*Inorganica Chimica Acta, 96* (1985) 21–27

# Macrocyclic Polyfunctional Lewis Bases.
# XI. Structure of Trichlorocuprates of Crown-Complexed Sodium.

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Received February 25, 1984

## Abstract

The structures of trichlorocuprates of benzo-15-crown-5 complexed sodium and dibenzo-18-crown-6 complexed sodium were determined from diffractometer data by direct methods and refined by least-squares to $R(F) = 0.059$ and $0.039$ respectively. Both complexes, $(C_{14}H_{20}O_5)_2Na_2Cu_2Cl_6$ and $(C_{20}H_{24}O_6)_2Na_2Cu_2Cl_6$, are centrosymmetric and consist of very similar $Cu_2Cl_6^{2-}$ units lying across the centre of symmetry. Two $Na^+$ cations, surrounded individually by crown ether ligands, are located on opposite sides of the anion. The dimeric structure of the anion is very characteristic for chlorocuprates of very bulky cations and resembles the anions present in tetraphenylphosphonium and tetraphenylarsonium chlorocuprates. This gives a further support to the 'super heavy' alkali metal cations concept.

## Introduction

The stability of numerous complex anions is strongly influenced by the size and charge [1] of the counter-ion. Illustrative examples are sodium complex halides such as chloromanganates, chlorocobaltates, chlorocuprates and chlorotellurates, all significantly less stable than complex halides of heavier alkali metals [2, 3]. Chlorocuprates [4], of which the potassium rubidium and cesium trichlorocuprates are known, are the most thoroughly studied complexes. Numerous ammonium and phosphonium chlorocuprates are also known. Sodium trichlorocuprate has not been obtained, probably due to the strong electrostatic field created by sodium ions which prevents the formation of the respective chlorocuprate [3]. In connection with this the formation of lithium trichlorocuprate seems surprising. However the crystal structure of this compound reveals the existence of a relatively large hydrated lithium cation $(Li{\cdot}H_2O)^+$ [5].

Recently we described the synthesis of trichlorocuprates of crown complexed sodium in which the cation size is significantly increased [6]; moreover, the interaction of the cation with the lone electron pairs of crown ether oxygens causes dispersion of its charge enabling an increase in chlorocuprate stabilities. A similar stabilization effect of carbonylate complex anions by the 18-crown-6 complexed sodium cation has also been described [7, 8].

The cation size strongly influences the structure of chlorocuprate anion in trichlorocuprates. For very bulky tetraphenylphosphonium [9] and tetraphenylarsonium [10] cations the trichlorocuprate anions are dimeric, with strictly tetracoordinated copper. For smaller cations the anionic part becomes polymeric, and the copper coordination changes to five for medium and to six for small cations as in $KCuCl_3$ and $NH_4CuCl_3$ [*cf.* 4].

The aim of this work was to determine the effect of crown complexed sodium cations on the structure of the trichlorocuprate anions.

## Experimental

Suitable crystals of trichlorocuprate of benzo-15-crown-5 complexed sodium **1** and of dibenzo-18-crown-6 complexed sodium **2** (Fig. 1) were prepared as described previously [6].

### *Crystallographic Data*

#### *Trichlorocuprate of benzo-15-crown-5 complexed sodium 1*

Photographs taken on a Weissenberg camera showed that the crystals belonged to the mono-

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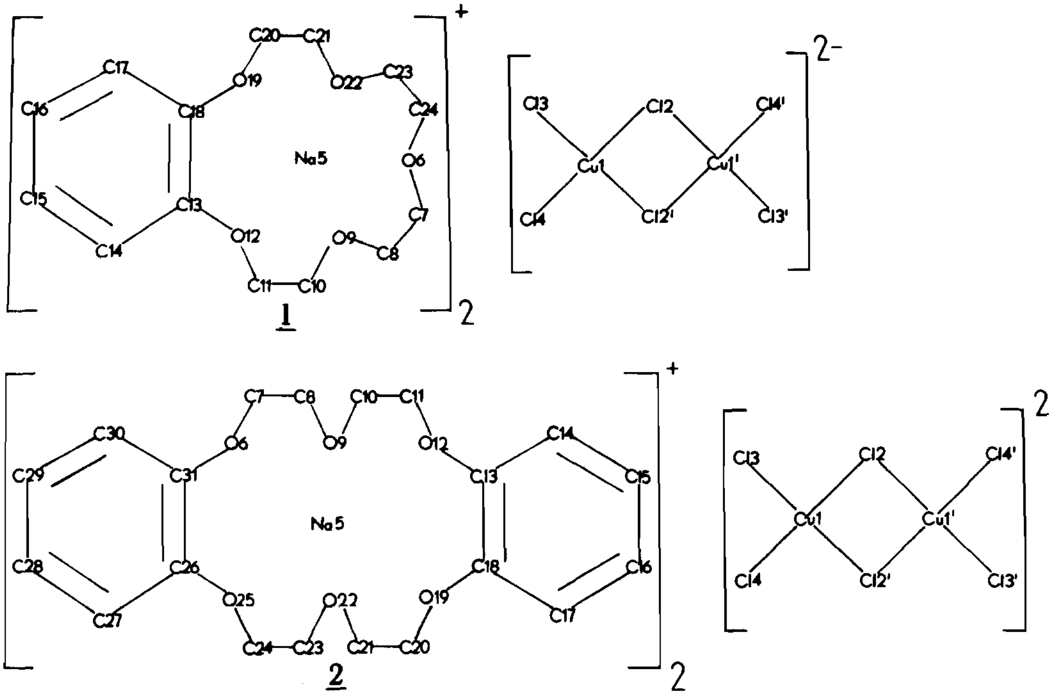

Fig. 1. The numbering schemes and formulas of complex 1 and 2.

clinic system and gave preliminary cell dimensions. Systematic absences h0l for l = 2n + 1 and 0k0 for k = 2n + 1 determined uniquely the centrosymmetric space group $P2_1/c$. A crystal of approximate dimensions 1.1 × 0.45 × 0.35 mm was mounted on a Stoe automated four-circle diffractometer with the $a$-axis parallel to the $\phi$-axis. Accurate cell dimensions were refined by a least-squares procedure based on $2\theta$ values for 20 high angle reflections measured on the diffractometer. Crystal data: $a$ = 9.805(3), $b$ = 9.449(3), $c$ = 21.382(7) Å, $\beta$ = 104.84(5)°, $V$ = 1915 Å$^3$, $D_x$ = 1.600 g cm$^{-3}$ for $Z$ = 2 units, $(C_{14}H_{20}O_5)_2$-$Na_2Cu_2Cl_6$, MW = 922.42, $F(000)$ = 940, $\mu$ = 58.9 cm$^{-1}$. The intensity data were collected to a limit of $2\theta$ = 128° with Cu–$K_\alpha$ radiation ($\lambda$ = 1.54179 Å) using the $\theta$:$2\theta$ scan technique. Of the total number of 3360 independent reflections 2454 with $I > 2\sigma(I)$ were classified as observed. Two standards measured every 40 reflections showed no significant deterioration in intensity during data collection (less than 2%). The intensities were corrected for Lorentz and polarisation effects. No absorption correction was applied.

### *Trichlorocuprate of dibenzo-18-crown-6 complexed sodium 2*

A set of Weissenberg photographs determined uniquely the $P2_1/n$ space group from the following systematic absences; h0l for h + l = 2n + 1 and 0k0 for k = 2n + 1, and allowed us to measure preliminary cell dimensions. The crystal selected for data collection had dimensions of 0.3 × 0.4 × 0.75 mm and was mounted on a Stoe diffractometer with its $c$-axis nearly parallel to the $\phi$-axis of the goniometer. Cell dimensions were accurately refined by a least-squares fit to 25 $2\theta$ values measured on the diffractometer. Crystal data: $a$ = 12.754(5), $b$ = 12.006(5), $c$ = 14.996(6) Å, $\beta$ = 92.80(5)°, $V$ = 2293 Å$^3$, $D_x$ = 1.603 g cm$^{-3}$ for $Z$ = 2 molecules of the formula $(C_{20}H_{24}O_6)_2Na_2Cu_2Cl_6$, MW = 1106.61, $F(000)$ = 1132, $\mu$ = 50.6 cm$^{-1}$. 3764 reflections were collected to a limit of $2\theta$ = 128°, and 3592 were considered as observed. Intensities of two standard reflections varied less than 4% during data collection. The intensities were corrected for Lorentz and polarisation effects. No absorption correction was applied.

### *Solution and Refinement of the Structures*

Both structures were solved by the MULTAN program [11], the 600 highest E values being used in both cases. The E-map calculated for complex 1 clearly showed the $Cu_2Cl_6^{2-}$ group placed around the centre of symmetry, the sodium position, and a fragment of the crown ring. By two subsequent iterations of isotropic refinement and difference Fourier synthesis all the remaining non-hydrogen atoms were found and the $R$ factor (= $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) dropped from 33 to 15.6%. A few more cycles of full-matrix anisotropic refinement reduced $R$ to 7.5%. At this stage the $\Delta F$ synthesis revealed all hydrogen atoms, which were then included in the refinement with isotropic temperature factors. The final $R$ value was 5.9%. Apart from the few peaks of *ca.* 0.6 e Å$^{-3}$ around the $Cu_2Cl_6^{2-}$ group the highest

TABLE I. Atomic Positional Parameters ($\times 10^4$) with E.s.d.'s in Parentheses for Non-hydrogen Atoms for Complex 1.

| | *x/a* | *y/b* | *z/c* | $U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 9236(1) | 5498(1) | 569(1) | 435 |
| Cl2 | 9823(2) | 6558(1) | −290(1) | 521 |
| Cl3 | 9697(2) | 7260(2) | 1260(1) | 586 |
| Cl4 | 7428(2) | 4580(2) | 855(1) | 735 |
| Na5 | 6975(3) | 6962(2) | 1637(1) | 484 |
| O6 | 7823(6) | 5757(5) | 2670(2) | 679 |
| C7 | 6896(12) | 4772(12) | 2847(5) | 894 |
| C8 | 5861(12) | 4252(9) | 2254(5) | 798 |
| O9 | 5117(5) | 5455(5) | 1929(2) | 632 |
| C10 | 4163(9) | 5119(8) | 1331(4) | 690 |
| C11 | 3484(8) | 6450(8) | 1018(4) | 590 |
| O12 | 4590(5) | 7453(4) | 1013(2) | 516 |
| C13 | 4177(7) | 8784(7) | 769(3) | 483 |
| C14 | 2873(9) | 9117(9) | 373(4) | 624 |
| C15 | 2551(10) | 10458(10) | 147(4) | 736 |
| C16 | 3553(10) | 11487(9) | 318(4) | 697 |
| C17 | 4874(10) | 11204(8) | 715(4) | 619 |
| C18 | 5194(7) | 9843(6) | 952(3) | 458 |
| O19 | 6475(5) | 9436(4) | 1352(2) | 497 |
| C20 | 7197(9) | 10498(8) | 1806(4) | 631 |
| C21 | 8444(9) | 9811(8) | 2242(4) | 654 |
| O22 | 7988(5) | 8611(5) | 2528(2) | 616 |
| C23 | 9121(10) | 7847(10) | 2939(4) | 727 |
| C24 | 8532(12) | 6629(11) | 3199(4) | 821 |

$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$, *cf.* [15].

TABLE II. Bond Distances (Å) and Angles (°) for Complex 1.

| | | | |
|---|---|---|---|
| Chlorocuprate anion | | | |
| Cu1–Cl2 | 2.292(2) | Cl2–Cu1–Cl2' | 87.8(1) |
| Cu1–Cl3 | 2.194(2) | Cl2–Cu1–Cl3 | 99.1(1) |
| Cu1–Cl4 | 2.196(2) | Cl2–Cu1–Cl4 | 141.5(1) |
| Cu1–Cl2' | 2.294(2) | Cl3–Cu1–Cl2' | 142.2(1) |
| Cu1–Cu1' | 3.306(1) | Cl3–Cu1–Cl4 | 98.9(1) |
| | | Cl4–Cu1–Cu2' | 98.3(1) |
| | | Cu1–Cl2–Cu1' | 92.2(1) |
| Coordination of Na$^+$ cation | | | |
| Na5–Cl3 | 2.992(3) | | |
| Na5–Cl4 | 2.905(3) | | |
| Na5–O6 | 2.434(5) | | |
| Na5–O9 | 2.513(6) | | |
| Na5–O12 | 2.422(5) | | |
| Na5–O19 | 2.434(5) | | |
| Na5–O22 | 2.465(5) | | |
| Crown part | | | |
| O6–C7 | 1.418(13) | C7–O6–C24 | 112.5(7) |
| O6–C24 | 1.427(10) | O6–C7–C8 | 109.4(8) |
| C7–C8 | 1.491(13) | C7–C8–O9 | 107.6(7) |
| C8–O9 | 1.431(10) | C8–O9–C10 | 113.4(6) |
| O9–C10 | 1.414(9) | O9–C10–C11 | 109.3(6) |
| C10–C11 | 1.498(11) | C10–C11–O12 | 107.8(6) |
| C11–O12 | 1.442(9) | C11–O12–C13 | 116.9(5) |
| O12–C13 | 1.382(7) | O12–C13–C14 | 125.2(6) |
| C13–C14 | 1.377(9) | O12–C13–C18 | 115.3(5) |
| C13–C18 | 1.396(9) | C14–C13–C18 | 119.5(6) |
| C14–C15 | 1.365(13) | C13–C14–C15 | 121.6(8) |
| C15–C16 | 1.364(13) | C14–C15–C16 | 118.8(8) |
| C16–C17 | 1.381(12) | C15–C16–C17 | 121.6(8) |
| C17–C18 | 1.388(9) | C16–C17–C18 | 119.5(7) |
| C18–O19 | 1.382(7) | C13–C18–C17 | 119.0(6) |
| O19–C20 | 1.448(9) | C13–C18–O19 | 116.4(5) |
| C20–C21 | 1.484(11) | C17–C18–O19 | 124.6(6) |
| C21–O22 | 1.414(10) | C18–O19–C20 | 115.7(5) |
| O22–C23 | 1.425(10) | O19–C20–C21 | 107.5(6) |
| C23–C24 | 1.460(14) | C20–C21–O22 | 108.7(6) |
| | | C21–O22–C23 | 112.9(6) |
| | | O22–C23–C24 | 108.2(8) |
| | | O6–C24–C23 | 108.3(6) |

density on the final difference Fourier map was 0.4 eÅ$^{-3}$. None of the positional parameters of the non-hydrogen atoms shifted more than 0.04$\sigma$ in the last cycle of refinement.

The E-map of complex 2 structure revealed all 31 non-hydrogen atoms. A few cycles of isotropic and anisotropic refinement diminished the R factor from 18.6 to 5.4% and allowed us to find all hydrogen atoms on the difference Fourier map. Hydrogen atoms were included in the refinement with isotropic temperature factors. After four more cycles of full-matrix refinement the R factor dropped to the final value of 3.6%. The highest electron density on the final difference Fourier map was 0.35 eÅ$^{-3}$, except for two peaks of 0.5 e Å$^{-3}$ in the vicinity of the $Cu_2Cl_6{}^{2-}$ anion. The largest shift of positional parameters of the heavy atoms in the last cycle of refinement was 0.05$\sigma$.

Calculated absorption correction in both structures yielded no lower *R* factor and did not improve the geometry, and was finally not taken into account. Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for all the non-hydrogen atoms were used. Atomic scattering factors for C, O, Cu, Cl and Na$^+$ were taken from Cromer and Mann [12] and for H from Stewart *et al.* [13]. All computations were performed on a CDC Cyber 175 computer at the Wissenschaftliche Rechenzentrum Berlin with an X-RAY system [14] and the MULTAN program [11].

The final positonal parameters are given in Tables I and V. Parameters for H-atoms and thermal parameters have been deposited as supplementary material.

## Results

### *Description of the Structures*

The bond lengths and angles for benzo-15-crown-5 and dibenzo-18-crown-6 complexes are collected in

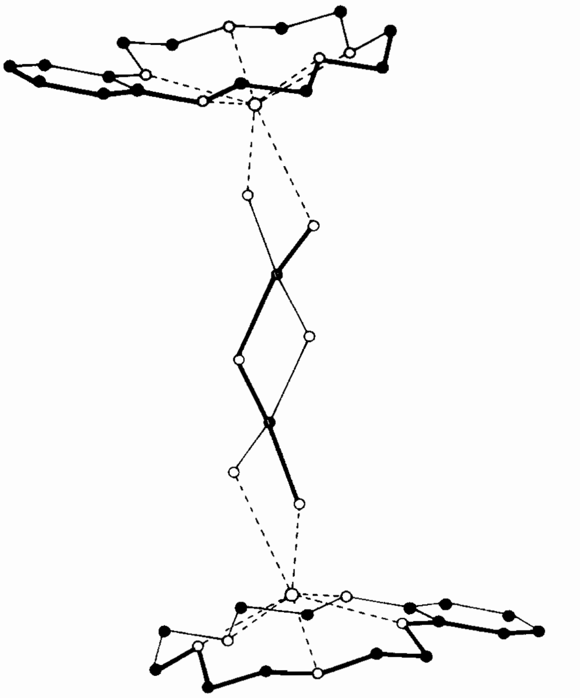

Fig 2 Structure of complex **1**.

TABLE III Selected Torsion Angles (°) for Complex **1**.

| | |
|---|---|
| Cl2–Cu1′–Cu1–Cl3 | 52 7 |
| Cl2–Cu1′–Cu1–Cl4 | 126 9 |
| C24–O6–C7–C8 | −161 1 |
| C7–O6–C24–C23 | 162 7 |
| O6–C7–C8–O9 | 58 5 |
| C7–C8–O9–C10 | −175 9 |
| C8–O9–C10–C11 | 177 7 |
| O9–C10–C11–O12 | −50 9 |
| C10–C11–O12–C13 | 177 1 |
| C11–O12–C13–C18 | −160 5 |
| O12–C13–C18–O19 | 0 2 |
| C13–C18–O19–C20 | 147 8 |
| C18–O19–C20–C21 | −173 0 |
| O19–C20–C21–O22 | 55 1 |
| C20–C21–O22–C23 | −177 9 |
| C21–O22–C23–C24 | 179 3 |
| O22–C23–C24–O6 | −60 9 |

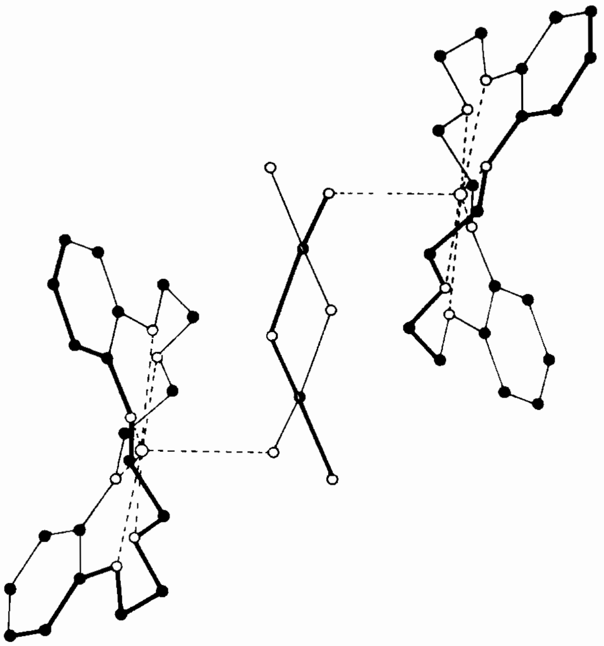

Fig 3 Structure of complex **2**.

Tables II and VI respectively (*cf* Fig 1) As shown in Figs 2 and 3, both structures contain discrete dimeric $Cu_2Cl_6^{2-}$ anions lying across the centres of symmetry and on both sides accompanied by two Na$^+$ cations and two crown ligands

The $Cu_2Cl_6^{2-}$ units are very similar in both structures and consist of $Cu_2Cl_2$ squares, built by two copper atoms and two bridging chlorines, and of two pairs of terminal chlorines at slightly shorter distances from copper, placed asymmetrically on both sides of the plane of the square so that the coordination around each copper atom is intermediate between planar and tetrahedral The details of the conformation of $Cu_2Cl_6^{2-}$ anions in the discussed structures are summarized in Table IX, together with relevant data for two other similar known structures

The benzo-15-crown-5 ligand exhibits some approximate symmetry, with the mirror perpendicular to the crown plane and bisecting the aromatic ring and the O6 atom The five oxygen atoms lie within 0 36 Å in one plane (Table IV) and torsion angles on both sides of the above mentioned mirror plane correspond in pairs with opposite signs, except for those about the bonds closest to the aromatic ring (Table III) The single C–C bonds have alternate *syn*-clinal conformations and C–O bonds exhibit anti-periplanar conformation (torsion angles 180 ± 7°), again except for the two closest to the aromatic ring, which are distorted by the planarity requirements of the ring

The dibenzo-18-crown-6 ring system exhibits approximate mm symmetry The six oxygen atoms lie in a plane, within a 0 21 Å margin All single C–C bonds are in syn–clinal conformation and all C–O bonds have anti-periplanar conformation torsion angles 180 ± 9° (Tables VII and VIII)

In both structures the Na$^+$ cation lies between the $Cu_2Cl_6^{2-}$ anion and the crown ring, and is irregularly coordinated by five (or six) oxygens and two (or one) terminal chlorines respectively In the structure of complex **2** only one chlorine atom is coordinated by a Na$^+$ cation (2 834 Å), and its bond to copper is slightly longer (2 246 Å) than the Cu–Cl

TABLE IV. Least-squares Planes with Deviations of Atom Positions (in Å) for Complex 1. Atoms defining the planes are asterisked.

| | |
|---|---|
| Aromatic ring | |
| C13* | −0.006 |
| C14* | 0.000 |
| C15* | 0.004 |
| C16* | −0.002 |
| C17* | −0.005 |
| C18* | 0.009 |
| O12 | −0.024 |
| O19 | 0.008 |
| Anion | |
| Cu1* | 0 |
| Cu1'* | 0 |
| Cl2* | 0 |
| Cl2'* | 0 |
| Cl3 | 1.316 |
| Cl4 | −1.345 |
| Oxygen atoms | |
| O6* | −0.362 |
| O9* | 0.271 |
| O12* | −0.081 |
| O19* | −0.160 |
| O22* | 0.332 |
| Na5 | −0.960 |

TABLE V. Atomic Positional Parameters (×10$^4$) with E.s.d.s in Parentheses for Non-hydrogen Atoms for Complex 2.

| | *x/a* | *y/b* | *z/c* | $U_{eq}$$^a$ |
|---|---|---|---|---|
| Cu1 | 8706(1) | 4780(1) | 9991(1) | 365 |
| Cl2 | 10040(1) | 5038(1) | 11046(1) | 446 |
| Cl3 | 7400(1) | 5514(1) | 10752(1) | 432 |
| Cl4 | 7805(1) | 3516(1) | 9224(1) | 548 |
| Na5 | 6985(1) | 7662(1) | 10035(1) | 461 |
| O6 | 9106(2) | 7829(3) | 9961(2) | 447 |
| C7 | 9690(3) | 8198(4) | 10755(3) | 468 |
| C8 | 9047(3) | 7912(4) | 11521(3) | 444 |
| O9 | 8080(2) | 8500(2) | 11418(2) | 409 |
| C10 | 7464(3) | 8400(4) | 12175(3) | 454 |
| C11 | 6518(3) | 9110(4) | 12034(3) | 463 |
| O12 | 5952(2) | 8712(2) | 11256(2) | 381 |
| C13 | 4970(3) | 9147(3) | 11077(3) | 322 |
| C14 | 4546(4) | 10035(4) | 11518(3) | 419 |
| C15 | 3532(4) | 10389(4) | 11276(3) | 462 |
| C16 | 2960(4) | 9864(4) | 10607(3) | 487 |
| C17 | 3386(3) | 8974(4) | 10156(3) | 439 |
| C18 | 4383(3) | 8617(3) | 10390(3) | 327 |
| O19 | 4892(2) | 7738(2) | 10009(2) | 397 |
| C20 | 4317(3) | 7136(4) | 9312(3) | 431 |
| C21 | 5029(3) | 6259(4) | 9005(3) | 404 |
| O22 | 5908(2) | 6779(2) | 8641(2) | 380 |
| C23 | 6569(3) | 6026(4) | 8203(3) | 415 |
| C24 | 7442(3) | 6681(4) | 7842(3) | 422 |
| O25 | 8003(2) | 7195(2) | 8586(2) | 380 |
| C26 | 8918(3) | 7732(3) | 8407(3) | 357 |
| C27 | 9251(4) | 7958(4) | 7559(3) | 455 |
| C28 | 10197(4) | 8505(4) | 7466(4) | 554 |
| C29 | 10800(4) | 8819(4) | 8196(4) | 615 |
| C30 | 10475(4) | 8603(4) | 9053(4) | 541 |
| C31 | 9525(3) | 8071(3) | 9154(3) | 386 |

$^a$$U_{eq}$ explained in Table I.

TABLE VI. Bond Distances (Å) and Angles (°) for Complex 2

| | | | |
|---|---|---|---|
| Chlorocuprate anion | | | |
| Cu1−Cl2 | 2.287(1) | Cl2−Cu1−Cl2' | 86.4(1) |
| Cu1−Cl2' | 2.294(1) | Cl2−Cu1−Cl3 | 98.0(1) |
| Cu1−Cl3 | 2.246(1) | Cl2−Cu1−Cl4 | 144.0(1) |
| Cu1−Cl4 | 2.194(1) | Cl3−Cu1−Cl2' | 150.0(1) |
| Cu1−Cu1' | 3.341(1) | Cl3−Cu1−Cl4 | 98.9(1) |
| | | Cl4−Cu1−Cl2' | 94.3(1) |
| | | Cu1−Cl2−Cu1' | 93.6(1) |
| Coordination of Na$^+$ cation | | | |
| Na5−Cl3 | 2.834(2) | | |
| Na5−O6 | 2.719(3) | | |
| Na5−O9 | 2.642(3) | | |
| Na5−O12 | 2.639(3) | | |
| Na5−O19 | 2.670(3) | | |
| Na5−O22 | 2.665(3) | | |
| Na5−O25 | 2.644(3) | | |
| Crown part | | | |
| O6−C7 | 1.442(5) | C7−O6−C31 | 116.9(3) |
| O6−C31 | 1.379(5) | O6−C7−C8 | 106.6(3) |
| C7−C8 | 1.485(6) | C7−C8−O9 | 108.0(4) |
| C8−O9 | 1.422(5) | C8−O9−C10 | 112.4(3) |
| O9−C10 | 1.418(5) | O9−C10−C11 | 108.4(4) |
| C10−C11 | 1.485(7) | C10−C11−O12 | 107.5(4) |
| C11−O12 | 1.425(5) | C11−O12−C13 | 117.0(3) |
| O12−C13 | 1.371(5) | O12−C13−C14 | 125.3(4) |
| C13−C14 | 1.380(6) | O12−C13−C18 | 115.0(3) |
| C13−C18 | 1.397(5) | C14−C13−C18 | 119.8(4) |
| C14−C15 | 1.390(6) | C13−C14−C15 | 119.6(4) |
| C15−C16 | 1.367(7) | C14−C15−C16 | 120.4(4) |
| C16−C17 | 1.392(7) | C15−C16−C17 | 120.3(4) |
| C17−C18 | 1.371(6) | C16−C17−C18 | 119.7(4) |
| C18−O19 | 1.378(5) | C13−C18−C17 | 120.2(4) |
| O19−C20 | 1.441(5) | C13−C18−O19 | 114.1(3) |
| C20−C21 | 1.479(6) | C17−C18−O19 | 125.6(4) |
| C21−O22 | 1.415(5) | C18−O19−C20 | 116.8(3) |
| O22−C23 | 1.417(5) | O19−C20−C21 | 106.4(3) |
| C23−C24 | 1.487(6) | C20−C21−O22 | 108.4(3) |
| C24−O25 | 1.436(5) | C21−O22−C23 | 113.4(3) |
| O25−C26 | 1.371(5) | O22−C23−C24 | 107.8(3) |
| C26−C27 | 1.387(6) | C23−C24−O25 | 107.3(3) |

*(continued overleaf)*

TABLE VI *(continued)*

| | | | |
|---|---|---|---|
| C26–C31 | 1 391(6) | C24–O25–C26 | 116 5(3) |
| C27–C28 | 1 385(7) | O25–C26–C27 | 125 1(4) |
| C28–C29 | 1 360(8) | O25–C26–C31 | 115 2(4) |
| C29–C30 | 1 395(8) | C27–C26–C31 | 119 8(4) |
| C30–C31 | 1 385(6) | C26–C27–C28 | 119 6(4) |
| | | C27–C28–C29 | 120 8(5) |
| | | C28–C29–C30 | 120 5(5) |
| | | C29–C30–C31 | 119 2(5) |
| | | O6–C31–C26 | 114 9(4) |
| | | O6–C31–C30 | 124 9(4) |
| | | C26–C31–C30 | 120 2(4) |

TABLE VII Selected Torsion Angles (°) for Complex **2**.

| | |
|---|---|
| Cl2–Cu1′–Cu1–Cl3 | –43 0 |
| Cl2–Cu1′–Cu1–Cl4 | 132 4 |
| C31–O6–C7–C8 | –176 1 |
| C7–O6–C31–C26 | 178 0 |
| O6–C7–C8–O9 | 61 5 |
| C7–C8–O9–C10 | 172 2 |
| C8–O9–C10–C11 | –175 5 |
| C10–C11–O12–C13 | –170 7 |
| O9–C10–C12–O12 | –60 6 |
| C11–O12–C13–C18 | 170 8 |
| O12–C13–C18–O19 | –0 3 |
| C13–C18–O19–C20 | –178 3 |
| C18–O19–C20–C21 | –179 0 |
| O19–C20–C21–O22 | 62 8 |
| C20–C21–O22–C23 | 171 1 |
| C21–O22–C23–C24 | –179 0 |
| O22–C23–C24–O25 | –61 1 |
| C23–C24–O25–C26 | –172 4 |
| C24–O25–C26–C31 | 170 5 |
| O25–C26–C31–O6 | 0 9 |

TABLE VIII Least Squares Planes with Deviations of Atoms (in Å) for Complex **2**

| Aromatic ring A | | Aromatic ring B | |
|---|---|---|---|
| C13[a] | –0 003 | C26[a] | –0 008 |
| C14[a] | 0 002 | C27[a] | 0 001 |
| C15[a] | 0 001 | C28[a] | 0 004 |
| C16[a] | –0 003 | C29[a] | –0 002 |
| C17[a] | 0 002 | C30[a] | –0 005 |
| C18[a] | 0 001 | C31[a] | 0 010 |
| O12 | –0 015 | O6 | 0 035 |
| O19 | –0 015 | O25 | –0 017 |
| Anion | | Oxygen atoms | |
| Cu1[a] | 0 | O6[a] | –0 017 |
| Cu1′[a] | 0 | O9[a] | –0 195 |
| Cl2[a] | 0 | O12[a] | 0 207 |
| Cl2′[a] | 0 | O19[a] | –0 010 |
| Cl3 | 1 106 | O22[a] | –0 201 |
| Cl4 | –1 289 | O25[a] | 0 217 |
| | | Na5 | –0 177 |

[a] Atoms defining the planes

bond to the 'free' terminal chlorine (2 194 Å) In the structure of complex **1** both terminal chlorine atoms are engaged in coordination around Na$^+$, with distances of 2 905 and 2 992 Å The coordination number of the Na$^+$ cation in both structures is 7

The Na$^+$ cation is enclosed to a greater degree within dibenzo-18-crown-6 ring than the benzo-15-crown-5 ring, the distances of Na$^+$ from the least-squares planes of the oxygen atoms are 0 177 and 0 960 Å respectively

## Discussion

Crystal structures of both compound **1** and compound **2** (Figs 2 and 3) consist of benzo-15-crown-5 complexed sodium cations or dibenzo-18-crown-6 complexed sodium cations, respectively, attached to the discrete hexachlorodicuprate $Cu_2Cl_6^{2-}$ anion The geometry of both compounds is centrosymmetric

In general, the structures of crown-complexed sodium cations are very similar to other examples [16, 17] The Na$^+$ cation is better enclosed within dibenzo-18-crown-6 (the Na$^+$–least-squares plane distance is 0 177 Å, Table VIII) than by benzo-15-crown-5 (the distance is equal to 0 960 Å, Table IV) The coordination number of the sodium cation is in both cases 7, the donor atoms being 5 or 6 crown oxygen atoms and 2 or 1 terminal chlorine atoms respectively

The electrostatic field around the complexed sodium cation is strongly reduced, due to Na$^+$ coordination to electron donating atoms and due to significant enlargement of its formal size The formation of trichlorocuprate of crown complexed sodium is thus possible in contrast to the 'free' sodium cation, which is not able to form chlorocuprates at all [1–3, 6] The reduction of the electrostatic field density around the complexed sodium cation, or the size of such a modified cation, can be deduced from the structural data obtained for the anionic part of both complexes

The structure of the anionic part of trichlorocuprates depends strongly on the counter-ion properties The existence of discrete dimeric $Cu_2Cl_6^{2-}$ anions in the both complexes is attributable to the presence of very large counter-ions Comparison of the structural parameters of the dimeric anions $Cu_2Cl_6^{2-}$ in our complexes, and in tetraphenylphosphonium and tetraphenylarsonium trichlorocuprate [9, 10], reveals their great similarity (Table IX) in all respects, including the coordination number 4 of copper atoms The structures of the anionic part of our complexes are thus comparable to the anion structure in trichlorocuprates of only very bulky tetraphenylphosphonium and tetraphenylarsonium cations, indicating a similarity in behaviour of crown-

$P_4Se_3$ and $As_4Se_3$ indicate that the rationalization proposed for $P_nAs_{4-n}S_3$ (n = 0–4) is not of general application, suggesting that the nature of the chalcogen atom also displays a strong influence Therefore it can be assumed that the gas-phase proton affinity of the $E_4X_3$ (E = P, As, X = S, Se) cage molecules is affected by the mutual interaction of the pnicogen and chalcogen atoms and by their structures Other compounds which contain phosphorus or arsenic and exhibit simple structures follow an opposite trend $PH_3$, for example, shows higher gas-phase proton affinity than $AsH_3$ [18] and $PPh_3$ [19] behaves in the same way with respect to $AsPh_3$ [20]

Turning to considerations on the chemical reactivity of the cage molecules with $d^{10}$ $M(np_3)$ (M = Ni, Pd) and $Pt(PPh_3)$, systems which have donor properties [21], it may be noted that according to the highest proton affinity of the apical pnicogen their interactions with the metal through either the apical or basal P atoms is determined probably by steric rather than electronic requirements The $Pt(PPh_3)$ moiety, in which the platinum has its coordination sphere occupied only to a small extent by the triphenylphosphine, interacts with the basal P atoms of the cage molecule The $M(np_3)$ complexes, in which the metal atom is surrounded by the skeleton of the ligand and the unique free coordination site to the metal is restricted by the six phenyl groups of the $np_3$ ligand [22], are forced by steric hindrance to interact with the apical pnicogen of the cage molecules, although the apical donor has the higher proton affinity The weak interaction that occurs between the metal–$np_3$ unit and the apical donor of the cage molecule [1] is in accordance with the above observations

Finally the different cleavages of the cage molecules by transition metal–ligand moieties afford complexes containing even-electron units, as found in the EIMS In this connection it is worthwhile to point out that the $[E_2X]^+$ (E = P, As, X = S, Se) and $[As_3]^+$ ions found in the mass spectra of the cage molecules probably have triangular structures, found for such units $\eta^3$ bonded to cobalt–triphos [5] or nickel–triphos [8] moieties Furthermore the cleavage of cage molecules in presence of metal–triphos (metal = rhodium or iridium) moieties allows us to isolate compounds with $E_3X_3$ (E = P, X = S, Se E = As, X = S) units that have not been found in mass spectra

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