TABLE I

Compound	Symmetry	Solvent[a]	Temp., °K.	Absorption bands, cm.$^{-1}$ I	II	III
$VO(acac)_2$	C_{2v}	2:5:5 ethanol:isopentane:ether	296	13,790	17,000	25,970
			77	12,980	17,920	. . .[b]
				13,580		
				14,180		
$VO(acac)_2$	C_{2v}	3:7 isopropyl alcohol:isopentane	296	13,380	16,940	25,700
			77	12,040	18,050	25,970
				12,980		
				13,600		
$(NH_4)_3[VOF_5]$	C_{4v}	Water	296	10,970	14,970	. . .
$(NH_4)_3[VOF_5]$	C_{4v}	1:1 water:propylene glycol	194	(8,480)	15,870	. . .
				11,830		
$[(CH_3)_4N]_3[VO(CN)_5]$	C_{4v}	1:1 water:propylene glycol	296	14,700	19,370	24,560
			194	(10,310)	20,660	24,810
				14,700		

[a] All solvent mixtures are *by volume*. [b] Region not investigated.

that the absorption maximum observed for many vanadyl complexes in the 24,500–30,000 cm.$^{-1}$ region, and assigned by previous workers[8,13,16] to the "third d–d band,"[23] might actually be the *first charge-transfer* band. We have experiments in progress to further test this hypothesis and to check out the possibility that the new bands observed at low temperature arise from vibrational fine structure.

However, there is some independent support for our hypothesis. (1) The relatively low intensity of this "third band" ($\epsilon < 100$) is in qualitative agreement with the partial forbiddance of this transition (from a filled bonding level to a half-filled nonbonding orbital). (2) It is observed[16,17] that this "third optical band" is relatively little shifted in $VO(acac)_2$ spectra obtained in a whole range of solvents which markedly shift the first two optical (room temperature) bands. If the third band were the third d–d transition, it is expected[16] that it would show a strong solvent effect. (3) In the vanadyl complexes $(NH_4)_3[VOF_5]$ and $[(CH_3)_4N]_3[VO(CN)_5]$, in which the vanadium is in a C_{4v} symmetry site, we observe at low temperature (at 194°K. in 1:1 water:propylene glycol) three optical bands at lower frequencies than the 25,000 cm.$^{-1}$ band, which is observed, for example, at 24,800 cm.$^{-1}$ in the cyano complex (see Table I). (4) Belford, Calvin, and Belford[24] observed the three predicted d–d bands in the very similar $Cu(acac)_2$ complex in the 11,300–18,800 cm.$^{-1}$ range and these bands were likewise found to be solvent dependent. (5) Recently[25] four d–d transitions were observed in the optical spectrum of bis-(3-phenylacetylacetonato)-copper at liquid nitrogen temperature and all occurred between 14,800 and 21,000 cm.$^{-1}$ with a familiar looking shoulder attached to an intense charge-transfer band at about 24,000 cm.$^{-1}$.

We plan extensive low-temperature investigations, employing organic glass and alkali halide matrices, of vanadyl and molybdenyl(V) complexes of C_{4v} and C_{2v} symmetry types. We would welcome communication from other workers who might suggest alternative explanations for our present observations.

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[23] In C_{4v} symmetry only three d–d bands are predicted.[13]

[24] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[25] G. Basu, R. L. Belford, and R. E. Dickerson, *Inorg. Chem.*, **1**, 438 (1962).

Stereochemistry of Ethylenediaminetetraacetato Complexes. The Chromium(III), Iron(III), and Gallium(III) Complex Acids[1]

Sir:

This report on the isostructural acid complexes formed by ethylenediaminetetraacetic acid (EDTA; H_4Y) with Cr(III), Fe(III), and Ga(III) is prompted by two recent papers[2,3] which differ materially in their characterizations of the Fe(III) acid. Stereochemical formulations from the earlier paper[3] for three chelate types pertinent to this discussion are summarized as follows: (1) $Fe(OH_2)Y^-$ as a sexadentate, seven-coordinate, aquo complex shown[4] to exist in $RbFe(OH_2)Y \cdot H_2O$, and considered to be the most stable anionic species; (2) the complex Fe(III) acid as a coupling of H^+ or H_3O^+ with the $Fe(OH_2)Y^-$ specified in (1); and (3) $Cr(OH_2)YH$ as a quinquedentate, six-coordinate, aquo complex having one free $\cdot CH_2COOH$ arm.

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[1] Supported by the National Science Foundation, the U. S. Public Health Service, and the Advanced Research Projects Agency. We thank also the Cornell Computing Center, R. C. Lesser, Director.

[2] J. L. Lambert, C. E. Godsey, and L. M. Seitz, *Inorg. Chem.*, **2**, 127 (1963).

[3] J. L. Hoard, G. S. Smith, and M. Lind in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 296–302.

[4] J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

TABLE I

	a, Å.	b, Å.	c, Å.	β, deg.
Ga(OH$_2$)YH	8.347 ± 0.005	8.840 ± 0.005	17.565 ± 0.010	99.86 ± 0.05
Fe(OH$_2$)YH	8.364 ± .005	8.942 ± .005	17.83 ± .010	99.46 ± .05
Cr(OH$_2$)YH	8.40 ± .01	8.82 ± .01	17.64 ± .02	99.9 ± .1

The first[5] and the third listed formulations are not presently in question. What we have to report, in full agreement on both points with Lambert, Godsey, and Seitz,[2] is that the Fe(III) acid in solutions of low pH behaves usually as a moderately strong acid (pK about[2] 2.2) and that crystalline Fe(OH$_2$)YH, with an infrared absorption spectrum indicative of a free ·CH$_2$COOH arm, is the usual polymorph, readily preparable despite its excessively large solubility in water.

Crystals of M(OH$_2$)YH, M = Cr, Fe, Ga, are monoclinic, with four molecules of no required symmetry in the unit cell. The space group is P2$_1$/c, and the lattice constants are given in Table I.

Using all three-dimensional data recordable with Mo Kα radiation by the counter technique, but from a crystal having less than 10% of the optimum volume, structure determination for Fe(OH$_2$)YH was readily achieved. Subsequent determination of structure for Ga(OH$_2$)YH utilized bigger and better crystals. The molecular configuration, as predicted[3] for Cr(OH$_2$)YH, is a dimensionally modified version of the quinquedentate octahedral configuration with *one* uncomplexed arm established[6] for Ni(OH$_2$)YH. Averaged bond distances, Fe–N = 2.22, Fe–O = 2.00 Å. in Fe(OH$_2$)YH are to be compared with Fe–N = 2.325, Fe–O = 2.057 Å. in the seven-coordinate Fe(OH$_2$)Y$^-$ anion. A large difference between M–N and M–O bond lengths occurs also in Ga(OH$_2$)YH: Ga–N = 2.12, Ga–O = 1.95 Å. In Cr(OH$_2$)YH, however, one may expect Cr–N to exceed Cr–O by no more than 0.04 Å. (the difference of the covalent radii for N and O) as is observed[7] for the sexadentate octahedral CoY$^-$ and for the bonds in the "square" girdle[6] of Ni(OH$_2$)YH$_2$.

Given inconsequential contributions from nitrogen atoms, the advantage to any Fe(III) complex of having five tightly held oxygen atoms becomes the more evident. We suggest that, in solution, a quinquedentate seven-coordinate bisaquo Fe(OH$_2$)$_2$YH with free arm is the preferred form of the complex acid, but that a water molecule is lost from each complex during crystallization. The Fe(OH$_2$)YH structural type is characterized by a high packing density (as EDTA complexes go), and the solubility of this phase, with allowance for ionization, seems excessively high unless the dissolving Fe(OH$_2$)YH molecules are largely transformed into other (neutral) species. Alternative or simultaneous crystallization of various salts at surprisingly low pH and cationic concentration, and some disproportionation of Fe(OH$_2$)YH during recrystallization, are usual. The distinctive color pattern—amber to deep brown depending upon concentration or crystal size—which characterizes the solutions (pH 1–7) and all crystalline complexes except the bright yellow Fe(OH$_2$)YH seems attributable to the seven-coordinate species.

Schwarzenbach and Heller[8] assigned pK < 1.5 to the Fe(III) acid by titrating the potassium salt with hydrochloric acid and noting that at low pH the curve was identical with that of KCl–HCl mixtures at the same formal concentrations. The sluggish kinetics of opening a chelate ring thus displayed encourages efforts to prepare crystals of an amber-brown complex acid crystallographically related to the ammonium salt—*i.e.*, the acid seemingly obtained[3] in small amount 5 years past.

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[5] Expanded evidence for an Fe(OH$_2$)Y$^-$ anion of the specified character is developed elsewhere: M. D. Lind and J. L. Hoard, *Inorg. Chem.*, in press, and M. J. Hamor, T. A. Hamor, and J. L. Hoard, *ibid.*, in press.

[6] G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 556 (1959); *cf.* Fig. 1 and 4. One protonated arm ·CH$_2$COOH is chelated to Ni.

[7] H. A. Weakliem and J. L. Hoard, *ibid.*, **81**, 549 (1959).

[8] G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

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The Structure of Neocarborane

Sir:

Hoffmann and Lipscomb[1] recently discussed the potential existence of three geometrical isomers for the icosahedral carborane system. In these structures (Fig. 1) the two carbon atoms are either adjacent (*ortho*), intermediate (*meta*), or opposite (*para*) to each other. To date two parent isomers of this class of compounds have been found which are called carborane[2,3] and neocarborane.[4] Efforts to establish their structures based on chemical and spectral evidence especially by n.m.r. studies have been conducted in this laboratory.

The theoretical ^{11}B n.m.r. spectra of the geometrical isomers can be qualitatively deduced from the environments of the individual boron atoms in their respective icosahedral configurations. All boron atoms of the *para* isomer (1,12) are geometrically equal in that each is adjacent to one of the carbon atoms. Therefore the spectrum should consist of only one doublet. The *meta* isomer (1,7), on the other hand, has three kinds of geometrically different boron atoms. Two of them (2,3) are affiliated with both carbons, six of them with only one carbon, and the remaining two (9,10) have no

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[1] R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 213 (1963).

[2] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *ibid.*, **2**, 1089 (1963).

[3] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

[4] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).