^{63}Cu NQR and Structural Studies of Complexes Formed Between Cu(I) Halides and *tris*(o-methoxyphenyl)- or *tris*(p-tolyl)phosphine Ligands*

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The crystal structure of [tri(o-methoxyphenyl)phosphine]$_2$Cu$_2$Br$_2$ shows it to be a halogen-bridged dimer with three-coordinated Cu(I) sites. The ^{63}Cu NQR frequency of the corresponding chloride indicates that it has a similar structure. The ^{63}Cu NQR frequencies of the complexes of tri(p-tolyl)phosphine, L$_3$Cu$_2$X$_2$, with cuprous chloride and bromide are consistent with their having halogen-bridged structures with both three- and four-coordinated Cu(I) sites analogous to those formed by triphenylphosphine and tri(m-tolyl)phosphine. Cu(I) sites. [CuBr(P(C$_7$H$_7$O)$_3$]$_2$; Triclinic, P $\bar{1}$, $Z=2$, $a=8.969(1)$, $b=10.510(2)$, $c=11.428(2)$ Å, $\alpha=99.46(1)$, $\beta=97.95(1)$, $\gamma=104.17(1)$°, $R=3.5\%$, $R_\omega=2.2\%$.

Introduction

We have previously shown [1], by a combination of X-ray crystallography and ^{63}Cu NQR spectroscopy, that the 1:1 complexes formed between tri(o-tolyl)phosphine and the cuprous halides have dimeric halogen-bridged structures with planar three-coordinated Cu(I) atoms analogous to those of tri(o-cyclohexyl)phosphine [2] rather than the tetrahedrally coordinated sites that are found in (Ph$_3$PCuCl)$_4$ [3] or (Ph$_3$PCuBr)$_4$ [4]. When the ratio of ligand to halide is increased, triphenylphosphine forms complexes such as (Ph$_3$P)$_3$CuX$_2$ [5, 6], where both three and four-coordinated sites are present, and the three-coordinated (Ph$_3$P)$_2$CuX [7]. In all these complexes the ^{63}Cu NQR frequency permits a clear distinction between the three-coordinated and the four-coordinated Cu(I) sites [1, 8–10]. We report here the results of a similar study of the complexes of *tris*(o-methoxyphenyl)phosphine and of tri(p-tolyl)phosphine.

Experimental

Preparations

[(*o*-CH$_3$OC$_6$H$_4$)$_3$PCuX]$_2$, X=Cl, **1**; X=Br, **2**, were prepared by refluxing 0.005 mole of ligand and 0.005 mole of CuX in acetonitrile for 1 hour. After cooling to room temperature, the solid complex was filtered off and recrystallised from either acetone or dichloromethane. [(*p*-CH$_3$C$_6$H$_4$)$_3$P]$_3$Cu$_2$X$_2$, X=Cl, **3**; X=Br, **4**, were prepared by the dropwise addition of a solution of 0.005 mole of CuX$_2$ in ethanol to a solution of the ligand (0.0125 mole) in ethanol at 60 °C. The resulting precipitate was purified by recrystallisation from acetone. **3** crystallizes with one molecule of acetone. Attempts to prepare the corresponding iodides of both series of complexes did not result in the formation of well-defined products. All four complexes gave satisfactory analyses (%): **1** C=56.01; H=4.74; C$_{21}$H$_{21}$O$_3$PCuCl=55.88, 4.69. **2** C=50.81; H=4.31; C$_{21}$H$_{21}$O$_3$PCuBr=50.87, 4.27. **3** C=67.31; H=5.88; C$_{63}$H$_{63}$P$_3$Cu$_2$Cl$_2$(CH$_3$)$_2$CO=67.80, 5.95. **4** C=62.81; H=5.33; C$_{63}$H$_{63}$P$_3$Cu$_2$Br$_2$=63.06, 5.29. We thank Dr K. Eder of the Geneva University Microanalytical laboratory for these analyses.

X-Ray Crystallography

Single crystals of **2** were obtained by slow evaporation from dichloromethane solution. The cell parameters (from 22 reflections with (22° < 2 θ < 29°) and diffracted intensities ($-9<h<9$, $-11<k<11$, $0<l<12$) were measured at room temperature on a STOE STADI4 diffractometer with graphite-monochromated Mo[Kα] radiation ($\lambda=0.71069$ Å). Two reference reflections, measured every 45 min, showed variations less than 2.8 σ(I).

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Table 1. Summary of crystal data, intensity measurement and structure refinement for **2**.

Formula	$[CuBr(P(C_7H_7O)_3)]_2$
Mol. wt.	495.8
Crystal system	Triclinic
Space Group	$P\bar{1}$
a (Å)	8.969 (1)
b (Å)	10.510 (2)
c (Å)	11.428 (2)
α (°)	99.46 (1)
β (°)	97.95 (1)
γ (°)	104.17 (1)
V (Å^3)	1012.2 (3)
Z	2
F (000)	500
Dc (gr · cm^{-3})	1.63
μ (MoKα) (mm^{-1})	3.150
$((\sin\theta)/\lambda)_{\max}$ (Å^{-1})	0.54
No. measured reflections	2837
No. observed reflections	2064
Criterion for observed	$\lvert F_o \rvert < 4\,\sigma(F_o)$
Refinement (on F)	Full-matrix
No. parameters	307
Weighting scheme	$\omega = 1/\sigma^2(F_o)$
Max. and average Δ/σ	0.036, 0.0013
Max. and min. $\Delta\rho$ (e · Å^{-3})	0.48, −0.55
S^1	1.98
R^2, ωR^3	0.035, 0.022

[1] $S = [\Sigma\{((F_o - F_c)/\sigma(F_o))^2\}/(N_{\text{ref}} - N_{\text{var}})]^{1/2}$; [2] $R = \lvert\lvert F_o \rvert - \lvert F_c \rvert/\Sigma \lvert F_o \rvert$; [3] $\omega R = \Sigma(\omega \lvert F_o \rvert - \lvert F_c \rvert)^{2/}\Sigma\, \omega \lvert F_o \rvert^2]^{1/2}$.

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

	x/a	y/b	z/c	U_{eq}*
Br	0.64644 (7)	0.41935 (6)	0.57351 (5)	0.0501 (3)
Cu	0.53450 (8)	0.59711 (6)	0.62346 (5)	0.0442 (3)
P	0.5308 (2)	0.7517 (1)	0.7766 (1)	0.0314 (5)
O (1)	0.2304 (4)	0.5584 (3)	0.7154 (3)	0.048 (2)
O (2)	0.6122 (5)	0.8927 (4)	0.5888 (3)	0.063 (2)
O (3)	0.7590 (4)	0.6352 (3)	0.8903 (3)	0.047 (2)
C (1)	0.3425 (5)	0.7889 (5)	0.7557 (4)	0.029 (2)
C (2)	0.2078 (6)	0.6824 (5)	0.7193 (4)	0.036 (2)
C (3)	0.0626 (7)	0.7060 (6)	0.6952 (5)	0.050 (3)
C (4)	0.0537 (8)	0.8363 (7)	0.7094 (6)	0.060 (3)
C (5)	0.1824 (8)	0.9411 (6)	0.7464 (5)	0.053 (3)
C (6)	0.3258 (7)	0.9174 (5)	0.7695 (5)	0.040 (2)
C (7)	0.1095 (8)	0.4438 (7)	0.6476 (6)	0.060 (3)
C (8)	0.6746 (6)	0.9137 (4)	0.7955 (4)	0.031 (2)
C (9)	0.7021 (6)	0.9665 (5)	0.6949 (4)	0.040 (2)
C (10)	0.8129 (8)	1.0849 (6)	0.7047 (5)	0.052 (3)
C (11)	0.9024 (7)	1.1517 (6)	0.8151 (6)	0.057 (3)
C (12)	0.8788 (7)	1.1018 (6)	0.9158 (6)	0.055 (3)
C (13)	0.7644 (7)	0.9831 (5)	0.9062 (5)	0.042 (2)
C (14)	0.654 (1)	0.9225 (9)	0.4788 (7)	0.093 (4)
C (15)	0.5505 (5)	0.7187 (4)	0.9290 (4)	0.028 (2)
C (16)	0.6625 (5)	0.6566 (4)	0.9689 (4)	0.030 (2)
C (17)	0.6741 (6)	0.6237 (5)	1.0810 (5)	0.038 (2)
C (18)	0.5748 (7)	0.6560 (5)	1.1557 (5)	0.045 (2)
C (19)	0.4667 (7)	0.7200 (5)	1.1213 (5)	0.043 (2)
C (20)	0.4558 (6)	0.7511 (5)	1.0082 (5)	0.038 (2)
C (21)	0.8630 (7)	0.5557 (6)	0.9148 (6)	0.050 (3)

* U_{eq} is the average of eigenvalues of U.

Table 3. Selected bond lengths (Å), bond angles and torsional angles (°) for **2**.

Bond lengths			
Cu–Cu′	3.0850 (9)	Cu–P	2.194 (1)
Br–Br′	3.807 (1)	P–C (1)	1.818 (5)
Cu–Br	2.356 (1)	P–C (8)	1.826 (4)
Cu–Br′	2.5406 (9)	P–C (15)	1.825 (5)
Bond angles			
Br–Cu–Br′	101.99 (3)	Cu–P–C (8)	115.8 (2)
Cu–Br–Cu′	78.01 (3)	Cu–P–C (15)	120.1 (2)
Br–Cu–P	141.38 (5)	C1–P–C (8)	104.6 (2)
Br′–Cu–P	116.53 (5)	C1–P–C (15)	102.6 (2)
Cu–P–C (1)	109.1 (1)	C8–P–C (15)	102.9 (2)
Torsional angles			
Br–Cu–P–C (1)	−150.5 (2)	C (7)–O (1)–C (2)–C (1)	−162.2 (5)
Br–Cu–P–C (8)	91.8 (2)	C (14)–O (2)–C (9)–C (8)	−166.5 (6)
Br–Cu–P–C (15)	−32.7 (2)	C (21)–O (3)–C (16)–C (15)	−171.3 (4)
Cu–P–C (1)–C (2)	45.5 (4)	Cu–P–C (8)–C (13)	−134.5 (4)
Cu–P–C (15)–C (16)	44.1 (4)		

Data were corrected for Lorentz and polarization effects and for absorption by analytical integration [11] from the crystal shape. The structure was solved by direct methods using MULTAN 87 [12]; all other calculations used XTAL [13] system and ORTEP [14] programs. Atomic scattering factors and anomalous dispersion terms were taken from [15]. All coordinates of the hydrogen atoms were observed and refined. A summary of crystal data, intensity measurement and structure refinement is given in Table 1. Final coordinates and selected geometrical parameters are reported in Tables 2 and 3, respectively.

NQR

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to har-

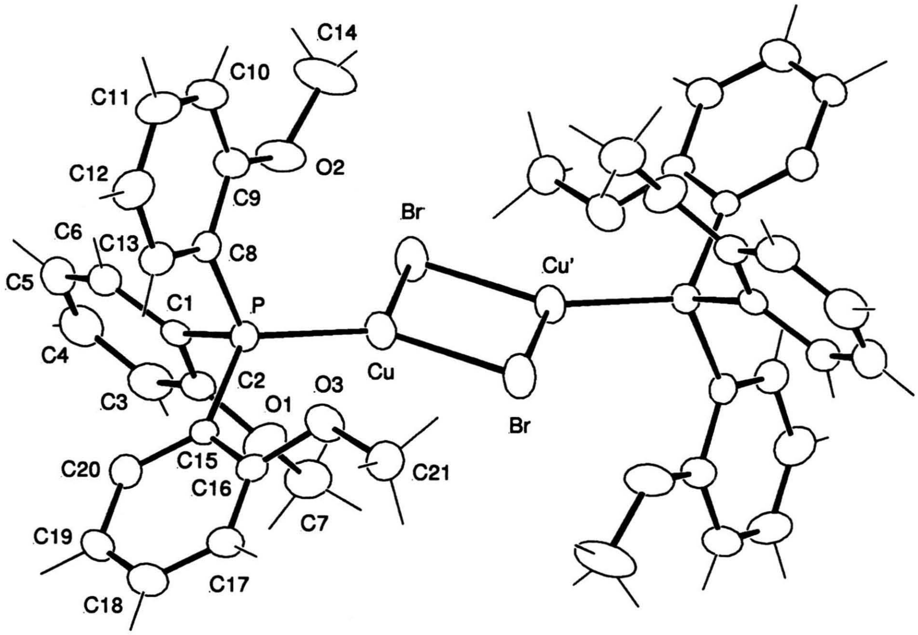

Fig. 1. Perspective view of the crystal structure of **2** with the atomic numbering. Ellipsoids are represented with 40% probability.

monics 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. Although results are only reported for ^{63}Cu, the resonances for the ^{65}Cu were always observed with frequencies equal to 0.925 times that of the ^{63}Cu, thus ensuring that the resonances have been correctly attributed.

Results and Discussion

X-Ray Crystallography

The [tri(*o*-methoxyphenyl)phosphine]$_2$Cu$_2$Br$_2$ structure (Fig. 1) does not differ essentially from that of its tri(o-tolyl) analogues [1]. The molecule is located about a center of inversion. Consequently the Cu$_2$Br$_2$ moiety is planar and, since the phosphorus atom is located in the same plane (deviation = 0.09 Å), the triphenylphosphine moieties are staggered (Figure 2). Contrary to the tri(o-tolyl) analogues, the co-ordination at the Cu(I) atom shows some distortions from a regular trigonal site: Both Cu-Br bonds differ by approximately 0.2 Å and the P-Cu-Br bond angles by more than 24° (Table 3). The three phenyl rings of the asymmetric unit form an almost regular propeller (angles between their mean planes and the Cu-P direction = 45.7, 49.9 and 51.1°). All the o-methoxy substituents are oriented toward the inner space of the molecule with their methyl group *trans* relative to the carbon atom bonded to the phosphorus (torsion angles

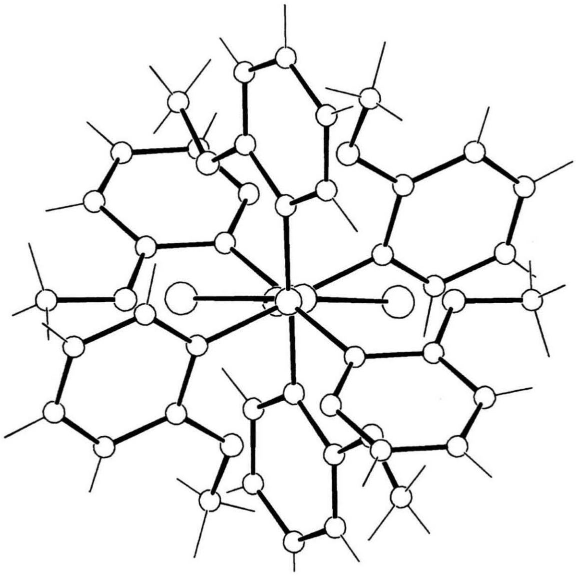

Fig. 2. Perspective view of **2** showing the pseudo $\bar{3}$ symmetry and the coplanarity of the methoxy substituent O(3)–C(15) with the Cu$_2$Br$_2$ plane.

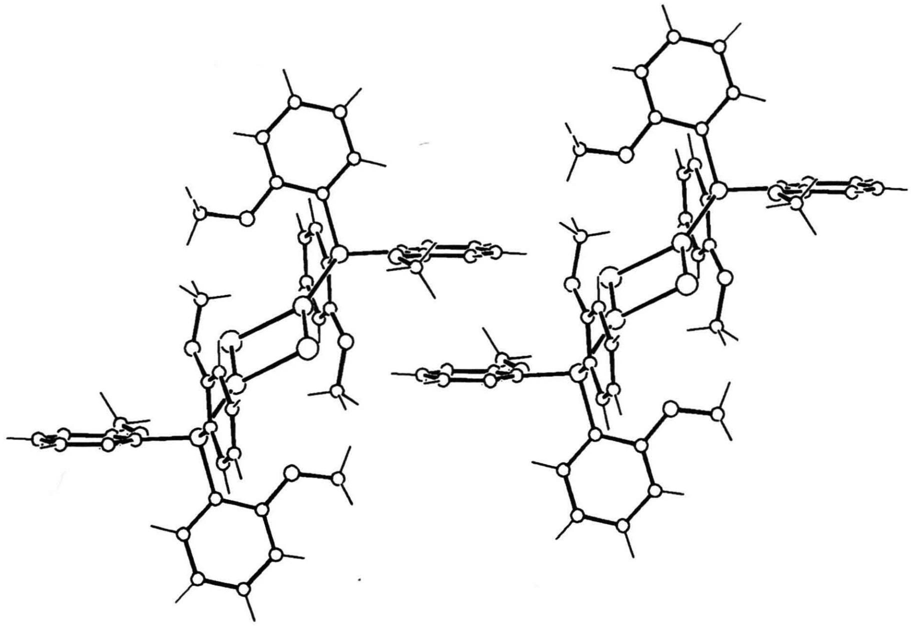

Fig. 3. View of the stacking interaction along the *c* direction for compound 2.

Table 4. ^{63}Cu NQR frequencies at 77 K of **1–4** together with the parameters of their temperature dependence.

Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K^{-1})	B (Hz K^{-2})
1	30.673	31.100	−4.32	−7.17
2	29.128	29.599	−5.50	−2.48
3	31.050*			
4	31.197	31.701	−6.32	4.93

* Measured at room-temperature.

CP-C-O-C methyl = −162.2(5), −166.5(6), −171.3(4)° for CP = C(1), C(8) and C(15) respectively).

Stacking interactions, involving the phenyl rings C(15)–C(20), occur along the c direction through the inversion center in 1/2, 1/2, 0 (mean interplane distance = 3.383(9) Å (Figure 3). This interaction leads the methoxy substituent O(3)–C(21) to be in the same plane as Cu_2Br_2 (deviations = 0.04 and 0.01 for O(3) and C(21) respectively, see also Fig. 2) and could explain the observed opening of the bond angles P-Cu-Br and Cu-P-C-C(15).

NQR

Table 4 shows the ^{63}Cu NQR frequencies of **1** to **4**, measured at 77 K. In all cases ^{65}Cu frequencies were observed at a frequency equal to 0.925 times that of the corresponding ^{63}Cu resonance. The temperature-dependence of these frequencies was observed in the range 77 K to room temperature. Except for **3**, whose signals were weak and could only be detected at room-temperature, the resonances were observable over the whole temperature range and showed no discontinuities indicative of a phase-change. For these three compounds the temperature-dependence could be expressed as a quadratic:

$$\nu_T = \nu_0 + A\,T + B\,T^2 \,. \qquad (1)$$

Table 1 shows the coefficients of this equation, which are typical of other complexes of this type.

The resonance frequencies of **1** and **2** fall in the same range as those of the corresponding complexes of tri(o-tolyl)phosphine and, as is almost always the case, the frequency of the chloride is higher than that of the bromide. However, although the molecular geometry of the Cu site in **2** is very similar to that of the tri(o-tolyl)-phosphine complex, the resonance frequency is 1.7 MHz lower. A possible explanation of this may reside in a weak interaction between the Cu(I) atom and the three oxygen atoms of the methoxy groups. These three atoms are arranged in an approximately equilateral triangle above the Cu(I) atom with Cu-O distances of 3.017, 3.117 and 3.320 Å respectively.

The molecular formulae of **3** and **4** suggest that their structures are analogous to those of $(Ph_3P)_3CuX_2$ [5, 6] and of tri(m-tolyl)phosphine [16], with both three- and four-coordinated sites. The single resonance frequency of **3** and **4** is typical of a three-coordinated site and is very similar to that observed in the analogous triphenylphosphine complexes, and, as usual, the frequency of the chloride is higher than that of the bromide. We were unable to observe resonances typical of a four-coordinated site that we would have expected in the region of 14 MHz [9], where, however, our spectrometer is less sensitive.

Conclusion

The crystal structure of **2** shows it to be a halogen-bridged dimer with three-coordinated Cu(I) sites. The ^{63}Cu NQR frequency of **1** indicates that it too has a similar structure. The ^{63}Cu NQR frequencies of **3** and **4** are consistent with the dimeric structures observed for the analogous complexes of triphenylphosphine [9, 10] and tri-m-tolylphosphine [11].

Supplementary Material

Complete Tables of atomic coordinates, displacement parameters, bond length, bond angles and torsion angles, least squares planes for compound **2** (5 pages) are available from the authors on request.

Acknowledgements

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- [1] S. Ramaprabhu, N. Amstutz, E. A. C. Lucken, and G. Bernardinelli, J. Chem. Soc. Dalton Trans. 871 (1993).
- [2] M. R. Churchill and F. J. Rotella, Inorganic Chem. **18,** 167 (1979).
- [3] M. R. Churchill and K. L. Kalra, Inorganic Chem. **13,** 1065 (1974).
- [4] M. R. Churchill and K. L. Kalra, Inorganic Chem. **13,** 1427 (1974).
- [5] V. G. Albano, P. L. Bellon, G. Cini, and M. Manassere, J. Chem. Soc. Dalton Trans. 171 (1972).
- [6] J. T. Gill, J. J. Mayerls, P. S. Welcker, D. F. Lewis, D. A. Uko, D. J. Barton, D. Stowens, and S. J. Lippard, Inorganic Chem. **15,** 1155 (1976).
- [7] P. H. Davis, R. L. Belford, and I. C. Paul, Inorganic Chem. **12,** 213 (1973).
- [8] T. Okuda, M. Hiura, K. Yamada, and H. Negita, Chemistry Letters **1977,** 367.
- [9] H. Negita, M. Hiura, K. Yamada, and T. Okuda, J. Molecular Structure **58,** 205 (1980).
- [10] T. Okuda, M. Hiura, and H. Negita, Bull. Chem. Soc. Japan **54,** 1920 (1981).
- [11] E. Blanc, D. Schwarzenbach, and H. D. Flack, J. Appl. Cryst. **24,** 1035 (1991).
- [12] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Univs. of York, England, and Louvain-la-Neuve, Belgium 1987.
- [13] S. R. Hall, H. D. Flack, and J. M. Stewart, Eds XTAL3.2 User's Manual, Universities of Western Australia and Maryland, 1992.
- [14] C. K. Johnson, ORTEP II; Report ORNL-5138; Oak ridge National Laboratory: Oak Ridge, TN (1976).
- [15] International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham 1974.
- [16] P. D. Akrivos, S. K. Hadjikakou, P. Karagiannidis, D. Mentzafos, and T. Terzis, Inorganica Chim. Acta **206,** 163 (1993).