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(15) The crystal structure of the dioxygen adduct of [Fe(TpivPP)-(THT)]·2(THT) has also been determined. Crystal and refinement data: monoclinic; $P2_1/c$; $Z = 4$; $a = 16.951$ (3), $b = 18.153$ (4), $c = 25.470$ (4) Å; $\beta = 107.14$ (8)°; $R = 0.17$, $R_w = 0.15$ for 1521 reflections having $I > \sigma_I$. The best data obtainable were severely limited in extent ($2\theta_{max} = 29.2°$) and quality, and the resultant structure analysis is therefore only semiquantitative. Dioxygen adopts the end-on bent bond mode of coordination found for Fe(TpivPP)(1-Me-imid)(O_2); the Fe-S separation is 2.49 (2) Å, the $Fe-N_{porph}$ separations are in the range of 1.99–2.00 Å, and the dihedral angle between the least-squares planes of the porphinato skeleton and THT axial base is 44°.

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Pentagonal-Bipyramidal Complexes. Crystal and Molecular Structures of Chloroaqua(2,6-diacetylpyridine bis(semicarbazone))manganese(II), -iron(II), -cobalt(II), and -zinc(II) Chloride Dihydrates

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The complexes $[M(DAPSC)(Cl)(H_2O)]^+Cl^-\cdot 2H_2O$, where M = Mn, Fe, Co, or Zn and DAPSC is 2,6-diacetylpyridine bis(semicarbazone), are isomorphous. The space group is *Ia* and there are four molecules per unit cell. The cell dimensions are a = 18.322 (3), 18.096 (2), 17.968 (3), and 18.038 (11); *b* = 13.076 (5), 13.111 (4), 13.139 (8), and 13.112 (5); and *c* = 8.128 (1), 8.061 (1), 8.052 (2), and 8.066 (3) Å, with β = 99.98 (1), 99.76 (1), 99.86 (2), and 100.28 (4)°, for the Mn, Fe, Co, and Zn complexes, respectively. The structures were solved by the heavy-atom method and refined by least-squares techniques to final unweighed *R* values of 0.039, 0.040, 0.039, and 0.058 for the Mn, Fe, Co, and Zn complexes. The cation $[M(DAPSC)(Cl)(H_2O)]^+$ is a pentagonal bipyramid with the metal ion in the center. The Cl and H_2O groups are axial, with the planar pentadentate ligand DAPSC forming the equatorial plane. An unusual feature of this series is the decrease in the axial M–Cl and $M-OH_2$ distances from Mn to Zn without the expected break. However, the M–equatorial donor distances increase from Co to Zn as predicted from the splitting pattern of the d orbitals in a pentagonal-bipyramidal field. This observation is discussed in terms of the nonbonded interactions between the axial and equatorial groups. A comparison of the dimensions of the $[M(DAPSC)(Cl)(H_2O)]^+$ ions with other seven-coordinate complexes is given.

Introduction

Seven-coordinate complexes of the elements scandium to zinc are relatively rare. The first, well-characterized, seven-coordinate species were the anionic ethylenediaminetetraacetato (EDTA) complexes of Mn(II)[2] and Fe(III)[3] and the *trans*-1,2-diaminocyclohexane-*N*,*N'*-tetraacetato (DCTA) complex of Fe(III).[4] In these three complexes the hexadentate ligand and a water molecule are coordinated to the central metal ion at the vertices of a somewhat irregular polyhedron.[5] Next, pentagonal-bipyramidal complexes of Fe(III) were synthesized using a pentadentate macrocycle[6] and were characterized by x-ray diffraction techniques.[7] In the above Mn(II) and Fe(III) complexes the metal ions are high-spin d^5 species which are spherically symmetric. Therefore, there is no crystal field stabilization for any particular geometry. The first, seven-coordinate complex with a nonspherical first-row transition-metal ion was a Ti(III) species[8] which was followed by a preliminary report on the pentagonal-bipyramidal $V(CN)_7^{-4}$ ion.[9a]

Previously, however, there has been no systematic investigation in which ligands were designed to produce seven-coordinate complexes consistently. Our earlier studies with thiosemicarbazones[10] and semicarbazones[11] suggested that 2,6-diacetylpyridine bis(semicarbazone), henceforth DAPSC, would be ideally suited to forming pentagonal-bipyramidal complexes with a variety of different metal ions. Indeed, the $(M(DAPSC)(H_2O)(Cl))^+Cl^-\cdot 2H_2O$, M = Mn, Fe, Co, and Zn, complexes were found to be isomorphous and all contained a pentagonal-bipyramidal cation.[12] The crystal structure of these complexes is presented in this report with the synthesis and characterization to be presented later.[13] Following our preliminary report,[12] seven-coordinate complexes of Ti(IV),[14] Mn(II),[15-17] Fe(II),[18,19] Fe(III),[20] Co(II),[21] and Zn(II)[22] have been reported. In addition, our own studies with DAPSC have yielded pentagonal-bipyramidal complexes of Ni(II),[23] Cu(II),[23] Cr(III),[24] Fe(III),[24] and Sc(III).[25] A related planar pentadentate ligand, 2,6-diacetylpyridine bis(2'-pyridylhydrazone), has produced pentagonal-bipyramidal complexes with Co(II)[26] and Zn(II).[26]

Experimental Section

Data Collection and Reduction. Preliminary precession photographs were taken of all four complexes. The photographs indicated that the four compounds were isomorphous. The crystals are monoclinic with the space groups *Ia* or *I*2/*a* as deduced from the systematic absences ($h + k + l = 2n + 1$ and $h0l$ if $h = 2n + 1$). In each case a second crystal was used to measure the intensity data with a Syntex $P\bar{1}$ diffractometer. The pertinent crystal data together with other details of the intensity measurements are given in Table I. A variable speed (1–24°/min) θ–2θ scan technique was used in measuring the intensity. A set of 4 standard reflections was measured after every 96 measurements and was used to correct for a small change in the intensities of the standards with time. In the Mn case the standards decreased by about 10% over the period of data collection, but the other three complexes showed variations of less than ±3%. Reflections with an intensity $I \geq k\sigma(I)$, see Table I for the various *k* values, were considered reliable and were used in the analysis. The remaining relections were flagged with a minus sign and were not used in the structure determination or refinement. No absorption corrections were made because of the small size of the crystals and the small value of μ.

Structure Determination and Refinement. The structure of the zinc complex was determined first. The intensity distribution for all four complexes was midway between the centric and acentric cases, suggesting that the correct space group was *Ia*. The *y* coordinate for the zinc atom was determined from the Patterson function, and the *x* and *y* coordinates were chosen to be $^1/_4$. The Fourier synthesis based

Table I. Crystallographic Data for the Isomorphic Complexes $[M(DAPSC)(H_2O)Cl]Cl\cdot 2H_2O$

	Mn	Fe	Co	Zn
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Ia*	*Ia*	*Ia*	*Ia*
a, Å	18.322 (3)	18.096 (2)	17.968 (3)	18.038 (11)
b, Å	13.076 (5)	13.111 (4)	13.139 (8)	13.112 (5)
c, Å	8.128 (1)	8.061 (1)	8.052 (2)	8.066 (3)
β, deg	99.98 (1)	99.76 (1)	99.86 (2)	100.28 (4)
Volume, $Å^3$	1917.9 (8)	1884.8 (6)	1872.9 (13)	1877.1 (6)
Mol wt, amu	457.18	458.08	461.17	467.61
Z	4	4	4	4
ρ(calcd), g/cm^3	1.584	1.615	1.636	1.655
ρ(obsd), g/cm^3	1.59	1.62	1.63	1.63
Crystal size	0.19 × 0.27 × 0.29	0.07 × 0.24 × 0.28	0.09 × 0.09 × 0.18	0.20 × 0.23 × 0.26
Radiation used	Mo	Mo	Mo	Cu
μ, cm^{-1}	10.4	11.4	12.8	13.5
2θ range, deg	0-35	0-50	0-50	0-110
No. of measd reflections	1271	1675	1671	1186
No. of reliable reflections	1200	1565	1524	1177
$k(k\sigma)$	2.00	2.00	1.50	1.50
F(low)	8.0	6.0	6.0	6.0
F(high)	32.0	24.0	24.0	24.0
Goodness of fit	1.07	0.87	1.02	1.47

on phases determined by the zinc atom showed four large peaks which could be interpreted as two chlorine atoms and two chlorine atoms generated by the pseudo-twofold axis. A Fourier synthesis calculated using phases determined by the zinc atom and one axial chlorine atom suggested that the atom trans to chlorine was not a chlorine, further support for the choice of *Ia* as the space group. The chlorine and the remaining nonhydrogen atoms were located easily in successive Fourier syntheses. The *R* value, $R = \sum||F_o| - |F_c||/\sum|F_o|$, was 0.17 at this point. Three least-squares cycles using individual isotropic thermal parameters reduced *R* to 0.11. A difference Fourier synthesis was calculated to locate the two waters of hydration. Only O(3), one of the water molecules, was included in the refinement at this point since the peak height of O(5), the other water molecule, was somewhat lower. Three least-squares cycles using anisotropic thermal parameters for the zinc and two chlorine atoms reduced *R* to only 0.10. The water molecule, O(5), was now included and three least-squares cycles using anisotropic thermal parameters for all the atoms reduced *R* to 0.063. A difference Fourier synthesis was now calculated and revealed unambiguous positions for 11 of the 21 hydrogen atoms. The 11 hydrogen atoms were now included in the structure factor calculation but their parameters were not varied. Three additional least-squares cycles reduced *R* to 0.058. In the final least-squares cycle the shifts in all the parameters were less than one-tenth of an esd so that the refinement was terminated.

The similarity of the cell constants and structure amplitudes for the Co(II) and Zn(II) complexes suggested that the two complexes were isomorphous. The Patterson function for the cobalt complex was essentially identical with that of the zinc complex. Therefore, the zinc parameters after the isotropic refinement were used as the starting parameters for the cobalt complex refinement. Three least-squares cycles using isotropic thermal parameters reduced *R* to 0.088, and then three cycles with anisotropic thermal parameters reduced *R* to 0.046. A difference Fourier synthesis revealed 13 of the hydrogen atoms which were then included in the calculations but were not refined. After three additional least-squares cycles, *R* was reduced to 0.039 and the refinement was terminated.

The Fe(II) and Mn(II) complexes used the Co(II) parameters as the starting point for the refinement. The refinement procedures were similar to the Co(II) case and gave *R* values of 0.040 for the Fe(II) and 0.039 for the Mn(II) complex. A difference Fourier synthesis using the Mn(II) data was used to locate all 21 hydrogen atoms.

The scattering factors were taken from the usual sources.[27] The details of the refinement are similar to those given previously.[10,11,26] All calculations were carried out on an IBM-370/165 using local programs written or modified by G.J.P.

The final positional and thermal parameters for the nonhydrogen atoms are given in Table II. The parameters for the hydrogen atoms in the Mn(II) complex are listed in Table III and are very similar to the values found in the other complexes. The bond distances and angles involving the nonhydrogen atoms are given in Tables IV and V and tables of observed and calculated structure amplitudes are available.[28]

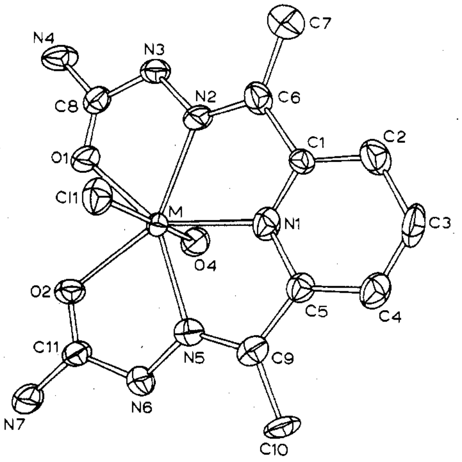

Figure 1. $[M(DAPSC)(H_2O)Cl]^+$ cations (M = Mn, Fe, Co, Zn). The Co(II) coordinates were used for this illustration. The Mn(II), Fe(II), and Zn(II) cations are essentially identical with the Co(II) cation. Hydrogen atoms are omitted for clarity.

Results and Discussion.

The complexes $[M(DAPSC)(H_2O)(Cl)]^+Cl^-\cdot 2H_2O$, M = Mn, Fe, Co, and Zn, form an isomorphous series containing a pentagonal-bipyramidal cation. The cation is illustrated in Figure 1 together with the atomic numbering and thermal ellipsoids. Since the complexes are isomorphous, packing effects will be relatively constant. Therefore, any differences in the dimensions of the cations should reflect changes in the interaction between the metal ion and the ligand. Consequently, in this series trends in the metal–ligand interaction in the unusual seven-coordinate pentagonal-bipyramidal geometry, henceforth PBP, can be observed.

There are five reported seven-coordinate Mn(II) structures,[5,15-17] which can be compared with our results. The equatorial Mn–N distances average 2.295 Å in our DAPSC complex compared with 2.267 Å in the 2,6-diacetylpyridine bis(picolinoylhydrazone), henceforth H_2DIP, complex,[17] 2.237 Å in the 15-membered N_3O_2 macrocycle,[16b] 2.26 Å in the 15-membered N_5 macrocycle,[15] 2.373 Å in the 17-membered N_5 macrocycle,[16a] and 2.377 Å in the EDTA complex.[5] The equatorial Mn–O distances average 2.221 Å for the DAPSC complex, 2.244 Å for the H_2DIP case,[17] 2.283 Å in the N_3O_2 macrocycle,[16b] and 2.240 Å in the EDTA structure.[5] If we neglect the Mn–EDTA complex which appears to be closer to a capped trigonal prism than PBP, we see that for the N_3O_2

Table II. Final Positional and Thermal Parameters (×10^4) for the Nonhydrogen Atoms in the [M(DAPSC)(Cl)(H_2O)]Cl·$2H_2O$ Complexes with M = Mn, Fe, Co, and Zn[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	2500[b]	10507 (1)	2500[b]	16 (1)	22 (1)	116 (2)	−1 (1)	32 (1)	2 (3)
Fe	2500[b]	10457 (1)	2500[b]	14 (1)	20 (1)	100 (1)	−1 (1)	27 (1)	2 (2)
Co	2500[b]	10437 (1)	2500[b]	13 (1)	17 (1)	91 (1)	−2 (1)	26 (1)	1 (2)
Zn	2500[b]	10452 (1)	2500[b]	14 (1)	27 (1)	70 (2)	−2 (1)	1 (2)	1 (3)
Cl1	3420 (2)	10355 (2)	5199 (4)	25 (1)	38 (2)	134 (5)	1 (2)	9 (3)	7 (5)
	3420 (1)	10320 (1)	5191 (3)	22 (1)	34 (1)	118 (3)	2 (1)	4 (2)	2 (3)
	3401 (1)	10310 (2)	5187 (3)	23 (1)	34 (1)	120 (4)	−1 (2)	9 (2)	−4 (3)
	3385 (2)	10337 (3)	5150 (4)	15 (1)	29 (2)	48 (5)	2 (2)	−21 (4)	−4 (5)
Cl2	342 (2)	5668 (2)	4171 (4)	21 (1)	49 (2)	234 (5)	9 (2)	62 (4)	14 (5)
	352 (1)	5698 (2)	4170 (3)	19 (1)	44 (1)	216 (3)	4 (1)	57 (2)	22 (3)
	345 (2)	5724 (2)	4162 (3)	18 (1)	42 (1)	218 (4)	2 (2)	68 (3)	18 (4)
	339 (2)	5692 (3)	4144 (5)	11 (1)	40 (2)	136 (7)	6 (3)	22 (4)	19 (7)
O1	3118 (4)	11762 (5)	1540 (10)	23 (2)	27 (5)	201 (13)	−5 (6)	73 (10)	11 (14)
	3103 (3)	11749 (4)	1635 (7)	23 (2)	30 (3)	163 (9)	−1 (4)	50 (6)	1 (9)
	3078 (4)	11735 (5)	1660 (8)	20 (2)	27 (4)	174 (10)	−4 (5)	50 (8)	1 (11)
	3084 (5)	11744 (7)	1607 (13)	14 (3)	26 (6)	100 (16)	2 (7)	26 (12)	1 (16)
O2	1882 (4)	11778 (5)	3441 (10)	22 (3)	30 (5)	175 (14)	−12 (6)	72 (10)	1 (13)
	1937 (3)	11745 (4)	3445 (7)	19 (2)	27 (3)	154 (9)	−4 (4)	56 (6)	−4 (9)
	1952 (3)	11740 (5)	3473 (8)	21 (2)	31 (4)	151 (10)	−6 (5)	69 (8)	−1 (11)
	1922 (5)	11754 (6)	3449 (12)	18 (4)	22 (6)	86 (16)	−9 (7)	28 (13)	2 (16)
O3	2341 (5)	13774 (6)	2509 (13)	59 (4)	38 (5)	195 (14)	2 (7)	104 (12)	12 (17)
	2386 (4)	13776 (4)	2572 (10)	59 (3)	38 (4)	180 (10)	7 (5)	116 (9)	9 (12)
	2376 (5)	13777 (5)	2606 (12)	53 (3)	53 (4)	165 (12)	7 (6)	110 (10)	−18 (15)
	2356 (7)	13776 (7)	2590 (14)	48 (6)	35 (6)	101 (16)	−9 (10)	69 (15)	2 (19)
O4	1726 (4)	10673 (5)	88 (10)	26 (2)	46 (5)	126 (13)	−6 (5)	8 (9)	8 (13)
	1758 (3)	10642 (4)	133 (7)	22 (2)	43 (3)	121 (9)	−9 (4)	12 (6)	4 (9)
	1744 (4)	10651 (5)	172 (8)	20 (2)	41 (4)	127 (11)	−6 (5)	18 (8)	1 (11)
	1752 (5)	10654 (7)	177 (11)	17 (3)	37 (6)	74 (15)	2 (7)	−4 (11)	−7 (15)
O5	4933 (5)	5774 (7)	1035 (11)	28 (3)	76 (6)	276 (17)	−27 (7)	96 (12)	7 (17)
	4956 (4)	5799 (5)	1077 (9)	22 (3)	68 (4)	260 (12)	−29 (6)	88 (9)	17 (12)
	4947 (5)	5802 (7)	1062 (11)	22 (3)	76 (5)	262 (15)	−30 (7)	113 (11)	22 (15)
	4933 (6)	5788 (9)	1060 (15)	19 (4)	63 (7)	202 (23)	−18 (9)	50 (15)	8 (22)
N1	2426 (5)	8746 (5)	2313 (12)	21 (2)	28 (4)	125 (14)	−3 (8)	12 (9)	−20 (16)
	2449 (4)	8767 (4)	2344 (9)	17 (2)	26 (3)	113 (9)	−3 (5)	17 (6)	−15 (11)
	2447 (5)	8775 (4)	2340 (11)	24 (2)	21 (3)	103 (10)	−7 (6)	32 (7)	6 (13)
	2444 (6)	8756 (6)	2315 (14)	12 (3)	19 (5)	55 (17)	−4 (10)	4 (11)	−8 (19)
N2	3418 (5)	9837 (7)	1209 (11)	25 (3)	27 (6)	134 (15)	6 (7)	47 (10)	−1 (14)
	3427 (3)	9855 (5)	1277 (7)	20 (2)	26 (4)	128 (10)	−3 (4)	37 (7)	−2 (10)
	3430 (4)	9868 (6)	1308 (9)	20 (3)	26 (5)	125 (12)	−5 (6)	47 (9)	12 (12)
	3420 (6)	9838 (9)	1235 (13)	15 (4)	18 (7)	72 (18)	−4 (8)	15 (13)	1 (18)
N3	3885 (6)	10537 (6)	746 (14)	22 (3)	34 (6)	183 (14)	−4 (7)	78 (10)	26 (15)
	3901 (5)	10571 (5)	800 (11)	21 (2)	26 (4)	187 (9)	−7 (4)	68 (7)	8 (10)
	3888 (6)	10585 (6)	838 (13)	17 (2)	26 (5)	173 (11)	−2 (6)	64 (9)	−3 (12)
	3886 (9)	10562 (8)	787 (19)	19 (4)	19 (7)	94 (18)	−4 (9)	32 (13)	7 (18)
N4	4097 (5)	12236 (8)	276 (13)	31 (4)	31 (7)	259 (21)	−7 (8)	49 (13)	66 (18)
	4076 (4)	12274 (6)	373 (9)	31 (3)	34 (5)	235 (15)	−7 (6)	65 (9)	58 (13)
	4045 (5)	12288 (7)	424 (11)	19 (3)	34 (6)	244 (18)	−1 (7)	80 (12)	47 (15)
	4054 (7)	12256 (10)	370 (17)	26 (5)	33 (8)	159 (30)	2 (10)	45 (19)	71 (24)
N5	1506 (4)	9872 (6)	3492 (10)	17 (2)	26 (6)	129 (14)	−3 (6)	35 (9)	−14 (13)
	1530 (3)	9884 (5)	3523 (7)	14 (2)	27 (4)	112 (10)	1 (4)	26 (7)	−15 (10)
	1525 (4)	9890 (6)	3533 (9)	15 (2)	32 (5)	107 (12)	−2 (5)	27 (9)	−4 (12)
	1506 (5)	9877 (8)	3493 (12)	9 (3)	20 (7)	46 (16)	−4 (8)	−4 (11)	−8 (17)
N6	1046 (5)	10584 (6)	4057 (12)	26 (3)	24 (7)	174 (16)	−6 (7)	33 (11)	−20 (14)
	1085 (4)	10605 (5)	4075 (8)	21 (2)	29 (4)	136 (11)	−7 (4)	37 (8)	−19 (10)
	1080 (5)	10622 (6)	4058 (10)	23 (3)	26 (5)	156 (13)	3 (6)	52 (10)	−21 (12)
	1062 (6)	10609 (8)	4026 (15)	8 (4)	28 (8)	96 (20)	−4 (8)	12 (13)	−18 (18)
N7	928 (5)	12280 (8)	4716 (13)	24 (3)	49 (7)	190 (20)	13 (8)	97 (13)	−16 (18)
	984 (4)	12301 (5)	4730 (9)	26 (2)	37 (5)	179 (13)	3 (5)	72 (9)	−30 (12)
	997 (5)	12306 (7)	4742 (11)	30 (3)	30 (6)	223 (16)	−14 (7)	87 (11)	−21 (14)
	968 (6)	12291 (9)	4725 (15)	14 (4)	25 (7)	137 (24)	6 (9)	35 (15)	−28 (21)
C1	2976 (5)	8219 (7)	1764 (13)	24 (3)	13 (6)	118 (16)	−1 (7)	16 (12)	2 (15)
	2996 (4)	8241 (5)	1787 (9)	24 (2)	21 (4)	93 (10)	4 (4)	21 (7)	−20 (9)
	3003 (5)	8251 (6)	1802 (10)	12 (3)	25 (5)	83 (12)	3 (5)	4 (9)	−18 (11)
	2984 (7)	8231 (9)	1784 (15)	14 (4)	18 (8)	42 (19)	−3 (9)	−16 (15)	−3 (18)
C2	2977 (6)	7152 (8)	1733 (14)	29 (4)	38 (8)	138 (19)	−9 (8)	25 (14)	−24 (18)
	2997 (4)	7172 (6)	1743 (10)	28 (2)	28 (5)	134 (13)	−3 (5)	34 (9)	−2 (12)
	2998 (5)	7197 (7)	1762 (12)	30 (3)	27 (6)	133 (16)	11 (7)	36 (11)	−1 (14)
	2995 (7)	7173 (11)	1757 (16)	16 (5)	29 (10)	54 (21)	−1 (11)	8 (16)	−11 (21)
C3	2401 (7)	6637 (7)	2271 (16)	37 (4)	31 (6)	138 (21)	−6 (9)	21 (15)	7 (21)
	2428 (5)	6660 (5)	2301 (11)	35 (3)	24 (4)	134 (13)	−13 (6)	23 (9)	16 (14)
	2408 (6)	6684 (7)	2324 (14)	34 (3)	19 (5)	146 (16)	−20 (8)	26 (12)	−17 (17)
	2412 (9)	6670 (9)	2281 (17)	30 (5)	21 (7)	60 (22)	−8 (13)	−29 (17)	2 (24)
C4	1834 (6)	7190 (9)	2858 (14)	28 (4)	28 (8)	138 (19)	−2 (8)	35 (14)	7 (18)
	1862 (4)	7204 (6)	2886 (10)	21 (2)	21 (5)	132 (13)	−5 (5)	24 (9)	11 (12)
	1853 (6)	7211 (8)	2889 (12)	31 (3)	25 (6)	128 (16)	−10 (7)	40 (11)	20 (14)
	1839 (7)	7199 (10)	2863 (17)	19 (5)	21 (8)	68 (22)	−11 (9)	−2 (17)	−5 (20)

Table II (*Continued*)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C5	1874 (5)	8247 (8)	2842 (13)	19 (3)	34 (7)	95 (17)	−11 (7)	20 (12)	5 (16)
	1895 (4)	8260 (5)	2883 (9)	14 (2)	31 (4)	89 (11)	−2 (5)	4 (8)	2 (10)
	1877 (5)	8273 (7)	2882 (11)	18 (3)	26 (5)	107 (14)	−1 (6)	7 (10)	7 (13)
	1872 (7)	8260 (9)	2856 (14)	14 (4)	18 (8)	24 (18)	−3 (9)	−11 (14)	6 (18)
C6	3553 (6)	8869 (9)	1207 (14)	27 (4)	34 (8)	119 (20)	1 (9)	12 (13)	−48 (18)
	3582 (4)	8897 (6)	1222 (10)	22 (2)	25 (5)	119 (12)	−2 (5)	15 (8)	−15 (11)
	3583 (5)	8910 (7)	1221 (12)	25 (3)	22 (5)	104 (14)	4 (6)	27 (10)	−7 (14)
	3569 (7)	8873 (11)	1226 (16)	11 (4)	30 (10)	52 (21)	−4 (10)	14 (15)	−48 (21)
C7	4251 (7)	8409 (10)	660 (17)	23 (5)	55 (9)	294 (25)	28 (10)	71 (17)	11 (23)
	4274 (5)	8463 (7)	667 (12)	20 (3)	37 (6)	272 (16)	8 (6)	56 (11)	−37 (15)
	4270 (7)	8472 (9)	615 (15)	27 (4)	48 (7)	233 (19)	3 (8)	46 (14)	−26 (18)
	4270 (8)	8443 (12)	686 (22)	11 (5)	40 (10)	188 (33)	21 (10)	26 (19)	−7 (27)
C8	3662 (6)	11551 (8)	882 (14)	21 (4)	47 (8)	112 (21)	−1 (8)	28 (16)	−11 (19)
	3652 (4)	11570 (5)	945 (9)	17 (2)	37 (4)	129 (12)	−1 (5)	37 (9)	−10 (11)
	3633 (5)	11569 (7)	983 (11)	17 (3)	33 (5)	114 (15)	−9 (6)	17 (11)	−1 (14)
	3634 (7)	11546 (10)	936 (15)	12 (5)	33 (10)	49 (23)	−8 (11)	−6 (17)	−2 (23)
C9	1322 (5)	8921 (8)	3455 (12)	20 (3)	40 (7)	107 (17)	−12 (7)	24 (12)	−8 (16)
	1334 (4)	8932 (6)	3512 (9)	19 (2)	32 (4)	99 (11)	−10 (5)	31 (8)	2 (11)
	1327 (5)	8948 (7)	3510 (11)	18 (3)	36 (5)	96 (14)	−12 (6)	16 (10)	9 (13)
	1311 (6)	8948 (10)	3467 (14)	9 (4)	24 (9)	32 (18)	−3 (9)	−22 (13)	−15 (20)
C10	627 (7)	8489 (9)	3942 (16)	27 (4)	47 (7)	204 (21)	−27 (9)	84 (15)	11 (20)
	631 (5)	8537 (6)	4012 (11)	22 (3)	42 (5)	174 (13)	−16 (6)	65 (10)	7 (12)
	626 (6)	8548 (8)	4039 (13)	17 (3)	35 (6)	168 (16)	−8 (7)	59 (12)	40 (15)
	620 (9)	8538 (12)	3949 (19)	20 (5)	31 (10)	121 (26)	−21 (11)	36 (19)	8 (25)
C11	1331 (6)	11575 (8)	4056 (14)	21 (4)	25 (7)	156 (19)	3 (8)	10 (14)	−23 (18)
	1374 (4)	11573 (5)	4064 (9)	17 (2)	27 (4)	115 (12)	2 (5)	23 (9)	−12 (11)
	1384 (5)	11578 (7)	4101 (11)	14 (3)	28 (5)	105 (15)	−3 (6)	21 (11)	5 (14)
	1355 (7)	11590 (10)	4044 (16)	14 (5)	25 (10)	46 (23)	−3 (10)	−5 (17)	12 (22)

[a] For each atom the coordinates correspond to the order of the metal atoms. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Coordinates chosen to define the origin.

Table III. Hydrogen Atom Parameters and Distances in $[Mn(DAPSC)(Cl)(H_2O)]Cl\cdot 2H_2O$[a]

Atom [bonded to]	Dist, Å	x	y	z	B, Å^2
H1[N4]	1.10	393	1299	68	4.8
H2[N4]	1.01	455	1204	−22	4.8
H3[N3]	1.01	431	1043	10	3.6
H4[N7]	0.94	52	1209	523	4.6
H5[N7]	0.91	113	1291	490	4.6
H6[N6]	1.05	65	1039	481	3.9
H7[C7]	1.08	435	885	−40	5.3
H8[C7]	0.98	450	792	149	5.3
H9[C7]	1.07	480	869	113	5.3
H10[C10]	1.08	42	879	501	4.5
H11[C10]	0.94	26	882	316	4.5
H12[C10]	0.89	53	785	422	4.5
H13[C2]	1.09	347	674	151	4.0
H14[C3]	1.01	252	588	237	4.3
H15[C4]	1.13	148	668	352	4.0
H16[O3]	0.85	239	1313	256	5.6
H17[O3]	0.93	277	1400	216	5.6
H18[O4]	1.01	193	1057	−98	4.4
H19[O4]	0.97	133	1114	−38	4.4
H20[O5]	0.88	511	597	14	6.0
H21[O5]	0.84	449	560	73	6.0

Table IV. Bond Distances (in Å) in the Four $[M(DAPSC)(H_2O)Cl]^+$ Cations

	Mn	Fe	Co	Zn
M–Cl1	2.532 (3)	2.507 (2)	2.476 (2)	2.433 (3)
M–O1	2.212 (7)	2.192 (5)	2.165 (6)	2.184 (9)
M–O2	2.220 (7)	2.175 (5)	2.186 (6)	2.207 (9)
M–O4	2.222 (8)	2.153 (6)	2.137 (6)	2.121 (9)
M–N1	2.310 (7)	2.220 (5)	2.189 (5)	2.229 (8)
M–N2	2.303 (9)	2.229 (6)	2.196 (7)	2.247 (10)
M–N5	2.273 (8)	2.195 (6)	2.186 (7)	2.222 (10)
O1–C8	1.241 (13)	1.240 (9)	1.235 (11)	1.239 (16)
O2–C11	1.231 (13)	1.230 (9)	1.233 (10)	1.224 (16)
N1–C1	1.358 (13)	1.345 (9)	1.345 (11)	1.325 (16)
N1–C5	1.335 (14)	1.335 (10)	1.352 (12)	1.357 (16)
N2–N3	1.351 (13)	1.371 (10)	1.347 (12)	1.358 (17)
N2–C6	1.290 (14)	1.290 (10)	1.293 (12)	1.294 (18)
N3–C8	1.398 (13)	1.398 (10)	1.383 (12)	1.381 (18)
N4–C8	1.348 (15)	1.331 (11)	1.326 (12)	1.331 (18)
N5–N6	1.385 (12)	1.365 (9)	1.363 (11)	1.367 (15)
N5–C9	1.288 (12)	1.297 (10)	1.287 (12)	1.267 (17)
N6–C11	1.397 (13)	1.373 (9)	1.368 (11)	1.389 (17)
N7–C11	1.350 (15)	1.351 (10)	1.337 (12)	1.331 (17)
C1–C2	1.395 (14)	1.402 (10)	1.385 (12)	1.387 (18)
C1–C6	1.488 (15)	1.495 (10)	1.491 (12)	1.481 (18)
C2–C3	1.385 (16)	1.367 (12)	1.395 (15)	1.369 (21)
C3–C4	1.413 (16)	1.395 (12)	1.385 (15)	1.395 (21)
C4–C5	1.385 (15)	1.386 (11)	1.396 (12)	1.392 (18)
C5–C9	1.492 (14)	1.497 (10)	1.480 (12)	1.503 (17)
C6–C7	1.545 (18)	1.510 (12)	1.516 (12)	1.517 (20)
C9–C10	1.507 (16)	1.489 (11)	1.512 (14)	1.471 (20)

donor set the Mn–N bond distance increases as the Mn–O bond length decreases. The metal ion appears to adjust to variations in the electron density in the equatorial plane by changing the metal donor distances. In essence the metal distances change so that an approximately constant charge is maintained on the metal ion.[29] The interplay between the axial and equatorial distances is somewhat more complicated and difficult to explain. The closely related DAPSC and H_2DIP complexes are difficult to compare because of the disorder in the axial Cl and H_2O groups in the latter structure. A comparison of the 15-membered N_3O_2 macrocycle with the 17-membered N_5 case (the axial ligands are N-bonded thiocyanates in both complexes) suggests that decreasing the axial distances increases the equatorial ones. However, because of the difference in the ring size the changes may not be related. Consequently, any observations regarding the interrelation between the axial and equatorial distances would be speculative.

The crystal structures of three PBP Fe(II) complexes[18,19] and four PBP Fe(III)[5,20,24] complexes have been reported in the literature. In the $Fe(DAPSC)(Cl)(H_2O)^+$ cation the axial Fe–Cl bond of 2.507 (2) Å is longer than in the $FeCl_2(DAPSC)^+$ complex, 2.344 Å, by slightly more than the change in the ionic radius.[30] The fact that the axial distances appear to reflect changes in the ion size more readily than the equatorial distances has been noted.[16b] In the Fe(II)–DAPSC

Table V. Bond Angles (deg) in the four $[M(DAPSC)(H_2O)(Cl)]^+$ Cations

	Mn	Fe	Co	Zn
Cl1-M-O1	93.4 (2)	92.1 (1)	92.8 (2)	93.3 (3)
Cl1-M-O2	93.6 (2)	91.9 (1)	90.4 (2)	91.1 (2)
Cl1-M-O4	177.8 (2)	176.4 (2)	176.2 (2)	176.2 (3)
Cl1-M-N1	90.1 (2)	89.6 (2)	90.0 (2)	90.7 (3)
Cl1-M-N2	86.3 (2)	85.3 (2)	85.8 (2)	87.4 (3)
Cl1-M-N5	96.8 (2)	96.1 (2)	95.3 (2)	96.2 (3)
O1-M-O2	83.6 (3)	78.4 (2)	76.4 (2)	78.5 (3)
O1-M-O4	84.5 (3)	84.3 (2)	83.6 (2)	83.1 (4)
O1-M-N1	138.1 (3)	140.5 (2)	141.8 (3)	140.4 (4)
O1-M-N2	70.3 (3)	71.4 (2)	71.9 (3)	71.9 (4)
O1-M-N5	152.5 (3)	149.0 (2)	146.8 (3)	148.2 (4)
O2-M-O4	86.8 (3)	87.9 (2)	87.3 (2)	86.8 (3)
O2-M-N1	137.8 (3)	141.0 (2)	141.7 (3)	140.9 (4)
O2-M-N2	153.9 (3)	149.5 (2)	147.8 (3)	150.2 (4)
O2-M-N5	70.3 (3)	71.5 (2)	71.4 (2)	71.1 (3)
O4-M-N1	91.1 (3)	92.8 (2)	93.7 (3)	93.0 (4)
O4-M-N2	92.3 (2)	92.9 (2)	94.5 (3)	92.8 (4)
O4-M-N5	85.4 (3)	87.3 (2)	86.9 (2)	86.2 (4)
N1-M-N2	68.3 (3)	69.4 (2)	70.3 (3)	68.9 (4)
N1-M-N5	67.5 (3)	69.6 (2)	70.4 (3)	69.9 (4)
N2-M-N5	135.7 (3)	139.0 (2)	140.7 (3)	138.7 (4)
M-O1-C8	119.0 (7)	118.4 (5)	117.8 (6)	116.9 (8)
M-O2-C11	118.8 (7)	118.0 (5)	117.9 (6)	118.7 (8)
M-N1-C1	119.3 (7)	120.3 (5)	120.2 (6)	120.9 (8)
M-N1-C5	120.3 (7)	120.3 (5)	119.7 (6)	119.0 (8)
C1-N1-C5	120.2 (9)	119.3 (6)	120.0 (7)	120.0 (10)
M-N2-N3	114.7 (7)	115.8 (5)	115.6 (6)	114.3 (9)
M-N2-C6	122.0 (7)	123.0 (5)	122.7 (6)	121.6 (9)
N3-N2-C6	122.2 (9)	120.5 (7)	121.3 (8)	122.9 (12)
N2-N3-C8	114.4 (9)	113.1 (7)	113.8 (9)	113.7 (12)
M-N5-N6	116.3 (6)	116.0 (4)	115.9 (5)	115.5 (7)
M-N5-C9	124.5 (6)	124.2 (5)	123.3 (6)	124.0 (8)
N6-N5-C9	119.0 (8)	119.5 (6)	120.5 (7)	120.3 (10)
N5-N6-C11	112.0 (8)	113.1 (6)	113.8 (7)	114.2 (10)
N1-C1-C2	121.1 (9)	121.7 (6)	121.1 (8)	122.6 (11)
N1-C1-C6	114.6 (9)	114.0 (6)	113.7 (7)	114.0 (11)
C2-C1-C6	124.2 (9)	124.3 (6)	125.1 (8)	123.4 (11)
C1-C2-C3	118.5 (10)	118.6 (7)	118.5 (9)	117.6 (12)
C2-C3-C4	120.1 (11)	119.8 (8)	120.4 (9)	121.4 (13)
C3-C4-C5	117.7 (10)	118.4 (7)	119.0 (9)	117.4 (12)
N1-C5-C4	122.4 (10)	122.2 (7)	121.0 (8)	121.1 (11)
N1-C5-C9	114.5 (9)	114.0 (6)	113.9 (7)	114.3 (10)
C4-C5-C9	123.1 (9)	123.7 (7)	125.1 (8)	124.6 (11)
N2-C6-C1	114.3 (9)	112.3 (6)	112.5 (8)	113.2 (11)
N2-C6-C7	123.5 (10)	125.0 (7)	125.4 (9)	123.3 (12)
C1-C6-C7	122.2 (10)	122.7 (7)	122.1 (8)	123.5 (12)
O1-C8-N3	120.9 (10)	120.6 (7)	120.4 (9)	122.3 (12)
O1-C8-N4	125.4 (10)	125.2 (7)	124.3 (9)	123.6 (12)
N3-C8-N4	113.7 (10)	114.0 (7)	115.2 (9)	114.0 (12)
N5-C9-C5	112.8 (9)	111.6 (6)	112.5 (8)	112.5 (10)
N5-C9-C10	125.8 (9)	125.3 (7)	124.9 (8)	126.3 (12)
C5-C9-C10	121.3 (9)	123.1 (6)	122.6 (8)	121.2 (11)
O2-C11-N6	122.2 (10)	121.0 (7)	120.2 (8)	120.1 (12)
O2-C11-N7	123.9 (10)	123.8 (7)	123.8 (8)	125.3 (12)
N6-C11-N7	113.8 (9)	115.2 (7)	115.8 (8)	114.6 (12)

complex the equatorial Fe–N bonds of 2.229 (6) and 2.195 (6) Å are significantly different. The difference in these two bonds can be rationalized in terms of the spin state of the ion and the splitting of the d orbitals in a PBP field.[31] The Jahn–Teller theorem[32] predicts that a high-spin d^6 ion in a PBP field will be unstable and will distort to remove the degeneracy of the two low-lying d_{xz} and d_{yz} orbitals. However, the distortion is not expected to alter the distances as much as in the Cr(III) and Ni(II) cases because the orbitals are not strongly antibonding. Two of the three Fe(II) macrocycles[18] show similar distortions which are not as evident in the corresponding Fe(III) complexes. An analysis of the Fe(II) vs. Fe(III) distances in the various PBP complexes reported to date suggests that the change can be explained without resorting to the proposed π-bonding arguments.[18]

For cobalt(II) there are crystal structures for only three PBP complexes.[21,26,33] The average Co–N and Co–O distances of

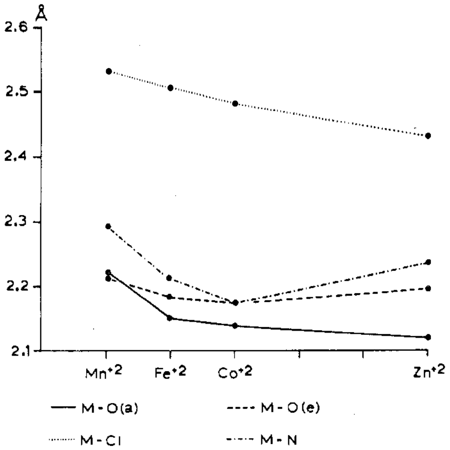

Figure 2. Trends in the metal–ligand distances in the complex $[M(DAPSC)(H_2O)Cl]^+$ cations, going from Mn(II) to Zn(II). Data for the corresponding Ni(II) and Cu(II) complexes are not available.

2.222 and 2.216 Å, respectively, in a cryptate[21] are similar to the corresponding averages of 2.190 and 2.176 Å in $[Co(DAPSC)(Cl)(H_2O)]^+$. In contrast the average Co–N distance is 2.245 Å in the 2,6-diacetylpyridine bis(2′-pyridylhydrazone) complex,[26] henceforth H_2dapp. Since all the equatorial donor atoms in H_2dapp are nitrogen atoms, the difference in the Co–N bond lengths could be an electroneutrality effect related to the better donor properties of the nitrogen atoms. However, the H_2dapp case is somewhat more complicated because a steric interaction between the hydrogen atoms on the terminal pyridine rings may prevent the formation of shorter Co–N bonds. There is a corresponding slight but not significant increase in the axial Co–O (to H_2O) bond distances in the DAPSC complex relative to that found in the H_2dapp case. In a purpurato–Co(II) complex[33] the axial Co–O (of H_2O) bonds are significantly different (2.146 (8) and 2.060 (9) Å) and the O–Co–O angle (of 168.8°) shows a significant deviation from linearity. The distortions in the purpurato complex may be related to the long Co–O bonds to the bidentate nitrate in the equatorial plane and illustrate the dependence of the axial distances on the equatorial bond lengths (vide infra).

Although crystal field effects are unimportant for the Zn(II) ion, there are only three crystal structure studies of seven-coordinate zinc(II) complexes.[26,33,34] The average Zn–N distance in $[Zn(DAPSC)(Cl)(H_2O)]^+$ is 2.233 Å which is slightly smaller than the average of 2.289 Å found in the $[Zn(H_2dapp)(H_2O)_2]^{2+}$ complex.[26] However, the axial Zn–O bonds average 2.104 Å in the latter complex compared to 2.121 Å in the DAPSC structure. These differences are similar to those observed in the Co(II) complexes and the significance and explanations have been given (vide supra).

We see that the metal–ligand distances in the PBP $[M(DAPSC)(Cl)(H_2O)]^+$ cations are similar to those reported for other seven-coordinate complexes. However, the changes in the bond distances with atomic number in our isomorphous series are fascinating. In Figure 2 the average M–donor distances are plotted vs. the atomic number, similar to various plots for octahedral complexes.[35] In a PBP complex the d orbitals are split into a 2,2,1 pattern with the three high energy orbitals being antibonding in nature.[31] Consequently, for high-spin PBP complexes a minimum in the metal–equatorial ligand distances is predicted to occur at Co(II) while the minimum metal–axial ligand distance will be for Cu(II). Indeed, we see that for the metal–equatorial ligand bonds there is a definite increase in the distances in the Zn(II) complex compared to the Co(II) case. However, the predicted trend in the metal–axial donor distances is not as apparent, if present

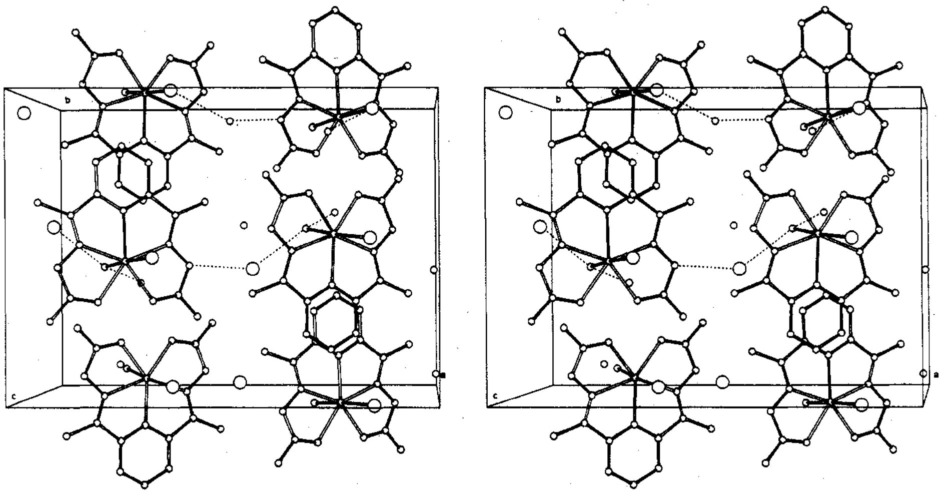

Figure 3. A stereoscopic packing diagram for the $[M(DAPSC)(H_2O)Cl]Cl{\cdot}2H_2O$ structures. The Co(II) coordinates were used for this illustration of the unit cell contents. The Mn(II), Fe(II), and Zn(II) structures are essentially identical with the Co(II) structure. Larger circles represent chlorine atoms. Dotted lines correspond to hydrogen bonds. Atomic numbering and hydrogen atoms are omitted for clarity.

Table VI. Nonbonded Contacts in the $[M(DAPSC)(H_2O)Cl]^+$ Cation

	Mn	Fe	Co	Zn
Cl-N1	3.429 (9)	3.337 (6)	3.304 (8)	3.319 (10)
Cl1-N2	3.312 (10)	3.216 (6)	3.186 (8)	3.236 (11)
Cl1-N5	3.597 (10)	3.503 (6)	3.450 (7)	3.467 (10)
Cl1-O1	3.460 (8)	3.390 (6)	3.368 (8)	3.363 (10)
Cl1-O2	3.470 (8)	3.374 (6)	3.314 (7)	3.317 (10)
O4-N1	3.234 (12)	3.168 (8)	3.156 (9)	3.155 (13)
O4-N2	3.264 (13)	3.177 (8)	3.182 (10)	3.164 (14)
O4-N5	3.049 (14)	3.002 (8)	2.974 (9)	2.969 (13)
O4-O1	2.980 (9)	2.915 (8)	2.868 (9)	2.856 (13)
O4-O2	3.053 (12)	3.005 (8)	2.985 (9)	2.975 (13)
N1-N2	2.589 (12)	2.534 (9)	2.525 (11)	2.533 (15)
N1-N5	2.548 (13)	2.519 (9)	2.522 (10)	2.550 (14)
N2-O1	2.601 (12)	2.579 (8)	2.561 (10)	2.601 (14)
N5-O2	2.587 (12)	2.553 (8)	2.552 (9)	2.574 (13)
O1-O2	2.955 (9)	2.761 (8)	2.690 (9)	2.777 (13)

Table VII. Least-Squares Planes for the $[M(DAPSC)(H_2O)Cl]^+$ Cations[a]

Atom	Mn	Fe	Co	Zn
Plane 1. Plane through the Planar Pentagonal Donor Set				
M	84	41	33	68
Cl	2609	2541	2505	2498
O1*	−93	−96	−116	−104
O2*	97	100	115	112
O4	−2134	−2108	−2096	−2047
N1*	7	5	−1	14
N2*	61	61	76	60
N5*	−72	−70	−74	−82
l	0.4582	0.4582	0.4594	0.4580
m	−0.0459	−0.0482	−0.0517	−0.0495
n	0.8877	0.8876	0.8867	0.8876
p	2.9985	2.9776	2.9220	2.9154
Plane 2. Plane through the Pyridine Ring				
M	141	103	111	130
O1	−129	−104	−104	−122
O2	347	336	390	376
N1*	−2	−1	−4	−2
N2	−115	−86	−77	−121
N5	165	152	180	167
C1*	1	3	7	−2
C2*	3	−3	−4	7
C3*	−6	1	−2	−8
C4*	5	1	6	4
C5*	−1	−1	−2	1
l	0.3702	0.3781	0.3704	0.3650
m	−0.0155	−0.0167	−0.0139	−0.0142
n	0.9288	0.9256	0.9288	0.9309
p	3.069	3.088	3.076	3.038

[a] The titles of the plane are followed by the deviations ($\times 10^3$ Å) of the atoms listed in the left-hand column. The atoms used to define the plane are denoted by asterisks. The deviation equals $lX + mY + nZ - p$, where p is the distance of the plane from the origin (in Å).

at all. The shortest axial M–Cl and $M{-}OH_2$ are observed in the zinc complex. Unfortunately, the absence of data for the corresponding Ni(II) and Cu(II) complexes makes an interpretation difficult. However, the nonbonded contacts given in Table VI suggest that these nonbonded interactions may be important in determining the metal–axial ligand distances. The nonbonded contacts in the Co(II) and Zn(II) complexes are very similar which suggests that the decrease in the axial M–donor distances is related, at least in part, to an expansion of the equatorial M–donor distances. Considering the values in Table VI, we see that decreasing the axial Co–donor distances could only be accomplished at the cost of increased repulsion between equatorial and axial donor atoms. The trends in axial and equatorial distances observed in the $M(DAPSC(Cl)(H_2O)$ series will occur whenever we have a macrocyclic or pseudomacrocyclic system where the donor atoms are constrained by the ligand geometry. In these cases the ligand donor atoms cannot assume positions which can simultaneously satisfy all the various electronic and steric requirements of both the metal ion and ligand.

The least-squares planes data in Table VII reveal small but significant deviations of the five donor atoms in the DAPSC ligand from planarity. The maximum deviation is 0.116 Å, found for O1 in the Co complex. These distortions from planarity give rise to an approximately helical arrangement of the DAPSC ligand around the metal ion. One side arm is tipped slightly down (3.3–3.6°) from the plane of the central pyridine ring, with the other side arm slightly above (5.2–5.8°) the central ring. However, the deviations from planarity are among the smallest found in PBP complexes, illustrating the rigidity and planarity of the DAPSC ligand.

A stereoview of the crystal packing is shown in Figure 3. The pyridine rings stack over each other with a slight displacement and tip (less than 2°) from being exactly parallel. The mean separation between the rings varies from 3.42 to 3.46 Å which is close to the usual value of about 3.3 Å found in graphite. There are also a number of hydrogen bonds involving the axial water, lattice waters, and ionic chlorides. The hydrogen bonds occur both between and within the columns of cations found in the crystal and serve to link the various components.

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Registry No. $(\mathrm{Mn(DAPSC)(H_2O)(Cl)})^{+}\mathrm{Cl}^{-}\cdot 2\mathrm{H_2O}$, 65484-11-9; $(\mathrm{Fe(DAPSC)(H_2O)(Cl)})^{+}\mathrm{Cl}^{-}\cdot 2\mathrm{H_2O}$, 43010-80-6; $(\mathrm{Co(DAPSC)(H_2O)(Cl)})^{+}\mathrm{Cl}^{-}\cdot 2\mathrm{H_2O}$, 43010-81-7; $(\mathrm{Zn(DAPSC)(H_2O)(Cl)})^{+}\mathrm{Cl}^{-}\cdot 2\mathrm{H_2O}$, 42936-39-0.

Supplementary Material Available: Listings of structure factor amplitudes (39 pages). Ordering information is given on any current masthead page.

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Selenite Complexes with Pentaamminecobalt(III): O- and Se-Bound Forms[1]

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The reaction of sodium selenite with aquopentaamminecobalt(III) chloride in ammoniacal solution leads to the formation of oxygen-bound selenitopentaamminecobalt(III) chloride–${}^{5}/_{2}$-water. The x-ray structure of this complex which crystallizes in the monoclinic system [space group $I2/a$; $a = 17.490$ (3), $b = 6.887$ (1), $c = 19.987$ (2) Å; $\beta = 94.19$ (1)°; $Z = 8$] has been refined to $R_1 = 0.024$ and $R_2 = 0.032$. The six-coordinate cobalt atom binds five ammonia ligands and an oxygen atom of the selenite anion. The selenite geometry is pyramidal with the longest Se–O bond, 1.707 (4) Å, being that to the oxygen atom coordinated to cobalt. There is a marginally significant negative trans effect in that the trans Co–N distance, 1.951 (3) Å, is 0.011 (5) Å less than the average cis Co–N distance 1.962 (4) Å. The reaction of sodium selenite with (dimethyl sulfoxide)pentaamminecobalt(III) perchlorate in methanol leads to a product whose chemical characterization and IR spectrum provide evidence that it is the selenium-bound selenitopentaamminecobalt(III) perchlorate.

Introduction

Following our discovery of a large ground-state structural trans effect in sulfitopentaamminecobalt(III) chloride[2] and our subsequent finding[3] that coordinated selenium seems to cause a larger trans effect than coordinated sulfur, we decided to prepare and study the selenium analogue of sulfitopentaamminecobalt(III). Our first attempts led to the formation of the oxygen-bound selenitopentaamminecobalt(III) cation, the structure of which we have determined by x-ray crystallography. Subsequent attempts appear to have produced the selenium-bound isomer of the complex cation, although we have not yet obtained a suitable material for x-ray studies. We report here the synthesis and characterization, including the crystal structure, of the oxygen-bound selenitopentaamminecobalt(III) chloride and the synthesis and partial characterization of selenium-bound selenitopentaamminecobalt(III) perchlorate.

Experimental Section

General Data. Common laboratory chemicals were of reagent grade. Visible–UV spectra were recorded on a Cary 14 spectrophotometer.

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