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Note

NQR studies of polyhalocuprate(I) anions

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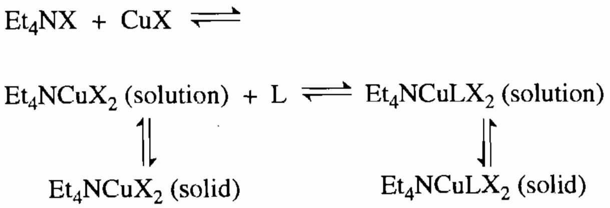
Abstract

Attempts to prepare the tricyclohexylphosphine or triphenylstibine analogues of the recently reported (triphenylphosphine)CuX_2^- anions were unsuccessful and instead resulted in the formation of a variety of polyhalocuprate anions. The structure of one of these, $[CH_3P(C_6H_5)_3]_2Cu_2I_4$, has been determined; monoclinic, $P2_1/c$; $a=16.715(3)$, $b=10.787(2)$, $c=23.196(3)$ Å, $\beta=98.59(1)°$, $Z=4$; $R=6.3\%$, $R_w=3.1\%$. The ^{63}Cu NQR spectra of twelve such polyhalocuprate anions were observed and the results compared with those of previously reported polyhalocuprates.

Keywords: Crystal structures; Copper complexes; Halide complexes; Anion complexes

1. Introduction

We have recently reported [1] the ^{63}Cu NQR frequencies of the triphenylphosphine dihalocuprate(I) complexes whose preparation and structures were reported by Bowmaker et al. [2]. We have likewise reported the preparation, structure and NQR spectra of the analogous complexes with *N*-alkylimidazolidine-2-thiones as the ligand [3]. Using the same methods as those employed by Bowmaker et al., we also attempted to form similar complexes with a variety of other ligands but these attempts all resulted in the formation of either the dihalocuprate anions $[CuCl_2]^-$ and $[CuBr_2]^-$ or the dinuclear tetrahalocuprates $[Cu_2Br_4]^{2-}$ and $[Cu_2I_4]^{2-}$. The preparative method is simply the mixing together of equimolecular proportions of the cuprous halide, the ligand and the halide of a bulky cation such as tetraalkylammonium, so that the outcome of the reaction depends on the various equilibrium constants and solubilities of the products.



$$\begin{tikzcd}
Et_4NX + CuX \arrow[r, shift left] & \arrow[l, shift left] \\
Et_4NCuX_2\text{ (solution)} + L \arrow[r, shift left] \arrow[d, shift left] & Et_4NCuLX_2\text{ (solution)} \arrow[l, shift left] \arrow[d, shift left] \\
Et_4NCuX_2\text{ (solid)} \arrow[u, shift left] & Et_4NCuLX_2\text{ (solid)} \arrow[u, shift left]
\end{tikzcd}$$

The ^{63}Cu NQR frequencies of the three possible products [1,3–5] are quite distinct and allowed us to determine rapidly which of them had in fact been formed. Whereas in some cases, depending on the cation employed and the halocuprate that was formed, the NQR spectrum of the product had already been observed [4,5], in others the halocuprate was previously unknown. We report here the results of the various attempts at forming the complex dihalocuprates, together with the NQR spectra of the previously unreported species. Furthermore in one case the product was a tetraiododicuprate that we had previously obtained on just one occasion in the course of a previous study [4] but had never been able to repeat the preparation. We have therefore determined its structure and report it here.

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2. Experimental

2.1. Preparations

The method was essentially that employed by Bowmaker et al. [2]. Thus 0.005 mol each of the cuprous halide, the alkylammonium or alkylphosphonium halide and, as ligand either tricyclohexylphosphine (method A) or triphenylstibine (method B), were dissolved in 25 ml of dry methylene chloride in an Erlenmeyer flask. The solution was filtered to remove any trace of undissolved material or precipitate and placed in a desiccator together with a second open Erlenmeyer flask containing diethylether. Crystals of the product slowly precipitated and were finally filtered off and dried. Two of the halocuprates were prepared directly (method C) by the reaction of 0.005 mol of each of the cuprous halide and the alkylammonium halide in acetonitrile, as in the case of $[NPr_4]_2[Cu_2I_4]$ [4].

2.2. X-ray crystallography

Crystals were grown at room temperature as above. Cell parameters and intensities were measured at room temperature on a Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Two reference reflections were monitored every 45 min and showed a decrease of intensities of about 10% during the data collection. All reflections were corrected for this drift. Data were corrected for Lorentz–polarization and for absorption [6]. The structure was solved by direct methods [7] and refined by least-squares with the XTAL program [8]. Atomic scattering factor and anomalous dispersion terms are taken from Ref. [9]. All coordinates of the hydrogen atoms have been calculated. A summary of crystal data, intensity measurements and structure refinements is given in

Table 1
Summary of crystal data, intensity measurement and structure refinement for **9**

Formula	$Cu_2I_4[PCH_3(C_6H_5)_3]$
Molecular weight	1189.4
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	16.715(3)
b (Å)	10.787(2)
c (Å)	23.196(3)
β (°)	98.59(1)
V (Å^3)	4135(1)
Z	4
$F(000)$	2256
D_c (g cm^{-3})	1.91
μ(Mo Kα) (mm^{-1})	4.088
A* min., max.	1.496, 2.417
$((\sin\theta)/\lambda)_{max}$ (Å^{-1})	0.55
Temperature (K)	298
No. measured reflections	5908
No. observed reflections	3297
Criterion for observed	$\|F_o\| > 4\sigma(F_o)$
Refinement (on F)	full-matrix
No. parameters	416
Weighting scheme	$\omega = 1/\sigma^2(F_o)$
Max., av. Δ/σ	0.025, 0.004
Max., min. $\Delta\rho$ (e Å^{-3})	1.4, −1.7
S	1.81
R^a, R_w^b (%)	6.3, 3.1

[a] $R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$.
[b] $R_w = [\Sigma(\omega\|F_o\| - \|F_c)^2/\Sigma\omega\|F_o\|^2]^{1/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) with e.s.d.s in parentheses for **9**

	x/a	y/b	z/c	U_{eq} [a]
I(1)	0.69228(8)	0.0257(1)	0.07273(5)	0.0921(6)
I(2)	0.75189(6)	−0.2335(1)	0.21497(4)	0.0645(5)
I(3)	0.90618(7)	−0.2109(1)	0.07417(5)	0.0810(5)
I(4)	0.64152(6)	0.1258(1)	0.25124(5)	0.0703(5)
Cu(1)	0.7858(1)	−0.1471(2)	0.11813(8)	0.075(1)
Cu(2)	0.6934(1)	−0.0183(2)	0.18172(8)	0.0699(9)
P(1)	0.0380(2)	0.1857(4)	0.1122(2)	0.047(2)
C(1)	0.1131(8)	0.067(1)	0.1221(7)	0.044(6)
C(2)	0.1430(9)	0.027(1)	0.1779(7)	0.050(7)
C(3)	0.202(1)	−0.061(2)	0.1842(7)	0.068(8)
C(4)	0.2349(8)	−0.111(1)	0.1387(8)	0.059(7)
C(5)	0.2039(9)	−0.068(1)	0.0858(7)	0.056(7)
C(6)	0.1446(9)	0.024(1)	0.0743(6)	0.053(7)
C(7)	0.0865(9)	0.333(1)	0.1015(6)	0.046(7)
C(8)	0.167(1)	0.344(2)	0.1153(8)	0.077(9)
C(9)	0.204(1)	0.449(2)	0.1093(9)	0.11(1)
C(10)	0.160(1)	0.553(2)	0.0885(8)	0.08(1)
C(11)	0.081(1)	0.541(2)	0.073(1)	0.12(1)
C(12)	0.0421(9)	0.436(2)	0.0806(8)	0.078(9)
C(13)	−0.0124(8)	0.196(1)	0.1743(6)	0.044(6)
C(14)	0.0105(8)	0.282(2)	0.2157(7)	0.066(7)
C(15)	−0.024(1)	0.284(2)	0.2650(8)	0.10(1)
C(16)	−0.082(1)	0.200(2)	0.2733(8)	0.09(1)
C(17)	−0.1064(9)	0.115(2)	0.2327(9)	0.077(9)
C(18)	−0.0721(9)	0.115(1)	0.1813(7)	0.061(7)
C(19)	−0.0352(7)	0.150(1)	0.0489(5)	0.048(6)
P(01)	0.5479(2)	0.0173(4)	0.6467(2)	0.046(2)
C(01)	0.4840(8)	0.149(1)	0.6281(6)	0.042(6)
C(02)	0.4921(9)	0.210(2)	0.5779(8)	0.083(9)
C(03)	0.436(1)	0.304(2)	0.5584(7)	0.090(9)
C(04)	0.377(1)	0.337(2)	0.591(1)	0.082(9)
C(05)	0.3757(9)	0.276(2)	0.6428(8)	0.070(8)
C(06)	0.4286(9)	0.183(1)	0.6619(6)	0.056(7)
C(07)	0.4949(8)	−0.120(1)	0.6226(7)	0.048(7)
C(08)	0.430(1)	−0.113(1)	0.5752(7)	0.061(8)
C(09)	0.3901(9)	−0.219(2)	0.5506(7)	0.067(8)
C(010)	0.419(1)	−0.329(2)	0.5713(8)	0.066(8)
C(011)	0.482(1)	−0.341(1)	0.6178(9)	0.078(9)
C(012)	0.5197(8)	−0.235(2)	0.6428(7)	0.061(7)
C(013)	0.6369(8)	0.025(1)	0.6140(6)	0.047(6)
C(014)	0.6518(9)	−0.058(1)	0.5716(7)	0.057(7)
C(015)	0.722(1)	−0.056(2)	0.5466(7)	0.078(9)
C(016)	0.778(1)	0.031(2)	0.5657(8)	0.09(1)
C(017)	0.767(1)	0.118(2)	0.6080(9)	0.10(1)
C(018)	0.696(1)	0.117(1)	0.6332(6)	0.069(7)
C(019)	0.5744(7)	0.008(1)	0.7230(5)	0.051(6)

[a] U_{eq} is the average of eigenvalues of U.

Table 3
Selected bond lengths (Å) and bond angles (°) for **9**

I(1)–Cu(1)	2.556(2)	I(3)–Cu(1)	2.485(2)
I(1)–Cu(2)	2.570(2)	I(4)–Cu(2)	2.487(2)
I(2)–Cu(1)	2.572(2)	Cu(1)–Cu(2)	2.678(3)
I(2)–Cu(2)	2.591(2)		
Av. P–C	1.79(2)		
Cu(1)–I(1)–Cu(2)	62.99(7)	I(3)–Cu(1)–Cu(2)	159.84(9)
Cu(1)–I(2)–Cu(2)	62.48(7)	I(1)–Cu(2)–I(2)	113.91(8)
I(1)–Cu(1)–I(2)	115.02(8)	I(1)–Cu(2)–I(4)	124.77(9)
I(1)–Cu(1)–I(3)	121.05(9)	I(1)–Cu(2)–Cu(1)	58.26(6)
I(1)–Cu(1)–Cu(2)	58.75(6)	I(2)–Cu(2)–I(4)	121.30(8)
I(2)–Cu(1)–I(3)	123.74(8)	I(2)–Cu(2)–Cu(1)	58.42(6)
I(2)–Cu(1)–Cu(2)	59.10(6)	I(4)–Cu(2)–Cu(1)	165.21(9)
Av. C–P–C	109.5(9)		

Table 1. The atomic coordinates are reported in Table 2. Selected geometrical parameters are reported in Table 3.

2.3. NQR

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802 digital thermometer and varied between 77 K and room temperature with an Artronix 5301-E temperature controller.

Table 4
Preparative methods

Halide	Cation	Method	Product	Number
Br	$N(n\text{-}C_3H_7)_4{}^+$	B	$N(C_3H_7)_4CuBr_2$	**1**
Br	$N(n\text{-}C_4H_9)_4{}^+$	B	$N(C_4H_9)_4CuBr_2$	**2**
Br	$P(C_6H_5)_4{}^+$	A	$P(C_6H_5)_4CuBr_2$	**3**
Br	$C_2H_5P(C_6H_5)_3{}^+$	A	$C_2H_5P(C_6H_5)_3CuBr_2$	**4**
Br	$n\text{-}C_3H_7P(C_6H_5)_3{}^+$	A	$C_3H_7P(C_6H_5)_3CuBr_2$	**5**
Br	$P(C_2H_5)_4{}^+$	A, B	$[P(C_2H_5)_4]_2Cu_2Br_4$	**6**
I	$N(n\text{-}C_5H_9)_4{}^+$	A, C	$[N(C_5H_9)_4]_2Cu_2I_4$	**7**
I	$N(cyclohexyl)_4{}^+$	A, C	$[N(C_6H_{11})_4]_2Cu_2I_4$	**8**
I	$CH_3P(C_6H_5)_3{}^+$	A	$[CH_3P(C_6H_5)_3]_2Cu_2I_4$	**9**
Br	$C_4H_9P(C_6H_5)_3{}^+$	A	$C_4H_9P(C_6H_5)_3CuBr_2$	**10**
Br	$N(C_2H_5)_4{}^+$	A, B	$[N(C_2H_5)_4]_2Cu_2Br_4$	**11**
I	$N(n\text{-}C_3H_7)_4{}^+$	A, B	$[N(C_3H_7)_4]_2Cu_2I_4$	**12**
I	$N(n\text{-}C_4H_9)_4{}^+$	A	$[N(C_4H_9)_4]_2Cu_2I_4$	**13**
I	$P(C_6H_5)_4{}^+$	A	$[P(C_6H_5)_4]_2Cu_2I_4$	**14**

Table 5
Chemical analyses

Number	Observed			Theory		
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
2	41.39	7.57	2.98	41.26	7.79	3.00
5	47.64	4.05		47.70	4.19	
7	39.05	7.10	2.54	39.00	7.20	2.27
8	42.95	7.66	2.12	42.89	7.80	2.08
9	38.33	3.02		38.38	3.05	

3. Results and discussion

3.1. Preparations

Table 4 summarizes the results of the various preparations, in all cases the product being a dihalocuprate or a tetrahalodicuprate. We had previously studied [4] the NQR spectra of compounds **10**–**14**; these spectra measured at 77 K and room temperature are sufficient to identify them with complete confidence. The preparation and crystal structures of **1**–**6** have also been previously reported [10–15], as has the ^{63}Cu NQR spectrum of **2** [5]. As will be seen below the NQR frequency of our sample of **2** differed by 0.2 MHz from the reported value. We have therefore confirmed the structure of **2** by chemical analysis and by the measurement of its unit-cell parameters which were found to be identical to those reported by Asplund et al. [11]. Compounds **7** and **8** have not been reported previously, their structure was therefore confirmed both by chemical analysis and by the identity of the product with that obtained by direct synthesis in the absence of a ligand. Compound **9** had a resonance frequency characteristic of the $[Cu_2I_4]^{2-}$ anion and is identical to that of a sample we once obtained by chance in an attempt to prepare $[CH_3P(C_6H_5)_3]_2CuI_3$ [5] but whose preparation we had never been able to repeat. Its structure was therefore confirmed by the X-ray analysis below.

Table 5 shows the results of the chemical analysis of **2**, **5**, **7**–**9**, performed by Dr H. Eder of the University of Geneva Microanalytical Service.

3.2. X-ray crystallography

The Cu_2I_4 anion adopts a diamond shape structure (Figs. 1 and 2). Each copper lies in an essentially trigonal-planar environment (distance Cu...plane of the three coordinated atoms = 0.062(2) and 0.016(2) Å for Cu(1) and Cu(2) respectively). The two coordination planes are bent around the I(1)...I(2) direction by 33.72(3)°. Both copper atoms have essentially the same coordinating environment with intracyclic Cu–I bond lengths about 0.09 Å longer than the extracyclic ones. No short distance nor stacking interaction was observed in the molecular packing. Similar folded, non-centrosymmetric structures for the Cu_2I_4 anion have been reported with the tetraphenylphosphonium [16] and tetraphenylphosphonium [17] cations.

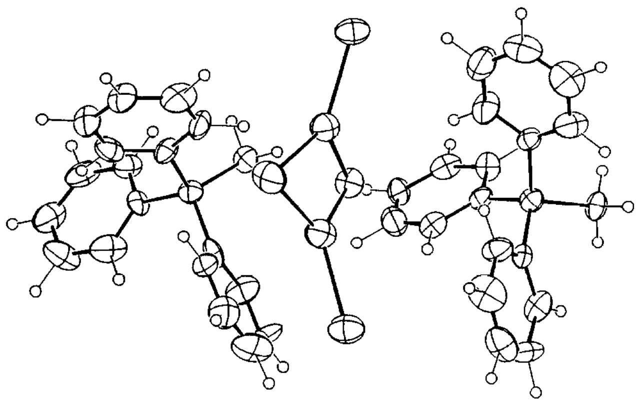

Fig. 1. ORTEP view of the $[PCH_3(C_6H_5)_3]Cu_2I_4$ (**9**). Ellipsoids are represented with 40% probability.

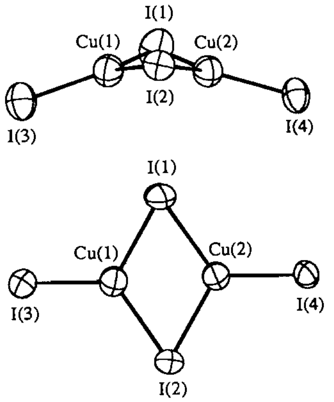

Fig. 2. Projections of the Cu_2I_4 moiety in **9** with atom numbering. Ellipsoids are represented with 50% probability.

Table 6
^{63}Cu NQR frequencies and their temperature dependence (Eq. (1))

Complex	ν_{77K} (MHz)	ν_{0K} (MHz)	A (KHz K^{-1})	B (Hz K^{-2})
1	29.381	29.512	−0.706	−15.300
2	28.677	28.761	−0.903	−4.394
3	29.328	29.583	−2.995	−3.368
4	29.425	29.607	−1.903	−6.132
5	29.383[a]	29.599	−2.399	−4.050
	29.545[a]	29.816	−3.101	−3.751
6	30.665[b]	31.189	−4.846	−24.993
7	24.921[c]	25.538	−5.470	0.784
8	25.868[d]	26.100	−2.263	−9.392
	25.658[d]	25.869	−1.793	−11.493
9	25.418	25.712	−3.475	−4.954
	25.248	25.528	−3.340	−5.444

[a] 77–267 K; $\nu(^{63}Cu)$ at 300 K = 28.502 MHz.
[b] 77–148 K.
[c] 77–201 K; $\nu(^{63}Cu)$ at 300 K = 23.698 MHz.
[d] 77–164 K; $\nu(^{63}Cu)$ at 300 K = 24.293 MHz.

3.3. NQR

Table 6 shows the ^{63}Cu NQR frequencies of **1**–**9**, measured at 77 K. In all cases the corresponding ^{65}Cu frequencies were observed at a frequency 0.925 times that of the corresponding ^{63}Cu resonance. Their temperature dependence was observed in the range 77 K to room temperature and the frequencies fitted to a quadratic:

$$\nu_T = \nu_0 + AT + BT^2 \qquad (1)$$

The coefficients A and B are also shown in Table 6.

Compounds **5**–**8** show phase changes in the 77–300 K temperature range. Both **5** and **8** have two resonances in the low-temperature region but only one resonance in the high-temperature phase. The crystal structure of **5**, determined at room temperature, shows the presence of only one crystallographically distinct dibromocuprate anion in the unit cell and the presence of just one ^{63}Cu resonance at room temperature is in agreement with this. In the low-temperature phase the crystal structure must be such that there are now two distinct dibromocuprate anions in the unit cell. For **8** on the other hand the splitting of the ^{63}Cu resonances is more likely to be due to a change from a structure having a centrosymmetric $[Cu_2I_4]^{2-}$ ion to a structure in which this symmetry element is lost. As shown both by its crystal structure [16] and by the NQR spectrum [4] **14** exists in both centrosymmetric and non-symmetric modifications while **9** has an unsymmetric structure with two ^{63}Cu resonances. For **6** the single ^{63}Cu resonance disappears at 140 K.

4. Supplementary material

Tables of atomic coordinates, displacement parameters, bond lengths, bond angles and torsional angles for compound **9** (5 pages) are available from the authors on request.

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