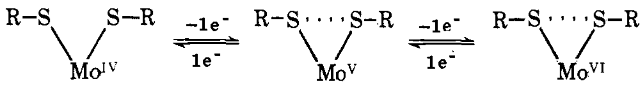
Melding our results with those in the literature leads to a fascinating possibility for redox processes in Mo-bis(thiolate) systems. As illustrated below, successive one-electron oxidation of Mo(IV) to (formally) Mo(V) and Mo(VI) may involve a substantial component of thiolate-disulfide oxidation. If this partial S-S bond formation occurs in Mo enzymes (and none of the existent data preclude such an occurrence), then it could explain, in part, the absence of identity between the spectroscopic, redox, and catalytic properties of Mo enzymes and their "model" systems. For example, the high g_z and low $A_z(^{95,97}Mo)$ value of the Mo(V) EPR signal in xanthine oxidase[5] may be attributable to strong delocalization of the unpaired electron into a partial S-S bond. The great range of redox potentials for different Mo enzymes (while also potentially explainable in other terms) could likewise be due to varying degrees of S-S bond formation in the different molybdenum enzymes. The presence of strategically juxtaposed sulfides in large-ring multisulfur organic heterocyclic compounds has been found to correlate with substantially lower potentials for one-electron oxidation and with increased reversibility in the electron-transfer process.[17-19] Similarly, the specific cis positioning of Mo-bound thiolates may be responsible for unusual reactivity and spectroscopic features of Mo sites in enzymes.



Regardless of the relevance of the above results to Mo enzymes, it is clear that more structural variety is possible in simple inorganic molybdenum systems than had heretofore been admitted. Recognition of this diversity may be crucial in the quest to determine the nature of the biological molybdenum sites.

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Supplementary Material Available: A list of atomic coordinates and thermal parameters for $MoO_2[SC(CH_3)_2CH_2NHCH_3]_2$ (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979,** *101,* 2772.
(2) Tullius, T. D.; Kurtz, D. M.; Conradson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc. 101,* **1979,** 2776.
(3) Cramer, S. P.; Hodgson, K. O.; Stiefel, E. I.; Newton, W. E. *J. Am. Chem. Soc.* **1978,** *100,* 2748.
(4) Berg, J. M.; Hodgson, K. O.; Cramer, S. P.; Corbin, J. L.; Elsberry, A.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1979,** *101,* 2774.
(5) Stiefel, E. I. *Progr. Inorg. Chem.* **1977,** *22,* 1. Stiefel E. I. In "Molybdenum and Molybdenum Containing Enzymes", Coughlan, M. P., Ed.; Pergamon Press: Elmsford, N.Y., and Oxford, 1980; Chapter 2, p 41.
(6) Bobrik, M. A.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1977,** *16,* 1851. This paper describes the X-ray data reduction and refinement procedures used in the investigation reported here.
(7) Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979,** *18,* 1626.
(8) Kepert, D. L. *Prog. Inorg. Chem.* **1977,** *23,* 1.
(9) An alternative description in terms of a severely distorted trigonal prism wherein the triangular faces have slid past each other is also possible. Detailed considerations of geometrical criteria and further structural documentation will be presented elsewhere.
(10) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, N.Y., 1960; p 260.
(11) Dance, I. G.; Wedd, A. G.; Boyd, I. W. *Aust. J. Chem.* **1978,** *31,* 519.
(12) Gillespie, R. J.; Passmore, J.; Ummat, P. K.; Vaidya, O. C. *Inorg. Chem.* **1971,** *10,* 1327.
(13) Salahub, D.; Foti, A. E.; Smith V. H., Jr. *J. Am. Chem. Soc.* **1978,** *100,* 7847.
(14) Chivers, T.; Proctor, J. *J. Chem. Soc., Chem. Commun.* **1978,** 642.
(15) Roesky, H. W.; Witt, M.; Krebs, B.; Jürgen-Korte, H. *Angew. Chem., Int. Ed. Engl.* **1979,** *18,* 415.
(16) Eisenberg, R. *Prog. Inorg. Chem.* **1970,** *12,* 295.
(17) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976,** *98,* 3055.
(18) Musker, W. K.; Roush, P. B. *J. Am. Chem. Soc.* **1976,** *98,* 6745.
(19) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. G.; Ryan, M. D.; Musker, W. K. *J. Am. Chem. Soc.* **1979,** *101,* 1040.
(20) NOTE ADDED IN PROOF. The crystal structure of $MoO_2[(CH_3)_2NCH_2C(CH_3)_2S]_2$ (2) has been solved. A structure of the skew-trapezoidal bipyramidal type is again found.

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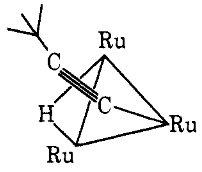
Synthesis, Structure, and Reactivity of Mercurial Derivatives of an Organoruthenium Cluster

Sir:

Hydrido organotrimetallic clusters of ruthenium are interesting model compounds for the study of transition metal cluster chemistry for several reasons. One reason is that they provide easily synthesized examples of thermally stable monohydride derivatives of the Ru_3 cluster with which to study the reactivity of the μ_2-hydrido bond. During the course of our studies on the general reactivity of $HRu_3(CO)_9(C_6H_9)$ (I)[1] we discovered that C_6H_5HgX (X = Br, I) reacts with I to give a halomercury(II) derivative $(C_6H_9)Ru_3(CO)_9HgX$ (II) and an equivalent amount of benzene:[2,3]



I

$$(C_6H_9)Ru_3(CO)_9H + C_6H_5HgX \xrightarrow[12\ h]{THF\ reflux} \underset{\text{II, 30-40\%,}}{(C_6H_9)Ru_3(CO)_9HgX} + C_6H_6 \quad (1)$$

II has been fully characterized and the data are summarized in Table I for the bromo and iodo derivatives. We subsequently found that reaction of the anion of I (generated in situ[4] with HgX_2 (X = Br, I) also gives II in comparable yields:

$$HRu_3(CO)_9(C_6H_9) \xrightarrow[THF\text{-}EtOH]{KOH} Ru_3(CO)_9(C_6H_9)^- + K^+ + HgX_2 \xrightarrow[18\ h]{25\ ^\circ C} II \quad (2)$$

Thus II is a common product from two apparently different reaction pathways.

The ^{13}C NMR of a 15% ^{13}CO-enriched sample of II shows five resonances at the low temperature limit (−24 °C) in the carbonyl region (Figure 1). This suggests that the cluster has the same overall summetry as I.[5] The lowest energy exchange process averages resonances *a* and *b* at +2 °C and arises from axial-radial exchange at the unique ruthenium atom, Ru(1) ($\Delta G^{\ddagger} = 12.7 \pm 0.5$ kcal/mol).[6] At +25 °C resonances *c*, *d*, and *e* have coalesced while the resonance arising from the average of (*a* + *b*) remains relatively sharp. This second stage of the CO-scrambling process arises from localized axial-radial exchange at Ru(2) and Ru(3) ($\Delta G^{\ddagger} = 14.8 \pm 0.5$ kcal/mol).[6] At +60 °C resonances (*a* + *b*) and (*c* + *d* + *e*) coalesce to a single broad resonance. This third stage of the exchange probably arises from the onset of intermetallic CO scrambling via CO-bridging intermediates in a typical Cotton-type CO-

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Table I. Spectroscopic and Analytical Data

compd	% C (calcd)	% H (calcd)	M⁺ MS[a] (calcd)	IR,[b] ν_{CO}, cm^{-1}
$Ru_3(CO)_9(C_6H_9)$-HgX (II) (X = Br)	19.80 (19.64)	1.12 (1.00)	917 (916.9)	2090 (w) 2050 (s) 2000 (s) 1995 (w)
II (X = I)	18.68 (18.70)	0.95 (0.90)	964 (963.9)	2060 (w) 2010 (s) 1980 (s) 1970 (s) 1940 (w)
$Ru_3(CO)_9(C_6H_9)$-HgO_2CCH_3 (III)	23.30 (22.80)	1.59 (1.35)	896 (896.08)	2060 (w) 2010 (s) 2000 (s) 1980 (s)

[a] M⁺ ions calculated using the ^{101}Ru isotope. $Ru_3{}^+$–CO fragments are observed from (M⁺) to (M⁺ − n(CO)) (n = 5). [b] KBr pellets, ±10 cm^{-1}.

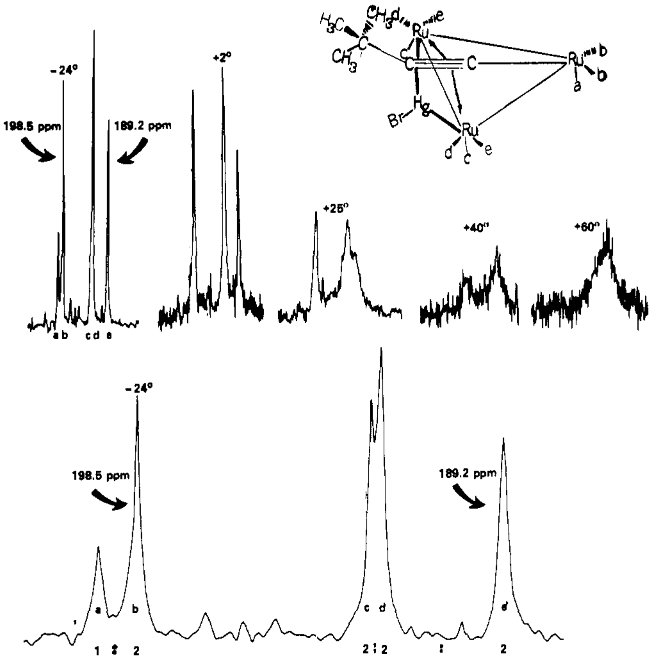

Figure 1. (a) ^{13}C NMR of the carbonyl region of $Ru_3(CO)_9(C_6H_9)HgBr$ in $CDCl_3$ at −24 °C. (b) Variable-temperature ^{13}C NMR of the carbonyl region of $Ru_3(CO)_9(C_6H_9)HgBr$ in $CDCl_3$ from −24 to +60 °C.

Table II. Selected Bond Distances (Ångstroms) and Angles (Degrees) with Their Estimated Standard Deviations

Hg–Ru(2)	2.733 (2)	Ru(3)–C(3)	1.86 (3)
Hg–Ru(3)	2.739 (2)	Ru(3)–C(10)	2.20 (2)
Ru(1)–Ru(2)	2.813 (3)	Ru(3)–C(11)	2.26 (2)
Ru(1)–Ru(3)	2.806 (2)	C(1)–O(1)	1.14 (3)
Ru(2)–Ru(3)	2.900 (3)	C(2)–O(2)	1.11 (3)
Hg–Br	2.505 (3)	C(3)–O(3)	1.19 (3)
Hg–Br[a]	3.084 (3)	C(4)–O(4)	1.15 (3)
Ru(1)–C(7)	1.92 (2)	C(5)–O(5)	1.14 (3)
Ru(1)–C(8)	1.90 (2)	C(6)–O(6)	1.15 (3)
Ru(1)–C(9)	1.89 (3)	C(7)–O(7)	1.14 (3)
Ru(1)–C(10)	1.96 (2)	C(8)–O(8)	1.12 (3)
Ru(2)–C(4)	1.91 (2)	C(9)–O(9)	1.15 (4)
Ru(2)–C(5)	1.92 (2)	C(10)–C(11)	1.31 (3)
Ru(2)–C(6)	1.89 (2)	C(11)–C(12)	1.48 (4)
Ru(2)–C(10)	2.19 (2)	C(12)–C(13)	1.56 (4)
Ru(2)–C(11)	2.25 (2)	C(12)–C(14)	1.53 (4)
Ru(3)–C(1)	1.93 (2)	C(12)–C(15)	1.57 (4)
Ru(3)–C(2)	1.89 (3)		
Ru(2)–Hg–Ru(3)	64.0 (1)	Ru(2)–C(6)–O(6)	178 (2)
Ru(2)–Ru(1)–Ru(3)	62.1 (1)	Ru(1)–C(7)–O(7)	177 (2)
Hg–Ru(2)–Ru(3)	58.1 (1)	Ru(1)–C(8)–O(8)	179 (2)
Ru(1)–Ru(2)–Ru(3)	58.8 (1)	Ru(1)–C(9)–O(9)	175 (3)
Ru(1)–Ru(3)–Ru(2)	59.1 (1)	Ru(1)–C(10)–C(11)	154 (2)
Hg–Ru(3)–Ru(2)	57.9 (1)	Ru(2)–C(10)–C(11)	76 (1)
Hg–Ru(2)–Ru(1)	99.4 (1)	Ru(3)–C(10)–C(11)	75 (1)
Hg–Ru(3)–Ru(1)	99.4 (1)	Ru(2)–C(11)–C(12)	135 (2)
Ru(2)–Hg–Br	146.1 (1)	Ru(3)–C(11)–C(12)	134 (2)
Ru(2)–Hg–Br[a]	108.1 (1)	C(10)–C(11)–C(12)	140 (2)
Ru(3)–Hg–Br	141.8 (1)	Ru(2)–C(11)–C(10)	70 (1)
Ru(3)–Hg–Br[a]	108.5 (1)	Ru(3)–C(11)–C(10)	71 (1)
Br–Hg–Br[a]	85.9 (1)	C(13)–C(12)–C(14)	109 (2)
Ru(3)–C(1)–O(1)	174 (2)	C(13)–C(12)–C(15)	107 (2)
Ru(3)–C(2)–O(2)	175 (2)	C(11)–C(12)–C(13)	112 (2)
Ru(3)–C(3)–O(3)	173 (2)	C(14)–C(12)–C(15)	108 (2)
Ru(2)–C(4)–O(4)	179 (2)	C(14)–C(12)–C(11)	110 (2)
Ru(2)–C(5)–O(5)	174 (2)	C(15)–C(12–C(11)	111 (2)

[a] indicates the atom in the equivalent position: −x, 2 − y, 2 − z.

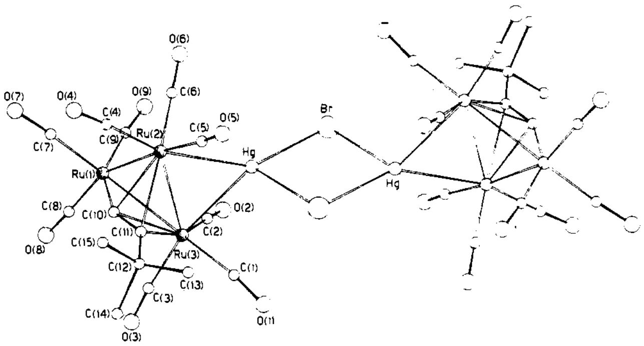

Figure 2. Solid-state structure of $[Ru_3(CO)_9(C_6H_9)HgBr]_2$.

exchange process.[7] The ^{13}C NMR results for II closely parallel those for I where the bridging hydride causes axial-radial exchange to be slower at Ru(2) and Ru(3) than at Ru(1).[8] Taken along with the fact that II is monomeric in solution,[9] these results suggest that II has the structure shown in Figure 1 with the mercury atom in a three-center bond bridging Ru(2) and Ru(3).

A single-crystal X-ray diffraction study has been undertaken on II; it has revealed that indeed the mercury bridges a Ru–Ru side of the starting cluster and that the compound exists as a dimer in the solid state. The formation of a dimer in the solid state suggests that the mercury atom possesses Lewis acid character.

Crystal data. $C_{30}H_{18}Br_2Hg_2O_{18}Ru_6$: mol wt 1833.87; triclinic; a = 9.434 (10), b = 14.631 (12), c = 9.423 (9) Å; α = 101.16 (8), β = 113.93 (9), γ = 86.85 (8)°; V = 1166 (2) Å^3; Z = 1; d_{calcd} = 2.612 g/cm^3; μ(Mo Kα) = 101.7 cm^{-1}; space group $P\bar{1}$ (from structural analysis). Diffraction intensities were measured in the $\theta/2\theta$ scan mode using Nb-filtered Mo Kα radiation on a Siemens on-line single-crystal diffractometer. A total of 3338 independent reflections was collected in the range $3 < \theta < 25°$; of these 2612 were considered observed [having $I > 2\sigma(I)$] and used in the analysis. The structure was solved by the heavy-atom method and refined by full-matrix least squares,[10] with anisotropic thermal parameters to an R value of 7.5% (observed reflections only).

The structure of the dimer is represented in Figure 2 and selected bond distances and angles in it are given in Table II. See the paragraph at the end of the paper regarding supplementary material.

Two tetranuclear metal clusters of three Ru and one Hg atoms, in a butterfly arrangement, are joined in a dimer by two bromines bridging the two Hg atoms asymmetrically (Hg–Br bond distances being of 2.505 and 3.084 Å). The two triangular wings HgRu(2)Ru(3) and Ru(1)Ru(2)Ru(3) share the hinge side Ru(2)Ru(3), the dihedral angle between the wings being of 127°. The Hg atom bridges Ru(2) and Ru(3) with bond distances of 2.733 and 2.739 Å and practically substitutes the hydride in I. It is interesting to note that the Ru(2)–Ru(3) side (2.900 Å) is longer than that in I (2.792 Å);[11] this is also consistent with the picture of a relatively polar Ru-Hg bridge bond where the mercury bears more positive charge than the hydride in I. Aside from this difference, the metal carbon framework of the cluster remains almost unchanged with respect to I. For example, the C(10)-C(11) bond length is 1.31 Å in II and 1.315 Å in I. Similarly, the Ru(1)-C(10) bond is 1.96 and 1.947 Å in II and I, respectively.

The reaction of II (X = Br) with $Ag(OOCCH_3)$ gives III in good yield (Table I):

$$(C_6H_9)Ru_3(CO)_9HgX + Ag(OOCCH_3) \xrightarrow{\text{THF}} \underset{\text{III}}{(C_6H_9)Ru_3(CO)_9Hg(OOCCH_3)} + AgX \quad (3)$$

However, direct reaction of $C_6H_5Hg(OOCCH_3)$ with I or I^- with $Hg(OOCCH_3)_2$ did not give III.

Under the reaction conditions for the synthesis of II (X = Br only) by the phenylmercuric halide plus hydride route, a byproduct is always obtained (10-20% yield) whose metal analysis (Ru = 33.0%, Hg = 23.9%, no bromine) and IR and mass spectra[12] are consistent with the formula $Hg_2Ru_6(CO)_{18}(C_6H_9)_2$ (IV). Independent experiments show that this compound is formed by reaction of II with I and is accompanied by cluster decomposition. IV is not formed in the synthesis of II from I^- and HgX_2 and is found in only trace amounts when I is reacted with C_6H_5HgI. IV is thermally unstable even in the solid state, slowly decomposing to mercury metal and a ruthenium containing residue. We are currently investigating the solid-state structure of IV.

Although there are many M-Hg-X and M-Hg-M (M = transition metal) derivatives in the literature,[13] II represents the first example of mercury atom briding two transition metals in a three-center bond. The fact that II is formed by both reaction of a phenylmercuric halide with a hydrido cluster and by reaction of a cluster anion with mercuric halides suggests the possibility that these reaction pathways could be of general use for synthesizing main group metal derivatives of transition metal clusters. The mercury derivatives reported here are interesting candidates for oxo or solvo mercuration catalysts and as intermediates for the synthesis of mixed transition metal clusters by oxidative addition of the mercury halogen bond to zerovalent platinum- and palladium-phosphine complexes.[14] We are currently exploring these possibilities. The chemistry observed here is reminiscent of that seen for the reaction of $(CO)_5MnH$ with $(C_6H_5)_3PAuCH_3$ to give CH_4 and a gold-manganese bond.[15] It is in sharp contrast, however, to the reaction of $HCCo_3(CO)_9$ with phenylmercuric halides where phenylation of carbinyl carbon occurs.[16]

Supplementary Material Available: The final atomic coordinates, the atomic thermal parameters and a complete listing of factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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References and Notes

(1) E. Sappa, O. Gambino, L. Milone, and G. Cetini, *J. Organomet. Chem.*, **39,** 169 (1972).

(2) The amount of benzene was evaluated by GC–MS of the reaction volatiles and compared with volatiles isolated from C_6H_5HgBr refluxing in THF.

(3) Reaction of 95% deuterated I synthesized from I^- with C_6H_5HgX gives C_6H_5D as <10% of the C_6H_6 formed, suggesting that the cleavage of the mercury–phenyl bond is not concerted but must involve either prior dissociation of the phenyl group or exchange with solvent of a protonated phenyl group on C_6H_5HgX. The recovered I from these reactions is still fully deuterated.

(4) We have fully characterized the anion of I as its tetraphenylarsonium salt: C. Barner Thorsen, J. Siegel, and E. Rosenberg, unpublished work.

(5) We have previously reported the variable-temperature ^{13}C NMR of I: E. Rosenberg, L. Milone, and S. Aime, *Inorg. Chim. Acta*, **15,** 53 (1975).

(6) Estimated from coalescence temperatures (±10 K) using the equation $\Delta G^{\ddagger}_c = 4.57(T_c)(9.97 - \log T_c/\delta\nu)$: D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(7) For a review of cluster carbonyl exchange processes, see S. Aime and L. Milone, *Prog. Nucl. Magn. Reson. Spectrosc.*, **11,** 149 (1977).

(8) The variable-temperature ^{13}C NMR of I^- shows that axial–radial exchange is more rapid at Ru(2) and Ru(3) than at Ru(1), thus demonstrating the effect of removing the bridging group on the axial–radial exchange (see ref **4**).

(9) Molecular weight by vapor pressure osmometry for $Ru_3(CO)_9(C_6H_9)HgBr$, 903 (calcd 916.8) in benzene.

(10) Computer programs used on a CYBER 7600 computer of the "Centro di Calcolo Interuniversitario dell' Italia Nord-Orientale," Bologna, were those of SHELX-76 system (G. M. Sheldrick, 1976, University of Cambridge, England). In the last stage of refinement a weighting scheme $1/[\sigma^2(F_o) + 0.003F_o^2]$ was adopted.

(11) M. Catti, G. Gervasio, and S. A. Mason, *J. Chem. Soc., Dalton Trans.*, 2260 (1977).

(12) We have been unable to obtain consistant C, H analysis for this compound. The mass spectrum shows a Ru_6 fragment at 1217 which corresponds to $Ru_6(CO)_{16}(C_6H_9)_2^+$: IR (KBr) ν_{CO} 2050 (w), 2010 (s), 1990 (m), 1980 (m).

(13) For a recent example of a MoHgMo cluster with cubane structure, see J. Deutcher, S. Fadel, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **16,** 704 (1977).

(14) V. I. Sokolov and G. Z. Suleimanov, *Inorg. Chim. Acta*, **25,** L149 (1977).

(15) C. M. Mitchell and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 102 (1972).

(16) D. Seyferth, J. E. Hallgren, B. J. Spohn, G. H. Williams, M. O. Nestle, and P. L. King, *J. Organomet. Chem.*, **65,** 99 (1974).

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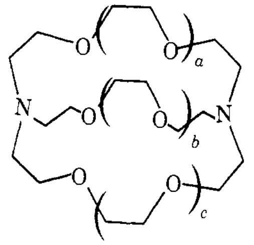
General Acid Catalyzed Dissociation of Metal Cryptates

Sir:

Recent kinetic studies on the dissociation of metal ions from complexes (cryptates) formed between cations and macrobicyclic ligands (cryptands) of the type **1-3**,[1] have involved NMR,[2-4] electrochemical,[5,6] relaxation,[7] and flow techniques,[8-10] including the use of strong acids to scavenge the free cryptand in equilibrium with the complex.[9,10]



1, $a = 1$; $b = c = 0$ (2.1.1)
2, $a = b = 1$; $c = 0$ (2.2.1)
3, $a = b = c = 1$ (2.2.2)

We have shown[9,10] that the dissociation of cryptates of a number of alkali and alkaline earth cations and Ag^+ are subject to varying degrees of catalysis by strong acids, both in water and methanol.[10] This was attributed to interaction between the proton and the lone pair of one of the nitrogen atoms, presumably in an exo conformation. Weaver and co-workers[6] have also found that the dissociation of europium and ytterbium cryptates is acid catalyzed.

We wish to report that the dissociation reactions are also catalyzed by general acids, HA. The catalytic activity of an

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