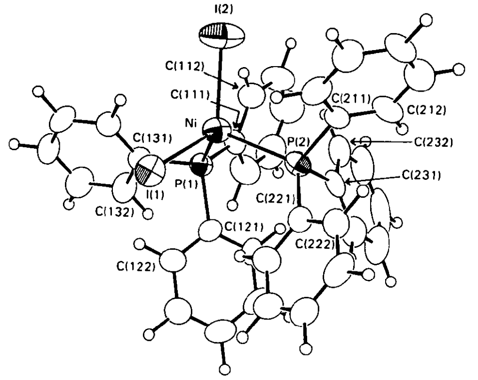

Fig. 1. Perspective view of $I_2Ni(PPh_3)_2$ (50% thermal ellipsoids). The numbering of C atoms in the phenyl rings is cyclic, C(*ijk*), where *i* is the number of the attached phosphorus, *j* = 1–3, and *k* = 1–6. H atoms, which have been given an artificial radius of 0·1 Å for clarity, carry the same number as the C atom to which they are attached.

latter angle is 123·3°, in the dibromide 126·3 (1)°, and in the diiodide herein, only 118·12 (6)°. In fact, in terms of the root-mean-square distortion (r.m.s.d.) of the angles at nickel from the tetrahedral ideal, the diiodide (r.m.s.d. 4·99°) is the least distorted molecule, the dichloride intermediate (r.m.s.d. 7·56°), and the dibromide the most distorted (r.m.s.d. 8·10°). These results emphasize the dangers of the assumption of simple structural patterns in a series of seemingly innocuous analogues. Since none of the three compounds are pairwise isomorphous it is certainly possible that differing intramolecular steric requirements of the triphenylphosphine ligands are at least partially responsible for the observed angles at nickel, but we have not pursued this possibility in any detail.

The Ni—I distances in $I_2Ni(PPh_3)_2$ are barely different, average 2·5307 (25) Å. In contrast, Ni—P(2) is longer than Ni—P(1) by 0·081 (4) Å, the average Ni—P distance being 2·382 (4) Å. This is longer than that observed in the dichloride (2·28 Å) and the dibromide (2·333 Å), a trend that can readily be correlated with the decreasing π-donor capability of the heavier halides. On the other hand, the changes in the average Ni—*X* distance [dichloride to dibromide, 0·07 Å (less than the difference in covalent radii), and dibromide to diiodide, 0·19 Å (exactly the difference in covalent radii)] do not easily fit with this pattern. A case could be made for a redetermination of $Cl_2Ni(PPh_3)_2$, for which only a rather inaccurate two-dimensional study is currently available (GHPV, 1963).

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Structure of Aqua[*N*,*N*′-bis(β-carbamoylethyl)-*trans*-1,2-cyclohexanediamine]copper(II) Perchlorate*

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Abstract. $[Cu(C_{12}H_{24}N_4O_2)(H_2O)](ClO_4)_2$, M_r = 536·81, monoclinic, $P2_1/c$, a = 15·445 (3), b = 11·412 (2), c = 13·745 (3) Å, β = 116·12 (2)°, V = 2175·5 (7) Å^3, Z = 4, D_x = 1·639 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 12·54 cm^{-1}, $F(000)$ = 1108, R = 0·054, wR = 0·059 for 2612 independent reflections at room temperature. The copper(II) ion is in a slightly distorted square pyramid with the diaminodiamide equatorial and the O atom of the aqua group axial. The perchlorate anions are disordered in the lattice.

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* Aqua(3-{2-[(2-carbamoylethyl)amino]cyclohexylamino}propionamide)copper(II) diperchlorate.

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Introduction. We have recently initiated a systematic structural study of copper(II) complexes of diaminodiamides. In previous papers we have reported the crystal structures of copper(II) complexes of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, bcen (Lee, Lu, Liu, Chung & Lee, 1984), *N,N'*-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine, bchtn (Lee, Hong, Liu, Chung & Lee, 1984), *N,N'*-bis(β-carbamoylethyl)trimethylenediamine, bctn (Hong, Lee, Lee, Chao & Chung, 1987), and *N,N'*-bis(β-carbamoylethyl)-*N*-methylethylenediamine, *N*-Mebcen (Lu, Shan, Chao & Chung, 1987). In this study, the title compound, $[Cu(L\text{-}2,Cy,2)(H_2O)](ClO_4)_2$, has been synthesized and the three-dimensional structure determination by X-ray diffraction methods has been completed.

Experimental. The ligand, *N,N'*-bis(β-carbamoylethyl)-*trans*-1,2-cyclohexanediamine (*L*-2,Cy,2), was prepared from *trans*-1,2-cyclohexanediamine (22·8 g; 0·2 mol) and acrylamide (28·4 g; 0·4 mol) in acetonitrile (100 cm³) by heating the mixture under reflux for 2 h. The solution was cooled and the product filtered off, washed with acetonitrile, recystallized from acetonitrile, and dried in air; m.p. 387–388 K (composition calc. for $C_{12}H_{26}Cl_2CuN_4O_{11}$: C, 26·81; H, 4·84; N, 10·43; O, 32·77; Cl, 13·22; Cu, 11·83%; found: C, 26·62; H, 4·56; N, 10·66; Cu, 11·61%). *L*-2,Cy,2 (6·4 g) was added to an aqueous solution of copper(II) perchlorate (9·3 g) and heated until it completely dissolved; the solution was filtered immediately while hot. After evaporation of the filtrate, blue crystals of $[Cu(L\text{-}2,Cy,2)(H_2O)](ClO_4)_2$ were formed. Single crystals were obtained by recrystallization in a mixture of water and ethanol, after slow evaporation of the solvent at room temperature. The crystals obtained are deep blue and rod-like.

A MicroVAXII computer-controlled Nicolet *R*3*m*/*V* diffractometer equipped with a graphite monochromator (Mo *K*α radiation) was used for intensity data collection. Lattice constants were obtained from a least-squares fit to the automatically centered settings for 18 reflections with $11{\cdot}96° \leq 2\theta \leq 21{\cdot}88°$. The space group $P2_1/c$ was unambiguously determined from the systematic absences $0k0$, $k = 2n+1$; $h0l$, $l = 2n+1$. $\theta/2\theta$ scan data were collected at room temperature (298 K) for two octants of the sphere ($-19 \leq h \leq 19$, $0 \leq k \leq 14$, $0 \leq l \leq 17$) out to the 2θ limit of 50°. A variable scan speed of 2·09–14·65° min^{-1} was used. Three standard reflections were monitored every 50 reflections and showed no signs of crystal deterioration. The data were corrected for Lorentz and polarization effects. 4431 reflections were collected, 3850 unique, of which 2612 observed reflections with $I > 3\sigma(I)$ were used for refinement of the structure. An empirical absorption correction based on 252 azimuthal (ψ) scans was applied to the data: R(before) = 5·23% and R(after) = 2·09% where R(before) and R(after) refer to the fit of the calculated intensities to the observed intensities of the azimuthal scans (*SHELXTL PLUS*; Sheldrick, 1986). The estimated maximum and minimum transmission factors were 0·994 and 0·666. The structure was solved by a direct method using *SHELXTL PLUS* (Sheldrick, 1986). Full-matrix least-squares refinement on F with anomalous-dispersion corrections for atoms with atomic numbers greater than 16. Neutral-atom scattering form factors from *International Tables for X-ray Crystallography* (1974) were used. The weights had the form $w = [\sigma^2(F) + gF^2]^{-1}$ with $g = 0{\cdot}00071$. All hydrogen atoms included in the refinement were placed in idealized positions (C—H = 0·96 Å, H—C—H = 109·4°) and fixed U (0·06 Å²) after the non-hydrogen atoms were refined anisotropically. During the course of structure refinement, it was found that all eight oxygen atoms of the two ClO_4^- ions had abnormally large thermal parameters and there were also a few electron density peaks of height greater than 0·95 e Å^{-3} very close to the Cl atoms, suggesting disordered ClO_4^- ions. Three sets of oxygen atoms could be located for each Cl atom. The oxygen occupancy factors were then refined with constraint on the bond length of Cl—O and the distance between oxygen atoms. The refinement yielded values of

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic displacement parameters* (Å²×10³)

	x	y	z	U_{eq}*
Cu	3424 (1)	5322 (1)	5308 (1)	40 (1)
N(1)	2146 (4)	4641 (5)	4332 (4)	44 (2)
N(2)	2716 (4)	6801 (4)	5220 (5)	43 (2)
N(3)	5790 (4)	7312 (5)	7199 (4)	52 (3)
N(4)	4397 (5)	1945 (5)	5427 (5)	57 (3)
O(1)	4091 (3)	3805 (4)	5612 (4)	49 (2)
O(2)	4682 (3)	5993 (4)	6261 (4)	48 (2)
O(3)	3819 (3)	5742 (5)	3831 (4)	58 (2)
C(1)	3781 (5)	2827 (6)	5195 (5)	46 (3)
C(2)	2748 (6)	2594 (6)	4419 (6)	55 (3)
C(3)	2028 (5)	3408 (6)	4593 (6)	54 (3)
C(4)	1401 (5)	5456 (6)	4325 (7)	58 (3)
C(5)	400 (6)	5238 (8)	3457 (9)	95 (5)
C(6)	−292 (7)	6191 (10)	3419 (12)	140 (8)
C(7)	66 (7)	7370 (10)	3341 (11)	127 (7)
C(8)	1050 (6)	7625 (8)	4246 (9)	92 (5)
C(9)	1751 (5)	6704 (6)	4282 (6)	51 (3)
C(10)	3283 (5)	7840 (6)	5169 (6)	50 (3)
C(11)	4165 (5)	8019 (6)	6181 (6)	50 (3)
C(12)	4893 (5)	7046 (6)	6541 (5)	43 (3)
Cl(1)	2046 (2)	4637 (2)	1310 (2)	70 (1)
O(4*A*)†	2140 (7)	5849 (6)	1693 (7)	94 (3)
O(5*A*)	2085 (7)	3886 (9)	2131 (7)	94 (3)
O(6*A*)	1249 (6)	4488 (10)	319 (6)	94 (3)
O(7*A*)	2938 (6)	4503 (9)	1180 (8)	94 (3)
Cl(2)	3202 (1)	5401 (1)	7893 (1)	46 (1)
O(8*A*)	3186 (9)	6597 (7)	7678 (10)	77 (2)
O(9*A*)	4125 (6)	5102 (9)	8808 (7)	77 (2)
O(10*A*)	2496 (8)	5082 (9)	5258 (10)	77 (2)
O(11*A*)	3102 (10)	4698 (11)	6999 (8)	77 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Only the coordinates of the oxygen atoms of set *A* for the perchlorate ions are listed (see text).

Table 2. *Selected bond lengths* (Å) *and bond angles* (°)

Cu—N(1)	1·992 (5)	Cu—N(2)	1·986 (5)
Cu—O(1)	1·963 (4)	Cu—O(2)	1·958 (4)
Cu—O(3)	2·412 (5)	N(1)—C(3)	1·484 (8)
N(1)—C(4)	1·477 (8)	N(2)—C(9)	1·484 (8)
N(2)—C(10)	1·493 (8)	N(3)—C(12)	1·314 (8)
N(4)—C(1)	1·325 (9)	O(1)—C(1)	1·250 (7)
O(2)—C(12)	1·260 (7)	C(1)—C(2)	1·501 (10)
C(2)—C(3)	1·546 (10)	C(4)—C(5)	1·501 (10)
C(4)—C(9)	1·534 (10)	C(5)—C(6)	1·509 (13)
C(6)—C(7)	1·476 (15)	C(7)—C(8)	1·508 (12)
C(8)—C(9)	1·494 (10)	C(10)—C(11)	1·471 (9)
C(11)—C(12)	1·501 (9)	Cl(1)—O(4*A*)	1·464 (7)
Cl(1)—O(5*A*)	1·397 (6)	Cl(1)—O(6*A*)	1·387 (6)
Cl(1)—O(7*A*)	1·472 (7)	Cl(2)—O(8*A*)	1·394 (7)
Cl(2)—O(9*A*)	1·467 (7)	Cl(2)—O(10*A*)	1·434 (7)
Cl(2)—O(11*A*)	1·418 (6)		

N(2)—Cu—N(1)	86·3 (2)	O(1)—Cu—N(1)	94·1 (2)
O(1)—Cu—N(2)	170·4 (2)	O(2)—Cu—N(1)	179·7 (1)
O(2)—Cu—N(2)	93·8 (2)	O(2)—Cu—O(1)	86·0 (2)
O(3)—Cu—N(1)	93·0 (2)	O(3)—Cu—N(2)	96·7 (2)
O(3)—Cu—O(1)	92·9 (2)	O(3)—Cu—O(2)	86·6 (2)
C(3)—N(1)—Cu	113·4 (4)	C(4)—N(1)—Cu	107·2 (4)
C(4)—N(1)—C(3)	114·9 (5)	C(9)—N(2)—Cu	107·8 (4)
C(10)—N(2)—Cu	111·1 (4)	C(10)—N(2)—C(9)	113·8 (5)
C(1)—O(1)—Cu	129·1 (5)	C(12)—O(2)—Cu	128·6 (4)
O(1)—C(1)—N(4)	118·6 (7)	C(2)—C(1)—N(4)	117·5 (6)
C(2)—C(1)—O(1)	123·9 (6)	C(3)—C(2)—C(1)	113·3 (6)
C(2)—C(3)—N(1)	111·0 (6)	C(5)—C(4)—N(1)	115·3 (6)
C(9)—C(4)—N(1)	107·4 (5)	C(9)—C(4)—C(5)	112·4 (7)
C(6)—C(5)—C(4)	111·9 (8)	C(7)—C(6)—C(5)	112·2 (9)
C(8)—C(7)—C(6)	112·9 (10)	C(9)—C(8)—C(7)	110·1 (8)
C(4)—C(9)—N(2)	105·8 (5)	C(8)—C(9)—N(2)	114·4 (6)
C(8)—C(9)—C(4)	113·1 (6)	C(11)—C(10)—N(2)	112·6 (6)
C(12)—C(11)—C(10)	117·1 (6)	O(2)—C(12)—N(3)	118·9 (6)
C(11)—C(12)—N(3)	117·8 (6)	C(11)—C(12)—O(2)	123·3 (6)

0·54 (1) (set *A*), 0·13 (1) (set *B*) and 0·337 (8) (set *C*) for the site factors of oxygen atoms bonded to Cl(1); and 0·51 (1) (set *A*), 0·143 (6) (set *B*) and 0·40 (1) (set *C*) for the oxygen atoms bonded to Cl(2). The final refined value for the Cl—O distance was 1·427 (2) Å, and the distance between the oxygen atoms was 2·330 (5) Å. The thermal parameters of C6 and C7 are also large compared with others. It was carefully checked that there was no disorder. The exact reason for the larger thermal parameters is not clear to us at present. For 272 variables and 2612 reflections the final agreement factors are $R = 0.054$, $wR = 0.059$; $(\Delta/\sigma)_{\max}$ in final refinement cycle was 0·06. The maximum height in final difference map was 0·51 e Å^{-3}, close to O(4*A*) (0·661 Å).

Discussion. The atomic coordinates and temperature factors are listed in Table 1. Bond lengths and angles are listed in Table 2.* The structure of this blue complex and the deviations of the atoms from the N_2O_2 plane are shown in Fig. 1, where it can be seen that the Cu^{II} ion is in a slightly distorted square pyramid with the diaminodiamide equatorial and the O atom of the aqua group axial. Cu^{II} is 0·08 Å out of the N_2O_2 plane toward the aqua group. The two asymmetric nitrogens, N(1) and N(2), are of the same *R* or *S* configuration. The diaminodiamide is in a planar coordination with the two terminal six-membered chelate rings in a stable chair form and the central five-membered chelate ring in a stable *gauche* form. The arrangement of the *L*-2,Cy,2 ligand in this complex appears to be relatively strain-free. In addition, the two N—Cu—O bond angles (179·7, 170·4°) are close to 180° and the CuN_2O_2 group is almost planar. Thus a strong Cu^{II}–ligand overlap is expected in this complex. The two perchlorate ions are not within the bonding distance of the cation. These perchlorate anions are disordered in the lattice. The equatorial Cu—N and Cu—O bond distances are typical for copper(II)–diaminodiamide complexes (Lee, Lu, Liu, Chung & Lee, 1984; Lee, Hong, Liu, Chung & Lee, 1984; Hong, Lee, Lee, Chao & Chung, 1987). The axial Cu—O bond distance (2·412 Å) is significantly longer than the equatorial Cu—O distances (1·958 and 1·963 Å).

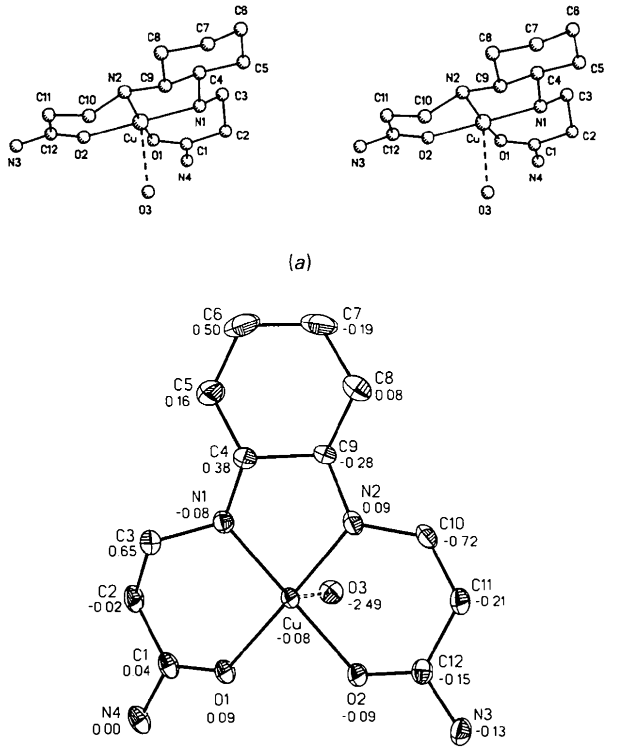

Fig. 1. The molecular structure of [Cu(*L*-2,Cy,2)(H_2O)](ClO_4)$_2$ excluding the perchlorate ions: (*a*) a stereoview; (*b*) an *ORTEP* drawing with the deviations of atoms from the N_2O_2 plane (Å) (the atom positions below the plane are indicated by negative signs).

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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 51029 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Both $[Cu(bcen)(NO_3)(H_2O)]NO_3.H_2O$ (Lee, Lu, Liu, Chung & Lee, 1984) and the title compound contain 6,5,6-membered chelate rings. Comparing the crystal structures of these two complexes, we find the following results: (1) for each of these two complexes, the two asymmetric nitrogens are of the same *R* or *S* configuration, and the central five-membered chelate ring adopts a stable *gauche* conformation; (2) the two terminal six-membered chelate rings of each of these two complexes are in stable chair forms; (3) the coordination numbers for these two complexes are different; $[Cu(bcen)(NO_3)(H_2O)]NO_3.H_2O$ is of the 4+2 type but $[Cu(L\text{-}2,Cy,2)(H_2O)](ClO_4)_2$ is five-coordinate. This difference may be due to the steric effects of the cyclohexane substituent on the central chelate ring.

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Structure of μ-Acetato-di-μ-carbonyl-bis[(2,2′-bipyridyl)carbonylruthenium(I)](*Ru–Ru*) Tetraphenylborate

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Abstract. $[Ru_2(\mu\text{-}O_2CCH_3)(CO)_2(\mu\text{-}CO)_2(bipy)_2]BPh_4$ (bipy = 2,2′-bipyridine), $[Ru_2(C_{10}H_8N_2)_2(C_2H_3O_2)(CO)_4][B(C_6H_5)_4]$, $M_r = 1004{\cdot}84$, monoclinic, $P2_1/c$, $a = 15{\cdot}900\ (3)$, $b = 17{\cdot}731\ (4)$, $c = 15{\cdot}739\ (7)$ Å, $\beta = 104{\cdot}16\ (3)°$, $V = 4302{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}55$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}668$ mm^{-1}, $F(000) = 2032$, $T = 295\ (1)$ K, $wR = 0{\cdot}033$ for 6115 unique reflections with $F_o \geq 4\sigma(F_o)$. The dimer consists of two Ru atoms bridged by two carbonyl ligands, an acetate ligand and a metal–metal bond, with the octahedral coordination around each metal atom completed by a terminal carbonyl and a chelate bipyridine ligand. The two octahedra thus formed share an edge *via* μ-CO ligands, resulting in the juxtaposition of two Ru atoms in an edge-sharing bioctahedron with an Ru—Ru distance of 2·709 (1) Å.

Introduction. Although a number of dimers containing the metal–metal bonded ruthenium(I)–ruthenium(I) unit are known, of which $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (Fischer & Vogler, 1962) represents the most widely studied, reliable synthetic routes to ruthenium(I) complexes are not available. To address this problem we have investigated the use of the readily available carboxylato polymer *catena*-$[Ru(O_2CMe)(CO)_2]$ [(1), Me = CH_3] (Crooks, Johnson, Lewis, Williams & Gamlen, 1969) as a precursor for ruthenium(I) dimers. Our investigations have illustrated the versatility of (1) and the acetonitrile derivative, $[Ru(O_2CMe)(CO)_2(NCMe)]_2$, in the syntheses of a range of neutral and cationic dimeric complexes containing isocyanide (Albers, Liles, Singleton, Stead & Steyn, 1986) and mono- and bidentate tertiary phosphorus ligands (Sherlock, Cowie, Singleton & Steyn, 1988; Singleton, Steyn & van Rooyen, 1988). The acetate complex provides the only readily accessible precursor for high-yield syntheses of the known carbonyl dimers, $[(\eta^2\text{-}C_5R_5)Ru(CO)_2]_2$ (R = H, Me), and the new polypyrazolylborato analogue, $[\{HB(pz)_3\}Ru(CO)_2]_2$ (pz = pyrazolyl) (Liles, Robinson, Singleton & Steyn, 1987). The extension of this study of reactions of (1) with a variety of diamine ligands led to the formation of a series of cationic bioctahedral structures with bridging carbonyl ligands. Confirmatory structural evidence has been

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