

counterion. For monatomic counterions, the bond length is longer than for polyatomic {2.00 (3), 2.004 (19) Å in $\text{Co}[\text{Au}(\text{CN})_2]_2$, Zyontz, Abrahams & Bernstein, 1981; 1.994 (11) Å in $\text{KCo}[\text{Au}(\text{CN})_2]_3$, Abrahams, Bernstein, Liminga & Eisenmann, 1980; 1.993–1.998 (22) Å in $\text{K}_5[\text{Au}(\text{CN})_2]_4[\text{Au}(\text{CN})_2\text{I}_2] \cdot 2\text{H}_2\text{O}$, Bertinotti & Bertinotti, 1972: *cf.* 1.939 (19) Å in a $\text{C}_{10}\text{H}_{10}\text{S}_4\text{Se}_2^{0.5+}$ salt, Kikuchi, Ishikawa, Saito, Ikemoto & Kobayashi, 1988; 1.88, 1.94 (2) Å in a potassium crown ether salt, Krasnova *et al.*, 1984}. This could be attributable to the effects of N...metal interactions. Secondly, for large counterions, the Au—C bond is longer for $\text{Au}(\text{CN})_4^-$ than for $\text{Au}(\text{CN})_2^-$; this may be a consequence of the better 'soft-soft' interactions for Au^+ . These conclusions must be regarded as tentative, but are supported by observations of AuCl_4^- and AuCl_2^- salts, with more ionic bonding and less sensitivity of the Au—X bond length to oxidation state; a large number of AuCl_4^- salts have Au—Cl bond lengths near the typical value of *ca* 2.27 Å (Jones, 1981), and various AuCl_2^- salts show similar values, *e.g.* 2.257 (4) Å for the Bu_4N^+ salt (Braunstein, Müller & Bögge, 1986), 2.269–2.286 (6) Å for the Et_4N^+ salt (Helgesson & Jagner, 1987), and 2.260 (14), 2.293 (15) Å for the py_2Au^+ salt (Adams, 1980).

Future, more extensive measurements may enable us to distinguish the effects of other factors such as hybridization and electrostatic interactions.

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Structure of [3,3'-(2,2-Dimethylpropylene)diiminodipropionamide]copper(II) Perchlorate Monohydrate

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Abstract. $[\text{Cu}(\text{C}_{11}\text{H}_{24}\text{N}_4\text{O}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $M_r = 524.8$, monoclinic, $P2_1/c$, $a = 16.757$ (4), $b = 11.290$ (3), $c = 11.531$ (3) Å, $\beta = 108.28$ (2)°, $U = 2071.4$ (9) Å³, $Z = 4$, $D_x = 1.683$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 1.37$ mm⁻¹, $F(000) = 1084$, $T = 295$ (3) K, $R = 0.035$, $wR = 0.026$ for 3128 observed reflections. The Cu atom has coordination number six, two O(carbamoyl), two N(diamine) and two O(ClO₄), forming a (4+2)-type complex. The central six-membered ring formed between the ligand and the Cu atom is in the

chair conformation whereas the other two rings are twisted chairs. The solvate water molecules are hydrogen bonded to molecules of the complex, holding them together. The H atoms attached to the amino groups, NH, are on the same side of the least-squares plane of the Cu-coordinated atoms.

Introduction. Previous papers (Liu & Chung, 1985, 1986; Chao & Chung, 1987, 1988; Lee, Lu, Liu, Chung & Lee, 1984; Lee, Hong, Liu, Chung & Lee,

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Cu	0.28659 (3)	-0.00724 (4)	0.01140 (4)	2.288 (23)
Cl(1)	0.35823 (6)	-0.31395 (10)	0.03468 (10)	3.25 (5)
Cl(2)	0.15958 (6)	0.26244 (9)	-0.04496 (10)	3.20 (5)
O(1)	0.3876 (1)	0.0203 (2)	-0.0382 (2)	2.82 (15)
O(2)	0.3646 (1)	0.0441 (2)	0.1701 (2)	2.84 (15)
O(W)	0.4508 (2)	0.2802 (3)	0.1152 (2)	4.32 (19)
O(11)	0.2808 (2)	-0.3756 (3)	-0.0053 (3)	5.04 (18)
O(12)	0.4169 (2)	-0.3789 (3)	0.1273 (3)	6.80 (25)
O(13)	0.3454 (2)	-0.2033 (3)	0.0854 (3)	5.17 (20)
O(14)	0.3883 (2)	-0.2933 (4)	-0.0647 (3)	8.16 (29)
O(21)	0.2458 (2)	0.2283 (3)	0.0096 (3)	4.72 (19)
O(22)	0.1350 (2)	0.2236 (3)	-0.1688 (3)	4.50 (19)
O(23)	0.1495 (2)	0.3858 (2)	-0.0395 (3)	5.78 (21)
O(24)	0.1099 (2)	0.2024 (3)	0.0170 (3)	6.49 (23)
N(1)	0.8106 (2)	0.4588 (3)	0.4241 (3)	2.27 (15)
N(2)	0.7896 (2)	0.0298 (3)	0.1618 (3)	2.25 (16)
N(3)	0.4620 (2)	0.4130 (3)	0.3444 (3)	3.14 (20)
N(4)	0.4081 (2)	0.1097 (3)	0.3610 (3)	4.20 (24)
C(1)	0.3485 (2)	0.0711 (3)	0.2651 (3)	2.65 (19)
C(2)	0.2608 (2)	0.0628 (4)	0.2721 (3)	2.97 (21)
C(3)	0.7838 (2)	0.4528 (3)	0.2890 (3)	2.81 (20)
C(4)	0.8593 (2)	0.3493 (3)	0.4737 (3)	2.63 (19)
C(5)	0.9016 (2)	0.1533 (3)	0.1108 (3)	2.57 (19)
C(6)	0.8392 (2)	0.1419 (3)	0.1819 (3)	2.66 (19)
C(7)	0.7474 (2)	0.0216 (4)	0.2573 (3)	3.10 (25)
C(8)	0.3107 (2)	0.4143 (4)	0.2604 (3)	2.94 (22)
C(9)	0.3902 (2)	0.4376 (3)	0.3621 (3)	2.35 (19)
C(10)	0.9714 (2)	0.0597 (4)	0.1519 (4)	3.33 (23)
C(11)	0.9416 (2)	0.2761 (4)	0.1391 (4)	3.81 (26)

*B*_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 2. Bond lengths (Å) and angles (°)

Cu—O(1)	1.973 (2)	Cu—O(2)	1.974 (2)
Cu—N(1)	2.028 (3)	Cu—N(2)	2.021 (3)
Cl(1)—O(11)	1.416 (3)	Cl(1)—O(12)	1.409 (3)
Cl(1)—O(13)	1.424 (3)	Cl(1)—O(14)	1.409 (3)
Cl(2)—O(21)	1.435 (3)	Cl(2)—O(22)	1.426 (3)
Cl(2)—O(23)	1.406 (3)	Cl(2)—O(24)	1.426 (3)
O(1)—C(9)	1.257 (4)	O(2)—C(1)	1.246 (4)
N(1)—C(3)	1.481 (5)	N(1)—C(4)	1.493 (5)
N(2)—C(6)	1.492 (5)	N(2)—C(7)	1.486 (5)
N(3)—C(9)	1.313 (5)	N(4)—C(1)	1.311 (5)
C(1)—C(2)	1.500 (5)	C(2)—C(3)	1.505 (5)
C(4)—C(5)	1.517 (5)	C(5)—C(6)	1.522 (5)
C(5)—C(10)	1.536 (5)	C(5)—C(11)	1.530 (5)
C(7)—C(8)	1.527 (6)	C(8)—C(9)	1.496 (5)
O(1)—Cu—O(2)	81.0 (1)	O(1)—Cu—N(1)	175.1 (1)
O(1)—Cu—N(2)	93.8 (1)	O(2)—Cu—N(1)	95.2 (1)
O(2)—Cu—N(2)	169.4 (1)	N(1)—Cu—N(2)	90.4 (1)
O(11)—Cl(1)—O(12)	109.9 (2)	O(11)—Cl(1)—O(13)	108.9 (2)
O(11)—Cl(1)—O(14)	110.0 (2)	O(12)—Cl(1)—O(13)	107.7 (2)
O(12)—Cl(1)—O(14)	111.1 (2)	O(13)—Cl(1)—O(14)	109.1 (2)
O(21)—Cl(2)—O(22)	106.9 (2)	O(21)—Cl(2)—O(23)	111.4 (2)
O(21)—Cl(2)—O(24)	108.5 (2)	O(22)—Cl(2)—O(23)	110.4 (2)
O(22)—Cl(2)—O(24)	108.9 (2)	O(23)—Cl(2)—O(24)	110.5 (2)
Cu—O(1)—C(9)	127.1 (2)	Cu—O(2)—C(1)	128.6 (2)
Cu—N(1)—C(3)	112.4 (2)	Cu—N(1)—C(4)	115.0 (2)
C(3)—N(1)—C(4)	108.3 (3)	Cu—N(2)—C(6)	114.1 (2)
Cu—N(2)—C(7)	115.1 (2)	C(6)—N(2)—C(7)	108.0 (3)
O(2)—C(1)—N(4)	120.3 (4)	O(2)—C(1)—C(2)	121.3 (3)
N(4)—C(1)—C(2)	118.4 (3)	C(1)—C(2)—C(3)	112.1 (3)
N(1)—C(3)—C(2)	113.3 (3)	N(1)—C(4)—C(5)	115.8 (3)
C(4)—C(5)—C(6)	112.6 (3)	C(4)—C(5)—C(10)	111.7 (3)
C(4)—C(5)—C(11)	105.7 (3)	C(6)—C(5)—C(10)	111.1 (3)
C(6)—C(5)—C(11)	106.9 (3)	C(10)—C(5)—C(11)	108.5 (3)
N(2)—C(6)—C(5)	115.6 (3)	N(2)—C(7)—C(8)	112.4 (3)
C(7)—C(8)—C(9)	109.8 (3)	O(1)—C(9)—N(3)	121.3 (3)
O(1)—C(9)—C(8)	120.3 (3)	N(3)—C(9)—C(8)	118.4 (3)

1984; Lee, Hong, Lee, Liu & Chung, 1985; Hong, Lee, Lee, Chao & Chung, 1987; Lu, Shan, Chao & Chung, 1987*a,b*; Lu, Tsai, Chao & Chung, 1987) have revealed the kinetic and structural data for a series of copper-diaminodiamide complexes. The title compound is one of these, and its structure as determined by X-ray diffraction is reported herein.

Experimental. The ligand, 6,6-dimethyl-4,8-diazaundecanediamide, was prepared by refluxing 0.2 mol of 2,2-dimethylpropylenediamine and 0.4 mol of acrylamide in acetonitrile (100 ml) for 2 h. The compound was purified by recrystallization from acetonitrile. Calc. for C₁₁H₂₄N₄O₂: C, 54.07, H, 9.89, N, 22.93; found: C, 53.68, H, 9.76, N, 23.12%. To an aqueous solution of copper(II) perchlorate (7.45 g), a stoichiometric amount of the ligand compound (4.88 g) was added. Gentle heating was applied until it was completely dissolved. Blue crystals were obtained by evaporation and cooling. A mixed solvent of water and methanol was used to grow the crystal which was later used for X-ray study.

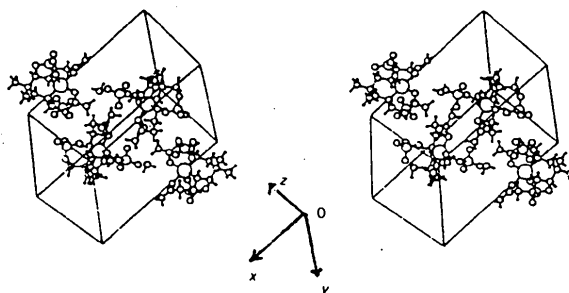


Fig. 1. A stereoview of the packing of the molecules in the unit cell. The origin of the unit cell is at the lower right corner in a right-handed coordinate system.

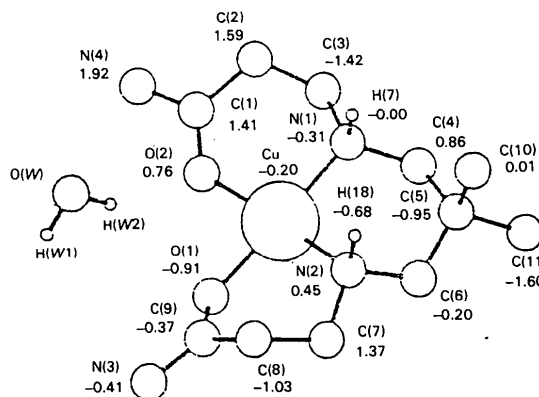


Fig. 2. Perspective view of the atom-numbering scheme of the molecule excluding the perchlorate ions and the H atoms except those attached to N(1) and N(2). Values below the atomic numbering are the displacements (Å) of atoms from the best plane through the coordinated O(1), O(2), N(1) and N(2) atoms. (Atom positions above the plane are indicated by negative signs.)

A blue crystal, $0.3 \times 0.4 \times 0.5$ mm, was used for the X-ray structure determination, using a Nicolet R3m/V four-circle single-crystal diffractometer, setting angles of 50 reflections ($15 < 2\theta < 31^\circ$) being used to determine unit-cell constants and crystal orientation. The time spent for background measurement is half of that used in scan. $[(\sin\theta)/\lambda]_{\max} = 0.60 \text{ \AA}^{-1}$ ($-19 \leq h \leq 18$, $0 \leq k \leq 12$, $0 \leq l \leq 13$), ω - 2θ scan, 0.6° above $K\alpha_2$ and 0.6° below $K\alpha_1$ respectively, 2θ scan speed = 3.26 to $14.65^\circ \text{ min}^{-1}$, graphite-monochromated Mo $K\alpha$ radiation. Intensities of three standard reflections, $\bar{1}50$, $\bar{7}33$, 243 , monitored every 50 reflections varied within 1%. Among 4243 reflections measured, 3128 were observed [$I > 2.5\sigma(I)$]. *NRCVAX* programs (Gabe, Le Page, White & Lee, 1987) for the VAX compiler were used to solve the structure. Empirical absorption correction based on azimuthal rotation from six reflections: 120, 130, 150, 260, 170, 3,10,0 (North, Phillips & Mathews, 1968) was applied. The minimum, maximum and average normalized correction factors were 0.9055, 1.0000 and 0.9585, respectively. The structure was solved by the heavy-atom method. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Final values for R and wR were 0.035 and 0.026 respectively, based on 3128 independent reflections, varying 288 parameters with anisotropic temperature factor for non-H atoms. $S = 3.45$, $(\Delta/\sigma)_{\max} = 0.4$, $(\Delta\rho)_{\max} = 0.37$ (7) (around perchlorate ion), $(\Delta\rho)_{\min} = -0.34$ (7) $e \text{ \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were used.

Discussion. The atomic parameters are listed in Table 1,* bond lengths and angles in Table 2. Fig. 1 shows a stereoview of the packing of the molecules in the unit cell, and Fig. 2 the numbering scheme of the complex, excluding the H atoms except for those attached to N(1) and N(2), with the displacements (\AA) of atoms from the least-squares plane through the four coordinated atoms given below the atomic labels, the equation being $-0.7816x - 7.059y + 8.699z = 0.1265$. The coordination bond distances of Cu—O(13) and Cu—O(21) between the Cu atom and two perchlorate ions are 2.464 (3) and 2.744 (3) \AA respectively. The atoms O(1), O(2), N(1) and N(2) are from the tetradentate ligand forming the equatorial plane, whereas two O atoms from the ClO_4 groups complete the (4 + 2) coordination sphere of Cu predicted from the Jahn–Teller effect. The central six-membered ring has a chair conformation with the NH in the axial position. The two lateral six-membered rings are in the twisted chair

* 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 51235 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (\AA) of some related compounds

Log K^*	Cu—O		Cu—N		
Central six-membered rings					
(1)	11.26	1.973 (2)	1.974 (2)	2.028 (3)	2.021 (3)
(2)	8.53	1.970 (7)	1.966 (7)	2.008 (7)	1.998 (10)
(3)	8.17	1.971 (8)	1.960 (9)	1.988 (10)	2.048 (9)
(4)	10.27	1.972 (4)	1.987 (4)	2.006 (5)	2.009 (4)
Average over last three		1.971 (8)		2.010 (18)	
Central five-membered rings					
(5)	12.58	1.957 (5)	1.974 (6)	1.983 (7)	2.002 (6)
(6a)	10.56	1.964 (8)	1.940 (8)	2.003 (10)	1.994 (10)
(6b)	10.56	1.934 (8)	1.946 (8)	1.981 (10)	1.988 (10)
(7)	9.25	1.945 (5)	1.952 (5)	2.010 (6)	1.977 (6)
Average over last four		1.952 (12)		1.992 (11)	

References: (1) [*N,N'*-bis(β -carbamoyl)ethyl]-2,2-dimethylpropylidiamine)copper(II) perchlorate monohydrate, this work; (2) [*N,N'*-bis(β -carbamoyl)ethyl]-2-hydroxytrimethylenediamine)copper(II) perchlorate (Lee, Hong, Liu, Chung & Lee, 1984); (3) [*N,N'*-bis(β -carbamoyl)ethyl]-*N*-methyltrimethylenediamine)copper(II) perchlorate monohydrate (Lu, Tsai, Chao & Chung, 1987); (4) {aqua[*N,N'*-bis(β -carbamoyl)ethyl]trimethylenediamine}perchlorato)copper(II) perchlorate monohydrate (Hong, Lee, Lee, Chao & Chung, 1987); (5) copper(II) complexes with *N,N'*-bis(β -carbamoyl)ethylenediamine (Lee, Lu, Liu, Chung & Lee, 1984); (6) the aqua and the perchlorato copper(II) complexes of *N,N'*-bis(β -carbamoyl)ethyl-*N*-methylethylenediamine (Lu, Shan, Chao & Chung, 1987); (7) μ -perchlorato-bis[*N,N'*-bis(β -carbamoyl)ethyl]-*N,N'*-dimethylethylenediamine)copper(II) perchlorate (Lu, Shan, Chao & Chung, 1987).

* K is the stability constant of the copper(II) diaminediamide in aqueous solution.

configuration. In this compound the hydrogen-bond lengths of O(*W*)—H...O(2), O(*W*)—H...O(14), O(*W*)...H—N(3), O(*W*)...H—N(4), N(1)—H...O(24), N(2)—H...O(22), N(3)—H...O(1) and N(4)—H...O(12) are 3.188, 2.935, 2.992, 3.055, 3.039, 3.118, 3.047 and 2.897 \AA respectively. The water molecules are involved in the extensive hydrogen-bonding scheme keeping the molecules (see Fig. 1) of the complex and the perchlorate ions in a stable form.

A comparison of the bond lengths between compounds having five-membered and six-membered central rings in some related diaminediamide copper(II) compounds is listed in Table 3. Bond distances of Cu—N and Cu—O for compounds in a six-membered central ring are in general longer than those in a five-membered ring. For compounds with a six-membered central ring, the average Cu—N and Cu—O bond lengths from previous work are equal to those of the present work within standard deviations. Furthermore, the effect is more obvious in Cu—O distances. They are longer by two e.s.d.'s whereas the Cu—N distances are longer by only one e.s.d. (see Table 3). The differences are not significant from a statistical viewpoint, but appear to be real. A very low R factor of 0.035 in the present study may indicate a high reliability in its bond lengths. This is because Cu—N are stronger bonds than Cu—O. The stronger bonds lead to higher stability constants for compounds with five-

membered rings. For compounds with only a different central ring size, the coordinated bond lengths in Cu^{II} complexes with *N,N'*-bis(β -carbamoyl)ethylenediamine, which has a five-membered central ring, are shorter than those in {aqua[*N,N'*-bis(β -carbamoyl)ethyl]trimethylenediamine}perchlorato}copper(II) perchlorate monohydrate, which has a six-membered central ring. Their stability constants are 12.58 and 10.27 respectively.

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The Structure of the Tetrahydrofuran Solvate of Tetrakis(2,6-diisopropylphenylisocyanide)nickel(II) Diperchlorate

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Abstract. [Ni(C₁₃H₁₇N)₄](ClO₄)₂·(C₄H₈O)₂, *M_r* = 1151.1, *Pbca*, *a* = 15.910 (9), *b* = 21.042 (9), *c* = 19.149 (12) Å, *V* = 6411 (6) Å³, *Z* = 4, *D_x* = 1.192 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 4.4$ cm⁻¹, *F*(000) = 2456, *T* = 295 K. The structure has been refined to *R* = 0.079 for 3055 unique reflections with *I* ≥ 2.5σ(*I*). The nickel complex is centrosymmetric with Ni lying on a centre of inversion. The coordination geometry is approximately square-planar about Ni. The Ni–C bonds are almost perpendicular, 92.2 (3)°. The isocyanide ligands are essentially linear with angles of 174.0 (7) and 174.3 (7)° respectively.

Introduction. Isocyanides polymerize under the catalytic action of nickel(II) salts (Drenth & Nolte, 1979; Millich, 1980). Poly(isocyanides) have a rigid helical structure and, therefore, are chiral. In the past a mechanism has been proposed for the polymerization of isocyanides, catalysed by nickel(II). It was concluded that the polymerization is initiated by a nucleophilic attack on a coordinated isocyanide and proceeds *via* a series of consecutive insertion reactions around the Ni^{II} centre (Drenth & Nolte, 1979; Nolte, Zwicker, Reedijk

& Drenth, 1978). However, intermediates of the polymerization reaction could not be isolated. Now we have been able to isolate and characterize the first intermediate, *i.e.* a square-planar nickel(II) isocyanide complex. The molecular and crystal structure of tetrakis(2,6-diisopropylphenylisocyanide)nickel(II) perchlorate is described, which is, as far as we know, the first X-ray analysis of a nickel(II) isocyanide complex. The scarce knowledge of nickel(II) isocyanide complexes can be ascribed to the high catalytic activity of Ni^{II} with respect to the polymerization of isocyanides.

Experimental. Crystals were obtained by slow cooling of a solution in tetrahydrofuran (THF) from room temperature to 253 K in a Dewar flask. Because of the extreme sensitivity to oxygen and the rapid deterioration in a solvent-free atmosphere, the crystals had to be sampled in a nitrogen atmosphere saturated with THF.

A yellow rod-shaped crystal (0.7 × 0.5 × 0.4 mm) was sealed under nitrogen in a capillary of Lindemann glass. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo *K* α radiation. Cell dimensions were obtained