

## Crystal Structures of Complexes with Zwitterionic Ligands

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**Summary** Crystal structure analysis of two copper(II) complexes of a betaine have shown that  $\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_2(\text{ClO}_4)^+$  contains a copper-copper bond, has bridging bidentate carboxy-groups, and both ionic and co-ordinated perchlorate, while  $\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_4(\text{ClO}_4)^+$  is monomeric and has only ionic perchlorate.

STUDIES of transition-metal complexes with positively charged ligands have shown that a positive charge remote from the donor atom does not fundamentally alter the co-ordinating ability of the ligand although its basicity is markedly reduced with respect to that of its neutral counterpart. In fact, such metal complexes have high thermal stability and are poorly soluble in most solvents. It appears that a positive charge on a ligand actually facilitates isolation of the complex by giving rise to a highly favourable lattice energy.<sup>1,2</sup>

Similar considerations apply to complexes with zwitterionic ligands.<sup>3</sup> We have investigated the crystal structures of two copper complexes with the betaine of glycine,  $\text{Me}_3\text{NCH}_2\text{CO}_2^-$ , to investigate the structural basis of the stability and possible Cu-Cu bonding in one of them as suggested by an anomalously low magnetic moment.<sup>4</sup>

$\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_2(\text{ClO}_4)^+$ , *crystal data*: monoclinic,  $C2$ ,  $Cm$  or  $C2/m$ ;  $a = 12.186$ ,  $b = 12.652$ ,  $c = 12.857$  Å;  $\beta = 100.00^\circ$ ;  $D_m = 1.65$  g cm<sup>-3</sup>,  $D_c = 1.69$  g cm<sup>-3</sup> for  $Z = 4$ ,  $M = 496.744$ .

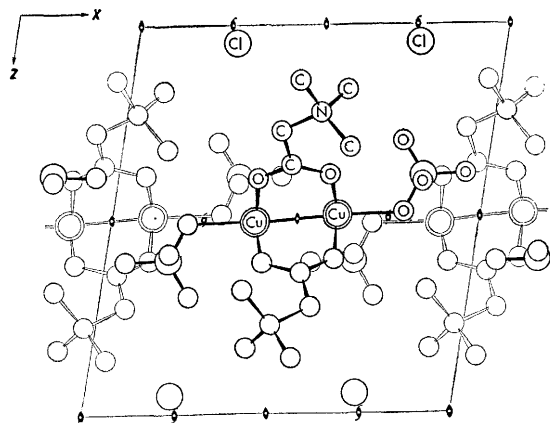


FIGURE 1.  $\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_2(\text{ClO}_4)_2$  projected down the unique  $b$ -axis. Copper and chlorine atoms on mirror plane at  $y = 0, 1/2$ ; quaternary ammoniums at  $y = 1/4, 3/4$ .

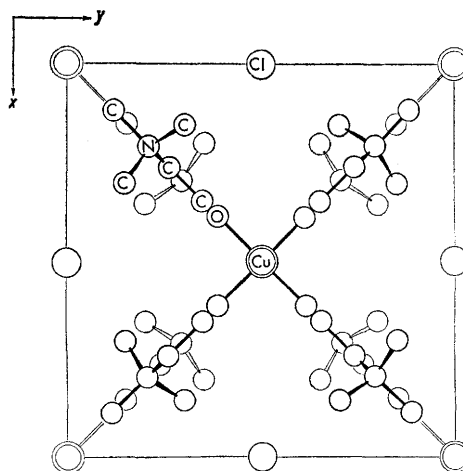


FIGURE 2.  $\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_4(\text{ClO}_4)_2$  projected down the unique  $c$ -axis.

A total of 797 non-zero independent intensities were recorded with a Hilger and Watts four-circle diffractometer using Mo- $K_\alpha$  radiation.

The structure was solved in the space group  $C2/m$  by Patterson and Fourier methods. The complex entity is a

dimer, lying centred at a  $2/m$  position. The copper atoms are bridged by four symmetry-related bidentate carboxy-groups in such a way that each copper is surrounded by a square-planar array of oxygen atoms, one from each group at a distance of 1.96(2) Å. The copper-copper bond distance is 2.652(7) Å. The dimeric ion is terminated at either end by a weak interaction [2.29(3) Å] with one of the oxygens of a perchlorate group. The copper-oxygen bond is rotated so that the perchlorates are brought into positions symmetrically located between, and close to the quaternary ammonium groups of the betaine ligands.

The structure also contains another type of perchlorate, purely ionic, which is arranged in columns along the unique  $b$ -axis and is surrounded by a rough cube of quaternary ammonium groups. Figure 1 shows a projection of the structure down the  $b$ -axis. The structure is similar to that of copper acetate monohydrate,<sup>5</sup> with perchlorate groups replacing the water molecules, though at a rather greater distance.

The structure is disordered, and the oxygens of the unco-ordinated perchlorate are not included at the present stage of refinement ( $R = 0.14$ ). The co-ordinated perchlorate too is disordered, taking up positions on both sides of the mirror plane with equal probability.

$\text{Cu}(\text{Me}_3\text{NCH}_2\text{CO}_2^-)_4(\text{ClO}_4)_2$ , crystal data: tetragonal,  $I4/mmm$ ,  $I\bar{4}2m$ ,  $I4m2$ ,  $I4mm$  or  $I422$ ;  $a = 11.711$ ,  $c = 11.695$  Å;  $D_m = 1.52$  g cm<sup>-3</sup>,  $D_c = 1.51$  g cm<sup>-3</sup> for  $Z = 2$ ,  $M =$

730.452. A total of 649 independent intensities were measured.

On the basis of chemical considerations, the structure was solved in  $I\bar{4}2m$ , which choice was justified in subsequent refinement ( $R = 0.09$ ). It consists of monomeric complex ions and free perchlorate groups. Four carbonyl groups co-ordinate strongly to the central copper through one oxygen [Cu-O distance 1.89(1) Å], resulting in a "square planar" entity of  $\bar{4}2m$  point symmetry. The four other carbonyl oxygens are 2.09(2) Å from the copper, being arranged at the corners of an elongated tetrahedron. The co-ordination is almost identical to that found in a complex with 6-aminohexanoic acid.<sup>6</sup> There are no other intermolecular contacts involving copper. The complex ions and the purely ionic perchlorate groups are stacked along the  $z$ -axis in separate, neatly interleaved chains. The perchlorate oxygens, which are disordered, are not shown in Figure 2.

In both structures the dimensions of the betaine ligands agree closely with those determined in betaine hydrochloride.<sup>7</sup> Copper-oxygen bond lengths are similar to those determined in comparable complexes.<sup>6,8</sup> Both structures are characterized by parallel columns of positive and negative groupings, with each ionic perchlorate surrounded by eight equidistant quaternary ammonium groups, six of which belong to separate molecular units.

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<sup>5</sup> J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 227.

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