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Coordination of the "Pendant-Arm" Macrocycle 6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane to Chromium(III). Crystal Structure and Physical Properties of the Hexacoordinated Complex Ion

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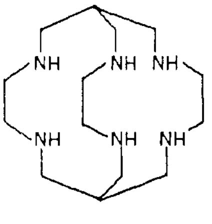
The ambidentate substituted cyclam 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane (diammac) acts as a sexidentate or quinquedentate ligand to chromium(III). The hexaamine $[Cr(diammac)](ClO_4)_3$ was synthesized, as well as isomers of the complex $[Cr(diammac)(OH)](ClO_4)_2$, where one pendant primary amine is not coordinated. In the hexaamine complex, the pendant primary amines occupy trans sites, defined by a crystal structure analysis. The $[Cr(diammac)](ClO_4)_3$ complex crystallizes in the monoclinic $P2_1/c$ space group, with $a = 16.653$ (3) Å, $b = 8.793$ (2) Å, $c = 17.842$ (4) Å, $\beta = 114.52$ (2)°, and $Z = 4$. The four secondary amines occupy a plane and the pendant primary amino groups occupy axial sites, forcing boat conformations on the six-membered rings to which the pendants are attached. There is considerable strain in the ligand, and the Cr–N bond lengths, Cr–N(equatorial) = 2.031 (5)–2.055 (5) Å and Cr–N(axial) = 2.067 (4) Å, are the shortest reported for a CrN_6^{3+} amine system. This "compression" is reflected in electronic spectra, with the ${}^4T_{2g} \leftarrow {}^4A_{2g}(O_h)$ and ${}^4T_{1g} \leftarrow {}^4A_{2g}(O_h)$ maxima (at 427 and 332 nm, respectively) at higher energy than for other hexaamines. The quasireversible Cr(III)/Cr(II) redox potential is also at a very negative potential. Spin-forbidden electronic transitions were also observed at 663 nm (to ${}^2T_{1g}$) and 681 nm (to ${}^2E_g$). The X-band EPR spectrum of seven lines between 1000 and 6000 G has been assigned for the paramagnetic complex, which shows a room-temperature magnetic moment of 3.87 μ_B. Two peaks near 680 nm, separated by less than 2 nm, are observed in the powder emission spectrum of $[Cr(diammac)]\ (ClO_4)_3$. Lifetimes in the temperature-independent region below 200 K are relatively long, being 150 μs for the protonated complex and rising significantly to 3.3 ms for the deuterated complex. Emission is observed at room temperature.

Introduction

Encapsulation of metal ions in macrocyclic ligands has attracted considerable attention over recent decades.[5] With saturated multidentate cyclic ligands, strategies have involved either trapping the metal ion within a macromonocycle,[6] inserting the metal ion in the cavity of a macrobicyclic ligand,[7] or employing a macromonocycle with pendant arms that carry suitable donor groups in addition to those in the macrocycle.[8] Macromonocycles may not occupy all coordination sites, particularly with octahedral metal ion geometries. This is avoided with sexidentate macrobicycles particularly, which encapsulate the metal ion in a cavity where the metal ion is coordinated in an essentially octahedral fashion and is rendered substitution-inert.[6] The macrobicyclic hexaamines based on sar (3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane (I)) form the most studied series.[9-11]



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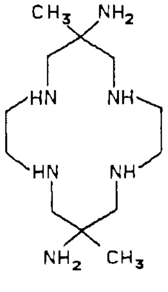

II

Macromonocycles with potentially coordinating pendants ("scorpiands")[12] may bind metal ions at axial sites in addition to encircling the metal ion with a set of donors from the macrocycle ring. When both axial sites are "blocked" by pendant donors, a metal ion may be considered effectively encapsulated in a manner not unlike that achieved by macrobicyclic ligands, although the single-strand "tails" in the former case may be more susceptible to dissociation. We have been investigating complexation by the potentially sexidentate disubstituted "cyclam" macromonocycle 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane (diammac (II)). This can be considered as a scorpiand ligand with two short tails, since the two extra amine donors are attached directly to the macrocyclic ring.[13] Nevertheless, they are available for metal ion binding, since octahedral complexes of Ni^{II},[14] Co^{III},[15] and Fe^{III}[16] with II as a sexidentate ligand have been reported.

Despite imparting inertness to encapsulated metal ions generally, macrobicycles of the sar type (I) are not usually strong ligand field donors, nor is there any evidence from crystal structure analyses of "compression" of coordination spheres; in fact, M–N distances are often slightly longer than observed in $[M(en)_3]^{n+}$ analogues (en = ethane-1,2-diamine).[9-11] By contrast, distinct compression of the coordination sphere has been observed for $[Co(diammac)]^{3+}$[15] and appears to occur for the Fe^{III} analogue,

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although comparative data for that metal ion are exceptionally sparse.[16] The possibility of diammac acting as a strong-field ligand and also exhibiting M–N distances shorter than normal generally is currently being addressed in our laboratories. Like the cobalt(III) system, where comparative data for hexaammine, tris(ethane-1,2-diamine), sar, and diammac have now been collected,[15] the chromium(III) system offers extensive data for comparisons. Herein we report the synthesis, X-ray crystal structure data, and redox, electronic, and photophysical data for the $[Cr(diammac)]^{3+}$ ion and make comparisons with other $CrN_6{}^{3+}$ systems.

Experimental Section

Syntheses. The synthesis of 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane (II) has been described previously;[13] the macrocycle is isolated conveniently as the hydrochloride salt, diammac·6HCl, or the free amine hydrate. The (hexaamine)chromium(III) cation can be prepared in two ways, the latter involving chromatographic purification.

Synthesis in Aprotic Solution. (a) (6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Chloride Trihydrate, $[Cr(diammac)]Cl_3 \cdot 3H_2O$. Anhydrous chromium(III) chloride (2.0 g) in dimethyl sulfoxide (100 mL) was heated to 100 °C, and diammac·$2.5H_2O$ (3.0 g) was added portionwise. The mixture was heated for 1 h and cooled, and the yellow product was filtered off and washed thoroughly with ethanol. The crude product was recovered in nearly quantitative yield. The product was recrystallized from hot water, or best by dissolving in cold dilute hydrochloric acid and precipitating with ethanol. Anal. Calcd for $C_{12}H_{36}Cl_3CrN_6O_3$: C, 30.7; H, 7.7; Cl, 22.7; Cr, 11.1; N, 17.9. Found: C, 31.0; H, 8.0; Cl, 22.9; Cr, 11.1; N, 18.1. The product may be recrystallized from cold dilute perchloric acid as the mixed dichloride perchlorate salt by addition of ethanol. Magnetic moment (278 K): 3.87 μ_B.

(b) *trans*-Aqua(6-amino-6-ammonio-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Chloride Trihydrate, $[Cr(diammacH^+)(OH_2)]Cl_4 \cdot 3H_2O$. The hexaamine trichloride crystallized from hot dilute hydrochloric acid as red-orange needles of the species with one pendant amine uncoordinated and protonated, assigned (vide infra) as a trans isomer from infrared spectroscopy. Anal. Calcd for $C_{12}H_{39}Cl_4CrN_6O_4$: C, 27.4; H, 7.5; Cl, 27.0; Cr, 9.9; N, 16.0. Found: C, 27.3; H, 7.7; Cl, 27.4; Cr, 9.9; N, 15.8. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 480 (sh, 27), 407 (45), 340 (35). Reaction in hot dilute perchloric acid yielded the mixed chloride perchlorate salt. Magnetic moment (278 K): 3.89 μ_B.

Synthesis Involving Chromatography. (a) *trans*-(6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)hydroxochromium(III) Perchlorate Sesquihydrate, *trans*-$[Cr(diammac)(OH)](ClO_4)_2 \cdot 1.5H_2O$. Anhydrous chromium(II) chloride (0.5 g) was added to a nitrogen-purged solution of diammac·6HCl (2.0 g) and triethylamine (5 mL) in absolute ethanol (250 mL). With the nitrogen supply maintained, the solution was stirred at room temperature for 3 h. The nitrogen supply was discontinued, and the solution was diluted to 500 mL with water and sorbed onto a column (20 × 3 cm) of Sephadex SP-C25 (Na^+ form) resin. The product was eluted with 0.5 M $NaClO_4$ solution, and the solution was evaporated to ca. 40 mL. On standing, the product precipitated as an orange-red powder, which was collected, washed with ethanol and then diethyl ether, and dried in a desiccator (0.3 g). Anal. Calcd for $C_{12}H_{34}Cl_2CrN_6O_{10.5}$: C, 26.1; H, 6.2; N, 15.2. Found: C, 26.1; H, 6.3; N, 14.85. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 488 (41), 380 (73), 293 (33). IR spectrum (KBr; $\bar{\nu}$, cm^{-1}): 800, 871, 905 ($-CH_2-$ rock); 3360 (–NH– stretch).

(b) *cis*-(6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)hydroxochromium(III) Perchlorate, *cis*-$[Cr(diammac)(OH)](ClO_4)_2$. In the above reaction, a second close-running band was eluted from the column with 0.5 M $NaClO_4$, and the solution was evaporated to ca. 50 mL. On standing, the product precipitated as a red powder, which was collected, washed with ethanol and then diethyl ether, and dried in a vacuum desiccator (0.4 g). Anal. Calcd for $C_{12}H_{31}Cl_2CrN_6O_9$: C, 27.4; H, 5.95; N, 15.95. Found: C, 27.3; H, 5.8; N, 15.6. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 486 (63), 376 (78), 320 (s, 30). IR spectrum (KBr; $\bar{\nu}$, cm^{-1}): 790, 860 ($-CH_2-$ rock); 3240, 3265, 3280, 3305 (–NH– stretch).

(c) (6,13-Diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate, $[Cr(diammac)](ClO_4)_3$. In the above reaction, a third slow-moving yellow band was eluted from the column with 1 M $NaClO_4$, and the solution was evaporated to ca. 50 mL. The yellow product crystallized on standing and was collected as above (0.4 g). A second crop was obtained by slow evaporation of the filtrate from the first crop to afford prismatic crystals suitable for X-ray analysis. Anal. Calcd for $C_{12}H_{30}Cl_3CrN_6O_{12}$: C, 23.7; H, 5.0; N, 13.8. Found: C, 24.0; H, 5.0; N, 13.55. Electronic spectrum [water; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 427 (55), 332 (52). IR spectrum (KBr; $\bar{\nu}$, cm^{-1}): 772, 796, 823 ($-CH_2-$ rock), 3050 (–NH– stretch). Complex interconversions between the hydroxo and aqua CrN_5O species and the CrN_6 species in acidic and basic media have been observed and will be pursued. In aqueous base, conversion of hydroxo species to ultimately the hexaamine is possible, improving the overall yield of this species. The hexaamines isolated from both procedures are spectroscopically identical, although care must be taken during recrystallizations to avoid cocrystallization of any hydroxo- or aqua-pentaamine species.

Table I. Crystallographic Data for $[Cr(diammac)](ClO_4)_3$

space group	$P2_1/c$	empirical formula	$C_{12}H_{30}Cl_3CrN_6O_{12}$
a, Å	16.653 (3)	fw	608.67
b, Å	8.793 (2)	Z	4
c, Å	17.842 (4)	abs coeff, cm^{-1}	8.21
β, deg	114.52 (2)	temp, K	294
V, $Å^3$	2377.0	λ, Å	0.71069
ρ_{calcd}, g cm^{-3}	1.701	$R(F_o)$, $R_w(F_o)$	0.061, 0.074

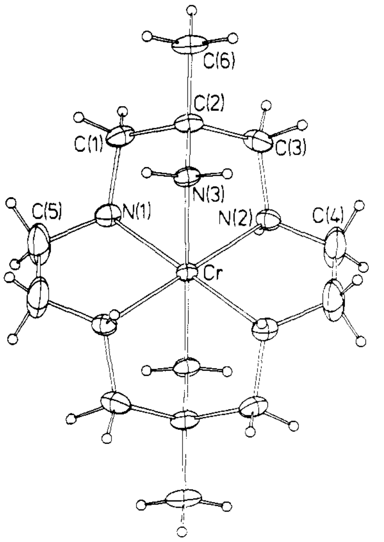

Figure 1. View of the molecular cation $[Cr(diammac)]^{3+}$.

Spectroscopy and Physical Methods. Electronic spectra were measured on a Hitachi 150-20 spectrophotometer. Infrared spectra of complexes dispersed in KBr disks were measured on Nicolet MX-1 FT-IR spectrometer. Electron spin resonance spectra were recorded on a Varian E9 spectrometer with solutions or glasses (10^{-3} M, MeOH–water (1:1)). Cyclic voltammetry was performed by using a BAS CV-27 controller and a conventional three-electrode configuration with a glassy-carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. All solutions, either aqueous or dry acetonitrile, were 0.1 M in $NaClO_4$ and were purged with nitrogen. Polarography was conducted on an AMEL Model 437 polarographic analyzer, with reference and counter electrodes as above. Room-temperature magnetic moments were measured by the Faraday method with $Hg[Co(NCS)_4]$ as calibrant. Photophysical measurements were taken on standard equipment described previously.[17] Excitation was achieved by 10-ns pulses from a standard N_2 laser operating at 10 Hz. Decay profiles were accumulated and averaged on a Tektronix 2430 digital scope and transferred to an IBM clone computer. The data were analyzed by using standard programs for nonlinear least-squares fitting.

Structure Determination. Crystal data are recorded in Table I. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer. Data were reduced and Lorentz, polarization, and decomposition corrections were applied by using a local data reduction program. The structure was solved by heavy-atom methods and refined by full-matrix least-squares analysis with SHELX-76.[18] Anisotropic thermal parameters were refined for all non-hydrogen atoms, excluding minor contributions to perchlorate oxygen disorder; $(x,y,z)_H$ were included and constrained at estimated values. The refinement and final discrepancy indices of the structure were adversely affected by the per-

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Table II. Positional Parameters ($\times 10^4$) for $[Cr(diammac)](ClO_4)_3$

	x	*y*	*z*
Cr(1)	0	10000	0
N(1)	761 (3)	9284 (5)	−575 (2)
N(2)	861 (3)	8881 (5)	1017 (2)
N(3)	766 (3)	11815 (5)	642 (2)
C(1)	184 (4)	8497 (7)	−1343 (4)
C(2)	780 (4)	11502 (6)	1469 (3)
C(3)	1217 (4)	9967 (6)	1708 (3)
C(4)	1509 (7)	8149 (13)	780 (5)
C(5)	1448 (6)	8349 (15)	23 (5)
C(6)	1316 (5)	12706 (8)	2095 (3)
Cr(2)	5000	5000	0
N(11)	5129 (3)	2779 (5)	−242 (3)
N(21)	3667 (3)	4591 (6)	−450 (3)
N(31)	4889 (3)	4727 (5)	1104 (3)
C(11)	4418 (5)	7290 (8)	788 (4)
C(21)	4112 (4)	5735 (8)	941 (4)
C(31)	3372 (4)	5032 (8)	183 (4)
C(41)	3532 (5)	3009 (10)	−727 (7)
C(51)	4239 (6)	2129 (10)	−574 (11)
C(61)	3825 (5)	5802 (10)	1654 (4)
Cl(1)	822 (1)	1171 (2)	3972 (1)
O(1)	1099 (9)	84 (15)	3593 (8)
O(2)	1369 (9)	2542 (14)	4269 (8)
O(3)	258 (7)	2339 (15)	3351 (6)
O(4)	309 (10)	599 (13)	4402 (8)
O(1′)	1518 (8)	2109 (15)	4511 (8)
O(2′)	29 (8)	1572 (17)	3318 (7)
O(3′)	743 (12)	443 (14)	4650 (8)
O(4′)	1417 (9)	188 (15)	3722 (9)
O(1″)	907 (22)	2600 (34)	3915 (19)
O(2″)	701 (24)	−7 (32)	3324 (21)
O(3″)	1397 (20)	826 (33)	4845 (17)
O(4″)	−63 (22)	738 (35)	4045 (20)
Cl(2)	3613 (1)	1173 (2)	1651 (1)
O(5)	2826 (12)	1929 (19)	1128 (10)
O(6)	4339 (10)	1382 (25)	1376 (11)
O(7)	3873 (9)	1953 (17)	2391 (8)
O(8)	3527 (9)	−499 (16)	1632 (10)
O(5′)	4262 (13)	2447 (22)	2041 (13)
O(6′)	3588 (13)	292 (27)	2266 (13)
O(7′)	3357 (14)	344 (22)	867 (12)
O(8′)	2794 (14)	2187 (25)	1426 (13)
O(5″)	3777 (13)	−324 (25)	2033 (15)
O(6″)	3585 (13)	1244 (27)	2482 (11)
O(7″)	4323 (12)	1984 (28)	1682 (16)
O(8″)	2822 (15)	1484 (24)	977 (14)
O(8″)	4155 (35)	771 (61)	1213 (27)
Cl(3)	2757 (1)	6593 (2)	3346 (1)
O(9)	2211 (16)	6315 (28)	2452 (15)
O(10)	3698 (15)	6375 (24)	3681 (14)
O(11)	2446 (14)	7912 (23)	3553 (13)
O(12)	2722 (19)	5685 (28)	4011 (15)
O(9′)	3043 (28)	5372 (39)	3024 (22)
O(10′)	2990 (26)	8300 (42)	3070 (24)
O(11′)	1797 (21)	6820 (34)	2883 (19)
O(12′)	3083 (23)	6387 (38)	4225 (21)
O(9″)	2317 (18)	5375 (27)	3704 (16)
O(10″)	2721 (18)	8196 (27)	3310 (16)
O(11″)	3812 (17)	6783 (28)	3562 (15)
O(12″)	2601 (19)	5563 (33)	2724 (20)
O(9*)	2543 (33)	6268 (61)	2558 (30)
O(10*)	7655 (30)	1569 (54)	1093 (24)
O(11*)	6668 (27)	2723 (46)	1512 (24)
O(12*)	5175 (34)	1140 (54)	1127 (30)

chlorate disorder. Scattering factors and anomalous dispersion corrections for Cr were taken from ref 19, and for all others the values supplied in SHELX-76 were used. Absorption correction was by numerical integration. Non-hydrogen atom coordinates are listed in Table II. The atomic labeling is shown in Figure 1, drawn with ORTEP.[20] Important non-hydrogen atom interatomic distances are given in Table III. Supplementary material has been deposited.

Table III. Bond Lengths and Angles for $[Cr(diammac)](ClO_4)_3$

Bond Lengths (Å)			
N(1)–Cr(1)	2.035 (4)	N(2)–Cr(1)	2.039 (4)
N(3)–Cr(1)	2.067 (4)	C(1)–N(1)	1.479 (7)
C(5)–N(1)	1.453 (9)	C(3)–N(2)	1.476 (7)
C(4)–N(2)	1.461 (9)	C(2)–N(3)	1.491 (6)
C(3)–C(2)	1.508 (8)	C(6)–C(2)	1.528 (7)
C(5)–C(4)	1.324 (11)	N(11)–Cr(2)	2.031 (5)
N(21)–Cr(2)	2.055 (5)	N(31)–Cr(2)	2.067 (5)
C(51)–N(11)	1.465 (10)	C(31)–N(21)	1.460 (9)
C(41)–N(21)	1.462 (10)	C(21)–N(31)	1.494 (8)
C(21)–C(11)	1.523 (11)	C(31)–C(21)	1.532 (9)
C(61)–C(21)	1.535 (8)	C(51)–C(41)	1.339 (13)

Bond Angles (deg)			
N(2)–Cr(1)–N(1)	86.9 (2)	N(3)–Cr(1)–N(1)	98.5 (2)
N(3)–Cr(1)–N(2)	80.5 (2)	C(1)–N(1)–Cr(1)	108.1 (4)
C(5)–N(1)–Cr(1)	105.6 (4)	C(5)–N(1)–C(1)	115.3 (7)
C(3)–N(2)–Cr(1)	108.8 (3)	C(4)–N(2)–Cr(1)	106.6 (4)
C(4)–N(2)–C(3)	115.9 (7)	C(2)–N(3)–Cr(1)	99.1 (3)
C(3)–C(2)–N(3)	104.7 (5)	C(6)–C(2)–N(3)	111.1 (5)
C(6)–C(2)–C(3)	110.2 (5)	C(2)–C(3)–N(2)	111.3 (4)
C(5)–C(4)–N(2)	118.9 (7)	C(4)–C(5)–N(1)	122.0 (7)
N(21)–Cr(2)–N(11)	86.6 (2)	N(31)–Cr(2)–N(11)	98.7 (2)
N(31)–Cr(2)–N(21)	81.0 (2)	C(51)–N(11)–Cr(2)	106.4 (5)
C(31)–N(21)–Cr(2)	107.8 (4)	C(41)–N(21)–Cr(2)	106.7 (5)
C(41)–N(21)–C(31)	117.4 (7)	C(21)–N(31)–Cr(2)	99.1 (3)
C(11)–C(21)–N(31)	103.9 (5)	C(31)–C(21)–N(31)	104.3 (5)
C(31)–C(21)–C(11)	114.2 (6)	C(61)–C(21)–N(31)	113.8 (5)
C(61)–C(21)–C(11)	110.9 (6)	C(61)–C(21)–C(31)	109.5 (6)
C(21)–C(31)–N(21)	112.6 (5)	C(51)–C(41)–N(21)	118.8 (7)
C(41)–C(51)–N(11)	120.9 (7)		

Results

Reaction of diammac and anhydrous chromic chloride in dimethyl sulfoxide yields the sexidentate complex in high yield, and microanalytically pure samples may be obtained by recrystallization from cold acidic solutions upon addition of alcohol. Reaction in ethanol employing chromous chloride involved chromatographic separation of products, which permitted identification of all complexed products and ready isolation of pure compounds. Three products were detected, with the species isolated containing the diammac as either a quinquedentate (both cis and trans isomers) or sexidentate ligand, with one or both of the pendant primary amines coordinated, respectively. The chemistry is complicated by the observation from spectroscopy that the $[Cr(diammac)]^{3+}$ cation undergoes facile hydrolysis of one pendant amino group in acid solution, the reaction occurring rapidly on heating. The amino group is rapidly recoordinated in base. This is in marked contrast to the behavior of the cobalt(III) analogue, which does not hydrolyze in aqueous acid.[15]

The hexacoordinated ligand is required to coordinate in a trans fashion, with the primary amines on opposite sides of the macrocyclic plane. However, the pentacoordinated ligand in $[Cr(diammac)(OH)]^{2+}$ may adopt a folded macrocycle geometry. That one product is indeed a cis isomer and not the higher symmetry trans isomer with the hydroxo ligand trans to the pendant primary amino group was indicated by infrared spectroscopy. The IR spectra of cis and trans isomers of cyclam complexes of octahedral metal ions have been well documented, with the N–H stretching vibrations (3300–3100 cm^{-1}) and the methylene rocking vibrations (900–800 cm^{-1}) being the areas of definition.[21] The cis isomer of the cyclam analogue reported here gives a spectrum with four peaks in the range 3300–3100 cm^{-1}, whereas the hexacoordinated and trans-pentacoordinated diammac complexes display a single vibration in that region. Moreover, the spectrum of the cis isomer in the region 900–800 cm^{-1} replicates the spectrum of *cis*-$[Rh(diammac)Cl]^{2+}$, whose symmetry has been confirmed by ^{13}C NMR spectroscopy.[22]

The electronic spectra of all chromium complexes at room temperature are consistent with $Cr^{III}N_6$ or $Cr^{III}N_5O$ chromophores.

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Spectra of the $[Cr(diammac)(OH)]^{2+}$ complexes display bands near 485 and 375 nm, corresponding to transitions from the $^4A_{2g}(O_h)$ groud state to $^4T_{2g}$ and $^4T_{1g}$ states, respectively. Maxima occur in positions like those for other CrN_5O species, though shifted slightly to higher energy. The first spin-allowed transition for $[Cr(diammac)]^{3+}$ occurs at 427 nm ($^4T_{2g} \leftarrow {}^4A_{2g}(O_h)$). This is the highest energy maximum reported for a series of (hexaamine)chromium(III) ions, whose values range from 462 nm (hexaammine)[23] to 439 nm (bis(1,4,7-triazacyclononane));[24,25] the trans cyclam diammine compound is known also,[26] but exhibits splitting with transitions at 445 nm (sh) and 420 nm. The high energy of the transition for diammac is tied to the short Cr–N bonds observed (see below). Also, the $^4T_{1g} \leftarrow {}^4A_{2g}$ transition (332 nm) is at higher energy than for other complexes. In addition to spin-allowed transitions, two spin-forbidden transitions were observed at 663 nm (ϵ 0.05 M^{-1} cm^{-1}), a relatively sharp band assigned to a transition to the $^2T_{1g}$ level, and at 681 nm (ϵ 0.18 M^{-1} cm^{-1}), assigned to a transition to the ^2E_g level. The position of this latter band accords with transitions involving the ^2E_g level observed in the emission spectrum discussed below.

The structure of $[Cr(diammac)]^{3+}$ consists of two complex cations, each located at a center of symmetry, and three perchlorate anions, each disordered over three sites and situated at general positions. There are no significant differences in the geometries of the two cations (Table III). Sexidentate coordination is apparent (Figure 1), with the four secondary amino groups occupying the equatorial plane and the pendant amino groups coordinating in axial sites of the octahedral coordination sphere, forcing boat conformations on the six-membered rings to which the pendants attach. There is considerable strain in the ligand as a result of the forced coordination of the pendant primary amines. It is evident from the large thermal motion of atoms C(4) and C(5) perpendicular to the five-membered ring and the near planarity of this ring that the refined geometry is in fact the average of two skew conformations; attempts to locate individual sites were unsuccessful. As the M–N bond length increases (Co^{III}–N = 1.94 Å;[15] Fe^{III}–N = 1.97 Å;[16] Rh^{III}–N = 2.04 Å;[22] Cr^{III}–N = 2.05 Å), this disorder of the ring becomes more facile. The equatorial Cr–N bonds are notably short, ranging from 2.031 (5) to 2.055 (5) Å, and are the shortest reported for a Cr^{III} hexaamine structure. The axial bonds, 2.067 (4) Å, although still short by comparison with other systems,[11,27,28] are longer than the equatorial bonds. Bond lengths and angles are given in Table III.

Electrochemistry on all chromium(III) complexes identified one-electron $Cr^{III/II}$ redox couples. Aqueous DC polarography of *cis*- and *trans*-$[Cr(diammac)(OH)]^{2+}$ and $[Cr(diammac)]^{3+}$ yielded $E_{1/2}$ values of −1.092, −1.05, and −1.26 V (vs Ag/AgCl), respectively (pH 10). The potential for the hexaamine, which is not markedly pH dependent, is comparable with those of the macrobicyclic sar analogues.[11] Cyclic voltammetry in aqueous solution indicated limited reversibility (ΔE = 150 mV and i_a/i_c = 0.7 at 100 mV/s, glassy carbon) for the hexaamine. A similar result was observed in acetonitrile ($E_{1/2}$ = −1.28 V and ΔE = 140 mV, i_a/i_c = 0.7 at 100 mV/s), suggesting that dissociation from the Cr^{II} ion occurs but is not markedly assisted by water alone. Both quinquedentate isomers exhibited irreversible behavior in cyclic voltammetry experiments.

The X-band electron paramagnetic resonance spectrum of $[Cr(diammac)](ClO_4)_3$ (Figure 2) displayed seven resonances between 1000 and 6000 G. A satisfactory spin Hamiltonian for an axially symmetric quartet ground state is[29]

$$\mathcal{H} = \beta\cdot\bar{H}\cdot g\cdot\bar{S} + D(S_z^2 - 5/4) \qquad (1)$$

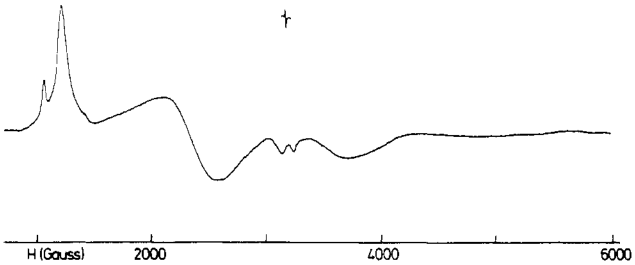

Figure 2. X-Band EPR spectrum of $[Cr(diammac)](ClO_4)_3$ recorded as a glass ($MeOH$–H_2O) at 77 K.

where the first and second terms are the Zeeman and axial zero-field-splitting terms, respectively. The energies of the components of the $^4A_{2g}$ ground state are as follows:[30] for $H = H_z$

$$E(3/2,-1/2) = g_\parallel\beta H/2 \pm (D + g_\parallel\beta H) \qquad (2)$$

$$E(-3/2,1/2) = -g_\parallel\beta H/2 \pm (D - g_\parallel\beta H) \qquad (3)$$

and for $H = H_x = H_y$

$$E(3/2,-1/2) = g_\perp\beta H/2 \pm (g_\perp^2\beta^2H^2 + D^2 - g_\perp\beta HD)^{1/2} \qquad (4)$$

$$E(1/2,-3/2) = -g_\perp\beta H/2 \pm (g_\perp^2\beta^2H^2 + D^2 + g_\perp\beta HD)^{1/2} \qquad (5)$$

Assignment of the spectrum was performed with working curves[31] comprising plots of magnetic resonance positions along both the *z* and *x*,*y* axes versus the spin-Hamiltonian parameter *D*. The *g* values were fixed in each curve. In the spectrum of $[Cr(diammac)](ClO_4)_3$, a $g_\parallel$ value of 1.98 may be immediately determined from the $-1/2 \rightarrow 1/2$, *z* resonance at 3230 G. The $-3/2 \rightarrow -1/2$, *z* and the $1/2 \rightarrow 3/2$, *z* resonances are expected to appear symmetrically ($\pm 2D/g_\parallel\beta$) on either side of the $-1/2 \rightarrow 1/2$, *z* transition. The peak at 1270 G is assigned as the $1/2 \rightarrow 3/2$, *z* transition (assuming a positive *D* value), yielding a zero-field splitting of $2D$ = 0.18 cm^{-1}. Furthermore, the $-3/2 \rightarrow -1/2$, *z* transition may then be accurately determined to lie at 5190 G. The spectrum shows a very broad band in this region in accordance with the above assignment. The *g* values of chromium(III) complexes are generally isotropic;[32] so, for $g_\perp$ = 1.98, the three $\Delta M_s = 1$ transitions $-3/2 \rightarrow -1/2$, $-1/2 \rightarrow 1/2$, and $1/2 \rightarrow 3/2$ in the *xy* plane can be assigned at 2350, 3130, and 4290 G, respectively. The remaining resonance at 1110 G is assigned as the $-3/2 \rightarrow 3/2$, *z* transition. The relative intensity of this peak is comparable with observations in spectra of other axially distorted Cr^{III} complexes.[33]

The powder emission spectrum of $[Cr(diammac)](ClO_4)_3$ at 10 K (excited at 450 nm) exhibits two peaks at 680.5 and 682.0 nm. The similar intensities of the two peaks might suggest emission from the two independent sites in the crystals. However, a strong temperature dependence of the relative intensities, increasing emission for the high-energy peak with increasing temperature, is most consistent with thermal population of the higher of the two coupled states. The insignificant differences in the geometries of the two crystallographically defined sites further support assignment of the two peaks as arising from the two components of the ^2E excited state,[34] split in second order due to the combined action of spin–orbit coupling and rhombic symmetry of the ligand field. The emission maxima shift from 680.5 and 682.0 nm to 680.3 and 681.5 nm upon N-deuteration. Lifetime measurements of the excited complex have been made both for normal and N-deuterated crystalline samples and for poly(vinyl

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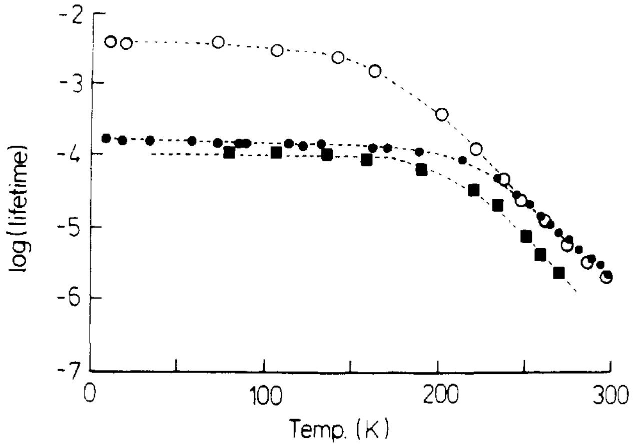

Figure 3. Temperature dependence of the lifetime of the excited state of $[Cr(diammac)](ClO_4)_3$ determined for the protonated (●) and deuterated (○) solid and for a poly(vinyl acetate) solution of the protonated complex (■).

acetate) (PVA) solutions of the hydrogenated species, from 10 to ca. 300 K (Figure 3). Lifetimes in the temperature-independent part (below 200 K) are over 150 μs for the nondeuterated crystals and 100 μs for the PVA matrix, increasing to 3.3 ms for the deuterated complex. Activation energies, extracted from Arrhenius plots, are 33.1 kJ mol^{-1} for the protonated complex and 35.2 kJ mol^{-1} for the deuterated complex in the solid state. Even at room temperature $[Cr(diammac)](ClO_4)_3$ shows an emission, with a lifetime of 2 μs in the PVA matrix.

Discussion

The complex cation $[Cr(diammac)]^{3+}$ represents a new type of CrN_6^{3+} molecular cation, where the chromium is encapsulated in a macrocyclic tetraamine ring and bound additionally by two axial nitrogen donors that are anchored to the ring. The sexidentate diammac ligand is a strong-field ligand that forms octahedral complexes with most metals of the first row of the periodic d block.[13-16,35] Consistently, the metal ion experiences bond length compression as a result of ligand demands. This has been observed previously in the cobalt(III) system[15] and also occurs with iron(III)[16] and rhodium(III),[22] for example. The Cr^{III}–N bonds are the shortest reported, and are up to 4 pm shorter than distances in $[Cr(en)_3]^{3+}$ and $[Cr(diAMsar)]^{3+}$ (diAMsar = 1,8-diaminosar).[11,28] This "compression" of the coordination sphere influences other properties; electronic maxima, for example, are shifted to higher energy compared with those of other hexaamines.

Comparisons of electronic maxima, redox potentials, and Cr–N bond distances for a number of CrN_6^{3+} compounds appear in Table IV. Whereas electronic maxima for the diammac complex are shifted substantially to higher energy, it is notable that the bis(1,4,7-triazacyclononane) complex is also shifted slightly, presumably again because of demands of the cyclic ligand in coordinating to an octahedral face.[24] The $Cr^{III/II}$ couple for diammac is over 400 mV more negative than the couple for $[Cr(en)_3]^{3+}$, but not appreciably different from values for other multidentate systems. At least with the macrobicyclic complexes, a very negative redox potential may be tied to the cavity being inappropriate for the larger Cr^{II} ion.[11] This consideration may be less important for the monocyclic diammac. The free-ion radius of Cr^{II} (89 pm) is appreciably larger than that of Cr^{III} (63 pm). The change is greater than for the cobalt system (free-ion radius 63 pm for Co^{III}, 72 pm for Co^{II}), and this may be tied to the generally quasireversible electrochemistry of Cr^{III} polyamines, and the appreciably lower stability of chromium(II) macrobicycles compared with cobalt(II) analogues. Substituent effects influence the redox couple of sar-type complexes (e.g.: 1,8-diamino, −1.33 V; 1,8-diammonio, −1.02 V),[11] so comparisons with the diammac and other complexes are modest at best.

Table IV. Comparisons of Selected Physical Properties of Saturated Chromium(III) Hexaamine Ions

N_6	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})[a]	$E_{1/2}$, V[b]	M–N, Å[c]	τ, μs[d,e]
$(NH_3)_6$	462, 346 (44, 37)[f]	−0.81[g]	2.064[h]	22 (460)[i]
$(en)_3$	457, 351 (86, 70)[j]	−0.84[g]	2.075[k]	20 (130)[l]
$(tacn)_2$	439, 340 (64, 88)[m]	−1.36[m]	...	340 (3200)[n]
$(cyclam)(NH_3)_2$	445, 420, 334 (32 sh, 36, 50)[o]	...	...	180[o] (...)
sar	457, 449, 347 (153, 156, 91)[p]	−1.36[p]	...	...
diAMsar	456, 447, 346 (203, 208, 109)[p]	−1.33[p]	2.07[p]	80 (310)[p,q]
diammac	427, 332 (55, 52)[r]	−1.26[r]	2.04_{eq}, 2.067_{ax}[r]	150 (3300)[r]

[a] Aqueous solution. [b] Versus Ag/AgCl. [c] Averaged distances. [d] Excited-state lifetime in the temperature-independent region (80 K) for crystalline solids. [e] Values in parentheses refer to N-deuterated samples. [f] Reference 23. [g] Friend, J. A.; Smith, P. W. *J. Phys. Chem.* **1959**, *63*, 314. [h] Reference 27. [i] Flint, C. D.; Matthews, A. P. *J. Chem. Soc., Chem. Commun.* **1971**, 954. [j] Reference 25. [k] Reference 28. [l] Reference 25. [m] Reference 24. [n] DMSO–water glass. Ditze, A.; Wasgestian, F. *J. Phys. Chem.* **1985**, *89*, 426. [o] Reference 26. [p] Reference 11. [q] Reference 41. [r] This work.

The shift in maxima to higher energy is the most prominent feature in the electronic spectrum of $[Cr(diammac)]^{3+}$. Intensities of the quartet–quartet transitions are not unusual, nor is there any splitting of the low-energy spin-allowed transition (as seen with sar or cyclam diammine)[7,26] evident. The deduced ligand field parameters for $[Cr(diammac)]^{3+}$ are $Dq = 2342$ cm^{-1}, $B = 620$ cm^{-1} (68% of B_0), and $C = 3301$ cm^{-1}. Transitions to the $^2T_{2g}$ and $^2T_{1g}$ levels are calculated on this basis to occur at 436 and 663 nm, respectively, with the latter spin-forbidden transition observed. For $[Cr(diammac)]^{3+}$ the room-temperature magnetic moment of 3.9 μ_B is near the spin-only value of 3.87 μ_B. The reduction of the g value from its spin-only value of 2.0023 allows an estimation of the spin–orbit coupling constant from EPR and electronic spectroscopy, using the formula[36]

$$\zeta = 3\Delta(g_e - g)/8$$

where Δ is the energy of the first spin-allowed transition. The value of ζ is 196 cm^{-1}, compared with 273 cm^{-1} for the free ion.

Chromium(III) complexes may exhibit excited lifetimes that are much longer than those of the well-studied ruthenium(II) systems,[37-39] although absorption/light-harvesting and excited-state redox potentials are less favorable. Nevertheless, chromium(III) complexes have been applied in solar energy conversion.[40] The well-studied $[Cr(phen)_3]^{3+}$ ion is a strong oxidant ($^*E_0 > +1$ V),[39] but turnover numbers in photochemical reactors are unfortunately very low due to the kinetic reactivity of the resulting chromium(II) complex. It was envisaged that encapsulated chromium(III) sar complexes would not suffer these problems, but unfortunately their photophysical properties are disappointing, as the lifetimes of the excited states are much too short at room temperature, the phosphorescent lifetime estimated to be less than 10 ns.[11,41] By contrast, $[Cr(diammac)]^{3+}$ exhibits emission from the ^2E_g state at 295 K with an appreciable phosphorescence lifetime of 2 μs. The excited-state redox potential for the $(^2E_g)[Cr(diammac)]^{3+}$ has been estimated as +0.8 V from

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$$E°(^*\mathrm{Cr(diammac)}^{3+}/\mathrm{Cr(diammac)}^{2+}) = E°(\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}) + E_{00}(^*\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+})$$

where $E_{00}(^*\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+})$ is the one-electron potential corresponding to the spectroscopic energy of the excited state (ca. 1.8 eV). The temperature-independent region for diammac extends to 200 K compared with 170 K for sar complexes.[11] The higher ligand field of diammac compared to sar leads to a relatively high-lying quartet excited state. This would be less easily populated from the ^2E_g excited state should deactivation occur through a mechanism of thermally induced back intersystem crossing. Alternative mechanisms may be considered, as detailed elsewhere.[26] Lifetimes at 77 K for $\mathrm{CrN_6}^{3+}$ ions in nondeuterated samples are extended considerably in the deuterated samples (Table IV).[11,41] The dramatic increase in the lifetime in the cold, temperature-independent region upon deuteration is in accordance with many other systems. This further substantiates the theory that the N–H stretching modes are responsible for radiationless deactivation.[42]

In parallel with the behavior around octahedral d^6 cobalt(III), the diammac sexidentate amine ligand leads to a "compressed" chromium(III) d^3 complex with physical properties reflecting this. Molecular mechanics calculations indicate that shortened bond lengths are a result of ligand demands,[15,43] so that "compression" should be generally observed with metal ions. This has now been seen for a range of octahedral metal ions.[15,16,22,35] Modest variations in physical properties of complexes of diammac appear generally, and may be turned to advantage in some applications.

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Supplementary Material Available: Tables of crystal data, thermal parameters, and hydrogen atom parameters and a unit cell diagram for $[\mathrm{Cr(diammac)}](\mathrm{ClO_4})_3$ (6 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

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Thermochemical Interpretation of Electrode Potentials for Transition-Metal Complexes

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Experimental and theoretical thermochemical quantities are interrelated to show how bond energies, solvation energies, and entropy changes lead to $E°$ values for several common transition-metal complex redox couples. Relevant conventions are described to demonstrate the relationship between gas-phase and solution thermochemistry of electron attachment reactions. Values of absolute electrode potentials for common reversible redox couples are estimated, and gas-phase electron attachment energies (experimental or theoretically estimated) are used to complete thermochemical cycles that lead to bond energy and solvation energy contributions to observed electrode potentials. A few common $\mathrm{M^{III}L}_x/\mathrm{M^{II}L}_x$ couples (L = $\mathrm{NH_3}$, bipyridine, cyclopentadienyl, $\mathrm{CN^-}$, acetylacetonate) are used to illustrate why the $E°$ values for couples involving widely varying ligand sets are usually within a range of ~2 V for a given metal despite the wide range (~20 V) of gas-phase electron attachment energies for the unsolvated complexes.

Introduction

Little experimental or theoretical attention has been given to detailed thermochemical interpretations of observed electrode potentials for oxidation–reduction couples involving transition-metal centers in coordination complexes, metalloproteins, and organometallic compounds. Typical textbook discussions[1] describe trends in $E°$ values as a function of the metal for a given ligand environment (e.g., the $[\mathrm{M(H_2O)_6}]^{3+/2+}$ series) and indicate the phenomenological dependence of $E°$ on the type of ligand. These treatments do little to relate compiled electrode potentials to general thermochemical concepts that might illuminate the reasons that a given redox couple has a particular $E°$ value. More advanced discussions[2] consider the thermochemical components of redox potentials and, for transition-metal couples, consider the role of ligand field effects in trends; however, these approaches are usually based on interpretation of relative *variations* of electrode potentials as the metal is changed rather than absolute values of the potentials. Some progress toward quantifying the role of bond energies and solvation in the determination of absolute electrode potentials can be made by using estimates based on rather simple models.[2f] Such analyses have clearly been limited by the absence of necessary gas-phase data for metal complexes, but this type of data has recently become more accessible through experimental studies.[3,4] The purpose of this article is to interrelate certain relevant thermochemical quantities for gas-phase and condensed-phase complexes to show how bond energies, entropy changes, and solvation energies lead to an $E°$ value for a given redox couple. The emphasis here is on redox couples for transition-metal complexes in which oxidized and reduced forms retain the same ligand coordination.

Some important conventions are discussed first to demonstrate the relationship between gas-phase and solution redox thermo-

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