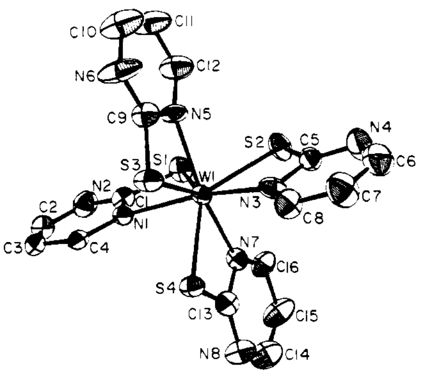

Figure 1. ORTEP drawing of the W(mpd)$_4$ molecules showing the numbering used in the tables. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 30% of the electron density.

Table V

Equations of Planes[a] for W(mpd)$_4$·$^1/_2$(diglyme)

P$_1$	S(3), W(1), N(5)	−0.9328	0.0456	−0.3576	−1.6592
P$_2$	S(1), W(1), N(1)	0.2987	0.5673	−0.7674	2.1958
P$_3$	S(2), W(1), N(3)	0.2916	0.6009	−0.7442	2.3160
P$_4$	S(4), W(1), N(7)	−0.9449	0.0731	−0.3190	−1.5626

Dihedral Angles, Deg

P$_1$/P$_2$	88.8	P$_2$/P$_3$	2.4
P$_1$/P$_3$	88.8	P$_2$/P$_4$	89.8
P$_1$/P$_4$	2.8	P$_3$/P$_4$	89.7

[a] The equation of the plane is of the form $AX + BY + CZ - D = 0$, where A, B, C, and D are constants and X, Y, and Z are orthogonalized coordinates.

Table VI. Lengths (Å) of *m* Edges

S(1)–N(1)	2.498 (7)	S(4)–N(7)	2.495 (8)
S(2)–N(3)	2.505 (8)	av	2.497 (5)
S(3)–N(5)	2.488 (8)		

spectively. Dihedral angles and equations for selected planes are presented in Table V.

The structure of W(mpd)$_4$·$^1/_2$(diglyme) was solved in the monoclinic space group $C2/c$. Each W(mpd)$_4$ molecule occupies a general position within the unit cell. The diglyme molecules sit on the inversion centers at ($^1/_4$, $^1/_4$, $^1/_2$), ($^3/_4$, $^3/_4$, $^1/_2$), ($^3/_4$, $^1/_4$, 0), and ($^1/_4$, $^3/_4$, 0) and show disordering of the O–CH$_3$ oxygen atoms. The tungsten atom is, of course, bonded to four mercaptopyrimidine ligands. Within experimental error the four ligands occupy two planes that are mutually perpendicular (see Table V) and contain the tungsten atom. The *m* edges[4] are equal within experimental error (Table VI) with a mean value of 2.497 (5) Å.

The structure of the W(mpd)$_4$ molecule has D_{2d} virtual symmetry and can be described as a dodecahedron with the *mmmm* arrangement of ligands. The A vertices are all occupied by sulfur atoms and the B vertices by ring nitrogen atoms. The angles[4] θ_A and θ_B have the mean values 36.2 ± 0.1 and 80.0 ± 0.2°. The former is very typical for all dodecahedral complexes while the latter is somewhat greater than the usual values, which are more commonly around 72°.

The excellent agreement of the observed ligand arrangement with that expected from the analysis of Burdett, Hoffmann, and Fay[3] is very gratifying. It would be interesting to know if there would be a reversal of site preferences for a d^0 complex such as Zr(mpd)$_4$. If so, it might also be expected that the wrapping pattern would change to *gggg*, as in the case[5] of Zr(8-oxoquinoline)$_4$, to minimize nonbonded contacts between the aromatic rings. We do not, however, plan such a study at present.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. W(mpd)$_4$·$^1/_2$(diglyme), 75701-22-3; W(CO)$_6$, 14040-11-0.

Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Division,
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Stability Quotients of Some Lanthanide Cryptates in Aqueous Solutions

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Received July 8, 1980

The ability of certain diazapolyoxabicyclic ligands ("cryptands") to form inclusion complexes ("cryptates") containing various alkali, alkaline-earth, transition-metal, and heavy-metal ions has been established by structural and thermodynamic studies.[1] The early reports[2] noted a variation in the stability of cryptates formed with a series of ions, e.g., the alkalis, which reaches a maximum when the estimated sizes of the cryptand cavity and the included ion are nearly the same. As more measurements were made,[3] including calorimetry,[4] other factors began to appear relevant for explaining the observations. Among these were (1) the relative importance of enthalpy and entropy in complex formation and cation solvation, (2) the cation charge, and (3) the nature of the complex formed in solution, i.e., whether the cation is completely enclosed, is partly enclosed with small anions also included, or perhaps is even an exterior complex.[5]

Lanthanide elements also form cryptates,[6–8] and crystal structures have been determined[8–10] in which each of the ions La^{3+}, Sm^{3+}, and Eu^{3+} are enclosed in the cryptand called [2.2.2] (see ref 11 for nomenclature). Electrochemical methods have been used to measure the effect of the metal

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(1) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.

(2) Lehn, J. M.; Sauvage, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6700.

(3) (a) Arnaud-Neu, F.; Spiess, B.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1977**, *60*, 2633. (b) Lehn, J. M.; Montavon, F. *Ibid.* **1978**, *61*, 67. (c) Mathieu, F.; Metz, B.; Moras, D.; Weiss, R. *J. Am. Chem. Soc.* **1978**, *100*, 4412.

(4) (a) Anderegg, G. *Helv. Chim. Acta* **1975**, *58*, 1218. (b) Kauffmann, E.; Lehn, J. M.; Sauvage, J. P. *Ibid.* **1976**, *59*, 1099.

(5) (a) Mei, E.; Popov, A. I.; Dye, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 6532. (b) Kauffmann, E.; Dye, J. L.; Lehn, J. M.; Popov, A. I. *Ibid.* **1980**, *102*, 2274. (c) Spiess, B.; Arnaud-Neu, F.; Schwing-Weill, M. J. *Helv. Chim. Acta* **1979**, *62*, 1531.

(6) Ganzow, O. A.; Kauser, A. R.; Triplett, K. M.; Weaver, M. J.; Yee, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 7087.

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(10) Ciampolini, M.; Dapporto, P.; Nardi, N. *J. Chem. Soc., Dalton Trans.* **1979**, 974.

(11) The shorthand nomenclature for cryptands was originated by Lehn.[1] The three numbers denote the ether oxygen in each strand of the bicyclic molecule. The cryptands used in this work are designated as follows: [2.1.1] represents 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane; [2.2.1] represents 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane; [2.2.2] represents 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane. The mathematical symbol for inclusion is used in naming cryptates.

Table I. Ionization Quotients for Cryptands[a] at 25 °C

[2.1.1]		[2.2.1]		[2.2.2]			
pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	medium	ref
7.85 (5)	10.64 (5)	7.50 (5)	10.53 (5)	7.28 (5)	9.60 (5)	0.05 M $(CH_3)_4NBr$	2
8.14 (1)	11.32 (7)	7.74 (4)	11.02 (1)	7.53 (4)	10.00 (1)	0.10 M $(CH_3)_4NClO_4$	3a
				7.31	9.71	0.10 M $(CH_3)_4NCl$	4a
7.86 (2)	10.48 (3)	7.68 (1)	10.75 (2)	7.59 (1)	9.95 (2)	0.25 M $(CH_3)_4NCl$	this work

[a] Estimated standard deviations in the last figure are given in parentheses.

Table II. Stability Quotients[a] for Some Lanthanide Cryptates in 0.25 M $(CH_3)_4NCl$ at 25 °C

element	trivalent radius, Å	log K_s [2.1.1]	log K_s [2.2.1]	log K_s [2.2.2]
La	1.06		6.59 (9)	6.45 (3)
Pr	1.01		6.58 (4)	6.37 (8)
Sm	0.96	6.8 (2)	6.76 (2)	5.94 (6)
Eu	0.95		6.8 (2)	5.90 (9)
Gd	0.94		6.7 (1)	
Tb	0.92		6.6 (1)	
Ho	0.89	6.21 (8)		6.2 (2)
Er	0.88		6.60 (8)	
Tm	0.87	6.8 (4)	6.88 (5)	
Yb	0.86	6.51 (9)		
Lu	0.85	6.55 (9)		

[a] K_s is defined in text. Least-squares estimated standard deviations in the last number are given in parentheses.

oxidation state on the thermodynamics and kinetics of the formation of Eu and Yb cryptates in aqueous solution.[12] Values of the stability quotients for $[\mathrm{Eu}^{3+}\subset 2.2.1]$ and $[\mathrm{Eu}^{3+}\subset 2.2.2]$ were determined indirectly and may be compared with the results we report here.

Using titrimetric methods similar to those of earlier workers,[2,3] we have measured the stabilities in water of a number of cryptates of the types $[\mathrm{Ln}^{3+}\subset 2.1.1]$, $[\mathrm{Ln}^{3+}\subset 2.2.1]$, and $[\mathrm{Ln}^{3+}\subset 2.2.2]$, where Ln represents various lanthanide elements. Slow reaction kinetics and a tendency for precipitation presented experimental difficulties to be overcome and somewhat limited the accuracy of the results. However, we have established the stability of these trivalent lanthanide complexes relative to those of lower valences and have shown that there is only a small effect of the variation of cation size among the lanthanides.

Stability quotients of cryptates can be determined by successive titration of solutions of pure cryptand and of cryptand plus a cation, because complexation affects the acid–base equilibria of these diamines. These equilibria can be represented by eq 1 and 2 in which L is the cryptand. The formation of the cryptate is given by eq 3. It is assumed that

$$\mathrm{LH_2}^{2+} \rightleftarrows \mathrm{LH}^+ + \mathrm{H}^+ \qquad (1)$$

$$\mathrm{LH}^+ \rightleftarrows \mathrm{L} + \mathrm{H}^+ \qquad (2)$$

$$\mathrm{L} + \mathrm{Ln}^{3+} \rightleftarrows [\mathrm{Ln}^{3+}\subset\mathrm{L}] \qquad (3)$$

because of the charge on the included atom, the protonation of the inclusion complex is negligible. From eq 1 and 2 the cryptand ionization quotients, K_1 and K_2, may be obtained. The stability quotient of the complex is written as eq 4. The

$$K_s = ([\mathrm{Ln}^{3+}\subset\mathrm{L}])/(\mathrm{Ln}^{3+})(\mathrm{L}) \qquad (4)$$

values in parentheses are concentrations; to convert K_s to the thermodynamic stability constant, activity coefficients would be needed.

Experimental Section

The cryptands were obtained from EM Laboratories and used without further purification. Lanthanides were introduced as the chlorides, made by dissolution of the sesquioxides (Kleber Labs, Alfa Inorganics) in HCl. Water was passed through a millipore filter and boiled to remove CO_2. The supporting electrolyte was 0.25 M $(CH_3)_4NCl$ (Eastman), and the titrant base was made by dissolving $(CH_3)_4NOH\cdot 5H_2O$ (Baker). The $(CH_3)_4N^+$ ion is used because it is not complexed by the cryptands.

The pH was measured with a Fischer Model 325 Research pH meter employing a Beckman glass electrode, a Corning calomel electrode containing saturated KCl solutions, and a salt bridge of 0.25 M $(CH_3)_4NCl$. The pH meter was calibrated with 10^{-4} M HCl in the supporting electrolyte. Ligand and lanthanide-ion solutions were about 0.0025 M. Titrations were carried out at 25.0 ± 0.1 °C. The solutions, contained in glass cells, were immersed in a water bath and covered with Ar gas to exclude CO_2.

Each solution was acidified with HCl to a pH of ~4, and 40.0 mL was then titrated with ~0.25 M base dispensed from a micrometer syringe (Wellcome Research Laboratories). Aqueous solutions of [2.1.1], [2.2.1], and [2.2.2] were titrated to a pH of ~11. Then, solutions in six separate vessels, each containing the same cryptand–lanthanide chloride combination were titrated to different pH values up to ~6.4. The use of separate vessels was required in order to allow the necessary 4–6 weeks for equilibrium to be reached; after steady pH values were obtained, the solutions were back-titrated with HCl to ensure that equilibrium had been attained. The pH maximum of 6.4 was needed to prevent the onset of precipitation of the cryptate and/or lanthanide hydroxide. The six data points thus obtained constituted the titration curve for formation of one cryptate. A variety of lanthanide ions were complexed with each of the three cryptands and the titration curves determined in each case. The curve for $[\mathrm{Ca}^{2+}\subset 2.2.1]$ was also measured for comparison of our techniques with others.

The titration curves obtained with the cryptand solutions were fitted by theoretical curves based on reactions 1 and 2 with use of the method of least squares[13] and with adjustment of the values of K_1 and K_2 to obtain the best agreement. These quotients were then used as constants in fitting calculated curves to the titrations in which complexing was occurring. These calculations were based on reactions 1–3 and the hydrolysis of the cations (eq 5). Published values[14] of the equilibrium

$$\mathrm{Ln}^{3+} + \mathrm{H_2O} \rightleftarrows \mathrm{LnOH}^{2+} + \mathrm{H}^+ \qquad (5)$$

quotients for reaction 5 were used and ranged from log $K = -8.3$ to -9.0. In the least-squares refinement K_s was varied to obtain the best fit to experiment.

Results and Discussion

The cryptand ionization quotients which we obtained are listed in Table I along with values from previous determinations, and the agreement is quite satisfactory. Values of log K_s for lanthanide cryptates are given in Table II, and the titration data are provided as supplementary material. The standard deviations estimated from the least-squares calculations are given in the table to show how well the data can be reproduced by use of the quotients. However, the accuracy

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(12) Yee, E. L.; Ganzow, O. A.; Weaver, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2278.

(13) The calculations were performed with use of the computer program by: Busing, W. R.; Levy, H. A. Report ORNL/TM-271, "ORGLS, A General Fortran Least Squares Program", Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(14) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976; p 137.

of these quotients is judged to be about ±0.3 log units. This is based on work on other cryptates by several authors, who obtained varying results, on the dependence of K_s on the K_1 and K_2 values used[15] and on the limitation imposed by our use of only a portion of the theoretically possible titration curve.[16] Relative accuracies within the series of lanthanide cryptates are probably better than that.

The range of values of log K_s for the lanthanide cryptates in Table II is small even though a variety of cryptands and lanthanide ions were included. Thus it appears that the matching of ligand-cavity size and ion size is not a dominant factor in determining stability in these cryptates.

While we have assumed that the cryptates are formed in accord with reaction 3, the exact composition of the complexes formed in these reactions is not known nor is it necessarily the same in each instance. From the crystal structures of the lanthanide cryptates with [2.2.2] it is seen that the cation can occupy the interior of the cryptand molecule and be bonded to both N atoms which are in the in–in configuration. Other studies[3c] have shown that the [2.2.2] cavity is about 1.3–1.4 Å in radius, considerably larger than the lanthanide ions; but the molecule is flexible and adapts to contain the cation. In fact it achieves a cavity radius of about 1.1–1.3 Å in the lanthanide cryptates studied. The presence of one or two anions (NO_3^- or ClO_4^-) between ligand strands is also observed in these crystals. In aqueous chloride solution it is probably H_2O which occupies these extra coordination sites, thereby requiring incomplete removal of solvent molecules from the lanthanide ions before their incorporation into the complexes. This, of course, affects the enthalpy of complexation and the stability of the complexes. No structures have been reported for lanthanide cryptates with ions smaller than Eu^{3+} (0.95 Å), but the smaller ions usually have fewer coordinating atoms. Consequently, these cryptates may include fewer H_2O molecules and be destabilized by the enthalpy of removal of more solvation molecules from the Ln^{3+} ion before its incorporation into the cryptates.

The only structures reported for cryptates of [2.2.1] and [2.1.1] are $[Co^{2+}\subset 2.2.1]$, $[Na^+\subset 2.2.1]$, $[K^+\subset 2.2.1]$, and $[Li^+\subset 2.1.1]$. From these some inferences may be drawn which are relevant to the nature of the complexes which these cryptands form with lanthanides. The [2.2.1] cavity size ranges widely, from 0.76 Å for Co^{2+} to 1.40 Å for K^+; thus it is quite possible that all the lanthanides form inclusion complexes in solution with [2.2.1]. In fact, some may have additional anions or H_2O molecules in the inner sphere as does the complex involving $[K^+\subset 2.2.1]$. The cavity in $[Li^+\subset 2.1.1]$ is about 0.75 Å, larger than the radius of Li^+ (0.60 Å); thus the optimum radius is at least this large, and the maximum should be large enough to accommodate most if not all the trivalent lanthanides. There is no direct evidence to indicate whether additional anions may be present in the complex. It is apparently not necessary to assume the formation of exterior complexes because of size limitations.

Yee et al.[12] have electrochemically reduced Eu^{3+} to Eu^{2+} to obtain $[Eu^{2+}\subset 2.2.1]$ and $[Eu^{2+}\subset 2.2.2]$ and have done pH titrations to obtain stability quotients. In 0.1 M $(C_2H_5)_4NClO_4$ the approximate values of log K_s of 9.3 ± 0.3 and 10.5 ± 0.5 were found for $[Eu^{2+}\subset 2.2.1]$ and $[Eu^{2+}\subset 2.2.2]$, respectively. We suggest that more accurate estimates of these stabilities may be obtained by combining our measurements of the stabilities of the trivalent cryptates with their measured redox couples; this yields log K_s values for the divalent cryptates of 10.2 and 13.0, respectively.

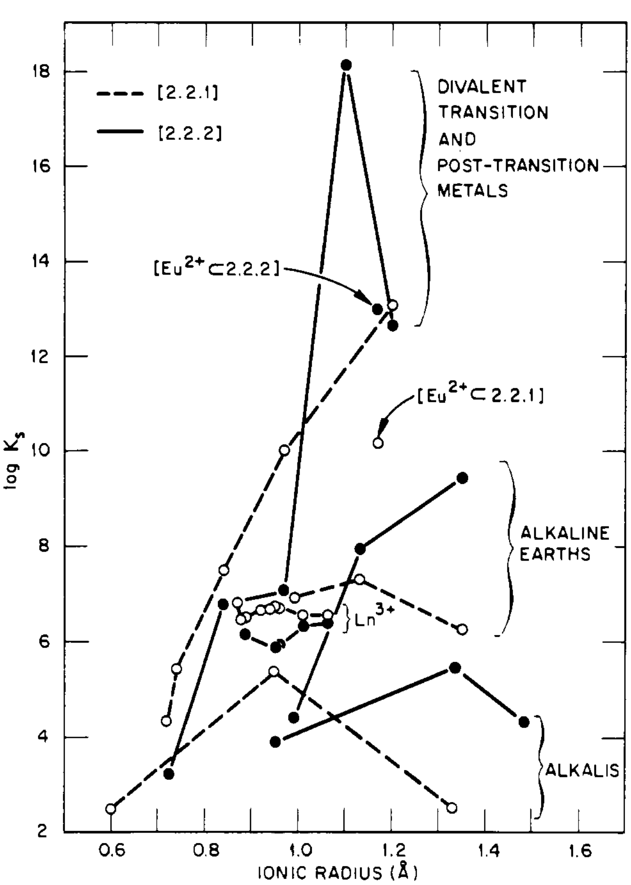

Figure 1. Logarithms of cryptate stability quotients vs. radii of the complexed ions. In order of increasing radii, the ions are as follows: *alkalis* Li^+, Na^+, K^+ with [2.2.1]; Na^+, K^+, Rb^+ with [2.2.2]; *alkaline earths* Ca^{++}, Sr^{++}, Ba^{++} with [2.2.1]; Ca^{++}, Sr^{++}, Ba^{++} with [2.2.2]; *transition and posttransition metals* Ni^{++}, Zn^{++}, Cu^{++}, Cd^{++}, Pb^{++} with [2.2.1]; Ni^{++}, Cu^{++}, Cd^{++}, Hg^{++}, Pb^{++} with [2.2.2]; *lanthanides* Tm^{3+}, Er^{3+}, Tb^{3+}, Gd^{3+}, Eu^{3+}, Sm^{3+}, Pr^{3+}, La^{3+} with [2.2.1]; Ho^{3+}, Eu^{3+}, Sm^{3+}, Pr^{3+}, La^{3+} with [2.2.2].

Formation quotients determined[2,3a,b] for various cryptates in aqueous solution are compared as a function of cation size in Figure 1. The monovalent alkali metal ions show the lowest cryptate stabilities, but a moderately strong dependence of stability on cation size, with peaks at Na^+ for [2.2.1] and at K^+ for [2.2.2]. The divalent alkaline-earth cryptates are generally more stable, and although the range of ion sizes is narrower, the variation of stability with ion size is consistent with the behavior of the alkali-metal cations. The divalent transition- and posttransition-metal cations, which fall in a lower range of ion sizes than the alkaline-earth metal ions, show the highest stabilities and the highest dependence on cation size. Values deduced above for Eu^{2+} cryptates (and included in Figure 1) indicate that the stabilities of divalent lanthanide cations are closer to the transition-metal ions than to the alkaline earths.

From these trends, it was expected that trivalent cations would show higher stabilities and an even greater sensitivity to cation size. It is therefore surprising to find that the trivalent lanthanides exhibit cryptate stabilities comparable to the alkaline earths, well below the divalent lanthanides, and with the lowest dependency yet observed on ion size. This would suggest that structural changes have been brought about by the increased charge that distinguish the trivalent cryptates from the monovalent and divalent ones; e.g., perhaps the trivalent cations, when complexed, retain more or all of their solvating water molecules in solution.

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(15) Our measurements with $[Ca^{2+}\subset 2.2.1]$ gave log K_s = 7.6; when we used the K_1 and K_2 values of Lehn and Sauvage,[2] the same data yielded log K_s = 7.2. Their data gave log K_s = 7.0.

(16) There is a lower limit to the size of log K_s which can be determined by this limited range of titration data because the complexation reaction does not cause significant deviation from the curve for the pure cryptand at low pH unless log K_s is ~5–6.

Acknowledgment. This research was sponsored by the Chemical Sciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy under contract (W-7405-eng-26) with the Union Carbide Corp.

Registry No. [2.1.1], 31250-06-3; [2.2.1], 31364-42-8; [2.2.2], 23978-09-8; La, 7439-91-0; Pr, 7440-10-0; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3.

Supplementary Material Available: A table containing the titration data for these cryptates (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Molecules with an M_4X_4 Core. 12.[1] Disruption of Tetrameric (Triphenylarsine)copper(I) Iodide in Acetonitrile Solution. Crystal Structure of $[(AsPh_3)(MeCN)CuI]_2$

Melvyn Rowen Churchill* and Joseph R. Missert

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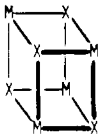
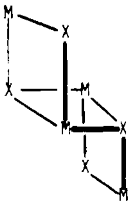
The complex $[(PPh_3)AgI]_4$ may be isolated as the "cubane-like" isomer (I) from chloroform/ether or as a steplike



I



II

or "chair" structure (II) from methylene chloride/ether.[2] To the best of our knowledge, this is the only reported case in which each of the skeletal forms has been confirmed structurally for a given $L_4M_4X_4$ species.

Far-infrared spectroscopic studies of $(Ph_3As)_4Cu_4X_4$ (X = Br, I) indicated that the samples studied had a *chairlike* configuration.[3] Unfortunately, the solvent from which they were crystallized was not explicitly stated. We later found[1] that crystallization of $[(AsPh_3)CuI]_4$ from benzene led to the formation of a *cubanelike* Cu_4I_4 core in crystals of stoichiometry $[(AsPh_3)CuI]_4 \cdot C_6H_6$. It seems probable, therefore, that $[(AsPh_3)CuI]_4$ also exists in both the cubanelike and steplike form.

In the course of recrystallizing $[(AsPh_3)CuI]_4$ from various solvents we have found that acetonitrile cleaves the tetrameric unit to form dimeric $[(AsPh_3)(MeCN)CuI]_2$, which has been characterized via a complete single-crystal X-ray diffraction study.

Experimental Section

$[(AsPh_3)(MeCN)CuI]_2$ can be prepared by dissolving $[(AsPh_3)CuI]_4 \cdot C_6H_6$ in hot acetonitrile and slowly evaporating the resulting solution. A more efficient synthesis is as follows.

Table I. Experimental Data for the X-ray Diffraction Study of $[(AsPh_3)(MeCN)CuI]_2$

A. Crystal Parameters at 24 °C[a]

cryst system: triclinic
space group: $P\bar{1}$
$a = 9.437$ (2) Å
$b = 9.500$ (2) Å
$c = 12.136$ (3) Å
$\alpha = 105.69$ (2)°
$\beta = 101.78$ (2)°
$\gamma = 98.52$ (1)°
$V = 1001.2$ (3) Å^3
$Z = 1$ (dimeric unit)
fw = 1075.5
$\rho_{calcd} = 1.78$ g cm^{-3}

B. Collection of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly ordered graphite, equatorial geometry
rflctns measd: $\pm h, +k, \pm l$
scan type: θ(cryst)–2θ(counter)
2θ range: 3–50°
scan speed: 2.0°/min
scan width: $[2.0 + \Delta(\alpha_2 - \alpha_1)]$°
rflctns collected: 3888 total data, 3553 independent data
stds: 3 collected every 97 data; no significant variations
abs coeff: $\mu = 44.2$ cm^{-1}

[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 $\{1\bar{7}2\}$, $\{1\bar{1}7\}$, $\{7\bar{2}1\}$, $\{161\}$, $\{2\bar{1}8\}$, $\{61\bar{1}\}$, $\{2\bar{7}2\}$, $\{23\bar{7}\}$, $\{62\bar{1}\}$, $\{361\}$, $\{31\bar{7}\}$, and $\{52\bar{2}\}$.

Table II. Positional Parameters, with Esd's, for $[(AsPh_3)(MeCN)CuI]_2$[a]

atom	*x*	*y*	*z*
Cu	0.00062 (5)	0.12927 (5)	0.08782 (4)
I	0.11131 (3)	0.13664 (3)	−0.09850 (2)
As	0.20619 (3)	0.25969 (4)	0.25285 (3)
N	−0.16294 (34)	0.24402 (36)	0.07422 (27)
C(1)	−0.25022 (45)	0.31144 (47)	0.06255 (34)
C(2)	−0.36568 (59)	0.39909 (65)	0.04688 (48)
C(11)	0.28303 (36)	0.46144 (36)	0.25390 (27)
C(12)	0.43140 (37)	0.53247 (39)	0.29434 (31)
C(13)	0.47717 (44)	0.67791 (45)	0.29691 (36)
C(14)	0.37278 (53)	0.75628 (45)	0.26084 (40)
C(15)	0.22660 (50)	0.68710 (49)	0.21933 (44)
C(16)	0.18125 (41)	0.53980 (44)	0.21440 (36)
C(21)	0.38773 (35)	0.18464 (34)	0.27490 (29)
C(22)	0.47661 (43)	0.20298 (44)	0.38513 (32)
C(23)	0.60947 (45)	0.15528 (47)	0.39473 (37)
C(24)	0.65303 (43)	0.08917 (46)	0.29535 (41)
C(25)	0.56428 (45)	0.06984 (47)	0.18694 (37)
C(26)	0.43127 (41)	0.11569 (43)	0.17505 (31)
C(31)	0.17190 (35)	0.30020 (38)	0.41017 (28)
C(32)	0.11839 (59)	0.18034 (50)	0.44432 (39)
C(33)	0.08910 (68)	0.20333 (61)	0.55432 (43)
C(34)	0.11078 (48)	0.34543 (60)	0.62977 (36)
C(35)	0.16259 (50)	0.46382 (51)	0.59682 (35)
C(36)	0.19529 (45)	0.44294 (42)	0.48780 (33)
H(12)	0.5026	0.4799	0.3207
H(13)	0.5795	0.7246	0.3231
H(14)	0.4033	0.8579	0.2651
H(15)	0.1555	0.7403	0.1936
H(16)	0.0794	0.4918	0.1836
H(22)	0.4471	0.2480	0.4543
H(23)	0.6709	0.1685	0.4708
H(24)	0.7443	0.0573	0.3024
H(25)	0.5940	0.0240	0.1180
H(26)	0.3696	0.0999	0.0984
H(32)	0.1014	0.0813	0.3921
H(33)	0.0536	0.1198	0.5776
H(34)	0.0895	0.3606	0.7048
H(35)	0.1768	0.5624	0.6488
H(36)	0.2338	0.5270	0.4664

[a] $B_{iso} = 6.0$ Å^2 for all hydrogen atoms.

Synthesis of $[(AsPh_3)(MeCN)CuI]_2$. A solution of copper(I) iodide (0.494 g, 0.0026 mol) and triphenylarsine (0.804 g, 0.0026 mol) in acetonitrile (75 mL) was refluxed under argon for 12 h. The hot solution was filtered. Slow evaporation of solvent from this solution yielded small colorless crystals of $[(AsPh_3)(MeCN)CuI]_2$. Crystals

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