Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

C—ON Bond Homolysis of Alkoxyamines Triggered by Paramagnetic Copper(II) Salts

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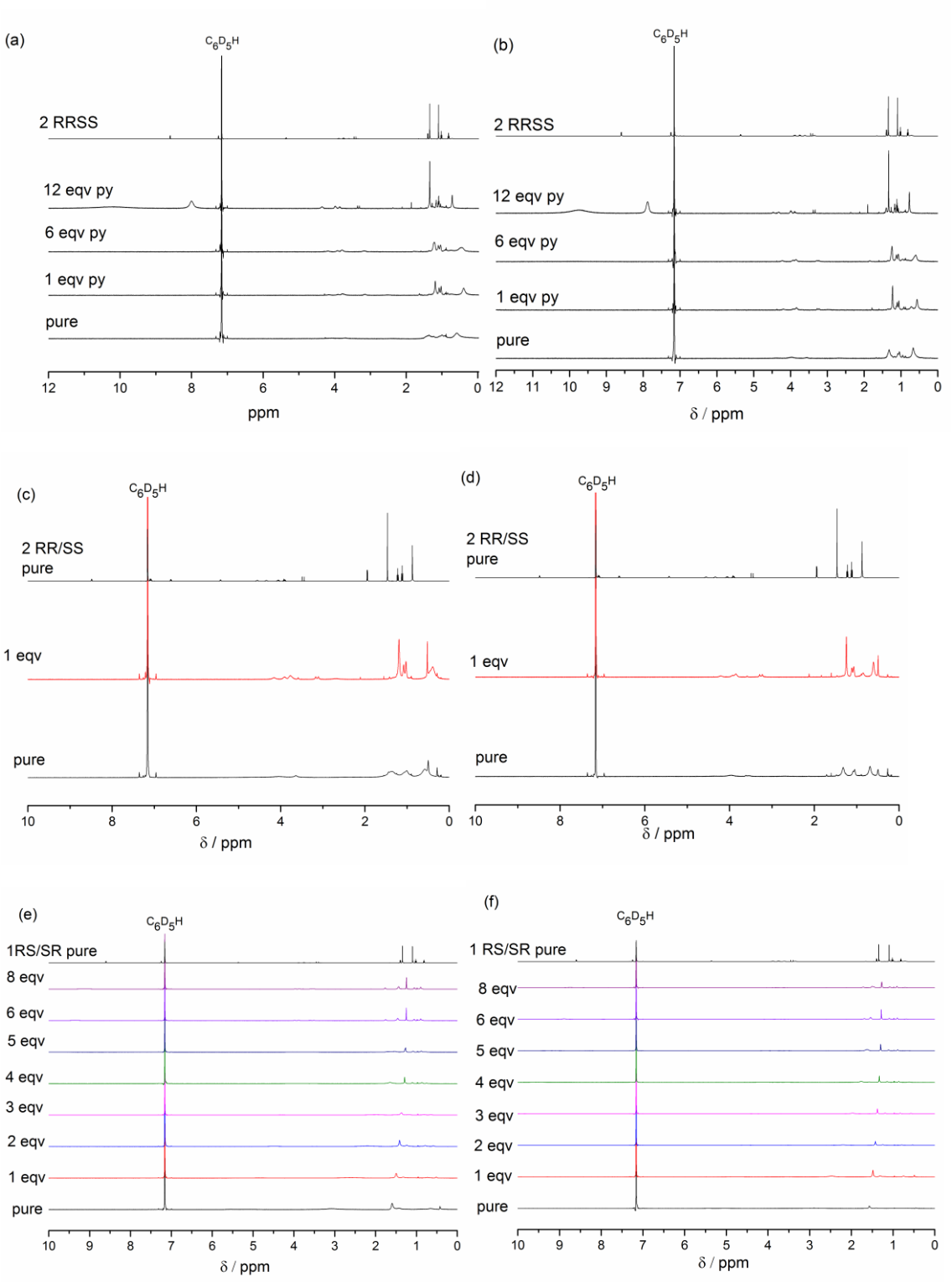
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pure
ppm
(b)
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6 eqv py
1 eqv py
pure
δ / ppm
(c)
C_6D_5H
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pure
1 eqv
pure
δ / ppm
(d)
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2 RR/SS
pure
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pure
δ / ppm
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5 eqv
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3 eqv
2 eqv
1 eqv
pure
δ / ppm
(f)
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δ / ppm

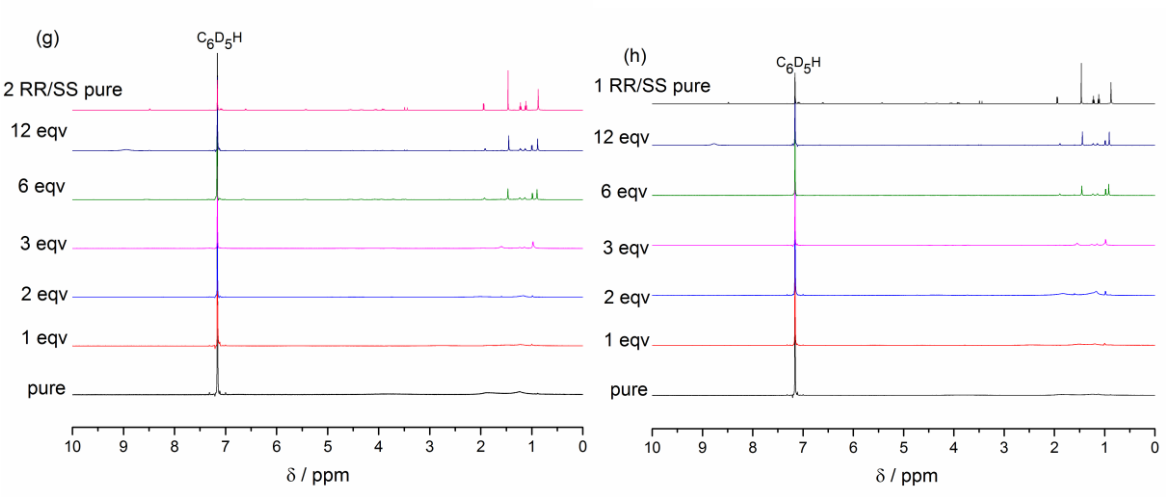


Figure 1SI. ^{1}H NMR spectra of *RSSR*-**7** (a and b), *RR*/*SS*-**7** (c and d), *RS*/*SR*-**8** (e and f) and (*RR*/*SS*)-**8** (g and h) at room temperature (left) and at 60 °C (right).

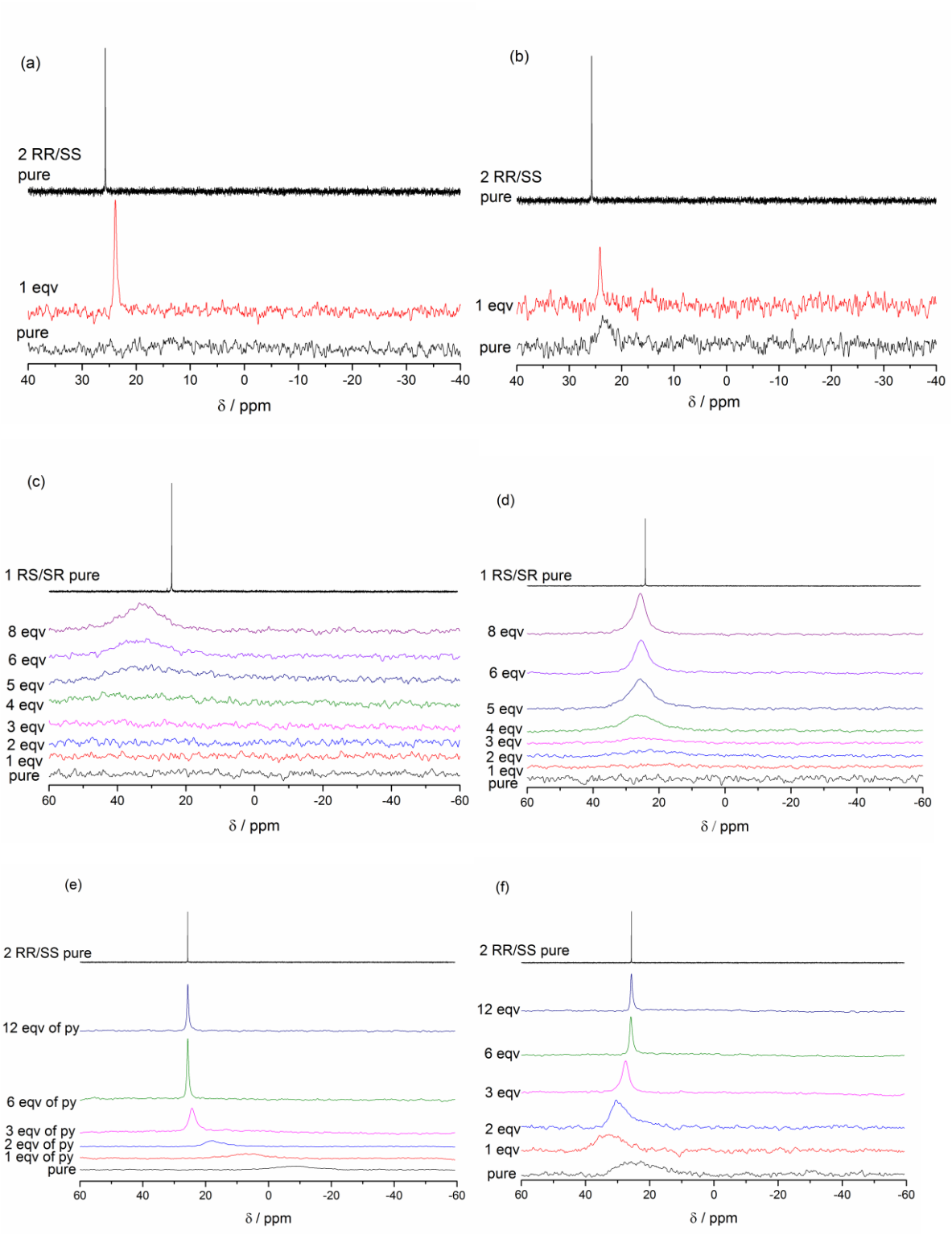


Figure 2SI. ^{31}P NMR spectra of *RR*/*SS*-**7** (a and b), *RS*/*SR*-**8** (c and d), and (*RR*/*SS*)-**8** (e and f) at room temperature (left) and at 60 °C (right).

Table 1SI. XRD data for complexes of $Cu(hfac)_2$ with alkoxyamines.

Compound	*RSSR*-**7**	β-*RSSR*-**7**	*RR/SS*-**7**	*RS/SR*-**8**	*RRSS*-**8**
Empirical formula	$C_{60}H_{78}Cu_2F_{24}N_4O_{16}P_2$	$C_{60}H_{78}Cu_2F_{24}N_4O_{16}P_2$	$C_{30}H_{39}CuF_{12}N_4O_8P$	$C_{30}H_{39}CuF_{12}N_2O_8P$	$C_{70}H_{80}Cu_3F_{36}N_4O_{20}P_2$
Formula weight	1756.28	1756.28	878.15	878.14	2233.94
Temperature, K	200(2)	296(2)	296(2)	200(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	P-1
Unit cell dimensions *a*, Å	13.1619(8)	12.3221(10)	10.6310(3)	9.5604(2)	9.3890(6)
b, Å	16.220(1)	15.6142(11)	11.8915(4)	19.9209(6)	17.402(1)
c, Å	18.945(1)	20.8147(17)	32.1197(11)	20.7180(6)	19.669(1)
α, °	90	90.00	90.00	90	63.746(2)
β, °	97.214(3)	96.154(3)	98.907(2)	96.103(1)	77.272(3)
γ, °	90	90.00	90.00	90	87.428(3)
Volume, $Å^3$	4012.5(5)	3981.7(5)	4011.6(2)	3923.4(2)	2806.2(3)
Z	2	2	4	4	1
Density (calcd.), $g \cdot cm^{-3}$	1.454	1.465	1.454	1.487	1.322
Abs. coefficient, mm^{-1}	0.686	0.691	0.686	0.701	0.705
F(000)	1796	1796	1796	1796	1129
Crystal size, mm	0.4 x 0.4 x 0.4	0.4 x 0.4 x 0.4	0.02 x 0.07 x 0.70	0.05 x 0.40 x 0.40	0.03 x 0.08 x 0.60
Θ range for data collection, °	2.4–27.5	1.6–26.1	2.49–19.78	1.4–27.5	1.2–25.7
Index ranges	$-16 \le h \le 16$, $-20 \le k \le 20$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-19 \le k \le 19$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-12 \le k \le 14$, $-38 \le l \le 38$	$-12 \le h \le 11$, $-25 \le k \le 25$, $-26 \le l \le 26$	$-11 \le h \le 11$, $-21 \le k \le 21$, $-23 \le l \le 23$
Reflections collected	55375	64925	25482	71583	74565
Independent reflections	8989 R(int) = 0.046	7903 R(int) = 0.047	6943 R(int)= 0.044	9027 R(int)= 0.045	10675 R(int)= 0.049
Completeness to θ, %	99.2	99.6	96.9	99.9	99.8
Data / restraints / parameters	8989 / 0 / 520	7903 / 0 / 557	6943/ 0 / 487	9027/ 0 / 521	10675 / 28 / 742
Goodness-of-fit on F^2	1.06	1.01	1.08	1.08	1.08
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0498$, $wR_2 = 0.1247$	$R_1 = 0.0674$, $wR_2 = 0.1854$	$R_1 = 0.0649$, $wR_2 = 0.1661$	$R_1 = 0.0582$, $wR_2 = 0.1591$	$R_1 = 0.0545$, $wR_2 = 0.1253$
Final R indices (all data)	$R_1 = 0.0784$, $wR_2 = 0.1553$	$R_1 = 0.1292$, $wR_2 = 0.2565$	$R_1 = 0.1192$, $wR_2 = 0.1993$	$R_1 = 0.0825$, $wR_2 = 0.1851$	$R_1 = 0.0950$, $wR_2 = 0.1301$
Largest diff. peak / hole, $e \cdot Å^{-3}$	0.52 / -0.93	0.60 / -1.17	0.52 / -0.50	0.99/–0.79	0.62/–0.41
CCDC	1483562	1505271	1483563	1483565	1483564

Complex β-*RSSR*-7 and its structure

It was found that recrystallization of *RSSR*-**7** from the mixture CH_2Cl_2/heptane (1:3) to quantitatively yield dark-green crystals of β-*RSSR*-**7**. The structure of the β-modification (Figure 3SI) is centrosymmetrical and very close to that of *RSSR*-**7**. In complex β-*RSSR*-**7**, copper atoms have an octahedron-distorted surrounding in which three O_{hfac} atoms and N_{Py} atom occupy equatorial positions (Cu–O 1.973(3), 1.968(3) 1.958(3) Å; Cu–N 2.001(5) Å), and the rest O_{hfac} atom as well as O atom of P=O fragment are located at axial positions (Cu–O3 2.351(4); Cu–O5 2.315(4) Å). Dihedral angle between planes of hfac-ligand is 63.0(2)°.

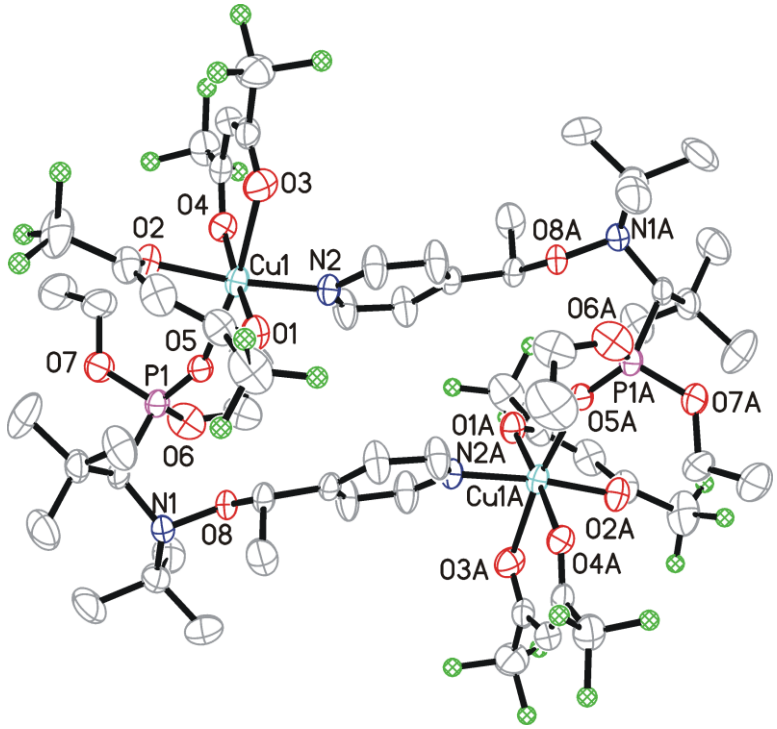


Figure 3SI. X-ray structures of β-*RSSR*-**7**.

Preparation of complexes

RSSR-**7.** Dark-green crystals were separated and air dried to quantitatively yield *RSSR*-**7** (0.044 g). Anal. calcd. for $C_{30}H_{39}CuF_{12}N_2O_8P$: C, 41.03; H, 4.48; N, 3.19; found: C, 41.07; H, 4.50; N, 3.14. IR (KBr, cm^{-1}): 3385 vw, 3142 vw, 2987 w, 2943 w, 2879 vw, 1670 m, 1647 s, 1622 w, 1597 w, 1552 m, 1529 m, 1500 m, 1470 m, 1427 w, 1398 w, 1369 w, 1259 vs, 1213 vs, 1198 vs, 1149 vs, 1109 m, 1068 m, 1032 m, 968 m, 831 w, 796 m, 769 vw, 742 w, 673 m, 623 w, 588 w, 528 vw, 438 vw.

β-*RSSR*-**7.** The fraction of *RSSR*-**7** was crystallized from the mixture CH_2Cl_2/heptane (1:3) to yield dark-green crystals of β-*RSSR*-**7** (0.044 g, ~100%). Anal. calcd. for $C_{30}H_{39}CuF_{12}N_2O_8P$: C, 41.03; H, 4.48; N, 3.19; found: C, 41.51; H, 4.43; N, 3.31. IR (KBr, cm^{-1}): 3437 w, 3138 vw, 2987 w, 2943 w, 2918 w, 2879 vw, 1670 m, 1647 s, 1622 w, 1593 w, 1552 m, 1527 m, 1500 m, 1483 m, 1471 m, 1427 w, 1398 w, 1369 w, 1352 w, 1319 w, 1257 vs, 1213 s, 1198 vs, 1151 vs, 1107 w, 1066 m, 1032 m, 966 w, 831 w, 796 m, 771 vw, 744 w, 671 w, 623 vw, 588 w, 577 w, 567 w, 528 vw.

RR/SS-**7.** Green crystals were separated, air dried, and crystallized from the mixture CH_2Cl_2/heptane (1:3) to yield *RS/SR*-**7** (0.039 g, 90%). Anal. calcd. for $C_{30}H_{39}CuF_{12}N_2O_8P$: C, 41.03; H, 4.48; N, 3.19; found: C, 41.21; H, 4.44; N, 3.25. IR (KBr, cm^{-1}): 3419 vw, 3138 vw, 3091 vw, 2983 w, 2939 w, 2914 w, 2877 vw, 1678 m, 1649 s, 1620 w, 1599 vw, 1551 m, 1529 m, 1498 m, 1483 m, 1466 m, 1425 w, 1396 w, 1367 w, 1354 w, 1336 w, 1308 w, 1255 vs, 1219 s, 1201 s, 1147 vs, 1111 w, 1097 w, 1082 m, 1066 m, 1032 m, 968 m, 941 w, 833 w, 795 m, 764 vw, 746 w, 675 w, 667 w, 640 vw, 617 w, 588 w, 577 w, 552 w, 528 vw, 505 vw, 436 vw. *Crystal growth:* A solution of *RR/SS*-**7** (0.010 g) in the mixture hexane/heptane (1:1; 2 mL) was kept in a freezer at –5 °C for 48 h. Light-green needles were separated and air dried.

RS/SR-**8.** After 24 h, green crystals were separated, air dried, and recrystallized from the mixture CH_2Cl_2/heptane (1:3) to yield *RS/SR*-**8** (0.040 g, 91%).[§] Anal. calcd. for $C_{30}H_{39}CuF_{12}N_2O_8P$: C, 41.03; H, 4.48; N, 3.19; found: C, 41.07; H, 4.43; N, 3.07. IR (KBr, cm^{-1}): 3441 vw, 3144 vw, 3001 w, 2982 w, 2939 w, 2875 vw, 1651 s, 1610 w, 1597 vw, 1576 w, 1554 w, 1547 m, 1525 m, 1493 m, 1475 m, 1396 w, 1367 w, 1352 vw, 1335 vw, 1259 vs, 1230 s, 1213 s, 1194 s, 1149 vs, 1109 w, 1084 w, 1057 m, 1022 m, 953 w, 876 vw, 835 vw, 795 w, 768 w, 742 w, 675 w 667 w, 617 vw, 588 w, 557 w, 528 vw, 484 vw, 436 vw. *RS/SR*-**8.** After 24 h, green crystals were separated, air dried, and recrystallized from the mixture CH_2Cl_2/heptane (1:3) to yield *RS/SR*-**8** (0.040 g, 91%).[#] Anal. calcd. for $C_{30}H_{39}CuF_{12}N_2O_8P$: C, 41.03; H, 4.48; N, 3.19; found: C, 41.07; H, 4.43; N, 3.07. IR (KBr, cm^{-1}): 3441 vw, 3144 vw, 3001 w, 2982 w, 2939 w, 2875 vw, 1651 s, 1610 w, 1597 vw, 1576 w, 1554 w, 1547 m, 1525 m, 1493 m, 1475 m, 1396 w, 1367 w, 1352 vw, 1335 vw, 1259 vs, 1230 s, 1213 s, 1194 s, 1149 vs, 1109

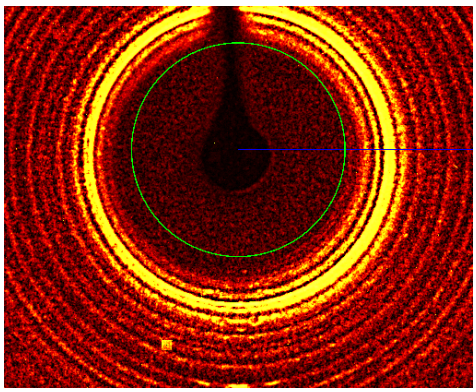
w, 1084 w, 1057 m, 1022 m, 953 w, 876 vw, 835 vw, 795 w, 768 w, 742 w, 675 w 667 w, 617 vw, 588 w, 557 w, 528 vw, 484 vw, 436 vw.

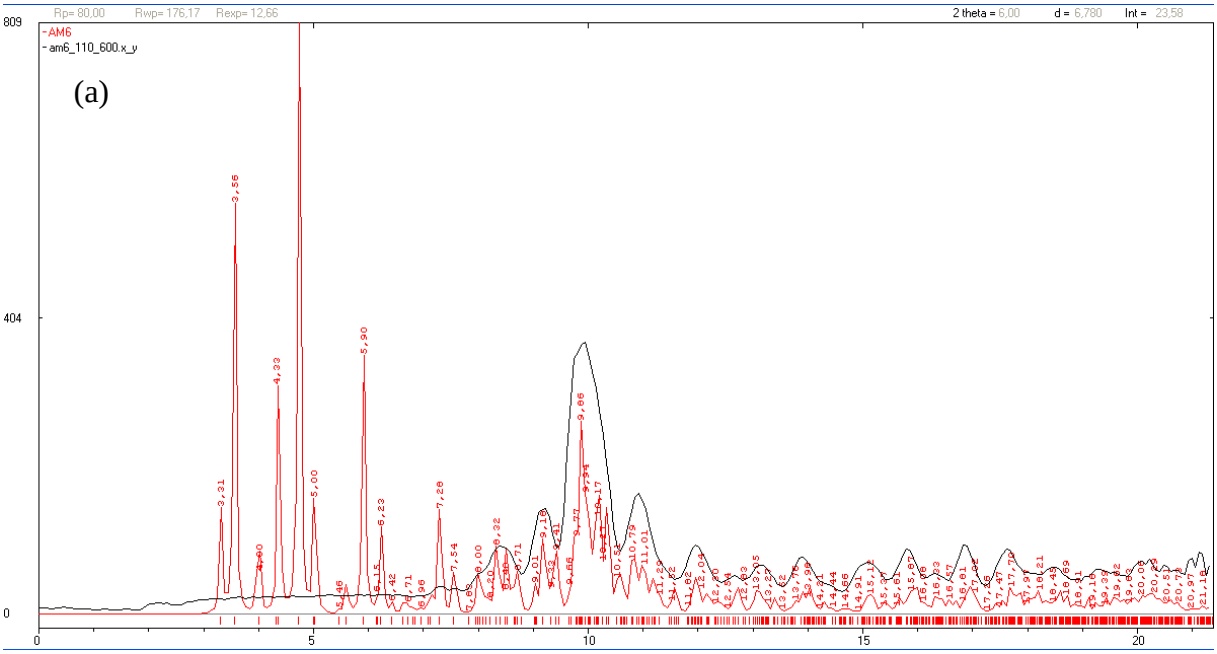
RRSS-**8.** Instead of freezing the solution was incubated for 24 h at room temperature in an open flat-bottom flask to obtain several green needlelike crystals. Their structure was solved by XRD structure analyses.

(*RR/SS*)-**8.** Here, the solution of $Cu(hfac)_2 \cdot H_2O$ was of 0.10 mmol (0.050 g). Instead of freezing the product was separated, air dried, and crystallized from the mixture CH_2Cl_2/heptane (1:3) to yield tightly intertwined very thin threadlike crystals (0.059 g, 87%). Anal. calcd. for $C_{40}H_{41}Cu_2F_{24}N_2O_{12}P$: C, 35.44; H, 3.05; N, 2.07; found: C, 35.62; H, 3.01; N, 1.96. IR (KBr, cm^{-1}): 3433 w, 3143 vw, 2987 w, 2970 w, 2947 vw, 2914 vw, 2879 vw, 1657 m, 1643 s, 1610 w, 1574 w, 1558 m, 1531 m, 1483 s, 1456 m, 1396 w, 1369 w, 1354 w, 1340 vw, 1257 vs, 1211 vs, 1149 vs, 1111 m, 1097 w, 1061 w, 1030 w, 997 vw, 976 w, 966 w, 928 vw, 804 m, 785 w, 766 vw, 746 w, 677 m, 640 vw, 625 vw, 594 w, 555 v w, 530 vw, 509 vw, 480 vw, 438 vw.

Powder X-ray Diffraction proved purity of the phases obtained

Powder XRD data were obtained at 296 K with a Bruker Kappa Apex II CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator, over the 2θ range 7–20° (R = 110 mm, cycle per ϕ with 600 s on the cycle, χ = 0 and -50°). The polycrystalline samples were ground with silicone grease prior to measurement.

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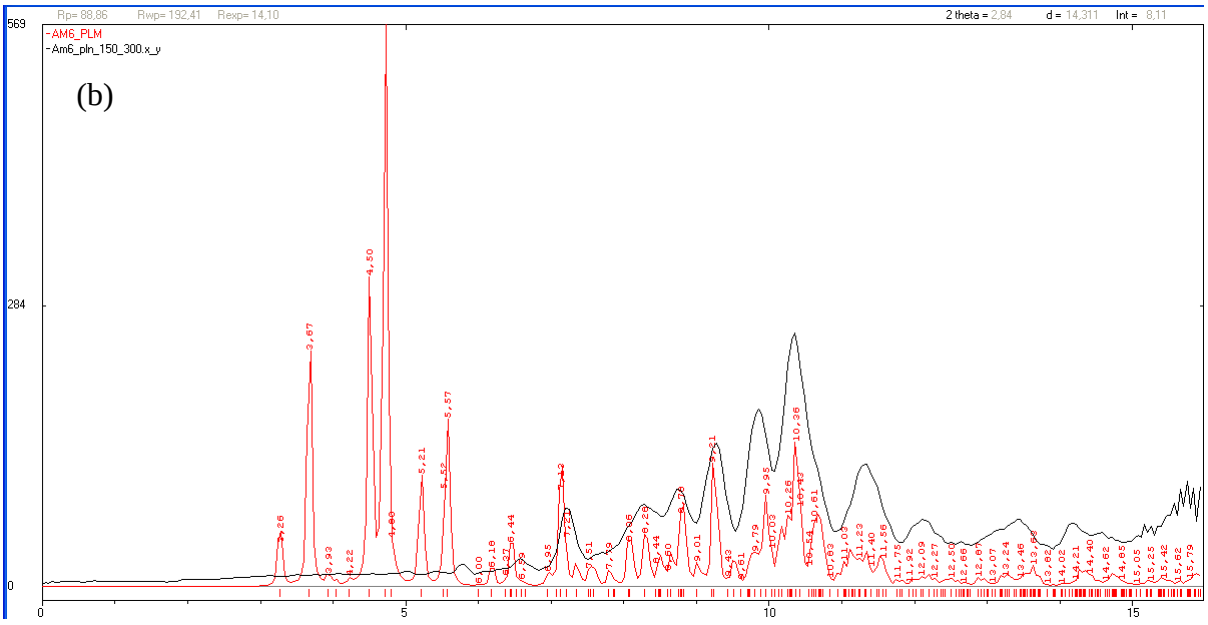
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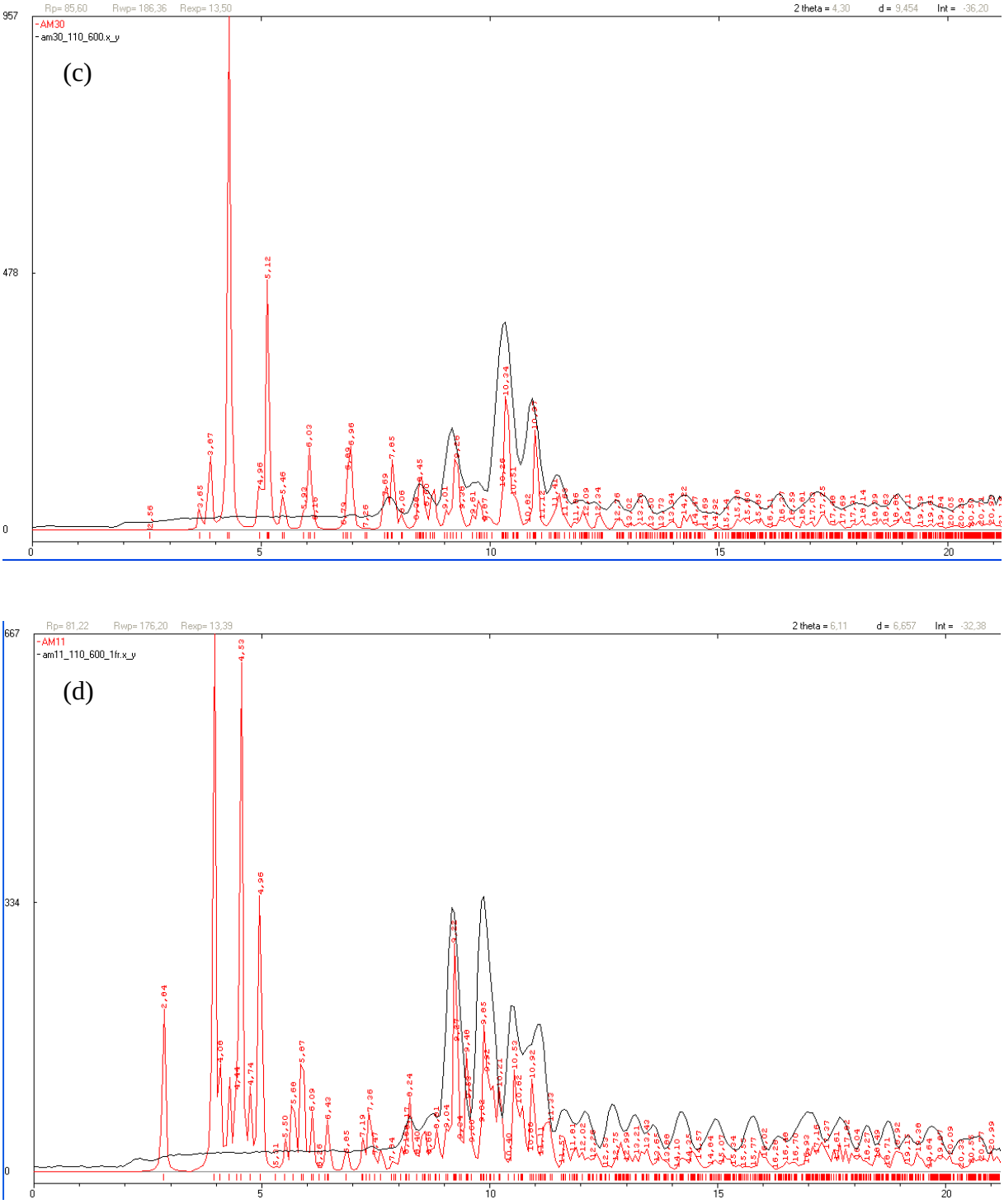

Figure 4SI. X-ray powder diffractograms for complexes *RSSR*-**7** (a), β-*RSSR*-**7** (b), *RR/SS*-**7** (c) and *RS/SR*-**8** (d).