# Synthesis and Crystal Structure of Tris-(2-picoline)copper(I) Perchlorate $(C_6H_7N)_3CuClO_4$; a Trigonal Copper(I) Ion

By Anita H. Lewin* and Rudolf J. Michl
(*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York* 11201)
and P. Ganis and U. Lepore
(*Istituto Chimico, Università di Napoli,* 80134, *Napoli, Italy*)

*Summary* Ionic copper(I) perchlorates, trico-ordinated by heterocyclic amines, have been prepared, characterized, and found to have trigonal hybridization about Cu; unusually high magnetic moments and Cu–N stretching frequencies are associated with some of these complexes.

We have isolated several copper(I) perchlorate complexes stablized by heterocyclic amines whose elemental analyses indicated the presence of three amine ligands per copper(I) perchlorate. The i.r. spectra of these complexes indicated that they were ionic perchlorates.[1] We concluded that we had on hand examples of the rare and unusual trico-ordinated copper(I)[2] and we report the $X$-ray structure determination of tris-(2-picoline)copper(I) perchlorate, $(C_6H_7N)_3CuClO_4$.

The amine copper(I) perchlorate complexes were prepared as previously reported.[3]† Slight hypsochromic shifts of the fundamental i.r. absorption modes of the ligands were observed, as expected.[4] The $Cu^I$–N stretching vibrations observed for these trico-ordinated amine copper(I) perchlorates (see Table) were at higher frequencies than those for analogous dico-ordinated $Cu^I$ complexes[5] and $Cu^{II}$ complexes.[6] Measurements of the magnetic susceptibilities showed relatively large values for some of the magnetic moments (see Table) which were *not* due to the presence of $Cu^{II}$ species.‡ Both the unusual Cu–N stretching frequencies and the abnormal magnetic moments may be associated with unusual conformations of the ligands due to the steric effect of the *ortho* groups.[5]

The crystal data for $(C_6H_7N)_3CuClO_4$, ($M$ = 426·0) are: prismatic, monoclinic crystals, space group $P2_1/c$; $a$ = 9·696 ± 0·004 Å, $b$ = 13·961 ± 0·007 Å, $c$ = 15·745 ± 0·010 Å, $\beta$ = 107° 39′ ± 5′; $Z$ = 4; $D_m$ = 1·39 g cm$^{-3}$, $D_c$ = 1·39 g cm$^{-3}$. 2333 non-zero independent reflections were measured with a Picker four-circle automated diffractometer using Mo-$K_\alpha$ radiation; least squares refinement brought the conventional $R$ to 0·105. The structure consists of $[Cu(2\text{-picoline})_3]^+$ and $[ClO_4]^-$ ions; the molecular

Table

*Properties of tri-amine copper*(I) *perchlorates*

| Amine | Formula of Complex | Colour | Far i.r. bands (cm$^{-1}$) | Magnetic moment $\mu_{eff}$ (to ±0·05) |
|---|---|---|---|---|
| 2-Picoline | $(C_7H_7)_3CuClO_4$ | tan | 425,375 | +0·06 |
| 2,5-Lutidine | $(C_8H_9)_3CuClO_4$ | grey | 400,306 | −0·13 |
| 2-Ethylpyridine | $(C_8H_9)_3CuClO_4$ | light brown | 277,259 | +0·72 |
| 2-Isopropylpyridine | $(C_8H_9)_3CuClO_4$ | white | 260,248 | +0·66 |

---

† Satisfactory elemental analyses were obtained for all complexes.

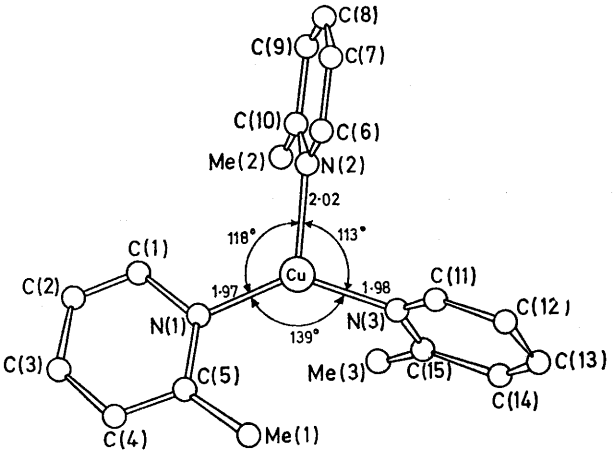

FIGURE *Structure of the cation* $Cu(C_6H_7N)_3^+$ *as viewed along the axis* Cu ------ $ClO_4^-$.

structure of the $Cu(2\text{-picoline})_3^+$ cation is reported in the Figure. The co-ordination about copper is distorted trigonal; the bond angles N–Cu–N are of 118, 113, and 139°, respectively. This deviation from a regular trigonal co-ordination can be rationalized as follows.

Two picoline rings (2 and 3 in the Figure) are nearly orthogonal to the co-ordination plane of Cu; the third picoline ring (1) is nearly coplanar with the same plane. This occurs in order to avoid contact interactions between Me(1) and Me(2) and/or Me(3), which would arise if ring 1 were orthogonal to the N(1)–N(2)–N(3) plane and the methyl group Me(1) were on the same side as Me(2) and Me(3). For this conformation, placing the methyl group Me(1) on the opposite side of Me(2) and Me(3) would also be unfavourable due to hindrance by the $ClO_4^-$ ion which is placed at 4·5 Å from Cu in the apical position of a trigonal pyramidal co-ordination of the metal. Due to this imposed conformation of the picoline ring (1), the angle N(1)–Cu–N(3) becomes enlarged (139°) to release the interaction Me(1)—Me(3) (3·9 Å).

The Cu–N bond lengths and the geometrical parameters of the picoline rings are quite normal. The perchlorate anions are disordered as has been found in other similar structures.[2,3]

(*Received, 2nd March* 1972; *Com.* 352.)

---

[1] B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 1963, 4586; B. J. Hathaway and A. E. Underhill, *ibid.*, 1961, 3091.

[2] P. G. Eller and P. W. R. Corfield, *Chem. Comm.*, 1971, 105.

[3] A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore, and G. Avitabile, *Chem. Comm.*, 1971, 1400.

[4] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.

[5] A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore, and G. Avitabile, to be submitted for publication to *J. Chem. Soc.*

[6] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, 1965, **21**, 105.