Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Separation of rare earths and other valuable metals from deep-eutectic solvents: a new alternative for the recycling of used NdFeB magnets

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Chemicals

Tricaprylmethylammonium chloride (Aliquat® 336, 88.2-90.6%), nitric acid (≥ 65%, p.a.), bis(2-ethylhexyl) phosphate (D2EHPA, 97%) and KSCN (99%) were obtained from Sigma-Aldrich (Diegem, Belgium). Cyanex® 923 (93%) was obtained from Cytec Industries (Canada), tri-*n*-butyl phosphate (97%) from Chem-Lab Analytical (Zedelgem, Belgium), choline chloride (99%), L(+)-lactic acid (90%), iron(III) chloride (98%), citric acid (99.6%), disodium ethylenediaminetetraacetate dihydrate (99%), sulfuric acid (96%), $CoCl_2 \cdot 6H_2O$ (99.9%) and oxalic acid (99%) were purchased from Acros Oganics (Geel, Belgium). Toluene (99.8%, HPLC grade) and hydrochloric acid (37%, reagent grade) were obtained from Fischer Chemical (UK). Boric acid (99%) was obtained from VWR Chemicals (Leuven, Belgium). Solvent 70 was obtained from Statoil (Norway). $NdCl_3 \cdot 6H_2O$ (99.9%) and $DyCl_3 \cdot 6H_2O$ (99.9%) were obtained from Strem Chemicals (Newburyport, USA). Standard solutions of individual elements (1000 mg L^{-1}) for ICP analysis and $CaCl_2 \cdot 2H_2O$ were obtained from Merck (Overijse, Belgium). Pure water (MilliQ, Millipore, >18 MΩ cm^{-1}) was employed to make all the dilutions. All chemicals were used as received without further purification.

Equipment

A disc mill (Benelux Scientific) was used to ground the magnet pieces, which were later sieved to obtain <400 µm powders. A planetary ball mill (Retsch PM4000, 5 mm stainless steel balls) was used to further grind the samples to obtain a particle size below 100 µm. The ball-milling conditions were: 30:1 ball-to-powder ratio (g/g), 2 h duration at 200 rpm. A muffle furnace was used for roasting (950 °C, 15 h). Leaching experiments were conducted in 4 mL vials, with magnetic stirring. After leaching, the samples were centrifuged in a Heraeus Megafuge 1.0 centrifuge at 5000 rpm during 3 min to separate the residue from the leachate. Solvent extraction experiments were carried out in temperature controllable Turbo Thermo Shakers (Model: TMS-200, Hangzhou Allsheng Instrument Co. Ltd, China). ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer, operating at a frequency of 300 MHz. Samples for ^{1}H NMR measurements were prepared in deuterated dimethyl sulfoxide (DMSO-d_6). UV-VIS absorption spectra were recorded with a Varian Cary 5000 spectrophotometer. The viscosity and density of the DES was measured using an automatic rolling-ball viscosity meter Lovis (Model 2000 M/ME, with a density measuring module MA 4500 ME, Anton Paar GmbH, Graz, Austria). A volumetric Karl Fischer titrator Mettler-Toledo DL39 with a Stromboli oven operating at 150 °C was used with HYDRANAL®-Composite 5 one-component reagent to

determine the water content of the DES. Analysis of the deep-eutectic solvent phase was performed using a Perkin Elmer Optima 8300 inductively coupled plasma optical emission spectrometer (ICP-OES) in dual view, with a GemTip CrossFlow II nebulizer, a Scott Spray Chamber Assembly, a sapphire injector and a Hybrid XLT ceramic torch. The calibration curve was constructed by fitting through the origin using standard solutions of Fe, Co, Nd and Dy prepared in a 1 M HNO_3 solution at four different concentrations: 2.5, 5, 10 and 20 mg L^{-1}. Samples of the deep-eutectic solvent phase were prepared by taking an aliquot of 300 µL and diluting it to 10 mL with a 1 M HNO_3 solution. A sample of 1 mL of this solution was further diluted to 10 mL with a 1 M HNO_3 solution in case of more concentrated solutions. All measurements were performed in triplicate.

Table S1. Composition (wt%) of three different NdFeB magnets determined with ICP-OES.

	Main composition (wt%)	
Element	Magnet 1	Magnet 2
Fe	58.52 ± 6.22	56.62 ± 5.67
Nd	22.96 ± 3.45	21.38 ± 4.96
Co	2.66 ± 0.10	2.76 ± 0.17
Dy	5.06 ± 0.56	0.26 ± 0.05
B	1.26 ± 0.09	1.30 ± 0.08
Nb	n.d.[a]	0.09 ± 0.04
Gd	1.86 ± 0.19	5.5 ± 0.9
Al	1.39 ± 0.05	4.00 ± 0.23
Pr	3.87 ± 0.07	5.47 ± 0.28
Si	0.05 ± 0.01	0.10 ± 0.05
Cu	n.d.[a]	0.10 ± 0.06
Ni	n.d.[a]	0.44 ± 0.09
Ga	0.22 ± 0.03	0.09 ± 0.01
Total	97.85	98.11

[a] n.d. = not detected (below detection limit)

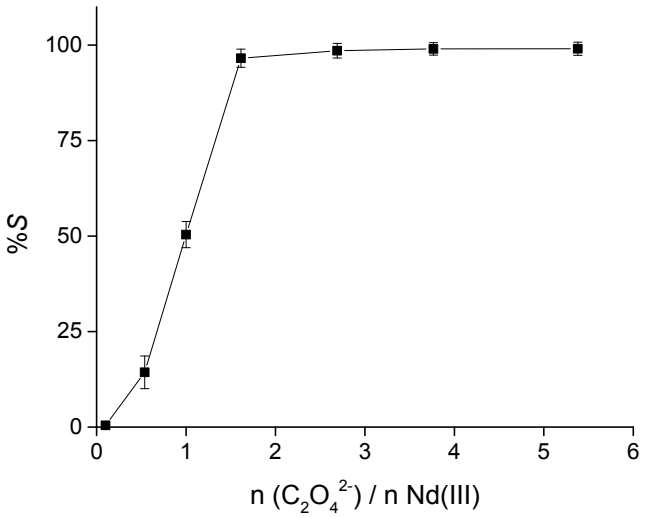

Fig. S1 Precipitation stripping of Nd from the eutectic mixture of choline chloride and lactic acid (molar ratio 1:2). Equilibration time 40 min, 25 °C and 2000 rpm.

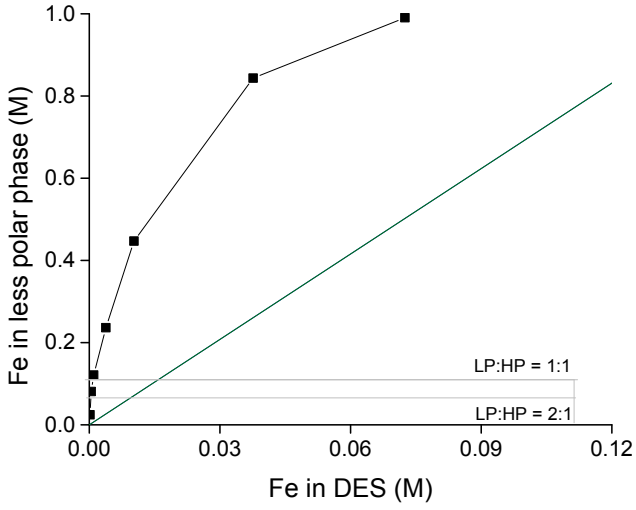

Fig. S2. McCabe-Thiele diagram for Fe from a mixture of Fe, Co, B, Nd and Dy in the DES choline chloride: lactic acid (molar ratio 1:2) with 0.9 M [A336][SCN] in toluene (phase contact time 20 min, LP:HP phase ratios between 0.05:1 and 10:1).

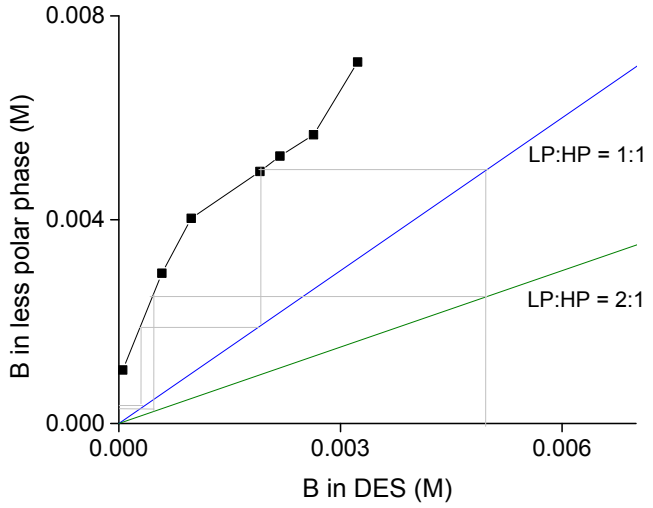

Fig. S3. McCabe-Thiele diagram for B from a mixture of Fe, Co, B, Nd and Dy in the DES choline chloride: lactic acid (molar ratio 1:2) with [A336][SCN] 0.9 M in toluene (phase contact time 20 min, LP:HP phase ratios between 0.25:1 and 10:1).

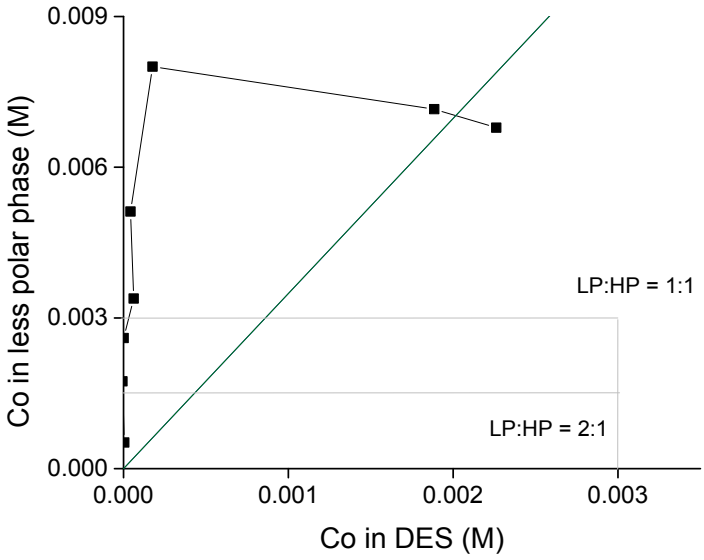

Fig. S4. McCabe-Thiele diagram for Co from a mixture of Fe, Co, B, Nd and Dy in the DES choline chloride : lactic acid (molar ratio 1:2) with 0.9 M [A336][SCN] in toluene (phase contact time 20 min, LP:HP phase ratios between 0.05:1 and 10:1).

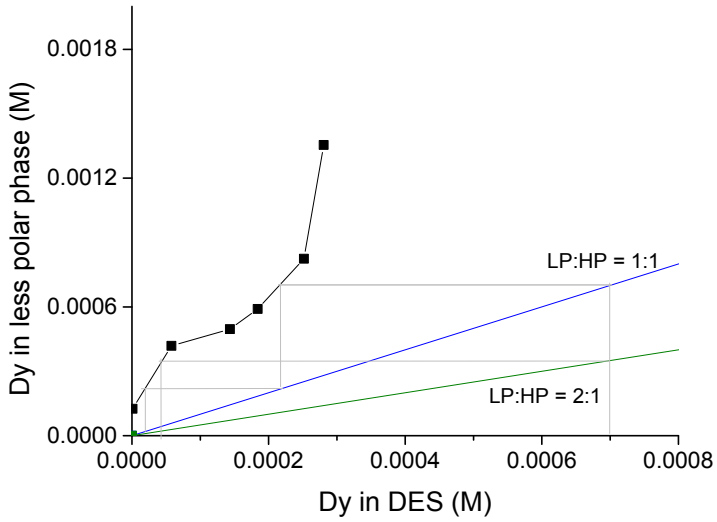

Fig. S5. McCabe-Thiele diagram for Dy from a mixture of Nd and Dy in the DES of choline chloride and lactic acid (molar ratio 1:2) with 0.9 M Cyanex® 923 in toluene (phase contact time 20 min, LP:HP phase ratios between 0.25:1 and 10:1).

Table S2. Fitting results of the EXAFS data for the $[Fe(SCN)_6]^{3-}$ complex in [A336][SCN], extracted from an aqueous phase*

Scattering path	*N*	*R* (Å)	σ^2 (Å^2)
Fe-N	6	2.076(3)	0.010(1)
Fe-C	6	3.085(46)	0.015(2)
Fe-S	6	4.503(29)	0.009(2)
Fe-N-C	12	3.254(13)	0.009(1)
Fe-S-C	12	4.614(19)	0.008(1)
Fe-S-N	12	4.937(11)	0.008(2)

*The data were Fourier-transformed between k = 3.0 and 12.9 Å^{-1} with a Gaussian rounded ends function and fitted to the model between R = 0 and 4.92 Å.

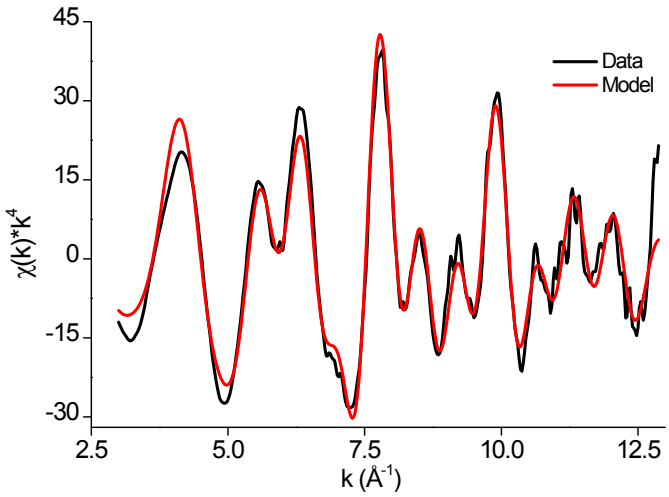

Fig. S6. EXAFS function $\chi(k)*k^4$ and model of the $[Fe(SCN)_6]^{3-}$ complex.

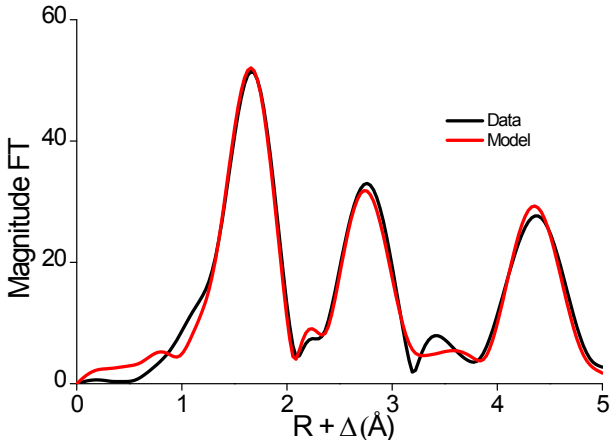

Fig. S7. Fourier transform and model of the $[Fe(SCN)_6]^{3-}$ complex. The data were Fourier -transformed between k = 3.0 and 12.9 $Å^{-1}$ with a Gaussian rounded ends function and fitted to the model between R = 0 and 4.92 Å.

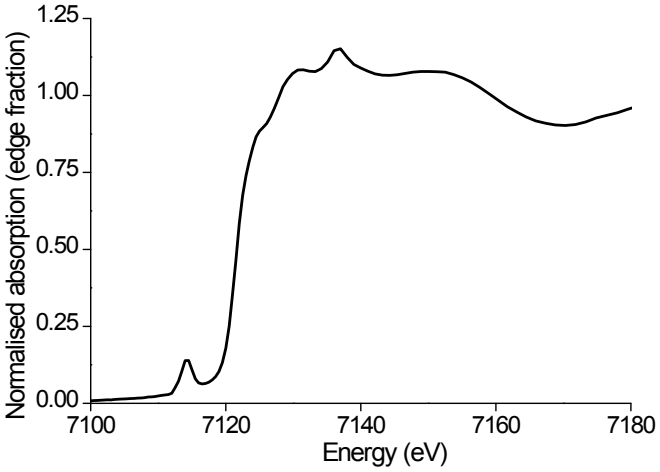

Fig. S8. X-ray absorption spectrum around the Fe K-edge of the less polar phase (0.9 M [A336][SCN] in toluene 0.9 M) of the extraction from the DES.

Table S3. Fitting results of the EXAFS function of cobalt extracted from aqueous solution to [A336][SCN].*

Scattering path	*N*	*R* (Å)	σ^2 (Å^2)
Co-N	4	1.962(4)	0.005(1)
Co-C	4	3.992(12)	0.004(1)
Co-S	4	4.606(9)	0.005(1)
Co-C-N	8	3.128(4)	0.004(1)
Co-S-C	8	4.776(15)	0.005(1)
Co-S-N	8	4.909(60)	0.005(1)

*The data were Fourier transformed between k = 4.0 and 13.0 Å^{-1} without any window function and fitted to the model between R = 0 and 5 Å.

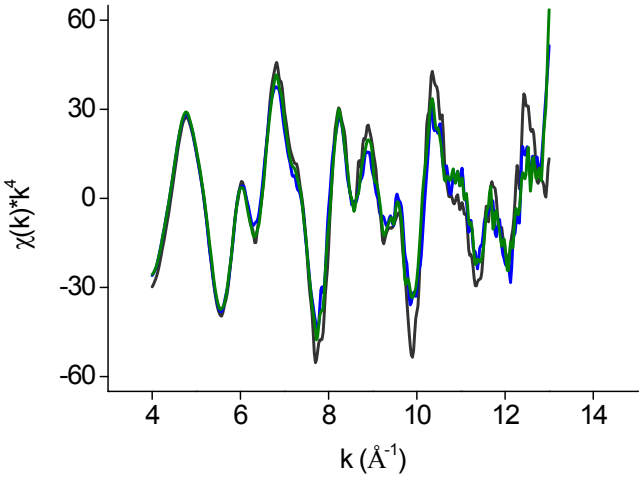

Fig. S9. EXAFS function $\chi(k)*k^4$ of the $[Co(SCN)_4]^{2-}$ complex in the ionic liquid [A336][SCN] as extracted from water (black), 5 M $CaCl_2$ (green) and DES (blue).