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Compounds of Iron(III) with *trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylic Acid: Structures of *trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylato)iron(III) Perchlorate and *trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylato)iron(III) *trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylic acid)dichloroiron(III) *trans*-1,4,8,11-Tetraazoniacyclotetradecane-6,13-dicarboxylic Acid Dichloride Tetraperchlorate Tetrahydrate

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The macrocyclic amino acid *trans*-1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylic acid ($diacH_2$) forms low-spin Fe^{III} cations *trans*-$[Fe(diac)]^+$ (with octahedral $diac^{2-}$ with two carboxylato oxygens coordinated *trans*) and *trans*-$[Fe(diacH_2)(X)_2]X$ ($X^- = Cl^-, NCS^-$; with planar tetradentate $diacH_2$). The cations are resistant to oxidative dehydrogenation when exposed to the atmosphere in acid solution. The carboxylic acid functions of $[Fe(diac)]^+$ readily form the methyl ester compound *trans*-$[Fe(dimest)Cl](ClO_4)_2$ (dimest = *trans*-6,13-bis(methoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane). Structures are reported for *trans*-$[Fe(diac)](ClO_4)$ with $diac^{2-}$ octahedrally coordinated by the macrocycle nitrogens and with the carboxylato oxygens coordinated *trans* [$C_{12}H_{20}ClFeN_4O_8$, $M_r = 441.6$, monoclinic, space group $I2/a$, $a = 12.676(3)$ Å, $b = 9.030(2)$ Å, $c = 15.103(4)$ Å, $\beta = 108.4(2)°$, $Z = 4$, Fe–N = 1.992(3) and 1.995(3) Å, Fe–O = 1.895(2) Å] and also for the extraordinary compound *trans*-$[Fe(diac)]$-*trans*-$[Fe(diacH_2)Cl_2][diacH_6]Cl_2(ClO_4)_4 \cdot 4H_2O$, which has three different centrosymmetric cations, *trans*-$[Fe(diac)]^+$, similar to the cation of the first compound [(Fe–N = 2.010(4) and 1.998(4) Å, Fe–O = 1.902(3) Å], *trans*-$[Fe(diacH_2)Cl_2]^+$ with square planar coordination of $diacH_2$ by the four macrocyclic nitrogens with *trans* coordinated chlorides [Fe–N = 1.992(4) and 2.004(4) Å, Fe–Cl = 2.248(1) Å], and $[diacH_6]^{4+}$ with the uncomplexed protonated ligand [$C_{36}H_{82}Cl_8Fe_2N_{12}O_{32}$, $M_r = 1590.4$, triclinic, space group $P\bar{1}$, $a = 9.474(2)$ Å, $b = 11.535(2)$ Å, $c = 15.487(3)$ Å, $\alpha = 71.67(1)°$, $\beta = 77.31(2)°$, $\gamma = 76.61(1)°$, $Z = 2$].

Introduction

Preparations and structural, magnetic, and spectroscopic properties have been reported for compounds of Fe^{II} and/or Fe^{III} with the tetra-secondary amine 1,4,8,11-tetraazacyclotetradecane (cyclam),[1-3] homologues with varying ring sizes,[3] *C*-methyl-substituted cyclams,[3,5] cyclam with substituent amine groups (*trans*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane = diam),[6,7] and various tetraaza cyclic immines.[3,4,8-20] The compounds $[Fe(diam)]Cl_2(ClO_4)$[7] and $[Fe(diam)](ClO_4)_3$[8] are the only compounds of cyclic tetraamines for which structures have been reported, although a number of compounds of tetrazamacrocycles with immine functions have been structurally characterized.[13-19] Immine (particularly α-diimine), porphyrin-like, and bipyridine-like ligands have a strong affinity for, and dominate the published amine chemistry of, low-spin Fe^{III}.

In oxygenated solution iron compounds of cyclam-like ligands with α-CH groups often readily oxidatively dehydrogenate to form immine derivatives, particularly if an α-diimine function can be formed.[8-11] However, the compounds with diam,[6,7] 1,4,7-triazacyclononane ligands,[21] and hexaaza clathrochelates[22] are resistant to ligand oxidation in aerated aqueous solution.

For both Fe^{II} and Fe^{III}, cyclic amine/immine compounds of low-, intermediate-, and high-spin ground states have been described.[23] Electrochemistry,[4,8,24] Mossbauer,[25] and ESR spectra[8] of a variety of tetraaza macrocycle compounds of iron have been reported.

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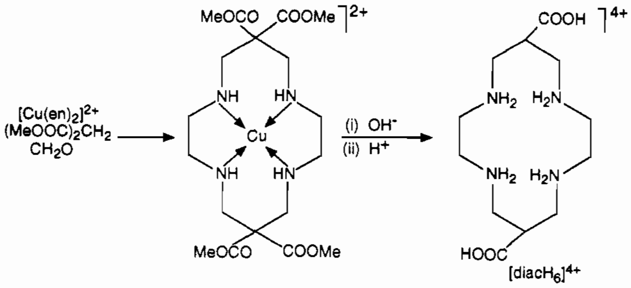
Scheme I



The macrocyclic amino acid *trans*-1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylic acid ($diacH_2$) has been prepared by the Cu^{II}-mediated sequence of reactions shown in Scheme I.[26] The initially formed Cu^{II} dicarboxylic acid compound has the carboxylate groups as axial substituents; this isomerizes in base to form the stable configuration with the substituent carboxylate groups equatorially oriented. Ni^{II} compounds of $diacH_2$ were similarly prepared.[26]

The isomeric Cu^{II} dicarboxylic acid cations $[Cu(diacH_2)]^{2+}$ readily esterified in acidic methanol to form isomeric 6,13-bis(methoxycarbonyl) (dimest) substituted complex cations, which reacted with ammonia and amines to form 6,13-dicarbamoyl (amido) substituted macrocyclic cations.[27]

Structures were reported for the Cu^{II} compounds as perchlorate salts of the isomeric cations $[Cu(diacH_2)]^{2+}$ with the dicarboxylic acid substituents axially (metastable) and equatorially oriented and for the stable configuration bis(methoxycarbonyl) cation $[Cu(dimest)]^{2+}$ with equatorially oriented substituents.[25]

The preparation of Cu^{II} compounds of other tetraazamacrocyles of various ring sizes from the reactions of linear tetraamines, formaldehyde, and diethyl malonate with *gem*-bis(ethoxycarbonyl), *gem*-bis(carboxylic acid), and mono(carboxylic acid) substituents have been reported, and the structure of a carboxylic acid substituted macrocyle has been determined.[28] A 6-amino-6-methyl-13-carboxylic acid substituted cyclam (amacH) has been prepared as the Cu^{II} compound, the ligand has been isolated, and preparation and structural studies of Co^{III} compounds have been reported.[29]

The macrocyclic amino acid $diacH_2$ is a member of a class of azamacrocycles with pendant donor functions.[30,31] These pendant donor groups are more commonly present as N-substituents, as for example for the *N*-(methoxycarbonyl) [*N*-(acetic acid)] substituted cyclic amines. These have aroused interest because they form complexes with high formation constants and often of low lability with a variety of cations, including lanthanides, which are of potential interest as NMR shift reagents.[32] With transition metal cations the tetra-*N*-(methoxycarbonyl)-substituted cyclic tetraamines form dinuclear complexes, with the macrocycle coordinated in an exocyclic fashion,[33,34] as well as mononuclear endocyclic coordinated ligands which have two coordinated carboxylato groups.[34,35] Structures with endocyclic coordinated macrocycles with the carboxylato groups coordinated have been reported for Ni^{II} or Cu^{II} for a 1,8-dimethoxycarbonyl-substituted cyclam[36] (and the 4,11-dimethyl homologue),[36] for a hexa-*C*-methyl-substituted cyclam,[37] and also for mono-*N*-(methoxycarbonyl) cyclic tetraamines.[38] The five-coordinate Cu^{II} compound of one di-*N*-(carboxymethyl)-substituted pyridyl tetraazamacrocycle has three of the four ring nitrogen atoms and both carboxylato group oxygen atoms coordinated.[39]

Coordination of the macrocycle nitrogens for these ligands with Ni^{II} is generally nonlabile, but the carboxylato groups are labile and in acid solution the carboxylato groups are rapidly and reversibly decoordinated and protonated. Similar behavior is shown by compounds of diam with Ni^{II}, the secondary amine nitrogens of the macrocycle being nonlabile and the coordinated primary amine groups labile.[40] The ligand $diacH_2$ with 6,13-di-*C*-carboxylic acid substituents is structurally related to the di-*N*-(carboxymethyl) cyclam macrocycles.

The formation constants of Fe^{III} with several per-*N*-(carboxymethyl)-substituted azamacrocycles have been reported.[41] The structure of [Fe(triac)] ($triacH_3$ = 1,5,9-tris(methoxycarbonyl)-1,5,9-triazacyclononane) has been determined.[42]

In this paper the preparations of compounds of $diacH_2$, $diac^{2-}$, and dimest with Fe^{III}, studies of magnetic, spectroscopic, and redox properties, and the structures of two of the compounds are reported. The compounds now described appear to be the first reported Fe^{III} compounds of a cyclic amine with *C*-carboxylato substituents.

Experimental Section

The ligand *trans*-1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylic acid was prepared as the tetrahydrochloride salt $[diacH_6]Cl_4\cdot2.5H_2O$ as previously described.[26]

Caution! The perchlorate salts described are potentially explosive and should be prepared in only small quantities.

***trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylato)-iron(III) Perchlorate, *trans*-$[Fe(diac)](ClO_4)$.** Iron(II) perchlorate hexahydrate (1 g), $[diacH_6]Cl_4\cdot2.5H_2O$ (0.8 g, diac:Fe^{II} 1:1.1 mol proportions), and sodium acetate (1.1 g, diac:CH_3COONa 1:6 mol proportions) were dissolved in 25 mL of water, and the solution was heated in a boiling water bath for several hours. The color slowly darkened, and dark orange crystals formed. Sodium perchlorate (2 g) was added, and the crystals were filtered from the cold solution after 1 d and washed with a little cold water and ethanol. These were recrystallized from boiling water containing a few drops of acetic acid, increasing the yield by the addition of sodium perchlorate to the hot filtered solution and then filtering out the *product* from the cold solution and washing as before; yield ca. 0.8 g, 85%. The reaction of diac with Fe^{II} occurred more rapidly in less acidic solution, as for example by dripping triethylamine into a hot solution of the ligand salt and iron(II) perchlorate until a permanent precipitate of hydrated iron(III) oxide just formed, but the product was contaminated with the oxide and the yield somewhat lower. Anal. Calcd for $C_{12}H_{22}ClFeN_4O_8$: C, 32.6; H, 5.0; N, 12.7. Found: C, 32.5; H, 5.0; N, 12.7.

***trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylic acid)-dichloroiron(III) Chloride, *trans*-$[Fe(diacH_2)Cl_2]Cl$.** Concentrated hydrochloric acid (1 mL) was added to a hot aqueous solution of $[Fe(diac)](ClO_4)$ (1 g in the minimum volume of water). The yellow-brown *product* was filtered from the cold solution and washed with a little cold dilute hydrochloric acid and then ethanol. Anal. Calcd for $C_{12}H_{24}Cl_3FeN_4O_4$: C, 32.0; H, 5.4; Cl, 23.6; N, 12.4. Found: C, 31.9; H, 5.3; Cl, 23.4; N, 12.5.

***trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylic acid)-dithiocyanatoiron(III) Thiocyanate Hemihydrate, *trans*-$[Fe(diacH_2)(NCS)_2](CNS)\cdot{}^1/_2H_2O$.** *trans*-$Fe(diacH_2)Cl_2]Cl$ (0.5 g) was dissolved

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Table I. Crystallographic Data

	compd	
	1	**2**
chem formula	$C_{12}H_{22}ClFeN_4O_8$	$C_{36}H_{82}Cl_8Fe_2N_{12}O_{32}$
fw	441.6	1590.4
space group	*I*2/*a* (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	12.676(3)	9.474(2)
b (Å)	9.030(2)	11.535(2)
c (Å)	15.103(4)	15.487(3)
α (deg)		71.67(1)
β (deg)	108.4(2)	77.31(2)
γ (deg)		76.61(1)
V (Å^3)	1640.2(7)	1543.0(1)
Z	4	2
T (°C)	−150	−150
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	2.04	1.65
μ (cm^{-1})	10.87	6.02
transm coeff	0.884–0.807	0.994–0.826
$R(F_o)$	0.0471	0.0433
$R_w(F_o)$	0.0524	0.0452

Table II. Positional Parameters and B_{iso} Values (Å^2) for Non-Hydrogen Atoms for *trans*-[Fe(diac)](ClO$_4$)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}[a]
Fe(1)	0.2500	0.7500	0.2500	1.01
N(1)	0.1540(2)	0.6761(4)	0.1266(2)	1.78
C(2)	0.0989(3)	0.8067(5)	0.0706(3)	2.68
C(3)	0.1769(3)	0.9335(5)	0.0936(3)	2.51
N(4)	0.2134(2)	0.9525(3)	0.1961(2)	1.75
C(5)	0.3053(3)	1.0646(4)	0.2278(3)	2.14
C(6)	0.0821(3)	0.5083(4)	0.2269(3)	1.80
C(7)	0.0705(3)	0.5588(4)	0.1286(3)	2.13
C(8)	0.0604(3)	0.6365(4)	0.2849(2)	1.47
O(9A)	0.1252(2)	0.7515(2)	0.2935(2)	1.38
O(9B)	−0.0132(2)	0.6315(3)	0.3207(2)	2.18
Cl(1)	0.7500	0.8597(1)	0.5000	1.84
O(11)[b]	0.6638(4)	0.7951(6)	0.5302(4)	1.60
O(12)	0.7102(5)	0.9932(7)	0.4555(4)	3.15
O(13)	0.6968(5)	0.8947(7)	0.3982(4)	3.17
O(14)	0.6641(5)	0.7572(7)	0.4938(5)	2.80

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid. [b] The disordered perchlorate oxygen atoms were refined with four sites at half-occupancy.

Table III. Positional Parameters and B_{iso} Values (Å^2) for Non-Hydrogen Atoms for *trans*-[Fe(diac)]-*trans*-[Fe(diacH$_2$)Cl$_2$][diacH$_6$]Cl$_2$(ClO$_4$)$_4$·4H$_2$O

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}[a]
Fe(1)	0.0000	0.0000	0.0000	0.95
N(11)	0.1924(5)	0.0478(4)	−0.0712(3)	1.27
C(12)	0.1555(6)	0.1485(5)	−0.1558(4)	1.59
C(13)	0.0411(6)	0.1122(5)	−0.1910(4)	1.65
N(14)	−0.0870(4)	0.0962(4)	−0.1136(3)	1.17
C(15)	−0.1990(6)	0.0436(5)	−0.1374(4)	1.52
C(16)	0.2082(6)	0.0900(5)	0.0753(4)	1.37
C(17)	0.2831(6)	0.0883(6)	−0.0217(4)	1.71
C(18)	0.0588(6)	0.1745(5)	0.0742(4)	1.27
O(19A)	−0.0394(4)	0.1447(3)	0.0414(2)	1.24
O(19B)	0.0334(4)	0.2687(3)	0.1006(2)	1.43
Fe(2)	0.0000	1.0000	0.5000	1.09
Cl(21)	−0.0313(2)	0.9651(1)	0.6536(1)	1.83
N(21)	0.2062(5)	1.0231(4)	0.4874(3)	1.37
C(22)	0.2033(6)	1.1472(5)	0.4992(4)	1.79
C(23)	−0.0840(6)	0.7627(5)	0.5503(4)	1.88
N(24)	0.0544(5)	0.8176(4)	0.5124(3)	1.35
C(25)	0.1734(6)	0.7438(5)	0.5655(4)	1.69
C(26)	0.3151(6)	0.7988(5)	0.5266(4)	1.75
C(27)	0.3071(7)	0.9244(6)	0.5434(4)	1.84
C(28)	0.4352(6)	0.7073(5)	0.5762(4)	2.01
O(29A)	0.4598(5)	0.7072(4)	0.6487(3)	3.14
O(29B)	0.5090(7)	0.6289(5)	0.5298(4)	4.99
N(1)	0.4563(5)	0.3352(4)	0.1698(3)	1.43
C(2)	0.5293(6)	0.4415(5)	0.1583(4)	1.54
C(3)	0.3046(6)	0.5927(6)	−0.1445(4)	1.60
N(4)	0.2333(5)	0.5944(4)	−0.0470(3)	1.35
C(5)	0.2526(6)	0.4676(5)	0.0213(4)	1.47
C(6)	0.2191(5)	0.4776(5)	0.1209(3)	1.25
C(7)	0.2870(6)	0.3629(6)	0.1898(4)	1.87
C(8)	0.0545(6)	0.5076(5)	0.1523(4)	1.43
O(9A)	0.0140(5)	0.4641(4)	0.2415(3)	2.29
O(9B)	−0.0286(4)	0.5686(3)	0.0985(3)	1.69
Cl(1)	0.1929(2)	0.6165(2)	0.3430(1)	3.15
O(11)	0.0403(6)	0.6382(5)	0.3810(3)	5.25
O(12)	0.2514(6)	0.4878(5)	0.359(4)	4.70
O(13)	0.2120(6)	0.6485(4)	0.2438(3)	3.45
O(14)	0.2662(8)	0.6922(6)	0.3683(4)	6.59
Cl(2)	0.5211(1)	1.0129(1)	0.2721(1)	1.70
O(21)	0.5621(5)	0.9114(4)	0.3486(3)	2.70
O(22)	0.6424(4)	1.0788(4)	0.2295(3)	2.48
O(23)	0.3987(5)	1.0979(4)	0.3033(3)	3.37
O(24)	0.4832(5)	0.9670(5)	0.2054(3)	3.03
Cl(3)	0.4116(1)	0.7515(1)	0.0076(1)	1.61
O(3)	0.2423(7)	0.4412(6)	0.6881(5)	7.11
O(4)	0.4625(7)	0.3012(6)	0.7869(7)	7.06

[a] See footnote *a* of Table II.

in hot water (10 mL) containing a few drops of acetic acid. Sodium thiocyanate (1 g) dissolved in a small volume of hot water was added, when the color slowly changed to intense purple, and the *product* crystallized. The solution was cooled in ice, and the purple crystals were filtered from the cold solution and washed with a little cold water and then propan-2-ol. Formulation as a hydrate is supported by weak absorption bands at 3524, 3439, and 1639 cm^{-1}. Anal. Calcd for $C_{15}H_{25}FeN_7O_{4.5}S_3$: C, 34.2; H, 4.8; N, 18.6; S, 18.2. Found: C, 34.4; H, 4.9; N, 18.5; S, 17.6.

***trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylic acid)iron(III) *trans*-(*trans*-1,4,8,11-Tetraazacyclotetradecane-6,13-dicarboxylato)dichloroiron(III) *trans*-(1,4,8,11-Tetraazoniacyclotetradecane-6,13-dicarboxylic acid) Dichloride Tetraperchlorate Tetrahydrate, *trans*-[Fe(diac)]-*trans*-[Fe(diacH$_2$)Cl$_2$][diacH$_6$]Cl$_2$(ClO$_4$)$_4$·4H$_2$O.** Iron(II) perchlorate hexahydrate (1 g) and [diacH$_6$]Cl$_4$·2.5H$_2$O (2 g) were dissolved in ethanol/water (20 mL of 1:1), and triethylamine was added to the solution until precipitation of iron(II) hydroxide commenced. The solution was allowed to evaporate for 2 d, while the color became brown and iron(III) hydroxide precipitated. Perchloric acid was added dropwise until the precipitate just dissolved, and the solution was allowed to evaporate for several days, while dark brown crystals of the *product* formed. These were filtered off and washed with ethanol. The structure was established by X-ray crystallography.

***trans*-(μ-Chloro)(*trans*-6,13-bis(methoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane)chloroiron(III) Perchlorate, (μ-Cl)[Fe(dimest)Cl](ClO$_4$)$_2$.** [Fe(diacH$_2$)Cl$_2$]Cl was dissolved in the minimum volume of boiling water, three volumes of methanol were added, followed by a few drops of concentrated hydrochloric acid, and the solution was refluxed for 30 min. Sodium perchlorate was added, and the yellow-brown *product* was filtered from the cold solution and washed with methanol. Anal. Calcd for $C_{14}H_{30}Cl_3FeN_4O_8$: C, 31.0; H, 5.2; N, 10.3. Found: C, 30.5; H, 5.2; N, 10.1.

Crystallography. The crystal of compound **1**, *trans*-[Fe(diac)](ClO$_4$), was grown by evaporation of a solution in dilute perchloric acid. The crystal of compound **2**, *trans*-[Fe(diac)]-*trans*-[Fe(diacH$_2$)Cl$_2$][diacH$_6$]Cl$_2$(ClO$_4$)$_4$·4H$_2$O, grew from the preparation solution and was not recrystallized.

Table I lists crystal data and details of the refinements for compounds **1** and **2**. Tables II and III list positional and thermal parameters. All X-ray crystallographic measurements were made using a Nicolet R3m diffractometer with graphite-monochromatized Mo Kα radiation. As the space group assignments were not unambiguous, the most symmetric possibilities were chosen. The structures were solved and refined without problems, supporting these assignments. The structures were solved by Patterson methods and subsequent difference Fourier maps.[43] Refinement was by a full-matrix least-squares method using anisotropic thermal parameters for non-hydrogen atoms. Disorder for the oxygen atoms of the perchlorate ion of compound **1** was modeled by half-occupancy of two sites. Hydrogen atoms were generally included in the refinement with fixed positional and isotropic thermal parameters. Special attention was given to the hydrogen atoms involved in hydrogen-bonding interactions for compound **2**. These were generally located from a difference synthesis

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(43) Structure solution and refinement used the program SHELX-76 (G. M. Sheldrick, SHELX-76 program for crystal structure determination, University of Cambridge, U.K., 1976).

of electronic density, and then their positional parameters were refined with fixed isotropic thermal parameters (B = 0.02 Å). The refined positions of the H atoms of O(4) using this procedure are not chemically meaningful.

Hydrogen atom site parameters and thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles are in the supplementary material.

Other Measurements. Magnetic susceptibilities were measured by the Faraday method at 298 K, using $Hg[Co(CNS)_4]$ as calibrant. Effective magnetic moments were calculated by making use of Pascal's constants for the diamagnetic corrections and assuming the Curie relationship. Spectroscopic measurements used Digilab FTS40 and Hewlett Packard 8452A spectrometers. Cyclic voltammetry measurements used an EG&G Princeton Applied Research Model 273 potentiostat. Microanalysis was by the Microanalytical Service, Otago University.

Results and Discussion

The reaction of iron(II) perchlorate with $[diacH_6]Cl_4$ in water with sufficient base added to produce a just slightly acid solution yielded orange *trans*-$[Fe(diac)](ClO_4)$ in high yield when exposed to the atmosphere. The structure of this compound, below, shows the macrocyclic ligand in hexadentate coordination, with the carboxylato groups coordinated *trans*. The cation is resistant to acid demetalation, the spectrum showing no change after boiling with 1 mol L^{-1} perchloric acid for some hours, and the compound crystallized unchanged from the solution. Demetalation in hydrochloric acid was faster, and the ligand hydrochloride crystallized from refluxing constant boiling hydrochloric acid after ca. 30 min (which is comparable with the rate for the Cu^{II} analogue).[26]

The cation *trans*-$[Fe(diac)]^+$ reacted over a period of minutes with hydrochloric acid to form a sparingly soluble yellow-brown compound of stoichiometry $Fe(diacH_2)Cl_3$. A structural determination (below) of an orange crystal which grew from one preparation showed discrete *trans*-$[Fe(diac)]^+$, *trans*-$[Fe(diacH_2)Cl_2]^+$, and $[diacH_6]^{4+}$ cations within the unit cell. The chloride compound is assigned the analogous *trans*-dichloro structure (although in view of the low solubility of the compound and apparent structure of the carbomethoxy compound, below, a μ-chloro chain polymeric structure is possible). The orange hexadentate dicarboxylato cation was rapidly re-formed in water.

Addition of thiocyanate to a solution of *trans*-$[Fe(diac)](ClO_4)$ resulted in a color change over minutes to intense purple. Intensely purple crystals of *trans*-$[Fe(diacH_2)(NCS)_2]CNS$ formed after addition of acid, and the same product crystallized when *trans*-$[Fe(diacH_2)Cl_2]Cl$ reacted with thiocyanate.

The orange aqueous solution of *trans*-$[Fe(diac)](ClO_4)$ slowly turned pink when dilute ammonia was added and then over a period of days deposited hydrated iron(III) oxide. The original complex was slowly re-formed when the oxide was redissolved in acid and the acidity then adjusted to faintly acidic. A deprotonation reaction producing an unstable red compound was also reported for the diam complex.[7]

The cation *trans*-$[Fe(diac)]^+$ was reduced and demetalated by amalgamated zinc in acid, again as reported for the diam compound.

The carboxylic acid functions of *trans*-$[Fe(diac)]^+$ readily esterified in acidified aqueous methanol to form the bis(methoxycarbonyl)-substituted macrocycle compound of stoichiometry $Fe(dimest)Cl(ClO_4)_2$ (dimest = 6,13-bis(methoxycarbonyl)-1,4,8,11-tetraazacyclotetradecane), most easily formulated with a μ-chloro–*trans*-dichloro chain structure. The ester functions rapidly hydrolyzed in water. Reaction with concentrated aqueous ammonia produced a red solution which rapidly deposited hydrated Fe^{III} oxide; the Cu^{II} analogue formed the dicarbamoyl (diamide) compound under these conditions.[26]

Spectra. The infrared spectrum of all the compounds showed absorption in the ν(NH) region and a sharp strong band in the "carboxyl" region: *trans*-$[Fe(diac)](ClO_4)$, 3258, 3176, and 1642; *trans*-$[Fe(diacH_2)Cl_2]Cl$, 3194, 3145, and 1792; *trans*-$[Fe(diacH_2)(NCS)_2](CNS)$, 3212, 1721; ($\mu$-Cl)-*trans*-$[Fe(dimest)Cl](ClO_4)_2$ 3212 and 1736 cm^{-1}. The Cu^{II} bis(carboxylato), bis(carboxylic acid), and bis(methoxycarbonyl) analogues (in the configuration with equatorially oriented substituents) showed absorption bands at 1587, 1734, and 1737 cm^{-1}, respectively.[26] The thiocyanato compound showed a very strong absorption band at 2058 cm^{-1}; cf. 2080 cm^{-1} for *trans*-$[Fe(cyclam)(NCS)_2](ClO_4)$. There was no indication of a separate band which could be attributed to ionic thiocyanate.

The electronic spectrum of *trans*-$[Fe(diac)](ClO_4)$ in water showed two d–d bands at 498 (35) and 428 (32) nm plus a charge-transfer band at 332 (ca. 1000) nm (molar absorbance, L mol^{-1} cm^{-1}, in parentheses). There was no significant change in the spectrum in 1 mol L^{-1} perchloric acid, and *trans*-$[Fe(diac)](ClO_4)$ crystallized from quite concentrated solutions of that acid; either the diaqua cation of the dicarboxylic acid ligand is not formed even in the concentrated acid or the spectrum is very similar to that of *trans*-$[Fe(diac)]^+$. The color changed from orange to red-orange (with bands at 522 (38) and 438 (43) nm) over a period of minutes in 2 mol L^{-1} sulfuric acid, suggesting that sulfato-coordinated species may be present. When hydrochloric acid was added to a solution of *trans*-$[Fe(diac)](ClO_4)$ in water, the color rapidly changed to brown and sparingly soluble brown *trans*-$[Fe(diacH_2)Cl_2]Cl$ slowly crystallized. Addition of hydrobromic acid produced neither the color change nor any crystalline product. The visible spectrum of the permanganate-colored solution of *trans*-$[Fe(diacH_2)(NCS)_2](CNS)$ in acetone was dominated by an intense iron–thiocyanato charge-transfer band at 556 nm (ϵ ca. 5000 L mol^{-1} cm^{-1}), with the d–d bands as weak poorly defined shoulders at ca. 340 and 480 nm.

Magnetic Properties. The effective magnetic moments (μ_{eff} at 298 K) for *trans*-$[Fe(diac)](ClO_4)$, 2.38 μ_B, *trans*-$[Fe(diacH_2)Cl_2]Cl$, 2.73 μ_B, *trans*-$[Fe(diacH_2)(NCS)_2](CNS)\cdot{}^1/_2H_2O$, 2.50 μ_B, and *trans*-$[Fe(dimest)Cl](ClO_4)_2$, 2.75 μ_B, are indicative of spin-paired Fe^{III}. The values show large unquenched orbital contributions, as is common for ^2T ground states; cf. the reported values for *trans*-$[Fe(cyclam)Cl_2]ClO_4$ of 2.71 μ_B and *trans*-$[Fe(cyclam)(NCS)_2]CNS$ of 2.30 μ_B.[1] The Fe^{III} cyclam compounds are spin-paired for all but the weakest *trans*-ligands.[1]

Electrochemistry. The cation $[Fe(diac)]^+$ was reversibly reduced with a reduction potential vs Ag/AgCl(satd) of –0.18 V in 0.1 mol L^{-1} aqueous $NaClO_4$. This value can be compared with –0.35 V reported for $[Fe(diam)]^{3+}$,[7] showing the effect of replacing two *trans* nitrogen by oxygen atoms in lowering the relative stability of the trivalent state. Reduction potentials for a variety of azamacrocyclic compounds of Fe^{III} have been reported.[23,24]

Structural Studies. The structures of *trans*-$[Fe(diac)](ClO_4)$, **1**, and of a crystal of **2** (which was isolated from one early attempt at preparation of the compounds) were determined by X-ray diffractometry; see Experimental Section for details. The crystal of **2** was found to contain discrete *trans*-$[Fe(diac)]^+$, *trans*-$[Fe(diacH_2)Cl_2]^+$, and $[diacH_6]^{4+}$ cations, all centrosymmetric, and symmetry-related pairs of Cl^-, two pairs of ClO_4^- anions, and two pairs of water molecules, all linked by a hydrogen-bonded network. The unit cell is shown in Figure 1. Significant dimensions are in the text or in the legends to the figures; full dimensions are in the supplementary material in Tables 4 and 9 (bond lengths) and 5 and 10 (bond angles). The *trans*-$[Fe(diac)]^+$ cations in the structures of compounds **1** and **2** have very similar geometries, with planar coordination of the tetraazamacrocycle nitrogen atoms and with carboxylato oxygen atoms coordinated *trans*. The cation $[Fe(diac)]^+$ of compound **2** is shown in Figure 2. The configuration of the chiral nitrogen centres is *RSRS*, as is usual for planar coordination of cyclam-like macrocycles. The conformation adopted has the six-membered chelate rings bearing the coordinated carboxylato substituents in a boat conformation, as required to permit coordination of these groups, and the five-

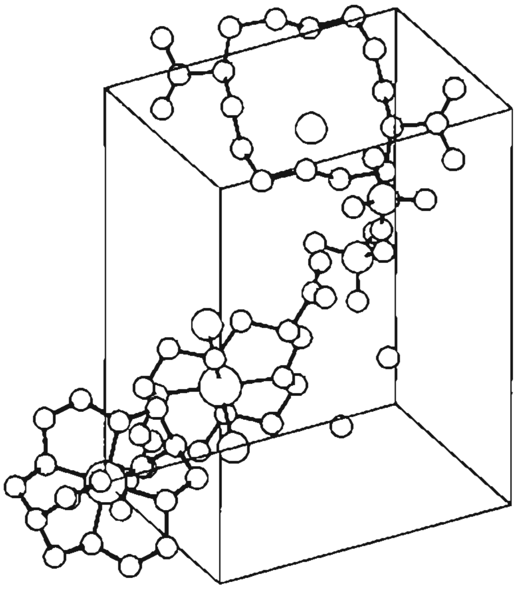

Figure 1. Contents of the unit cell for compound **2**.

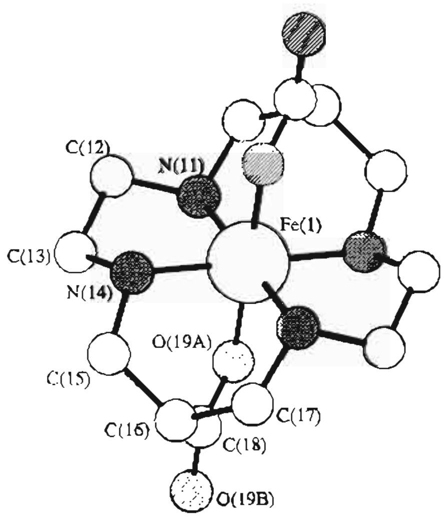

Figure 2. Cation $[Fe(diac)]^+$ of compound **2**. Selected dimensions for this cation (Å, deg): C(18)–O(19A), 1.306(7); C(18)–O(19B), 1.236(6); N(11)–Fe(1)–N(14), 86.9(2); O(19A)–Fe(1)–N(11), 89.0(1); O(19A)–Fe(1)–N(14), 90.8(2); O(19A)–C(18)–O(19B), 121.6(4). Selected dimensions for the similar cation $[Fe(diac)]^+$ of compound **1** (Å, deg): C(8)–O(9A), 1.304(4); C(18)–O(19B), 1.219(4); N(1)–Fe(1)–N(4), 86.0(1); N(1)–Fe(1)–O(9A), 89.8(1); N(4)–Fe(1)–O(9B), 91.3(1); O(9A)–C(8)–O(9B), 121.1(3).

Table IV. Deviations (Å) from Planes Containing the Four Nitrogen Atoms

	cation			
atom	*trans*-$[Fe(diac)]^{+a}$	*trans*-$[Fe(diac)]^{+b}$	*trans*-$[Fe(diacH_2)Cl_2]^+$	$[diacH_6)]^{4+}$
C(2)	–0.18	–0.33	–0.33	–1.13
C(3)	0.51	0.43	0.39	0.92
C(5)	0.78	0.84	0.80	0.55
C(6)	1.74	1.74	0.39	–0.54
C(7)	0.99	0.92	0.80	–1.19
C(8)	2.56	2.56	1.18	0.89
O(9A)	1.89	1.90	2.23	0.80
O(9B)		3.79	0.38	1.30

[a] Compound **1**. [b] Compound **2**.

membered chelate rings in a gauche conformation (see Table IV for deviations of atoms from the FeN_4 planes). The macrocyclic ring conformation is similar to that found for octahedrally coordinated compounds of diam with several metal ions, including Fe^{III},[7,41,42] except that for the diam compounds the coordinated amino nitrogen is a direct substituent on the ring, forming new five-membered chelate rings, while for $diac^{2-}$ the carboxyl carbon is interposed between the ring and coordinated oxygen, forming new six-membered chelate rings. The conformations of the macrocycle for these compounds is discussed further below.

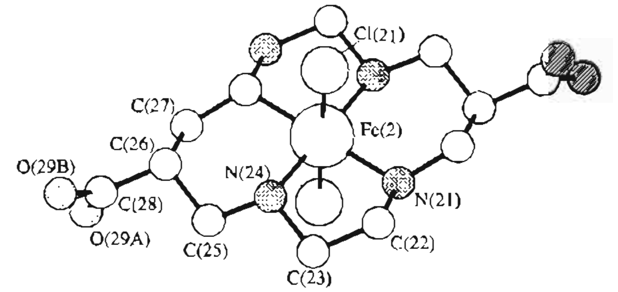

Figure 3. Cation $[Fe(diacH_2)Cl_2]^+$ of compound **2**. Selected dimensions for this cation (Å, deg): C(28)–O(29A), 1.307(7); C(28)–O(29B), 1.197(7); N(21)–Fe(2)–N(24), 85.6(2); Cl(21)–Fe(2)–N(21), 91.2(1); Cl(21)–Fe(2)–N(24), 88.8(1); O(29A)–C(28)–O(29B), 124.0(4).

The cation *trans*-$[Fe(diacH_2)Cl_2]^+$ of compound **2**, shown in Figure 3, has *trans* coordinated chloride ions, with the same macrocycle configuration and with the usual conformation of cyclam-like macrocycles, with the carboxylic acid substituents as equatorial substituents on the chair-conformation six-membered chelate rings, an arrangement similar to that found for the stable β-isomer of $[Cu(diacH_2)](ClO_4)_2$.[26]

The Fe–N distances of 1.992(3), 1.995(3) and 2.010(4), 1.998(4) Å for the $[Fe(diac)]^+$ cations of **1** and **2**, respectively, and 1.992(4), 2.004(4) Å for the *trans*-$[Fe(diacH_2)Cl_2]^+$ cation of **2** are closely similar and significantly longer than those for *trans*-$[Fe(diam)]^{3+}$ of 1.969(2) and 1.974(2) Å (secondary N) and 1.984(2) Å (primary N). Metal–nitrogen distances for M^{III} cations with hexadentate diam are appreciably shorter than found for *trans*-bis(ligand)–cyclam compounds, an effect attributed to the minimal intraligand interactions for the hexadentate diam ligand, which permits adoption of M–N distances closer to optimal; the distances are longer for penta- and tetradentate diam compounds with Co^{III}.[44] The structure of *trans*-$[Co(amac)](ClO_4)_2$, with a 6-amino-13-carboxylato-substituted cyclam,[29] shows $Co–N_{sec}$ distances longer than for *trans*-$[Co(diam)]^{3+}$ and comparable with those of pentadentate diam compounds with the same nitrogen configuration.[44] The Fe–N distances are similar for the tetra- and hexadentate diac compounds and longer than for the diam compound, confirming that the additional bulk of the carboxylato group of $diac^{2-}$, relative to the amine group of diam, nullifies this effect. Mean Cu–N distances for the $[Cu(diacH_2]^{2+}$ cations with carboxylic acid groups equatorial [2.018(4) Å] or axial [2.005(2) Å] and for $[Cu(dimest)]^{2+}$ with axial methoxy substituents [2.023(3) Å] are slightly longer than the Fe–N distances for the Fe^{III} cations.[26]

The structure has been reported for the high-spin Fe^{III} compound [Fe(triac)], which has C_3 symmetry, closer to trigonal prismatic than octahedral, with Fe–N distances of 2.181(3) and Fe–O distances of 1.962(2) Å.[42]

For a carboxylato group of $diac^{2-}$ to be able to coordinate, the six-membered chelate ring bearing the substituent has to adopt a (strained) boat conformation. There is no indication from the infrared spectra that these groups are coordinated for Cu^{II} or Ni^{II},[26] although the carboxylato groups of di-*N*-(methyoxycarbonyl)-substituted cyclams normally coordinate. The equivalent carboxylate group is coordinated for the Co^{III} cation *trans*-$[Co(amac)]^+$.[29] The observed coordination of the carboxylate groups for $[Fe(diac)]^+$ suggests that the higher charge on these M^{III} cations may be a factor determining whether coordination of the *C*-carboxylato substituents is energetically favored.

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(44) Curtis, N. F.; Robinson W. T.; Weatherburn, D. C. *Aust. J. Chem.* **1992**, *45*, 1663.

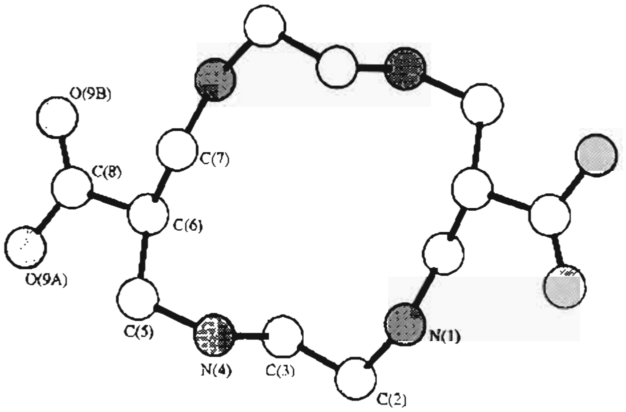

Figure 4. Cation $[diacH_6]^{4+}$ of compound **2**. Selected dimensions for this cation (Å, deg): C(8)–O(9A), 1.314(6); C(8)–O(9B), 1.213(6); O(9A)–C(8)–O(9B), 124.5(5)°.

The uncomplexed ligand cation $[diacH_6]^{4+}$ of compound **2**, shown in Figure 4, is also centrosymmetric, hence with coplanar nitrogen atoms. The macrocycle is in an *exo* conformation; the "cavity" defined by the four nitrogen atoms is larger than for the complexes with Fe^{III} or Cu^{II}, with N(1)–N(1)′ = 5.46 Å and N(4)–N(4)′ = 5.34 Å, but with the lone pair directed away from the center. The cation is hydrogen bonded to chloride and water [N(1)–H(1A)–Cl(3) = 0.95, 2.19 Å; O(2)–H(O2)–O(4) = 1.12, 1.79 Å]; strong interactions between protonated polyazamacrocycles and anions are common.

The conformation of the macrocycle of the cations $[Fe(diac)]^+$, *trans*-$[Fe(diacH_2)Cl_2]^+$, and $[diacH_6)]^{4+}$ can be characterized by the sets of endocyclic torsion angles and compared with those for cyclam,[45] di-[46] and tetraprotonated[45] cyclam, tetraprotonated diam,[46,47] and tetra-*N*-(methoxycarbonyl)-substituted cyclam $tetacH_4{\cdot}6H_2O$[48,49] and the coordination compounds of these macrocycles. All the macrocycles and their protonated cations (and many of their metal ion complexes) crystallize with required centrosymmetry. Cyclam and $[cyclamH_2]^{2+}$ adopt endocyclic arrangements, very similar to that generally observed for square-planar coordinated cyclam and $diacH_2$ in the *RSRS* configuration and apparently stabilized by intracyclic hydrogen bonding, with a "cavity" size (center–N) of ca. 2.06 Å.[50,51] The same arrangement is found for $tetacH_4{\cdot}6H_2O$,[48,49] $[diamH_4](ClO_4)_4{\cdot}6H_2O$,[46] and $[diamH_4]_3[Fe(CN)_6]_4$,[47] which have two *trans* ring nitrogen atoms protonated, the other two protons being associated with two *trans* carboxyl or the primary amine substituents, respectively. The conformation adopted by $[diacH_6]^{4+}$ is rectangular exodentate, with the nitrogen atoms adjacent to the "corner" atoms, and related to that of 1,4,8,11-tetraoxacyclotetradecane.[52] Tetraprotonated cyclam in $[cyclamH_4]Cl_4$ also adopts a rectangular exodentate arrangement but with two of the nitrogen atoms at "corner" sites and with each NH^+ group hydrogen bonded to a chloride ion.[45]

Conclusion

The tetraaza macrocyclic amino acid $diacH_2$ forms low-spin compounds with Fe^{III}, as the hexadentate deprotonated ligand $diac^{2-}$ with *trans* coordination of the carboxylato groups or as the neutral tetradentate, planar tetraazamacrocycle $diacH_2$ for the *trans*-dichloro and -dithiocyanato cations. Coordination of the carboxylato groups is labile, and in acid the carboxylato groups are rapidly protonated if a coordinating anion such as chloride or thiocyanate is present. The carboxylic acid substituents are readily esterified to form the bis(methoxycarbonyl) derivative. The cation is very resistant to acid demetalation. Unlike the Cu^{II} cations, the Fe^{III} cations are rapidly demetalated in basic solution, with deposition of hydrated Fe^{III} oxides. The compounds of $diac^{2-}$ and $diacH_2$ with Fe^{III} are indefinitely stable in solution in acidified oxygenated water, although compounds of Fe^{III} with other cyclam-like macrocycles with α-CH groups are generally very subject to oxidative dehydrogenation to form immine macrocycles. The only other substituted cyclam reported to form compounds similarly resistant to oxidation is the structurally related ligand diam.

The structural studies show the same *RSRS* configuration and very similar Fe–N distances for the cation $[Fe(diac)]^+$, for which the macrocycle has the six-membered chelate ring folded into a boat conformation to enable the carboxylato group to be coordinated, and the *trans*-dichloro tetradentate-macrocycle cation *trans*-$[Fe(diacH_2)Cl_2]^+$, which has the usual conformation of cyclam-like macrocycles.

A most unusual compound with fully protonated ($[diacH_6]^{4+}$), tetradentate (*trans*-$[Fe(diacH_2)Cl_2]^+$), and hexadentate (*trans*-$[Fe(diac)]^+$ diac within the one crystal structure provides an opportunity to compare dimensions for these arrangements. The macrocycle with all four nitrogen atoms protonated adopts an *exo* conformation with the nitrogen atoms coplanar.

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Supplementary Material Available: Tables 1–9, crystal data and details of structure refinement, hydrogen atom site and thermal parameters, anisotropic parameters, bond lengths, and bond angles (11 pages). Ordering information is given on any current masthead page.

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