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Macrobicyclic Chromium(III) Hexaamine Complexes

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The syntheses and characterization of the macrobicyclic hexaamine chromium(III) complexes of diamsar (1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) and sar (3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) ligands (**1–3**) are reported. The complexes were isolated as stable, paramagnetic, and monomeric salts. [Cr(diamsar)]$Cl_3 \cdot H_2O$ crystallized in the space group $P2_1/c$, ($Z = 4$, $a = 9.474$ (2) Å, $b = 13.331$ (3) Å, $c = 18.221$ (5) Å, $\beta = 92.756$ (0)°) with the octahedral cation in the C_3-*lel* conformation and an average Cr–N distance of 2.070 (3) Å. The complexes are high-spin d^3 with room-temperature magnetic moments near the spin-only value of 3.87 μ_B. The aqueous electrochemistry exhibits a quasi-reversible Cr(III/II) couple below −1 V for each complex and a further irreversible Cr(II/0) reduction near −1.6 V; the chromium(II) complexes are not stable in the coulometric time scales (minutes). The Cr(III) electronic spectra show the expected spin-allowed absorption bands of ${}^4T_{2g} \leftarrow {}^4A_{2g}$ and ${}^4T_{1g} \leftarrow {}^4A_{2g}$ origin as well as weak spin-forbidden bands of ${}^2E_g$, ${}^2T_{1g} \leftarrow {}^4A_g$ origin in the visible region. The first of these (${}^4T_{2g}$ transition) is split by −400 cm^{-1} and is relatively high in intensity, and the splitting is probably due to the lowered symmetry (D_3). Cr(sar)$^{3+}$ and Cr(diamsar)$^{3+}$ emit rather strongly at 77 K ($\phi_P^{H_2O} \approx 0.02$), but give no detectable emission above 273 K. Photodecomposition of Cr(diamsar)$^{3+}$ is $\sim 10^4$-fold smaller than that of the Cr(en)$_3^{3+}$ ion, and possible reasons for this are discussed.

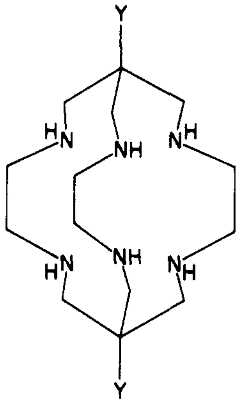
Introduction

Encapsulation of the inert d^6 metal ions Co(III), Rh(III), Ir(III), and Pt(IV) as nearly octahedral complexes in saturated hexacoordinate amine macrobicycles has been achieved recently,[8-11] by template synthesis about the M(en)$_3^{n+}$ precursor (en = 1,2-ethanediamine) with formaldehyde and ammonia or nitromethane in basic solution.[12] Amine Cr(III)–N bond lengths (average 2.09 Å) are longer than Co(III)–N bond lengths (average 1.97 Å) but are similar to Pt(IV)–N bond lengths (average 2.08 Å).[13] Therefore, encapsulation of Cr(III) in a macrobicyclic amine ligand, already achieved for Co(III) and Pt(IV), should be chemically feasible. However our attempts at encapsulation of the inert d^3 Cr(en)$_3^{3+}$ precursor were not successful due to the rapid dissociation of intermediate imine species formed during the reaction.[14] Nevertheless, recently, Endicott et al.[15] claimed to have synthesized Cr(sep)$^{3+}$ by such a route.

This paper now explores the synthesis of Cr(III) macrobicyclic complexes via the free ligands (**1–3**) and the Cr(II) oxidation state. Structural, electrochemical, spectroscopic, photochemical, photophysical, and magnetic properties are also reported.

Experimental Section

Detailed syntheses and characterization of the metal-free ligands will be published elsewhere.[16]



1 (Y = H) **2** (Y = NH_2) **3** (Y = NH_3^+)

(1,8-Diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)chromium(III) Chloride Monohydrate. Diamsar ligand[16] (3.0 g) was dissolved in dry dimethyl sulfoxide (25 mL) and the solution warmed on a steam bath. Zinc powder (0.1 g) and anhydrous chromic chloride (1.51 g) were added, and the solution was gently warmed for 5 min. The resulting green-yellow solution was added to a large volume of water and filtered. The filtrate was sorbed on a column of Dowex 50W-X2 (H^+ form) resin, and washed with water and 1 M HCl. Elution with 3 M HCl gave a major yellow band, which was collected and evaporated to dryness by using a rotary evaporator. The yellow solid was redissolved in a large volume of water and rechromatographed on SP Sephadex C-25 (Na^+ form) cation-exchange resin. After being washed with water and 0.1 M NaCl solution, the column was eluted with 0.3 M NaCl solution and the major yellow band collected. This eluate was sorbed on a column of Dowex 50W-X2 (H^+ form) resin, washed with 0.5 M HCl, and eluted with 3 M HCl solution. The yellow solid obtained upon evaporation of the solvent was crystallized from aqueous propan-2-ol solution, following the addition of 2 equiv of lithium hydroxide, as yellow needles (2.5 g). Anal. Calcd for $C_{14}H_{36}Cl_3CrN_8O$: C, 34.25; H, 7.39; N, 22.83; Cr, 10.59; Cl, 21.67. Found: C, 34.7; H, 7.3; N, 23.2; Cr, 10.3; Cl, 21.6.

(3,6,10,13,19-Hexaazabicyclo[6.6.6]eicosane)chromium(III) Trifluoromethanesulfonate. Sar ligand[16] (3.0 g) was dissolved in dry dimethyl sulfoxide (25 mL) and the solution warmed on a steam bath. Zinc powder (0.1 g) and anhydrous chromic chloride (1.73 g) were added, and the solution was gently heated for 2 min. The mixture was chromatographed and the yellow solid isolated from aqueous HCl as described for the diamsar analogue except for the additions of LiOH.

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The yellow chloride salt was recrystallized as the trifluoromethanesulfonate salt from water upon addition of excess Na CF_3SO_3 and cooling (2.0 g). Anal. Calcd for $C_{17}H_{32}CrF_9N_6O_9S_3$: C, 26.05; H, 4.12; N, 10.73; Cr, 6.63; S, 12.27. Found: C, 26.3; H, 4.4; N, 10.7; Cr, 6.6; S, 12.3.

Photochemical experiments were carried out by using an ILC Cermax xenon illuminator (150 W) with 450-nm light dispersed by a Bausch and Lomb monochromator ($f = 3.6$). The total number of photons absorbed was measured by ferrioxalate actinometry. The disappearance of chromium(III) complexes was monitored by HPLC on a Zorbax ODS column (Du Pont; 25 × 0.46 cm). The eluent was an aqueous solution of THF (10%), acetic acid (1%), sodium heptasulfonate monohydrate (0.88%), and methanesulfonic acid (0.02%), adjusted to pH 3.1 with tetramethylammonium hydroxide. Phosphorescence lifetime measurements were carried out with a nitrogen laser pumped dye laser (Molectron DL11). Signals were detected by an EMI 9816B photomultiplier through a Spex double-mate monochromator, and were displayed with a Tektronix 7834 oscilloscope.[17] The complexes were dissolved in appropriate solvents ($\sim 10^{-4}$ M) and deaerated with high-purity N_2. The temperature of the Dewar containing the sample was monitored with a thermocouple. The complexes were deuterated at the N centers in neutral D_2O, and the level of deuteration was checked by IR spectroscopy and FAB mass spectrometry.

Electrochemical studies were performed by using a conventional three-electrode configuration with *iR* compensation and a PAR Model 170 electrochemical system. For rapid-scan cyclic voltammograms a Tektronix C-70 oscilloscope camera connected to a Tektronix 5031 storage oscilloscope and the PAR Model 170 system were used. Working electrodes were a dropping mercury electrode (DME), a hanging mercury drop electrode (HMDE) and stationary Pt or Au electrodes. The reference electrode was a saturated calomel or a silver/silver chloride electrode and was separated from the working and auxiliary electrodes in an electrode bridge with a fine-porosity frit. The auxiliary electrode was a platinum coil. Solutions were degassed with solvent-saturated argon through a standard purge tube. Double glass distilled water or dried analytical grade organic solvents were employed. Sodium perchlorate (0.1 M), sodium trifluoromethanesulfonate (0.1 M), or tetramethylammonium trifluoromethanesulfonate (0.1 M) were used as electrolytes. Complex concentrations close to millimolar were used throughout. Coulometric analyses were performed with a PAR Model 337A coulometry cell system using either a stirred mercury pool or platinum basket working electrode and an Amel Model 551 potentiostat and Model 731 digital integrator.

Room-temperature magnetic moments were determined by both the standard Gouy method and the Faraday method. Details of the instrumental methods and a full temperature-dependent study of the magnetism will be published elsewhere.[18]

Visible absorption spectra were recorded with a Cary 17 spectrophotometer. Visible absorption spectra of electrochemially reduced solutions in water were determined by circulating the solution from the coulometry cell through a flow cell in a Hewlett-Packard 8450A spectrophotometer. Infrared spectra (KBr disks) were recorded with a Perkin-Elmer 457 spectrometer.

Crystal Structure Analysis. A crystal needle of $[Cr(diamsar)]Cl_3 \cdot H_2O$ of dimensions 0.09 × 0.09 × 0.30 mm^3 was mounted on a glass fiber and coated with cyanoacrylate glue. Lattice parameters at 25 °C were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD-4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation.

Crystal data: $C_{14}H_{36}Cl_3CrN_8O$, fw 490.85, monoclinic space group $P2_1c$, $a = 9.474$ (2) Å, $b = 13.331$ (3) Å, $c = 18.221$ (5) Å, $\beta = 92.756$ (0)°, $D_c = 1.418$ g cm^{-3}, $V = 2290.93$ Å^3, $Z = 4$, μ(Mo Kα) = 8.57 cm^{-1}, λ(Mo Kα) = 0.7107 Å, $F(000) = 940$ e. Intensity data were collected in the range $1.5 < \theta < 24.5$ by using an $\omega - n/3\theta$ scan, where n (=6) was optimized by profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures employed were $(0.9 + 0.35 \tan \theta)°$ and $(2.40 + 0.5 \tan \theta)$ mm respectively. Three standard reflections, monitored after every hour of data collection, indicated that by completion of the data collection no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed by using the program SUSCAD.[19] Absorption corrections were applied with the program ABSORB.[19] Maximum and minimum transmission factors were estimated to be 0.94 and 0.84, respectively. Of the 3182 reflections collected, 704 with $I > 2.5\sigma(I)$ were considered unobserved and not used in the calculations.

Table I. Positional Parameters for $[Cr(diamsar)]Cl_3 \cdot H_2O$, Excluding Hydrogen Atoms[a]

atom	x	y	z
Cr	25097 (5)	26242 (3)	12940 (2)
Cl(1)	2353 (1)	4321 (1)	−595 (1)
Cl(2)	9256 (1)	4727 (1)	3687 (1)
Cl(3)	4212 (1)	3932 (1)	3252 (1)
O(1)	2931 (5)	−2041 (5)	998 (3)
N(1)	−1841 (3)	3854 (1)	1863 (2)
N(2)	6853 (3)	1346 (2)	754 (2)
N(3)	840 (2)	2922 (2)	550 (1)
N(4)	2199 (2)	4001 (2)	1792 (1)
N(5)	1127 (3)	1964 (2)	1994 (1)
N(6)	2792 (2)	1374 (2)	645 (1)
N(7)	4065 (2)	3377 (2)	754 (1)
N(8)	4058 (3)	2115 (2)	2056 (1)
C(1)	−419 (3)	3495 (2)	1682 (2)
C(2)	−220 (4)	2522 (3)	2124 (2)
C(3)	−512 (3)	3287 (3)	854 (2)
C(4)	688 (3)	4297 (2)	1895 (2)
C(5)	5438 (3)	1740 (2)	914 (2)
C(6)	5429 (3)	1784 (2)	1754 (2)
C(7)	5368 (3)	2794 (2)	569 (2)
C(8)	4293 (3)	1037 (2)	574 (2)
C(9)	3015 (3)	4775 (2)	1386 (2)
C(10)	4400 (3)	4315 (2)	1179 (2)
C(11)	606 (3)	2017 (2)	74 (2)
C(12)	2028 (3)	1572 (3)	−74 (2)
C(13)	1928 (3)	1716 (3)	2690 (2)
C(14)	3376 (4)	1329 (2)	2506 (2)

[a] All coordinates are ×10^4 except those for Cr (×10^5).

The structure was solved and refined by application of the heavy-atom technique. Successive difference syntheses located all non-hydrogen atoms of the structure, including one water molecule. In the refinement by full-matrix least-squares techniques, the hydrogen atoms were either fixed at their found positions (water and NH_2 sites) or allowed to ride in fixed orientation to their connections (NH and CH_2 sites; $d = 0.95$ Å). A weighting scheme was applied and refined, converging at $w = 0.97/(\sigma^2(F_o) + 0.0074(F_o)^2)$. Refinement converged with $R = 0.0313$ and $R_w = 0.0350$ at which state the largest peak in the final difference map was <0.4 e Å^{-3}. All scattering factors and anomalous terms were taken from ref 20. The final positional parameters are listed in Table I. The thermal parameters, hydrogen parameters, and observed and calculated structure factors are available as supplementary material.

Results

Encapsulation of chromium(III) in the macrobicyclic hexaamine ligands diamsar and sar has been achieved by direct reaction of the ligand with chromium(III) chloride in dimethyl sulfoxide in the presence of Zn powder. The yellow, paramagnetic, and monomeric complexes $[Cr(sar)](CF_3SO_3)_3$ and $[Cr(diamsar)]Cl_3 \cdot H_2O$ were isolated as analytically pure samples.

The encapsulation of the metal ion by the macrobicyclic ligands was established by an X-ray crystallographic analysis of $[Cr(diamsar)]Cl_3 \cdot H_2O$. A perspective view of the cation is shown in Figure 1, and Table II contains selected bond lengths and angles. In the crystal, the cation is surrounded by three chloride ions hydrogen bonded to adjacent pairs of NH groups (e.g. N(5)–H and N(6)–H, Figure 1). The same pattern has been found for $[Co(sep)]Cl_3 \cdot H_2O$,[8] where the apical moieties are not aminomethane, but single nitrogen atoms (sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane). The hydrogen-bonding pattern is completed by each chloride having an additional link either to the water molecule or to an NH_2 group (Table II). The overall symmetry of the cation is only C_3 with catoptric caps, whereas the monodeprotonated cobalt(III) dinosar[9] (dinosar = 1,8-dinitro-sar) and cobalt(III) and cobalt(II) sepulchrate species have caps of the same chirality. The ethylene-

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Table II. Bond Distances (Å) and Angles (deg) for $[Cr(diamsar)]Cl_3.H_2O$

Bond Distances

N(3)–Cr	2.072 (2)	C(2)–C(1)	1.533 (4)	C(9)–N(4)	1.505 (4)
N(5)–Cr	2.069 (3)	C(2)–C(1)	1.534 (4)	C(13)–N(5)	1.484 (4)
N(7)–Cr	2.071 (2)	C(7)–C(5)	1.539 (5)	C(12)–N(6)	1.490 (4)
C(1)–N(1)	1.482 (4)	C(10)–C(9)	1.512 (5)	C(10)–N(7)	1.497 (4)
C(3)–N(3)	1.501 (4)	C(14)–C(13)	1.519 (5)	C(14)–N(8)	1.496 (4)
C(4)–N(4)	1.506 (4)	N(4)–CrB	2.074 (2)	C(3)–C(1)	1.532 (5)
C(2)–N(5)	1.505 (4)	N(6)–CrAl	2.068 (2)	C(6)–C(5)	1.533 (5)
C(8)–N(6)	1.503 (4)	N(8)–CrCr	2.085 (2)	C(8)–C(5)	1.541 (4)
C(7)–N(7)	1.511 (4)	C(5)–N(2)	1.482 (4)	C(12)–C(11)	1.508 (4)
C(6)–N(8)	1.499 (4)	C(11)–N(3)	1.495 (4)		

Hydrogen Bonds

Cl(1)–N(3)	3.189 (3)	C6(2)[b]–O(1)	3.209 (3)	Cl(3)–N(4)	3.199 (3)
Cl(1)–N(7)	3.141 (3)	Cl(2)[b]–N(5)	3.144 (3)	Cl(3)–N(8)	3.258 (3)
Cl(1)[a]–N(1)	3.374 (3)	Cl(2)[b]–N(6)	3.209 (3)	Cl(3)[b]–O(1)	3.244 (3)

Bond Angles

N(4)–Cr–N(3)	89.8 (1)	N(5)–Cr–N(3)	89.9 (1)
N(5)–Cr–N(4)	90.0 (1)	N(6)–Cr–N(3)	84.1 (1)
N(6)–Cr–N(4)	171.1 (1)	N(6)–Cr–N(5)	96.5 (1)
N(7)–Cr–N(3)	97.7 (1)	N(7)–Cr–N(4)	84.2 (1)
N(7)–Cr–N(5)	170.3 (1)	N(7)–Cr–N(6)	90.2 (1)
N(8)–Cr–N(3)	171.5 (1)	N(8)–Cr–N(4)	96.2 (1)
N(8)–Cr–N(5)	84.1 (1)	N(8)–Cr–N(6)	90.7 (1)
N(8)–Cr–N(7)	88.9 (1)	C(3)–N(3)–Cr	117.3 (2)
C(11)–N(3)–Cr	108.1 (2)	C(11)–N(3)–C(3)	111.7 (2)
C(4)–N(4)–Cr	116.2 (2)	C(9)–N(4)–Cr	107.8 (2)
C(9)–N(4)–C(4)	113.3 (2)	C(2)–N(5)–Cr	116.9 (2)
C(13)–N(5)–Cr	108.0 (2)	C(13)–N(5)–C(2)	112.2 (3)
C(8)–N(6)–Cr	116.1 (2)	C(12)–N(6)–Cr	106.8 (2)
C(12)–N(6)–C(8)	113.5 (2)	C(7)–N(7)–Cr	117.7 (2)
C(10)–N(7)–Cr	107.2 (2)	C(10)–N(7)–C(7)	113.0 (2)
C(6)–N(8)–Cr	116.5 (2)	C(14)–N(8)–Cr	106.5 (2)
C(14)–N(8)–C(6)	113.6 (2)	C(2)–C(1)–N(1)	104.3 (2)
C(3)–C(1)–N(1)	105.5 (2)	C(3)–C(1)–C(2)	111.3 (3)
C(4)–C(1)–N(1)	109.7 (2)	C(4)–C(1)–C(2)	113.0 (3)
C(4)–C(1)–C(3)	112.4 (3)	C(1)–C(2)–N(5)	114.8 (3)
C(1)–C(3)–N(3)	114.4 (3)	C(1)–C(4)–N(4)	115.4 (2)
C(6)–C(5)–N(2)	105.1 (3)	C(7)–C(5)–N(2)	105.3 (3)
C(7)–C(5)–C(6)	111.8 (3)	C(8)–C(5)–N(2)	109.3 (3)
C(8)–C(5)–C(6)	112.8 (3)	C(8)–C(5)–C(7)	112.0 (3)
C(5)–C(6)–N(8)	115.1 (2)	C(5)–C(7)–N(7)	113.5 (3)
C(5)–C(8)–N(6)	115.1 (2)	C(5)–C(7)–N(7)	113.5 (3)
C(5)–C(8)–N(6)	115.7 (2)	C(10)–C(9)–N(4)	108.4 (2)
C(9)–C(10)–N(7)	107.7 (2)	C(12)–C(11)–N(3)	108.2 (2)
C(11)–C(12)–N(6)	108.2 (3)	C(14)–C(13)–N(5)	108.5 (3)
C(13)–C(14)–N(8)			

[a] Symmetry transformation $^1/_2 + x, 1 - y, 1 - z$. [b] Symmetry transformation $x, ^1/_2 - y, ^1/_2 + z$.

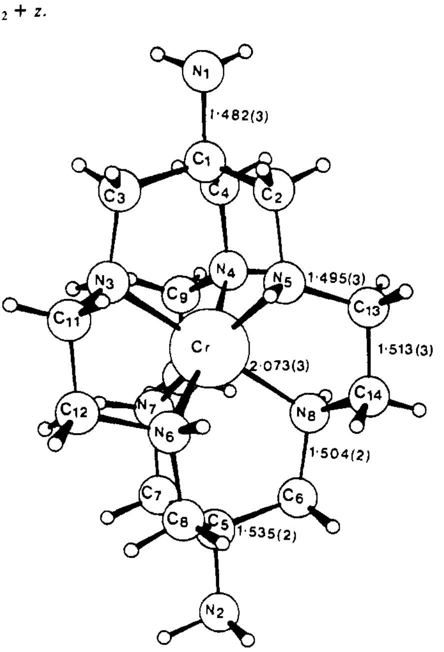

Figure 1. ORTEP diagram of the $Cr(diamsar)^{3+}$ cation.

Table III. Comparison of Phosphorescence Lifetimes [$\tau_P(^2E \rightarrow {}^4A_2)$, μs] and Quantum Yield of Photodecomposition (ϕ_{PD}) of $Cr(diamsar)^{3+}$ and $Cr(en)_3{}^{3+}$ in Acetate Buffer at pH 5.0

	$Cr(diamsar)^{3+}$	$Cr(sar)^{3+}$	$Cr(en)_3{}^{3+}$
$\tau_{295}(OH_2)$	*a*	*a*	1.5 (lit.[b] 1.85)
$\tau_{77}(OH_2)$	65	60	22
$\tau_{295}(OD_2)$	*a*		2.1 (lit.[c] 2.27)
$\tau_{77}(OD_2)$	790		130
$\phi_{PD}(OH_2, 295\ K)$[d]	2×10^{-5}		0.38 (lit.[c] 0.40)[c]

[a] Not detected. [b] Reference 25. [c] Reference 29. [d] A 450-nm excitation.

diamine rings of the chromium(III) complex have the *lel* conformation with the C–C bond nearly parallel to the three-fold axis resulting in C_3-*lel* symmetry. In both cobalt(III) and cobalt(II) sepulchrate structures the ethylenediamine rings also have the *lel* conformation. The D_3-*ob* conformation has been observed for the deprotonated cobalt(III) dinosar complex.[9] The average chromium to nitrogen distance in the encapsulated ion (2.070 (3) Å) is very similar to that of the $Cr(NH_3)_6{}^{3+}$ ion (2.064 (3) Å),[21] consistent with the result found for the cobalt analogues that the metal to ligand bond lengths are little perturbed by chelation and encapsulation. The average bond lengths in the ligand chain are shown in Figure 1 and they differ by less than one combined standard deviation, but bond angles in the ligand and about the metal are strained. The twist angle ϕ is ~50° compared to 60° for an octahedral complex.[22]

The pK_a values for the uncoordinated ammonium groups of $[Cr(di(amH)sar)]Cl_5 \cdot H_2O$ are 2.03 ± 0.03 and 4.48 ± 0.02 (potentiometric titration; 25 °C; $\mu \sim 0.1$). At high pH, one coordinated amine is deprotonated ($pK_a = 12.0 \pm 0.1$; spectrophotometric titration; 25 °C; $\mu = 1$ M, NaCl).

The complexes have high-spin d^3 electronic configurations like the parent $Cr(en)_3{}^{3+}$ and $Cr(NH_3)_6{}^{3+}$ ions. They exhibit magnetic moments of 3.74 μ_B for $Cr(diamsar)^{3+}$, 3.80 μ_B for $Cr(di(amH)sar)^{5+}$ and 3.78 μ_B for $Cr(sar)^{3+}$ at 298 K. This compares with a room-temperature moment of 3.83 μ_B for $Cr(en)_3{}^{3+}$,[23] and the spin-only value of 3.87 μ_B.

The electronic spectra of the complexes in room-temperature aqueous solution have the following absorption maxima for the $Cr(diamsar)^{3+}$ ion (in cm^{-1}, extinction coefficients ($M^{-1}\ cm^{-1}$) in parentheses): 14 590 (0.8), 15 090 (0.5), 15 450 (0.6), 15 570 (sh) (of ^2E_g, $^2T_{1g} \leftarrow {}^4A_{2g}$ origin), 21 950 (203), 22 350 (208) (of $^4T_{2g} \leftarrow {}^4A_{2g}$ origin), 28 940 (109) (of $^4T_{1g} \leftarrow {}^4A_{2g}$ origin). Spectral changes resulting from protonation of the amino caps ($Cr(di(amH)sar)^{5+}$) are only small. The spectrum for $Cr(sar)^{3+}$ is also similar. The respective absorption maxima are as follows: 14 620 (~0.8), 15 160 (~0.7), 15 440 (~0.6), 15 550 (sh), 21 860 (153), 22 250 (156), 28 820 (91).

In aqueous solution, unlike $Cr(en)_3{}^{3+}$,[24,25] $Cr(diamsar)^{3+}$ and $Cr(sar)^{3+}$ gave no detectable phosphorescence from the doublet states above 273 K. No emission for $Cr(diamsar)^{3+}$ was detected either in various solvents such as D_2O, CH_3OH, CD_3OD, CH_3CN, and DMF or in rigid matrices such as polystyrene at the same temperatures. However, very weak phosphorescence ($\phi_P \sim 10^{-4}$) was observed from crystalline powders of $Cr(diamsar)Cl_3 \cdot H_2O$ and $Cr(diamsar\text{-}d_{10})Cl_3 \cdot D_2O$ at 298 K. The lack of emission from the solutions of $Cr(diamsar)^{3+}$ at 298 K, even after deuteration, is surprising in view of its structural similarity with $Cr(en)_3{}^{3+}$ and the supposed $Cr(sepulchrate)^{3+}$ ion, which both emit at room temperature.[15] Some aspects of this behavior in relation to the structural modification of the cage are currently under investi-

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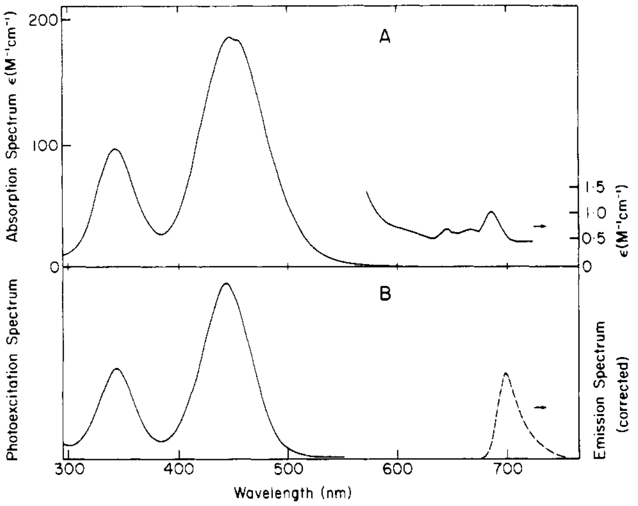

Figure 2. (A) Absorption spectrum of Cr(diamsar)$^{3+}$ in water at 295 K. (B) Photoexcitation spectrum and emission spectrum, corrected for spectral response, of Cr(diamsar)$^{3+}$ in water (1×10^{-5} M complex) at 77 K.

Table IV. Isotope Effects and Apparent Activation Energies (E_a*, kJ) of the Phosphoresence Lifetimes (μs) of Cr(diamsar)$^{3+}$

	Cr(diamsar-d_{10})$^{3+}$			Cr(diamsar)$^{3+}$		
	CH_3CN	D_2O	cryst	CH_3CN	H_2O	cryst
τ_{77}	420	790	310	105	65	80
τ_{203}	8	12	290	1.5	1.2	60
τ_{295}	*a*	*a*	13	*a*	*a*	1.0
$E_a{}^{*b}$	34	37	38	29	30	32

[a] Emission not detected ($\phi_P < 10^{-5}$), $\tau_{298} < 10$ ns by extrapolation from Figure 3. [b] E_a* derived from the data of Figure 3.

gation.[26,27] At 77 K both Cr(sar)$^{3+}$ and Cr(diamsar)$^{3+}$ emit rather strongly ($\phi_P{}^{H_2O} \approx 0.02$) (Table III). For Cr(diamsar)$^{3+}$ under these conditions, the phosphorescence lifetimes are longer than for Cr(en)$_3{}^{3+}$ in both the H_2O and D_2O matrices (Table III). The lifetimes of the excited states are also lengthened by deuteration. The photoexcitation and emission spectra of Cr(diamsar)$^{3+}$ in water at 77 K, both corrected for spectral response, are shown in Figure 2B. The fact that the photoexcitation spectrum differs little from the absorption spectrum rules out the presence of emitting impurities and shows that Cr(diamsar)$^{3+}$ is the emitting species. The origin of the emission is entirely due to phosphorescence. Since phosphorescence appears simultaneously with the laser excittion pulse (rise time 2 ns), we conclude that intersystem crossing is a rapid process with a rate constant exceeding 5×10^8 s^{-1}, and probably approaching 10^{11} s^{-1}, as observed with some other Cr(III) complexes.[28] As the temperature increases the phosphorescence intensities and the lifetimes decrease proportionately. Figure 3 shows the change of phosphorescence lifetimes of Cr(diamsar)$^{3+}$ and Cr(diamsar-d_{10})$^{3+}$ from 77 to 298 K in various media. In solution, the phosphorescence lifetimes are strongly dependent on temperature, and between 150 and 230 K, they span 3 orders of magnitude. Table IV shows the effect of deuteration on the lifetimes of phosphorescence. In CH_3CN at 77 K, the phosphorescence lifetime of Cr(diamsar-d_{10})$^{3+}$ is four times longer than that of the non-deuterated species. The lifetimes of the excited states are further lengthened in deuterated solvents such as D_2O where the ratio of τ_P differs now by 1 order of magnitude (Table III). In methanol/water (3:1) the change of phosphorescence lifetimes with temperature for Cr(diamsar)$^{3+}$ and Cr(en)$_3{}^{3+}$ differ dramatically (Figure 3). At <130 K, they have essentially the same lifetime, ~100 μs, but at 200 K the lifetimes differ by 2 orders of magnitude. Also, the temperature dependence of τ for Cr(di(amH)sar^{5+} in 0.2 M HCl was almost identical with that of Cr(diamsar)$^{3+}$ in H_2O (pH 5). Arrhenius plots obtained from the data of Figure 3 show that the activation energies (E_a*) are relatively insensitive to the solvent media. Also allowing for experimental uncertainty (10%), E_a* for the deuterated complex is only about 500 cm^{-1} (6 kJ/mol) higher than that for Cr(diamsar)$^{3+}$. The photodecomposition of the Cr(diamsar)$^{3+}$ ion was monitored by HPLC. The results reported in Table III show that $\phi_{PD'}$ (295 K) is appreciably smaller than that reported[29] for Cr(en)$_3{}^{3+}$ and somewhat smaller than that reported for Cr(sep)$^{3+}$.[15] This is not surprising in view of the kinetic inertness of the caged metal ions generally.

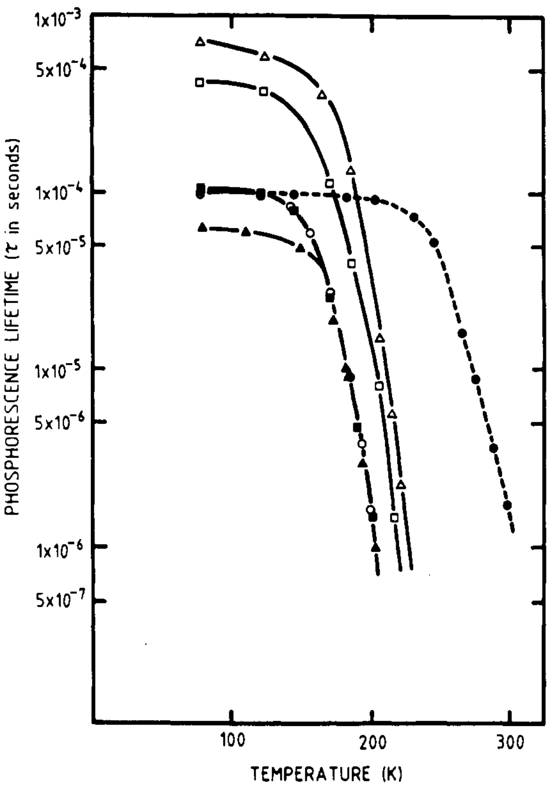

Figure 3. Phosphorescence lifetimes as a function of temperature. Cr(diamsar)$^{3+}$: ■, in CH_3CN; ▲, in H_2O; ○, in $MeOH/H_2O$ (3:1). Cr(diamsar-d_{10})$^{3+}$: □, in CH_3CN; △ in D_2O. Cr(en)$_3{}^{3+}$: ●, $MeOH/H_2O$ (3:1).

The cyclic voltammetry of the Cr(diamsar)$^{3+}$ complex is characterized in water by a reversible one-electron couple at −1.35 V (vs. the saturated (KCl) calomel electrode, HMDE, 50 mV/s, 70 mV peak to peak, $i_{pf}/i_{pb} = 1.0$). The couple shifts to −1.04 V vs. SCE in acid solution, due to protonation of the cap amine groups which forms the Cr(di(amH)sar)$^{5+}$ ion. The one-electron nature of the couple was established by dc wave-height comparisons with the analogous Co(III/II) couple.[30] Variable-frequency ac polarography indicates that the Cr(III/II) couple is also quasi-reversible in the time scale of that technique, like the cobalt analogues. However with the Cr(III) cage complexes, adsorption effects interfered more severely than with the cobalt(III) system. Reduction in water at 293 K was also nearly reversible in the coulometric time scale. This was ascertained by visible absorption spectroscopy, since reoxidation of the reduced solution gave largely the absorption spectrum of Cr(diamsar)$^{3+}$, albeit with a little additional impurity. The nature of the decomposition has not been ascertained yet, but fragmentation of the cage structure is likely, by analogy with reductions of cobalt(II) and platinum(IV) analogues.[30,11] A second irreversible wave was

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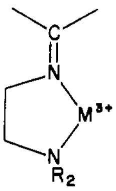
observed near the solvent limit at −1.6 V vs. SCE for Cr(di(amH)sar)$^{5+}$. From dc wave-height comparisons, this appears to be a two-electron reduction and is presumably the Cr(II/0) irreversible reduction. No reductions of the free ligand occurred prior to the solvent limit in water.[31]

The voltammetric behavior of $Cr(sar)^{3+}$ was similar but not identical with that of the diamsar analogue. A Cr(III/II) couple was observed at −1.38 V vs. SCE in water, with a further wave near −1.6 V. The first couple was irreversible in the coulometric time scale and at slow speeds in cyclic voltammetry, but a reverse wave was observed at scan speeds ≥10 V/s. Effects that govern the voltammetric behavior of the sar and diamsar complexes must be subtle, since the size of the cavity in each of the ligands is essentially the same. Investigation of the $Cr(sar)^{3+}$ ion in aprotic solvents indicated no oxidation waves up to the solvent limit ($\sim$+2 V in CH_3CN), so there is at present no evidence for the formation of Cr(IV) Complexes.

Discussion

Analogous inert amine complexes of cobalt(III) and chromium(III) have been reported, and complexes with multidentate and macromonocyclic amine lignds are known for both metal ions.[32,33] The earlier reports[8,9] of stable macrobicyclic amine complexes of cobalt(III) implied that similar compounds of chromium(III) should be formed readily by using the template synthesis found for the cobalt systems. This synthesis proceeds in a stepwise manner[12] and involves imine intermediates such as **4**. With



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Co(III) these intermediates readily undergo nucleophilic attack at the imine carbon by ammonia or $^-CH_2NO_2$, leading eventually to the macrobicycle. Attempts to carry out this synthesis with $Cr(en)_3^{3+}$, however, were not successful, a failure that we attributed to the relatively rapid dissociation of imine ligands of Cr(III) such as **4**.[14] The ready loss of amine ligands in the presence of aldehydes and base is demonstrable for Cr(III) complexes.[14] It is also reflected in a general way for such unsaturated N donors. For example, $(NH_3)_5CrN{\equiv}CCH_3^{3+}$ loses CH_3CN in aqueous solution with a rate constant of 2.10^{-3} s^{-1} at 25 °C. In this respect the reported synthesis of $Cr(sep)^{3+}$ by Endicott et al.[15] is surprising although small quantities of the capped $Cr(sep)^{3+}$ ion might be formed by such a route.

Clearly, a different approach was necessary, and the simple substitution reaction employed for macromonocyclic amines was the most obvious. Since encapsulation of cobalt renders even the normally labile cobalt(II) state substitutionally inert,[8,9] extreme conditions were necessary to obtain free macrobicyclic ligand from the readily prepared cobalt complexes.[16] However, once this was achieved, ligand substitution on labile transition-metal complexes has generally provided the macrobicyclic complexes smoothly. The macrobicyclic ligands readily accommodate ions of various sizes. Metal–amine bond lengths between 1.97 and 2.27 Å have been observed.[22] The incorporation of the inert chromium(III) ion in the ligand cavity was therefore accomplished via a trace of the labile Cr(II) state generated by Zn^0, followed by rapid reoxidation.

The template syntheses of $Co(sep)^{3+}$ and $Co(dinosar)^{3+}$ proceed in a remarkably stereospecific manner.[12] The crystal structures of $Co(sep)^{+3}$[8] and the monodeprotonated $Co(dinosar)^{3+}$ ion[9] have caps of the same chirality, although the ethylenediamine chelate five-ring conformations are lel_3 and ob_3 respectively. In this respect, the $Cr(diamsar)^{3+}$ ion follows suit, except that the caps are catoptric and the overall symmetry is only C_3. The coordination geometry of all structurally analyzed $M^{II}(di(amH)sar)^{4+}$ complexes is D_3-lel_3.[22]

The chromium(II) macrobicycles are appreciably less stable than the corresponding cobalt(II) macrobicyclic complexes while the M(III) ions are both very robust. The variation in the stability of the divalent complexes is probably a consequence of the larger size of the Cr^{2+} ion, which is accommodated less readily by the cage cavity.[22] The reduction potentials of the chromium(III) macrobicyclic complexes are appreciably more negative than those for the cobalt(III) analogues ($\sim$−0.8 V) in keeping with the lower accessibility of the divalent state for Cr(III) complexes.[30] It may be related in part to geometric constraints arising in the M(II) oxidation state of the former complexes. Both sar and diamsar complexes of Cr(II) have limited stability, decomposing possibly with cleavage of the macrobicycles.[31] The Cr(III/II) redox couple is sensitive to 1,8-substituents, with potentials at −1.35 V vs. SCE $(NH_2)_2$, −1.04 V vs. SCE $(NH_3^+)_2$, −1.38 V vs. SCE $(H)_2$. This behavior parallels that observed for Co(III/II) complexes, where an extensive study has been reported, and the substituent effects have been shown to be transmitted inductively.[30,34]

The most prominent spectral differences with respect to the structurally similar $Cr(en)_3^{3+}$[24] ion are the high intensity of the low-energy spin-allowed quartet–quartet transition relative to the high-energy one ($\sim$2 fold) and the resolved splitting ($\sim$400 cm^{-1}) of the low-energy one in the cage complexes (Figure 2A). An increase in the line width of the doublet absorption, $^2E_g \leftarrow {}^4A_{2g}$ (O–O) (in O_h), relative to that of the $Cr(en)_3^{3+}$ complex is also evident. The deduced ligand field parameters for $Cr(diamsar)^{3+}$ and $Cr(sar)^{3+}$ are Dq = 2200 cm^{-1}, B = 640 cm^{-1} (62% of B_0), and C = 3300 cm^{-1} and Dq = 2200 cm^{-1}, B = 630 cm^{-1} (62% of B_0), and C = 3300 cm^{-1}, respectively.[35] Transitions to $^2T_{2g}$ and $^2T_{1g}$ are calculated on this basis to occur at $\sim$15000 and $\sim$23000 cm^{-1} for $Cr(diamsar)^{3+}$ and $Cr(sar)^{3+}$, respectively. This analysis is based on identical ligand field parameters for ^4F and ^2G free ion states and does not include the Trees corrections and is therefore of limited accuracy. The observed splitting of the low-energy quartet–quartet transition is not yet fully analyzed and understood, and at least two possibilities have to be taken into account: a splitting due to a trigonal distortion of the octahedral field or the partial superimposition of absorptions arising from transitions of $^4T_{2g}$ and $^2T_{2g} \leftarrow {}^4A_{2g}$ origins (O_h). Of these possibilities the former is probably the more likely, but a detailed spectral analysis including low-temperature and single-crystal electronic and magnetic circular dichroism (MCD) experiments is in progress to help resolve the question.[27,35]

The lack of emission from the ^2E state of $Cr(diamsar)^{3+}$ at 295 K is unusual in the context of emission from the ^2E state of $Cr(en)_3^{3+}$. If we extrapolate the curves in Figure 3 to room temperature, the phosphorescence lifetime of $Cr(diamsar)^{3+}$ and its deuterated analogue in CH_3CN, H_2O, and D_2O would be less than 10 ns. With the available experimental setup, where the weak phosphorescence of anthracene can be measured,[17] the absence of detectable phosphorescence of $Cr(diamsar)^{3+}$ at room temperature indicates that ϕ_P is less than 10^{-5}. Our spectroscopic and photophysical results are in sharp contrast to the results of similar experiments[15] with $Cr(sep)^{3+}$, $Cr(en)_3^{3+}$, and $Cr(NH_3)_6^{3+}$. The correspondence in the photochemistry for the last three complexes was believed to imply a common mechanism for the decay of the excited ^2E states of chromium(III) amines.[15] At least, this idea has to be refuted on the basis of the results of the sar-type cage complexes, which are structurally related to both $Cr(sep)^{3+}$ and $Cr(en)_3^{3+}$.[26]

The lifetimes of the excited states have been extended in minor ways; for example, in CH_3CN deuteration of the diamsar ligand lengthens the excited-state lifetime of the Cr(III) (^2E) by a factor of 4 in the temperature range where a plateau is observed. Table

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IV also shows a further increase in the lifetime of the ^{2}E state of the deuterated complex in D_2O, but neither of these effects is especially significant in this context. Also, at low temperature (77 K) the lifetimes of the crystals are shorter than those of the solutions. This could be caused by exciton trapping in defect sites.

The excited states of the sar-type hexaamine cage complexes of chromium(III) are potentially powerful oxidants ($E(^{*}\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}) \sim 0.8$ V), and Cr^{2+} is a powerful reductant in the ground state. In this context the very short lifetimes at room temperature are particularly undesirable for bimolecular reactions. A more thorough understanding of these usually short lifetimes at room temperature is needed, and possibilities for ligand modifications to increase the lifetimes are currently under investigation.

Photodecomposition and photoanation of chromium(III) complexes have been widely studied.[36–39] A central question and point of controversy is the mechanism of relaxation of the lowest lying excited doublet states and, related to this problem, the question of whether the ^{2}E or the usually slightly higher energy thermally equilibrated lowest quartet excited state ($^{4}T_{2g}{}^{0}$) or both are responsible for photosubstitution. Table III shows that photodecomposition (ϕ_{PD}) of Cr(diamsar)$^{3+}$ is very small. Cr(diamsar)$^{3+}$ is, photochemically, more inert than other chromium(III) complexes[38] by at least 2 orders of magnitude and over $\sim 10^4$-fold more stable than Cr(en)$_3{}^{3+}$. This photochemical stability of the sar-type hexaamine–chromium(III) cage complexes is not surprising since dissociative as well as associative substitution of the cage complexes is hindered. As with the cage complexes of other metal ions, we have found no evidence of an increased coordination number and that is very much expected from the known chemistry to date. In this respect, Endicott's recent proposal[15,40] that such an associative species is needed for decay of the excited doublet states of chromium(III) amines is inconsistent with the current chemistry and the small cavity of the cage. Clearly, the origin of these effects needs further examination and additional spectroscopic studies; for example, studies of the temperature dependence of the infrared and Raman spectra are presently being undertaken in the hope that they will reveal information about the decay path.

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Registry No. [Cr(diamsar)]Cl$_3$·H$_2$O, 99583-52-5; [Cr(sar)](CF$_3$SO$_3$)$_3$, 99593-38-1; [Cr(di(amH)sar)]Cl$_5$, 99583-53-6; D$_2$, 7782-39-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom parameters, and structure factors for [Cr(diamsar)]Cl$_3$·H$_2$O (18 pages). Ordering information is given on any current masthead page.

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Notes

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Nature of Intervalence Charge-Transfer Bands in Prussian Blues

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There has been considerable current interest in the electrochemistry of Prussian blue (PB)[1–4] and its related complexes.[3,5,6] In the case of PB, it has been conclusively shown that the electron-transfer reactions observed at about 0.2 V and 1.0 V vs. SCE are due to the high-spin iron (Fe^{3+}) and the low-spin iron (Fe^{II}) ions, respectively.[2c]

The large intervalence charge-transfer band, i.e. Fe^{3+}–NC–Fe^{II} → Fe^{2+}–NC–Fe^{III} was first discussed by Robin on the basis of the result using a colloidal form of PB prepared by adding a stoichiometric amount of $K_4Fe^{II}(CN)_6$ to an $Fe^{3+}(ClO_4)_3$ solution.[7] In our previous spectroelectrochemical study,[2d] it was emphasized that Berlin green, which has long been used as the conventional name for the oxidized forms of PB, is merely a partially oxidized form of PB, but that the fully oxidized form can be prepared as in the pure state by an electrochemical oxidation at SnO_2 electrodes. The color of the fully oxidized form was visually yellow-brown,[2d,i] as has long been expected.[8] Iron(3+) hexacyanoferrate(III), Prussian brown, had not until then been prepared chemically in the pure state. Ellis et al. reported an absorption spectrum at 1.1 V vs. SCE (saturated calomel electrode) where the absorption band due to the intervalence charge transfer persisted in the oxidized form of PB and about one-third of the ferrocyanide ions remained unoxidized.[1b] Similar results have been recently reported by Rosseinsky et al.[4] However, our previous paper clearly showed that no appreciable absorption band due to the intervalence charge transfer was found in the spectrum obtained at 1.4 V vs. SCE (see Figure 5 in ref 2d).

It has also been briefly described that the peak position of the intervalence charge-transfer band was remarkably shifted toward longer wavelengths not only for the partially oxidized form of PB, i.e. Berlin green, but also for the partially reduced form of PB.[2d] On the other hand, it has been reported in a recent paper by Rosseinsky that the shift of the charge-transfer band was observed for the partially oxidized form of PB, but was not observed for the partially reduced form.[4d]

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