452	161
H1(C3)	359	555	271
H2(C3)	291	482	331
H1(C4)	517	287	328
H2(C4)	565	381	441

The occupancy factors of the water molecule were determined from the heights of the peaks on the difference-Fourier maps and by means of the least-squares refinement, different fractional weights being assigned to the oxygen atom of the water molecule. The final weighting schemes

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[9] N. Bresciani Pahor, M. Calligaris, L. Randaccio, V. Ricevuto, and U. Belluco, *Inorg. Chim. Acta*, 1975, **14**, L17; N. Bresciani Pahor and P. Delise, *Cryst. Struct. Comm.*, 1975, **4**, 483.

were: $w = 1/(A + B|F_o| + C|F_o|^2)$, where $A = 5.1$, $B = 1.0$, $C = 0.006$ for (I), $A = 16.6$, $B = 1.0$, $C = 0.005$ for (II) and $A = 10.0$, $B = 1.0$, $C = 0.005$ for (III), chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$.

Final atomic positional parameters are listed in Tables 1, 2, and 3 together with their estimated standard deviations calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme used for the atoms is shown in Figures 1 and 2. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21615 (14 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 10.

TABLE 3

(*a*) Atomic positional parameters of non-hydrogen atoms ($\times 10^4$) for (III) with estimated standard deviations in parentheses

	x	y	z
Pd	1 111(0)	2 097(1)	457(1)
N(1)	113(6)	2 209(14)	1 032(17)
N(2)	1 355(6)	3 687(11)	1 594(15)
N(3)	2 078(5)	1 907(10)	111(14)
N(4)	1 033(6)	418(9)	−553(16)
N(5)	−276(9)	2 552(16)	202(26)
N(6)	−718(13)	2 799(29)	−569(42)
C(1)	2 090(7)	3 830(14)	1 416(23)
C(2)	2 439(6)	2 629(15)	1 341(19)
C(3)	2 228(8)	648(13)	114(21)
C(4)	1 734(9)	60(14)	−1 086(21)
C(5)	592(8)	341(16)	−1 909(22)
C(6)	709(11)	1 336(20)	−3 184(26)
C(7)	774(9)	−383(14)	812(20)
C(8)	675(14)	−1 684(17)	305(44)
C(9)	1 004(6)	4 759(12)	911(15)
C(10)	1 017(10)	4 807(14)	−922(17)
C(11)	1 176(8)	3 515(16)	3 341(17)
C(12)	1 270(9)	4 589(15)	4 373(21)
N(7)	2 595(6)	2 772(11)	6 224(16)
O(1)	2 817(7)	3 227(13)	4 992(14)
O(2)	2 574(10)	3 387(12)	7 459(16)
O(3)	2 420(11)	1 811(13)	6 326(25)
O(4)	3 802(18)	425(42)	7 380(51)

(*b*) Co-ordinates ($\times 10^3$) of hydrogen atoms, numbered according to the atom to which they are bonded

	x	y	z
H(N3)	220	226	−97
H1(C1)	213	431	33
H2(C1)	228	435	238
H1(C2)	296	275	108
H2(C2)	240	219	248
H1(C3)	275	50	−31
H2(C3)	217	26	122
H1(C4)	183	39	−228
H2(C4)	180	−91	−110
H1(C5)	67	−52	−254
H2(C5)	7	36	−157
H1(C7)	119	−42	171
H2(C7)	35	−3	133
H1(C9)	50	476	131
H2(C9)	126	555	134
H1(C11)	233	124	267
H2(C11)	291	236	216

Calculations.—All calculations were carried out on a CDC 6200 computer with programs described in ref. 11. A local program was used to obtain best molecular planes whose equations were calculated according to ref. 12.

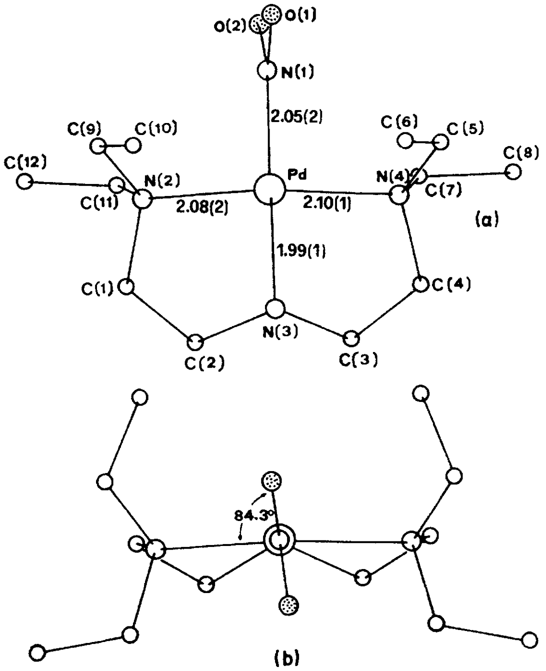

FIGURE 1 (a) Numbering scheme for the $[NO_2Pd(Et_4dien)]^+$ cation together with co-ordination bond lengths, and (b) a side view of the cation

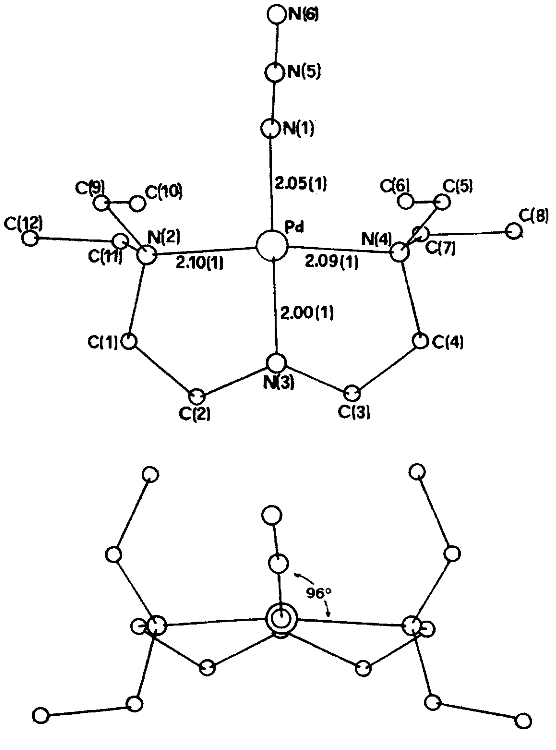

FIGURE 2 (a) Numbering scheme for the $[N_3Pd(Et_4dien)]^+$ cation together with co-ordination bond lengths, and (b) a side view of the cation

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[10] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[11] V. Albano, A. Domenicano, and A. Vaciago, *Gazzetta*, 1966, **3**, 565.

[12] V. Schomaker, J. Waser, R. F. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

DISCUSSION

Nitro-derivatives.—The arrangement of the donor atoms around palladium is similar in both nitro-derivatives (I) and (II), being nearly square-planar and with a slight tetrahedral distortion. However the two cations exhibit significant geometrical differences (Figures 1 and 3). In fact the plane of the NO_2^- group is nearly perpendicular to the co-ordination plane in the Et_4dien derivative (I) whereas the two planes are nearly parallel in the dien complex (II); the interplanar angles are 84.3 and 15.8°. Furthermore, the Pd-N co-ordination bond lengths, involving the terdentate ligand, are equal, in the $[NO_2Pd(dien)]^+$ cation, ranging from 2.041(4) to 2.047(6) Å, whereas, in $[NO_2Pd(Et_4dien)]^+$, the Pd-N(3) distance [1.99(1) Å] is significantly shorter than Pd-N(2) and Pd-N(4) [2.08(2) and 2.10(1) Å]. Since the overall conformation of the dien and (Et_4dien) ligands appears to be the same (*cf.* Figures 1 and 3), this difference may be ascribed only to the steric effect of the ethyl groups on the co-ordination bond lengths. This is also suggested by the values of the Pd-N(4)-C(5) and Pd-N(2)-C(9) angles (116 and 117°) which are larger than the other angles around N(2) and N(4). The interaction of the ethyl groups with NO_2^- would push away the N(2) and N(4) atoms from palladium, allowing a better approach of N(3) to the metal atom, so as to leave unaltered the rigid conformation of the terdentate ligand. An analogous geometrical feature has been found in the octahedral compound [3] $[(N_3)_3Rh^{III}(Et_4dien)]$, where Rh-N(3) is 2.027 Å *vs.* 2.163 and 2.159 Å for Rh-N(2) and Rh-N(4). Similar, although less enhanced effects, have been observed in some octahedral Co^{III} complexes containing dien when this acts as a *mer*-ligand [4,13] whereas there is no significant difference in the three bond lengths [13,14] when it behaves as a *fac*-terdentate ligand. Some data indicating such a trend are reported in Table 4. Some π-bonding between palladium *d* orbitals and nitrogen antibonding *p* orbitals is possible both for compound (I), in which the NO_2 group lies in the co-ordination plane of palladium and d_{yz} orbitals are involved, and also for compound (II), where the plane of the NO_2^- group is normal to the co-ordination plane and d_{xy} orbitals can interact (Figure 4). The Pd-N distances give no evidence for π-bonding, however, since the Pd-NO_2 distances are not shorter than Pd-N. This result differs from that in $[Pd(NH_3)_3NO_2]^+$, where Pd-NO_2 is significantly shorter than Pd-NH_3.[15]

The geometry of the nitrite ion has been found [16] to be characterized by an N-O bond length of 1.236 Å and by a

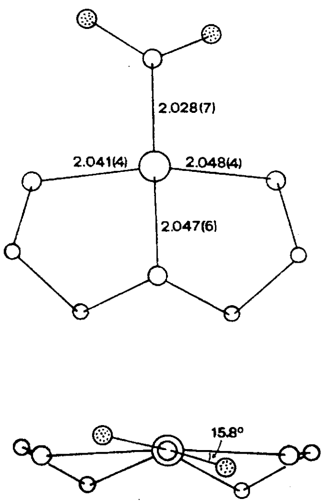
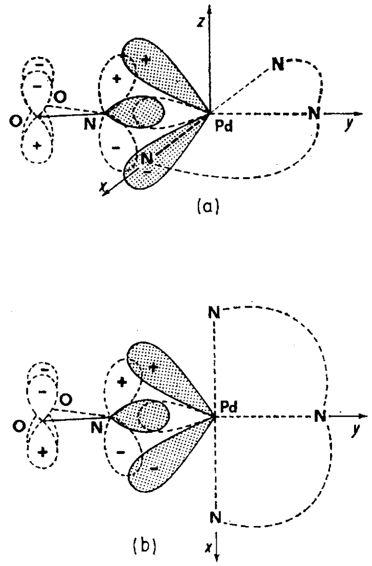


FIGURE 3 (a) Schematic diagram of the $[NO_2Pd(dien)]^+$ cation together with co-ordination bond lengths (for the numbering scheme see Figure 1), and (b) a side view of the cation



(a)

(b)

FIGURE 4 σ–π bonding scheme for the Pd–NO_2 grouping in (a) ' coplanar,' and (b) ' normal ' orientation of the NO_2 group

TABLE 4

Co-ordination bond lengths (Å) involving the (dien) ligand in *mer*- and *fac*-conformations

	mer-$[Co(dien)(N_3)_3]$ [a]	*mer*-[Co(dien)enCl] [b]	*fac*-[Co(dien)en] [b]	*fac*-$[Co(dien)_2]^{3+}$ [c]	
Co–N(2)	1.964(6)	1.97(1)	1.993(7)	1.957(5)	1.951(5)
Co–N(3)	1.930(6)	1.93(1)	1.974(7)	1.970(4)	1.968(4)
Co–N(4)	1.960(6)	1.98(1)	1.944(7)	1.969(4)	1.970(4)

[a] Ref. 4. [b] Ref. 13. [c] Ref. 14.

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[13] A. R. Gainsford, D. A. House, and W. J. Robinson, *Inorg. Chim. Acta*, 1971, **5**, 595.

[14] M. Konno, F. Marumo, and Y. Saito, *Acta Cryst.*, 1973, **B29**, 739.

[15] E. P. Boer, V. B. Carter, and J. W. Turley, *Inorg. Chem.*, 1971, **10**, 651.

[16] M. R. Truter, *Acta Cryst.*, 1954, **7**, 73.

bond angle of 115.4°. These values are very similar to those found for $[NO_2Pd(dien)]^+$ where the N–O distances are 1.241(7) and 1.208(7) Å and the angle is 118.5(7)°.

On the basis of such results it may be assumed that the hypothesis of double-bond character in the Pd–NO_2 bond is somewhat questionable, although we cannot exclude that the extent of the back-donation is such that bond lengths and angles are scarcely influenced.

TABLE 5

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses for the nitro-complexes

(*a*) Bond lengths	(II)	(I)
Pd–N(1)	2.053(15)	2.028(7)
Pd–N(2)	2.082(16)	2.041(4)
Pd–N(3)	1.988(11)	2.047(6)
Pd–N(4)	2.098(13)	2.048(4)
N(1)–O(1)	1.16(3)	1.241(7)
N(1)–O(2)	1.23(3)	1.208(7)
N(2)–C(1)	1.55(2)	1.482(11)
N(3)–C(9)	1.45(3)	
N(2)–C(11)	1.52(2)	
N(3)–C(2)	1.50(3)	1.496(8)
N(3)–C(3)	1.45(2)	1.484(7)
N(4)–C(4)	1.47(2)	1.518(12)
N(4)–C(5)	1.50(3)	
N(4)–C(7)	1.52(3)	
C(1)–C(2)	1.51(3)	1.529(9)
C(3)–C(4)	1.57(3)	1.529(9)
C(5)–C(6)	1.49(3)	
C(7)–C(8)	1.53(3)	
C(9)–C(10)	1.55(3)	
C(11)–C(12)	1.56(3)	
N(5)–O(3)	1.19(2)	1.230(11)
N(5)–O(4)	1.19(2)	1.212(13)
N(5)–O(5)	1.20(3)	1.251(9)
(*b*) Bond angles		
Pd–N(1)–O(1)	123(1)	120.0(4)
Pd–N(1)–O(2)	116(1)	121.5(4)
Pd–N(2)–C(1)	105(1)	107.9(4)
Pd–N(2)–C(9)	117(1)	
Pd–N(2)–C(11)	108(1)	
Pd–N(3)–C(2)	108(1)	105.8(5)
Pd–N(3)–C(3)	108(1)	107.5(4)
Pd–N(4)–C(4)	107(1)	109.3(3)
Pd–N(4)–C(5)	116(1)	
Pd–N(4)–C(7)	106(1)	
O(1)–N(1)–O(2)	121(2)	118.5(7)
N(1)–Pd–N(2)	94.4(6)	95.1(2)
N(1)–Pd–N(3)	178.2(7)	179.4(2)
N(1)–Pd–N(4)	94.3(6)	95.9(2)
N(2)–Pd–N(3)	85.8(6)	85.3(2)
N(2)–Pd–N(4)	169.6(6)	167.2(2)
N(2)–C(1)–C(2)	109(1)	109.1(5)
N(2)–C(9)–C(10)	118(2)	
N(2)–C(11)–C(12)	116(2)	
N(3)–Pd–N(4)	85.3(5)	83.6(2)
N(3)–C(2)–C(1)	106(2)	106.4(6)
N(3)–C(3)–C(4)	107(2)	105.6(6)
N(4)–C(4)–C(3)	109(2)	108.1(6)
N(4)–C(5)–C(6)	115(2)	
N(4)–C(7)–C(8)	114(2)	
C(1)–N(2)–C(9)	104(1)	
C(1)–N(2)–C(11)	107(1)	
C(2)–N(3)–C(3)	117(2)	117.1(6)
C(4)–N(4)–C(5)	108(1)	
C(4)–N(4)–C(7)	110(1)	
O(3)–N(5)–O(4)	125(2)	120.9(7)
O(3)–N(5)–O(5)	117(2)	116.8(9)
O(4)–N(5)–O(5)	117(2)	122.3(9)

We therefore believe that the 'normal' and 'coplanar' orientations of the NO_2^- group in the two cations are mainly due to the steric hindrance of the ethyl groups which impose a 'normal' orientation. Bond lengths and angles are reported in Table 5 and equations of relevant mean planes in Table 6.

TABLE 6

Equations of least-squares planes and distances (Å) of relevant atoms from the planes in square brackets. Equations are referred to crystal axes and x, y, z are fractional co-ordinates

(*a*) $[Pd(Et_4dien)NO_2]^+$

Plane (1): Pd, N(1)—(4)

$$0.072x - 4.926y + 7.357z = -0.793$$

[Pd −0.053, N(1) −0.018, N(2) 0.049, N(3) −0.026, N(4) 0.048, C(1) −0.075, C(2) 0.610, C(3) 0.580, C(4) −0.087]

Plane (2): Pd, N(1), O(1), O(2)

$$3.329x + 9.148y + 4.374z = 2.316$$

[Pd 0.004, N(1) −0.016, O(1) 0.006, O(2) 0.006]

(*b*) $[Pd(dien)NO_2]^+$

Plane (1): Pd, N(1)—(4)

$$-8.820x + 3.623y + 14.710z = 2.343$$

[Pd −0.049, N(1) −0.035, N(2) 0.065, N(3) −0.047, N(4) 0.065, C(1) −0.093, C(2) 0.571, C(3) 0.635, C(4) −0.017]

Plane (2): Pd, N(1), O(1), O(2)

$$-10.102x + 3.450y + 12.955z = 1.607$$

[Pd 0.004, N(1) −0.016, O(1) 0.006, O(2) 0.006]

(*c*) $[Pd(Et_4dien)N_3]^+$

Plane (1): Pd, N(1)—(4)

$$2.716x - 5.124y + 7.455z = -0.356$$

[Pd −0.076, N(1) 0.008, N(2) 0.033, N(3) 0.003, N(4) 0.033, C(1) 0.009, C(2) 0.685, C(3) 0.685, C(4) −0.024]

Plane (2): Pd, N(1), N(5), N(6)

$$2.847x + 10.469y + 2.881z = 2.643$$

[Pd 0.000, N(1) 0.002, N(5) −0.005, N(6) 0.003]

Azido-derivative.—The molecular structure of compound (III), $[N_3Pd(Et_4dien)]NO_3$, is similar to that of the analogous nitro-derivative, if we exclude the azide and nitrite ligands. Only slight differences are observed in the geometrical arrangement of the donor atoms, since no tetrahedral distortion has been observed, the palladium atom being displaced 0.1 Å from the co-ordination plane. The azide group co-ordinates to the metal atom with Pd–N–N 123(1)°, and is nearly linear [N–N–N 172(3)°]. The plane of the Pd–N_3 grouping (planar within ±0.003 Å) is nearly perpendicular to the co-ordination plane (96°). This orientation, as in the case of the $[NO_2Pd(Et_4dien)]^+$ cation, appears mainly to be determined by the interactions of the azide group with the ethyl groups of the terdentate ligand. Unfortunately, we did not succeed in obtaining suitable crystals of $[N_3Pd(dien)]NO_3$ for *X*-ray data collection. The geometries of some typical co-ordinated azide derivatives are reported in Table 7. The angles a–b suggest essentially sp^2 hybridization of the N(1) atom. Furthermore the two N–N distances are not equal, with few exceptions. These exceptions are difficult to rationalize in terms of the electronic structure of the N_3–M grouping, although we feel that the high thermal motion of the terminal nitrogen atoms may play an important role in causing an apparent shortening of the bond lengths. In other cases the geometry approaches that reported for covalent azides. The possibility suggested by Maxwell[17] of an orbital overlap between an azide π orbital and a suitable metal d orbital may not be excluded. The available structural results, however, do not support this hypothesis.

TABLE 7

Co-ordination geometry of the azido-group to metal atoms [a]

	a/Å	b/Å	c/Å	a–b/°	b–c/°
$[(N_3)_3Rh^{III}(Et_4dien)]$ [b]	2.061	1.184	1.153	124.4	175.9
	2.058	1.193	1.156	128.3	175.4
	2.065	1.186	1.148	126.4	176.0
$[(N_3)_3Co^{III}(dien)]$ [c]	1.954(6)	1.201(9)	1.173(11)	118	
	1.922(7)	1.188(20)	1.172(30)	122	177 (mean)
	1.966(6)	1.196(9)	1.153(10)	118	
$[Br(N_3)Cu^{II}(Et_4dien)]$ [d]	1.927(6)	1.145(8)	1.144(9)	125.4(5)	175.5(10)
$[N_3Co^{III}(tetraen)](NO_3)_2$ [e, f]	1.957(6)	1.209(7)	1.152(7)	119.0(5)	176.4(9)
$[N_3Pd^{II}(Et_4dien)]NO_3$ [g]	2.08(1)	1.13(2)	1.15(4)	123(2)	172(3)
N_3H [h]		1.24	1.13		110
N_3Me [h]		1.26	1.10		135
N_3^- [h]		1.15	1.15		180

[a] Bonds are identified as M–N–N–N, where bond M–N is a, and two N–N bonds, in order, are b and c. [b] Ref. 3. [c] Ref. 4. [d] Ref. 1. [e] tetraen = Tetraethylenepentamine. [f] Ref. 17. [g] Present work. [h] E. Cartmell and G. W. A. Fowles, 'Valency and Molecular Structure,' Butterworth, London, 1966.

TABLE 8

Bond lengths (Å) and angles (°) for (III), with estimated standard deviations in parentheses

(*a*) Distances

Pd–N(1)	2.077(12)	N(4)–C(7)	1.57(2)
Pd–N(2)	2.101(13)	N(5)–N(6)	1.15(4)
Pd–N(3)	1.985(10)	C(1)–C(2)	1.53(2)
Pd–N(4)	2.089(11)	C(3)–C(4)	1.58(2)
N(1)–N(5)	1.13(2)	C(5)–C(6)	1.59(3)
N(2)–C(1)	1.50(2)	C(7)–C(8)	1.54(3)
N(2)–C(9)	1.52(2)	C(9)–C(10)	1.59(2)
N(2)–C(11)	1.57(2)	C(11)–C(12)	1.52(2)
N(3)–C(2)	1.52(2)	N(7)–O(1)	1.26(2)
N(3)–C(3)	1.45(2)	N(7)–O(2)	1.27(2)
N(4)–C(4)	1.54(2)	N(7)–O(3)	1.14(2)
N(4)–C(5)	1.47(2)		

(*b*) Angles

Pd–N(1)–N(5)	123(1)	N(2)–C(9)–C(10)	114(1)
Pd–N(2)–C(1)	106(1)	N(2)–C(11)–C(12)	116(1)
Pd–N(2)–C(9)	113(1)	N(3)–Pd–N(4)	85.0(5)
Pd–N(2)–C(11)	107(1)	N(3)–C(2)–C(1)	106(1)
Pd–N(3)–C(2)	108(1)	N(3)–C(3)–C(4)	106(1)
Pd–N(3)–C(3)	108(1)	N(4)–C(4)–C(3)	106(1)
Pd–N(4)–C(4)	107(1)	N(4)–C(5)–C(6)	115(1)
Pd–N(4)–C(5)	116(1)	N(4)–C(7)–C(8)	112(2)
Pd–N(4)–C(7)	103(1)	C(1)–N(2)–C(9)	110(1)
N(1)–Pd–N(2)	93.6(5)	C(1)–N(2)–C(11)	110(1)
N(1)–Pd–N(3)	174.2(5)	C(2)–N(3)–C(3)	115(1)
N(1)–Pd–N(4)	94.7(5)	C(4)–N(4)–C(5)	107(1)
N(1)–N(5)–N(6)	172(3)	C(4)–N(4)–C(7)	112(1)
N(2)–Pd–N(3)	86.1(5)	O(1)–N(7)–O(2)	120(1)
N(2)–Pd–N(4)	170.0(5)	O(1)–N(7)–O(3)	124(2)
N(2)–C(1)–C(2)	111(1)	O(2)–N(7)–O(3)	116(2)

The co-ordination bond lengths are similar to those of the corresponding nitro-derivative, the Pd–N(3) distance [1.99(1) Å] being significantly shorter than Pd–N(2) and Pd–N(4) [2.10(1) and 2.09(1) Å]. Bond lengths and angles are listed in Table 8.

Terdentate Ligands.—The overall conformation of the terdentate ligand (Figures 1, 3, and 4) in the three compounds is nearly the same. The Pd–N–C–C–N groups have envelope-shapes with a nearly gauche conformation of the ethylene bridge.

Crystal Packing.—The crystal structure of all the three compounds is built up by discrete anions NO_3^- and cations $[XPd(chel)]^+$. The Et_4dien compounds are isomorphous, with NO_3^- anions which undergo a large thermal motion; no hydrogen-bonding scheme may be detected in either compound. However, in the crystal structure of $[NO_2Pd(dien)]NO_3$ weak hydrogen bonds may be assumed to be present. The O(3) and O(5) atoms of the NO_3^- ion are involved in short contacts with the N(3) and N(4) atoms of the cation as well as O(1) and O(2) nitrite atoms with the N(2) and N(4) atoms. Corresponding distances are reported in Table 9.

TABLE 9

Intermolecular distances (Å), with estimated standard deviations in parentheses

N(3) ··· O(3)	2.93(1)	$N(2) \cdots O(1)^{III}$	3.11(1)
N(3) ··· O(5)	3.18(1)	$N(2) \cdots O(2)^{III}$	3.15(1)
$N(4) \cdots O(4)^{I}$	3.01(1)	$O(2) \cdots N(4)^{IV}$	3.034(6)
$O(5) \cdots N(4)^{II}$	3.01(1)		

Roman numerals as superscripts refer to the following equivalent positions:

I	$x, \frac{1}{2} - y, \frac{1}{2} + z$	III	$-x, \frac{1}{2} + y, \frac{1}{2} - z$
II	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	IV	$1 - x, -y, 1 - z$

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[17] I. E. Maxwell, *Inorg. Chem.*, 1971, **10**, 1782.