Copper(I) Complexes: Synthesis and Crystal Structure of Tetrapyridine Copper(I) Perchlorate $(C_5H_5N)_4CuClO_4$†

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Summary The tetrapyridine copper(I) cation has been synthesized, characterized and found to have a regular tetrahedral structure; no infrared active Cu–N stretching vibration was observed.

WE have prepared several relatively stable copper(I) perchlorate complexes which have nitrogen heterocycle ligands. The unexpected properties of some of these compounds suggested an investigation of their structure; we

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† Taken from the dissertation of R. J. Michl submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry (1971).

report here the synthesis and the *X*-ray structure determination of tetrapyridine copper(I) perchlorate, $(C_5H_5N)_4CuClO_4$.[1]

Amine copper(I) perchlorate complexes were prepared by the reduction of copper(II) perchlorate hexahydrate with electrolytic copper in the appropriate amine (see Table).[2‡]

TABLE

Tetra-amine copper(I) *perchlorates*

Amine	Formula of complex	Colour
Pyridine	$(C_5H_5N)_4CuClO_4$	yellow
4-Picoline	$(C_6H_7N)_4CuClO_4$	light brown
Quinoline	$(C_9H_7N)_4CuClO_4$	green

The isolated complexes were diamagnetic. Their i.r. spectra showed that the fundamental modes of the ligands were shifted to slightly higher frequency, as expected,[3] and that they were ionic perchlorates.[4] No Cu–N stretching vibration could be located in the far i.r. region, for these complexes, although numerous studies have shown that Cu^{II}–N stretching vibrations occur in the region 230—270 cm^{-1}.[5]

$(C_5H_5N)_4$ $CuClO_4$ (*M* 479·4) has colourless, prismatic, tetragonal crystals space group $I\bar{4}$, $a = b = 12{\cdot}460 \pm 0{\cdot}010$ Å, $c = 6{\cdot}960 \pm 0{\cdot}005$ Å, $Z = 2$; $D_m = 1{\cdot}47$ g cm^{-3}, $D_c = 1{\cdot}48$ g cm^{-3}. Cu and Cl are in special positions 000 and 0 $\frac{1}{2}$ $\frac{1}{4}$ on $\bar{4}$, which is compatible with a tetrahedral or a square-planar co-ordination. 425 non-zero, independent, reflections were measured with a Picker four-circle automated diffractometer using Mo-K_α radiation; least-squares refinement has so far reduced *R* to 0·06 and is being continued. The structure consists of separated tetrapyridine copper cations [$Cu(py)_4^+$] and perchlorate (ClO_4^-) counterions. The closest Cu........Cl and Cu........Cu distances are 6·40 and 6·96 Å, respectively.

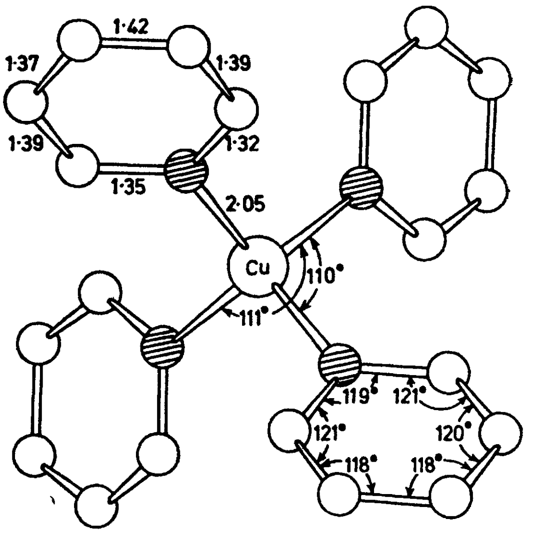

FIGURE. *Molecular geometry of the* $Cu(py)_4^+$ *cation.*

The perchlorate anions are disordered, but this is not unusual[6] and will be described elsewhere.[7] The Figure shows the molecular structure and the most relevant geometric parameters of the $Cu(py)_4^+$ cations.

The co-ordination about copper is almost exactly tetrahedral with two independent bond angles N–Cu–N of 110° and 111°. The Cu–N bond length is 2·05 ± 0·01 Å, which is normal. The S_4 symmetry of the isolated cation is retained in the crystal.

To our knowledge this is the only authentic example of a symmetric, tetrahedral copper(I) cation co-ordinated by nitrogen.§

Investigations of analogous tri- and di-ligated copper(I) species will be reported on separately.

(*Received, August 2nd,* 1971; *Com.* 1335.)

‡ Satisfactory elemental analyses were obtained for all three complexes.

§ The tetrakis(methyl cyanide)copper(I) cation has been reported;[8] it was assumed to be tetrahedral.

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