124·7 (12)° between planes C5C6C8C9C10C11 (plane 1) and C4C7N1N3 (plane 2). The small displacements of atoms C4 and C7 from plane 1 [−0·047 (10), 0·131 (7) Å], C2, N2, C12 atoms from plane 2 [0·052 (10), 0·116 (10), 0·332 (12) Å respectively], and unequal equivalent torsion angles [e.g. C2N3C4C5 = −65·8 (10) and C2N1C7C6 = 48·8 (10)°] indicate small distortion of the benzodiazepine ring. Both diazepine N atoms are protonated in the crystal, but the N1−C2 = 1·311 (2) and N3−C2 = 1·369 (8) Å bonds are not equal; this suggests that N1−C2 has significant double-bond character in solution, consistent with NMR results (Brzezinska, unpublished data). The N2−C2 bond, 1·301 (8) Å, is also shorter than a normal single N−C bond, e.g. N2−C12 = 1·463 (10) Å. These data indicate the presence of an aminodiazepine ion. The ionic form of the compound is stabilized by hydrogen bonds N1···Cl(1) = 3·284 (20) Å   [HN1···Cl(1) = 2·93 (32) Å, N−HN1···Cl(1) = 112·2 (54)°, N1 from the molecule at x, y, z], N2···Cl(1) = 3·202 (24) Å [HN2···Cl(1) = 2·29 (20) Å,   N2−HN2···Cl(1) = 157·7 (46)°],

N3···Cl(1) = 3·389 (24) Å   [HN3···Cl(1) = 2·34 (17) Å, N3−HN3···Cl = 154·6 (57)°, the N2 and N3 atoms from the molecule at −x, ½+y, ½−z]. These interactions in the crystal (see Fig. 2) result in the formation of chains of type [molecule 1···Cl(1)··· molecule 3]ₙ and [molecule 2···Cl(2)···molecule 4]ₙ, which are connected only by van der Waals forces.

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Structure of Y₂BaCuO₅: a Refinement by Single-Crystal X-ray Diffraction

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Abstract. $M_r = 458·7$, orthorhombic, *Pbnm*, $a = 7·1276$ (8), $b = 12·1742$ (9), $c = 5·6564$ (7) Å, $V = 490·82$ (9) Å³, $Z = 4$, $D_x = 6·21$ Mg m⁻³, $\lambda(Ag\ K\alpha) = 0·56087$ Å, $\mu = 19·2$ mm⁻¹, $F(000) = 828$, $T = 300$ K, $R = 0·020$ for 1661 unique observed reflections. Seven O atoms are bonded similarly to each Y atom, 11 O atoms to the Ba atom. Five O atoms coordinate pyramidally to the Cu atom which is shifted 0·23 Å from the basal plane towards the apex of the coordination pyramid. Bond lengths are: Y−O 2·276 (2)−2·378 (2), Ba−O 2·609 (2)−3·244 (2), and Cu−O 1·972 (2)−2·205 (2) Å.

Experimental. Crystals grown by sintering a mixture of BaCO₃, Y₂O₃ and CuO at 1203 K for 40 h in air. Details of data collection and structure refinement are summarized in Table 1. The structure was refined by full-matrix least squares; the initial values of the positional parameters were those reported by Michel & Raveau (1982).

Table 1. *Experimental details*

Crystal	Green, needle along c, $0.1 \times 0.07 \times 0.2$ mm
Crystal faces	Approximately $(0\bar{1}0)$, $(1\bar{1}0)$, (140), $(\bar{1}20)$, $(\bar{1}40)$, (001), $(00\bar{1})$
Diffractometer	Rigaku AFC-3, graphite monochromator
Scan	ω mode, width $1.8°$, speed $2°$ min^{-1}, 2θ range $3-70°$, $(\sin\theta)/\lambda < 1.02$ $Å^{-1}$
Standards	600, $\bar{6}00$, 060, $0\bar{6}0$, 006; every 50 reflections; gradual decrease (probably in source intensity): $1.0 \to 0.98$ in F
hkl range	$0-14$, $-24-24$, $0-11$, and additional $\bar{h}0l$
Reflections measured	4993 (2352 unique)
observed	3241 (1661 unique): $|F_o| > 3\sigma(|F_o|)$, $R_{int} = 0.023$
Corrections	Lp, stability (linearly), absorption (numerical integration)
Transmission factors	$0.16-0.43$
Unit cell	32 reflections, $20.0 < \theta < 22.5°$
Function minimized	$\sum w(F_o - F_c)^2$, $w^{-1} = \sigma^2(|F_o|) + (0.025|F_o|)^2$
Parameters refined	50
Extinction parameter	$0.14(1) \times 10^{-4}$
R; wR, S	0.020, 0.035, 1.07
Max. shift/e.s.d.	0.02
$\Delta\rho$	$+2.7$ and -2.7 e $Å^{-3}$ (near the Ba atom)

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^5$, $\times 10^4$ *for* O) *with e.s.d.'s*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Y(1)	$0.11635(4)$	$0.28822(2)$	0.2500	$449(9)$
Y(2)	$0.39588(4)$	$0.07387(2)$	0.2500	$446(9)$
Ba	$0.06977(3)$	$0.09520(2)$	0.7500	$808(7)$
Cu	$0.28736(6)$	$0.34059(4)$	0.7500	$522(13)$
O(1)	$0.1656(2)$	$0.4323(2)$	$0.5070(3)$	$79(5)$
O(2)	$0.3563(2)$	$0.2277(2)$	$0.5041(4)$	$90(6)$
O(3)	$0.0798(3)$	$0.1004(2)$	0.2500	$78(8)$

The atomic coordinates of some atoms differ from but are symmetry equivalent to those reported by Michel & Raveau (1982) and Hazen *et al.* (1987).

Table 3. *Bond lengths (Å) and angles (°)*

Y(1)—O(1)	$2.305(2)$	Ba—O(1^{ii})	$3.063(2)$
Y(1)—O(2)	$2.352(2)$	Ba—O(1^{iv})	$3.244(2)$
Y(1)—O(2^i)	$2.326(2)$	Ba—O(2)	$2.951(2)$
Y(1)—O(3)	$2.301(2)$	Ba—O(2^{iv})	$3.005(2)$
Y(2)—O(1^{ii})	$2.297(2)$	Ba—O(3)	$2.8298(4)$
Y(2)—O(1^{iii})	$2.365(2)$	Ba—O(3^v)	$2.609(2)$
Y(2)—O(2)	$2.378(2)$	Cu—O(1)	$1.972(2)$
Y(2)—O(3)	$2.276(2)$	Cu—O(2)	$2.016(2)$
		Cu—O(3^{vi})	$2.205(2)$

O(1)—Y(1)—O(1^{vii})	$78.20(8)$	O(1^{ii})—Y(2)—O(2)	$100.71(8)$
O(1)—Y(1)—O(2)	$75.07(7)$	O(1^{ii})—Y(2)—O(2^{vii})	$161.99(8)$
O(1)—Y(1)—O(2^{vii})	$120.86(7)$	O(1^{ii})—Y(2)—O(3)	$85.28(8)$
O(1)—Y(1)—O(2^i)	$124.20(7)$	O(1^{iii})—Y(2)—O(1^x)	$71.09(5)$
O(1)—Y(1)—O(2^{viii})	$78.91(7)$	O(1^{iii})—Y(2)—O(2)	$118.22(7)$
O(1)—Y(1)—O(3)	$140.65(8)$	O(1^{iii})—Y(2)—O(2^{vii})	$76.71(7)$
O(2)—Y(1)—O(2^{vii})	$75.32(7)$	O(1^{iii})—Y(2)—O(3)	$144.03(7)$
O(2)—Y(1)—O(2^i)	$156.76(7)$	O(2)—Y(2)—O(2^{vii})	$74.39(8)$
O(2)—Y(1)—O(2^{viii})	$100.83(6)$	O(2)—Y(2)—O(3)	$76.75(8)$
O(2)—Y(1)—O(3)	$76.77(8)$	O(1)—Cu—O(1^{xi})	$88.37(8)$
O(2^i)—Y(1)—O(2^{viii})	$73.47(6)$	O(1)—Cu—O(2)	$90.71(9)$
O(2^i)—Y(1)—O(3)	$80.04(8)$	O(1)—Cu—O(2^{xi})	$166.91(9)$
O(1^{ii})—Y(2)—O(1^{ix})	$78.53(8)$	O(1)—Cu—O(3^{vi})	$103.39(8)$
O(1^{ii})—Y(2)—O(1^{iii})	$119.95(7)$	O(2)—Cu—O(2^{xi})	$87.24(10)$
O(1^{ii})—Y(2)—O(1^x)	$76.31(7)$	O(2)—Cu—O(3^{vi})	$89.52(9)$

Symmetry operations: (i) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (ii) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, z; (iii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$; (iv) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (v) $-x$, $-y$, $1-z$; (vi) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (vii) x, y, $\frac{1}{2}-z$; (viii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (ix) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; (x) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (xi) x, y, $\frac{1}{2}-z$.

Systematic absences were carefully examined: neither $0kl$ with $k = $ odd nor $h0l$ with $h + l = $ odd were observed with few exceptions which were confirmed by ψ-scan technique to be a result of multiple reflection. Hazen, Finger, Angel, Prewitt, Ross, Mao, Hadidiacos, Hor, Meng & Chu (1987) observed several weak $0kl$ with $k = $ odd, and proposed the possible space group $P2_1nm$ for slightly non-stoichiometric crystals; this space group, however, was ruled out for the present crystal. Two space groups, $Pbnm$ (centrosymmetric) and $Pbn2_1$ (non-centrosymmetric), are possible from the extinction rules above. Refinements were attempted separately for both space groups; they converged at nearly the same R value, and resulted in quite similar atomic coordinates; accordingly, the space group $Pbnm$ was selected. A least-squares fit of site occupancies showed no atomic deficiency within experimental accuracy and only a 2.5% deficiency in the O(1) site (see Fig. 1); therefore, full occupancy of all atoms was assumed in the final refinement.

Positional and equivalent isotropic thermal parameters are given in Table 2;* geometrical details in Table 3. Fig. 1 shows a projection of the structure along c and the numbering scheme of the atoms. Atomic scattering factors, and f', f'' values taken from *International Tables for X-ray Crystallography* (1974); for O^{2-}, values of Tokonami (1965) were used. All calculations performed on a FACOM M-380R computer at ISSP, The University of Tokyo. Programs used were *UNICS*II (Sakurai, 1967), *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979), *ORTEP* (Johnson, 1965) and those prepared at ISSP.

Related literature. The structure of the title compound was first determined by means of powder dif-
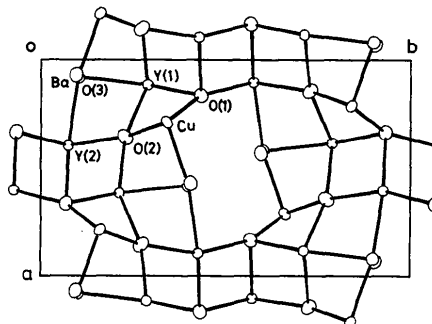
Fig. 1. A projection of the structure along c. Thermal displacement ellipsoids are drawn at the 90% probability level.

fraction (Michel & Raveau, 1982) and then by single-crystal diffractometry (Hazen *et al.*, 1987).

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Tetraaquatrinitratopraseodymium–4,4'-Bipyridine–Water (1/2/1)

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Abstract. $[Pr(NO_3)_3(H_2O)_4].2C_{10}H_8N_2.H_2O$, $M_r = 729.4$, orthorhombic, $P2_12_12_1$, $a = 7.142$ (3), $b = 16.119$ (12), $c = 24.816$ (24) Å, $V = 2857$ (6) Å^3, $Z = 4$, $D_x = 1.695$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 140$ cm^{-1}, $F(000) = 1452$, $T = 294$ K, $R = 0.051$ for 1270 observed reflections. The compound is isostructural with the neodymium analogue [Al-Rasoul & Drew (1987). *Acta Cryst.* C**43**, 2081–2084] apart from having larger [32, 34 (2)°] dihedral angles between the rings of the 4,4'-bpy molecules. The complex contains ten-coordinate Pr with three bidentate nitrate ligands [Pr–O 2.52–2.75 (3) Å] and four aqua ligands [Pr–O 2.46–2.48 (2) Å], and has approximate twofold symmetry. The complex, the 4,4'-bpy molecules, and the lattice water molecule are linked *via* a three-dimensional system of hydrogen bonds.

Experimental. Preparation: Weakley (1982). Intensity data from multi-film Weissenberg photographs (layers 0–4*kl*, *h*0–5*l*), scanned by microdensitometer (SERC Service, Daresbury Laboratory, Warrington, England); crystal dimensions $0.17 \times 0.17 \times 0.45$ and $0.15 \times 0.15 \times 0.39$ mm; merging $R = 0.094$ before, 0.068 after absorption correction (transmission factors 0.091 to 0.375); range of indices $0 \le h \le 8$, $0 \le k \le 19$, $0 \le l \le 30$. The data films showed sharp reflections to high angles ($2\theta_{max} = 143°$) but in many festoons the reflections were all weak or absent. The only *systematic*

absence appeared to be 0*kl* for *k* odd [the absences in *h*00 and 00*l* were taken to be special cases of the general weakness of *h*0*l* reflections with ($h + l$) odd], but attempts to solve the structure in space groups *Pbm2*, *Pb2$_1$m* and *Pbmm* were unsuccessful (Weakley, 1984). The similarity of the cell parameters to those of the Nd compound (Al-Rasoul & Drew, 1987) prompted a successful structure solution in $P2_12_12_1$: Pr coordinates from Patterson synthesis, other non-H atoms from difference syntheses (problem of false mirror symmetry from situation of Pr at $z \simeq 0.25$); anisotropic thermal parameters for Pr, NO$_3$, water O atoms; 4,4'-bpy C, N isotropic; H atoms included at calculated positions riding on C atoms; blocked-matrix least-squares refinement (on F) converged at $R = 0.051$, $wR = 0.070$, 250 parameters, 1270 independent data, function minimized $\sum w(\Delta F)^2$; $w = [1 + 0.00545F^2]^{-1}$, max. $\Delta/\sigma = 0.18$ in last cycle, final $\Delta\rho$ synthesis flat to ± 0.90 e Å^{-3}. All calculations by use of *SHELX*76 (Sheldrick, 1976), which incorporated atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1, and selected dimensions in Table 2.† The labelling of atoms is shown in Fig. 1.

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† Lists of structure factors, anisotropic thermal parameters, remaining bond lengths and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51462 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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