

Inorganic Chemistry

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Figure S-1. Packing diagram of $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$ in $P2_12_12_1$.

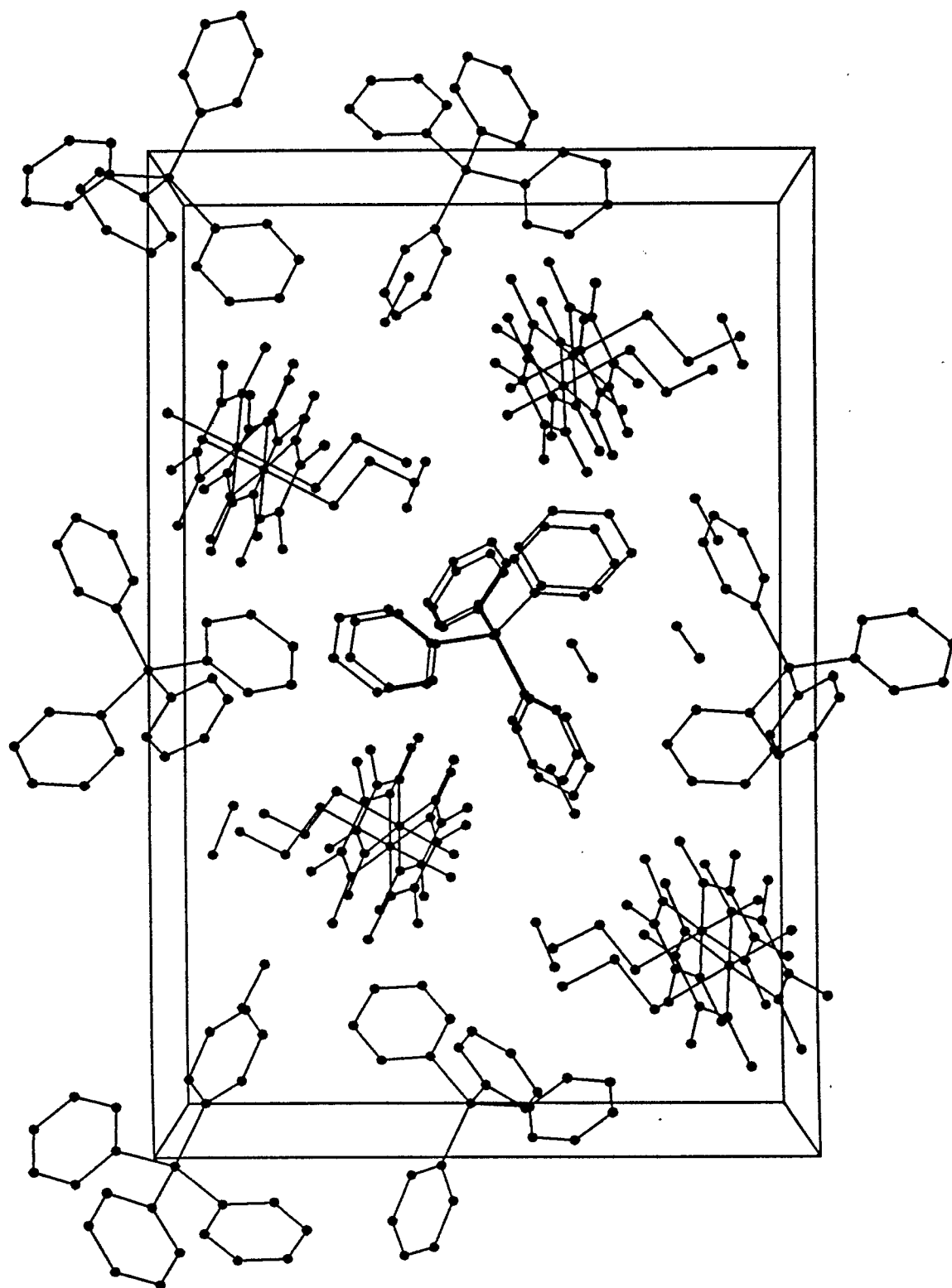


Table S-1. Crystallographic Data for [AsPh₄][EtSCo(DH)₂CH₃]

empirical formula	C ₃₈ H ₅₄ AsCoN ₄ O ₇ S
color	orange-red
crystal size (mm)	0.26 × 0.44 × 0.45
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.091 (2)
<i>b</i> (Å)	17.098 (6)
<i>c</i> (Å)	26.505 (2)
volume (Å ³)	4120 (2)
<i>Z</i>	4
formula weight	844.76
density (calc.)	1.36 mg m ⁻³
absorption coefficient	1.31 mm ⁻¹
F(000)	1768
diffractometer	Siemens P4
radiation	Mo K _α (λ = 0.71073 Å)
temperature (K)	173
monochromator	highly oriented graphite crystal
2θ Range (deg)	3.0-45.0
scan type	omega
standard reflections	3 measured every 97 reflections
index ranges	-1 < <i>h</i> < 9 -1 < <i>k</i> < 18 -1 < <i>l</i> < 28
reflections collected	3952
independent reflections	3729 (R _{int} = 4.28 %)
absorption correction	semi-empirical
min./max. transmission	0.267/0.355
system	Siemens SHELXTL 93
solution	direct methods
refinement method	full-matrix least-squares on F ²
hydrogen atoms	riding model, isotropic U (20% greater than bonded atom).
data/restraints/parameters	3728/0/469
final R indices [I > 2σ(I)]	R = 4.34 % R _w = 9.96 %
R Indices (all data)	R = 5.51 % R _w = 11.34 %
goodness-of-fit	1.033
absolute structure parameter	0.00 (2)
largest difference peak	0.60 eÅ ⁻³
largest difference hole	-0.35 eÅ ⁻³

Table S-2. Bond Lengths (Å) of [AsPh₄][EtSCo(DH)₂CH₃]

Co-N(4)	1.852(6)	C(12)-C(13)	1.386(9)
Co-N(2)	1.853(6)	C(13)-C(14)	1.384(10)
Co-N(1)	1.876(6)	C(14)-C(15)	1.359(11)
Co-N(3)	1.886(7)	C(15)-C(16)	1.392(11)
Co-C(1)	2.005(7)	C(16)-C(17)	1.383(10)
Co-S	2.342(2)	C(18)-C(23)	1.379(10)
N(1)-C(4)	1.296(10)	C(18)-C(19)	1.399(10)
N(1)-O(1)	1.344(7)	C(19)-C(20)	1.380(11)
N(2)-C(6)	1.321(11)	C(20)-C(21)	1.380(11)
N(2)-O(2)	1.370(7)	C(21)-C(22)	1.381(12)
N(3)-C(8)	1.277(10)	C(22)-C(23)	1.389(12)
N(3)-O(3)	1.353(7)	C(24)-C(25)	1.363(10)
N(4)-C(10)	1.303(10)	C(24)-C(29)	1.406(10)
N(4)-O(4)	1.354(7)	C(25)-C(26)	1.369(10)
S-C(2)	1.821(8)	C(26)-C(27)	1.375(11)
C(2)-C(3)	1.529(11)	C(27)-C(28)	1.384(11)
C(4)-C(6)	1.444(11)	C(28)-C(29)	1.385(10)
C(4)-C(5)	1.489(12)	C(30)-C(35)	1.367(11)
C(6)-C(7)	1.467(11)	C(30)-C(31)	1.405(11)
C(8)-C(10)	1.447(11)	C(31)-C(32)	1.390(10)
C(8)-C(9)	1.518(11)	C(32)-C(33)	1.355(12)
C(10)-C(11)	1.492(10)	C(33)-C(34)	1.394(13)
As-C(30)	1.906(7)	C(34)-C(35)	1.370(11)
As-C(24)	1.909(7)	O(5)-C(36)	1.383(9)
As-C(18)	1.919(7)	O(6)-C(37)	1.395(11)
As-C(12)	1.926(7)	O(7)-C(38)	1.398(9)
C(12)-C(17)	1.374(10)		

Table S-3. Bond Angles (°) of [AsPh₄][EtSCo(DH)₂CH₃]

N(4)-Co-N(2)	179.8(3)	C(8)-C(10)-C(11)	124.7(8)
N(4)-Co-N(1)	98.5(3)	C(30)-As-C(24)	110.6(3)
N(2)-Co-N(1)	81.4(3)	C(30)-As-C(18)	110.9(3)
N(4)-Co-N(3)	81.5(3)	C(24)-As-C(18)	108.9(3)
N(2)-Co-N(3)	98.6(3)	C(30)-As-C(12)	109.1(3)
N(1)-Co-N(3)	177.4(3)	C(24)-As-C(12)	109.3(3)
N(4)-Co-C(1)	88.1(3)	C(18)-As-C(12)	108.0(3)
N(2)-Co-C(1)	91.7(3)	C(17)-C(12)-C(13)	121.9(7)
N(1)-Co-C(1)	87.2(3)	C(17)-C(12)-As	118.5(5)
N(3)-Co-C(1)	90.3(3)	C(13)-C(12)-As	119.6(5)
N(4)-Co-S	94.0(2)	C(14)-C(13)-C(12)	118.3(7)
N(2)-Co-S	86.2(2)	C(15)-C(14)-C(13)	120.9(7)
N(1)-Co-S	92.3(2)	C(14)-C(15)-C(16)	120.1(7)
N(3)-Co-S	90.2(2)	C(17)-C(16)-C(15)	120.1(7)
C(1)-Co-S	177.9(2)	C(12)-C(17)-C(16)	118.7(7)
C(4)-N(1)-O(1)	121.2(7)	C(23)-C(18)-C(19)	120.8(7)
C(4)-N(1)-Co	117.0(5)	C(23)-C(18)-As	119.3(6)
O(1)-N(1)-Co	121.8(5)	C(19)-C(18)-As	119.8(5)
C(6)-N(2)-O(2)	117.5(6)	C(20)-C(19)-C(18)	119.3(7)
C(6)-N(2)-Co	117.2(5)	C(21)-C(20)-C(19)	120.0(8)
O(2)-N(2)-Co	125.1(5)	C(20)-C(21)-C(22)	120.7(8)
C(8)-N(3)-O(3)	122.0(7)	C(21)-C(22)-C(23)	120.1(8)
C(8)-N(3)-Co	116.3(5)	C(18)-C(23)-C(22)	119.2(8)
O(3)-N(3)-Co	121.7(5)	C(25)-C(24)-C(29)	121.3(7)
C(10)-N(4)-O(4)	118.3(6)	C(25)-C(24)-As	120.0(6)
C(10)-N(4)-Co	116.8(5)	C(29)-C(24)-As	118.6(6)
C(2)-S-Co	107.6(3)	C(25)-C(26)-C(27)	119.9(8)
C(3)-C(2)-S	109.7(6)	C(26)-C(27)-C(28)	120.6(8)
N(1)-C(4)-C(6)	112.6(7)	C(27)-C(28)-C(29)	120.2(7)
N(1)-C(4)-C(5)	123.9(7)	C(28)-C(29)-C(24)	117.8(8)
C(6)-C(4)-C(5)	123.5(8)	C(35)-C(30)-C(31)	120.3(7)
N(2)-C(6)-C(4)	111.8(7)	C(35)-C(30)-As	120.2(6)
N(2)-C(6)-C(7)	124.8(7)	C(31)-C(30)-As	119.2(6)
C(4)-C(6)-C(7)	123.4(8)	C(32)-C(31)-C(30)	118.4(8)
N(3)-C(8)-C(10)	113.0(7)	C(33)-C(32)-C(31)	120.9(9)
N(3)-C(8)-C(9)	124.8(7)	C(32)-C(33)-C(34)	120.1(7)
C(10)-C(8)-C(9)	122.2(7)	C(35)-C(34)-C(33)	119.9(9)
N(4)-C(10)-C(8)	112.4(7)	C(30)-C(35)-C(34)	120.4(9)
N(4)-C(10)-C(11)	123.0(7)		

Table S-4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$

atom	x	y	z	$U_{\text{equiv}} \text{\AA}^2$
Co	7579(1)	8566(1)	3022(1)	21(1)
N(1)	6019(7)	7987(3)	2747(2)	24(2)
N(2)	6319(8)	8590(3)	3572(2)	28(2)
N(3)	9106(8)	9188(3)	3287(2)	26(2)
N(4)	8832(7)	8543(3)	2471(2)	25(2)
O(1)	6069(7)	7702(3)	2275(2)	37(2)
O(2)	6647(7)	8910(3)	4032(2)	32(1)
O(3)	9012(6)	9517(3)	3750(2)	31(1)
O(4)	8531(7)	8188(3)	2026(2)	31(1)
S	8614(3)	7454(1)	3397(1)	26(1)
C(1)	6635(10)	9517(4)	2721(3)	31(2)
C(2)	9447(10)	6872(4)	2897(3)	31(2)
C(3)	10109(11)	6127(5)	3121(4)	48(3)
C(4)	4876(9)	7881(4)	3031(3)	28(2)
C(5)	3523(10)	7463(5)	2865(3)	42(2)
C(6)	5047(10)	8224(5)	3525(3)	30(2)
C(7)	3962(10)	8133(6)	3931(3)	44(2)
C(8)	10233(9)	9281(4)	3006(3)	28(2)
C(9)	11593(10)	9745(5)	3150(3)	42(2)
C(10)	10078(10)	8912(4)	2518(3)	25(2)
C(11)	11210(9)	8935(5)	2110(3)	37(2)
As	8430(1)	4782(1)	4824(1)	21(1)
C(12)	7373(8)	5748(4)	4916(2)	20(2)
C(13)	7641(9)	6371(4)	4595(2)	25(2)
C(14)	6886(10)	7063(4)	4676(3)	33(2)
C(15)	5904(10)	7129(5)	5060(3)	31(2)
C(16)	5626(9)	6493(5)	5374(3)	30(2)
C(17)	6371(9)	5797(4)	5303(2)	26(2)
C(18)	10308(8)	5025(4)	4532(3)	20(2)
C(19)	11141(8)	5642(5)	4727(3)	27(2)
C(20)	12456(10)	5836(4)	4498(3)	35(2)
C(21)	12923(9)	5430(5)	4078(3)	44(2)
C(22)	12104(9)	4816(6)	3889(3)	40(2)
C(23)	10781(10)	4612(5)	4116(3)	36(2)
C(24)	7364(9)	4127(4)	4370(2)	26(2)
C(25)	6503(9)	4452(5)	4005(3)	28(2)
C(26)	5749(9)	3983(5)	3675(3)	28(2)
C(27)	5902(10)	3184(5)	3701(3)	35(2)
C(28)	6791(10)	2847(5)	4065(3)	34(2)
C(29)	7563(11)	3312(4)	4401(3)	32(2)
C(30)	8661(10)	4282(4)	5461(3)	29(2)
C(31)	7563(10)	3767(4)	5632(3)	34(2)
C(32)	7712(11)	3442(5)	6110(3)	40(2)
C(33)	8865(11)	3632(5)	6410(3)	38(2)
C(34)	9939(11)	4149(5)	6238(3)	43(2)
C(35)	9827(10)	4465(5)	5764(3)	33(2)
O(5)	1231(8)	6093(3)	11211(2)	51(2)
C(36)	1117(12)	6444(5)	11679(3)	54(3)
O(6)	705(7)	6753(4)	10271(2)	53(2)

Table S-4 (cont.) Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$

atom	x	y	z	$U_{\text{equiv}} \text{\AA}^2$
C(37)	1660(13)	6428(7)	9917(3)	75(3)
O(7)	9052(7)	3793(3)	8469(2)	41(2)
C(38)	9101(11)	4112(5)	7983(3)	48(2)

Table S-5. Anisotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) of $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$

atom	U11	U22	U33	U12	U13	U23
Co	24(1)	19(1)	20(1)	0(1)	-1(1)	-1(1)
N(1)	28(4)	24(3)	21(3)	-2(3)	-8(3)	2(3)
N(2)	46(5)	12(3)	26(3)	1(3)	-2(3)	2(4)
N(3)	35(4)	16(3)	25(3)	0(3)	-3(3)	0(3)
N(4)	40(5)	15(3)	19(3)	-1(3)	-6(3)	-7(4)
O(1)	51(4)	35(3)	25(3)	-7(2)	-10(3)	-5(3)
O(2)	35(3)	34(3)	26(3)	-7(2)	-3(3)	-4(3)
O(3)	48(4)	22(3)	22(3)	-2(2)	-5(3)	-3(3)
O(4)	38(3)	31(3)	23(2)	-8(2)	2(3)	-5(3)
S	35(1)	19(1)	25(1)	2(1)	-2(1)	1(1)
C(1)	38(5)	21(4)	35(4)	4(3)	-9(5)	6(4)
C(2)	28(5)	27(4)	37(5)	2(4)	4(4)	-4(4)
C(3)	53(6)	31(5)	61(6)	5(4)	2(5)	13(5)
C(4)	23(5)	24(4)	37(5)	8(4)	-8(4)	3(4)
C(5)	30(5)	46(5)	51(5)	8(4)	-12(5)	-8(6)
C(6)	28(5)	21(4)	40(5)	8(4)	3(4)	13(4)
C(7)	30(5)	58(6)	45(5)	5(5)	13(5)	2(5)
C(8)	26(5)	21(4)	38(5)	9(4)	-6(4)	-9(4)
C(9)	41(5)	42(5)	44(4)	-3(4)	-5(5)	-16(6)
C(10)	30(5)	18(4)	26(4)	6(3)	2(4)	10(4)
C(11)	34(5)	39(5)	39(4)	5(4)	6(4)	-6(5)
As	21(1)	18(1)	24(1)	0(1)	-2(1)	0(1)
C(12)	15(4)	21(4)	24(4)	-3(3)	-1(4)	-4(4)
C(13)	22(4)	31(4)	23(3)	-2(3)	-5(4)	-2(5)
C(14)	44(6)	21(4)	35(4)	8(3)	5(4)	-2(4)
C(15)	33(5)	26(4)	35(4)	-6(4)	-2(4)	9(4)
C(16)	22(4)	40(5)	29(4)	-1(4)	4(4)	3(5)
C(17)	30(5)	18(4)	30(4)	3(3)	-5(4)	-5(4)
C(18)	7(4)	20(4)	31(4)	5(3)	-2(3)	3(3)
C(19)	19(4)	29(4)	33(4)	4(4)	1(4)	2(4)
C(20)	30(5)	27(4)	49(5)	-5(4)	-6(5)	-3(5)
C(21)	24(5)	56(6)	52(5)	21(5)	14(4)	12(5)
C(22)	34(5)	49(5)	36(4)	-1(5)	18(4)	20(5)
C(23)	41(5)	32(5)	34(4)	4(4)	-2(4)	10(5)
C(24)	23(4)	30(4)	25(4)	-3(3)	6(4)	1(4)
C(25)	26(4)	30(4)	29(4)	2(3)	-2(4)	2(5)
C(26)	29(5)	38(5)	16(4)	-5(4)	-6(4)	-3(4)
C(27)	28(5)	37(5)	40(5)	-11(4)	-4(5)	-6(5)
C(28)	42(6)	27(4)	34(4)	-10(4)	-7(5)	-2(5)
C(29)	31(5)	26(4)	39(4)	-5(4)	-12(5)	-3(5)
C(30)	36(5)	20(4)	30(4)	-9(3)	-2(4)	11(4)
C(31)	24(5)	39(5)	40(4)	4(4)	2(4)	-6(5)
C(32)	45(6)	36(5)	39(5)	14(4)	9(5)	9(5)
C(33)	63(7)	26(4)	26(4)	5(4)	5(5)	24(5)
C(34)	56(7)	36(5)	36(5)	-3(5)	-16(5)	17(6)
C(35)	35(5)	26(4)	38(5)	-1(4)	-4(4)	0(4)
O(5)	84(6)	36(3)	33(3)	-6(3)	11(4)	-2(4)
C(36)	66(8)	34(5)	62(6)	-4(5)	9(6)	-3(6)
O(6)	48(4)	55(4)	56(4)	-5(3)	3(4)	-5(4)
C(37)	71(7)	93(8)	62(6)	-30(6)	-6(7)	13(8)
O(7)	49(4)	40(3)	33(3)	-2(3)	0(3)	-21(3)

Table S-5 (cont.) Anisotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) of
[AsPh₄][EtSCo(DH)₂CH₃]

atom	U11	U22	U33	U12	U13	U23
C(38)	58(6)	33(5)	54(5)	-4(5)	-2(5)	-7(5)

Table S-6. H-Atom Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) of $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$

atom	x	y	z	U
H(2A)	7469(7)	9145(3)	4013(2)	38
H(4A)	7809(7)	7895(3)	2103(2)	37
H(1A)	6441(10)	9427(4)	2370(3)	38
H(1B)	7284(10)	9957(4)	2757(3)	38
H(1C)	5728(10)	9624(4)	2893(3)	38
H(2B)	8720(10)	6744(4)	2648(3)	37
H(2C)	10211(10)	7170(4)	2736(3)	37
H(3B)	10550(11)	5823(5)	2857(4)	58
H(3C)	9340(11)	5829(5)	3278(4)	58
H(3D)	10842(11)	6258(5)	3368(4)	58
H(5A)	3649(10)	7278(5)	2526(3)	51
H(5B)	2709(10)	7821(5)	2877(3)	51
H(5C)	3332(10)	7029(5)	3085(3)	51
H(7A)	4301(10)	8414(6)	4223(3)	53
H(7B)	3852(10)	7590(6)	4014(3)	53
H(7C)	3032(10)	8341(6)	3825(3)	53
H(9A)	11470(10)	9944(5)	3486(3)	51
H(9B)	11727(10)	10174(5)	2921(3)	51
H(9C)	12439(10)	9410(5)	3139(3)	51
H(11A)	10869(9)	8645(5)	1823(3)	45
H(11B)	12114(9)	8713(5)	2230(3)	45
H(11C)	11372(9)	9470(5)	2014(3)	45
H(13A)	8314(9)	6316(4)	4318(2)	30
H(14A)	7078(10)	7507(4)	4465(3)	40
H(15A)	5390(10)	7612(5)	5115(3)	37
H(16A)	4916(9)	6540(5)	5641(3)	36
H(17A)	6197(9)	5355(4)	5519(2)	31
H(19A)	10793(8)	5929(5)	5014(3)	32
H(20A)	13050(10)	6252(4)	4631(3)	42
H(21A)	13822(9)	5577(5)	3914(3)	52
H(22A)	12461(9)	4521(6)	3606(3)	48
H(23A)	10193(10)	4190(5)	3987(3)	43
H(25A)	6435(9)	5010(5)	3977(3)	34
H(26A)	5119(9)	4210(5)	3424(3)	33
H(27A)	5383(10)	2857(5)	3467(3)	42
H(28A)	6865(10)	2287(5)	4086(3)	41
H(29A)	8213(11)	3088(4)	4647(3)	38
H(31A)	6740(10)	3645(4)	5420(3)	41
H(32A)	6997(11)	3072(5)	6229(3)	48
H(33A)	8931(11)	3422(5)	6745(3)	46
H(34A)	10754(11)	4279(5)	6452(3)	51
H(35A)	10580(10)	4811(5)	5644(3)	40
H(5D)	1561(8)	6034(3)	10913(2)	61
H(36A)	1373(12)	6069(5)	11934(3)	65
H(36B)	1782(12)	6880(5)	11696(3)	65
H(36C)	130(12)	6624(5)	11734(3)	65
H(6A)	650(7)	6465(4)	10532(2)	64
H(37A)	1465(13)	6657(7)	9593(3)	90
H(37B)	2657(13)	6536(7)	10013(3)	90
H(37C)	1515(13)	5873(7)	9899(3)	90

Table S-6 (cont.) H-Atom Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) of $[\text{AsPh}_4][\text{EtSCo}(\text{DH})_2\text{CH}_3]$

atom	x	y	z	U
H(7D)	8513(7)	3443(3)	8603(2)	49
H(38A)	9218(11)	4670(5)	8003(3)	58
H(38B)	9918(11)	3890(5)	7804(3)	58

Table S-7. Elemental Analyses

		% C	% H	% N
		Calcd/ Found	Calcd/ Found	Calcd/ Found
pyCo(DH) ₂ (4-MePhS)	C ₂₀ H ₂₆ CoN ₅ O ₄ S	48.88 48.75	5.33 5.35	14.25 14.22
pyCo(DH) ₂ (3,5-Me ₂ PhS)	C ₂₁ H ₂₈ CoN ₅ O ₄ S	49.90 49.84	5.58 5.62	13.85 13.72
pyCo(DH) ₂ (2,6-Me ₂ PhS)	C ₂₁ H ₂₈ CoN ₅ O ₄ S	49.90 49.66	5.58 5.59	13.85 13.97
Me ₂ PhPCo(DH) ₂ CH ₃ •0.5H ₂ O	C ₁₇ H ₂₈ CoN ₄ O ₄ P •0.5H ₂ O	45.24 45.06	6.48 6.18	12.41 12.46
AsPh ₄ [EtSCo(DH) ₂ CH ₃]•H ₂ O	C ₃₅ H ₄₂ AsCoN ₄ O ₄ S •H ₂ O	54.83 54.58	5.78 5.80	7.31 7.29
AsPh ₄ [3,5-Me ₂ PhSCo(DH) ₂ CH ₃] •1.5H ₂ O	C ₄₁ H ₄₆ AsCoN ₄ O ₄ S •1.5H ₂ O	57.81 57.79	5.80 5.78	6.58 6.56
Co((DO)(DOH)pn)(<i>i</i> -C ₃ H ₇ OCS ₂) ₂	C ₁₉ H ₃₃ CoN ₄ O ₄ S ₄	40.13 40.22	5.85 5.91	9.85 9.81
Co((DO)(DOH)pn)(4-MePhSO ₂) ₂	C ₂₅ H ₃₃ CoN ₄ O ₆ S ₂	49.34 49.37	5.46 5.52	9.21 9.22
[<i>N</i> -MeImdCo((DO)(DOH)pn)Cl]PF ₆	C ₁₅ H ₂₅ ClCoF ₆ N ₆ O ₂ P	32.12 32.14	4.49 4.52	14.99 14.91
[<i>N</i> -MeImdCo((DO)(DOH)pn)- (4-MePhS)]PF ₆	C ₂₂ H ₃₂ CoF ₆ N ₆ O ₂ PS	40.75 40.72	4.97 5.05	12.96 12.90
[<i>N</i> -MeImdCo((DO)(DOH)pn)- (4-MePhSO ₂)]PF ₆	C ₂₂ H ₃₂ CoF ₆ N ₆ O ₄ PS	38.83 38.84	4.74 4.69	12.35 12.37
3,5-Me ₂ PhSCo((DO)(DOH)pn)CH ₃	C ₂₀ H ₃₁ CoN ₄ O ₂ S	53.32 53.30	6.94 6.86	12.44 12.37
EtSCo((DO)(DOH)pn)CH ₃ •0.5H ₂ O	C ₁₄ H ₂₇ CoN ₄ O ₂ S •0.5H ₂ O	43.86 43.90	7.36 7.33	14.61 14.62
[Me ₂ PhPCo((DO)(DOH)pn)CH ₃]PF ₆	C ₂₀ H ₃₃ CoF ₆ N ₄ O ₂ P ₂	40.28 40.39	5.58 5.61	9.39 9.46
[<i>i</i> -C ₃ H ₇ OCS ₂ Co(C ₁ py)]ClO ₄	C ₂₁ H ₃₁ ClCoN ₅ O ₇ S ₂	40.42 40.33	5.01 4.99	11.22 11.22
[4-MePhSO ₂ Co(C ₁ py)]ClO ₄	C ₂₄ H ₃₁ ClCoN ₅ O ₈ S	44.76 45.02	4.85 4.83	10.88 10.89
[4-MePhSCo(C ₁ py)]ClO ₄	C ₂₄ H ₃₁ ClCoN ₅ O ₆ S	47.10 46.23	5.11 5.06	11.44 11.17
[3,5-Me ₂ PhSCo(C ₁ py)]ClO ₄	C ₂₅ H ₃₃ ClCoN ₅ O ₆ S	47.97 47.83	5.31 5.36	11.19 11.15

Table S-8. ^1H NMR Data.

[NEt₄][3,5-Me₂PhS]. (DMSO-*d*₆): δ 1.14 (t, 12H), 1.98 (s, 6H), 3.19 (q, 8H), 6.02 (s, 1H), 6.62 (s, 2H).

[NEt₄][4-MePhS]. (CD₃CN): δ 1.14 (m, 12H), 2.06 (s, 3H), 3.10 (q, 8H), 6.53 (d, 2H), 7.00 (d, 2H).

[NEt₄][2,6-Me₂PhS]. (DMSO-*d*₆): δ 1.14 (t, 12H), 2.18 (s, 6H), 3.17 (q, 8H), 6.23 (t, 1H), 6.67 (d, 2H).

pyCo(DH)₂(4-MePhS). (CDCl₃): δ 2.02 (s, 12H), 2.13 (s, 3H), 6.87 (d, 2H), 7.27 (m, 4H), 7.69 (t, 1H), 8.47 (s, 2H, br), 18.40 (s, 2H, br).

pyCo(DH)₂(3,5-Me₂PhS). (CDCl₃): δ 2.01 (s, 12H), 2.25 (s, 6H), 6.91 (s, 1H), 7.03 (s, 2H), 7.26 (t, 2H), 7.69 (t, 1H), 8.45 (d, 2H), 18.57 (s, 2H).

pyCo(DH)₂(2,6-Me₂PhS). (CDCl₃): δ 2.08 (s, 12H, br), 2.33 (s, 6H), 6.88 (d, 2H), 7.06 (t, 1H), 7.26 (s, 2H, br, obscured), 7.68 (t, 1H), 8.44 (s, 2H, br), 18.50 (s, 2H).

Me₂PhPCo(DH)₂CH₃. (CDCl₃): δ 1.04 (d, 3H), 1.40 (s, 6H), 1.93 (d, 12H), 7.11 (t, 2H), 7.36 (m, 3H), 18.06 (s, 2H).

[AsPh₄][EtSCo(DH)₂CH₃·H₂O]. (DMSO-*d*₆): δ 0.06 (s, 3H), 0.85 (t, 3H), 1.47 (q, 2H), 2.00 (s, 12H), 7.79 (m, 16H), 7.92 (m, 4H), 18.65 (s, 2H).

[AsPh₄][3,5-Me₂PhSCo(DH)₂CH₃·H₂O]. (DMSO-*d*₆): δ 0.14 (s, 3H), 1.76 (s, 12H), 2.06 (s, 6H), 6.43 (s, 2H), 6.49 (s, 1H), 7.78 (m, 16H), 7.93 (m, 4H), 18.66 (s, 2H).

Co((DO)(DOH)pn)(*i*-C₃H₇OCS₂)₂. (CDCl₃): δ 1.30 (s, 6H), 1.32 (s, 6H), 2.31 (m, 2H), 2.41 (s, 6H), 2.45 (s, 6H), 3.83 (m, 4H), 5.67 (quintet, 2H), 19.07 (s, 1H).

Co((DO)(DOH)pn)(4-MePhSO₂)₂. (DMSO-*d*₆): δ 1.91 (s, 6H), 2.29 (s, 6H), 2.32 (s, 6H), 2.50 (m, 2H+DMSO), 3.92 (m, 4H), 6.95 (d, 4H), 7.12 (d, 4H), 17.80 (s, 1H).

[N-MeImdCo((DO)(DOH)pn)(4-MePhS)]PF₆. (CDCl₃): δ 2.16, 2.16, 2.19 (m, s, 10H), 2.33 (s, 6H), 2.64 (m, 1H), 3.67 (s, 3H), 3.98 (m, 4H), 6.29 (s, 1H), 6.80 (s, 1H), 6.91 (d, 2H), 7.05 (d, 2H), 7.15 (s, 1H), 18.91 (s, 1H).

[N-MeImdCo((DO)(DOH)pn)(4-MePhSO₂)]PF₆. (CDCl₃, sl. sol): δ 2.23 (s, 6H), 2.38 (s, 3H), 2.59 (s, 6H), 3.66 (s, 3H), 4.13 (m, 4H), 6.14 (s, 1H), 6.78 (s, 1H), 7.07 (s, 1H), 7.17 (s, 4H), 18.17 (s, 1H). (DMSO-*d*₆, v.sol): δ 2.18, (s, 6H), 2.34 (s, 3H), 2.57 (s, 6H), 3.60 (s, 3H), 3.91 (m, 4H), 6.30 (s, 1H), 7.09 (d, 2H), 7.25 (m, 4H), 18.27 (s, 1H).

[N-MeImdCo((DO)(DOH)pn)Cl]PF₆. (DMSO-*d*₆): δ 1.86 (m, 1H), 2.42 (m, 1H), 2.52 (s, 6H, overlap), 2.68 (s, 6H), 3.60 (s, 3H), 4.04 (m, 4H), 6.28 (s, 1H), 7.22 (s, 1H), 7.27 (s, 1H), 18.89 (s, 1H).

[N-MeImdCo((DO)(DOH)pn)(3,5-Me₂PhS)]PF₆. (CDCl₃): δ 2.10 (m, 1H), 2.19 (s, 6H), 2.26 (s, 6H), 2.34 (s, 6H, br), 2.65 (m, 1H), 3.68 (s, 3H), 4.02 (m, 4H), 6.29 (s, 1H, br), 6.81 (s, 3H), 7.01 (s, 1H, br), 7.17 (s, 1H, br), 18.92 (s, 1H).

3,5-Me₂PhSCo((DO)(DOH)pn)CH₃. (DMSO-*d*₆): δ 0.38 (s, 3H), 1.89 (m, 1H), 1.93 (s, 6H), 1.97 (s, 6H), 2.10 (s, 6H), 2.4 (m, 1H), 3.65 (m, 4H), 6.39 (s, 2H), 6.65 (s, 1H), 19.34 (s, 1H).

[Me₂PhPCo((DO)(DOH)pn)CH₃]PF₆. (CDCl₃): δ 1.01 (d, 3H), 1.42 (d, 6H), 2.05 (d, m, 7H), 2.09 (d+m, 7H), 3.63 (m, 4H), 7.08 (t, 2H), 7.48 (m, 3H), O·H-O (too broad).

EtSCo((DO)(DOH)pn)CH₃. (DMSO-*d*₆): δ 0.28 (s, 3H), 0.88 (t, 3H), 1.28 (q, 2H), 1.90 (m, 1H), 2.15 (s, 6H), 2.27 (s, 6H), 2.32 (m, 1H), 3.69 (m, 4H), 19.41 (s, 1H).

Table S-8 cont. ^1H NMR Data.

[*i*-C₃H₇OCS₂Co(C₁py)]ClO₄. (CDCl₃): δ 1.36 (s, 3H), 1.38 (s, 3H), 2.40 (s, 6H), 2.54 (s, 6H), 3.18 (s, 1H), 3.67 (d, 2H), 4.27 (m, 4H), 5.68 (m, 1H), 7.10 (t, 1H), 7.35 (d, 1H), 7.63 (t, 1H), 8.14 (d, 1H), 19.04 (s, 1H).

[4-MePhSO₂Co(C₁py)]ClO₄. (CDCl₃): δ 2.08 (s, 6H), 2.39 (s, 3H), 2.46 (s, 6H), 3.12 (m, 1H), 3.65 (d, 2H), 4.41 (m, 4H), 7.05 (t, 1H), 7.21 (q, overlap, 4H), 7.35 (d, 1H), 7.63 (t, 1H), 7.88 (d, 1H), 18.78 (s, 1H).

[4-MePhSCo(C₁py)]ClO₄. (CDCl₃): δ 2.12 (s, 6H), 2.16 (s, 3H), 2.25 (s, 6H), 3.26 (m, 1H), 3.69 (d, 2H), 4.32 (m, 4H), 6.93 (d, 2H), 7.06 (m, 3H), 7.38 (d, 1H), 7.62 (t, 1H), 8.09 (d, 1H), 19.29 (s, 1H).

[3,5-Me₂PhSCo(C₁py)]ClO₄. (CDCl₃): δ 2.12 (s, 6H), 2.26 (s, 12H), 3.26 (m, 1H), 3.70 (d, 2H), 4.33 (m, 4H), 6.83 (d, 2H), 7.01 (s, 1H), 7.07 (t, 1H), 7.38 (d, 1H), 7.62 (t, 1H), 8.10 (d, 1H, br), 19.29 (s, 1H).

Table S-9. ^1H NMR Shifts of Sulfur Compounds and of Cobaloximes

compound	S-ligand signals	oxime CH_3	axial CH_3	NMR solvent
$[\text{CH}_3\text{SCo}(\text{DH})_2\text{CH}_3]^{-a}$	1.28	2.18	0.69	$\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (1:1)
CH_3S^{-a}	1.95			$\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (1:1)
$\text{CH}_3\text{SSCH}_3^a$	2.43			$\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (1:1)
CH_3SH^a	2.05			$\text{CD}_3\text{OD}/\text{D}_2\text{O}$ (1:1)
EtSSEt	2.70, 1.32 ^b			CDCl_3
EtSH^b	2.55(2H), 1.39 (m, 1H), 1.33 (t, 3H)			CDCl_3
EtSCH_3^b	2.52, 2.10 (s), 1.27			CDCl_3

^aRef. 1. ^bRef. 2.**Table S-10.** ^1H NMR shifts of $[\text{LCo}((\text{DO})(\text{DOH})\text{pn})\text{CH}_3]^{(0/+)}$ in CD_3OD

L	axial CH_3	N- CH_2	imine CH_3	oxime CH_3	EtS (CH_2S)	EtS (CH_3)
EtS^-	0.57	3.74	2.32	2.23	1.72	1.05
H_2O	0.79	3.79	2.42	2.30		
PMe_3	0.99 ^a	3.81	2.41	2.29		
$\text{PMe}_3 + 1$ equiv	0.99 ^a	3.78	<i>b</i>	2.29	2.50 ^c	1.27 ^c
NaSEt						
$\text{PMe}_3 + 1$ equiv	0.58 ^a	3.75 ^d	<i>b</i>	2.22 ^d	1.74 ^d	1.05 ^{d,e}
NaSEt , later ^d						

^aDoublet. ^bSignal disappeared (D-exchange). ^c NaSEt . ^dSolution color changed from yellow to green. Additional signals given represent a minor species. ^eShoulder.**Table S-11.** NaSEt interaction with $[\text{N-MeImdCo}(\text{N-CH}_2\text{-CHEL})]\text{ClO}_4$ in CD_3OD

NaSEt	H2	H4	H5	N-Me	axial CH_2	imine CH_3	oxime CH_3 's	EtS- (CH_2S)	Et S- (CH_3)
none	7.47	7.25	6.73	3.77	5.77 5.49	2.34	2.28 2.06		
2.4 equiv	7.58 ^a	7.06 ^a	6.94 ^a	3.73 ^a	5.52 5.24	2.23	2.03 2.00	2.68 ^b 2.50	1.28 ^b 1.17

^aFree *N-MeImd*. ^bSignals for EtSSEt .**References**

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