

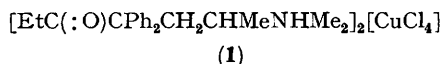
Novel Methadone Salt containing a Discrete, Square-planar CuCl_4^{2-} Anion: X-Ray Crystal and Molecular Structure of Bis(1-methyl-4-oxo-3,3-diphenylhexyldimethylammonium) Tetrachlorocuprate(II)

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Summary The crystal and molecular structure of a novel, dark green methadone salt, bis-(1-methyl-4-oxo-3,3-diphenylhexyldimethylammonium)tetrachlorocuprate(II) (**1**), which has a high energy $d-d$ electronic absorption maximum at $15,700\text{ cm}^{-1}$ in the solid state, and lacks a thermochromic transition, is reported; crystal packing forces, and not hydrogen bonding, are responsible for the discrete, square-planar geometry about copper(II) in the CuCl_4^{2-} anion.

As part of our work on the characterization of co-ordination compounds of hallucinogenic drugs and related ligands,¹ including the geometry and environment of the tetrachlorocuprate(II) anion,² we report the first metal-ion complex of methadone, a synthetic narcotic analgesic,^{3,4} with multiple actions quantitatively similar to morphine and heroin. This dark green salt was studied because of its novel composition, its high energy, solid-state $d-d$ electronic absorption maximum at $15,700\text{ cm}^{-1}$ (which shifts markedly to lower energies in non-co-ordinating solvents *e.g.*, $11,400\text{ cm}^{-1}$ in acetone, $11,100$ in methylene chloride, $10,700$ in nitromethane, $10,000$ in dimethylsulphoxide, and $9,000$ in dimethylformamide), its lack of thermochromism² (m.p. $124-128^\circ\text{C}$), and its atypical e.s.r. spectrum⁵ in the solid state, $g_z = 2.356$ and $g_{xy} = 2.063$ at 77 K ($g_z = 2.199$ and $g_{xy} = 2.084$ at 77 K , in dimethylformamide).



The molecular structure of (**1**), prepared by the addition of stoichiometric quantities of methadone hydrochloride and CuCl_2 to acetone-ether followed by slow evaporation of the resultant orange solution, has been determined by X-ray diffraction methods. The complex crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 16.602(11)$, $b = 9.739(2)$, $c = 12.650(2)\text{ \AA}$, $\beta = 93.08(2)^\circ$; $U = 2042.2\text{ \AA}^3$, $D_c = 1.34$, $D_m = 1.35\text{ g cm}^{-3}$, $Z = 2$, $M = 826.25$ for $\text{Cu}_{42}\text{H}_{58}\text{N}_2\text{O}_2\text{Cl}_4$. The structure was solved by conventional Patterson and Fourier methods and refined by least-square methods to $R = 5.0\%$ ($R_w = 4.7\%$), using 3240 independent reflections with $I > 3\sigma(I)$ collected with a Syntex $P2_1$ diffractometer using $\text{Mo-K}\alpha$ radiation, see Figure.†

The copper atom is situated on a crystallographic centre of symmetry with square-planar co-ordination of the

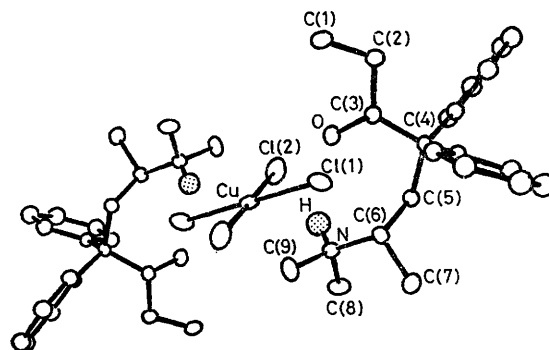


FIGURE. Molecular structure of bis(1-methyl-4-oxo-3,3-diphenylhexyldimethylammonium) tetrachlorocuprate(II) (**1**). Stippled sphere hydrogen on N(1). The numbering corresponds to that in the table of atomic co-ordinates.†

chlorine atoms; the Cu-Cl distances are $2.283(1)$ and $2.253(1)\text{ \AA}$ with angles of 89.5 and 90.5° . Chlorine atoms from neighbouring anions do not occupy octahedral sites on the CuCl_4^{2-} chromophore as Cu-Cl' distances are greater than 6 \AA ,² a result due in part to the large, bulky methadone cation. In addition, no interactions short enough² to be interpreted as hydrogen bonding between the Cl and H-N of the methadone cation are observed as the N-Cl(1) and N-Cl(2) distances are $3.471(3)$ and $3.600(3)\text{ \AA}$, respectively, suggesting that crystal packing forces are the primary factors imposing the unusual, square-planar geometry on the CuCl_4^{2-} anion. Because thermochromic transitions observed upon heating have been ascribed to extensive hydrogen bonding to the CuCl_4^{2-} anion,² the lack of a thermochromic transition in this salt is consistent with the absence of any hydrogen bonding (*vide supra*). The dark green colour of this complex and concomitant high energy $d-d$ electronic absorption maximum ($15,700\text{ cm}^{-1}$) are characteristic of discrete square-planar CuCl_4^{2-} chromophores.⁶ The variable temperature bulk magnetic susceptibility data ($300-4\text{ K}$) conform to the Curie-Weiss Law, $\chi = C/(T - \theta)$ with $C = 2.502\text{ c.g.s. units}$ and $\theta = -0.37\text{ K}$. The effective magnetic moment of 1.79 B.M. at room temperature is consistent with a discrete, square-planar CuCl_4^{2-} anion.⁵ The decrease in magnetic moment to 1.73 B.M. at 4 K , as well as the negative Weiss constant, suggests a small degree of antiferromagnetic interaction which can be attributed to lattice effects throughout the crystallites.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

A detailed description of the structure, and electronic and magnetic properties of this complex and other tetrachlorometallate(II) salts of methadone will appear elsewhere. Dickinson (University of Texas at Arlington) for the susceptibility measurements.

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