TABLE I

CONDUCTANCE PARAMETERS FOR Bu$_4$NBr IN METHANOL AT 25°

Λ_0	$\mathring{a}$	K_A	σ_Λ
95.31 ± 0.02	2.85 ± 0.02		0.02
95.32 ± 0.02	2.84 ± 0.03		0.03
95.38 ± 0.02	3.2 ± 0.1	2.8 ± 0.6	0.01
95.42 ± 0.01	3.4 ± 0.1	4.3 ± 0.4	0.007

When the data for the nitrobenzene–methanol mixtures[2] were analyzed by the computer program for associated electrolytes negative $\mathring{a}$ or K_A resulted, or the standard deviations of the parameters were larger than the parameters. These data covered too narrow a concentration range for any kind of meaningful interpretation. On the other hand, the data of Witschonke and Kraus[9] for this salt in pure nitrobenzene had the necessary precision and concentration range. Their data gave $K_A = 56 \pm 3$ and $\mathring{a} = 4.9 \pm 0.7$ and $\sigma_A = 0.03$. Thus the $\mathring{a}$ is reasonable, the fit is good, and the K_A is large enough so that the assumption of association of this salt in nitrobenzene is justified. When treated as an unassociated electrolyte in nitrobenzene an $\mathring{a}$ of 0.12 results which is unreasonably low indicating considerable association.

Considering the above analysis the only experimental result needing explanation is why Bu$_4$NBr is associated in nitrobenzene and not in methanol or nitromethane[10] although these solvents have about the same dielectric constant. Stabilization of the free ions by solvation will explain the lack of association in methanol, but solvation of the free ions by nitromethane and not by nitrobenzene is unlikely. Hyne's[1] suggestion of an interaction between the nitrobenzene molecule and the Bu$_4$NBr ion pair is one possible explanation. The dimensions involved could be correct for nitrobenzene but not for nitromethane.

Acknowledgment.—We wish to acknowledge the technical assistance of Mr. C. Zawoyski. This work was supported by a contract with the Office of Saline Water, U. S. Department of the Interior.

(9) C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc., **69**, 2472 (1947).

(10) R. L. Kay, S. C. Blum, and H. I. Schiff, J. Phys. Chem., **67**, 1223 (1963).

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The Enthalpy of Transformation, δ-Al$_2$O$_3$ to α-Al$_2$O$_3$

Sir:

It is well known that in the oxygen bomb calorimetry of aluminum compounds, a part of the reaction product sometimes occurs in the form of δ-Al$_2$O$_3$. This is a metastable phase of tetragonal but so far not fully determined structure,[1] whose enthalpy of transformation to the stable form α-Al$_2$O$_3$ (corundum) has not yet been established. As a result, there may be some uncertainty associated with the adopted value of the heat of combustion of aluminum to form Al$_2$O$_3$.[2]

We have recently become interested in the possible use of high-temperature solution calorimetry for the study of the thermochemistry of certain inorganic solids. Of particular interest to us are solids such as Al$_2$O$_3$, which cannot be dissolved in the common room-temperature

(1) H. P. Rooksby, J. Appl. Chem., **8**, 44 (1958).
(2) R. C. King and G. T. Armstrong, private communication.

solvents. We have found that this oxide dissolves readily in a lead–cadmium borate melt (composition approximately 9PbO·3CdO·4B$_2$O$_3$). Using this solvent we have determined the heats of solution of α-Al$_2$O$_3$ and of δ-Al$_2$O$_3$ at 705°. For α-Al$_2$O$_3$ we have carried out several determinations with α-Al$_2$O$_3$ of different origin. The mean value of the enthalpy of solution is $+7.6 \pm 0.2$ kcal./mole.

We used two different specimens of δ-Al$_2$O$_3$ (I and II), both obtained as reaction products in a bomb-calorimetric study of Al$_4$C$_3$.[2] Duplicate samples of these specimens were dissolved in the same solvent at the considered temperature. The enthalpies of solution were as follows: I, 4.9, 5.0; II, 4.5, 5.1; mean, $+4.9 \pm 0.3$ kcal./mole.

Finally we converted a small sample of δ-Al$_2$O$_3$ to α- by heating it for 0.5 hr. at 1450°. The enthalpy of solution of this product was 7.4 kcal./mole, *i.e.*, within the range of the results obtained for the several other samples of α-Al$_2$O$_3$.

Thus we have for the process: Al$_2$O$_3(\delta)$ = Al$_2$O$_3(\alpha)$; $\Delta H°_{978} = -2.7 \pm 0.4$ kcal./mole.

Experimental details of this work will be incorporated in a more extensive study of the various forms of Al$_2$O$_3$ and will be published elsewhere.

Acknowledgment.—We are indebted to Drs. G. T. Armstrong and R. C. King of the National Bureau of Standards for providing us with the samples of δ-Al$_2$O$_3$. This work has been supported in part by the National Science Foundation (GP-1993).

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Stereochemistry of the 1,2-Diaminocyclohexane-N,N'-tetraacetatoaquoferrate(III) Ion,[1] Fe(OH$_2$)Z$^-$

Sir:

Inasmuch as 1,2-diaminocyclohexane-N,N'-tetraacetic acid (hereafter DCTA or H$_4$Z) generally forms more stable complexes[2] with metal ions than does the closely related ethylenediaminetetraacetic acid (EDTA or H$_4$Y), one must suppose that the cyclohexane ring of DCTA somehow promotes chelation. It is clear, on the other hand, that the constraints imposed by multiple ring formation must be no less important for chelation by DCTA than by EDTA, and constraints of just this kind are assigned primary responsibility for the unconventional stereochemistry of the sexadentate seven-coordinate aquo complexes, Fe(OH$_2$)Y$^-$ and Mn(OH$_2$)Y^{2-}, formed by EDTA with Fe(III)[3,4] and Mn-

(1) Support of this study by the National Science Foundation, the National Institutes of Health, and the Advanced Research Projects Agency is gratefully acknowledged. We thank also the Cornell Computing Center Mr. Richard C. Lesser, Director.

(2) *Cf.*, S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 572–576, for tabulated stability constants of DCTA and EDTA chelates and Chapter 4 for discussion of chelate stabilities.

(3) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, Inorg. Chem., **3**, 34 (1964).

(4) *Cf.* J. L. Hoard, G. S. Smith, and M. D. Lind in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, pp. 296–302, for *a priori* analysis predicting the existence of seven-coordinate Fe(OH$_2$)Y$^-$.
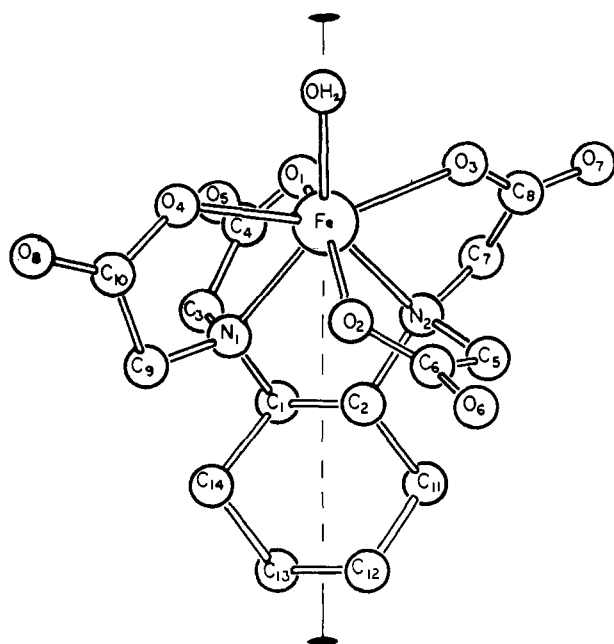
Fig. 1.—Idealized model in perspective of the sexadentate seven-coordinate aquo complex, $Fe(OH_2)Z^-$, with the twofold axis vertical. The complexed oxygen atoms, O_1 - - - O_4, have coordinates measured parallel to the twofold axis from an origin at Fe as follows: O_1 and O_2, -0.11 Å.; O_3 and O_4, $+0.56$ Å.

(II).[5] That both of these conclusions can be valid simultaneously is demonstrated by our determination of structure, using three-dimensional X-ray analysis, of the calcium salt $Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$ containing the anionic $Fe(III)$–DCTA chelate, $Fe(OH_2)Z^-$.

$Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$ crystallizes in the monoclinic space group $C2/c$ with $a = 34.34 \pm 0.02$, $b = 8.844 \pm 0.011$, $c = 13.527 \pm 0.017$ Å., $\beta = 91.02 \pm 0.05°$, and a unit cell content of four Ca^{2+}, eight $Fe(OH_2)Z^-$, and thirty-six H_2O. Intensity data, measured by counter methods out to $(\sin \theta)/\lambda = 0.65$ with Mo $K\alpha$ radiation, were utilized in the heavy-atom technique for structure determination. Least-squares refinement of positional and anisotropic thermal parameters gives a residual of 0.094 for the approximately 92% of the data which are definitely above background.

The $Fe(OH_2)Z^-$ ion, as given by the analysis and illustrated in Fig. 1, is a sexadentate seven-coordinate aquo complex which approximates closely to the symmetry required by a twofold axis through OH_2, Fe, the midpoint of the C–C bond shared by the ethylenediamine and cyclohexane rings, and the midpoint of the opposite C–C bond in the cyclohexane ring. The atoms N_1, N_2, Fe, and O of H_2O are coplanar, but O_3 and O_4 are, respectively, -0.99 and $+0.99$ Å. from this plane in positions corresponding to a rotation of 29° about the twofold axis. Consequently, the coordination group of $Fe(OH_2)Z^-$ is geometrically intermediate between the NbF_7^{2-} configuration[6] which, suitably modified, is utilized[5] by $Mn(OH_2)Y^{2-}$, and the pentagonal bipyramid which, in an asymmetric form, is utilized[3] by $Fe(OH_2)Y^-$. The "chair" form with standard bond parameters is assumed by the cyclohexane ring. Ethylenediamine and glycinate ring

geometry in $Fe(OH_2)Z^-$ is very like that in $Mn(OH_2)Y^-$, and is suggestive of slightly more cumulative strain than in $Fe(OH_2)Y^-$. Lengths of the complexing bonds in $Fe(OH_2)Z^-$ conform, nonetheless, to the pattern observed[3] in $Fe(OH_2)Y^-$. When averaged in agreement with C_2-2 symmetry, one obtains Fe–O (O_1 and O_2) = 2.017, $Fe–OH_2$ = 2.090, Fe–O (O_3 and O_4) = 2.092, Fe–N = 2.29 Å., all with $\sigma < 0.005$ Å. Passing over differences in detail, we note that the averaged length of the five Fe–O bonds comes out just 0.005 Å. larger for $Fe(OH_2)Z^-$ than for $Fe(OH_2)Y^-$, while the comparatively unimportant Fe–N bonds are 0.035 Å. shorter in the DCTA complex. Over-all comparisons of the two configurations suggest little or no difference in the energy of complex formation for the DCTA and EDTA chelates.

A principal source of stability[2] for both chelates is the large increase in entropy associated with the release during chelation of water molecules (five in the present case) from the hydrated $Fe(OH_2)_6{}^{3+}$. The accompanying and partially off-setting decrease in the (partial molar) entropy of the chelating agent is confidently expected to be of lower magnitude for DCTA than for EDTA primarily because the cyclohexane ring in DCTA functions as a relatively severe constraint of the number of configurations available to the *free* complexing species. The stability constant of $Fe(OH_2)Z^-$ is unreported, but a value of about 10^{27}, as compared with $10^{25.1}$ for $Fe(OH_2)Y^-$, is made plausible by the tabulated data[2] for the chelates of Mn^{2+} and many other ions.

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Kinetics of the Addition of Grignard Reagents to Ketones[1]

Sir:

The 1,2-addition of Grignard reagents to carbonyl groups has been the subject of extensive study for many years.[2] Recently data have been interpreted in terms of the product arising from a low concentration of a complex between a dimeric Grignard reagent and a ketone,[3,4] from a complex between dialkylmagnesium and ketone,[5] or from the reaction of a Grignard reagent with a 1:1 complex between a Grignard reagent and a ketone.[6] In this communication data are presented which are consistent with a mechanism involving product arising from a complex between ketone I and methylmagnesium bromide with an equilibrium constant for complex formation of 6.2 1./mole.

2,4-Dimethyl-4'-methylmercaptobenzophenone (I), m.p. 53–54°, displays a strong absorption with λ_{max} 315 mμ (ϵ 2.5 × 10^4) in diethyl ether. An additional band, λ_{max} 360 mμ, is observed when methylmagnesium

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(6) The coordination group about Ca^{2+} in $Ca[Fe(OH_2)Z]_2 \cdot 9H_2O$, comprising five water molecules and two carbonyl oxygen atoms, approximates closely to the idealized $(C_{3v}\text{-}mm2)$ NbF_7^{2-} configuration as described by J. L. Hoard, *J. Am. Chem. Soc.*, **61**, 1252 (1939).

(1) Research supported by the U.S. Army Research Office (Durham).
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