

Metal Ion-Aromatic Complexes. VIII. The Crystal and Molecular Structure of Naphthalene-Tetrakis(silver perchlorate) Tetrahydrate and Anthracene-Tetrakis(silver perchlorate) Monohydrate

Sir:

During the course of a systematic study of the structure of metal ion-aromatic complexes we have prepared and determined the crystal structures of two new complexes of unexpected stoichiometry (naphthalene-4AgClO₄·4H₂O and anthracene-4AgClO₄·H₂O), re-

described as a partially opened hinge in which the leaves of the hinge are the aromatic entities and the pin is the Ag(I). It might be expected based upon free valence⁶ that anthracene or naphthalene would form a 1:2 complex in which the two silvers are bound to the aromatic π system at the 9,10 positions or at the α,α' positions, respectively. Neither of these compounds is found, but rather the 1:4 complexes are obtained.

Naphthalene-4AgClO₄·4H₂O and anthracene-4AgClO₄·H₂O were prepared by mixing together a solution of the appropriate aromatic in toluene and a silver perchlorate-toluene⁷ solution, followed by addi-

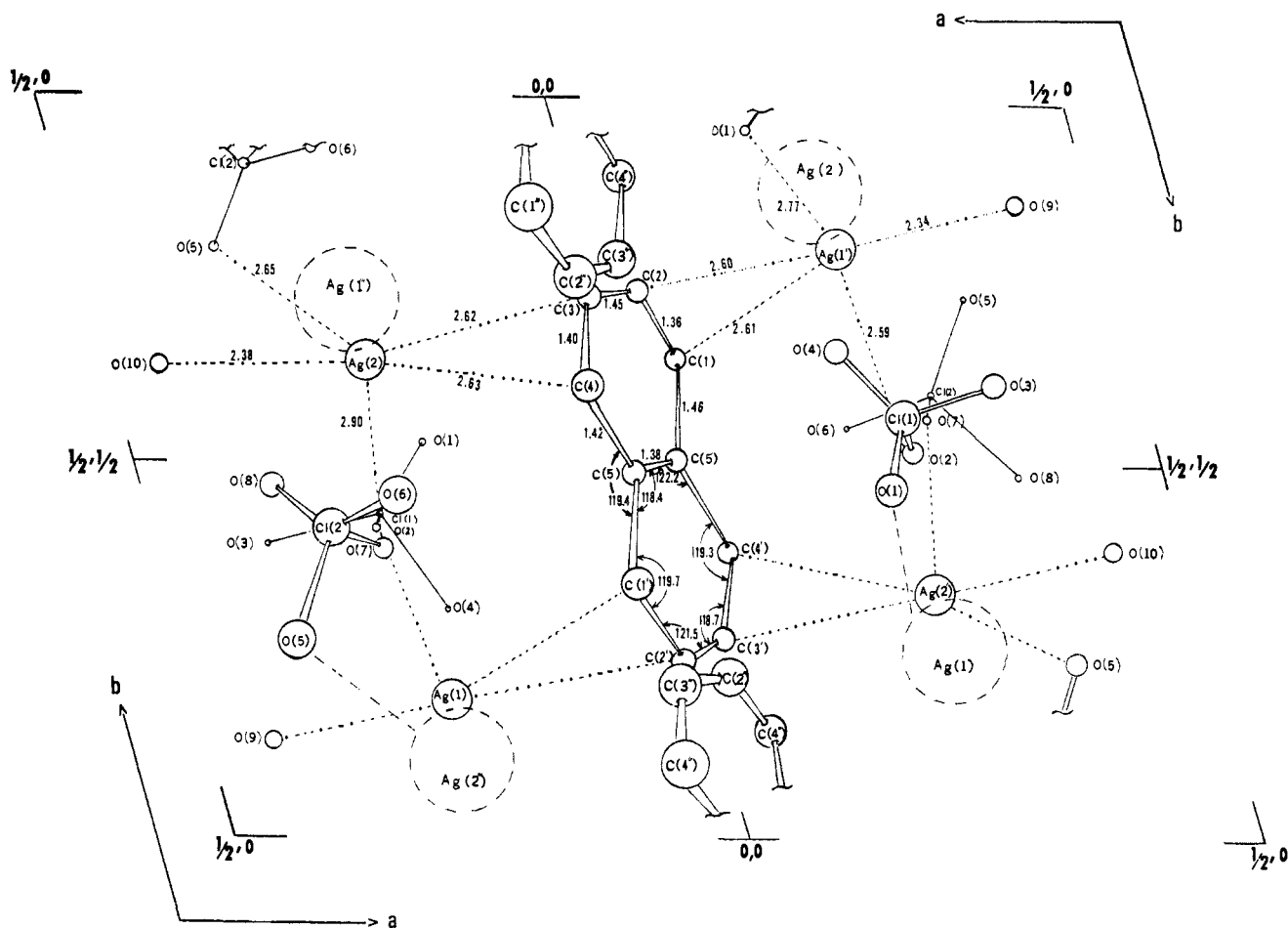


Figure 1. A perspective view of the structure of naphthalene-4AgClO₄·4H₂O down the *b* axis showing the sheets and the molecular interactions. The Ag atoms represented by large dotted circles are at $z = 1/2$, while the small solid circles represent Ag atoms at $z = 0$. A chain of AgClO₄ is Cl(2)-O(5)-Ag(2)-O(7)-Cl(2)-O(5)-Ag(2). The hydrate sheets are composed of O(9) and O(10). A crystallographic center of symmetry is midway between C(5) and C(5').

markable geometry, and novel bonding. The 1:1 aromatic Ag(I)¹ complexes have been known for some time, and two crystal structures have been determined.^{2,3} However, only recently have such compounds with other stoichiometries been well characterized and their structures reported, e.g., (cyclohexylbenzene)₂-AgClO₄⁴ and (*m*-xylene)₂-AgClO₄.⁵ These structures may be

(1) (a) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954); (b) L. J. Andrews and R. M. Keifer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 2.

(2) H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958).

(3) R. W. Turner and E. L. Amma, *ibid.*, **88**, 3243 (1966).

(4) E. A. Hall and E. L. Amma, *Chem. Commun.*, 622 (1968).

(5) E. A. Hall, I. F. Taylor, Jr., and E. L. Amma, *J. Am. Chem. Soc.*, **91**, 5745 (1969).

tion of pentane to the cloud point. The final solution was allowed to evaporate under controlled conditions. The colorless naphthalene and yellow-green anthracene complexes were unstable in air and light sensitive. They were placed in thin-walled glass capillaries for diffraction studies. Naphthalene-4AgClO₄·4H₂O was found to be triclinic: $A\bar{1}$; $a = 11.870(1) \text{ \AA}$, $b = 9.247(1) \text{ \AA}$, $c = 11.123(1) \text{ \AA}$, $\alpha = 88.93(1)^\circ$, $\beta = 96.88$

(6) (a) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, New York, N. Y., 1959, p 242; (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 330.

(7) Toluene does not form a stable crystalline complex with AgClO₄ at room temperature: E. A. Hall and E. L. Amma, submitted for publication.

of hydrate oxygens into a two-stranded ribbon. The ribbons are then stacked parallel to *c* with only van der Waals distances between them. The anthracene molecules are assembled one above the other in the channels between ribbons with the center of the molecule on a crystallographic center of symmetry and separated from neighboring molecules by 5.3 Å. The long molecular symmetry axis makes an angle of 25° with the *ab* plane, whereas the short axis makes an angle of 44° with this plane. Each anthracene is bonded *via* its π orbitals to silver atoms of four different ribbons with the shortest Ag–C distances of 2.51 (1) and 2.48 (1) Å. These Ag–C interactions are with the 1,4,5,8 positions. There is no metal–carbon bond to the points of predicted highest electron density⁶ of the ring, the 9,10 positions. The 2.48- and 2.45-Å Ag–C distances are very similar to the shortest Ag–C distances observed by us in a number of aromatic–Ag(I)^{2–5} complexes and are independent of stoichiometry, anion, and packing considerations. This arrangement gives each silver a coordination number of four: two interactions to oxygen atoms of two different perchlorate groups, one to a hydrate, and one to the aromatic. It is interesting to note that the C(2)–C(3) distance is elongated 0.07 Å (7 std dev) from free anthracene while the other C–C distances are unchanged.⁹

An alternate description of these crystalline complexes would be in terms of a clathrate in which the aromatic is a guest in the water and AgClO₄ host lattice. However, the similarity in Ag–C distances found in the anthracene complex to other Ag–C^{1–5} distances makes such a formulation unattractive. On the other hand, this description for the naphthalene complex might be acceptable. It seems to us more logical to think in terms of all the Ag–aromatic complexes as related in some way, particularly since the structures of anhydrous and hydrated silver perchlorate are not well known.

The orientations of metal to aromatic above are those predicted by Fukui, *et al.*,¹⁰ based upon a MO charge-transfer model.

Acknowledgment. This research was supported by National Science Foundation Grant GP-12282.

(10) K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Jap.*, **34**, 1076 (1961).

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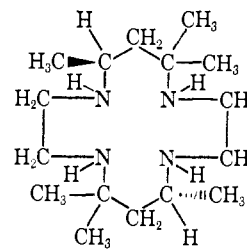
Macrocyclic Effect on the Stability of Copper(II) Tetramine Complexes

Sir:

The *chelate effect*¹ has long been known in coordination chemistry to lead to increased stability of complexes. In this work we report a *macrocyclic effect* in which the stability of a copper complex is additionally enhanced by coordination to a tetramine macrocyclic ligand compared to similar noncyclic tetramine ligands.

The macrocyclic ligand used was the *meso* isomer of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, designated *tet a* by Curtis² and *meso*-1,7-CTH

(1) For a recent review see A. E. Martell in *Advances in Chemistry Series*, No. 62, American Chemical Society, Washington D. C., 1967, p. 272.



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tet *a* or *meso*-1,7-CTH

by Busch and coworkers³ (structure I). Copper(II) reacts with this ligand to form a red complex² and we have also isolated a blue complex as a perchlorate salt. The Cu(*tet a*)²⁺_{blue} complex is not as stable thermodynamically or kinetically as Cu(*tet a*)²⁺_{red}, and the blue complex will convert to the red complex in aqueous solution. The stability constants of these complexes were measured by competition with hydrogen ion in aqueous solution. The red complex is extremely sluggish in its acid dissociation reaction at 25°, and a number of months was required to reach equilibrium. Table I

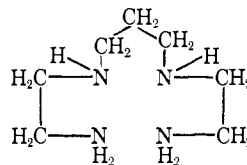
Table I. Stability Constants for the 1:1 Complexes of Tetramines with Copper(II)^a

Ligands		Log <i>K</i>	Ref
Noncyclic			
tpt	N[(CH ₂) ₃ NH ₂] ₃	13.1	<i>b</i>
3,3,3-tet	NH ₂ (CH ₂) ₃ NH(CH ₂) ₃ NH(CH ₂) ₃ NH ₂	17.3 (20°)	<i>c</i>
tren	N[(CH ₂) ₂ NH ₂] ₃	18.8 (20°)	<i>d</i>
trien	NH ₂ (CH ₂) ₂ NH(CH ₂) ₂ NH(CH ₂) ₂ NH ₂	20.1	<i>e</i>
2,3,2-tet	NH ₂ (CH ₂) ₂ NH(CH ₂) ₃ NH(CH ₂) ₂ NH ₂	23.9	<i>f</i>
Macrocyclic			
<i>tet a</i> (blue)		20	
<i>tet a</i> (red)		28	

^a 0.1 *M* ionic strength, 25.0°. Abbreviations are: tpt, 3,3',3''-triaminotripropylamine; 3,3,3-tet, N,N'-di(3-aminopropyl)propylenediamine; tren, 2,2',2''-triaminotriethylamine; trien, N,N'-di(2-aminoethyl)ethylenediamine; 2,3,2-tet, N,N'-di(2-aminoethyl)propylenediamine. ^b A. Dei, P. Paoletti, and A. Vacca, *Inorg. Chem.*, **7**, 865 (1968). ^c P. Teyssié, G. Anderegg, and G. Schwarzenbach, *Bull. Soc. Chim. Belges*, **71**, 177 (1962). ^d J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950). ^e L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Chem. Soc.*, 5115 (1961). ^f D. C. Weatherburn, E. J. Billo, J. P. Jones, and D. W. Margerum, submitted for publication.

gives the stability constants determined for the red and blue *tet a* complexes and for comparison the constants for other tetramine noncyclic ligands.

The macrocyclic complex Cu(*tet a*)²⁺_{red} is 10,000 times more stable than the noncyclic red complex Cu(2,3,2-tet)²⁺ which has a similar sequence of chelate rings (structure II). This large increase in stability can-



II
2, 3, 2-tet

not be attributed to the usual chelate effect in terms of

(2) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(3) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).