Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Synthesis and Interconversions of Reduced, Alkali-Metal Supported Iron-Sulfur-Carbonyl Complexes

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Synthesis of Starting Materials

[$Fe_3(CO)_{12}$]. This cluster was used as a starting material, and it was prepared by slight modification of the reported procedure.[1] A Schlenk flask was charged with 5.0 mL (37 mmol) [$Fe(CO)_5$], and was reacted with 3.7 mL of NEt_3 in 27 mmol of deoxygenated H_2O at 80 °C overnight to form a dark red solid of [NEt_3H][$HFe_3(CO)_{11}$]. The product was collected on a glass frit and washed thoroughly with water. The hydride complex was further reacted with 45 mL of a 1:1 H_2O/HCl solution in MeOH for 4 h. A dark green precipitate formed, which was collected by filtration and washed with 50 mL each of H_2O, MeOH and pentane. The green material was confirmed by IR to be [$Fe_3(CO)_{12}$]. Yield: 3.8 g (61%). IR (ν_{CO} in cm^{-1}): 1975, 1854, 1810.

[μ_2-$(SPh)_2Fe_2(CO)_6$] (1). This complex was synthesized by a slightly modified version of a published procedure.[2] In a well-ventilated fume hood, 0.61 mL (5.9 mmol) of PhSH was dissolved in 100 mL of benzene. To this solution, 0.98 g (1.9 mmol) of [$Fe_3(CO)_{12}$] was added and the reaction heated at 80 °C for 1 h. Next, the benzene was removed in vacuo and the resulting red material was washed thoroughly with pentane until the washes were no longer yellow. The product **1** was confirmed to be pure by TLC. IR (ν_{CO} in cm^{-1}): 2072, 2032, 2006, 1969. Yield: 0.984 g (67.6%).

Preparation of KC_8. In a typical reaction, 1.02 g of potassium metal was added to a Schlenk flask. Without the use of solvent, 2.44 g of dried graphite (prepared under vacuum overnight) was added to the flask. These two solids were heated to 160 °C under vacuum, mixing the heterogeneous materials every 10 minutes. As the potassium melted and mixed with graphite, it became a golden brown powder. Yield: 3.44 g (quantititave).

IR and ^{13}CNMR data

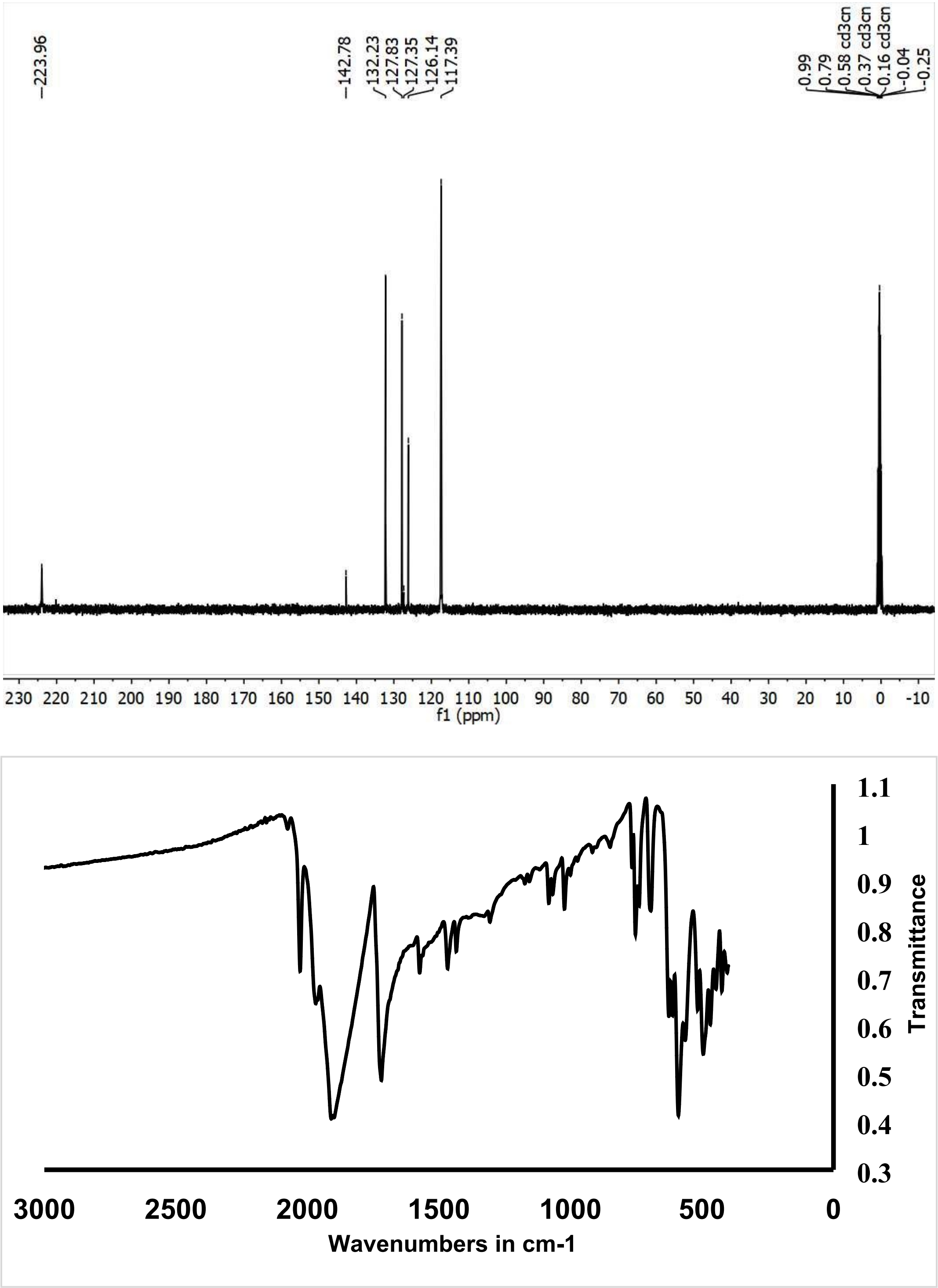

Figure S1. ^{13}C NMR (500 MHz, obtained in CD_3CN) and solid state IR spectrum (298 K, ATR crystal) of $K[Fe_2(SPh)(CO)_6(\mu\text{-}CO)]$ (**2**).

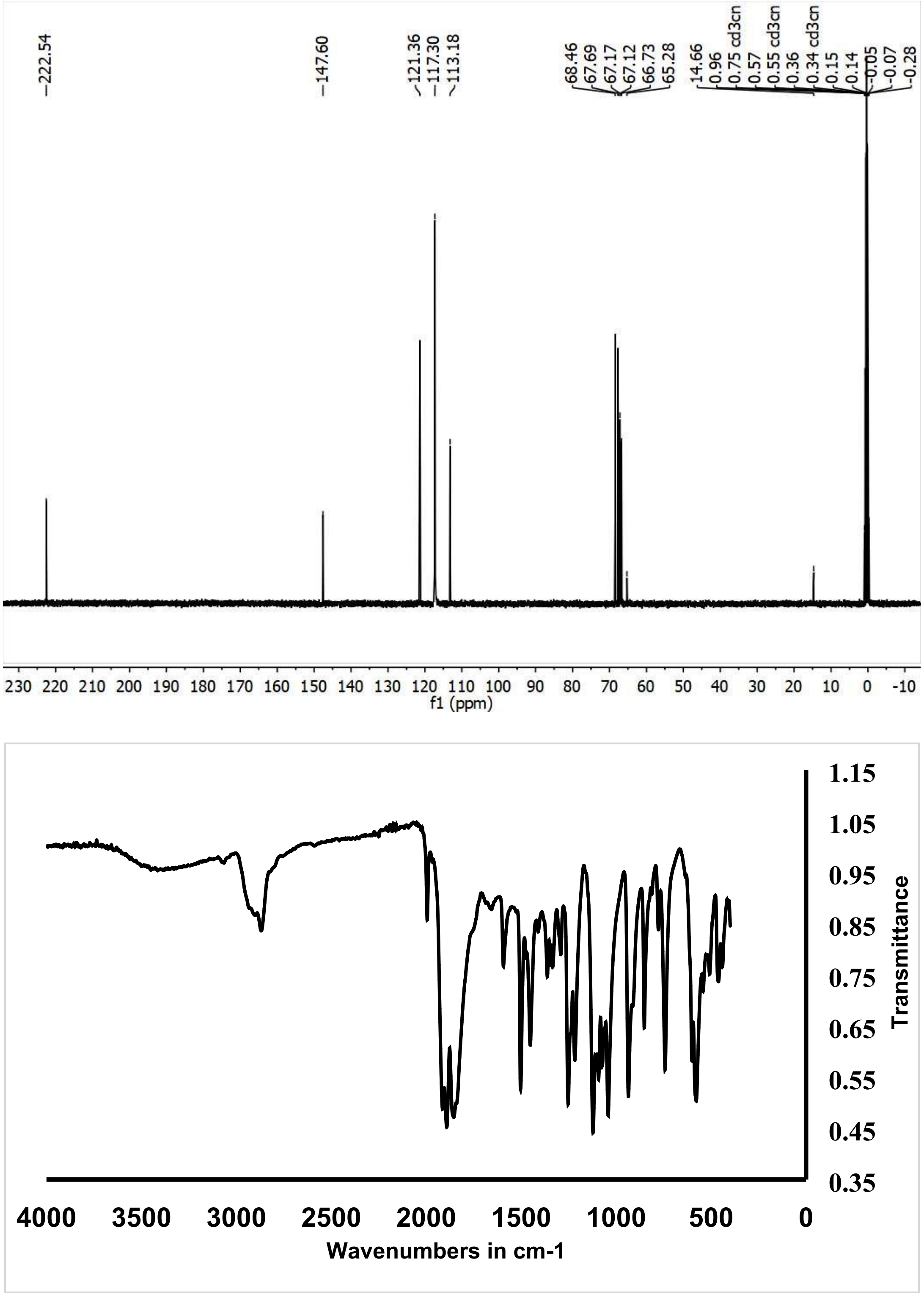

Figure S2. ^{13}C NMR (500 MHz, obtained in CD_3CN) and solid state IR spectrum (298 K, ATR crystal) of $[K(\text{benzo-15-crown-5})_2]_2[Fe_3(\mu_3\text{-}S)(CO)_9]$ (**3**).

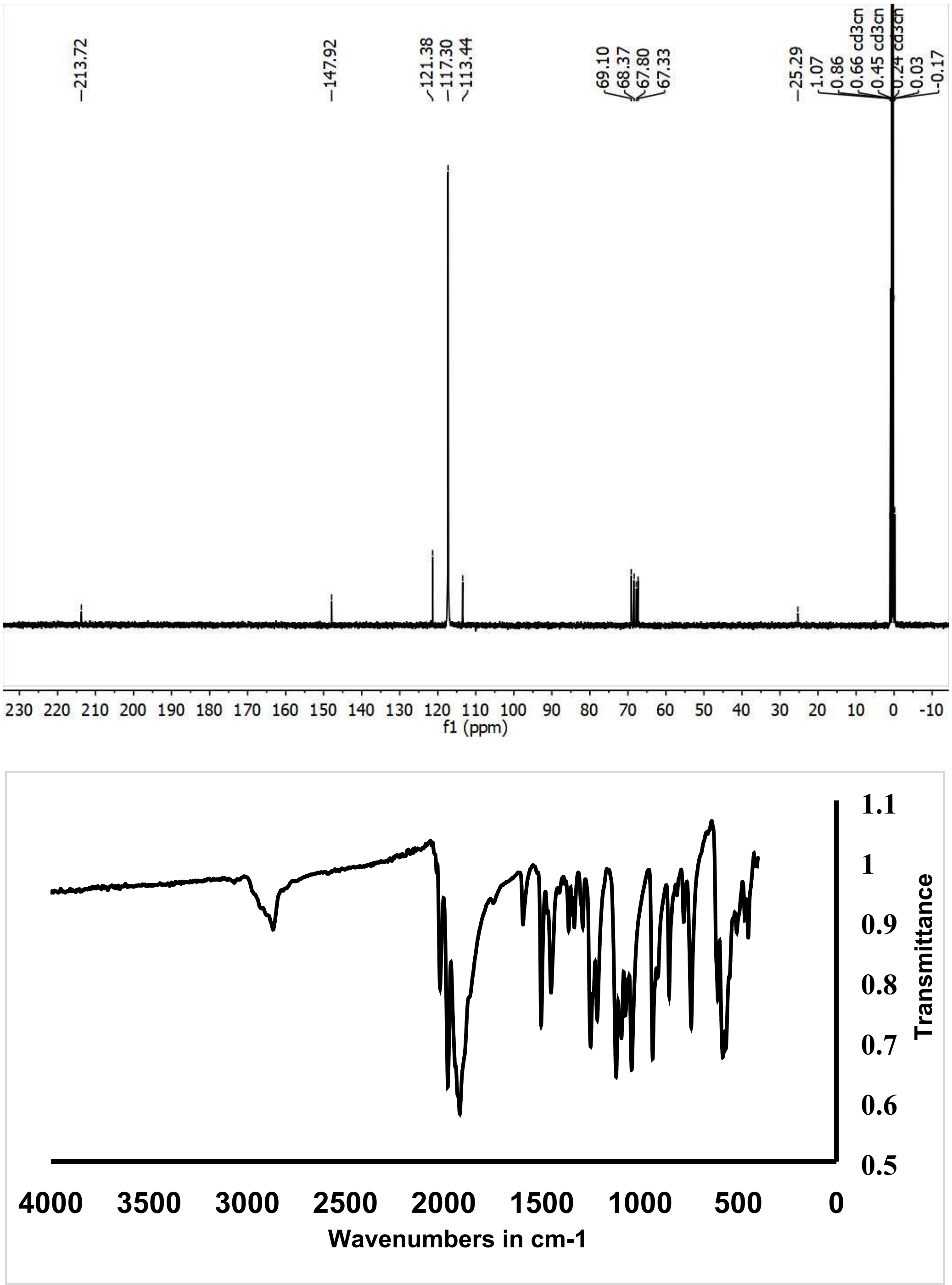

Figure S3. ^{13}C NMR (500 MHz, obtained in CD_3CN) and solid state IR spectrum (298 K, ATR crystal) of $[K(\text{benzo-15-crown-5})_2]_2[((Fe_2S_2)(CO)_6)_2Fe]$ (**5**).

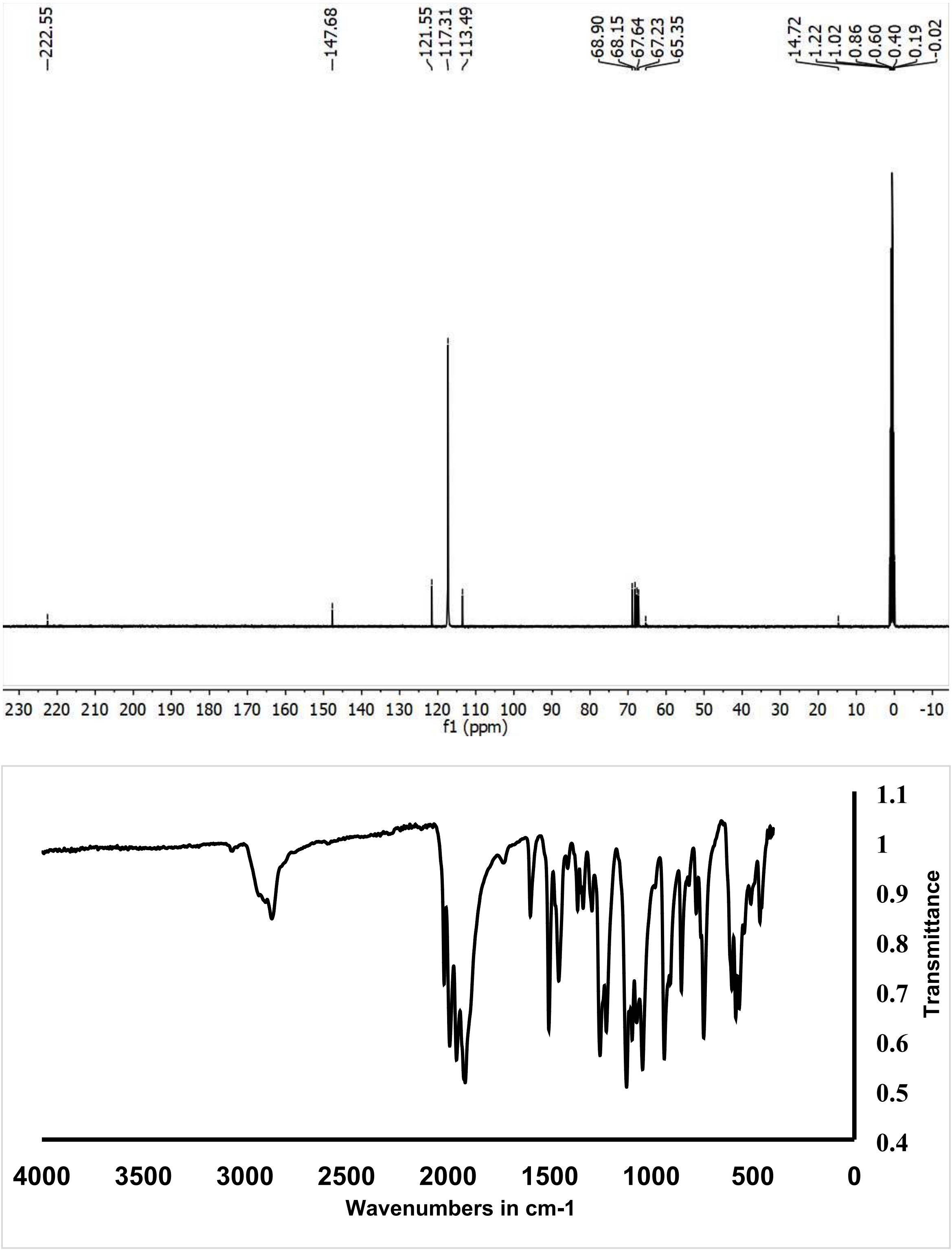

Figure S4. ^{13}C NMR (500 MHz, obtained in CD_3CN) and solid state IR spectrum (298 K, ATR crystal) of $[K(\text{benzo-15-crown-5})_2]_2[((Fe_2S)(CO)_6)_2(\mu{-}S)_2]$ (**6**).

X-ray Data Collection

For complex **2** the data were collected on a Rigaku SCX-Mini diffractometer with a Mercury 2 CCD using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). For complexes **3**, **5**, and **6**, the data were collected on a Rigaku ACF-12 with a Saturn 724+ CCD using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å). All frames of data were collected using ω-scans with a scan range of 0.5° and a counting time of 45 seconds per frame. The data were collected at 100 K using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 2. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.1 The structure was solved by direct methods using Superflip and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. Structure analysis was aided by use of the programs (2009) PLATON and WinGX. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{\mathrm{eq}}$ of the attached atom ($1.5 \times U_{\mathrm{eq}}$ for methyl hydrogen atoms). For complex **3**, a large region with disordered solvent molecules was observed; attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to this solvent molecule were removed by use of the utility SQUEEZE in (2009) PLATON. Structure analysis was aided by use of the programs (2009) PLATON as incorporated into WinGX.

Table S1. Selected crystal data and refinement parameters for new complexes reported herein.

	K[Fe_2S] **(2)**	**K_2[Fe_3S]** **(3)**	**K[(Fe_2S_2)$_2$Fe]** **(5)**	**K_2[(Fe_2S)$_2$(μ_2-S)]** **(6)**
Formula	$C_{13}H_5Fe_2KO_7S$	$C_{67}H_{83}Fe_3K_2NO_{29}S$	$C_{72}H_{90}Fe_5K_2O_{33}S_4$	$C_{68}H_{80}Fe_4K_2O_{32}S_4$
FW	456.03	1644.15	1969.12	1839.16
Color	Brown	Red	Red	Red
Habit	Needle	Needle	Plate	Plate
T (K)	100	100	100	100
Lattice	Orthorhombic	Triclinic	Triclinic	Triclinic
Space Group	P*nma*	*P*-1	*P*-1	*P*-1
a (Å)	20.059(5)	14.1536(11)	14.8881(13)	11.403(2)
b (Å)	12.787(3)	15.8852(13)	15.2863(13)	12.306(2)
c (Å)	12.502(3)	20.397(2)	20.8167(18)	15.455(3)
α (deg)	90	93.487(3)	92.417(3)	111.685(5)
β (deg)	90	90.553(3)	96.261(3)	90.900(5)
γ (deg)	90	115.373(4)	115.604(3)	96.876(5)
V (Å^3)	3206.8(14)	4152.9(6)	4225.7(6)	1996.4(7)
Z	8	2	2	1
d_{calc} (g/cm^3)	1.889	1.315	1.548	1.530
μ (mm^{-1})	2.231	0.717	1.119	1.005
GOF on F^2	1.036	1.058	1.058	1.063
R indices [I > 2σ(I)]	R_1 = 0.0411, wR_2 = 0.0975	R_1 = 0.0480, wR_2 = 0.1082	R_1 = 0.0748, wR_2 = 0.1992	R_1 = 0.0539, wR_2 = 0.1199
R indices all data	R_1 = 0.0529, wR_2 = 0.1046	R_1 = 0.0710, wR_2 = 0.1181	R_1 = 0.0932, wR_2 = 0.2120	R_1 = 0.0754, wR_2 = 0.1297

References

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(3) CrystalClear 1.40 (2008). Rigaku Americas Corportion, The Woodlands, TX.

(4) Superflip. (2007). A program for crystal structure solution. Palatinus, L. and Chapuis, G. *J. Appl. Cryst.* 40, 786-790.

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(6) Sluis, P. v. d. and Spek, A. L. (1990). SQUEEZE. *Acta Cryst*. A46, 194-201.

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(8) Spek, A. L. (2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. *Acta Cryst*. D65, 148-155.

(9) $Rw(F^2) = \{\Sigma\, w(|F_o|^2 - |F_c|^2)^2/\Sigma\, w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.

$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.

$S = [\Sigma w(|F_o|^2 - |Fc|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

(10) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.