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Molecules with an M_4X_4 Core. 11.[1] The Unexpected Isolation of the Cubane-like Isomer of Tetrameric (Triphenylarsine)copper(I) Iodide. Crystal Structure of $[(AsPh_3)CuI]_4{\cdot}C_6H_6$

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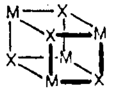
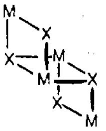
Tetrameric (triphenylarsine)copper(I) iodide crystallizes from benzene as the 1:1 solvate $[(AsPh_3)CuI]_4{\cdot}C_6H_6$. This species crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 14.605$ (2) Å, $b = 18.446$ (3) Å, $c = 28.524$ (5) Å, $\beta = 93.25$ (1)°, $V = 7672$ (2) Å^3, ρ(obsd) = 1.80 g cm^{-3}, and ρ(calcd) = 1.788 g cm^{-3} for formula weight 2064.874 and $Z = 4$. X-ray diffraction data were collected with a Syntex $P2_1$ four-circle automated diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement techniques. All 90 nonhydrogen atoms were located accurately, the final discrepancy indices being $R_F = 6.6\%$ and $R_{wF} = 4.9\%$ for all 4857 reflections with $4° < 2\theta < 35°$ (Mo Kα radiation). The Cu_4I_4 core takes up a cubane-like geometry rather than the predicted step (or "chair") structure. Copper–iodine bonds are 2.667 (2)–2.724 (2) Å in length, while copper–arsenic distances range from 2.366 (3) to 2.384 (3) Å. Intramolecular copper⋯copper contacts vary from 2.781 (3) to 2.900 (3) Å, while (nonbonding) iodine⋯iodine separations range from 4.314 (2) to 4.515 (2) Å. The possible approximate S_4 axis through the $[(AsPh_3)CuI]_4$ molecule is broken by minor rotations of the phenyl groups about their As–C(α) bonds.

Introduction

The tetrameric (phosphine)copper(I) halides and (phosphine)silver(I) halides have recently been subjected to intensive single-crystal X-ray diffraction studies both by our research group[1-9] and by Teo and Calabrese.[10-12] Complete structural studies have now appeared for the species $[(PEt_3)CuX]_4$ (X = Cl,[2] Br,[2] I[3]), $[(PPh_3)CuX]_4$ (X = Cl,[4] Br,[5] I[6]), $[(PMePh_2)CuI]_4$,[7] $[(PEt_3)AgX]_4$ (X = Cl,[8] Br,[8] I[9]), and $[(PPh_3)AgX]_4$ (X = Cl,[10] Br,[11] I[12]). There has also been interest in analogous complexes with nitrogen donor ligands including $[(pip)CuI]_4$,[13] $[(py)CuI]_4$,[14] and $[(morph)CuI]_4$.[15] While most of these complexes have a cubane-like M_4X_4 core (I), the step (or "chair") structure (II) is observed for $[(PPh_3)CuBr]_4$[5] and $[(PPh_3)CuI]_4$;[6] in addition, both the cubane-like and the step structure have been characterized for $[(PPh_3)AgI]_4$.[12]



I



II

Recently Teo and Barnes[16] reported the results of far-infrared spectroscopic studies on a variety of (pnicogen ligand)–(coinage metal)–halogen cluster systems and concluded, on the basis of these results, that "...each of $(Ph_3As)_4Cu_4X_4$ (X = Br, I) should adopt a chair-like configuration". Since $[(AsEt_3)CuI]_4$[3,17,18] is (to our knowledge) the only tetrameric (arsine)copper(I) halide complex to be examined crystallographically and since examples of the step (or "chair") conformation are rare, we decided to undertake an X-ray diffraction study of $[(Ph_3As)CuI]_4$. Our results (below) show, however, that this species crystallizes from benzene as the *cubane-like* isomer.

Experimental Section

Synthesis of $[(AsPh_3)CuI]_4{\cdot}C_6H_6$. A suspension of copper(I) iodide (0.796 g, 0.0026 mol) was refluxed in an equimolar solution of triphenylarsine (0.495 g, 0.0026 mol) in benzene (52 mL) for 12 h. The hot solution was filtered and benzene removed by slow evaporation (25 °C, 4 days), yielding large colorless crystals of $[(AsPh_3)CuI]_4{\cdot}C_6H_6$. Crystals are best obtained from the initial reaction mixture; attempted recrystallization was unsuccessful.

Table I. Experimental Data for the X-ray Diffraction Study of $[(AsPh_3)CuI]_4{\cdot}C_6H_6$

A. Crystal Parameters at 24 °C[a]

crystal system: monoclinic
space group: $P2_1/c$ [C_{2h}^5; No. 14]
$a = 14.6053$ (20) Å
$b = 18.4459$ (31) Å
$c = 28.5238$ (47) Å
$\beta = 93.252$ (12)°
$V = 7672.2$ (21) Å^3
$Z = 4$
formula wt 2064.874
ρ(calcd) = 1.788 g cm^{-3}
ρ(obsd) = 1.80 g cm^{-3}

B. Collection of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα (λ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial geometry
reflections measd: $+h$, $+k$, $\pm l$
2θ range: 4.0–35.0°
scan mode: wandering ω scan
scan speed: 1.5°/min
scan width: 1.0° (0.7° offset for bgd)
reflections collected: 5566 total, yielding 4857 independent data
standards: 3 collected every 97 data; no significant variations
absorption coeff: $\mu = 46.1$ cm^{-1}; empirical correction made (see text)

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of the 24 reflections of the forms $\{1,7,\overline{12}\}$, $\{49\bar{6}\}$, $\{5,0,14\}$, $\{822\}$, $\{673\}$, $\{80\bar{8}\}$, and $\{5,2,\overline{13}\}$, all with $2\theta = 23$–$25°$.

Collection and Processing of X-ray Diffraction Data. The crystal chosen for the analysis had dimensions of 0.3 × 0.2 × 0.2 mm. Preliminary photographic studies provided approximate unit cell dimensions, showed C_{2h} Laue symmetry, and revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$; the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is strongly indicated. The crystal was transferred to a Syntex $P2_1$ automated diffractometer. Crystal alignment and determination of the orientation matrix and accurate cell dimensions were carried out as described previously.[19] Both θ–2θ and ω scans were monitored graphically for selected reflections along (and close to) each of the principal reciprocal axes. As a result of the rather long c axis (and concomitantly short c^* spacings), we elected to collect data via the "wandering ω-scan" technique[20] rather than by the customary θ–2θ method. Details of the data collection appear in Table I.

Data were corrected for absorption ($\mu = 46.1$ cm^{-1}) with an empirical method based on a series of ψ scans. The method has been described previously.[21] The reflections used to obtain the normalized absorption curves, their 2θ values, and their maximum:minimum intensity ratios were as follows: $03\bar{5}$, $2\theta = 9.76°$, (max)/(min) = 1.174; $06\bar{7}$, 16.66°, 1.159; $17\bar{9}$, 20.31°, 1.110.

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Table II. Final Positional and Isotropic Thermal Parameters[a] for Atoms in $[(AsPh_3)CuI]_4 \cdot C_6H_6$, with Esd's

atom	*x*	*y*	*z*	B,[a] Å^2	atom	*x*	*y*	*z*	B,[a] Å^2
A. Atoms in the $[(AsPh_3)CuI]_4$ Molecule									
I(1)	0.09895 (8)	0.15123 (6)	0.06975 (4)	4.48	C(231)	0.1572 (11)	0.3732 (9)	0.2161 (6)	4.7 (4)
I(2)	0.36840 (8)	0.17772 (6)	0.00983 (4)	4.32	C(232)	0.1421 (13)	0.3747 (10)	0.2650 (7)	7.1 (5)
I(3)	0.33551 (8)	0.20424 (6)	0.16532 (4)	4.64	C(233)	0.1883 (15)	0.4296 (12)	0.2935 (7)	8.4 (6)
I(4)	0.23332 (8)	0.36811 (6)	0.06016 (4)	4.45	C(234)	0.2421 (14)	0.4780 (11)	0.2735 (7)	7.8 (6)
As(1)	0.50754 (11)	0.32517 (9)	0.09927 (5)	3.74	C(235)	0.2582 (14)	0.4770 (11)	0.2282 (8)	8.6 (6)
As(2)	0.09510 (11)	0.30752 (9)	0.17312 (6)	3.89	C(236)	0.2165 (13)	0.4210 (11)	0.1986 (6)	7.0 (5)
As(3)	0.12672 (12)	0.25340 (9)	−0.05458 (6)	4.21	C(311)	0.0204 (12)	0.3148 (10)	−0.0571 (6)	5.7 (4)
As(4)	0.32049 (12)	0.00776 (9)	0.09732 (6)	3.95	C(312)	0.0237 (17)	0.3812 (14)	−0.0775 (8)	10.8 (7)
Cu(1)	0.36407 (14)	0.26859 (11)	0.08238 (7)	4.75	C(313)	−0.0557 (21)	0.4320 (15)	−0.0738 (10)	13.4 (9)
Cu(2)	0.18878 (14)	0.25759 (11)	0.11623 (7)	4.71	C(314)	−0.1368 (18)	0.4077 (15)	−0.0577 (9)	11.6 (8)
Cu(3)	0.20443 (14)	0.23864 (11)	0.02030 (7)	4.92	C(315)	−0.1386 (16)	0.3392 (14)	−0.0397 (8)	9.5 (6)
Cu(4)	0.28165 (14)	0.13212 (11)	0.08511 (7)	4.90	C(316)	−0.0603 (15)	0.2911 (11)	−0.0393 (7)	8.0 (5)
C(111)	0.5121 (10)	0.3962 (8)	0.1491 (5)	3.8 (4)	C(321)	0.0783 (11)	0.1639 (8)	−0.0831 (5)	4.4 (4)
C(112)	0.4881 (11)	0.4690 (9)	0.1389 (6)	4.8 (4)	C(322)	0.1178 (11)	0.1009 (9)	−0.0667 (5)	4.9 (4)
C(113)	0.4860 (12)	0.5192 (10)	0.1770 (6)	6.2 (5)	C(323)	0.0842 (12)	0.0317 (10)	−0.0858 (6)	6.4 (5)
C(114)	0.5105 (13)	0.4999 (11)	0.2220 (7)	7.2 (5)	C(324)	0.0135 (13)	0.0343 (10)	−0.1198 (6)	6.4 (5)
C(115)	0.5305 (14)	0.4254 (12)	0.2313 (7)	8.3 (6)	C(325)	−0.0260 (12)	0.1008 (11)	−0.1364 (6)	6.8 (5)
C(116)	0.5314 (12)	0.3708 (10)	0.1948 (7)	6.9 (5)	C(326)	0.0061 (11)	0.1660 (9)	−0.1176 (6)	4.8 (4)
C(121)	0.6102 (10)	0.2649 (8)	0.1202 (5)	4.1 (4)	C(331)	0.1968 (11)	0.2945 (9)	−0.1019 (6)	4.6 (4)
C(122)	0.5929 (12)	0.1897 (10)	0.1212 (6)	5.9 (5)	C(332)	0.2671 (13)	0.3440 (10)	−0.0879 (6)	6.5 (5)
C(123)	0.6683 (14)	0.1446 (10)	0.1384 (6)	7.0 (5)	C(333)	0.3188 (12)	0.3786 (10)	−0.1229 (6)	6.6 (5)
C(124)	0.7533 (13)	0.1720 (10)	0.1516 (6)	6.5 (5)	C(334)	0.3003 (13)	0.3696 (11)	−0.1701 (7)	7.0 (5)
C(125)	0.7683 (14)	0.2476 (12)	0.1502 (7)	8.5 (6)	C(335)	0.2331 (16)	0.3196 (13)	−0.1836 (8)	10.1 (7)
C(126)	0.6935 (14)	0.2948 (10)	0.1352 (6)	6.8 (5)	C(336)	0.1756 (15)	0.2825 (11)	−0.1495 (8)	8.9 (6)
C(131)	0.5579 (11)	0.3789 (8)	0.0486 (5)	4.4 (4)	C(411)	0.2775 (10)	−0.0369 (8)	0.1544 (5)	3.8 (4)
C(132)	0.6284 (12)	0.4314 (9)	0.0567 (6)	5.8 (5)	C(412)	0.2476 (11)	0.0106 (9)	0.1883 (6)	5.0 (4)
C(133)	0.6617 (12)	0.4679 (9)	0.0170 (6)	5.8 (5)	C(413)	0.2190 (12)	−0.0194 (10)	0.2320 (6)	5.7 (4)
C(134)	0.6256 (11)	0.4538 (9)	−0.0285 (6)	5.3 (5)	C(414)	0.2258 (11)	−0.0947 (10)	0.2387 (6)	5.8 (4)
C(135)	0.5536 (12)	0.4044 (9)	−0.0356 (6)	5.7 (5)	C(415)	0.2542 (11)	−0.1411 (9)	0.2048 (6)	5.6 (4)
C(136)	0.5169 (11)	0.3677 (8)	0.0039 (6)	4.6 (4)	C(416)	0.2811 (11)	−0.1121 (9)	0.1608 (5)	4.8 (4)
C(211)	−0.0042 (11)	0.3722 (9)	0.1494 (6)	4.6 (4)	C(421)	0.4506 (10)	−0.0126 (8)	0.1014 (5)	4.0 (4)
C(212)	−0.0414 (13)	0.3563 (10)	0.1051 (7)	6.9 (5)	C(422)	0.4896 (14)	−0.0514 (11)	0.1401 (7)	7.5 (5)
C(213)	−0.1123 (15)	0.4021 (12)	0.0837 (7)	8.6 (6)	C(423)	0.5843 (15)	−0.0712 (11)	0.1399 (7)	8.8 (6)
C(214)	−0.1435 (12)	0.4597 (10)	0.1120 (6)	6.3 (5)	C(424)	0.6379 (12)	−0.0494 (10)	0.1031 (7)	6.5 (5)
C(215)	−0.1033 (12)	0.4764 (9)	0.1556 (6)	6.1 (5)	C(425)	0.5972 (12)	−0.0076 (9)	0.0672 (6)	5.8 (4)
C(216)	−0.0315 (11)	0.4317 (9)	0.1755 (6)	5.3 (5)	C(426)	0.5036 (11)	0.0114 (8)	0.0655 (5)	4.4 (4)
C(221)	0.0329 (10)	0.2394 (8)	0.2129 (5)	3.9 (4)	C(431)	0.2756 (12)	−0.0615 (9)	0.0494 (6)	5.1 (4)
C(222)	−0.0334 (11)	0.2629 (9)	0.2435 (6)	5.4 (5)	C(432)	0.3367 (12)	−0.1132 (10)	0.0329 (6)	6.3 (5)
C(223)	−0.0754 (12)	0.2072 (10)	0.2708 (6)	6.3 (5)	C(433)	0.2994 (14)	−0.1653 (11)	−0.0025 (7)	7.5 (5)
C(224)	−0.0554 (12)	0.1352 (10)	0.2652 (6)	6.1 (5)	C(434)	0.2119 (14)	−0.1593 (11)	−0.0167 (7)	7.2 (5)
C(225)	0.0122 (13)	0.1128 (11)	0.2353 (7)	7.4 (5)	C(435)	0.1502 (14)	−0.1083 (12)	−0.0009 (7)	8.2 (6)
C(226)	0.0560 (12)	0.1663 (10)	0.2073 (6)	5.9 (5)	C(436)	0.1830 (13)	−0.0581 (9)	0.0357 (6)	6.1 (5)
B. Carbon Atoms in the Benzene of Crystallization									
Bz(1)	0.5731 (17)	0.1994 (13)	0.2689 (8)	9.7 (6)	Bz(4)	0.6291 (18)	0.2049 (13)	0.3601 (8)	10.5 (7)
Bz(2)	0.5147 (15)	0.2307 (12)	0.3029 (8)	9.6 (6)	Bz(5)	0.6919 (17)	0.1716 (14)	0.3324 (9)	11.3 (7)
Bz(3)	0.5399 (19)	0.2358 (15)	0.3561 (10)	12.6 (8)	Bz(6)	0.6572 (17)	0.1690 (13)	0.2829 (9)	10.8 (8)

[a] "Equivalent isotropic thermal parameters", provided for noncarbon atoms, correspond to the average mean-square displacement along the three principal axes of the vibration ellipsoid.

Table III. Anisotropic Thermal Parameters[a] for the Heavy Atoms of the $[(AsPh_3)CuI]_4 \cdot C_6H_6$ Complex

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I(1)	4.29 (6)	4.37 (7)	4.73 (6)	−1.07 (5)	0.01 (5)	−0.09 (5)
I(2)	5.01 (7)	4.06 (6)	3.93 (6)	0.07 (5)	0.62 (5)	−0.16 (5)
I(3)	5.13 (7)	5.14 (7)	3.62 (6)	−0.53 (5)	−0.16 (5)	0.46 (5)
I(4)	5.64 (7)	3.28 (6)	4.43 (6)	−0.16 (5)	0.37 (5)	0.17 (5)
As(1)	4.15 (10)	3.58 (9)	3.43 (9)	−0.63 (8)	−0.15 (7)	0.24 (7)
As(2)	3.88 (9)	4.02 (10)	3.80 (9)	−0.14 (8)	0.46 (7)	−0.01 (8)
As(3)	4.44 (10)	4.36 (10)	3.77 (9)	−0.41 (8)	−0.27 (7)	0.34 (8)
As(4)	4.76 (10)	3.62 (9)	3.48 (9)	−0.19 (8)	0.34 (8)	0.39 (7)
Cu(1)	4.60 (12)	4.96 (12)	4.65 (12)	−1.08 (10)	−0.04 (9)	−0.06 (10)
Cu(2)	4.98 (12)	4.62 (12)	4.62 (12)	−0.10 (10)	1.08 (9)	−0.35 (9)
Cu(3)	5.51 (13)	4.95 (12)	4.21 (12)	−0.31 (10)	−0.42 (9)	0.09 (9)
Cu(4)	5.64 (13)	4.04 (12)	5.04 (12)	0.03 (10)	0.34 (10)	0.63 (10)

[a] The anisotropic thermal parameters have units of Å^2 and enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + hka^*b^*B_{12} + \ldots)]$.

Redundant and equivalent data were averaged [$R(I) = 2.37\%$] and converted to unscaled $|F_o|$ values following correction for Lorentz and polarization factors. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. All calculations were performed on the CDC 6600-Cyber 173 computing system at the State University of New York at Buffalo. Programs used include the following: LSHF (full-matrix least-squares refinement, by B. G. DeBoer), JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP by J. A. Ibers), STAN1 (distances and angles, with esd's, by B. G. DeBoer), and ORTEP-II (thermal ellipsoid plotting programs, by C. K. Johnson). The analytical scattering factors of Cromer and Mann[22a]

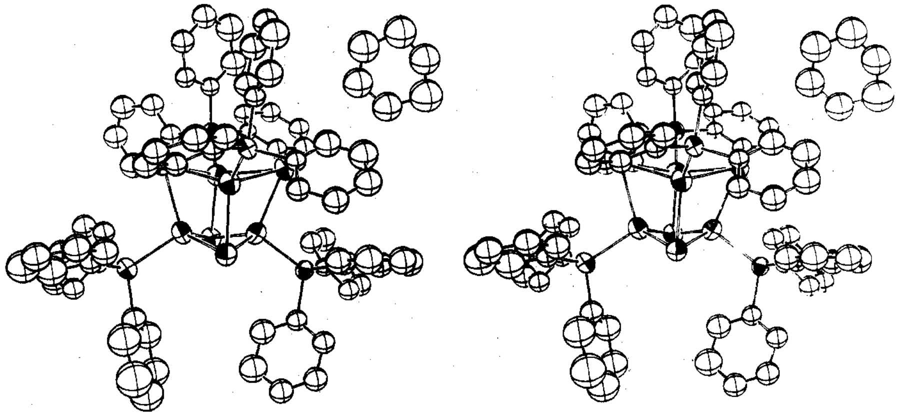

Figure 1. Stereoscopic view of the $[(AsPh_3)CuI]_4 \cdot C_6H_6$ structure, emphasizing the cubane-like connectivity of the Cu_4I_4 core and showing the interaction between the $[(AsPh_3)CuI]_4$ molecule and benzene of crystallization (ORTEP-II diagram; 50% ellipsoids).

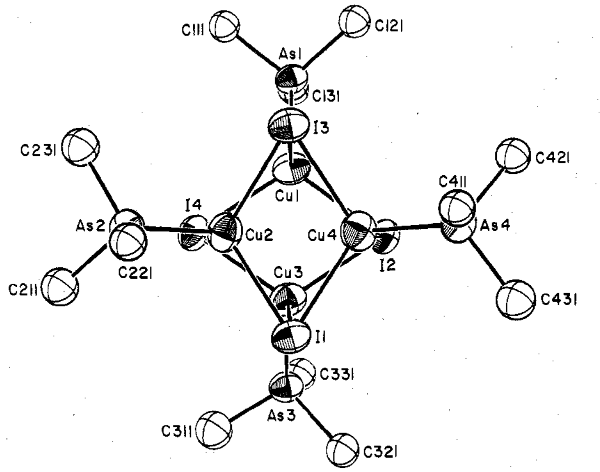

Figure 2. Labeling of atoms in the $[(AsC_3)CuI]_4$ portion of the $[(AsPh_3)CuI]_4$ molecule, looking along the pseudo-S_4 axis of the molecule (ORTEP-II diagram; 50% ellipsoids).

for neutral copper, iodine, arsenic, and carbon were corrected for both $\Delta f'$ and $\Delta f''$.[22b] The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$.

The positions of the 12 heavy atoms ($As_4Cu_4I_4$) were determined from a three-dimensional Patterson map. Full-matrix least-squares refinement of positional and isotropic thermal parameters for these atoms (49 parameters in all) led to $R_F = 34.6\%$ and $R_{wF} = 44.0\%$. The carbon atoms of the 12 phenyl rings and of a benzene molecule of crystallization were located via a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. Least-squares refinement of positional parameters for all 90 non-hydrogen atoms, anisotropic thermal parameters for heavy (Cu, As, I) atoms, and isotropic thermal parameters for the light (C) atoms (421 parameters in all) led to final convergence [$(\Delta/\sigma)_{max} < 0.1$] with $R_F = 6.6\%$, $R_{wF} = 4.9\%$, and GOF = 1.75 for all 4857 independent reflections (none rejected). It should be noted that core limitations on the computer necessitated the "blocking" of parameters into three sets for the least-squares process. The contributions of hydrogen atoms were not included in the calculations.

The largest peak on a final difference-Fourier map was 1.1 e Å^{-3} in height and was associated possibly with anisotropic thermal motion of the solvent molecule. The structure is thus complete. The usual tests of $\langle w(|F_o| - |F_c|)^2 \rangle$ against $|F_o|$, $(\sin \theta)/\lambda$, index identity, or sequence number showed the weighting scheme to be satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

Crystals of $[(AsPh_3)CuI]_4 \cdot C_6H_6$ are composed of discrete tetrameric $[(AsPh_3)CuI]_4$ units and benzene molecules which are mutually separated by normal van der Waals distances. Figure 1 shows a stereoscopic view of the tetrameric $[(AsPh_3)CuI]_4$ molecule (emphasizing its cubane-like geometry) and also indicates the placement of the benzene of crystallization relative to the tetrameric molecule.

Interatomic distances and their esd's are shown in Table IV; bond angles, with esd's, are given in Table VI, while significant least-squares planes are collected in Table V. The labeling of atoms in the $[(AsC_3)CuI]_4$ core of the molecule is illustrated in Figure 2; Figure 3 shows a stereoscopic view of the entire $[(AsPh_3)CuI]_4$ molecule viewed down this same pseudo-S_4 axis.

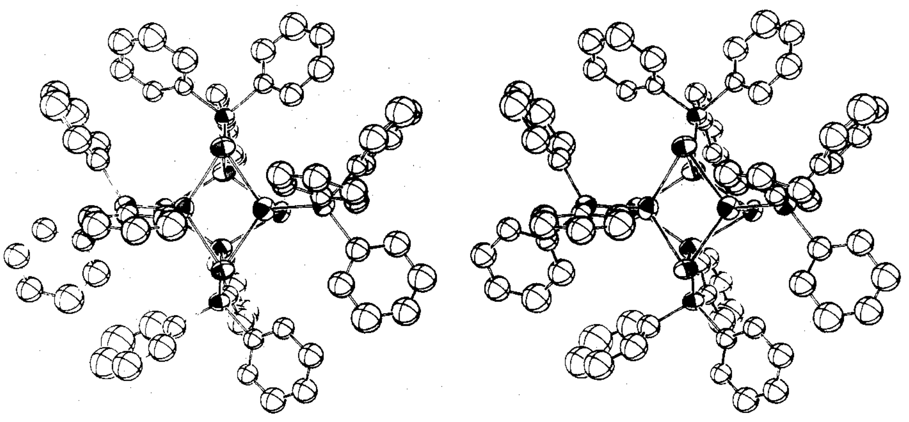

Figure 3. Stereoscopic view of the entire $[(AsPh_3)CuI]_4$ molecule, viewed down the pseudo-S_4 axis (ORTEP-II diagram; 50% ellipsoids).

Table IV. Interatomic Distances (in Å) with Esd's for $[(AsPh_3)CuI]_4 \cdot C_6H_6$

	A. Copper–Copper Distances		
Cu(1)···Cu(2)	2.794 (3)	Cu(2)···Cu(3)	2.781 (3)
Cu(1)···Cu(3)	2.900 (3)	Cu(2)···Cu(4)	2.850 (3)
Cu(1)···Cu(4)	2.793 (3)	Cu(3)···Cu(4)	2.883 (3)
	B. Copper–Iodine Distances		
Cu(1)···I(1)	4.433 (2)	Cu(3)···I(3)	4.503 (2)
Cu(1)–I(2)	2.667 (2)	Cu(3)–I(4)	2.668 (2)
Cu(1)–I(3)	2.700 (2)	Cu(3)–I(1)	2.685 (2)
Cu(1)–I(4)	2.698 (2)	Cu(3)–I(2)	2.678 (2)
Cu(2)···I(2)	4.378 (2)	Cu(4)···I(4)	4.461 (2)
Cu(2)–I(3)	2.680 (2)	Cu(4)–I(1)	2.703 (2)
Cu(2)–I(4)	2.694 (2)	Cu(4)–I(2)	2.689 (2)
Cu(2)–I(1)	2.670 (2)	Cu(4)–I(3)	2.724 (2)
	C. Copper–Arsenic Distances		
Cu(1)–As(1)	2.366 (3)	Cu(3)–As(3)	2.377 (3)
Cu(2)–As(2)	2.368 (3)	Cu(4)–As(4)	2.384 (3)
	D. Iodine–Iodine Distances		
I(1)···I(2)	4.406 (2)	I(2)···I(3)	4.515 (2)
I(1)···I(3)	4.388 (2)	I(2)···I(4)	4.314 (2)
I(1)···I(4)	4.471 (2)	I(3)···I(4)	4.456 (2)
	E. Arsenic–Carbon Distances		
As(1)–C(111)	1.932 (15)	As(3)–C(311)	1.921 (18)
As(1)–C(121)	1.933 (15)	As(3)–C(321)	1.955 (16)
As(1)–C(131)	1.932 (16)	As(3)–C(331)	1.897 (16)
As(2)–C(211)	1.968 (16)	As(4)–C(411)	1.960 (15)
As(2)–C(221)	1.952 (15)	As(4)–C(421)	1.933 (15)
As(2)–C(231)	1.914 (16)	As(4)–C(431)	1.958 (16)
	F. Carbon–Carbon Distances		
C(111)–C(112)	1.414 (22)	C(211)–C(212)	1.377 (25)
C(112)–C(113)	1.429 (24)	C(212)–C(213)	1.446 (29)
C(113)–C(114)	1.361 (27)	C(213)–C(214)	1.424 (28)
C(114)–C(115)	1.427 (30)	C(214)–C(215)	1.381 (26)
C(115)–C(116)	1.449 (29)	C(215)–C(216)	1.427 (25)
C(116)–C(111)	1.398 (24)	C(216)–C(211)	1.398 (23)
C(121)–C(122)	1.412 (24)	C(221)–C(222)	1.408 (22)
C(122)–C(123)	1.444 (26)	C(222)–C(223)	1.447 (25)
C(123)–C(124)	1.373 (27)	C(223)–C(224)	1.370 (27)
C(124)–C(125)	1.411 (29)	C(224)–C(225)	1.404 (26)
C(125)–C(126)	1.443 (29)	C(225)–C(226)	1.440 (26)
C(126)–C(121)	1.380 (25)	C(226)–C(221)	1.402 (24)
C(131)–C(132)	1.423 (23)	C(231)–C(232)	1.425 (25)
C(132)–C(133)	1.427 (24)	C(232)–C(233)	1.442 (29)
C(133)–C(134)	1.398 (24)	C(233)–C(234)	1.339 (30)
C(134)–C(135)	1.396 (24)	C(234)–C(235)	1.326 (31)
C(135)–C(136)	1.443 (23)	C(235)–C(236)	1.447 (29)
C(136)–C(131)	1.393 (22)	C(236)–C(231)	1.352 (25)
C(311)–C(312)	1.358 (32)	C(411)–C(412)	1.393 (22)
C(312)–C(313)	1.499 (39)	C(412)–C(413)	1.447 (23)
C(313)–C(314)	1.370 (41)	C(413)–C(414)	1.405 (25)
C(314)–C(315)	1.365 (37)	C(414)–C(415)	1.371 (24)
C(315)–C(316)	1.447 (32)	C(415)–C(416)	1.441 (23)
C(316)–C(311)	1.380 (28)	C(416)–C(411)	1.400 (22)
C(321)–C(322)	1.368 (23)	C(421)–C(422)	1.409 (25)
C(322)–C(323)	1.461 (25)	C(422)–C(423)	1.431 (30)
C(323)–C(324)	1.378 (26)	C(423)–C(424)	1.403 (28)
C(324)–C(325)	1.425 (27)	C(424)–C(425)	1.388 (25)
C(325)–C(326)	1.387 (25)	C(425)–C(426)	1.409 (24)
C(326)–C(321)	1.401 (22)	C(426)–C(421)	1.390 (22)
C(331)–C(332)	1.414 (24)	C(431)–C(432)	1.404 (25)
C(332)–C(333)	1.435 (26)	C(432)–C(433)	1.476 (26)
C(333)–C(334)	1.368 (27)	C(433)–C(434)	1.323 (29)
C(334)–C(335)	1.386 (31)	C(434)–C(435)	1.395 (29)
C(335)–C(336)	1.486 (32)	C(435)–C(436)	1.455 (27)
C(336)–C(331)	1.395 (27)	C(436)–C(431)	1.388 (25)
Bz(1)–Bz(2)	1.446 (33)	Bz(4)–Bz(5)	1.386 (36)
Bz(2)–Bz(3)	1.545 (36)	Bz(5)–Bz(6)	1.476 (37)
Bz(3)–Bz(4)	1.420 (38)	Bz(6)–Bz(1)	1.388 (35)

Table V. Least-Squares Planes[a] within the $[(AsPh_3)CuI]_4$ Molecule

atom	dev, Å	atom	dev, Å
	Plane I: $0.9727X + 0.2013Y - 0.1151Z = 8.0009$		
C(111)	0.023 (15)	C(114)	0.030 (20)
C(112)	0.001 (16)	C(115)	−0.007 (21)
C(113)	−0.028 (18)	C(116)	−0.019 (19)
	Plane II: $-0.3425X + 0.0785Y + 0.9362Z = 0.6143$		
C(121)	−0.013 (15)	C(124)	−0.008 (19)
C(122)	−0.007 (17)	C(125)	−0.012 (21)
C(123)	0.018 (19)	C(126)	0.022 (19)
	Plane III: $-0.6732X + 0.7312Y + 0.1100Z = -0.1351$		
C(131)	−0.035 (16)	C(134)	−0.015 (17)
C(132)	0.015 (17)	C(135)	−0.004 (17)
C(133)	0.011 (17)	C(136)	0.029 (16)
	Plane IV: $0.7040X + 0.5832Y - 0.4052Z = 2.0811$		
C(211)	−0.014 (16)	C(214)	−0.031 (18)
C(212)	−0.007 (19)	C(215)	0.010 (18)
C(213)	0.029 (21)	C(216)	0.013 (17)
	Plane V: $0.6767X + 0.0950Y + 0.7301Z = 4.9354$		
C(221)	0.004 (15)	C(224)	−0.022 (18)
C(222)	−0.008 (17)	C(225)	0.017 (19)
C(223)	0.017 (18)	C(226)	−0.008 (17)
	Plane VI: $0.7670X - 0.6123Y + 0.1919Z = -1.5193$		
C(231)	−0.022 (16)	C(234)	−0.011 (21)
C(232)	−0.001 (19)	C(235)	−0.012 (22)
C(233)	0.017 (21)	C(236)	0.028 (19)
	Plane VII: $0.2696X + 0.3442Y + 0.8994Z = 0.6159$		
C(311)	0.026 (18)	C(314)	−0.020 (27)
C(312)	−0.052 (25)	C(315)	−0.008 (23)
C(313)	0.050 (29)	C(316)	0.005 (21)
	Plane VIII: $-0.7044X - 0.0495Y + 0.7080Z = -2.7247$		
C(321)	−0.002 (15)	C(324)	0.002 (18)
C(322)	−0.001 (16)	C(325)	−0.005 (19)
C(323)	0.001 (18)	C(326)	0.005 (16)
	Plane IX: $-0.6572X + 0.7531Y - 0.0295Z = 2.1879$		
C(331)	−0.008 (16)	C(334)	0.026 (19)
C(332)	0.007 (18)	C(335)	−0.027 (24)
C(333)	−0.016 (18)	C(336)	0.018 (22)
	Plane X: $0.9189X + 0.0896Y + 0.3842Z = 5.1164$		
C(411)	0.007 (15)	C(414)	0.014 (17)
C(412)	0.005 (16)	C(415)	−0.002 (17)
C(413)	−0.015 (17)	C(416)	−0.009 (16)
	Plane XI: $0.2042X + 0.8423Y + 0.4989Z = 2.5811$		
C(421)	−0.027 (15)	C(424)	−0.015 (18)
C(422)	0.024 (20)	C(425)	0.014 (17)
C(423)	−0.004 (22)	C(426)	0.007 (15)
	Plane XII: $-0.2759X - 0.6354Y + 0.7212Z = 0.6641$		
C(431)	−0.017 (17)	C(434)	−0.002 (20)
C(432)	−0.005 (18)	C(435)	−0.020 (21)
C(433)	0.014 (20)	C(436)	0.029 (18)

[a] Equations to planes are expressed in orthonormal coordinates (X, Y, Z) which are related to the fractional coordinates (x, y, z) via the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The Cu_4I_4 moiety defines a tetrahedrally distorted cubane-like arrangement of alternating copper(I) and iodide ions. Each d^{10} copper(I) ion is in a tetrahedral coordination environment, being linked to three (μ_3-bridging) iodide ions and a terminal triphenylarsine ligand.

The 12 copper–iodine distances range from 2.667 (2) to 2.724 (2) Å. The average value of 2.688 [17] Å[23] may be compared with those of 2.6767 (15) Å in $[(AsEt_3)CuI]_4$,[3] 2.6837 (13) Å in $[(PEt_3)CuI]_4$,[3] and 2.698 [58] Å[23] in $[(PMePh_2)CuI]_4$.[9] Copper–arsenic distances range from 2.366 (3) to 2.384 (3) Å, the average value being 2.374 [8] Å[23] as compared to 2.3612 (17) Å in $[(AsEt_3)CuI]_4$.[3]

The principal distortion of the Cu_4I_4 core from a truly cubic

Bond Angles (in deg) for $[(\mathrm{AsPh_3})\mathrm{CuI}]_4\cdot\mathrm{C_6H_6}$

A. Angles within the $\mathrm{Cu_4I_4}$ Core

I(2)–Cu(1)–I(3)	114.53 (8)	I(1)–Cu(3)–I(2)	110.49 (8)	Cu(2)–I(1)–Cu(3)	62.56 (7)	Cu(1)–I(3)–Cu(2)	62.58 (7)
I(2)–Cu(1)–I(4)	107.04 (8)	I(2)–Cu(3)–I(4)	107.60 (8)	Cu(2)–I(1)–Cu(4)	64.06 (7)	Cu(1)–I(3)–Cu(4)	61.99 (6)
I(3)–Cu(1)–I(4)	111.25 (8)	I(4)–Cu(3)–I(1)	113.29 (8)	Cu(3)–I(1)–Cu(4)	64.71 (7)	Cu(2)–I(3)–Cu(4)	63.66 (7)
I(3)–Cu(2)–I(4)	112.04 (8)	I(1)–Cu(4)–I(2)	109.59 (8)	Cu(1)–I(2)–Cu(3)	65.72 (7)	Cu(1)–I(4)–Cu(2)	62.43 (7)
I(3)–Cu(2)–1(1)	110.21 (8)	1(1)–Cu(4)–I(3)	107.94 (8)	Cu(1)–I(2)–Cu(4)	62.87 (7)	Cu(1)–I(4)–Cu(3)	65.41 (7)
I(1)–Cu(2)–I(4)	112.93 (8)	I(2)–Cu(4)–I(3)	113.03 (8)	Cu(3)–I(2)–Cu(4)	64.99 (7)	Cu(2)–I(4)–Cu(3)	62.48 (6)

B. Arsenic–Copper–Iodine Angles

As(1)–Cu(1)–I(2)	112.06 (9)	As(3)–Cu(3)–I(1)	106.38 (9)	As(2)–Cu(2)–I(1)	109.84 (9)	As(4)–Cu(4)–I(1)	111.95 (9)
As(1)–Cu(1)–I(3)	101.22 (8)	As(3)–Cu(3)–I(2)	109.40 (9)	As(2)–Cu(2)–I(3)	105.13 (9)	As(4)–Cu(4)–I(2)	107.38 (9)
As(1)–Cu(1)–I(4)	110.76 (9)	As(3)–Cu(3)–I(4)	109.65 (9)	As(2)–Cu(2)–I(4)	106.32 (9)	As(4)–Cu(4)–I(3)	107.00 (9)

C. Copper–Arsenic–Carbon Angles

Cu(1)–As(1)–C(111)	116.3 (4)	Cu(3)–As(3)–C(311)	116.4 (5)	Cu(2)–As(2)–C(211)	116.3 (5)	Cu(4)–As(4)–C(411)	116.2 (4)
Cu(1)–As(1)–C(121)	118.2 (5)	Cu(3)–As(3)–C(321)	114.9 (5)	Cu(2)–As(2)–C(221)	117.0 (5)	Cu(4)–As(4)–C(421)	114.9 (5)
Cu(1)–As(1)–C(131)	116.4 (5)	Cu(3)–As(3)–C(331)	115.8 (5)	Cu(2)–As(2)–C(231)	114.4 (5)	Cu(4)–As(4)–C(431)	117.3 (5)

D. Carbon–Arsenic–Carbon Angles

C(111)–As(1)–C(121)	99.7 (6)	C(311)–As(3)–C(321)	102.1 (7)	C(211)–As(2)–C(221)	103.4 (6)	C(411)–As(4)–C(421)	103.2 (6)
C(111)–As(1)–C(131)	101.7 (6)	C(311)–As(3)–C(331)	101.9 (7)	C(211)–As(2)–C(231)	98.6 (7)	C(411)–As(4)–C(431)	101.3 (7)
C(121)–As(1)–C(131)	101.8 (6)	C(321)–As(3)–C(331)	103.8 (7)	C(221)–As(2)–C(231)	104.7 (6)	C(421)–As(4)–C(431)	101.8 (7)

E. Internal Angles of the Phenyl Rings

C(116)–C(111)–C(112)	123.0 (15)	C(216)–C(211)–C(212)	123.1 (15)
C(111)–C(112)–C(113)	118.4 (14)	C(211)–C(212)–C(213)	119.9 (17)
C(112)–C(113)–C(114)	122.1 (17)	C(212)–C(213)–C(214)	116.2 (17)
C(113)–C(114)–C(115)	118.0 (18)	C(213)–C(214)–C(215)	122.9 (17)
C(114)–C(115)–C(116)	123.0 (18)	C(214)–C(215)–C(216)	119.7 (16)
C(115)–C(116)–C(111)	115.4 (17)	C(215)–C(216)–C(211)	117.8 (15)
C(126)–C(121)–C(122)	122.8 (15)	C(226)–C(221)–C(222)	123.0 (15)
C(121)–C(122)–C(123)	116.0 (15)	C(221)–C(222)–C(223)	116.2 (15)
C(122)–C(123)–C(124)	122.8 (17)	C(222)–C(223)–C(224)	121.7 (16)
C(123)–C(124)–C(125)	119.7 (18)	C(223)–C(224)–C(225)	121.2 (17)
C(124)–C(125)–C(126)	119.2 (18)	C(224)–C(225)–C(226)	119.0 (17)
C(125)–C(126)–C(121)	119.3 (17)	C(225)–C(226)–C(221)	118.6 (15)
C(136)–C(131)–C(132)	121.3 (14)	C(236)–C(231)–C(232)	119.1 (16)
C(131)–C(132)–C(133)	117.9 (15)	C(231)–C(232)–C(233)	118.3 (17)
C(132)–C(133)–C(134)	121.5 (15)	C(232)–C(233)–C(234)	119.6 (19)
C(133)–C(134)–C(135)	119.7 (15)	C(233)–C(234)–C(235)	123.2 (20)
C(134)–C(135)–C(136)	120.3 (15)	C(234)–C(235)–C(236)	119.1 (19)
C(135)–C(136)–C(131)	119.0 (14)	C(235)–C(236)–C(231)	120.5 (17)
C(316)–C(311)–C(312)	119.7 (19)	C(416)–C(411)–C(412)	123.1 (14)
C(311)–C(312)–C(313)	119.2 (22)	C(411)–C(412)–C(413)	118.3 (15)
C(312)–C(313)–C(314)	120.3 (25)	C(412)–C(413)–C(414)	118.3 (15)
C(313)–C(314)–C(315)	117.8 (25)	C(413)–C(414)–C(415)	122.9 (16)
C(314)–C(315)–C(316)	122.6 (22)	C(414)–C(415)–C(416)	119.4 (15)
C(315)–C(316)–C(311)	119.6 (19)	C(415)–C(416)–C(411)	118.0 (14)
C(326)–C(321)–C(322)	123.3 (15)	C(426)–C(421)–C(422)	121.4 (15)
C(321)–C(322)–C(323)	119.3 (14)	C(421)–C(422)–C(423)	118.3 (17)
C(322)–C(323)–C(324)	117.1 (16)	C(422)–C(423)–C(424)	120.7 (18)
C(323)–C(324)–C(325)	122.3 (17)	C(423)–C(424)–C(425)	118.4 (17)
C(324)–C(325)–C(326)	119.9 (16)	C(424)–C(425)–C(426)	122.6 (16)
C(325)–C(326)–C(321)	118.1 (15)	C(425)–C(426)–C(421)	118.4 (14)
C(336)–C(331)–C(332)	119.7 (16)	C(436)–C(431)–C(432)	124.3 (16)
C(331)–C(332)–C(333)	119.5 (16)	C(431)–C(432)–C(433)	117.0 (16)
C(332)–C(333)–C(334)	123.3 (17)	C(432)–C(433)–C(434)	117.8 (18)
C(333)–C(334)–C(335)	116.8 (18)	C(433)–C(434)–C(435)	126.1 (19)
C(334)–C(335)–C(336)	122.9 (20)	C(434)–C(435)–C(436)	117.9 (18)
C(335)–C(336)–C(331)	117.4 (18)	C(435)–C(436)–C(431)	116.7 (16)

geometry (i.e., true O_h symmetry save for atom identity) involves symmetric and opposing distortions of the I–Cu–I and Cu–I–Cu angles from the idealized (cube) value of 90°. The I–Cu–I angles vary from 107.04 (8) to 114.53 (8)°, averaging 110.83 [244]°—i.e., close to the ideal angle of 109.47° expected for tetrahedral coordination about the Cu(I) ion; similarly, the As–Cu–I angles range from 101.22 (8) to 112.06 (9)°, averaging 108.09 [314]°. In compensation for the increased I–Cu–I bond angles, the 12 Cu–I–Cu angles range from 61.99 (6) to 65.72 (7)°, averaging 63.62 [131]°.

Iodine···iodine contacts within the $[(\mathrm{AsPh_3})\mathrm{CuI}]_4$ molecule range from 4.314 (2) to 4.515 (2) Å, averaging 4.425 [71] Å—close to the predicted van der Waals contact of ~4.3 Å for I···I[24] and in good agreement with average I···I contacts of 4.4237 (15) Å in $[(\mathrm{AsEt_3})\mathrm{CuI}]_4$,[3] 4.3800 (11) Å in $[(\mathrm{PEt_3})\mathrm{CuI}]_4$[3], and 4.406 [80] Å in $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$.[9]

The six nonbonding Cu···Cu distances range from 2.781 (3) to 2.900 (3) Å, averaging 2.834 [51] Å. This is not as short as the Cu···Cu distance of 2.7826 (24) Å found in $[(\mathrm{AsEt_3})\mathrm{CuI}]_4$[3] but is significantly shorter than the average Cu···Cu distance in analogous tetrameric (*phosphine*)copper(I) iodides—viz., 2.9272 (20) Å in $[(\mathrm{PEt_3})\mathrm{CuI}]_4$[3] and 2.930 [78] Å in $[(\mathrm{PMePh_2})\mathrm{CuI}]_4$.[9]

The 12 independent As–C(sp^2) distances range from 1.897 (16) to 1.968 (16) Å, averaging 1.938 [21] Å; this may be compared to the As–C(sp^3) distance of 1.829 (27) Å in $[(\mathrm{AsEt_3})\mathrm{CuI}]_4$.[3]

The local geometry about each arsenic atom corresponds to C_{3v} symmetry. The Cu–As–C(α) angles are each greater than the ideal tetrahedral angle of 109.47°; individual angles vary from 114.4 (5) to 118.2 (5)°, averaging 116.2 [11]°. The C(α)–As–C(α') angles are correspondingly reduced, with a range from 98.6 (7) to 104.7 (6)° and an average value of 102.0 [17]°. Carbon–carbon distances within the phenyl rings average 1.407 [35] Å; individual values are given Table IV.

Conclusions

Tetrameric (triphenylphosphine)copper(I) iodide crystallizes from benzene as $[(AsPh_3)CuI]_4 \cdot C_6H_6$, in which the Cu_4I_4 core has a tetrahedrally distorted cubane-like geometry of approximate T_d symmetry. The far-infrared spectroscopic studies of Teo and Barnes[16] suggest that they studied a $[(AsPh_3)CuI]_4$ complex in which the Cu_4I_4 core had a step structure. It therefore appears that $[(AsPh_3)CuI]_4$ joins $[(PPh_3)AgI]_4$[12] as a second example of a tetrameric (pnicogen ligand)–(coinage metal)–halide complex which exists in both cubane-like and step (or "chair") structures. Further studies are underway in attempting to isolate the step isomer in crystalline form.

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Registry No. $[(AsPh_3)CuI]_4 \cdot C_6H_6$, 69439-90-3.

Supplementary Material Available: A list of data processing formulas and structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 10: Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1979**, *18*, 166.
(2) Churchill, M. R.; DeBoer, B. G.; Mendak, S. J. *Inorg. Chem.* **1975**, *14*, 2041.
(3) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1899.
(4) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1065.
(5) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.
(6) Churchill, M. R.; DeBoer, B. G.; Donovan, D. J. *Inorg. Chem.* **1975**, *14*, 617.
(7) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267.
(8) Churchill, M. R.; Donahue, J.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 2752.
(9) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1975**, *14*, 2502.
(10) Teo, B.-K; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.
(11) Teo, B.-K.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 185.
(12) Teo, B.-K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2474.
(13) Schramm, V. *Inorg. Chem.* **1978**, *17*, 714.
(14) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2153.
(15) Schramm, V.; Fischer, K. F. *Naturwissenschaften* **1974**, *61*, 500.
(16) Teo, B.-K.; Barnes, D. M. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 681.
(17) This species was first examined by Wells in 1936.[18] The structure was redone by Churchill and Kalra in 1974.[3]
(18) Wells, A. F. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1936**, *94*, 447.
(19) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.
(20) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1950.
(21) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.
(22) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101, (b) pp 149–50.
(23) Esd's on average distances, shown in square brackets, are calculated via the formula $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$, where d_i is the ith distance and $\bar{d}$ is the average of N such distances.
(24) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

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Some New Types of Quadruply Bonded Dirhenium Compounds Containing Bridging Carboxylato Groups

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It has been found that when $Re_2(piv)_4Cl_2$ (piv = the pivalato group, $(CH_3)_3CCO_2$) is heated at temperatures of 220 °C or above, decomposition occurs, and the two chief products, which may be isolated in crystalline form by fractional sublimation, are $Re_2(piv)_2Cl_4$ (**1b**) and $Re_2(piv)_3Cl_3$ (**2**). Both of these compounds have been characterized thoroughly, including X-ray crystallographic structure determination. Compound **1** crystallizes in space group *Cmcm* with $a = 14.062$ (3) Å, $b = 11.935$ (8) Å, $c = 11.147$ (5) Å, $V = 1870$ (2) Å^3, and $Z = 4$. The molecule has rigorous *mm* (C_{2v}) symmetry with Re_2Cl_4 lying in one of the mirror planes and the Re–Re bond being bisected by the other. The full symmetry is close to D_{2h}, neglecting the orientations of the methyl groups. Important distances are Re–Re = 2.209 (2) Å, Re–Cl = 2.23 (1), 2.34 (1) Å, and Re–O = 2.02 (1) Å. The molecules are linked into chains by coordination of Cl atoms of one molecule to axial positions on neighboring molecules with Re⋯Cl = 2.90 (1) Å. The longer intramolecular Re–Cl distances are to the Cl atoms that form these bridges. Compound **2** crystallizes in space group *Cc* with $a = 13.877$ (4) Å, $b = 13.445$ (5) Å, $c = 13.497$ (3) Å, $\beta = 106.56$ (2)°, $V = 2414$ (1) Å^3, and $Z = 4$. The structure consists of infinite chains of $Re_2(piv)_3Cl_2$ units linked by bridging Cl atoms coordinated in axial positions of adjacent $Re_2(piv)_3Cl_2$ units, at Re⋯Cl distances of 2.63 and 2.68 Å. Some important distances are Re–Re = 2.229 (2) Å, Re–Cl = 2.28 (1) Å, and Re–O = 2.03 (3) Å.

Introduction

In the course of current studies of the $Re_2(O_2CCMe_3)_4X_2$ (X = Cl, Br) compounds,[1,2] we have observed that these are thermally labile and give rise to mixed pivalato/halo complexes with different compositions. Using the chloro compound, $Re_2(piv)_4Cl_2$, where we introduce the abbreviation piv for $(CH_3)_3CCO_2$, we have examined these thermal transformations in more detail and determined the conditions under which good yields of two new compounds, $Re_2(piv)_2Cl_4$ and $Re_2(piv)_3Cl_3$, can be isolated. We have also thoroughly characterized these compounds, including determination of their crystal structures.

Experimental Section

Preparation of $Re_2(piv)_4Cl_2$. This was done following the method in the literature.[3]

Preparation of 1a and 2. The thermolysis reactions of $Re_2(piv)_4Cl_2$ were carried out in an evacuated 20 × 0.7 cm Pyrex tube which was inserted into a tube furnace with $^1/_2$ its length exposed for condensation