Table 10
Dihedral Angles for Various Planes in $[Co(PHENSC)(H_2O)_2](NO_3)_2$

Plane (1)	*Plane (2)*	*Angle (deg)*
Phen	Side (1)	3.7
Phen	Side (2)	3.4
Side (1)	Side (2)	7.0

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Table 9

Least–Squares Planes for [Co(PHENSC) $(H_2O)_2$] $(NO_3)_2$[a]

Atom	*PHEN*	*Side (1)*	*Side(2)*	*Donors*
Co	86	-153	-22	25
O(1)	-85	-589	-27*	-160
O(2)	198	8*	10	47*
N(1)	-9*	-358	4	19*
N(2)	20	-347	-3*	-38*
N(3)	17	-345	-36*	-92
N(4)	93	-311	33*	-79
N(5)	75	-19*	-155	-38*
N(6)	80	25*	-207	-92
N(7)	65	-13*	-247	-180
N(10)	15*	-175	-94	11*
C(2)	-13*	-442	60	30
C(3)	-11*	-512	139	90
C(4)	19*	-469	184	164
C(5)	9*	-368	117	181
C(6)	2*	-291	46	157
C(7)	-25*	-162	-127	47
C(8)	2*	-74	-171	14
C(9)	18*	-87	-157	-8
C(11)	-6*	-254	-46	47
C(12)	-10*	-234	-43	84
C(13)	5*	–330	33	77
C(14)	4*	–398	107	135
C(15)	–19	–457	31*	–27
C(16)	14	–414	1*	–102
C(17)	51	0*	–194	–39
C(18)	111	–2*	–147	–77
l	–0.4190	–0.4771	–0.3684	–0.3971
m	0.2731	0.2631	0.2994	0.3111
n	0.8659	0.8386	0.8802	0.8634
p	6.628	6.278	7.177	6.830

[a] *The title of the plane is followed by the deviations (x 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 X,Y, and Z are the orthogonal coordinates (in Å) relative to a, b, and c sin β; l, m and n are the direction cosines ; and p is the distance of the plane from the origin (in Å).*

Table 7

Bond Distances (in Å) for hydrogens of [Co(PHENSC) $(H_2O)_2](NO_3)_2$ With Estimated Standard Deviations

H(1) – O(3)	0.90(7)
H(2) – O(3)	0.62(7)
H(3) – O(4)	0.83(6)
H(4) – O(4)	0.58(8)
H(5) – C(3)	0.95(6)
H(6) – C(4)	0.92(7)
H(7) – C(5)	0.53(8)
H(8) – C(6)	0.95(6)
H(9) – C(7)	0.97(6)
H(10) – C(8)	0.88(5)
H(11) – C(17)	0.94(6)
H(12) – C(15)	0.90(6)
H(13) – N(3)	1.06(7)
H(14) – N(6)	1.11(7)
H(15) – N(7)	0.82(7)
H(16) – N(7)	0.82(8)
H(17) – N(4)	0.82(6)
H(18) – N(4)	0.89(7)

Table 8

Hydrogen Bonds in [Co(PHENSC) $(H_2O)_2](NO_3)_2$

			Dist, Å		*Ange, deg*
Bond D–H ····· A	Position of A	D–H	H ···· A	D ···· A	D–H–A
O(3)–H(1) ····· O(1)	2 - x, - y, 1 - z	0.90(7)	1.91(7)	2.757 (6)	158(7)
O(3)–H(2) ····· O(5)	1 - x, 1/2 + y, 1/2 - z	0.62(7)	2.37(7)	2.947(8)	158(8)
O(4)–H(3) ····· O(10)	x,y.z	0.83(6)	2.05(6)	2.860(7)	166(6)
O(4)–H(3) ····· N(9)	x,y,z	0.83(6)	2.68(6)	3.498(7)	168(5)
N(3)–H(13) ····· O(7)	1 - x, -1/2 + y, 1/2 - z	1.06(7)	2.67(7)	3.511(7)	137(5)
N(6)–H(14) ····· O(9)	1 - x, -1/2 + y, 1/2 - z	1.11(7)	1.67(7)	2.776(7)	174(6)
N(6)– H(15) ···· O(10)	1 - x, -1/2 + y, 1/2 - z	0.82(7)	2.56(7)	3.241(8)	142(6)
N(7)–H(16) ···· O(7)	1 - x, -1/2 + y, 1/2 - z	0.82(8)	2.12(8)	2.878(8)	156(7)
N(4)–H(17) ···· O(7)	1 - x, -1/2 + y, 1/2 - z	0,82(6)	2.17(6)	2.978(9)	170(6)
N(4)–H(18) ···· O(6)	1 + x, -1/2 -y, 1/2 + z	0.89(7)	2.03(7)	2.887(8)	162(6)

Table 5 Continued

N(3)-C(16)-N(4)	114.2(6)
N(5)-C(17)-C(9)	113.6(5)
O(2)-C(18)-N(6)	121.2(6)
O(2)-C(18)-N(7)	123.7(6)
N(6)-C(18)-N(7)	115.1(6)

In the Nitrate Ions

O(5)-N(8)-O(6)	122.8(6)
O(5)-N(8)-O(7)	120.1(6)
O(6)-N(8)-O(7)	117.1(6)
O(8)-N(9)-O(9)	119.5(5)
O(8)-N(9)-O(10)	122.6(5)
O(9)-N(9)-O(10)	117.9(5)

Table 6
Final Hydrogen Atom Parameters for [Co(PHENSC) $(H_2O)_2$]$(NO_3)_2$.
The positional parameters are x 10^{+3}
and B is the isotropic thermal parameter.

ATOM	X	Y	Z	B
H(1)	–354(9)	152(7)	473(3)	5.6(1.8)
H(2)	–406(8)	250(7)	451(2)	4.6(1.6)
H(3)	–189(7)	125(6)	286(2)	3.6(1.4)
H(4)	–241(10)	23(8)	297(3)	7.0(2.0)
H(5)	274(7)	314(6)	435(2)	3.3(1.4)
H(6)	230(8)	526(7)	402(3)	5.3(1.7)
H(7)	–32(9)	642(8)	364(3)	7.0(2.0)
H(8)	–232(7)	717(6)	312(2)	3.2(1.4)
H(9)	–514(8)	619(6)	280(2)	4.3(1.5)
H(10)	–679(6)	432(5)	275(2)	2.0(1.2)
H(11)	–728(8)	181(6)	302(2)	4.3(1.6)
H(12)	174(8)	87(6)	442(2)	3.9(1.4)
H(13)	–176(8)	–119(7)	438(3)	5.2(1.7)
H(14)	–736(9)	–45(8)	333(3)	6.3(2.0)
H(15)	–645(8)	–241(7)	363(3)	5.3(1.8)
H(16)	–516(10)	–274(8)	398(3)	7.3(2.1)
H(17)	–67(7)	–305(6)	466(2)	2.8(1.4)
H(18)	107(9)	–327(7)	485(3)	5.3(1.8)

Table 4

Bond Distances (in Å) in $[Co(PHENSC)(H_2O)_2](NO_3)_2$ With Estimated Standard Deviations

		In the Cation:	
Co-O(3)	2.113(4)	Co-O(4)	2.119(4)
Co-N(1)	2.139(5)	Co-N(10)	2.164(5)
Co-N(2)	2.348(5)	Co-N(5)	2.227(5)
Co-O(2)	2.138(4)		
C(2)-C(15)	1.460(9)	C(9)-C(17)	1.446(9)
C(15)-N(2)	1.268(8)	C(17)-N(5)	1.278(8)
N(2)-N(3)	1.353(7)	N(5)-N(6)	1.340(7)
N(3)-C(16)	1.356(9)	N(6)-C(18)	1.371(8)
C(16)-N(4)	1.320(9)	C(18)-N(7)	1.322(8)
C(16)-O(1)	1.225(8)	C(18)-O(2)	1.212(8)
N(1)-C(2)	1.314(8)	N(10)-C(9)	1.329(8)
N(1)-C(13)	1.333(7)	N(10)-C(11)	1.323(8)
C(2)-C(3)	1.404(9)	C(9)-C(8)	1.381(9)
C(13)-C(14)	1.388(8)	C(11)-C(12)	1.406(9)
C(3)-C(4)	1.368(9)	C(8)-C(7)	1.381(10)
C(4)-C(14)	1.397(9)	C(7)-C(12)	1.377(10)
C(5)-C(6)	1.337(10)	C(11)-C(13)	1.412(9)
C(5)-C(14)	1.449(9)	C(6)-C(12)	1.423(10)
		In the Nitrate Ions:	
N(8)-O(5)	1.219(8)	N(9)-O(8)	1.216(7)
N(8)-O(6)	1.216(8)	N(9)-O(9)	1.259(7)
N(8)-O(7)	1.254(8)	N(9)-O(10)	1.234(7)

Table 5

Bond Angles (in deg) in $[Co(PHENSC)(H_2O)_2](NO_3)_2$ With Estimated Standard Deviations

In the Cation	
O(2)-Co-O(3)	88.6(2)
O(2)-Co-O(4)	89.8(2)
O(2)-Co-N(2)	77.8(2)
O(2)-Co-N(5)	70.7(2)
O(3)-Co-O(4)	176.2(2)
O(3)-Co-N(1)	92.0(2)
O(3)-Co-N(2)	93.4(2)
O(3)-Co-N(5)	89.4(2)
O(3)-Co-N(10)	89.7(2)
O(4)-Co-N(1)	91.2(2)
O(4)-Co-N(2)	89.6(2)

Table 5 Continued

O(4)-Co-N(5)	86.8(2)
O(4)-Co-N(10)	89.3(2)
N(1)-Co-N(2)	69.4(2)
N(1)-Co-N(10)	73.4(2)
N(5)-Co-N(10)	68.7(2)
Co-O(2)-C(18)	119.4(4)
Co-N(1)-C(2)	122.9(4)
Co-N(1)-C(13)	117.8(4)
Co-N(2)-N(3)	120.1(4)
Co-N(2)-C(15)	117.2(4)
Co-N(5)-N(6)	115.6(4)
Co-N(5)-C(17)	122.0(4)
Co-N(10)-C(9)	122.6(4)
Co-N(10)-C(11)	117.1(4)
C(2)-N(1)-C(13)	119.2(5)
N(3)-N(2)-C(15)	122.8(5)
N(2)-N(3)-C(16)	128.5(5)
N(6)-N(5)-C(17)	122.4(5)
N(5)-N(6)-C(18)	112.8(5)
C(9)-N(10)-C(11)	120.4(5)
N(1)-C(2)-C(3)	121.7(6)
N(1)-C(2)-C(15)	115.3(5)
C(3)-C(2)-C(15)	123.0(6)
C(2)-C(3)-C(4)	119.0(6)
C(3)-C(4)-C(14)	119.6(6)
C(6)-C(5)-C(14)	122.3(6)
C(5)-C(6)-C(12)	122.0(6)
C(8)-C(7)-C(12)	120.1(6)
C(7)-C(8)-C(9)	119.2(6)
N(10)-C(9)-C(8)	121.0(6)
N(10)-C(9)-C(17)	113.0(5)
C(8)-C(9)-C(17)	126.0(6)
N(10)-C(11)-C(12)	122.3(6)
N(10)-C(11)-C(13)	116.1(5)
C(12)-C(11)-C(13)	121.7(6)
C(6)-C(12)-C(7)	126.4(6)
C(6)-C(12)-C(11)	116.5(6)
C(7)-C(12)-C(11)	117.0(6)
N(1)-C(13)-C(11)	115.6(5)
N(1)-C(13)-C(14)	123.4(5)
C(11)-C(13)-C(14)	121.0(5)
C(4)-C(14)-C(5)	126.5(6)
C(4)-C(14)-C(13)	117.0(6)
C(5)-C(14)-C(13)	116.5(6)
N(2)-C(15)-C(2)	115.2(5)
O(1)-C(16)-N(3)	122.3(6)
O(1)-C(16)-N(4)	123.5(6)

Table 3

Final Thermal Parameters (x 10^{+4} except for Co which is x 10^{+5}) for $[Co(PHENSC)(H_2O)_2](NO_3)_2$. The Form of the Thermal Parameter is exp $[-2\pi^2(U_{11}h^2a^{*2}+U_{22}h^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$

ATOM	U11	U22	U33	U12	U13	U23
Co	312(4)	223(4)	329(5)	3(3)	- 81(3)	15(4)
O(1)	49(3)	49(3)	60(4)	6(2)	- 13(2)	17(2)
O(2)	60(3)	29(2)	55(4)	0(2)	- 24(2)	9(2)
O(3)	52(3)	39(2)	36(4)	2(2)	- 4(2)	2(2)
O(4)	46(2)	34(2)	42(4)	3(2)	- 7(2)	- 6(2)
O(5)	67(3)	81(4)	76(5)	21(3)	- 1(3)	20(3)
O(6)	90(4)	68(4)	74(5)	- 27(3)	- 12(3)	- 18(3)
O(7)	88(4)	32(3)	95(5)	1(2)	- 10(3)	-18(3)
O(8)	55(3)	78(4)	46(4)	9(2)	- 14(2)	0(3)
O(9)	40(2)	50(3)	72(5)	- 7(2)	- 10(2)	23(3)
O(10)	50(3)	66(3)	61(4)	- 16(2)	- 3(2)	8(3)
N(1)	26(2)	27(2)	34(4)	0(2)	- 3(2)	- 3(2)
N(2)	47(3)	26(3)	39(4)	1(2)	- 11(2)	4(2)
N(3)	45(3)	34(3)	48(5)	4(2)	- 12(2)	9(2)
N(4)	70(4)	29(3)	64(5)	2(3)	- 21(3)	9(3)
N(5)	33(3)	29(3)	40(4)	- 2(2)	- 8(2)	- 1(2)
N(6)	36(3)	31(3)	55(5)	- 4(2)	- 10(2)	0(3)
N(7)	41(3)	34(3)	87(6)	- 8(2)	- 7(3)	6(3)
N(8)	46(3)	45(3)	45(5)	- 2(2)	- 1(2)	- 5(3)
N(9)	34(3)	45(3)	41(4)	0(2)	2(2)	- 4(2)
N(10)	42(3)	27(3)	28(4)	3(2)	- 3(2)	0(2)
C(2)	33(3)	37(3)	34(5)	- 1(3)	1(2)	- 3(3)
C(3)	35(3)	45(4)	39(5)	- 5(3)	- 10(3)	0(3)
C(4)	40(4)	41(4)	46(5)	- 11(3)	- 3(3)	- 5(3)
C(5)	68(5)	37(4)	38(5)	- 8(3)	10(3)	3(3)
C(6)	70(5)	28(3)	44(5)	- 4(3)	0(3)	14(3)
C(7)	53(4)	40(4)	40(5)	14(3)	- 3(3)	13(3)
C(8)	41(4)	47(4)	38(5)	9(3)	- 11(3)	9(3)
C(9)	35(3)	37(3)	30(5)	5(3)	- 5(3)	3(3)
C(11)	52(4)	27(3)	28(5)	2(3)	2(3)	2(2)
C(12)	54(4)	27(3)	37(5)	6(3)	5(3)	6(3)
C(13)	34(3)	26(3)	30(4)	- 5(2)	0(2)	0(2)
C(14)	42(3)	31(3)	33(5)	- 7(3)	5(3)	2(3)
C(15)	21(3)	37(3)	43(5)	2(2)	- 7(2)	- 2(3)
C(16)	49(4)	42(4)	36(5)	1(3)	- 8(3)	- 1(3)
C(17)	27(3)	42(4)	34(5)	9(3)	- 6(2)	0(3)
C(18)	29(3)	33(3)	46(5)	0(2)	- 3(3)	- 1(3)

Table 2

Final Positional Parameters (x 10^{+4} except for Co which is x 10^{+5}) for $[Co(PHENSC)(H_2O)_2](NO_3)_2$

ATOM	X	Y	Z
Co	-28691(11)	13009(8)	37633(3)
O(1)	2090(6)	- 1098(5)	4696(2)
O(2)	- 3701(5)	-630(4)	3924(2)
O(3)	-3904 (6)	1928 (4)	4447(2)
O(4)	-1995(5)	643(4)	3059(2)
O(5)	-5366(7)	- 259(6)	613(2)
O(6)	-7766(8)	- 225(6)	222(2)
O(7)	-6697(7)	1536(5)	492(2)
O(8)	196(6)	3144(5)	2616(2)
O(9)	-802 (6)	4131(5)	1953(2)
O(10)	-2183(6)	2578(5)	2274(2)
N(1)	- 898(6)	2704(5)	3838(2)
N(2)	- 502(7)	387(5)	4187(2)
N(3)	- 516(7)	- 876(5)	4336(2)
N(4)	274(8)	-2760(5)	4710(2)
N(5)	-5441(5)	1021(5)	3421(2)
N(6)	-6089(6)	-173(5)	3473(2)
N(7)	-5587(7)	-2211 (5)	3785(3)
N(8)	-6596(7)	323(6)	442(2)
N(9)	-926(6)	3275 (5)	2292(2)
N(10)	- 3782(6)	3059(5)	3389(2)
C(2)	548(8)	2455(6)	4076(2)
C(3)	1791(8)	3413(6)	4140(2)
C(4)	1474(8)	4643(7)	3959(3)
C(5)	- 566(9)	6149(7)	3478(2)
C(6)	-2061 (9)	6316(7)	3239(3)
C(7)	-4810 (9)	5360(7)	2946(3)
C(8)	-5852 (8)	4287(7)	2936(2)
C(9)	--5297 (8)	3140(6)	3162(2)
C(11)	-2774 (8)	4081(6)	3402(2)
C(12)	-3248(8)	5288(6)	3187(2)
C(13)	-1198(7)	3900(6)	3657(2)
C(14)	- 50(8)	4912(6)	3700(2)
C(15)	757 (7)	1122(6)	4264(2)
C(16)	703 (8)	- 1558(6)	4593(2)
C(17)	- 6233(7)	1938(6)	3185(2)
C(18)	- 5030 (7)	- 1004(6)	3740(2)

Table 1

Crystal Data for [Co (PHENSC) $(H_2O)_2$] $(NO_3)_2$

Formula	$C_{16}H_{18}O_{10}N_{10}Co$
Molecular Weight	569.32
Space Group	$P2_1/c$
a,Å	8.012(3)
b,Å	10.257(9)
c,Å	26.260(15)
α, deg	90*
β, deg	92.71(4)
γ, deg	90*
Volume,Å^3	2155(2)
z	4
D_m, g cm^{-3}	1.714
D_c,g cm^{-3}	1.754
Crystal size, mm	0.25x0.09x0.09
μ, cm^{-1}	8.7
Radiation Used	Mo Kα - graphite monochromator
2 θ Range	0 - 45^o
No. of Measured Reflections	2824
No. of Reliable Reflections	2103
K [in I $\langle$ Kσ (I)]	2.0
F(low)	14.0
F (high)	56.0
Goodness of Fit	2.0
R	0.044

* Reguired by symmetry of space group.

O-Co-O angles (axial) are 176.1°, 168.8°, 174.2°, and 176.2°, respectively, and only the purpurato-Co(II) complex shows a significant deviation from linearity. The axial Co-O (to H_2O) bond distances of (2.113(4), 2.119(4) Å) and O-Co-O angle (axial) of 176.2° in $[Co(PHENSC)(H_2O)_2]^{2+}$ again are indistinguishable from other seven-coordinate cobalt complexes.

The least squares planes data are given in Table 9. The deviations of the five donor atoms from the pentagonal plane are from -0.038 to 0.034 Å in $[Co(BIPYSC)(H_2O)_2](NO_3)_2$,[13] from -0.038 to 0.047 Å in $[Co(PHENSC)(H_2O)_2](NO_3)_2$, from -0.068 to 0.069 Å in $[Co(DAPSAH)(H_2O)](NO_3)_2$. H_2O,[12] from -0.100 to 0.111 Å in $[Co(DAPBH)(H_2O)(NO_3)](NO_3)$ [11] from -0.116 to 0.115 Å in $[Co(DAPSC)(H_2O)Cl]Cl.\ 2H_2O$,[5] from -0.140 to 0.160 Å in $[CoL(NO_3)(H_2O)_2].2H_2O$ (L-purpurate),[15] and from -0.364 to 0.363 Å in $[Co(H_2DAPP)(H_2O)_2]Cl_2$.[10] Therefore, the maximum and minimum deviations from planarity are found in $[Co(H_2DAPP)(H_2O)_2]Cl_2$ and $[Co(BIPYSC)(H_2O)_2(NO_3)_2$, respectively; but the deviation for $Co(PHENSC)(H_2O)_2](NO_3)_2$ is very close to that found for $[Co(BIPYSC)(H_2O)_2](NO_3)_2$. Dihedral angles for $[Co(PHENSC)(H_2O)_2]^{2+}$ are given in Table 10. The two side arms are twisted slightly (side (1), 3.7° and side (2), 3.4°) relative to the 1,10-phenanthroline ring.

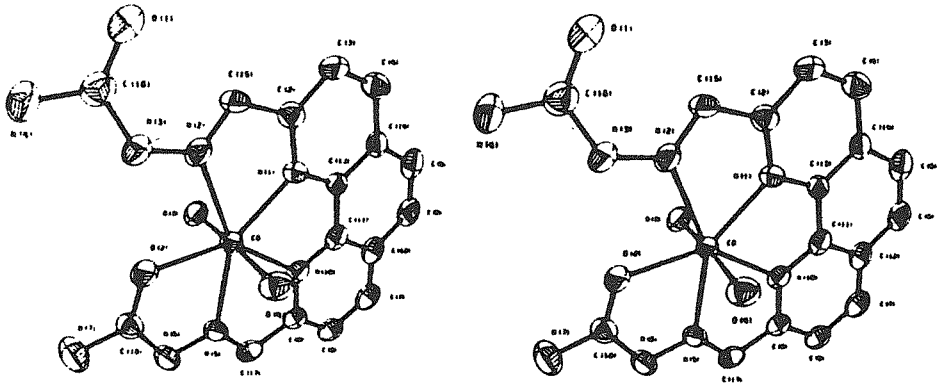

Figure 1. Stereoscopic view of $[Co(PHENSC)(H_2O)_2](NO_3)_2$.

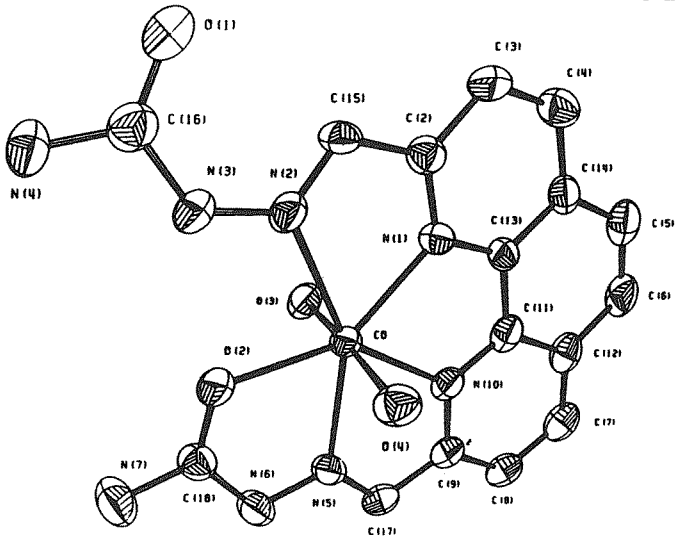

Figure 2. An ORTEP view of $[Co(PHENSC)(H_2O)_2](NO_3)_2$ showing the atomic numbering and the thermal ellipsoids (50% probability level).

tion. Another hexadentate ligand, 2,9-diformyl-1, 10-phenanthroline bis (semicarbazone), PHENSC, was used to prepare $[Co(PHENSC)(H_2O)_2](NO_3)_2$, which was studied by X-ray diffraction.

A. Experimental Section

Preparation of $[Co(PHENSC)(H_2O)_2](NO_3)_2$

The ligand 2,9-diformyl-1,10-phenanthroline bis(semicarbazone) was prepared from 1,10-phenanthroline-2,9-dicarboxaldehyde and semicarbazide hydrochloride. Equimolar amounts of cobalt nitrate hexahydrate and 2,9-diformyl-1,10-phenanthroline bis (semicarbazone) were heated in 95% ehtanol for one-half hour. Addition of a small amount of water and continued heating gave a clear solution within one hour. After filtering, orange crystals were obtained by slow evaporation of the solvent.

Data Collection and Reduction

Preliminary photographs indicated that the space group was $P2_1/c$. The unit cell dimensions are reported in Table 1, and the intensity data were measured using a Syntex $P\bar{1}$ diffractometer. The pertinent crystal data, together with some details of the intensity measurements, are given in Table 1. The $\theta - 2\theta$ scan technigue with a variable scan rate of 1 to 24^o/min was used in measuring the intensity. Four standard reflections were measured every 96 reflections to monitor the beam and crystal stability. Scale factors varying from 0.988 to 1.024 were used to place all the data on approximately the same scale.

Structure Determination and Refinement

The position of the cobalt atom was determined from the Patterson function and the remaining non-hydrogen atoms from successive Fourier syntheses. The R value ($R = \Sigma \| F_{obs} | - | F_{cal} \| \Sigma | F_{obs} |$) was 0.17 at the start of the least-squares refinement. After three cycles, the R value was 0.093. Anisotropic thermal refinement gave an R of 0.060 after three cycles. A difference Fourier synehtesis gave reasonable positions for all the eighteen hydrogen atoms. Three additional least squares cycles, in which the H atoms were included in the structure factors calculation but were not refined, reduced R to 0.047. Three more cycles, in which all the atoms were refined, reduced R to the final value of 0.044.

The scattering factors were taken from the usual sources.[14] The final positional parameters and thermal parameters for the non-hydrogen atoms are given in Tables 2 and 3, respectively. The bond distances and angles are given in Tables 4 and 5, respectively. The hydrogen atom parameters and distances are given in Tables 6 and 7, respectively.

B. Results and Discussion

The crystal consists of $[Co(PHENSC)(H_2O)_2]^{2+}$ cation, illustrated in Figures 1 and 2. The cobalt atom is in the center of a pentagonal bipyramidal arrangement consisting of five of the six donor atoms of the planar ligand in the equatorial plane and two axial water molecules. The NO_3^- anions are joined by hydrogen bonds (see Table 8). The range of D-H···A angles and the variation of the H···A and D···A distances indicate the presence of both strong and weak hydrogen bonds. The $[Co(PHENSC)(H_2O)_2](NO_3)_2$ and $[Co(BIPYSC)(H_2O)_2](NO_3)_2$ are the only two seven-coordinate cobalt complexes with hexadentate ligands which have been characterized by X-ray diffraction studies. The two hexadentate ligands act as pentadentate ligands because the size of Co(II) ion is too small to form bonds to all six donors in the equatorial plane. In the four cobalt complexes with planar pentadentate ligands (as mentioned above), the Co-N bond distances range from 2.171 to 2.268 Å ; the Co-O bond distances range from 2.150 to 2.253 Å . In $[Co(BIPYSC)(H_2O)_2](NO_3)_2$, the average Co-N bond distance is 2.222 Å , and the Co-O bond distance in the plane is 2.191 Å .[13] We found is $[Co(PHENSC)(H_2O)_2](NO_3)_2$ the Co-O bond distance in the plane is 2.138 Å , and the average Co-N bond length is 2.220 Å , which are similar to the values in the other seven-coordinate cobalt complexes. The axial Co-O (to H_2O) bond distances are (2.146(4), 2.153(4) Å) in $[Co(H_2DAPP)(H_2O)_2]^{2+}$, (2.060(9), 2.146(8) Å) in the purpurato-Co(II) complex,[15] (2.110(6), 2.125(6) Å) in $[Co(DAPSAH)(H_2O)_2]^{2+}$ and (2.131(6), 2.159(6) Å) in $[Co(BIPYSC)(H_2O)_2]^{2+}$.[13] The

The Crystal Structure of Diaqua [2,9-Diformyl-1 10-Phenanthrol line bis (semicarbazone)]COBALT(II), Nitrate, $[Co(PHENSC)(H_2O)_2](NO_3)_2$

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ABSTRACT

A pentagonal-bipyramidal complex of Co(II), $[Co(PHENSC)(H_2O)_2](NO_3)_2$, was synthesized using the PHENSC, a hexadentate ligand, 2,9-diformyl-1,10-phenanthroline bis(semicarbazone), and characterized by X-ray diffraction. The cobalt atom is in the center of a pentagonal bipyramidal arrangement cosisting of five of the six donor atoms of the planar ligand in the equatorial plane and two axial water molecules. The complex crystallizes in the monoclinic space group $P2_1/c$, with a = 8.012(3), b=10.257(9), c=26.260(15) Å, β=92.71(4)°, and four molecule per unit cell. The position of the cobalt atom was determined from the patterson function and the remaining non-hydrogen atom from successive Fourier Syntheses. A difference Fourier Synthesis gave reasonable positions for all the eighteen hydrogen atoms. The final R value for 2103 reflections is 0.044. The NO_3^- anions are joined by hydrogen bonds. The range of D···H···A angles and the variation of the H···A and D···A distances indicate the presence of both strong and weak hydrogen bonds.

INTRODUCTION

The most extensively studied hexadentate chelating agent is probably ethylenediaminetetraacetic acid (EDTA or H_4Y). Hoard and co-workers have determined the geometry of seven coordinate aqua complexes of the type $[M(EDTA)(H_2O)]^{n-}$ with M= Fe(III), Mg(II), Mn(II) [1-3] They have noted that two kinds of geometries can be obtained, viz., pentagonal-bipyramid and capped trigonal prism. Trans 1,2-diaminocyclohexane-N,N'-tetraacetic acid (DCTA) also functions as a hexadentate ligand in $Ca[Fe(H2O)(DCTA)]_2 \cdot 2H_2O$. The $[Fe(H_2O)(DCTA)]^-$ is a seven-coordinate aqua complex.[4]

The ligand 2,6-diacetylpyridine bis (semicarbazone), DAPSC, was postulated to be ideally suited to form pentagonal-bipyramidal complexes with a variety of different metal ions.[5-9] Indeed, the complexes $[M(DAPSC)(H_2O)(Cl)]Cl.2H_2O$, where M=Mn(II), Fe(II), Co(II), and Zn(II), were found to be isomorphous, each cation assuming a pentagonal-bipyramidal shape.[5] In addition, $[Cu(DAPSC)(H_2O)_2](NO_3)_2.H_2O$,[6] $[Ni(DAPSC)(H_2O)_2(NO_3)_2.H_2O$,[6] $[Cr(DAPSC)(H_2O)_2](NO_3)_2(OH).H_2O$,[7] $[Fe(DAPSC)Cl_2]Cl.2H_2O$,[7] $[Sc(DAPSC)(H_2O)](NO_3)_2(OH)$,[8] and $[Mn(DAPSC(H_2O)_2](NO_3)_2$[9] are best described as pentagonal-bipyramidal compexes. A few other planar, pentadentate ligands such as 2,6-diacetylpyridine bis (2'-pyridylhydrazone (H_2DAPP); 2,6-diacetylpyridine bis(bezonic acid hydrazone) (DAPBH); and 2,6-diacetylpyridine bis (salicylic acid hydrazone) (DAPSAH) also have been prepared and found to yield the pentagonal-biypramidal complexes $[M(H_2DAPP),(H_2O)_2]Cl_2$[10] [M= Co(II), Zn(II)]; $[Co(DAPBH)(H_2O)(NO_3)](NO_3)$,[11] $[Ni(DAPBH)(H_2O)_2](NO_3)_2.2H_2O$;[11] and $[Co(DAPSAH)(H_2O)_2](NO_3)_2.H_2O$.[12]

A pentagonal-bipyramidal complex of Co(II), $[Co(BIPYSC)(H_2O)_2](NO_3)_2$,[13] was synthesized using the BIPYSC, a hexadentate ligand 6,6'-diformyl-2,2'-bipyridine bis (semicarbazone) related to DAPSC and characterized by a single-crystal X-ray investiga-