Supporting Information

Novel Cu(I)-Selective Chelators Based on a Bis(phosphorothioyl)amide Scaffold

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Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **7**.

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Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8**.

Table S18. Torsion angles [deg] for **8**.

NMR spectra of metal-ion-complexes of compounds 6, 7, and 8

Fig. S1. ^{13}C-MAS NMR spectra at 125 MHz: a. compound **6**. b. **6**-Hg(II) complex. c. **6**-Zn(II) complex.

Fig. S2. ^{31}P-MAS NMR spectra at 202 MHz: a. compound **7**. b. **7**-Ni(II) complex.

Fig. S3. ^{31}P-NMR spectra in DMSO-d_6 of 8-Cu(I) complex at 241 MHz.

X-ray crystal structures of BTPA/BOPA analogues 6, 7 and 8

Table S1. Crystal data and structure refinement for **6** (CCDC 911195).

Identification code	aa53
Empirical formula	C_{12} H_{28} N_2 P_2 S_6
Formula weight	454.66
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.9500(2) A alpha = 90 deg. b = 9.3645(3) A beta = 100.133(2) deg. c = 19.1773(6) A gamma = 90 deg.
Volume	2112.58(10) A^3
Z, Calculated density	4, 1.429 Mg/m^3
Absorption coefficient	0.796 mm^-1
F(000)	960
Crystal size	0.28 x 0.28 x 0.22 mm
Theta range for data collection	3.09 to 25.68 deg.
Limiting indices	-14<=h<=14, 0<=k<=11, 0<=l<=23
Reflections collected / unique	8145 / 3999 [R(int) = 0.0350]

Completeness to theta = 25.68 99.5 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.8443 and 0.8078

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 3999 / 0 / 208

Goodness-of-fit on F^2 1.090

Final R indices [I>2sigma(I)] R1 = 0.0551, wR2 = 0.1509

R indices (all data) R1 = 0.0723, wR2 = 0.1654

Largest diff. peak and hole 0.956 and -0.510 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **6**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
P(1)	7959(1)	3024(1)	1322(1)	29(1)
S(1)	7728(1)	2991(1)	283(1)	44(1)
S(2)	7314(1)	1124(1)	1699(1)	39(1)
S(3)	9668(1)	2803(1)	1812(1)	36(1)
C(1)	8610(3)	516(4)	2247(2)	41(1)
C(2)	9639(3)	904(4)	1940(3)	46(1)
N(1)	7528(3)	4497(3)	1601(2)	36(1)

P(2)	7058(1)	4997(1)	2286(1)	29(1)
S(4)	7296(1)	7037(1)	2476(1)	38(1)
S(5)	7673(1)	3822(1)	3228(1)	37(1)
S(6)	5350(1)	4345(1)	2150(1)	37(1)
C(3)	5349(3)	4132(5)	3086(2)	41(1)
C(4)	6327(3)	3124(5)	3394(2)	42(1)
N(2)	2435(2)	3411(4)	-3(2)	34(1)
C(5)	2959(4)	3603(5)	782(2)	50(1)
C(6)	2294(4)	4596(5)	1172(2)	43(1)
C(7)	1190(4)	2974(5)	-116(2)	46(1)
C(8)	675(4)	3076(5)	-908(2)	53(1)
C(9)	979(5)	1556(6)	209(3)	73(2)
C(10)	3236(4)	2589(5)	-389(2)	50(1)
C(11)	4247(4)	3459(6)	-459(2)	52(1)
C(12)	3598(5)	1169(6)	-55(4)	76(2)

Table S3. Bond lengths [A] and angles [deg] for **6**.

P(1)-N(1)	1.597(3)
P(1)-S(1)	1.9635(13)
P(1)-S(3)	2.1025(13)
P(1)-S(2)	2.1158(13)
S(2)-C(1)	1.804(4)
S(3)-C(2)	1.797(4)
C(1)-C(2)	1.498(6)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
N(1)-P(2)	1.588(3)
P(2)-S(4)	1.9563(14)

P(2)-S(6)	2.1013(12)
P(2)-S(5)	2.1315(13)
S(5)-C(4)	1.817(4)
S(6)-C(3)	1.806(4)
C(3)-C(4)	1.537(6)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
N(2)-C(10)	1.518(5)
N(2)-C(7)	1.521(5)
N(2)-C(5)	1.537(5)
N(2)-H(2C)	0.87(4)
C(5)-C(6)	1.505(6)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(9)	1.507(6)
C(7)-C(8)	1.538(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.483(7)
C(10)-C(12)	1.506(7)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

N(1)-P(1)-S(1)	110.98(13)
N(1)-P(1)-S(3)	106.26(13)
S(1)-P(1)-S(3)	113.83(6)
N(1)-P(1)-S(2)	116.97(12)
S(1)-P(1)-S(2)	109.79(6)
S(3)-P(1)-S(2)	98.52(5)
C(1)-S(2)-P(1)	97.89(13)
C(2)-S(3)-P(1)	96.76(14)
C(2)-C(1)-S(2)	112.0(3)
C(2)-C(1)-H(1A)	109.2
S(2)-C(1)-H(1A)	109.2
C(2)-C(1)-H(1B)	109.2
S(2)-C(1)-H(1B)	109.2
H(1A)-C(1)-H(1B)	107.9
C(1)-C(2)-S(3)	109.3(3)
C(1)-C(2)-H(2A)	109.8
S(3)-C(2)-H(2A)	109.8
C(1)-C(2)-H(2B)	109.8
S(3)-C(2)-H(2B)	109.8
H(2A)-C(2)-H(2B)	108.3
P(2)-N(1)-P(1)	135.6(2)
N(1)-P(2)-S(4)	112.39(12)
N(1)-P(2)-S(6)	106.79(13)
S(4)-P(2)-S(6)	114.41(6)
N(1)-P(2)-S(5)	115.38(12)
S(4)-P(2)-S(5)	109.22(6)
S(6)-P(2)-S(5)	97.95(5)
C(4)-S(5)-P(2)	98.65(13)
C(3)-S(6)-P(2)	94.52(13)
C(4)-C(3)-S(6)	108.5(3)

C(4)-C(3)-H(3A)	110.0
S(6)-C(3)-H(3A)	110.0
C(4)-C(3)-H(3B)	110.0
S(6)-C(3)-H(3B)	110.0
H(3A)-C(3)-H(3B)	108.4
C(3)-C(4)-S(5)	110.3(3)
C(3)-C(4)-H(4A)	109.6
S(5)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4B)	109.6
S(5)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
C(10)-N(2)-C(7)	118.6(3)
C(10)-N(2)-C(5)	110.7(3)
C(7)-N(2)-C(5)	112.9(3)
C(10)-N(2)-H(2C)	107(3)
C(7)-N(2)-H(2C)	102(2)
C(5)-N(2)-H(2C)	104(3)
C(6)-C(5)-N(2)	113.6(3)
C(6)-C(5)-H(5A)	108.9
N(2)-C(5)-H(5A)	108.9
C(6)-C(5)-H(5B)	108.9
N(2)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(9)-C(7)-N(2)	114.2(4)
C(9)-C(7)-C(8)	113.3(4)
N(2)-C(7)-C(8)	109.6(3)
C(9)-C(7)-H(7)	106.4
N(2)-C(7)-H(7)	106.4

C(8)-C(7)-H(7)	106.4
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(12)	110.2(4)
C(11)-C(10)-N(2)	111.1(4)
C(12)-C(10)-N(2)	113.6(4)
C(11)-C(10)-H(10)	107.2
C(12)-C(10)-H(10)	107.2
N(2)-C(10)-H(10)	107.2
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **6**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
P(1)	28(1)	28(1)	31(1)	6(1)	4(1)	-1(1)
S(1)	63(1)	40(1)	29(1)	2(1)	4(1)	3(1)
S(2)	30(1)	37(1)	48(1)	14(1)	-1(1)	-9(1)
S(3)	27(1)	31(1)	47(1)	4(1)	3(1)	-5(1)
C(1)	40(2)	32(2)	50(2)	14(2)	4(2)	4(2)
C(2)	32(2)	34(2)	71(3)	3(2)	5(2)	1(2)
N(1)	46(2)	26(2)	38(2)	8(1)	12(1)	2(1)
P(2)	24(1)	30(1)	33(1)	5(1)	4(1)	1(1)
S(4)	37(1)	33(1)	43(1)	-2(1)	7(1)	0(1)
S(5)	25(1)	49(1)	37(1)	11(1)	2(1)	1(1)
S(6)	24(1)	45(1)	40(1)	4(1)	-1(1)	-4(1)
C(3)	30(2)	49(2)	46(2)	6(2)	12(2)	1(2)
C(4)	36(2)	47(2)	45(2)	14(2)	10(2)	-6(2)
N(2)	32(2)	33(2)	37(2)	6(1)	3(1)	5(1)
C(5)	51(3)	55(3)	42(2)	-6(2)	2(2)	6(2)
C(6)	46(2)	47(2)	38(2)	4(2)	15(2)	-3(2)
C(7)	40(2)	47(3)	52(3)	2(2)	8(2)	-8(2)
C(8)	39(2)	66(3)	50(3)	2(2)	0(2)	-15(2)
C(9)	64(3)	65(3)	93(4)	33(3)	21(3)	-13(3)
C(10)	53(3)	57(3)	42(2)	-6(2)	10(2)	11(2)
C(11)	43(2)	72(3)	42(2)	4(2)	13(2)	12(2)
C(12)	84(4)	50(3)	96(4)	-11(3)	26(3)	9(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6**.

	x	y	z	U(eq)
H(1A)	8674	946	2724	49
H(1B)	8579	-534	2300	49
H(2A)	9615	411	1481	56
H(2B)	10335	597	2264	56
H(3A)	5453	5071	3326	49
H(3B)	4614	3726	3160	49
H(4A)	6191	2168	3176	51
H(4B)	6355	3022	3911	51
H(2C)	2390(30)	4280(50)	-170(20)	29(10)
H(5A)	3010	2658	1017	60
H(5B)	3741	3977	817	60
H(6A)	2161	5499	912	65
H(6B)	2725	4780	1647	65
H(6C)	1563	4158	1210	65
H(7)	793	3708	130	56
H(8A)	1012	2340	-1170	79
H(8B)	834	4022	-1087	79
H(8C)	-149	2932	-972	79
H(9A)	1228	783	-72	110
H(9B)	165	1451	217	110
H(9C)	1406	1511	694	110
H(10)	2817	2393	-878	60
H(11A)	4778	3464	-8	78
H(11B)	4009	4439	-589	78
H(11C)	4621	3048	-829	78
H(12A)	4194	756	-285	113
H(12B)	2944	522	-113	113
H(12C)	3894	1304	451	113

Table S6. Torsion angles [deg] for **6**.

N(1)-P(1)-S(2)-C(1)	-110.5(2)
S(1)-P(1)-S(2)-C(1)	121.92(16)
S(3)-P(1)-S(2)-C(1)	2.71(16)
N(1)-P(1)-S(3)-C(2)	143.0(2)
S(1)-P(1)-S(3)-C(2)	-94.57(17)
S(2)-P(1)-S(3)-C(2)	21.55(17)
P(1)-S(2)-C(1)-C(2)	-33.9(3)
S(2)-C(1)-C(2)-S(3)	56.7(4)
P(1)-S(3)-C(2)-C(1)	-47.0(3)
S(1)-P(1)-N(1)-P(2)	152.9(3)
S(3)-P(1)-N(1)-P(2)	-82.9(3)
S(2)-P(1)-N(1)-P(2)	25.8(4)
P(1)-N(1)-P(2)-S(4)	155.5(3)
P(1)-N(1)-P(2)-S(6)	-78.3(3)
P(1)-N(1)-P(2)-S(5)	29.3(4)
N(1)-P(2)-S(5)-C(4)	-118.7(2)
S(4)-P(2)-S(5)-C(4)	113.60(16)
S(6)-P(2)-S(5)-C(4)	-5.78(16)
N(1)-P(2)-S(6)-C(3)	150.29(18)
S(4)-P(2)-S(6)-C(3)	-84.69(15)
S(5)-P(2)-S(6)-C(3)	30.67(15)
P(2)-S(6)-C(3)-C(4)	-54.4(3)
S(6)-C(3)-C(4)-S(5)	57.3(4)
P(2)-S(5)-C(4)-C(3)	-27.6(3)
C(10)-N(2)-C(5)-C(6)	171.2(4)
C(7)-N(2)-C(5)-C(6)	-53.1(5)
C(10)-N(2)-C(7)-C(9)	69.9(5)
C(5)-N(2)-C(7)-C(9)	-62.1(5)
C(10)-N(2)-C(7)-C(8)	-58.5(5)
C(5)-N(2)-C(7)-C(8)	169.6(4)
C(7)-N(2)-C(10)-C(11)	157.1(4)

C(5)-N(2)-C(10)-C(11)	-70.0(5)
C(7)-N(2)-C(10)-C(12)	-78.0(5)
C(5)-N(2)-C(10)-C(12)	55.0(5)

Symmetry transformations used to generate equivalent atoms:

Table S7. Crystal data and structure refinement for **7** (CCDC 911194).

Identification code	aa49
Empirical formula	C12 H28 N2 O4 P2 S2
Formula weight	390.42
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.1970(16) A alpha = 90 deg. b = 11.374(2) A beta = 90 deg. c = 19.694(4) A gamma = 90 deg.
Volume	1836.1(6) A^3
Z, Calculated density	4, 1.412 Mg/m^3
Absorption coefficient	0.481 mm^-1
F(000)	832
Crystal size	0.40 x 0.40 x 0.30 mm

Theta range for data collection	2.69 to 27.46 deg.
Limiting indices	-10<=h<=10, -14<=k<=14, -25<=l<=25
Reflections collected / unique	4155 / 4155 [R(int) = 0.0330]
Completeness to theta = 27.46	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8691 and 0.8308
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4155 / 0 / 208
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1109
R indices (all data)	R1 = 0.0452, wR2 = 0.1139
Absolute structure parameter	-0.17(10)
Largest diff. peak and hole	0.426 and -0.567 e.A^-3

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **7**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)

P(1)	1425(1)	5591(1)	758(1)	15(1)
P(2)	-578(1)	4508(1)	-286(1)	17(1)
S(1)	1596(1)	5478(1)	1750(1)	22(1)
S(2)	723(1)	5001(1)	-1059(1)	23(1)
O(1)	1418(2)	6935(2)	493(1)	20(1)
O(2)	3147(2)	5226(2)	424(1)	18(1)
O(3)	-2491(2)	4800(2)	-408(1)	21(1)
O(4)	-787(3)	3095(2)	-238(1)	24(1)
N(1)	-90(3)	4921(2)	458(1)	20(1)
N(2)	-2109(3)	4546(2)	2218(1)	16(1)
C(1)	3057(3)	7293(3)	310(2)	22(1)
C(2)	3831(3)	6182(2)	27(2)	20(1)
C(3)	-3500(3)	3797(2)	-242(1)	19(1)
C(4)	-2439(3)	2721(3)	-364(2)	21(1)
C(5)	-1964(4)	3941(3)	2908(1)	23(1)
C(6)	-259(4)	4016(3)	3202(2)	29(1)
C(7)	-2682(3)	3713(3)	1662(1)	19(1)
C(8)	-1489(4)	2711(3)	1582(2)	24(1)
C(9)	-4413(4)	3300(3)	1794(2)	28(1)
C(10)	-3100(3)	5682(3)	2265(1)	22(1)
C(11)	-2192(4)	6513(3)	2740(2)	28(1)
C(12)	-3336(4)	6236(3)	1569(2)	30(1)

Table S9. Bond lengths [A] and angles [deg] for **7**.

P(1)-N(1)	1.572(2)
P(1)-O(2)	1.6113(19)
P(1)-O(1)	1.615(2)
P(1)-S(1)	1.9631(10)
P(2)-N(1)	1.588(2)
P(2)-O(4)	1.619(2)
P(2)-O(3)	1.621(2)
P(2)-S(2)	1.9414(10)
O(1)-C(1)	1.450(3)
O(2)-C(2)	1.453(3)
O(3)-C(3)	1.447(3)
O(4)-C(4)	1.440(3)
N(2)-C(7)	1.522(4)
N(2)-C(5)	1.527(3)
N(2)-C(10)	1.528(4)
N(2)-H(2C)	0.87(4)
C(1)-C(2)	1.520(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.520(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.515(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800

C(6)-H(6C)	0.9800
C(7)-C(8)	1.510(4)
C(7)-C(9)	1.517(4)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.522(4)
C(10)-C(11)	1.523(4)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
N(1)-P(1)-O(2)	114.42(12)
N(1)-P(1)-O(1)	109.52(13)
O(2)-P(1)-O(1)	96.59(10)
N(1)-P(1)-S(1)	113.56(9)
O(2)-P(1)-S(1)	109.07(8)
O(1)-P(1)-S(1)	112.54(8)
N(1)-P(2)-O(4)	105.51(13)
N(1)-P(2)-O(3)	108.68(12)
O(4)-P(2)-O(3)	96.28(11)
N(1)-P(2)-S(2)	119.93(9)
O(4)-P(2)-S(2)	112.96(9)
O(3)-P(2)-S(2)	110.80(9)
C(1)-O(1)-P(1)	110.07(17)
C(2)-O(2)-P(1)	111.45(16)
C(3)-O(3)-P(2)	110.93(16)

C(4)-O(4)-P(2)	112.51(17)
P(1)-N(1)-P(2)	133.55(15)
C(7)-N(2)-C(5)	112.6(2)
C(7)-N(2)-C(10)	114.0(2)
C(5)-N(2)-C(10)	111.6(2)
C(7)-N(2)-H(2C)	107(2)
C(5)-N(2)-H(2C)	107(2)
C(10)-N(2)-H(2C)	104(2)
O(1)-C(1)-C(2)	104.2(2)
O(1)-C(1)-H(1A)	110.9
C(2)-C(1)-H(1A)	110.9
O(1)-C(1)-H(1B)	110.9
C(2)-C(1)-H(1B)	110.9
H(1A)-C(1)-H(1B)	108.9
O(2)-C(2)-C(1)	105.2(2)
O(2)-C(2)-H(2A)	110.7
C(1)-C(2)-H(2A)	110.7
O(2)-C(2)-H(2B)	110.7
C(1)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8
O(3)-C(3)-C(4)	105.8(2)
O(3)-C(3)-H(3A)	110.6
C(4)-C(3)-H(3A)	110.6
O(3)-C(3)-H(3B)	110.6
C(4)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
O(4)-C(4)-C(3)	105.8(2)
O(4)-C(4)-H(4A)	110.6
C(3)-C(4)-H(4A)	110.6
O(4)-C(4)-H(4B)	110.6
C(3)-C(4)-H(4B)	110.6
H(4A)-C(4)-H(4B)	108.7
C(6)-C(5)-N(2)	112.7(2)
C(6)-C(5)-H(5A)	109.0

N(2)-C(5)-H(5A)	109.0
C(6)-C(5)-H(5B)	109.0
N(2)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(9)	113.0(3)
C(8)-C(7)-N(2)	110.2(2)
C(9)-C(7)-N(2)	111.0(2)
C(8)-C(7)-H(7)	107.5
C(9)-C(7)-H(7)	107.5
N(2)-C(7)-H(7)	107.5
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	111.0(3)
C(12)-C(10)-N(2)	111.3(2)
C(11)-C(10)-N(2)	107.6(2)
C(12)-C(10)-H(10)	109.0
C(11)-C(10)-H(10)	109.0
N(2)-C(10)-H(10)	109.0

C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for **7**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
P(1)	14(1)	16(1)	16(1)	0(1)	3(1)	-1(1)
P(2)	14(1)	14(1)	22(1)	-1(1)	-1(1)	-1(1)
S(1)	21(1)	31(1)	16(1)	0(1)	2(1)	-2(1)
S(2)	21(1)	30(1)	19(1)	-2(1)	0(1)	-3(1)
O(1)	19(1)	15(1)	27(1)	2(1)	2(1)	2(1)
O(2)	15(1)	16(1)	24(1)	2(1)	5(1)	1(1)
O(3)	13(1)	17(1)	34(1)	2(1)	-3(1)	0(1)
O(4)	18(1)	12(1)	41(1)	-1(1)	-5(1)	-1(1)
N(1)	19(1)	24(1)	18(1)	-1(1)	3(1)	-6(1)
N(2)	13(1)	20(1)	16(1)	1(1)	1(1)	0(1)
C(1)	20(1)	19(1)	28(1)	2(1)	-1(1)	-4(1)
C(2)	16(1)	20(1)	24(1)	2(1)	4(1)	-5(1)

C(3)	17(1)	19(1)	22(1)	-2(1)	0(1)	-3(1)
C(4)	17(1)	18(1)	26(1)	-2(1)	-2(1)	-4(1)
C(5)	28(2)	27(2)	15(1)	2(1)	3(1)	-1(1)
C(6)	34(2)	35(2)	19(1)	2(1)	-7(1)	0(1)
C(7)	18(1)	24(1)	15(1)	-2(1)	-3(1)	-1(1)
C(8)	25(1)	23(1)	24(1)	-3(1)	1(1)	2(1)
C(9)	20(1)	33(2)	32(2)	-6(1)	-3(1)	-7(1)
C(10)	20(1)	24(2)	23(1)	0(1)	2(1)	0(1)
C(11)	28(2)	26(2)	32(2)	-9(1)	0(1)	1(1)
C(12)	33(2)	30(2)	28(2)	4(1)	-4(1)	9(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **7**.

	x	y	z	U(eq)
H(2C)	-1130(50)	4780(30)	2103(18)	24(9)
H(1A)	3663	7578	713	27
H(1B)	3034	7923	-37	27
H(2A)	3561	6086	-460	24
H(2B)	5032	6208	77	24
H(3A)	-4480	3774	-535	23
H(3B)	-3853	3833	239	23
H(4A)	-2747	2077	-51	25
H(4B)	-2561	2440	-837	25
H(5A)	-2741	4310	3228	28
H(5B)	-2271	3104	2858	28
H(6A)	531	3735	2865	44
H(6B)	-193	3528	3610	44
H(6C)	-14	4835	3319	44
H(7)	-2688	4164	1226	23
H(8A)	-1524	2211	1987	36
H(8B)	-385	3027	1525	36

H(8C)	-1783	2245	1182	36
H(9A)	-4732	2732	1444	42
H(9B)	-5154	3976	1781	42
H(9C)	-4470	2926	2242	42
H(10)	-4193	5500	2465	27
H(11A)	-1088	6648	2565	43
H(11B)	-2127	6162	3194	43
H(11C)	-2777	7263	2766	43
H(12A)	-3739	7042	1623	45
H(12B)	-4130	5775	1309	45
H(12C)	-2292	6249	1327	45

Table S12. Torsion angles [deg] for **7**.

N(1)-P(1)-O(1)-C(1)	-138.16(19)
O(2)-P(1)-O(1)-C(1)	-19.3(2)
S(1)-P(1)-O(1)-C(1)	94.51(18)
N(1)-P(1)-O(2)-C(2)	111.69(19)
O(1)-P(1)-O(2)-C(2)	-3.25(19)
S(1)-P(1)-O(2)-C(2)	-119.88(17)
N(1)-P(2)-O(3)-C(3)	-93.5(2)
O(4)-P(2)-O(3)-C(3)	15.3(2)
S(2)-P(2)-O(3)-C(3)	132.76(16)
N(1)-P(2)-O(4)-C(4)	115.2(2)
O(3)-P(2)-O(4)-C(4)	3.8(2)
S(2)-P(2)-O(4)-C(4)	-111.94(19)
O(2)-P(1)-N(1)-P(2)	-38.5(3)
O(1)-P(1)-N(1)-P(2)	68.6(2)
S(1)-P(1)-N(1)-P(2)	-164.61(18)
O(4)-P(2)-N(1)-P(1)	120.9(2)
O(3)-P(2)-N(1)-P(1)	-136.8(2)
S(2)-P(2)-N(1)-P(1)	-7.9(3)

P(1)-O(1)-C(1)-C(2)	34.2(3)
P(1)-O(2)-C(2)-C(1)	23.2(3)
O(1)-C(1)-C(2)-O(2)	-34.9(3)
P(2)-O(3)-C(3)-C(4)	-28.2(3)
P(2)-O(4)-C(4)-C(3)	-20.3(3)
O(3)-C(3)-C(4)-O(4)	29.6(3)
C(7)-N(2)-C(5)-C(6)	121.6(3)
C(10)-N(2)-C(5)-C(6)	-108.8(3)
C(5)-N(2)-C(7)-C(8)	-60.3(3)
C(10)-N(2)-C(7)-C(8)	171.4(2)
C(5)-N(2)-C(7)-C(9)	65.6(3)
C(10)-N(2)-C(7)-C(9)	-62.7(3)
C(7)-N(2)-C(10)-C(12)	-47.3(3)
C(5)-N(2)-C(10)-C(12)	-176.2(2)
C(7)-N(2)-C(10)-C(11)	-169.1(2)
C(5)-N(2)-C(10)-C(11)	62.1(3)

Table S13. Crystal data and structure refinement for **8** (CCDC 911196).

Identification code	aa75
Empirical formula	$C_6 H_{13} N P_2 S_6$
Formula weight	353.47
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.2348(4) A alpha = 90 deg.
	b = 16.6337(8) A beta = 106.102(2) deg.
	c = 10.4261(5) A gamma = 90 deg.

Volume	1372.09(11) A^3
Z, Calculated density	4, 1.711 Mg/m^3
Absorption coefficient	1.198 mm^-1
F(000)	728
Crystal size	0.25 x 0.25 x 0.25 mm
Theta range for data collection	2.37 to 28.40 deg.
Limiting indices	-10<=h<=10, -22<=k<=17, -13<=l<=12
Reflections collected / unique	10250 / 3325 [R(int) = 0.0245]
Completeness to theta = 28.40	96.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7539 and 0.7539
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3325 / 0 / 137
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0624
R indices (all data)	R1 = 0.0262, wR2 = 0.0633
Largest diff. peak and hole	0.586 and -0.481 e.A^-3

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	1634(1)	1388(1)	5382(1)	12(1)
S(2)	3674(1)	2230(1)	8103(1)	11(1)
S(3)	5581(1)	1846(1)	5551(1)	14(1)
S(4)	6266(1)	-566(1)	9492(1)	11(1)
S(5)	8258(1)	-43(1)	7395(1)	11(1)
S(6)	7359(1)	1447(1)	9258(1)	13(1)
P(1)	4097(1)	1484(1)	6592(1)	7(1)
P(2)	6559(1)	441(1)	8374(1)	7(1)
C(1)	1450(2)	2452(1)	7294(2)	13(1)
N(1)	4636(2)	555(1)	7287(1)	7(1)
C(2)	570(2)	1706(1)	6610(2)	15(1)
C(3)	8391(2)	-1067(1)	8048(2)	15(1)
C(4)	8238(2)	-1045(1)	9463(2)	15(1)
C(5)	3906(2)	-162(1)	6452(1)	10(1)
C(6)	2395(2)	-510(1)	6822(2)	16(1)

Table S15. Bond lengths [A] and angles [deg] for **8**.

S(1)-C(2)	1.8188(16)
S(1)-P(1)	2.0768(5)
S(2)-C(1)	1.8294(16)
S(2)-P(1)	2.1085(5)
S(3)-P(1)	1.9410(5)
S(4)-C(4)	1.8167(15)
S(4)-P(2)	2.0938(5)

S(5)-C(3)	1.8261(16)
S(5)-P(2)	2.1075(5)
S(6)-P(2)	1.9353(5)
P(1)-N(1)	1.7124(13)
P(2)-N(1)	1.6835(12)
C(1)-C(2)	1.513(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
N(1)-C(5)	1.4998(18)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.515(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.516(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(2)-S(1)-P(1)	97.46(5)
C(1)-S(2)-P(1)	97.26(5)
C(4)-S(4)-P(2)	95.74(5)
C(3)-S(5)-P(2)	98.90(5)
N(1)-P(1)-S(3)	112.74(5)
N(1)-P(1)-S(1)	106.40(4)
S(3)-P(1)-S(1)	110.16(2)
N(1)-P(1)-S(2)	106.97(4)
S(3)-P(1)-S(2)	119.73(2)
S(1)-P(1)-S(2)	99.38(2)
N(1)-P(2)-S(6)	110.86(5)
N(1)-P(2)-S(4)	103.44(5)

S(6)-P(2)-S(4)	120.24(2)
N(1)-P(2)-S(5)	110.10(5)
S(6)-P(2)-S(5)	112.17(2)
S(4)-P(2)-S(5)	99.11(2)
C(2)-C(1)-S(2)	109.78(11)
C(2)-C(1)-H(1A)	109.7
S(2)-C(1)-H(1A)	109.7
C(2)-C(1)-H(1B)	109.7
S(2)-C(1)-H(1B)	109.7
H(1A)-C(1)-H(1B)	108.2
C(5)-N(1)-P(2)	116.86(9)
C(5)-N(1)-P(1)	117.22(9)
P(2)-N(1)-P(1)	118.11(7)
C(1)-C(2)-S(1)	107.99(10)
C(1)-C(2)-H(2A)	110.1
S(1)-C(2)-H(2A)	110.1
C(1)-C(2)-H(2B)	110.1
S(1)-C(2)-H(2B)	110.1
H(2A)-C(2)-H(2B)	108.4
C(4)-C(3)-S(5)	109.19(11)
C(4)-C(3)-H(3A)	109.8
S(5)-C(3)-H(3A)	109.8
C(4)-C(3)-H(3B)	109.8
S(5)-C(3)-H(3B)	109.8
H(3A)-C(3)-H(3B)	108.3
C(3)-C(4)-S(4)	110.03(11)
C(3)-C(4)-H(4A)	109.7
S(4)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4B)	109.7
S(4)-C(4)-H(4B)	109.7
H(4A)-C(4)-H(4B)	108.2
N(1)-C(5)-C(6)	112.43(12)
N(1)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5A)	109.1

N(1)-C(5)-H(5B)	109.1
C(6)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.9
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters (A^2 x 10^3) for **8**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	11(1)	13(1)	10(1)	-2(1)	-2(1)	4(1)
S(2)	11(1)	9(1)	11(1)	-3(1)	2(1)	2(1)
S(3)	18(1)	11(1)	16(1)	3(1)	10(1)	0(1)
S(4)	12(1)	10(1)	11(1)	3(1)	5(1)	4(1)
S(5)	10(1)	11(1)	14(1)	1(1)	6(1)	1(1)
S(6)	11(1)	10(1)	15(1)	-5(1)	-1(1)	0(1)
P(1)	8(1)	6(1)	7(1)	0(1)	2(1)	1(1)
P(2)	6(1)	7(1)	7(1)	0(1)	1(1)	1(1)
C(1)	12(1)	14(1)	15(1)	-2(1)	4(1)	4(1)
N(1)	6(1)	5(1)	9(1)	0(1)	-1(1)	0(1)
C(2)	10(1)	17(1)	18(1)	-2(1)	4(1)	0(1)
C(3)	17(1)	11(1)	17(1)	1(1)	8(1)	6(1)
C(4)	15(1)	14(1)	16(1)	5(1)	5(1)	9(1)
C(5)	11(1)	6(1)	11(1)	-4(1)	0(1)	0(1)
C(6)	11(1)	9(1)	24(1)	0(1)	2(1)	-2(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8**.

	x	y	z	U(eq)
H(1A)	893	2639	7968	16
H(1B)	1365	2886	6628	16
H(2A)	-633	1823	6167	18
H(2B)	626	1273	7274	18
H(3A)	7471	-1398	7480	18
H(3B)	9484	-1311	8040	18
H(4A)	9201	-743	10042	18
H(4B)	8272	-1600	9814	18
H(5A)	4789	-581	6567	12
H(5B)	3559	-3	5500	12
H(6A)	2710	-632	7779	23
H(6B)	2029	-1004	6312	23
H(6C)	1469	-119	6613	23

Table S18. Torsional angles [deg] for **8**.

C(2)-S(1)-P(1)-N(1)	92.77(7)
C(2)-S(1)-P(1)-S(3)	-144.73(6)
C(2)-S(1)-P(1)-S(2)	-18.14(6)
C(1)-S(2)-P(1)-N(1)	-118.28(7)
C(1)-S(2)-P(1)-S(3)	111.95(6)
C(1)-S(2)-P(1)-S(1)	-7.82(6)
C(4)-S(4)-P(2)-N(1)	135.77(7)
C(4)-S(4)-P(2)-S(6)	-99.97(6)
C(4)-S(4)-P(2)-S(5)	22.42(6)
C(3)-S(5)-P(2)-N(1)	-105.66(7)

C(3)-S(5)-P(2)-S(6)	130.38(6)
C(3)-S(5)-P(2)-S(4)	2.36(6)
P(1)-S(2)-C(1)-C(2)	39.46(11)
S(6)-P(2)-N(1)-C(5)	175.70(9)
S(4)-P(2)-N(1)-C(5)	-54.12(10)
S(5)-P(2)-N(1)-C(5)	50.99(11)
S(6)-P(2)-N(1)-P(1)	27.28(9)
S(4)-P(2)-N(1)-P(1)	157.46(6)
S(5)-P(2)-N(1)-P(1)	-97.43(7)
S(3)-P(1)-N(1)-C(5)	-87.08(10)
S(1)-P(1)-N(1)-C(5)	33.77(11)
S(2)-P(1)-N(1)-C(5)	139.28(9)
S(3)-P(1)-N(1)-P(2)	61.23(8)
S(1)-P(1)-N(1)-P(2)	-177.92(6)
S(2)-P(1)-N(1)-P(2)	-72.41(8)
S(2)-C(1)-C(2)-S(1)	-59.49(12)
P(1)-S(1)-C(2)-C(1)	46.55(11)
P(2)-S(5)-C(3)-C(4)	-33.62(12)
S(5)-C(3)-C(4)-S(4)	57.53(14)
P(2)-S(4)-C(4)-C(3)	-49.20(12)
P(2)-N(1)-C(5)-C(6)	111.27(12)
P(1)-N(1)-C(5)-C(6)	-100.02(13)

NMR spectra of metal-ion-complexes of compounds 6, 7, and 8

In solution NMR, spectra consist of a series of very sharp transitions, due to averaging of anisotropic (aniso) NMR interactions by rapid random tumbling.[27] By contrast, solid-state NMR spectra are very broad, as the full effects of anisotropic or orientation-dependent interactions are observed in the spectrum. In solid, the thermal molecular rotations are strongly restricted. Therefore, here we applied magic-angle spinning (MAS), method to obtain spectra of metal-ion complexes of **6** and **7**. In the ^{13}C-MAS-NMR spectrum of compound **6** and its Hg(II) and Zn(II) complexes, each

of the carbons at the dithio ring is observed, but changes of the spectrum from Hg to Zn complex imply on the structural differences (Fig. S1).

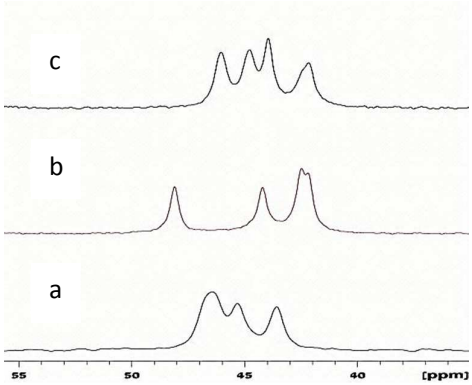

Fig. S1. ^{13}C-MAS NMR spectra at 125 MHz: a. compound **6**. b. **6**-Hg(II) complex. c. **6**-Zn(II) complex.

^{31}P-MAS-NMR spectrum of compound **7** (Fig. S2) exhibits iso peaks at 74 ppm J = 1250 Hz and an aniso pattern similar to **6**. The ^{31}P-MAS-NMR spectrum of **7**-Ni(II) complex exhibits very large anisotropy signals, which may be attributed to a polymeric structure.

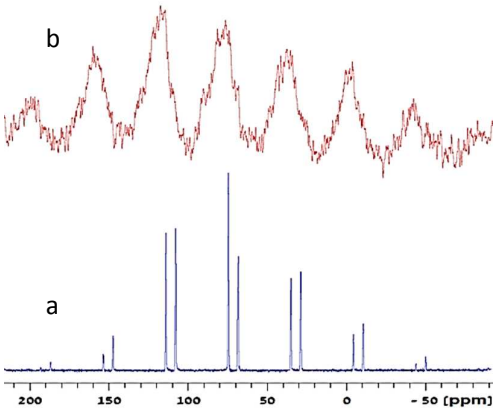

Fig. S4. ^{31}P-MAS NMR spectra at 202 MHz: a. compound **7**. b. **7**-Ni(II) complex.

The ssNMR spectra of chelators **6** and **7** and complexes of **6** with Hg(II) and Zn(II) have less aniso signals than ^{31}P-MAS-NMR spectra of **6**/**7**-Ni(II) complexes which is attributed to a polymeric structure.

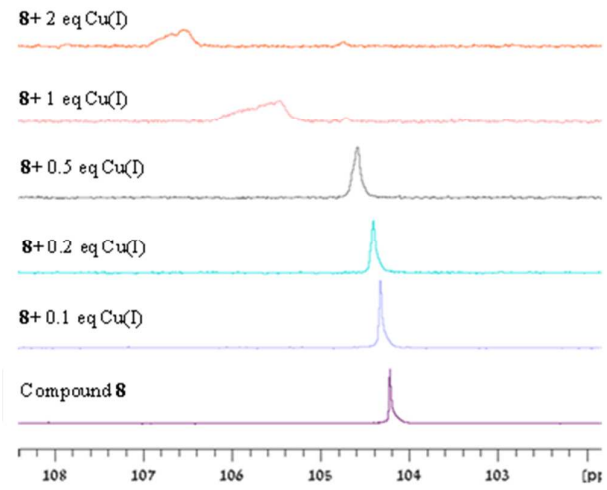

Fig. S3. ^{31}P-NMR spectra in DMSO-d_6 of **8**-Cu(I) complex at 241 MHz.