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 density[6] 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 $AgClO_4$ 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.

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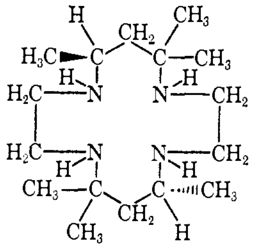
Macrocyclic Effect on the Stability of Copper(II) Tetramine Complexes

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 Curtis[2] and *meso*-1,7-CTH by Busch and coworkers[3] (structure I). Copper(II) reacts with this ligand to form a red complex[2] and we have also isolated a blue complex as a perchlorate salt. The Cu(tet *a*)$^{2+}{}_{\text{blue}}$ complex is not as stable thermodynamically or kinetically as Cu(tet *a*)$^{2+}{}_{\text{red}}$, 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 gives the stability constants determined for the red and blue tet *a* complexes and for comparison the constants for other tetramine noncyclic ligands.



I

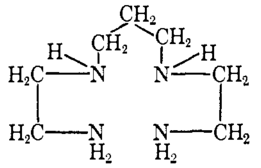
tet *a* or *meso*-1,7-CTH

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

	Ligands	Log *K*	Ref
Noncyclic			
tpt	$N[(CH_2)_3NH_2]_3$	13.1	*b*
3,3,3-tet	$NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$	17.3 (20°)	*c*
tren	$N[(CH_2)_2NH_2]_3$	18.8 (20°)	*d*
trien	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	20.1	*e*
2,3,2-tet	$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$	23.9	*f*
Macrocyclic			
tet *a* (blue)		20	
tet *a* (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.

The macrocyclic complex Cu(tet *a*)$^{2+}{}_{\text{red}}$ 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 cannot be attributed to the usual chelate effect in terms of



II

2, 3, 2-tet

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(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.

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

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

changes in translational entropy and we have termed it the macrocyclic effect. The stability of the complex is greatly increased despite the more restricted geometry which the macrocycle forces on the copper–nitrogen bonds. The macrocyclic effect, which adds stability beyond that of chelation, is about 10 times larger than the chelate effect observed for copper(II) and amine complexes. The configuration and solvation of the free macrocyclic ligand compared to the noncyclic ligand undoubtedly are very important to this effect.

The Cu(tet a)$^{2+}{}_{\text{blue}}$ complex is believed to have the macrocycle in a folded form. The blue complex reacts more rapidly with acid and is thermodynamically less stable than the square-planar Cu(tet a)$^{2+}{}_{\text{red}}$ complex.

The stability constants (concentration constants) for red and blue forms of Cu(tet a)$^{2+}$ were evaluated from the conditional stability constants measured in hydrochloric acid and from the protonation constants. Correction factors for the copper(II) chloride complexes were used.[4]

The most basic protonation constant was determined by a solvent extraction method and gave $\log K_1 = 12.6 \pm 0.1$. Values for K_2 and K_3 were determined by potentiometric titrations ($\log K_2 = 10.4 \pm 0.1$ and $\log K_3 = 0.8 \pm 0.2$). A value of K_4 was estimated using $\log K_3 - \log K_4 = 0.8$, as is the case for cyclam (1,4,8,11-tetraazacylotetradecane).[5]

The conditional stability constant ($K' = 10^{6.8}$) for the red complex in 0.1 M hydrochloric acid at 25° was obtained by extrapolation from a plot of $\log K'$ *vs.* the reciprocal of absolute temperature. The constant at each temperature was obtained by spectrophotometrically (for the red complex, ϵ 140 M^{-1} cm^{-1} at 520 mμ) determining the amount of complex remaining in solution after 47 days at 50 and 75°, and after 14 and 10 days, respectively, at 100 and 130°. The stability constant in Table I was calculated from this extrapolated value ($\log K = 28$ at 25°, $\mu = 0.1$). Other values obtained in a similar manner but with 0.2 to 0.6 M HCl were in agreement. Solutions with higher acid concentration (2–8 M HCl) were equilbrated for 133 days at 26° and the stability constant was significantly larger, $\log K = 30.8 \pm 0.4$, under these conditions.

The stability constant of the blue complex was determined spectrophotometrically (ϵ 193 M^{-1} cm^{-1} at 650 mμ) from a solution of copper(II) and tet a after 15 days at 25° (final pH 2.51). At this acidity the rate of formation of the red complex is negligible, and the fact that equilibrium was established between copper and the blue complex was ascertained from kinetic experiments followed potentiometrically and spectrophotometrically.

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(5) K. H. Mayer, Dissertation, Munich, 1960.

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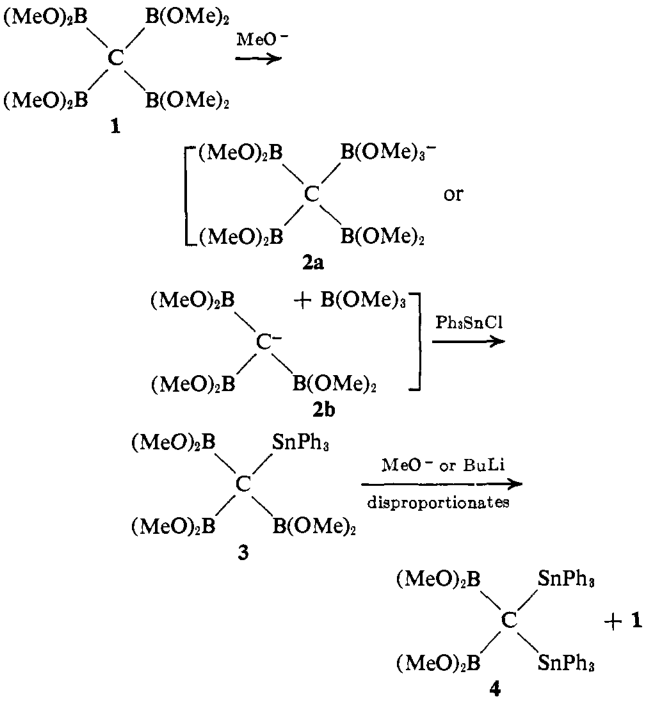
Boron–Tin and Boron–Lead Tetrametallomethanes

Sir:

Octamethyl methanetetraboronate (**1**) reacts with suitable bases to form an anionic intermediate, presumably the tris(dimethoxyboryl)methide ion (**2b**) or its methyl borate complex **2a**, which has been shown to undergo alkylation by alkyl halides[1] or condensation with aldehydes and ketones.[2] We have now extended this chemistry to prepare tetrametallomethanes having one or two tin and three or two boron atoms around the central carbon.



A solution of 3.0 g (10 mmol) of methanetetraboronic ester (**1**) in 15 ml of tetrahydrofuran was stirred under nitrogen with 0.42 g (11 mmol) of dry lithium methoxide, beginning at room temperature and heating to reflux 10 min. The resulting orange solution was added from a dropping funnel in 10 min to a stirred refluxing solution of 5.8 g (15 mmol) of triphenyltin chloride in 20 ml of tetrahydrofuran, and refluxing was continued an additional 15 min. To ensure acidity, 0.2 ml of dimethoxyboron chloride was then added, as well as 3 ml of 2,2-dimethoxypropane to reverse any accidental boronic ester hydrolysis. The solution was decanted from the lithium chloride and concentrated under vacuum. The semisolid residue was recrystallized from 30 ml of methanol and 5 ml of acetone to yield 3.0 g (52%) of triphenylstannyltris(dimethoxyboryl)methane (**3**), mp 155–156°; nmr (CCl$_4$) τ 2.83 (m, 15, C$_6$H$_5$) and 6.66 (s, 18, CH$_3$O).[3] Triphenyltin bromide gave a somewhat better yield (65%) of **3**.

Base-catalyzed interchange of electrophiles in Ph$_3$SnC[B(OMe)$_2$]$_3$ (**3**) is unusually facile and results in disproportionation. One gram (1.7 mmol) of **3** in 10 ml of tetrahydrofuran was treated with 1.2 ml (1.9 mmol) of 1.6 M butyllithium at −75° and allowed to warm to room temperature, then treated with 0.2 ml (2 mmol) of dimethoxyboron chloride and 1 ml of 2,2-dimethoxypropane, concentrated, and crystallized from 40 ml of hot methanol to yield 0.69 g (93%) of bis(triphenylstannyl)bis(dimethoxyboryl)methane (**4**), mp 159–160°; nmr (CCl$_4$) τ 2.87 (m, 30, C$_6$H$_5$) and 6.66 (s, 12, CH$_3$O).[3]

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(3) Elemental analyses were correct for C, H, B, and Sn or Pb.