Kennard, Watson, Brammer, Orpen & Taylor, 1987). C—C distances in the Cp ring average 1.41 (3) Å and in the Cp* ring 1.41 (2) Å and C—C(H₃) distances are 1.515 (14) Å, all within normal ranges. The bonding about scandium is the same as seen in similar compounds (Shapiro, Bercaw, Marsh & Schaefer, 1989; Bunel, Bercaw & Schaefer, 1987): Sc—Cp is 2.20 Å and Sc—Cp* the same. The Sc—C distances to the ring C atoms show the 'tilt' of the rings with respect to the vector, Sc—Cp center, caused by the Si(CH₃)₂ bridge, with Sc—C8 = 2.444 (7), and Sc—C10 and Sc—C11 2.560 (8) Å; in the Cp ring, Sc—C19 is 2.461 (8), Sc—C21 is 2.585 (8) and Sc—C22 is 2.541 (8) Å. The Sc—C1 distance is 2.253 (8) Å, nearly the same as found in a quite similar compound [2.271 (7) Å; Bunel et al. (1987)]. In that compound the coordination about C1 was nearly planar and electron density was found both above and below the plane, where a bonded H atom would be; consequently, in that structure, we placed half-H atoms in both positions. The present compound shows a slightly more tetrahedral C atom, with no residual electron density on the Sc, Si2, Si3 side of C1, so we have considered C1 as a normal C atom, even though the angles about it involving Sc, Si2 and Si3 are 118, 116 and 119°. In a difference map calculated after final refinement, but with H1 omitted from the structure-factor calculation, the largest peak (0.90 e Å⁻³) was 0.95 Å from C1, with Sc—, Si2— and Si3—C—(peak) angles 99, 89 and

107°. Thus we conclude that, although the heavy-atom geometry about C1 is nearly planar, the coordination in the present compound is best described as distorted tetrahedral, with the H atom clearly positioned on one side.

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Structure of N,N-[Bis(2-pyridylmethyl)-γ-aminobutyrato]copper(II) Bromide Methanol Solvate

BY DIANE M. STEARNS, LUCAS R. HOFFMAN AND WILLIAM H. ARMSTRONG*

Department of Chemistry, University of California, Berkeley, California 94720, USA

Abstract. [Cu(C₁₆H₁₈N₃O₂)]Br.CH₄O, $M_r = 459.83$, orthorhombic, $P2_12_12_1$, $a = 10.452$ (4), $b = 12.197$ (7), $c = 14.984$ (6) Å, $V = 1910$ (3) Å³, $Z = 4$, $D_m = 1.61$ (1), $D_x = 1.599$ g cm⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 32.37$ cm⁻¹, $F(000) = 932$, $T = 174$ K, $R = 0.0396$, $wR = 0.0419$, 1146 observed reflections $[I > 3\sigma(I)]$. The title compound is a polymeric species in the solid state, with a unit cell consisting of two segments of one-dimensional chains. The ligand, a derivative of γ-aminobutyric acid in which the amino group is substituted with two 2-pyridylmethyl moieties, coordinates to one copper atom through the three nitrogen atoms and to another copper atom through the two carboxylate oxygen atoms. The copper(II) atom has a pseudo square-pyramidal geometry, distorted by a distant sixth interaction to a carboxylate oxygen atom [Cu—O(2), 2.770 (7) Å].

Introduction. The title compound, hereafter referred to as [Cu{GABA(mpy)₂}]Br, is the first to be structurally characterized with this substituted γ-amino-

butyric acid ligand. The compound is an extended chain in the solid state. The ligand with its four-carbon carboxylate 'tail' spans between two copper(II) atoms instead of wrapping around a single copper(II) atom. This same coordination has been found in the unsubstituted analog, copper(II) di-γ-aminobutyrate (Takenaka, Oshima, Yamada & Watanabé, 1973), as well as in two structures of copper(II) with ligands containing the same N(CH$_2$)$_3$CO$_2^-$ fragment: copper(II) glutamate dihydrate (Gramaccioli & Marsh, 1966) and *catena*-tetraaqua-di-μ$_3$-(N-salicylidene-DL-glutamato)-tricopper(II) heptahydrate (Korhonen, Hämäläinen & Turpeinen, 1984), although the latter is not a one-dimensional chain. The ligand with one less methylene group, β-alanine, binds copper in a different fashion. Bis(β-alaninato)copper(II) tetrahydrate is bidentate through the amine and one carboxylate oxygen atom; the second carboxylate bridges to another copper(II) atom (Mitsui, Iitaka & Sakaguchi, 1976). This coordination mode is expected since in this case a stable six-membered chelate ring is formed.

Experimental. The ligand, N,N-bis(2-pyridyl-methyl)-γ-aminobutyric acid, was prepared from γ-aminobutyric acid and picolyl chloride hydrochloride by the method of Toftlund & Yde-Andersen (1981). [Cu{GABA(mpy)$_2$}]Br was obtained from the reaction of the ligand and CuBr$_2$ in methanol (Hoffman & Armstrong, 1989). Blue single crystals were obtained by the slow evaporation of methanol. Crystal suitable for X-ray diffraction, 0.56 × 0.46 × 0.31 mm, was cut from a larger block. D_m measured by flotation in a mixture of CCl$_4$ and CHBr$_3$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, unit-cell constants refined from 24 reflections (23.3 ≤ 2θ ≤ 24.9°). Data collection: 3 ≤ 2θ ≤ 45°, index ranges 0 ≤ h ≤ 11, 0 ≤ k ≤ 13, 0 ≤ l ≤ 16; θ–2θ scan technique with Mo Kα radiation at 174 K. 1470 total reflections; systematic absences: (h00), h ≠ 2n; (0k0), k ≠ 2n; (00l), l ≠ 2n; 1450 unique reflections; 1146 reflections with $I > 3\sigma(I)$. Intensities and orientation checked by three reflections (346, 515, 172) every hour. Intensity loss was 3.2% over total exposure time of 10.2 h. Empirical absorption correction was applied (maximum, 0.9981; minimum, 0.9286). Maximum sinθ/λ = 0.538 Å^{-1}. Heavy-atom positions calculated using the *SHELXS*86 package (Sheldrick, 1986). Further structure solution and refinement *via* standard full-matrix least squares and Fourier techniques with a Digital Equipment Micro-VAX computer using locally modified Enraf–Nonius *SDP* software (Frenz, 1985). Function minimized was $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$; p factor = 0.03. Non-hydrogen atoms refined with anisotropic thermal parameters. Hydrogen atoms (including those of

methanol solvate) located on difference Fourier map, positions of hydrogen atoms bound to carbon atoms calculated using idealized geometry and C—H atom distances of 0.95 Å, but not refined; isotropic thermal parameters assigned by $B(H) = 1.3 \times B_{eq}(C)$. The screw axis makes the molecular chain chiral. Refinement of the other enantiomer resulted in a higher R factor. Final number of parameters refined was 226, $R = 0.0396$, $wR = 0.0419$, e.s.d. of an observation of unit weight was 1.84, maximum shift/e.s.d. on final cycle = 0.00σ; largest peaks on final difference Fourier map were $(\Delta\rho)_{max} = 0.89$ and $(\Delta\rho)_{min} = -0.49$ e Å^{-3}. Extinction coefficient was not refined. Atomic scattering factors and anomalous corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. An *ORTEP* diagram of a fragment of the [Cu{GABA(mpy)$_2$}]Br chain with the atom-numbering scheme is shown in Fig. 1. A stereoscopic view of the extended unit cell is shown in Fig. 2.
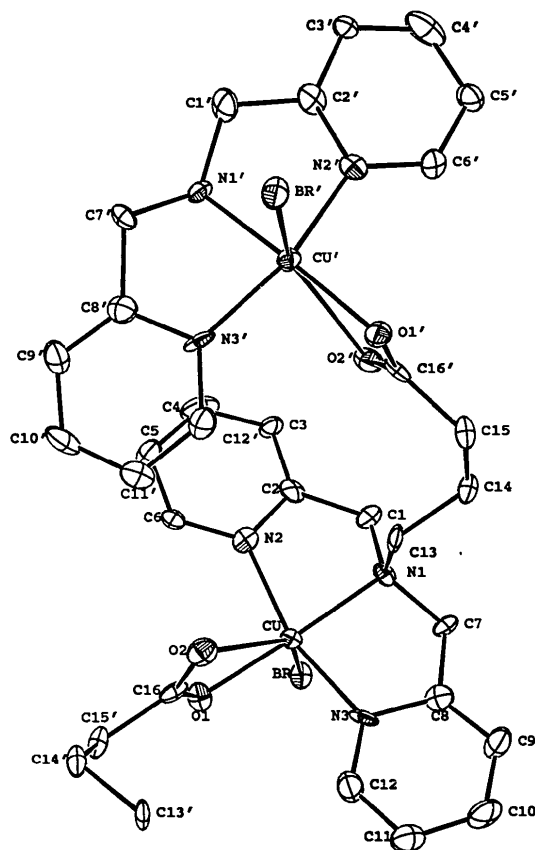

Fig. 1. *ORTEP* drawing of two molecules of [Cu{GABA-(mpy)$_2$}]Br showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms and the methanol solvate are omitted for clarity.

Atomic coordinates and final equivalent isotropic thermal parameters are listed in Table 1.* Selected interatomic distances and angles are given in Table 2.

The copper(II) atom is coordinated in a pseudo-square-pyramidal geometry, the basal plane consisting of N(1), N(2), N(3) and O(1), and the apical position occupied by bromide. The second carboxylate oxygen atom, O(2), is weakly coordinating with a Cu—O(2) bond length of 2.770 (7) Å. The Br—Cu—O(2) angle is 145.4 (1)°. The bis(2-pyridylmethyl)amino moiety binds in a meridional fashion. The angle between the two coordination planes defined by N(1)–Cu–N(2) and N(1)–Cu–N(3) is 9.4 (7)°. There is no crystallographically imposed symmetry around the copper atom, but there is a pseudo-mirror plane through N(1)–Br–O(1)–O(2), ignoring the carboxylate tail. The dihedral angle between N(1)–N(2)–N(3) and O(1)–C(16)–O(2) is 87.6 (4)°. Within a given ligand, the angle between the planes of two pyridine rings N(2)–C(2)–C(3)–C(4)–C(5)–C(6) and N(3')–C(8')–C(9')–C(10')–C(11')–C(12') is 17.7 (4)°.

A methanol of solvation is hydrogen bonded to each GABA(mpy)$_2$ ligand, but is not associated between the two chains of the unit cell. The hydrogen atom of the methanol solvate, H(104), is 2.40 (1) Å from the O(1) carboxylate atom. The oxygen atom of the methanol solvate, O(100), is 2.88 (1) Å from the O(1) atom and 3.86 (1) Å from the bromine atom.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, selected interatomic distances and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54462 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
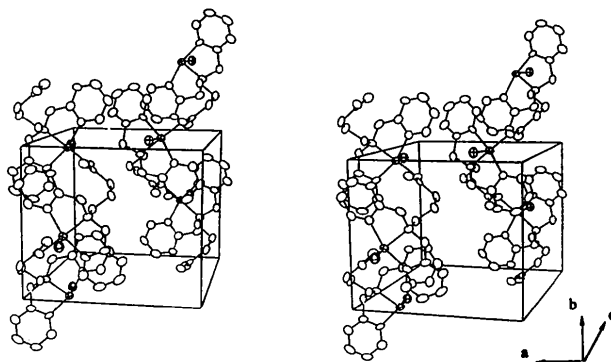
Table 1. *Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Cu	0.9746 (1)	0.21493 (8)	0.16363 (8)	2.13 (2)
Br	0.9671 (1)	0.17918 (7)	0.34417 (7)	2.77 (2)
O(1)	1.3630 (6)	0.1590 (5)	−0.1707 (4)	2.3 (1)
O(2)	1.3943 (6)	0.1511 (6)	−0.0253 (4)	2.9 (2)
O(100)	0.6590 (8)	0.3446 (9)	0.2995 (6)	7.7 (3)
N(1)	1.0913 (7)	0.0878 (6)	0.1331 (5)	2.3 (2)
N(2)	1.1428 (7)	0.2944 (6)	0.1657 (5)	2.0 (2)
N(3)	0.8399 (7)	0.1040 (6)	0.1315 (5)	2.0 (2)
C(1)	1.209 (1)	0.1086 (9)	0.1849 (7)	2.8 (2)
C(2)	1.2439 (9)	0.2284 (8)	0.1799 (6)	2.4 (2)
C(3)	1.3657 (9)	0.2665 (9)	0.1915 (7)	2.9 (2)
C(4)	1.385 (1)	0.3768 (9)	0.1871 (7)	3.9 (3)
C(5)	1.286 (1)	0.4479 (8)	0.1700 (8)	3.4 (3)
C(6)	1.1645 (9)	0.4025 (8)	0.1602 (7)	2.6 (2)
C(7)	1.0205 (9)	−0.0117 (7)	0.1581 (6)	2.0 (2)
C(8)	0.8825 (9)	0.0006 (8)	0.1258 (6)	2.4 (2)
C(9)	0.813 (1)	−0.0837 (9)	0.0969 (7)	2.9 (2)
C(10)	0.688 (1)	−0.063 (1)	0.0699 (8)	3.9 (3)
C(11)	0.640 (1)	0.0416 (9)	0.0769 (8)	3.7 (3)
C(12)	0.719 (1)	0.1224 (9)	0.1087 (7)	3.3 (3)
C(13)	1.117 (1)	0.0901 (7)	0.0353 (6)	2.1 (2)
C(14)	1.1990 (9)	−0.0039 (8)	0.0004 (8)	3.4 (3)
C(15)	1.252 (1)	0.0215 (7)	−0.0918 (7)	2.4 (2)
C(16)	1.3456 (8)	0.1191 (7)	−0.0943 (6)	1.7 (2)
C(100)	0.626 (1)	0.268 (1)	0.365 (1)	6.7 (4)

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Cu—Br	2.741 (2)	O(100)—C(100)	1.396 (18)
Cu—N(1)	2.025 (8)	C(1)—C(2)	1.507 (14)
Cu—N(2)	2.007 (7)	C(2)—C(3)	1.366 (14)
Cu—N(3)	2.011 (7)	C(3)—C(4)	1.362 (16)
Cu—O(1)	1.933 (6)	C(4)—C(5)	1.374 (15)
Cu—O(2)	2.770 (7)	C(5)—C(6)	1.390 (14)
N(1)—C(1)	1.479 (12)	C(7)—C(8)	1.502 (13)
N(1)—C(7)	1.470 (11)	C(8)—C(9)	1.347 (14)
N(1)—C(13)	1.489 (12)	C(9)—C(10)	1.385 (15)
N(2)—C(2)	1.346 (12)	C(10)—C(11)	1.380 (16)
N(2)—C(6)	1.341 (12)	C(11)—C(12)	1.373 (15)
N(3)—C(8)	1.350 (13)	C(13)—C(14)	1.527 (14)
N(3)—C(12)	1.327 (13)	C(14)—C(15)	1.520 (15)
O(1)—C(16)	1.258 (11)	C(15)—C(16)	1.540 (13)
O(2)—C(16)	1.216 (11)		

Br—Cu—N(1)	96.81 (22)	C(7)—N(1)—C(13)	110.9 (7)
Br—Cu—N(2)	94.98 (20)	C(2)—N(2)—C(6)	117.7 (8)
Br—Cu—N(3)	96.27 (21)	C(8)—N(3)—C(12)	118.4 (8)
Br—Cu—O(1)	93.15 (18)	N(1)—C(1)—C(2)	109.9 (8)
Br—Cu—O(2)	145.45 (14)	N(2)—C(2)—C(1)	113.5 (8)
O(1)—Cu—O(2)	52.33 (22)	N(2)—C(2)—C(3)	123.3 (9)
O(1)—Cu—N(1)	170.04 (28)	C(1)—C(2)—C(3)	123.2 (9)
O(1)—Cu—N(2)	98.26 (27)	C(2)—C(3)—C(4)	117.8 (9)
O(1)—Cu—N(3)	97.22 (28)	C(3)—C(4)—C(5)	121.4 (10)
O(2)—Cu—N(1)	117.72 (26)	C(4)—C(5)—C(6)	117.1 (9)
O(2)—Cu—N(2)	89.55 (24)	N(1)—C(7)—C(8)	108.0 (7)
O(2)—Cu—N(3)	90.31 (25)	N(2)—C(6)—C(5)	122.6 (9)
N(1)—Cu—N(2)	81.13 (29)	N(3)—C(8)—C(7)	113.8 (8)
N(1)—Cu—N(3)	81.50 (30)	N(3)—C(8)—C(9)	122.4 (9)
N(2)—Cu—N(3)	160.29 (29)	C(7)—C(8)—C(9)	123.8 (9)
Cu—N(1)—C(1)	104.6 (6)	C(8)—C(9)—C(10)	119.0 (10)
Cu—N(1)—C(7)	105.8 (5)	C(9)—C(10)—C(11)	119.3 (10)
Cu—N(1)—C(13)	108.4 (5)	C(10)—C(11)—C(12)	118.0 (10)
Cu—N(2)—C(2)	113.7 (6)	N(3)—C(12)—C(11)	122.9 (10)
Cu—N(2)—C(6)	128.5 (6)	C(13)—C(14)—C(15)	111.3 (8)
Cu—N(3)—C(8)	113.5 (6)	C(14)—C(15)—C(16)	114.3 (8)
Cu—N(3)—C(12)	127.9 (7)	O(1)—C(16)—O(2)	126.1 (8)
C(1)—N(1)—C(7)	115.3 (7)	O(1)—C(16)—C(15)	114.4 (8)
C(1)—N(1)—C(13)	111.4 (7)	O(2)—C(16)—C(15)	119.5 (8)

Fig. 2. Stereoscopic view of the unit cell for [Cu{GABA-(mpy)$_2$}]Br. Hydrogen atoms and the methanol solvate are omitted for clarity.

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Structures of Dimethylammonium Metal(III) Sulfate Hexahydrates (Metal = Al, Cr)

BY N. GALEŠIĆ

'Rudjer Bošković' Institute, POB 1016, 41001 Zagreb, Yugoslavia

AND V. B. JORDANOVSKA

Institute of Chemistry, University 'Kiril and Metodij', 91000 Skopje, Yugoslavia

Abstract. (I) $[Al(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$, $M_r = 373.28$, monoclinic, $P2_1/n$, $a = 6.408\,(1)$, $b = 10.752\,(1)$, $c = 11.134\,(2)$ Å, $\beta = 100.44\,(1)°$, $V = 754.4\,(2)$ Å^3, $Z = 2$, $D_x = 1.643$, $D_m = 1.62$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 4.7$ cm^{-1}, $F(000) = 392$, $T = 295$ K, $R = 0.040$ for 1680 reflections with $I > 4\sigma(I)$. (II) $[Cr(H_2O)_6]^{3+}.C_2H_8N^+.2SO_4^{2-}$, $M_r = 398.29$, monoclinic, $P2_1/n$, $a = 6.391\,(8)$, $b = 10.748\,(3)$, $c = 11.40\,(1)$ Å, $\beta = 100.87\,(6)°$, $V = 769\,(1)$ Å^3, $Z = 2$, $D_x = 1.720$, $D_m = 1.64$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 10.5$ cm^{-1}, $F(000) = 414$, $T = 295$ K, $R = 0.038$ for 1666 reflections with $I > 4\sigma(I)$. The Al and Cr atoms are octahedrally coordinated by the water molecules showing Al—Ow and Cr—Ow bond lengths ranging from 1.874 (2) to 1.891 (2) Å and from 1.953 (2) to 1.967 (2) Å, respectively. The dimethylammonium cations are disordered, with each NH_2 group having two centrosymmetric positions. The hydrogen bonds between O atoms of a sulfate anion acting as acceptors, water molecules and a dimethylammonium cation acting as a donor range from 2.586 (3) to 2.87 (1) Å.

Introduction. Trivalent metal cations (most often Al^{3+} and Cr^{3+}) form not only a variety of double sulfates with univalent alkaline and ammonium cations, but also with univalent guanidinium and

substituted ammonium cations such as $(NH_3OH)^+$ and $(NH_3CH_3)^+$. Also, the corresponding alums have been studied extensively (Haussühl, 1961; Fletcher & Steeple, 1964; Ledsham & Steeple, 1969; Ledsham, Steeple & Hughes, 1970; Bol'shakova, Zalogina & Selivanova, 1971; Abdeen, Will, Schäfer, Kirfel, Bargouth, Recker & Weiss, 1981; Serezhkin, 1984; and references therein).

There are only a few reports about double sulfates of Al^{III} and Cr^{III} with dimethylammonium cations. Recently, Kirpichnikova, Andreev, Ivanov, Shuvalov & Varikash (1988) reported on the synthesis, dielectric and optical properties of dimethylammonium aluminium sulfate hexahydrate; Jordanovska (1989) reported syntheses, thermal decompositions and X-ray powder determinations of the dimethylammonium sulfate hexahydrates of Al and Cr. Continuing our work on the double salts, the crystal structure analyses of the Al and Cr salts were undertaken.

Experimental. The two title compounds were obtained as transparent colourless and violet monocrystals, respectively, by evaporation at room temperature of aqueous mixed solutions of the metal (III) sulfates and dimethylammonium sulfate in the molar ratio 1:5 (Jordanovska, 1989). Kirpichnikova *et al.* (1988) synthesized the dimethylammonium aluminium sulfate hexahydrate from a solution