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Pentagonal-Bipyramidal Complexes. Synthesis and Crystal Structures of Diaqua[2,6-diacetylpyridine bis(semicarbazone)]chromium(III) Hydroxide Dinitrate Hydrate and Dichloro[2,6-diacetylpyridine bis(semicarbazone)]iron(III) Chloride Dihydrate

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The planar pentadentate ligand 2,6-diacetylpyridinebis(semicarbazone), DAPSC, was synthesized and used to prepare pentagonal-bipyramidal complexes of Cr(III) and Fe(III). The two complexes were characterized by x-ray diffraction techniques. The $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$ complex crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions $a = 8.621$ (2) Å, $b = 13.854$ (5) Å, $c = 17.467$ (6) Å, and $\beta = 90.33$ (3)°. The $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ complex forms monoclinic crystals with the space group $P2_1/c$ and four molecules in the unit cell with dimensions $a = 12.317$ (1) Å, $b = 12.960$ (2) Å, $c = 14.225$ (2) Å, and $\beta = 119.82$ (1)°. The unweighted R values are 0.045 for 1982 reflections in the Cr(III) case and 0.048 for 2204 reflections in the Fe(III) case. In both complexes the cations are pentagonal bipyramids in which the planar DAPSC ligand forms the pentagonal plane and either two water molecules (in the Cr(III) complex) or two chloride ions (in the Fe(III) case) occupy the axial positions. The magnetic moments in solution were determined by NMR techniques and give 3.2 unpaired electrons in the Cr(III) complex and 3.3 unpaired electrons in the Fe(III) complex. However, in the solid state the Fe(III) complex gives a magnetic moment corresponding to 4.90 unpaired electrons. The Cr(III) cation is appreciably distorted which is expected on the basis of the Jahn–Teller theorem. There is only a very slight distortion in the Fe(III) cation, consistent with the observed moment and the ordering of the energy levels in pentagonal-bipyramidal complexes.

Pentagonal-bipyramidal (henceforth PBP) complexes of the first-row transition elements were rare when we began our investigation of planar pentadentate ligands. The only reported seven-coordinate complexes of the elements Sc to Zn were a Ti(III),[3] a Mn(II),[4] and four Fe(III)[5,6] complexes although a V(III),[7] Mn(II),[8] Ti(IV),[9] Fe(II),[10] Fe(III),[11] and Co(II)[12] complexes have been reported recently. Our approach was to utilize a planar pentadentate ligand to force the metal ion to adopt a PBP arrangement. Our earlier studies with thiosemicarbazones[13] and semicarbazones[14] suggested that 2,6-diacetylpyridine bis(semicarbazone), henceforth DAPSC, would be an ideal ligand for producing PBP complexes. Molecular models indicated that the five donor atoms of DAPSC would all be about 2.1 Å from a central metal ion. The use of DAPSC has resulted in the synthesis of PBP complexes of Fe(II),[15] Co(II),[15] Ni(II),[16] Cu(II),[16] and Zn(II)[15] while another planar pentadentate ligand has given PBP complexes of Co(II) and Zn(II).[17] The Fe(II) complex was obtained from the reaction of $FeCl_3\cdot 6H_2O$ which also yields the Fe(III) complex $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ reported herein and a third product as yet unidentified.

To extend our investigations of PBP complexes to other elements, we studied the reaction of DAPSC with $Cr(NO_3)_3\cdot 9H_2O$. Since Cr(III) and high-spin Fe(III) have about the same radius, we anticipated that a PBP Cr(III) complex similar to the Fe(III) case could be prepared. Indeed, one of the products from the reaction is a PBP Cr(III) cation $[Cr(DAPSC)(H_2O)_2]^{3+}$, the first example of a seven-coordinate chromium complex. A preliminary account of the Cr(III) complex has appeared[18] and the present report presents full details of both the Cr(III) and the Fe(III) complexes.

Experimental Section

Materials. 2,6-Diacetylpyridine was obtained from Pfaltz & Bauer and used as supplied. All other solvents and chemicals were reagent grade.

Preparation of the Ligand DAPSC. To 1.954 g of 2,6-diacetylpyridine (11.97 mmol) dissolved in 100 ml of 95% ethanol was added 2.670 g of semicarbazide hydrochloride (23.94 mmol) and 1.964 g of sodium acetate (23.94 mmol). The mixture was stirred, water was added until all of the solids dissolved, and the solution was heated. The fluffy white precipitate which formed after about 1 min was removed by filtration and washed with a dilute ethanol solution of sodium hydroxide. The yield was 2.70 g or about 81% of DAPSC. The melting point is not well defined but the compound turns brown at ~265 °C and no melting occurs below 300 °C.

Preparation of $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$. A mixture of DAPSC (0.693 g, 2.5 mmol) and $Cr(NO_3)_3\cdot 9H_2O$ (1.000 g, 2.5 mmol) in ethanol–benzene (170–20 ml) was heated and stirred. After about 1 h, the clear green-black solution was filtered, cooled

Table I. Crystal Data for $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^- \cdot H_2O$, I, and $[Fe(DAPSC)_2Cl_2]^+Cl^- \cdot 2H_2O$, II

	I	II
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	8.621 (2)	12.317 (1)
b, Å	13.854 (5)	12.960 (2)
c, Å	17.467 (6)	14.225 (2)
β, deg	90.33 (3)	119.82 (1)
Vol, Å^3	2086 (1)	1970.0 (5)
Mol wt	524.34	475.52
Z	4	4
d(calcd), g/cm^3	1.669	1.603
d(measd), g/cm^3	1.67	1.61
Crystal size, mm^3	0.14 × 0.17 × 0.31	0.10 × 0.10 × 0.25
Radiation used	Mo	Mo
μ, cm^{-1}	6.6	12.2
2θ range, deg	0–45	0–45
No. of independent reflections	2759	2594
No. of "reliable" reflections	1982	2204

overnight, and filtered again. Slow evaporation of the filtrate gave two successive crops of a crude product. One portion of the crude product was recrystallized from aqueous ethanol to give brown crystals with an infrared spectrum similar to those of other PBP complexes of DAPSC, i.e., broad absorption at 1610–1680 cm^{-1}, with ill-defined peaks at 1610, 1630–1640, and 1680 cm^{-1}. Subsequent x-ray analysis showed the brown crystals to have a composition $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^- \cdot H_2O$. Another portion of the crude solid was recrystallized from water to yield brown monoclinic crystals with space group $P2_1/n$ and a = 11.2 Å, b = 14.5 Å, c = 11.7 Å, and $\beta \approx 100°$.

Preparation of $[Fe(DAPSC)Cl_2]^+Cl^- \cdot 2H_2O$. To $FeCl_3 \cdot 6H_2O$ (0.675 g, 2.5 mmol) dissolved in water was added 2,6-diacetylpyridine (0.408, 2.5 mmol). Upon heating, the 2,6-diacetylpyridine dissolved and then semicarbazide hydrochloride (0.558 g, 5.0 mmol) was added. The color changed from orange to deep red, and the solution was left at room temperature for 24 h. Greenish black crystals of $[Fe(DAPSC)(H_2O)Cl]^+Cl^- \cdot 2H_2O$ were collected by filtration. The yield was 0.26 g or 31% based on the starting $FeCl_3 \cdot 6H_2O$. The filtrate was left for 48 h at room temperature after which 0.53 g of $[Fe(DAPSC)Cl_2]^+Cl^- \cdot 2H_2O$ (45% yield) as red needlelike crystals was obtained. After several days, reddish black platelike crystals of a third product were formed.

Magnetic Measurements. The magnetic moments of both complexes were determined in a 2% *tert*-butyl alcohol–water solution by NMR techniques.[19] The average of five measurements was 4.05 ± 0.03 μ_B for the chromium compound and 4.22 ± 0.01 μ_B for the iron complex. The magnetic moment of the iron complex in the solid state was determined to be 5.81 μ_B by the Faraday method (D.W.W. at the Ohio State University).

Data Collection and Reduction. Preliminary Weissenberg and precession photographs taken of both complexes were used to determine the space groups and approximate unit cell dimensions. The unit cell dimensions reported in Table I and the intensity data were measured using a Syntex $P\bar{1}$ diffractometer. The pertinent crystal data, together with details of the intensity measurements, are also given in Table I. A variable-speed (1 to 24°/min) θ–2θ scan technique was used for measuring the intensity. A series of four standard reflections was measured after each 96 measurements and showed only a slight variation (±3% for the chromium complex and ±1% for the iron complex) with time. The intensity was equal to (scan rate)(total scan counts − background counts)/(background to scan ratio), with σ(intensity) = [total scan counts + ((background count)/(background to scan ratio)^2)]$^{1/2}$. Reflections with an intensity greater than or equal to $m\sigma$(intensity), where m = 2.0 for Cr and 1.8 for the Fe case, were used in the analysis. The remaining reflections (flagged with a minus sign in the supplementary tables) were not used in the structure determination or refinement. Absorption corrections were deemed unnecessary because of the small value of μr (0.25–0.10 for I and 0.35–0.12 for II). Any errors due to absorption will mainly affect the thermal parameters and not significantly change the bond distances and angles.

Structure Determination and Refinement. Both structures were solved by the heavy-atom method and refined by least-squares

Table II. Final Positional and Thermal Parameters for the Nonhydrogen Atoms in $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^- \cdot H_2O$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	11 108 (9)	12 394 (5)	36 641 (4)	742 (9)	221 (3)	182 (2)	−23 (14)	102 (8)	44 (7)
O(1)	1 517 (3)	−166 (2)	3 631 (2)	83 (5)	21 (2)	30 (1)	1 (5)	26 (4)	4 (3)
O(2)	3 346 (3)	1 135 (2)	3 102 (2)	100 (5)	23 (2)	32 (1)	−6 (5)	37 (4)	4 (3)
O(3)	104 (3)	1 233 (2)	2 643 (2)	137 (5)	37 (2)	21 (1)	−34 (6)	5 (4)	5 (3)
O(4)	2 122 (3)	1 306 (2)	4 666 (2)	105 (5)	34 (2)	22 (1)	−22 (6)	0 (4)	8 (3)
N(5)	2 274 (4)	2 777 (3)	3 410 (2)	88 (6)	34 (2)	24 (2)	4 (7)	19 (5)	3 (3)
N(1)	−347 (4)	2 463 (2)	3 968 (2)	73 (6)	25 (2)	22 (1)	13 (6)	20 (5)	2 (3)
N(2)	−839 (4)	660 (2)	4 111 (2)	74 (6)	27 (2)	18 (1)	−18 (6)	10 (5)	8 (3)
C(11)	4 200 (5)	1 831 (3)	2 936 (3)	105 (8)	29 (3)	25 (2)	−9 (8)	19 (6)	6 (4)
N(7)	5 567 (4)	1 751 (3)	2 610 (2)	91 (6)	37 (2)	42 (2)	−13 (7)	56 (6)	2 (4)
N(6)	3 717 (4)	2 743 (3)	3 109 (2)	93 (6)	25 (2)	36 (2)	−11 (6)	36 (5)	6 (3)
C(19)	1 624 (5)	3 568 (3)	3 610 (3)	99 (8)	31 (3)	25 (2)	1 (7)	15 (6)	0 (4)
C(10)	2 309 (7)	4 565 (4)	3 557 (3)	167 (10)	28 (3)	56 (3)	−30 (9)	56 (9)	−14 (5)
C(5)	61 (5)	3 399 (3)	3 917 (3)	108 (8)	26 (3)	23 (2)	15 (7)	7 (6)	−1 (4)
C(4)	−963 (6)	4 130 (3)	4 129 (3)	134 (9)	27 (3)	30 (2)	24 (8)	2 (7)	−5 (4)
C(3)	−2 408 (5)	3 878 (4)	4 398 (3)	107 (8)	43 (3)	33 (2)	45 (9)	28 (7)	−3 (5)
C(2)	−2 830 (5)	2 925 (4)	4 460 (3)	93 (8)	44 (3)	29 (2)	21 (8)	21 (7)	−3 (4)
C(1)	−1 760 (5)	2 224 (3)	4 240 (2)	68 (7)	34 (3)	18 (2)	11 (7)	2 (6)	1 (4)
C(6)	−2 304 (5)	1 184 (3)	4 302 (2)	63 (6)	38 (3)	23 (2)	13 (9)	8 (5)	10 (4)
C(7)	−3 545 (5)	776 (3)	4 566 (3)	81 (7)	45 (3)	29 (2)	−33 (8)	16 (6)	15 (4)
N(3)	−895 (4)	−334 (2)	4 165 (2)	86 (6)	28 (2)	18 (1)	−18 (6)	11 (5)	1 (3)
N(4)	609 (4)	−1 663 (3)	3 917 (2)	96 (6)	25 (2)	35 (2)	13 (6)	37 (5)	3 (3)
C(8)	413 (5)	−702 (3)	3 896 (2)	99 (8)	31 (3)	18 (2)	−9 (8)	−12 (6)	3 (4)
O(5)	3 006 (4)	115 (3)	7 375 (2)	189 (7)	47 (2)	57 (2)	115 (7)	−1 (6)	−19 (4)
O(6)	788 (4)	652 (2)	7 728 (2)	116 (6)	42 (2)	39 (2)	5 (6)	10 (5)	−7 (3)
O(7)	2 598 (4)	1 638 (2)	7 413 (2)	118 (6)	37 (2)	67 (2)	2 (6)	25 (6)	−7 (3)
N(8)	2 132 (5)	807 (3)	7 503 (2)	142 (8)	41 (2)	31 (2)	29 (7)	−19 (6)	−12 (4)
O(8)	1 355 (4)	2 190 (3)	1 508 (2)	169 (7)	86 (3)	33 (2)	−43 (8)	5 (5)	21 (4)
O(9)	631 (5)	3 999 (3)	1 696 (3)	204 (9)	72 (3)	121 (3)	−56 (9)	110 (9)	8 (5)
O(10)	3 753 (4)	2 699 (3)	5 261 (3)	134 (7)	79 (3)	69 (2)	−31 (8)	26 (6)	−56 (4)
O(11)	1 630 (5)	3 338 (3)	5 595 (3)	185 (8)	87 (3)	75 (2)	42 (9)	2 (7)	−23 (5)
O(12)	3 810 (7)	4 013 (3)	5 860 (4)	471 (15)	50 (3)	135 (4)	27 (11)	−318 (13)	−38 (6)
N(9)	3 032 (5)	3 376 (3)	5 577 (3)	211 (10)	39 (3)	51 (2)	−19 (8)	−80 (8)	−14 (4)

[a] All values are $\times 10^{+4}$, except those for the Cr atom which are $\times 10^{+5}$. The estimated standard deviation is given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Final Hydrogen Atom Parameters and Distances in $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$[a]

Atom-[bonded to]	Dist, Å	x	y	z	B, Å^2
H(1)[N(3)]	0.75 (6)	−90 (7)	−30 (5)	459 (4)	12.0 (1.9)
H(2)[N(4)]	0.84 (4)	144 (5)	−189 (3)	374 (2)	3.6 (1.1)
H(3)[N(4)]	0.81 (5)	−3 (6)	−203 (3)	409 (3)	5.5 (1.3)
H(4)[N(6)]	0.86 (5)	418 (6)	326 (3)	296 (3)	5.4 (1.3)
H(5)[N(7)]	0.82 (5)	609 (5)	223 (3)	251 (3)	5.1 (1.3)
H(6)[N(7)]	0.87 (5)	591 (5)	122 (4)	240 (3)	5.4 (1.2)
H(7)[C(2)]	0.91 (4)	−375 (4)	273 (3)	466 (2)	2.3 (1.0)
H(8)[C(3)]	1.01 (5)	−316 (6)	440 (4)	455 (3)	7.1 (1.5)
H(9)[C(4)]	0.91 (4)	−73 (5)	477 (3)	414 (2)	3.9 (1.1)
H(10)[C(7)]	0.87 (4)	−345 (5)	66 (3)	505 (2)	4.3 (1.1)
H(11)[C(7)]	1.08 (5)	−439 (6)	118 (4)	424 (3)	8.1 (1.5)
H(12)[C(7)]	0.99 (5)	−384 (5)	15 (3)	432 (3)	5.5 (1.3)
H(13)[C(10)]	0.97 (5)	248 (6)	466 (4)	303 (3)	7.3 (1.5)
H(14)[C(10)]	0.91 (6)	186 (7)	501 (4)	387 (3)	8.8 (1.7)
H(15)[C(10)]	0.92 (5)	311 (6)	452 (3)	390 (3)	6.2 (1.3)
H(16)[O(3)]	0.80 (5)	−29 (6)	74 (4)	250 (3)	6.7 (1.4)
H(17)[O(3)]	0.77 (5)	58 (5)	148 (3)	233 (3)	5.8 (1.3)
H(18)[O(4)]	0.98 (5)	253 (5)	190 (4)	488 (3)	5.5 (1.3)
H(19)[O(4)]	0.70 (5)	202 (5)	97 (3)	496 (3)	4.8 (1.2)
H(20)[O(8)]	0.95 (5)	81 (6)	190 (4)	109 (3)	7.3 (1.5)
H(21)[O(8)]	0.98 (4)	89 (5)	283 (3)	158 (3)	4.1 (1.2)
H(22)[O(9)]	0.81 (7)	99 (8)	415 (5)	211 (4)	10.7 (2.1)

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance, the positional parameters ($\times 10^{+3}$), and the isotropic thermal parameter. The estimated standard deviations are in parentheses.

techniques. The heavy-atom position was determined from a Patterson function and the remaining nonhydrogen atoms in successive Fourier syntheses. The R value ($=\sum \| F_o| - |F_c\| / \sum |F_o|$) was 0.23 for the Cr complex and 0.20 for the Fe complex at the start of the least-squares refinement. After three cycles using individual isotropic thermal parameters, R was 0.10 (Cr) and 0.11 (Fe). After further refinement using anisotropic thermal parameters, R was reduced to 0.069 (Cr) and to 0.056 (Fe). A difference Fourier synthesis was used to locate the hydrogen atom positions. Three additional cycles in which the hydrogen atom contributions with fixed parameters were included in the structure factor calculation reduced R to 0.053 (Cr) and 0.048 (Fe). In the Cr case three additional cycles were calculated (all the parameters were varied) and R was reduced to 0.045. The final parameters are given in Tables II–V. Tables of observed and calculated structure amplitudes are available.[20]

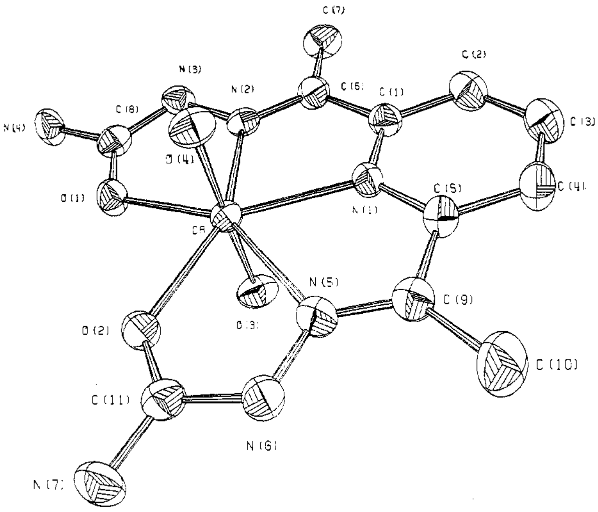

Figure 1. View of the $[Cr(DAPSC)(H_2O)_2]^{3+}$ cation, showing the atomic numbering and thermal ellipsoids.

The quantity minimized in the least-squares calculations was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = F_o/F_{low}$ if $F_o < F_{low}$, $w^{1/2} = 1$ if $F_{low} < F_o < F_{high}$, and $w^{1/2} = F_{high}/F_o$ if $F_{high} < F_o$. The values of F_{low} and F_{high} were 34.3 and 85.8 (Cr) and 8.5 and 65.0 (Fe). The goodness of fit was 1.2 and 2.0, respectively. The atomic scattering factors for the nonhydrogen atoms were taken from Hanson, Herman, Lea, and Skillman,[21] except that for Fe which was from Doyle and Turner's[22] compilation. The hydrogen atom curve was from Stewart, Davidson, and Simpson.[23] All the calculations were carried out on an IBM 370/165 using programs written or modified by G.J.P.

Results and Discussion

The crystals of both compounds consist of the pentagonal-bipyramidal $[Cr(DAPSC)(H_2O)_2]^{3+}$ or $[Fe(DAPSC)Cl_2]^+$ cations hydrogen bonded to anions and water molecules. The PBP nature of the two cations is easily seen in Figures 1 and 2 which also show the atomic numbering and thermal ellipsoids. The individual bond distances and angles in the

Table IV. Final Positional and Thermal Parameters for the Nonhydrogen Atoms in $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	1641 (1)	1290 (1)	3370 (1)	30 (1)	46 (1)	22 (1)	4 (1)	29 (1)	0 (1)
Cl(1)	1676 (1)	3096 (1)	3164 (1)	74 (2)	47 (1)	39 (1)	5 (2)	65 (2)	−3 (2)
Cl(2)	1526 (1)	−501 (1)	3366 (1)	52 (1)	48 (1)	39 (1)	5 (2)	52 (2)	8 (2)
Cl(3)	6810 (1)	1459 (2)	3668 (1)	51 (1)	108 (2)	70 (1)	4 (3)	81 (2)	28 (3)
O(1)	1382 (3)	1397 (3)	4741 (3)	39 (4)	67 (3)	30 (3)	8 (6)	36 (5)	3 (5)
O(2)	3448 (3)	1304 (3)	4678 (3)	39 (4)	70 (3)	32 (3)	8 (6)	36 (5)	0 (5)
N(1)	570 (4)	1252 (4)	1592 (3)	51 (5)	40 (3)	31 (3)	11 (7)	47 (6)	7 (6)
N(2)	−378 (4)	1316 (4)	2804 (3)	40 (4)	48 (4)	32 (3)	5 (6)	43 (6)	3 (6)
N(3)	−701 (4)	1296 (4)	3591 (4)	44 (5)	66 (4)	35 (3)	8 (7)	50 (7)	0 (6)
N(4)	69 (5)	1269 (4)	5427 (4)	72 (5)	59 (4)	37 (3)	−4 (7)	75 (7)	3 (6)
N(5)	2929 (4)	1207 (4)	2718 (4)	40 (4)	45 (4)	37 (3)	−2 (7)	40 (6)	−4 (6)
N(6)	4155 (4)	1213 (4)	3487 (4)	43 (4)	59 (4)	47 (4)	−4 (7)	54 (7)	−3 (6)
N(7)	5538 (4)	1271 (5)	5317 (4)	32 (5)	74 (4)	56 (4)	11 (7)	35 (7)	2 (7)
C(1)	−675 (5)	1275 (5)	1072 (4)	41 (5)	40 (4)	26 (4)	5 (8)	20 (7)	2 (7)
C(2)	−1375 (6)	1272 (5)	−48 (5)	55 (6)	50 (4)	33 (4)	7 (9)	27 (8)	6 (7)
C(3)	−780 (6)	1252 (5)	−640 (5)	84 (7)	42 (4)	27 (4)	−4 (9)	34 (8)	1 (7)
C(4)	529 (6)	1232 (5)	−99 (5)	89 (7)	35 (4)	36 (4)	1 (9)	71 (9)	5 (7)
C(5)	1180 (5)	1235 (4)	1020 (4)	55 (5)	33 (4)	34 (4)	−5 (8)	54 (8)	−1 (6)
C(6)	−1222 (5)	1296 (5)	1793 (5)	44 (5)	48 (4)	38 (4)	14 (8)	37 (8)	6 (7)
C(7)	−2599 (6)	1270 (7)	1360 (5)	40 (5)	145 (9)	44 (5)	16 (11)	24 (9)	−18 (11)
C(8)	321 (5)	1322 (4)	4622 (4)	52 (5)	34 (4)	35 (4)	−1 (8)	50 (7)	1 (6)
C(9)	2556 (6)	1223 (5)	1697 (5)	70 (6)	38 (4)	40 (4)	−8 (8)	76 (9)	−2 (7)
C(10)	3387 (6)	1238 (6)	1214 (6)	82 (7)	89 (6)	56 (5)	14 (12)	107 (11)	6 (10)
C(11)	4363 (5)	1265 (5)	4521 (4)	45 (5)	43 (4)	46 (4)	5 (8)	48 (8)	8 (7)
O(3)	5976 (5)	3662 (5)	2507 (4)	104 (5)	114 (6)	72 (4)	−13 (9)	58 (8)	32 (8)
O(4)	3465 (6)	4052 (7)	1896 (5)	130 (6)	214 (10)	111 (6)	−13 (13)	82 (10)	−72 (12)

[a] All values are $\times 10^{+4}$. The estimated standard deviation is given in parentheses. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Hydrogen Atom Parameters and Distances in $[Fe(DAPSC)Cl_2]^+Cl^- \cdot 2H_2O$[a]

Atom[bonded to]	Dist, Å	x	y	z	B, Å^2
H(1)[N(3)]	0.97	−159	133	337	3.5
H(2)[N(4)]	0.86	66	129	609	3.6
H(3)[N(4)]	0.90	−67	118	541	3.6
H(4)[N(6)]	1.00	488	130	336	3.6
H(5)[N(7)]	0.97	576	130	608	4.2
H(6)[N(7)]	0.84	618	121	524	4.2
H(7)[C(2)]	0.91	−223	126	−41	3.7
H(8)[C(3)]	1.01	−122	120	−146	3.9
H(9)[C(4)]	0.97	79	129	−64	3.8
H(10)[C(7)]	0.92	−268	101	193	5.5
H(11)[C(7)]	0.92	−286	184	158	5.5
H(12)[C(7)]	0.93	−316	96	70	5.5
H(13)[C(10)]	1.10	436	143	180	4.8
H(14)[C(10)]	1.08	376	48	121	4.8
H(15)[C(10)]	0.92	315	133	49	4.8
H(16)[O(3)]	0.79	526	373	235	6.6
H(17)[O(3)]	1.09	623	289	287	6.6
H(18)[O(4)]	1.17	401	420	284	9.5
H(19)[O(4)]	1.07	349	323	201	9.5

[a] The hydrogen atom is given followed by the atom to which it bonded in brackets, the corresponding bond distance, the positional parameters ($\times 10^{+3}$), and the isotropic thermal parameter.

Table VI. Intramolecular Distances (Å) in the $M(DAPSC)X_2$ Cations [M = Cr, X = H_2O; M = Fe, X = Cl]

	M = Cr(III)	M = Fe(III)
M–N(1)	2.177 (3)	2.196 (4)
M–N(2)	2.023 (3)	2.200 (5)
M–N(5)	2.397 (4)	2.203 (6)
M–O(1)	1.979 (3)	2.131 (4)
M–O(2)	2.173 (3)	2.074 (4)
M–O(3)	1.978 (3)	
M–O(4)	1.953 (3)	
M–Cl(1)		2.362 (2)
M–Cl(2)		2.325 (2)
N(1)–C(1)	1.351 (5)	1.331 (8)
N(1)–C(5)	1.347 (6)	1.355 (8)
C(1)–C(2)	1.394 (6)	1.385 (8)
C(2)–C(3)	1.375 (7)	1.364 (10)
C(3)–C(4)	1.378 (7)	1.400 (10)
C(4)–C(5)	1.395 (6)	1.381 (8)
C(5)–C(9)	1.472 (6)	1.476 (10)
C(1)–C(6)	1.464 (6)	1.481 (9)
C(6)–C(7)	1.496 (6)	1.489 (10)
C(9)–C(10)	1.506 (7)	1.488 (11)
N(2)–C(6)	1.306 (6)	1.290 (7)
N(5)–C(9)	1.280 (6)	1.288 (7)
N(2)–N(3)	1.381 (5)	1.362 (7)
N(5)–N(6)	1.354 (5)	1.355 (7)
N(3)–C(8)	1.326 (6)	1.379 (7)
N(6)–C(11)	1.366 (6)	1.364 (7)
C(8)–O(1)	1.294 (5)	1.236 (8)
C(11)–O(2)	1.248 (5)	1.254 (8)
C(8)–N(4)	1.342 (6)	1.328 (8)
C(11)–N(7)	1.315 (6)	1.321 (8)

Nonbonded Contacts in $[Cr(DAPSC)(H_2O)]^{3+}$

O(3)–O(1)	2.863 (4)	O(4)–O(1)	2.773 (4)
O(3)–O(2)	2.906 (4)	O(4)–O(2)	2.944 (4)
O(3)–N(1)	2.901 (5)	O(4)–N(1)	2.925 (4)
O(3)–N(2)	2.808 (4)	O(4)–N(2)	2.869 (4)
O(3)–N(5)	3.137 (5)	O(4)–N(5)	2.998 (5)

Nonbonded Contacts in $[Fe(DAPSC)Cl_2]^+$

Cl(1)–O(1)	3.290 (4)	Cl(2)–O(1)	3.202 (4)
Cl(1)–O(2)	3.181 (4)	Cl(2)–O(2)	3.189 (5)
Cl(1)–N(1)	3.088 (5)	Cl(2)–N(1)	3.157 (5)
Cl(1)–N(2)	3.271 (6)	Cl(2)–N(2)	3.133 (5)
Cl(1)–N(5)	3.122 (6)	Cl(2)–N(5)	3.213 (6)

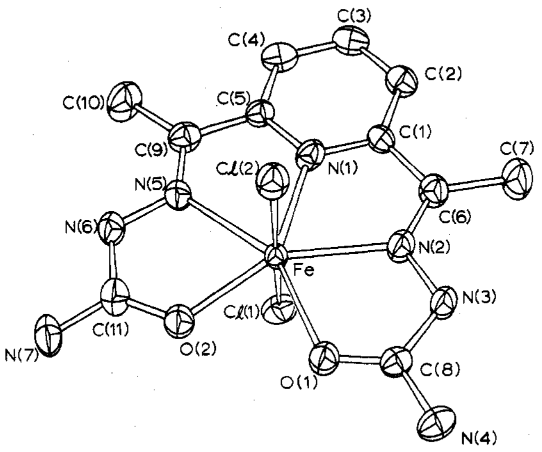

Figure 2. View of the $[Fe(DAPSC)Cl_2]^+$ cation, showing the atomic numbering and the thermal ellipsoids.

Table VII. Bond Angles in the $M(DAPSC)X_2$ Cations [M = Cr, X1 = O(3), X2 = O(4); M = Fe, X1 = Cl(1), X2 = Cl(2)]

	M = Cr	M = Fe
X1–M–X2	177.5 (1)	173.6 (1)
X1–M–O(1)	92.7 (1)	94.0 (1)
X1–M–O(2)	88.8 (1)	91.4 (1)
X1–M–N(1)	88.4 (1)	85.2 (1)
X1–M–N(2)	89.1 (1)	91.5 (1)
X1–M–N(5)	91.1 (1)	86.2 (1)
X2–M–O(1)	89.7 (1)	91.8 (1)
X2–M–O(2)	90.9 (1)	92.8 (1)
X2–M–N(1)	90.0 (1)	88.5 (1)
X2–M–N(2)	92.3 (1)	87.6 (1)
X2–M–N(5)	86.5 (1)	90.4 (1)
O(1)–M–O(2)	76.4 (1)	76.1 (2)
O(1)–M–N(2)	76.6 (1)	71.2 (2)
O(2)–M–N(5)	66.6 (1)	72.6 (2)
N(1)–M–N(5)	66.2 (1)	70.1 (2)
N(1)–M–N(2)	74.5 (1)	69.9 (2)
M–O(1)–C(8)	115.0 (3)	119.9 (4)
M–O(2)–C(11)	125.5 (3)	119.9 (4)
M–N(1)–C(1)	114.7 (3)	120.3 (4)
M–N(1)–C(5)	125.6 (3)	119.9 (4)
M–N(2)–N(3)	116.8 (2)	116.0 (4)
M–N(2)–C(6)	122.4 (3)	123.1 (4)
M–N(5)–N(6)	115.3 (3)	114.0 (4)
M–N(5)–C(9)	121.7 (3)	123.2 (4)
N(1)–C(1)–C(2)	121.8 (4)	121.7 (6)
C(1)–C(2)–C(3)	118.1 (4)	119.5 (6)
C(2)–C(3)–C(4)	120.7 (4)	119.2 (6)
C(3)–C(4)–C(5)	118.8 (4)	118.9 (6)
C(4)–C(5)–N(1)	121.0 (0)	121.0 (6)
C(5)–N(1)–C(1)	119.6 (4)	119.8 (5)
N(1)–C(1)–C(6)	114.4 (4)	114.3 (5)
N(1)–C(5)–C(9)	114.6 (4)	114.1 (5)
C(2)–C(1)–C(6)	123.8 (4)	124.0 (6)
C(4)–C(5)–C(9)	124.3 (4)	124.9 (6)
C(1)–C(6)–C(7)	122.4 (4)	122.0 (6)
C(5)–C(9)–C(10)	121.9 (4)	121.9 (6)
C(1)–C(6)–N(2)	113.6 (4)	112.3 (5)
C(5)–C(9)–N(5)	111.5 (4)	112.7 (5)
N(2)–C(6)–C(7)	123.9 (4)	125.7 (6)
N(5)–C(9)–C(10)	126.6 (4)	125.4 (6)
C(6)–N(2)–N(3)	120.6 (3)	120.9 (5)
C(9)–N(5)–N(6)	122.7 (4)	122.7 (5)
N(2)–N(3)–C(8)	109.2 (3)	112.9 (5)
N(5)–N(6)–C(11)	113.6 (4)	114.0 (5)
N(3)–C(8)–O(1)	122.4 (4)	119.4 (5)
N(6)–C(11)–O(2)	118.8 (4)	119.4 (5)
N(3)–C(8)–N(4)	118.6 (4)	115.8 (5)
N(6)–C(11)–N(7)	116.7 (4)	117.6 (6)
O(1)–C(8)–N(4)	119.0 (4)	124.8 (6)
O(2)–C(11)–N(7)	124.5 (4)	123.0 (6)

cations are tabulated in Tables VI and VII.

A comparison of the individual distances in the $[Fe(DAPSC)Cl_2]^+$ cation reveals that the ion has almost C_2 symmetry, the pseudo-twofold axis passing through the Fe–N(1)–C(3) atoms. In the DAPSC ligand only the N(1)–C(1) vs. N(1)–C(5) and the C(2)–C(3) vs. C(3)–C(4)

Table VIII. Hydrogen Bonds in $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ and $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)OH^-\cdot H_2O$

Bond D-H···A[a]	Position of A	Distances, Å D-H	H···A	D···A	Angles, deg D-H···A
	In $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$				
N(3)-H(1)···Cl(3)	$1-x, y, z$	0.97	2.22	3.128 (6)	154
N(4)-H(2)···Cl(1)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0.86	2.68	3.477 (5)	153
N(4)-H(3)···Cl(2)	$-x, -y, 1-z$	0.90	2.60	3.339 (6)	140
N(4)-H(3)···Cl(3)	$1-x, y, z$	0.90	2.87	3.527 (6)	130
N(6)-H(4)···Cl(3)	x, y, z	1.00	2.20	3.166 (6)	161
N(7)-H(5)···O(3)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	0.97	1.91	2.887 (7)	173
N(7)-H(6)···Cl(2)	$1-x, -y, 1-z$	0.84	2.68	3.294 (6)	130
N(7)-H(6)···Cl(3)	x, y, z	0.84	2.74	3.417 (6)	139
O(3)-H(16)···O(4)	x, y, z	0.79	2.02	2.812 (10)	174
O(3)-H(17)···Cl(3)	x, y, z	1.09	2.11	3.201 (7)	176
	In $[Cr(DAPSC)(H_2O)_2]^{3+}(NO_3^-)_2OH^-\cdot H_2O$				
N(3)-H(1)···N(2)	$-x, -y, 1-z$	0.75	2.75	3.384 (5)	143
N(3)-H(1)···N(3)	$-x, -y, 1-z$	0.75	2.80	3.419 (5)	142
N(4)-H(2)···O(8)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	0.84	2.33	3.154 (5)	166
N(4)-H(3)···O(11)	$-x, -y, 1-z$	0.81	2.35	3.140 (6)	167
N(6)-H(4)···O(6)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	0.86	2.09	2.930 (5)	165
N(7)-H(5)···O(7)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	0.82	2.05	2.859 (5)	171
N(7)-H(6)···O(5)	$1-x, -y, 1-z$	0.87	2.11	2.862 (5)	144
O(3)-H(16)···O(6)	$-x, -y, 1-z$	0.80	2.02	2.798 (5)	165
O(3)-H(17)···O(8)	x, y, z	0.77	1.86	2.622 (5)	168
O(4)-H(18)···O(10)	x, y, z	0.98	1.66	2.601 (5)	161
O(4)-H(19)···N(3)	$-x, -y, 1-z$	0.70	2.01	2.669 (4)	155
O(8)-H(20)···O(10)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	0.95	2.35	3.121 (6)	138
O(8)-H(20)···O(12)	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$	0.95	2.18	2.973 (7)	141
O(8)-H(21)···O(9)	x, y, z	0.98	1.65	2.605 (6)	163

[a] Donor-hydrogen···acceptor. D-H is at x, y, z and A is in the position given.

bonds show possibly significant deviations from C_2 symmetry. Of the various metal–ligand bonds, the two Fe–Cl and the two Fe–O bonds are significantly different. These differences may be related to the stronger hydrogen bonds to Cl(2) (see Table VIII) compared to Cl(1). A similar lengthening of Zn–Cl bonds has already been reported.[24] The longer Fe–Cl(2) distance is reflected in the nonbonded contacts which show a smaller variation compared to those involving Cl(1). The nonbonded contacts may in turn influence the two Fe–O bond distances.

The distortions from C_2 symmetry in the Cr cation are much more pronounced. In fact, all five bonds in the equatorial plane appear to be significantly different. However, except for the N(2)–N(3), N(3)–C(8), and C(8)–O(1) bonds, there are no significant differences in the DAPSC ligand dimensions in the two compounds. The short Cr–O(1) bond could cause the C(8)–O(1) bond to lengthen with concomitant changes in the other two bonds. Although there is extensive hydrogen bonding in the Cr case, the differences in bond lengths are much larger than could be rationalized in that way. The Cr(III) case is also more complicated since a number of peroxido complexes are known[25,26] where the coordination polyhedra are ambiguous. If the O_2 groups are considered to be bidentate,[27] then the structures are formally seven-coordinate; however, a monodentate π-bonded model has also been proposed.[28] If we exclude the peroxido compounds, no seven-coordinate complexes of chromium have been reported. The average Cr–N distance of 2.199 Å agrees well with the average Fe–N distances of 2.200 Å, as expected from other structural studies of the two ions.[29] There are four seven-coordinate Fe(III) structures reported[5,11] which can be compared with our results. Two of the structures involve macrocycles formed using diacetylpyridine (one is a refinement of the earlier iron macrocycle structure[6]) and contain very similar ligand features. The Fe–N bonds in seven-coordinate complexes average 2.325 Å in $Li_2[Fe(OH_2)EDTA]$,[5a] 2.290 Å in $Ca[Fe(OH_2)DCTA]\cdot 8H_2O$,[5b] 2.235 Å in the redetermination[11] of the 15-membered macrocycle,[6] and 2.239 Å in the corresponding 16-membered macrocycle.[11] These four values are all slightly longer than the average of 2.200 Å found in our study. In all cases the Fe–N bonds in seven-coordinate complexes are always slightly shorter than in the eight-coordinated naphthyridine complex,[30] where the Fe–N average is 2.35 Å. A more detailed comparison of our results with the two macrocycles is rather interesting. In our study the three Fe–N bonds are not significantly different which is not the case in the macrocycles. In the 15-membered macrocycle the Fe–N(of pyridine) bond is shorter (2.198 (13) Å) than the two Fe–N(of C=N) bonds [2.259 (13) and 2.248 (13) Å]. In the 16-membered case the reverse is true [Fe–N(of py) = 2.251 (10) Å and Fe–N(of C=N) = 2.237 (13) and 2.228 (11) Å]. These differences have been attributed to steric constraints within the macrocyclic ring. Since the DAPSC ligand has slightly more flexible steric requirements than the macrocycle, the pattern of Fe–N distances in the three compounds is not surprising. The Fe–O distances in the pentagonal plane which average 2.102 Å are slightly longer than in the Cr case (average is 2.076 Å) but similar to those found (2.119[5a] and

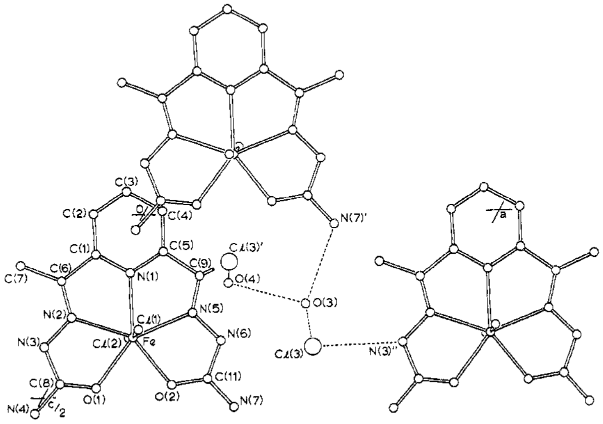

Figure 3. View down the *b* axis of the $[Fe(DAPSC)Cl_2]^+Cl^-\cdot 2H_2O$ complex, illustrating the crystal packing. Only partial contents of the unit cell are shown and C(10) has been omitted for clarity.

2.092 Å[5b]) in the other seven-coordinate complexes. The difference in the M–O and M–N distances must be a combination of differences in radii between O and N and ligand geometry. In summary the average metal–ligand distances in the two complexes are reasonable on the basis of the small amount of data available. However, the effects of ligand geometry (especially in the case of macrocyclic ligands) are very important and perturb the distances.

The two most intriguing features of these complexes, aside from the unusual PBP geometry, are the distortions in the Cr case and the spin state in the iron complex. The Cr(III) ion is a d^3 system and the solution magnetic moment of $4.05 \pm 0.03\ \mu_B$ corresponds to 3.2 unpaired electrons which is very close to the spin-only value. In the Cr(III) case, the usual energy level diagrams for PBP geometry[31] would require placing one electron in either the antibonding $x^2 - y^2$ or xy orbital. Since the two orbitals would be degenerate in a regular pentagonal bipyramid, a Jahn–Teller distortion[32] occurs to remove the degeneracy. The result is the observed asymmetry in the pentagonal plane.

The magnetic behavior of the Fe(III) complex is intriguing since the solution and solid-state moments were different. This result was unexpected but explicable in terms of the relative positions of Cl^- and H_2O in the spectrochemical series. In the solid state with the weak-field ligand Cl^- in the axial positions, the high-spin configuration is found. In solution if the chloride ions are replaced by the slightly stronger field ligand water, the splittings increase and the intermediate spin state is observed. The effect is surprising since the difference between Cl^- and H_2O in the spectrochemical series is not large and further studies are in progress. In any case, the symmetrical high-spin state found in the solid for the Fe(III) complex would not require any ligand distortion. Consequently, the Fe(III) cation is much more symmetrical than the corresponding Cr(III) case.

A final point which might be noted is the composition of the Cr(III) complex, namely, the appearance of the hydroxide ion. Both the starting materials (i.e., $Cr(NO_3)_3{\cdot}9H_2O$) as well as the solvents used contained water. Since many hydroxochromium(III) species are known,[33] the final composition is not unusual. The fact that the hydroxide ion is not bonded to the Cr(III) is a bit unusual but must reflect, to an extent, the relative solubilities of the possible solution species.

In conclusion, we see that PBP complexes of Cr(III) can be prepared and characterized. Therefore, seven-coordinate Cr(III) species are possible intermediates in substitution reactions. Furthermore, these PBP Cr(III) complexes provide the first example of a Jahn–Teller distortion in PBP complexes.

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Registry No. I, 57956-24-8; II, 59187-95-0; DAPSC, 59169-68-5; 2,6-diacetylpyridine, 1129-30-2; semicarbazide hydrochloride, 563-41-7.

Supplementary Material Available: Listing of structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(2) This paper is abstracted from a dissertation submitted by D.W.W. to the Graduate School of the University of Florida in partial fulfillment of the requirements for the Ph.D. degree in chemistry.
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