**Table II.** Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³)

| atom | *x* | *y* | *z* | *U*[a] |
|---|---|---|---|---|
| Cl | 2339 (1) | 7438 (1) | 2059 (1) | 55 (1)* |
| $H_a$ | 2060 (15) | 6473 (38) | 1373 (13) | 43 (11) |
| $H_b$ | 2628 (23) | 8575 (57) | 1555 (21) | 95 (20) |
| $H_c$ | 1669 (15) | 8747 (38) | 1674 (13) | 44 (12) |
| Al | −1156 (1) | 10168 (2) | 683 (1) | 52 (1)* |
| Cl(1) | −1810 (1) | 11504 (2) | 647 (1) | 83 (1)* |
| Cl(2) | −539 (1) | 11030 (2) | 377 (1) | 84 (1)* |
| Cl(3) | −1459 (1) | 8481 (2) | 295 (1) | 91 (1)* |
| Cl(4) | −824 (1) | 9683 (2) | 1381 (1) | 87 (1)* |
| N(11) | 1778 (2) | 7026 (4) | 750 (1) | 46 (1)* |
| N(12) | 1946 (2) | 6166 (4) | 1101 (1) | 44 (1)* |
| N(21) | 2366 (2) | 9110 (4) | 885 (1) | 44 (1)* |
| N(22) | 2712 (2) | 9093 (4) | 1304 (1) | 46 (1)* |
| N(31) | 1394 (2) | 9137 (4) | 1042 (1) | 42 (1)* |
| N(32) | 1435 (1) | 9155 (4) | 1509 (1) | 45 (1)* |
| C(1) | 4838 (3) | 9514 (8) | 635 (3) | 185 (5) |
| C(2) | 4767 (3) | 10786 (8) | 465 (3) | 214 (5) |
| C(3) | 5021 (3) | 11823 (8) | 730 (3) | 175 (4) |
| C(4) | 5345 (3) | 11587 (8) | 1164 (3) | 152 (4) |
| C(5) | 5417 (3) | 10315 (8) | 1334 (3) | 201 (5) |
| C(6) | 5163 (3) | 9278 (8) | 1069 (3) | 188 (5) |
| C(11) | 1608 (2) | 6294 (5) | 374 (2) | 62 (2)* |
| C(12) | 1669 (2) | 5003 (6) | 484 (2) | 67 (2)* |
| C(13) | 1889 (2) | 4932 (4) | 955 (2) | 45 (2)* |
| C(14) | 2068 (2) | 3805 (5) | 1272 (2) | 54 (2)* |
| C(15) | 2678 (3) | 3767 (8) | 1381 (3) | 149 (5)* |
| C(16) | 1871 (4) | 3949 (7) | 1724 (2) | 121 (4)* |
| C(17) | 1854 (4) | 2563 (6) | 1042 (3) | 148 (5)* |
| C(21) | 2609 (2) | 9825 (5) | 604 (2) | 55 (2)* |
| C(22) | 3107 (2) | 10236 (6) | 841 (2) | 64 (2)* |
| C(23) | 3169 (2) | 9759 (5) | 1291 (2) | 53 (2)* |
| C(24) | 3621 (2) | 9868 (6) | 1700 (2) | 71 (2)* |
| C(25) | 4006 (3) | 10963 (7) | 1625 (3) | 108 (3)* |
| C(26) | 3926 (3) | 8570 (7) | 1762 (3) | 139 (4)* |
| C(27) | 3400 (3) | 10196 (9) | 2139 (2) | 121 (4)* |
| C(31) | 948 (2) | 9815 (5) | 871 (2) | 51 (2)* |
| C(32) | 709 (2) | 10257 (5) | 1223 (2) | 57 (2)* |
| C(33) | 1026 (2) | 9818 (5) | 1628 (2) | 46 (2)* |
| C(34) | 970 (2) | 9973 (6) | 2127 (2) | 57 (2)* |
| C(35) | 1513 (2) | 10302 (8) | 2433 (2) | 95 (3)* |
| C(36) | 582 (3) | 11091 (7) | 2164 (2) | 101 (3)* |
| C(37) | 746 (3) | 8701 (7) | 2278 (2) | 119 (4)* |
| B | 1792 (2) | 8540 (6) | 755 (2) | 45 (2)* |

[a] Asterisks indicate equivalent isotropic *U* defined as one-third of the trace of the orthongalized $\mathbf{U}_{ij}$ tensor.

graphs. Intensity data were collected with the use of graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz and polarization effects. The structure was solved by using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[8] Systematic absences were consistent with the space groups *Cc* (No. 9) and *C*2/*c* (No. 15), but consideration of the *E* value statistics suggested the choice *C*2/*c* (No. 15). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions ($d_{C-H}$ = 0.96 Å; $U_{iso}$(H) = 1.2$U_{iso}$(C)). Block-diagonal least-squares refinement converged to *R* = 0.0529 ($R_w$ = 0.0705). Atomic coordinates and thermal parameters are listed in Table II.

**Acknowledgment** is made to the National Science Foundation (Grant CHE 90-07512) for support of this research, and we thank one of the reviewers for helpful comments.

**Supplementary Material Available:** Tables SI–SVI, listing crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters, and an ORTEP drawing for $[\{\eta^3\text{-HB(3-Bu}^t\text{pzH)}_3\}\text{Cl}][\text{AlCl}_4]\cdot\text{C}_6\text{H}_6$ (11 pages); a listing of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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(8) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, Göttingen, Federal Republic of Germany, 1981.

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# Beryllium Salicylate Dihydrate

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## Introduction

Beryllium and its compounds are considered extremely dangerous owing to their latent toxicity[1-3] and *should be handled cautiously or not at all.*[4] Most chemists seem to opt for the second solution: Already as early as 1975, theoretical papers on organoberyllium chemistry outnumbered the experimental reports.[5] Nevertheless, the lack of experimental work on beryllium chemistry leads to the embarrassing situation that knowledge of the interaction of one of the perhaps most toxic metal cations with ligands present in biological systems or in the environment is very limited indeed. Even the nature of a very simple beryllium compound, beryllium salicylate, which is of interest in this respect and has been known since the beginning of the century,[6] appears to be in doubt: The salt has been formulated as a dihydrate $Be(C_6H_4OCO_2)\cdot 2H_2O$ with the beryllium cation complexed by a phenolate and a carboxylate oxygen atom. In other reports, however, beryllium salicylate is proposed to be a trihydrate, $Be(C_6H_4OCO_2)\cdot 3H_2O$,[8] or to have the curious stoichiometry $BeOH(C_6H_4OHCO_2)\cdot 2H_2O$.[9]

Salicylic acid has been regarded as one of the simplest model ligands for humic substances occurring in natural waters. A recent potentiometric study of the complex formation of beryllium(II) with salicylate and hydroxide ions gives insight into the complex equilibria present in aqueous solutions of beryllium salicylate.[10] No crystal structure determination of beryllium salicylate has been reported, however. For the species $BeOH(C_6H_4OHCO_2)\cdot 2H_2O$, only the crystal parameters (*a* = 7.068 Å, *b* = 7.950 Å, *c* = 9.443 Å, α = 100°10′, β = 102°36′, γ = 112°34′) were determined by powder photographs.[9] We therefore decided to synthesize beryllium salicylate and try to obtain single crystals of this compound suitable for X-ray structure determination.

## Experimental Section

**General Data.** All experiments were carried out in pure, fully desalinated water. Reagents were of p.a. quality. Elemental analyses were performed by the microanalytical laboratory of the Anorganisch-chemisches Institute, by standard procedures. NMR spectra were obtained on Bruker WP100SY ($^1$H) and Jeol CX400 ($^9$Be) instruments.

**Preparation.** A 3.01-g (17.00-mmol) sample of $BeSO_4\cdot 4H_2O$ is dissolved in 30 mL of water. A 2.35-g (17.01-mmol) sample of salicylic acid is added to the solution followed by 5.36 g (17.00 mmol) of $Ba(OH)_2\cdot 8H_2O$ in small portions. Upon addition of the barium hydroxide, precipitation of $BaSO_4$ occurs. The reaction mixture is stirred for 12 h at room temperature and then heated under reflux for 2 h. The hot solution (pH 4.8) is filtered and left to cool to room temperature. The resulting clear solution is evaporated under reduced pressure until precipitation of a white solid occurs. The solid is filtered and dried in a vacuum. A 1.98-g yield of $Be(C_6H_4OCO_2)\cdot 2H_2O$ (mp >350 °C) is isolated (yield 64%). Anal. Calcd for $BeC_7H_8O_5$: C, 46.41; H, 4.45. Found: C, 44.94; H, 4.56. $^1$H NMR [$D_2O$, 20 °C, internal standard *tert*-butyl alcohol (δ

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(1) Skilleter, D. N. *Chem. Br.* **1990**, *26*, 26.
(2) Petzow, G.; Zorn, H. *Chem.-Ztg.* **1974**, *98*, 236.
(3) Seidel, A. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer: Berlin, 1986; Supplement Vol. A1, p 300.
(4) Martin, R. B. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Marcel Dekker, Inc.: New York and Basel, Switzerland, 1986; Vol. 20, p 44.
(5) Schmidbaur, H. In *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer: Berlin, 1987; Be, Organoberyllium Compounds, Part 1, Preface.
(6) Rosenheim, A.; Lehmann, F. *Justus Liebigs Ann. Chem.* **1924**, *440*, 153.
(7) Jones, F. E.; Hamer, W. E.; Davies, C. W.; Bury, C. R. *J. Phys. Chem.* **1930**, *34*, 563.
(8) Asmussen, R. W.; Rancke Madsen, E. *Z. Anorg. Allg. Chem.* **1933**, *212*, 321.
(9) Venkatasubramanian, K. *Anal. Chem.* **1960**, *32*, 1052.
(10) Maeda, M.; Murata, Y.; Ito, K. *J. Chem. Soc., Dalton Trans.* **1987**, 1853.

**Table I.** Crystallographic Data for $Be(C_6H_4OCO_2)(OH_2)_2$

chem formula: $BeC_7H_8O_5$
fw = 181.151
$a$ = 9.176 (2) Å
$b$ = 12.397 (1) Å
$c$ = 7.183 (2) Å
$\beta$ = 107.16 (2)°
$V$ = 780.73 Å$^3$
$Z$ = 4

space group: $P2_1/c$ (No. 14)
$T$ = 23 ± 1 °C
$\lambda$ = 0.71069 Å
$\rho_{calcd}$ = 1.541 g cm$^{-3}$
$\mu$(Mo K$\alpha$) = 1.2 cm$^{-1}$
$R(F_o)$ = 0.031
$R_w(F_o^2)$ = 0.029

**Table II.** Fractional Atomic Coordinates and Isotropic Equivalent Thermal Displacement Parameters for $Be(C_6H_4OCO_2)(OH_2)_2$

| atom | $x/a$ | $y/b$ | $z/c$ | $U$(eq), Å$^2$ |
|---|---|---|---|---|
| Be | 0.9294 (2) | 0.6253 (2) | 0.2917 (3) | 0.026 |
| O1 | 0.8105 (1) | 0.69290 (7) | 0.1319 (1) | 0.024 |
| O2 | 0.8370 (1) | 0.36652 (8) | 0.0201 (1) | 0.030 |
| O3 | 0.9261 (1) | 0.50134 (7) | 0.2227 (1) | 0.028 |
| O4 | 0.8983 (1) | 0.63101 (9) | 0.5026 (2) | 0.038 |
| O5 | 1.1046 (1) | 0.67056 (9) | 0.3205 (2) | 0.026 |
| C1 | 0.7035 (2) | 0.5325 (1) | −0.0450 (2) | 0.021 |
| C2 | 0.6989 (2) | 0.6435 (1) | −0.0060 (2) | 0.021 |
| C3 | 0.5756 (2) | 0.7044 (1) | −0.1154 (2) | 0.033 |
| C4 | 0.4581 (2) | 0.6568 (1) | −0.2578 (2) | 0.037 |
| C5 | 0.4611 (2) | 0.5475 (1) | −0.2959 (2) | 0.030 |
| C6 | 0.5830 (2) | 0.4866 (1) | −0.1907 (2) | 0.026 |
| C7 | 0.8276 (2) | 0.4623 (1) | 0.0691 (2) | 0.021 |

= 1.2 ppm)]: $\delta$ = 6.6–6.8 ppm, m, 2 H; $\delta$ = 7.3 ppm, m, 1 H; $\delta$ = 7.6 ppm, m, 1 H. $^9$Be NMR [$D_2O$, 60 °C, external standard $Be(H_2O)_4^{2+}$ ($\delta$ = 0.00)]: $\delta$ = 3.00 ppm, s.

**X-ray Structure Determination.** Information relating to data collection and structure refinement is summarized in Table I. Data collection was performed with use of an Enraf-Nonius CAD4 diffractometer (graphite monochromator, $\theta$–$\theta$ scan). Data were corrected for Lorentz–polarization effects, but no absorption correction was applied. A total of 1696 intensity data were measured up to $((\sin\theta)/\lambda)_{max}$ = 0.616 Å$^{-1}$. After equivalent data were merged ($R_{int}$ = 0.010), 1292 of the remaining 1525 independent structure factors were considered "observed" ($F_o \geq 4\sigma(F_o)$) and used for refinement. The structure was solved by direct methods (SHELXS-86)[11] and refined by full-matrix least-squares techniques (SHELX-76).[12] All hydrogen atoms could be located and were refined isotropically, while other atoms were refined with anisotropic displacement parameters (number of refined parameters was 150). The function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F_o)$. Final $R$ and $R_w$ values were 0.031 and 0.029, respectively. Residual electron density was +0.16/−0.22 e Å$^{-3}$. The final atomic positional parameters and isotropic equivalent displacement parameters are listed in Table II.

## Results

The title compound has been prepared by the reaction of beryllium sulfate with equivalent amounts of salicylic acid and barium hydroxide in aqueous solution according to the following equation:

$$BeSO_4 + Ba(OH)_2 + 1,2\text{-}C_6H_4(OH)COOH \rightarrow BaSO_4 + Be[C_6H_4O(COO)]\cdot 2H_2O$$

After filtration of the $BaSO_4$ precipitate, the beryllium complex can be crystallized from the filtrate at pH 4.8 in good yield. Its identity was established by microanalysis, by NMR spectroscopy, and by a single-crystal X-ray diffraction study. Single crystals could be grown by slow cooling of a hot saturated solution of beryllium salicylate dihydrate. The X-ray structure investigation showed that the beryllium salicylate prepared via the "barium route" described in the Experimental Section can be formulated as $Be(C_6H_4OCO_2)(OH_2)_2$. The beryllium(II) cation lies at the center of a slightly distorted tetrahedron formed by the two oxygens of the water molecules and the deprotonated carboxyl and phenolic oxygen atoms of the salicylate ligand (Figure 1), which thus acts as a chelating ligand. The Be–O bond lengths range from 1.572 (2) (Be–$O_{hydroxy}$) to 1.658 (2) Å (Be–$O_{water}$) (Table III). These distances are at the lower end of the range given for beryllium(II) coordinated by four oxygen atoms (1.60–1.69 Å).[13] The four hydrogen atoms of the water molecules are engaged in hydrogen bonds to the hydroxyl oxygen and the carboxyl oxygens (Table IV). The short H···O and O–H···O distances are of the same order as the values determined for comparable beryllium compounds[14,15] and indicate strong hydrogen bonds.

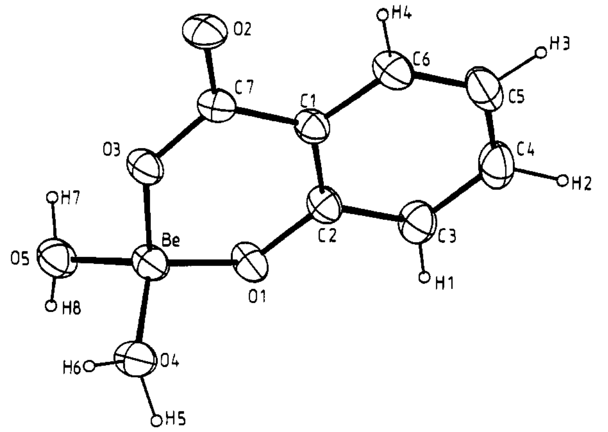

**Figure 1.** Crystal structure of $Be(C_6H_4OCO_2)(OH_2)_2$ with atomic numbering (ORTEP, displacement parameters at the 50% probability level; H atoms with arbitrary radii).

**Table III.** Interatomic Distances (Å) and Angles (deg) in the Crystal Structure of $Be(C_6H_4OCO_2)(OH_2)_2$

| | | | |
|---|---|---|---|
| Be–O1 | 1.572 (2) | Be–O3 | 1.612 (2) |
| Be–O4 | 1.623 (2) | Be–O5 | 1.658 (2) |
| O1–C2 | 1.344 (2) | O2–C7 | 1.248 (2) |
| O3–C7 | 1.296 (2) | C1–C2 | 1.407 (2) |
| C1–C6 | 1.399 (2) | C1–C7 | 1.475 (2) |
| C2–C3 | 1.394 (2) | C3–C4 | 1.381 (2) |
| C4–C5 | 1.385 (2) | C5–C6 | 1.376 (2) |
| O1–Be–O3 | 109.7 (1) | O1–Be–O4 | 112.5 (1) |
| O3–Be–O4 | 109.6 (1) | O1–Be–O5 | 110.4 (1) |
| O3–Be–O5 | 106.9 (1) | O4–Be–O5 | 107.4 (1) |
| Be–O1–C2 | 120.6 (1) | Be–O3–C7 | 124.2 (1) |
| C2–C1–C6 | 118.9 (1) | C2–C1–C7 | 122.0 (1) |
| C6–C1–C7 | 119.1 (1) | O1–C2–C1 | 122.1 (1) |
| O1–C2–C3 | 118.9 (1) | C1–C2–C3 | 119.0 (1) |
| C2–C3–C4 | 120.9 (1) | C3–C4–C5 | 120.5 (2) |
| C4–C5–C6 | 119.3 (2) | C1–C6–C5 | 121.5 (1) |
| O2–C7–O3 | 120.4 (1) | O2–C7–C1 | 120.7 (1) |
| O3–C7–C1 | 118.9 (1) | | |

$Be(C_6H_4OCO_2)(OH_2)_2$ is soluble in water only to a very small extent. The $^9$Be NMR[16] spectrum of the solution shows a singlet at 3.00 ppm. $Be(H_2O)_4^{2+}$ and cationic aquo/hydroxopoly/beryllium species formed in the hydrolysis of beryllium(II) (such as $Be_3(OH)_3^{3+}$ and $Be_2(OH)^{3+}$),[17,18] however, are known to exhibit narrow resonances at ca. 0.0 ppm. The considerable chemical shift thus observed for $Be(C_6H_4OCO_2)(OH_2)_2$ as compared to $Be(H_2O)_4^{2+}$ indicates—in agreement with previous studies[10,19]—complexation of the metal ion by the salicylate ligand in aqueous solution. Considering the narrow shift range typical for $^9$Be resonances (−20 ppm – +20 ppm), it is remarkable that the complexation of beryllium(II) through a carboxyl oxygen atom and a phenolate oxygen atom causes a considerable chemical shift ($\Delta\delta$ = 3 ppm), whereas the $^9$Be chemical shift is nearly insensitive to variations in the hydroxide/water environment of $Be(H_2O)_4^{2+}$ or its condensation products.[20] For an aqueous solution of Be(L-AspH)$_2$—a compound of crucial importance for the under-

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(11) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985.

(12) Sheldrick, G. M. *SHELX-76*, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(13) International Tables for X-Ray Crystallography; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1985; Vol. III.

(14) Robl, C.; Kinkeldey, D. *Z. Naturforsch.* **1990**, *45B*, 931.

(15) Robl, C.; Hentschel, S. *Z. Naturforsch.* **1990**, *45B*, 1499.

(16) Kotz, J. C.; Schaeffer, R.; Clouse, A. *Inorg. Chem.* **1967**, *6*, 620.

(17) Kakihana, H.; Sillen, L. G. *Acta Chem. Scand.* **1956**, *10*, 985.

(18) Bertin, F.; Thomas, G.; Merlin, J.-C. *Bull. Soc. Chim. Fr.* **1967**, 2393.

(19) Schubert, J.; Lindenbaum, A. *J. Biol. Chem.* **1954**, *208*, 359.

(20) Akitt, J. W.; Duncan, R. H. *J. Chem. Soc., Faraday Trans. I* **1980**, *76*, 2212.

**Table IV.** Hydrogen Bonds (X-H···Y) for $Be(C_6H_4OCO_2)(OH_2)_2$[a]

| X-H···Y | X-H, Å | H···Y, Å | X···Y, Å | X-H···Y, deg |
|---|---|---|---|---|
| O4-H5···O1(a) | 0.965 | 1.628 | 2.592 | 178.4 |
| O4-H6···O3(b) | 0.874 | 1.843 | 2.704 | 167.7 |
| O5-H7···O2(c) | 0.908 | 1.809 | 2.695 | 164.5 |
| O5-H8···O2(d) | 0.936 | 1.744 | 2.672 | 171.1 |

[a] Symmetry positions of atom Y: (a) $x$, $1.5 - y$, $0.5 + z$; (b) $2 - x$, $1 - y$, $1 - z$; (c) $2 - x$, $1 - y$, $-z$; (d) $2 - x$, $0.5 + y$, $0.5 - z$.

standing of the toxicity of beryllium[1]—the $^9Be$ NMR shows one singlet at ca. 0.8 ppm.[21] The observation of only one $^9Be$ singlet does not exclude the presence of other beryllium-containing species in solution, however, because fast ligand exchange on the NMR time scale could cause averaged spectra.

## Discussion

The present investigation proves the identity of the sample $Be(C_6H_4OCO_2)(OH_2)_2$ as a chelate complex, but of course, does not exclude the existence of $Be(C_6H_4OCO_2)\cdot 3H_2O$ and $Be(OH)(C_6H_4OHCO_2)\cdot 2H_2O$, which may well be components of the complex equilibria present in aqueous solutions of beryllium(II).[10] Small modifications of the preparation of beryllium salicylate could lead to different products. The straightforward formation of $Be(C_6H_4OCO_2)(OH_2)_2$ at pH 4.8 is noteworthy as compared to the behavior of other divalent metal ions toward the salicylate ligand. Although many salicylate salts of the stoichiometry $M(C_6H_4OHCO_2)_2$ (M = divalent metal ion) are known,[22-25] only a few salts of the stoichiometry $M(C_6H_4OCO_2)$ have been isolated.[26] To the best of our knowledge, no beryllium compound of the stoichiometry $Be(C_6H_4OHCO_2)_2$ has been reported. In light of the ubiquitous availability of phenolic and carboxylic groups in many natural products, the finding of strong bonding of $Be^{2+}$ to these functions is very important. This is particularly true since the chelation appears to persist in aqueous solution under physiological conditions of temperature, concentration, and pH and may thus be relevant for metal transport and for fixation at specific coordination sites in biopolymers.

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**Supplementary Material Available:** Tables giving details of the structure analysis, atomic positions, anisotropic thermal parameters, and hydrogen atom parameters (5 pages); a table of observed and calculated structure amplitudes (8 pages). Ordering information is given on any current masthead page.

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(21) Schmidbaur, H.; Kumberger, O. Unpublished results.
(22) Klug, H. P.; Alexander, L. E.; Sumner, G. G. *Acta Crystallogr.* **1958**, *11*, 41.
(23) Clark, G. L.; Kao, H. *J. Am. Chem. Soc.* **1948**, *70*, 2153.
(24) Gupta, M. P.; Saha, A. P. *Ind. J. Phys. A* **1979**, *53*, 460.
(25) Debuyst, R.; Dejehet, F.; Dekandelaer, M.-C.; Declercq, J. P.; Meersche, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1979**, *76*, 1117.
(26) Gerngross, O.; Kersap, H. *Justus Liebigs Ann. Chem.* **1914**, *406*, 245.

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# Encapsulation of Silver(I) by the Crown Thioether Ligand 1,3,6,9,11,14-Hexathiacyclohexadecane (16S6). Synthesis and Structure of $[Ag(16S6)][ClO_4]$

Broer de Groot and Stephen J. Loeb*

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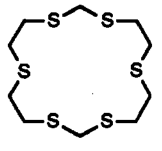
**Table I.** Crystallographic Data for $[Ag(16S6)][ClO_4]$

| | | | |
|---|---|---|---|
| chem formula | $C_{10}H_{20}AgClO_4S_6$ | $\rho$(calcd), g/cm$^{-3}$ | 1.86 |
| fw | 540.04 | $Z$ | 8 |
| $a$, Å | 9.842 (2) | $\mu$, cm$^{-1}$ | 18.10 |
| $b$, Å | 25.748 (4) | $\lambda$, Å | 0.71069 |
| $c$, Å | 15.217 (2) | $T$, °C | 23 |
| space group | *Pbca* (No. 61) | $R(F_o)$, % | 5.59 |
| $V$, Å$^3$ | 3856 (2) | $R_w(F_o)$, % | 6.48 |

Although the most common coordination numbers for Ag(I) are 2 and 4,[1] the complexing of Ag(I) by crown thioether ligands has produced a variety of homoleptic thioether complexes of higher coordination numbers. For example, six-coordination has been achieved for $[Ag(18S6)]^+$ (18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane)[2] and $[Ag(9S3)_2]^+$ (9S3 = 1,4,7-trithiacyclononane),[3-5] five-coordination was observed in the dimeric complex $[Ag_2L_2]^{2+}$ (L = 2,5,7,10-tetrathia[12](2,5)thiophene),[6] and four-coordination was found for $[Ag_3(9S3)_3]^{3+}$, $[Ag_2(15S5)_2]^{2+}$ (15S5 = 1,4,7,10,13-pentathiacyclopentadecane), and $[Ag(TT[9]OB)_2]^+$ (TT[9]OB = 2,5,8-trithia[9]-*o*-benzenophane).[5,7,8] Of these thioether macrocycles, only 18S6 acts as a classical macrocyclic ligand, providing all the donor atoms from a single ligand and encapsulating the $Ag^+$ ion to form a simple mononuclear species. We have recently demonstrated that the thioether macrocycle 1,3,6,9,11,14-hexathiacyclohexadecane (16S6) can act as a tetradentate ligand in which four of the six S atoms define a tetrahedral coordination sphere.[9]



**16S6**

We describe herein the synthesis and X-ray structure determination of $[Ag(16S6)][ClO_4]$, in which the thioether macrocycle 16S6 acts as a tetradentate ligand for Ag(I). This results in encapsulation of the Ag(I) ion in a homoleptic thioether coordination sphere with distorted tetrahedral geometry.

## Experimental Section

1,3,6,9,11,14-Hexathiacyclohexadecane (16S6) was prepared by the published method.[9] $AgClO_4$, $CH_3CN$, and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of $N_2$ by using standard Schlenk techniques, and all solvents were degassed prior to use. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.1 and 75.4 MHz, respectively, on a Brüker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Microanalytical Services, New Westminister, British Columbia, Canada. Cyclic voltammetric experiments were performed by using a BAS CV-27 potentiostat with a platinum-disk working electrode, a Ag/AgCl reference electrode, and $[NBu_4][PF_6]$ as the supporting electrolyte. All potentials are quoted versus ferrocene/ferrocenium, $Fc/Fc^+$.

**Preparation of $[Ag(16S6)][ClO_4]$.** *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive.* To a stirred

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(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980; pp 968–972.
(2) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *Polyhedron*, **1989**, *8*, 513–518.
(3) Clarkson, J. A.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 950–951.
(4) Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartman, J. R.; Wolf, R. E., Jr.; Yagbasan, R.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040–4046.
(5) Küppers, H.-J.; Wieghardt, K.; Tsay, Y.-H.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575–576.
(6) Blake, A. J.; Gould, R. O.; Reid, G.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1990**, 974–976.
(7) Lucas, C. R.; Liu, S.; Newlands, M. J.; Charland, J.-P.; Gabe, E. J. *Can. J. Chem.* **1990**, *68*, 644–649.
(8) de Groot, B.; Loeb, S. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1755–1757.
(9) de Groot, B.; Loeb, S. J. *Inorg. Chem.* **1989**, *28*, 3573–3578.