

Bis(*N*-isopropyl-2-methyl-1,2-propanediamine)nitrocopper(II) Nitrite

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Abstract. $[\text{Cu}(\text{C}_7\text{H}_{18}\text{N}_2)_2(\text{NO}_2)]\text{NO}_2$, $\text{C}_{14}\text{H}_{36}\text{CuN}_5\text{O}_2^+$. NO_2^- , Ic , $a = 9.212$ (4), $b = 23.531$ (7), $c = 9.979$ (3) Å, $\beta = 95.98$ (3)°, $Z = 4$, $D_m = 1.28$ (1), $D_x = 1.28$ Mg m^{-3} . The structure contains five-coordinate Cu^{II} complex cations and nitrite ions. The Cu^{II} coordination is effected by four N atoms of two diamine ligands and one N atom of a nitrite ion. The coordination can be described as trigonal bipyramidal. The anisotropic thermal parameters for the nitrite N and O atoms indicate that these atoms undergo significant thermal motion or are disordered in the crystal. The structure was refined to an R of 0.051 for 1117 independent observed reflections.

Introduction. The structure of the title compound has been determined as part of our investigation of diamine complexes of copper(II) nitrite (Luukkonen, 1973; Pajunen & Belinskij, 1970; Pajunen & Kivekäs, 1979; Pajunen & Näsäkkälä, 1978; Pajunen & Pajunen, 1977). The compound was prepared by a method described by Pajunen & Pajunen (1971). Cell data were obtained by least squares from diffractometer setting angles of 14 reflections. Intensities were collected in the range $3 < 2\theta < 58^\circ$ on a Syntex $P2_1$ diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.7107$ Å). Of the 1583 independent reflections collected, 1117 with $I > 3\sigma(I)$ were considered observed and used in the structure analysis. The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and difference syntheses. The x and z coordinates of Cu were fixed at 0.5 and held constant throughout the computations. The structure was refined by block-diagonal least squares with *XRAY* 76 (Stewart, 1976). All H atoms were identified in a difference map in chemically reasonable positions. They were included in the final cycles with fixed positions and isotropic temperature factors of $U = 0.06$ Å². Scattering factors of Cromer & Mann (1968) for the non-hydrogen atoms and of Stewart, Davidson & Simpson (1965) for H were used. The refinement converged at $R = 0.051$ and $R_w = 0.054$. The weighting scheme was $w = (F_o/30)^2$ if $F_o \leq 30$ and $w = (30/F_o)^2$ if $F_o > 30$. A final difference map was essentially featureless, the highest peaks

(< 0.38 e Å⁻³) occurring in the vicinity of the uncoordinated nitrite ion. Final parameters for non-hydrogen and H atoms are given in Tables 1 and 2 respectively.*

Discussion. Bond lengths and angles are listed in Table 3. Fig. 1 illustrates a *PLUTO* (Motherwell, 1976) drawing of the complex cation. The crystals are composed of positively charged bis(*N*-isopropyl-2-methyl-1,2-propanediamine)nitrocopper(II) cations and nitrite ions. The coordination of the Cu atom is trigonal

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34726 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) of the non-hydrogen atoms

	x	y	z
Cu	5000	6031 (1)	5000
O(1)	5496 (11)	4953 (5)	4044 (9)
O(2)	4701 (16)	4836 (4)	5580 (21)
O(3)	4497 (31)	7687 (6)	4619 (26)
O(4)	4943 (39)	8372 (5)	4979 (49)
N(1)	6094 (8)	6021 (4)	6987 (7)
N(2)	3675 (11)	6618 (4)	5852 (9)
N(3)	3972 (8)	6029 (4)	3145 (9)
N(4)	6487 (10)	6612 (4)	4172 (10)
N(5)	5025 (51)	5160 (8)	4900 (53)
N(6)	5245 (46)	7955 (6)	5118 (56)
C(1)	5563 (14)	6483 (5)	7686 (14)
C(2)	3912 (15)	6599 (6)	7384 (13)
C(3)	3078 (12)	6099 (6)	7835 (11)
C(4)	3452 (20)	7119 (8)	7971 (14)
C(5)	7753 (10)	6052 (7)	7028 (12)
C(6)	8323 (14)	5573 (7)	6344 (15)
C(7)	8430 (15)	5951 (8)	8536 (14)
C(8)	4627 (14)	6516 (6)	2334 (10)
C(9)	6236 (12)	6548 (5)	2703 (10)
C(10)	7096 (13)	6014 (7)	2388 (15)
C(11)	6853 (16)	7082 (5)	1965 (12)
C(12)	2347 (11)	6004 (5)	2914 (9)
C(13)	1687 (12)	6045 (7)	1473 (12)
C(14)	1825 (11)	5503 (4)	3763 (12)

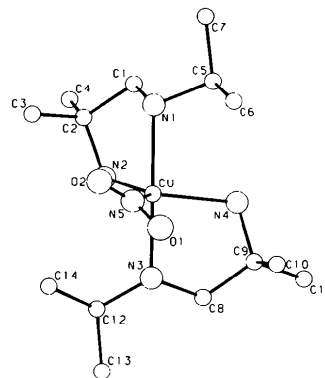
Table 2. Fractional atomic coordinates ($\times 10^3$) of the H atoms

	x	y	z		x	y	z
H(N1)	593	569	740	H(N3)	413	570	275
H(N2)	274	655	557	H(N4)	741	651	445
H'(N2)	392	698	558	H'(N4)	632	696	443
H(C1)	578	642	868	H(C8)	416	688	254
H'(C1)	609	684	744	H'(C8)	444	643	135
H(C3)	322	607	883	H(C10)	690	596	136
H'(C3)	201	615	753	H'(C10)	814	610	261
H''(C3)	348	577	738	H''(C10)	683	566	281
H(C4)	227	712	771	H(C11)	791	714	229
H'(C4)	348	703	901	H'(C11)	675	701	97
H''(C4)	389	740	770	H''(C11)	629	743	217
H(C5)	804	641	664	H(C12)	195	632	346
H(C6)	939	558	645	H(C13)	189	571	98
H'(C6)	795	521	671	H'(C13)	60	611	147
H''(C6)	787	567	544	H''(C13)	202	639	92
H(C7)	806	556	884	H(C14)	73	554	379
H'(C7)	950	593	858	H'(C14)	202	514	330
H''(C7)	803	626	899	H''(C14)	224	546	474

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

Cu—N(1)	2.129 (7)	C(2)—C(4)	1.440 (23)
Cu—N(2)	2.083 (10)	C(5)—C(6)	1.444 (21)
Cu—N(3)	1.990 (8)	C(5)—C(7)	1.586 (18)
Cu—N(4)	2.160 (10)	C(8)—C(9)	1.491 (17)
Cu—N(5)	2.052 (20)	C(9)—C(10)	1.534 (18)
N(1)—C(1)	1.407 (16)	C(9)—C(11)	1.592 (17)
N(1)—C(5)	1.526 (12)	C(12)—C(13)	1.504 (15)
N(2)—C(2)	1.522 (15)	C(12)—C(14)	1.558 (15)
N(3)—C(8)	1.560 (15)	N(5)—O(1)	1.11 (5)
N(3)—C(12)	1.492 (12)	N(5)—O(2)	1.08 (4)
N(4)—C(9)	1.468 (14)	N(6)—O(3)	1.02 (4)
C(1)—C(2)	1.544 (18)	N(6)—O(4)	1.03 (2)
C(2)—C(3)	1.500 (20)		
N(1)—Cu—N(2)	82.4 (3)	C(1)—C(2)—C(4)	113.3 (12)
N(1)—Cu—N(3)	179.2 (4)	C(3)—C(2)—C(4)	111.3 (12)
N(1)—Cu—N(4)	96.1 (3)	C(3)—C(2)—N(2)	107.5 (10)
N(1)—Cu—N(5)	91.6 (14)	C(4)—C(2)—N(2)	111.4 (11)
N(2)—Cu—N(3)	98.0 (3)	N(1)—C(5)—C(6)	111.3 (10)
N(2)—Cu—N(4)	99.1 (4)	N(1)—C(5)—C(7)	108.2 (9)
N(2)—Cu—N(5)	133.8 (15)	C(6)—C(5)—C(7)	101.8 (12)
N(3)—Cu—N(4)	84.6 (4)	N(3)—C(8)—C(9)	109.7 (8)
N(3)—Cu—N(5)	87.6 (14)	N(4)—C(9)—C(8)	107.5 (9)
N(4)—Cu—N(5)	127.1 (14)	C(8)—C(9)—C(10)	115.4 (10)
Cu—N(1)—C(1)	107.3 (7)	C(8)—C(9)—C(11)	108.6 (9)
Cu—N(1)—C(5)	113.6 (6)	C(10)—C(9)—C(11)	109.5 (10)
Cu—N(2)—C(2)	111.2 (7)	C(10)—C(9)—N(4)	105.0 (9)
Cu—N(3)—C(8)	107.9 (6)	C(11)—C(9)—N(4)	110.7 (9)
Cu—N(3)—C(12)	121.1 (6)	C(13)—C(12)—N(3)	116.4 (8)
Cu—N(4)—C(9)	106.0 (6)	C(14)—C(12)—N(3)	107.8 (8)
Cu—N(5)—O(1)	118.9 (29)	C(13)—C(12)—C(14)	116.8 (9)
Cu—N(5)—O(2)	131.9 (37)	C(1)—N(1)—C(5)	110.4 (9)
N(1)—C(1)—C(2)	115.2 (10)	C(8)—N(3)—C(12)	112.6 (8)
C(1)—C(2)—N(2)	103.7 (10)	O(1)—N(5)—O(2)	109.2 (21)
C(1)—C(2)—C(3)	109.2 (11)	O(3)—N(6)—O(4)	111.4 (45)

bipyramidal, which is unusual for Cu^{II} complexes (Hathaway & Billing, 1970). The Cu atom is surrounded by four N atoms of two diamine ligands and one N atom of a nitrite ion at the corners of a slightly dis-

Fig. 1. The complex Cu^{II} cation with H atoms omitted.

torted trigonal bipyramid. The Cu—N distances are in the range 1.990 (8)—2.160 (10) Å.

The N atom of the nitrite ion N(5) and two N atoms from different diamine molecules N(2) and N(4) are in a plane from which the Cu atom deviates by only 0.002 (2) Å. The two other N atoms of the diamine molecules, N(1) and N(3), lie on a line (passing through the Cu atom) which makes an angle of 9.0 (5)° with the normal to this plane.

The angles formed by the two N atoms of each diamine molecule with the Cu atom are significantly less than 90°, 82.4 (3) and 84.6 (4)° for N(1)—Cu—N(2) and N(3)—Cu—N(4) respectively, and this causes the trigonal-bipyramidal coordination polyhedron to be distorted.

The normal coordination geometry for bis-diamine—Cu complexes is 4 + 1 or 4 + 2 with a square-planar arrangement of four N atoms at normal bonding distances; e.g. in the corresponding L-

lactatobis(*N*-isopropyl-2-methyl-1,2-propanediamine)-copper(II) L-lactate monohydrate (Ahlgren & Hämäläinen, 1978), the Cu atom has normal 4 + 1 coordination. The trigonal-bipyramidal configuration can be considered a distortion of the square-planar arrangement through movement of the two *trans* N atoms [N(2) and N(4)] within the plane containing them, Cu, and the atom at the apex of the square pyramid [N(5)] to positions such that the angles made with the Cu and the apical atom are about 120°. In this structure N(2)—Cu—N(5) is 133.8 (15)° and N(4)—Cu—N(5) is 127.1 (14)°.

Each of the five-membered Cu—diamine rings is in an unsymmetrical *gauche* configuration. The complex cation has approximate C₂ symmetry, the axis passing through N(5) and Cu. All interionic contacts are normal, the shortest being 2.93 (2) Å between N(2) and O(3).

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Bis(*tri-tert*-butylphosphine)platinum(0)

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Abstract. C₂₄H₅₄P₂Pt, [Pt(C₁₂H₂₇P)₂], monoclinic, P2₁/n, *a* = 8.630 (2), *b* = 13.733 (7), *c* = 12.049 (6) Å, β = 93.74 (3)°, *Z* = 2, *D_m* = 1.40, *D_x* = 1.396 Mg m⁻³, μ(Mo Kα) = 5.27 mm⁻¹, λ(Mo Kα) = 0.71069 Å. The structure was refined from 1804 observed reflections measured on a diffractometer; *R* = 0.046. The Pt—P distance is 2.249 (3) Å.

Introduction. Although crystal structures of two-coordinated complexes of zerovalent Pt or Pd with phosphines have been reported (Otsuka, Yoshida, Matsumoto & Nakatsu, 1976; Immirzi, Musco, Zambelli & Carturan, 1975), no data on this type of

compound involving the bulky *tri-tert*-butylphosphine group were available. Therefore, a structural determination was carried out for the title compound, Pt[P(*tert*-Bu)₃]₂.

The space group was determined by photographic methods. The crystal used, which was approximately cubic with edges of 0.11 mm, was mounted on a Syntex P2₁ automatic diffractometer. 15 automatically centred reflections were used in a least-squares refinement to give the cell constants and the orientation matrix. Two reflections (011 and 110) were measured after every 48 reflections to monitor the stability of the data collection; the intensities of these checking