

Table S1. Separation factors of M^{n+} metal ions extracted with $HP=2 \times 10^{-2}$ mol/dm³ ligand in $[C_1C_4im^+][Tf_2N^-]$ applying EtG and H_2O .

SF	Fe	H_2O	Ni	Cu	H_2O	Eu	H_2O	Gd	H_2O	Lu	H_2O	Hg	H_2O	Tl	H_2O	Bi	H_2O
Al	22.7	3.3×10^{-3}	9.3×10^{-2}	30.2	2×10^{-2}	6.2	3.8×10^{-2}	19.7	8×10^{-2}	19.3	3×10^{-2}	0.24	1.74	8.8	4×10^{-2}	9.2	0.3
Fe			4×10^{-3}	1.3	5.9	0.27	11.53	0.86	24.6	0.84	9.75	1×10^{-2}	525.6	0.38	12.5	0.4	92.3
Ni			—	324.2	—	66.3	—	211	—	207	—	2.55	—	94.5	—	98.8	—
Cu						0.2	1.9	0.65	4.11	0.63	1.63	7×10^{-3}	87.8	0.29	2.08	0.30	15.4
Eu								3.2	2.13	3.12	0.84	4×10^{-2}	45.5	1.42	1.08	1.48	8.0
Gd										0.97	0.39	1.2×10^{-2}	21.35	0.44	0.5	0.46	3.75
Lu												1.2×10^{-2}	53.7	0.45	1.27	0.47	9.43
Hg														36.9	2×10^{-2}	38.6	0.17
Tl																1.04	7.4

Table S2. Initial concentrations of metal ions used in competitive extraction after 7 and 6.3-fold dilution.

M^{n+}	Li^+	Na^+	K^+	Ca^{2+}	Ag^+	Tl^+	Sr^{2+}	Ba^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Hg^{2+}
$[M^{n+}]_{in}$ mg/dm ³	0.39±0.03 0.23±0.01	0.56±0.02 0.79±0.02	0.92±0.02 1.14±0.01	1.12±0.04 1.79±0.06	2.85±0.02 3.94±0.04	1.44±0.05 2.44±0.26	0.25±0.02 2.11±0.01	3.37±0.01 5.23±0.04	1.46±0.01 2.32±0.01	1.52±0.05 2.82±0.02	1.19±0.01 1.89±0.02	6.73±0.04 13.22±2.4
M^{n+}	Pb^{2+}	Al^{3+}	Bi^{3+}	Fe^{3+}	Cr^{3+}	Mg^{2+}	La^{3+}	Ce^{3+}	Eu^{3+}	Gd^{3+}	Lu^{3+}	
$[M^{n+}]_{in}$ mg/dm ³	5.54±0.05 9.85±0.18	1.52±0.03 2.74±0.06	1.28±0.05 2.96±0.32	1.17±0.01 2.06±0.16	0.98±0.01 1.53±0.04	0.68±0.06 0.98±0.01	1.89±0.01 2.55±0.02	0.1±0.02 —	3.71±0.03 6.01±0.04	2.16±0.01 3.08±0.04	2.82±0.01 4.39±0.02	

Table S3. Separation factors of M^{n+} metal ions extracted with $HP=2 \times 10^{-2}$ mol/dm³ ligand in $[C_1C_{10}im^+][Tf_2N^-]$ applying H₂O and glycerol, 1:1.

SF	Mg	Al	K	Ca	Cr	Fe	Co	Ni	Cu	Zn	Sr	Ag	Cd	Ba	La	Ce	Eu	Gd	Lu	Hg	Tl	Pb	Bi
Li	1.7	0.7	0.5	2.3	1.2	1x10 ⁻³	0.3	1.3	5x10 ⁻³	4.4	21.7	1.04	1.5	1.03	0.9	0.87	1.6	0.7	0.35	1.52	0.05	0.98	0.1
Mg		0.4	0.3	1.3	0.7	7x10 ⁻⁴	0.14	0.75	3x10 ⁻³	2.5	12.6	0.6	1.5	0.6	0.53	0.5	0.92	0.42	0.2	0.88	3x10 ⁻²	0.6	6x10 ⁻²
Al			0.72	3.3	1.72	2x10 ⁻³	0.35	0.54	7x10 ⁻³	6.2	30.6	1.47	2.17	1.46	1.3	1.2	2.23	1.02	0.5	2.15	6x10 ⁻²	1.4	0.14
K				4.5	0.46	2.4x10 ⁻³	0.48	2.52	1x10 ⁻²	8.6	42.2	2.03	3.0	2.02	1.7	1.7	3.08	1.4	0.7	2.9	9x10 ⁻²	1.9	0.2
Ca					0.52	5x10 ⁻⁴	0.1	0.55	2x10 ⁻²	1.9	9.3	0.44	0.66	0.44	0.39	0.37	0.68	0.31	0.15	0.65	2x10 ⁻²	0.42	4x10 ⁻²
Cr						1x10 ⁻³	0.2	1.06	4x10 ³	3.6	17.8	0.85	1.26	0.85	0.74	0.72	1.3	0.6	0.3	1.25	4x10 ⁻²	0.8	8x10 ⁻²
Fe							199.8	1x10 ³	4.4	3x10 ³	1.7x10 ⁴	832	1x10 ³	826	723	693	1x10 ³	576	282	1x10 ³	38.6	784	82.7
Co								5.2	2x10 ⁻²	17.6	86.4	4.2	6.1	4.1	3.6	3.4	6.3	2.8	1.4	6.07	0.2	3.9	0.4
Ni									4x10 ⁻³	3.4	16.7	0.8	1.2	0.8	0.7	0.7	1.2	0.56	0.3	1.2	3x10 ⁻²	0.76	8x10 ⁻²
Cu										792	3x10 ⁴	187	274	184	161	155	281	132	63	271	8.63	175	18.5
Zn											4.9	0.24	0.2	0.23	0.2	0.2	0.35	0.16	8x10 ⁻²	0.34	1x10 ⁻²	0.22	2x10 ⁻²
Sr												4x10 ⁻²	7x10 ⁻²	4x10 ⁻²	4x10 ⁻²	4x10 ⁻²	7x10 ⁻²	3x10 ⁻²	1.6x10 ⁻²	7x10 ⁻²	2x10 ⁻³	4x10 ⁻²	4x10 ⁻³
Ag													1.4	1	0.86	0.83	1.5	0.7	0.34	1.4	4x10 ⁻²	0.94	9x10 ⁻²
Cd														0.67	0.58	0.56	1.02	0.46	0.23	0.98	3x10 ⁻²	0.63	6x10 ⁻²
Ba															0.87	0.83	1.52	0.69	0.34	1.47	4x10 ⁻²	0.94	0.1
La																0.95	1.7	0.8	0.4	1.6	5x10 ⁻²	1	0.1
Ce																	1.8	0.83	0.4	1.7	5x10 ⁻²	1.1	0.1
Eu																		0.45	0.22	0.96	3x10 ⁻²	0.6	6x10 ⁻²
Gd																			0.47	2.1	6x10 ⁻²	1.3	0.13
Lu																				4.3	0.13	2.77	0.3
Hg																					3x10 ⁻³	0.64	6x10 ⁻²
Tl																						20.3	2.2
Pb																							0.1

Table S4. Initial concentrations of metal ions used in competitive extraction test applying H₂O and glycerol, 1:1.

M^{n+}	Li^+	Na^+	K^+	Ca^{2+}	Ag^+	Tl^+	Sr^{2+}	Ba^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}	Hg^{2+}	
$[M^{n+}]_{in}$ mg/dm ³	0.50±0.01	2.55±0.02	3.10±0.02	4.37±0.02	7.21±0.10	5.16±0.16	12.67±0.89	10.45±0.06	4.37±0.14	5.08±0.01	3.40±0.02	26.69±0.88	
M^{n+}	Pb^{2+}	Al^{3+}	Bi^{3+}	Fe^{3+}	Cr^{3+}	Mg^{2+}	La^{3+}	Ce^{3+}	Eu^{3+}	Gd^{3+}	Lu^{3+}	Zn^{2+}	Cd^{2+}
$[M^{n+}]_{in}$ mg/dm ³	17.95±0.10	5.99±0.01	12.48±0.30	4.48±0.20	2.85±0.01	1.87±0.01	10.21±0.01	12.39±0.04	8.20±0.02	7.26±0.01	11.41±0.04	4.42±0.02	9.63±0.04

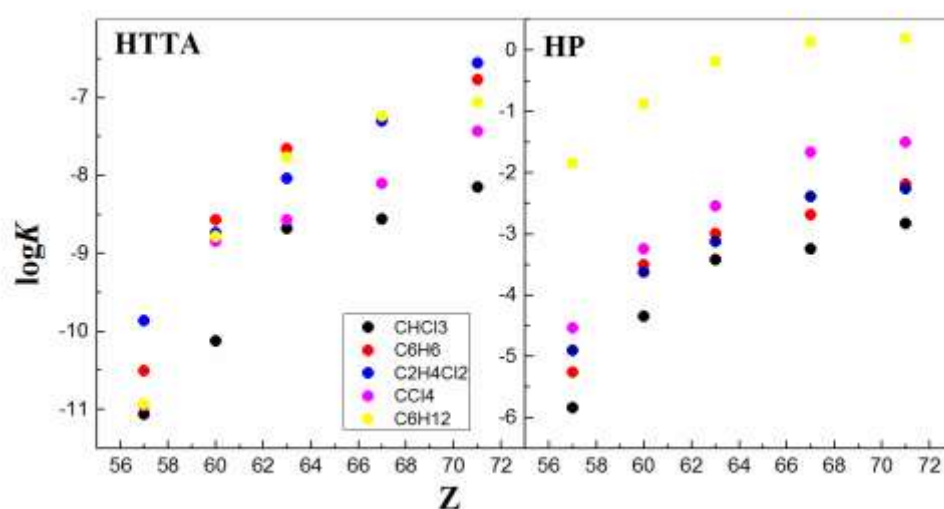


Figure S1. LogK vs. Z.

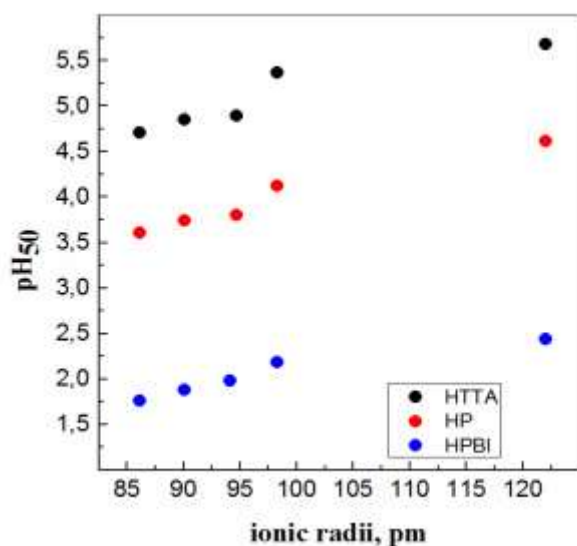


Figure S2. pH₅₀ in the solvent extraction of lanthanoids with HL in CHCl₃ as a function of the ionic radius.

Table S5. Concentrations of the investigated Gd³⁺ ions using the SpinCount program, part of the Bruker Xenon software.

Sample	Concentration [mol/dm ³] found in frozen solutions, 120 K
c	9.1×10^{-3}
a	1.05×10^{-6}
b	1.7×10^{-7}
1	2.6×10^{-4}
2	4.6×10^{-4}
3	2.5×10^{-4}

Notes: ¹For the calculation of the molar concentrations in the SpinCount program, a spin number S=1/2 was used for solutions 1, 2 and 3, with a single transition -1/2 ↔ +1/2. A spin number S=7/2 is used for solutions a, b and c, where multiple allowed transitions are observed.

²The investigated volume of the extracting phase is small, i.e. no 100% LP phase.

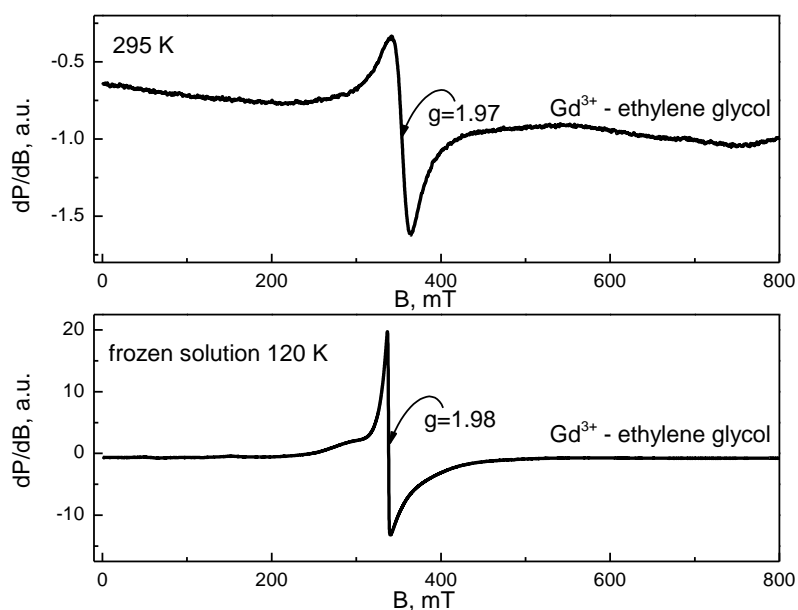


Fig. S3. EPR spectra of Gd^{3+} ion in ethylene glycol at room temperature and in the frozen state at 120 K: $[\text{Gd}^{3+}] = 3 \times 10^{-3} \text{ mol/dm}^3$.

Table S6. Concentrations of the investigated Gd^{3+} ions using the SpinCount program, part of the Bruker Xenon software.

Sample	Concentration $[\text{mol/dm}^3]$ found in frozen solutions, 120 K
C	Background spectrum
A	4.115×10^{-4}
B	4.075×10^{-4}
1	2.239×10^{-7}
2	3.93×10^{-8}
3 *	Background spectrum
ZERO	1.4×10^{-2}

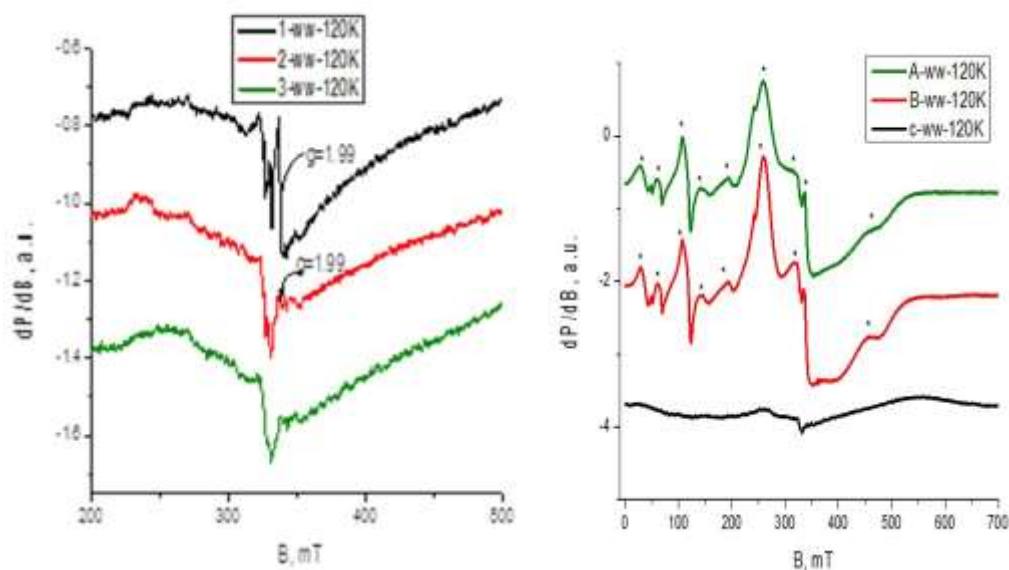


Fig. S4. EPR spectra of frozen solutions of complexes of Gd^{3+} ($[\text{Gd}^{3+}]_{\text{in}} = 6 \times 10^{-4} \text{ mol/dm}^3$) with ligands $[\text{HP}] = 2.5 \times 10^{-2} \text{ mol/dm}^3$ (A, B and C) and $[\text{HTTA}] = 3 \times 10^{-2} \text{ mol/dm}^3$ (1, 2 and 3) obtained after solvent

extraction from EtG, respectively, in the following diluents $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ (A: $\text{pH}_{\text{eq}}=1.98$ and 1: $\text{pH}_{\text{eq}}=2.60$), $[\text{C}_1\text{C}_{10}\text{im}^+][\text{Tf}_2\text{N}^-]$ (B: $\text{pH}_{\text{eq}}=2.02$ and 2: $\text{pH}_{\text{eq}}=2.57$), CHCl_3 , (C: $\text{pH}_{\text{eq}}=1.98$ and 3: $\text{pH}_{\text{eq}}=2.21$). On the left: range of the magnetic field 0–700 mT, on the right: range of the magnetic field 300–360 mT.

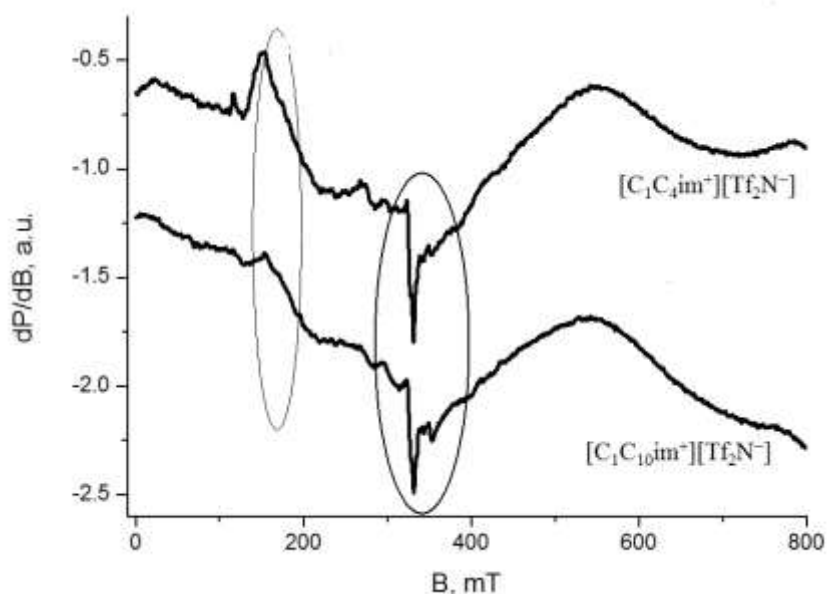


Fig. S5. EPR spectra of Cr^{3+} obtained after solvent extraction with $\text{HP}=2 \times 10^{-2} \text{ mol/dm}^3$ in $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]$ and $[\text{C}_1\text{C}_{10}\text{im}^+][\text{Tf}_2\text{N}^-]$ recorded in frozen solutions: MP phase – $[\text{Cr}^{3+}]_{\text{in}}=6 \times 10^{-4} \text{ mol/dm}^3$ and 0.1 MES in EtG. Calculated % E is 71.23% and 54.60% – ICP-OES based on an average of three parallel determinations.

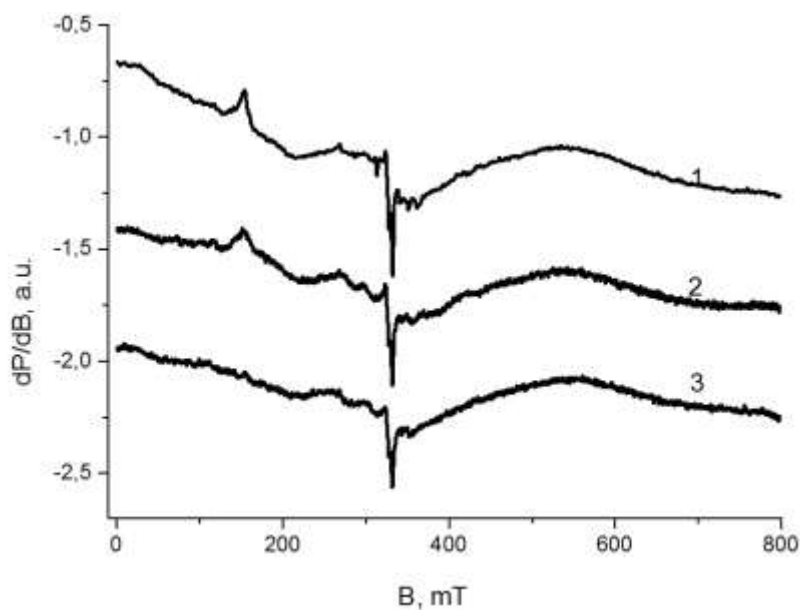


Fig. S6. EPR spectra of Cr^{3+} obtained after solvent extraction with $\text{HP}=2 \times 10^{-2} \text{ mol/dm}^3$ in $[\text{C}_1\text{C}_{10}\text{im}^+][\text{Tf}_2\text{N}^-]/\text{EtG}$ (1), $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]/\text{EtG}$ (2) and $[\text{C}_1\text{C}_4\text{im}^+][\text{Tf}_2\text{N}^-]/\text{H}_2\text{O}$ (3) recorded in frozen solutions: MP phase – $[\text{Cr}^{3+}]_{\text{in}}=1 \times 10^{-3} \text{ mol/dm}^3$ and 0.1 MES in EtG. Calculated % E is 99.04% (1) and 99.57% (2) and below 0.5 % (3) – ICP-OES based on an average of three parallel determinations.

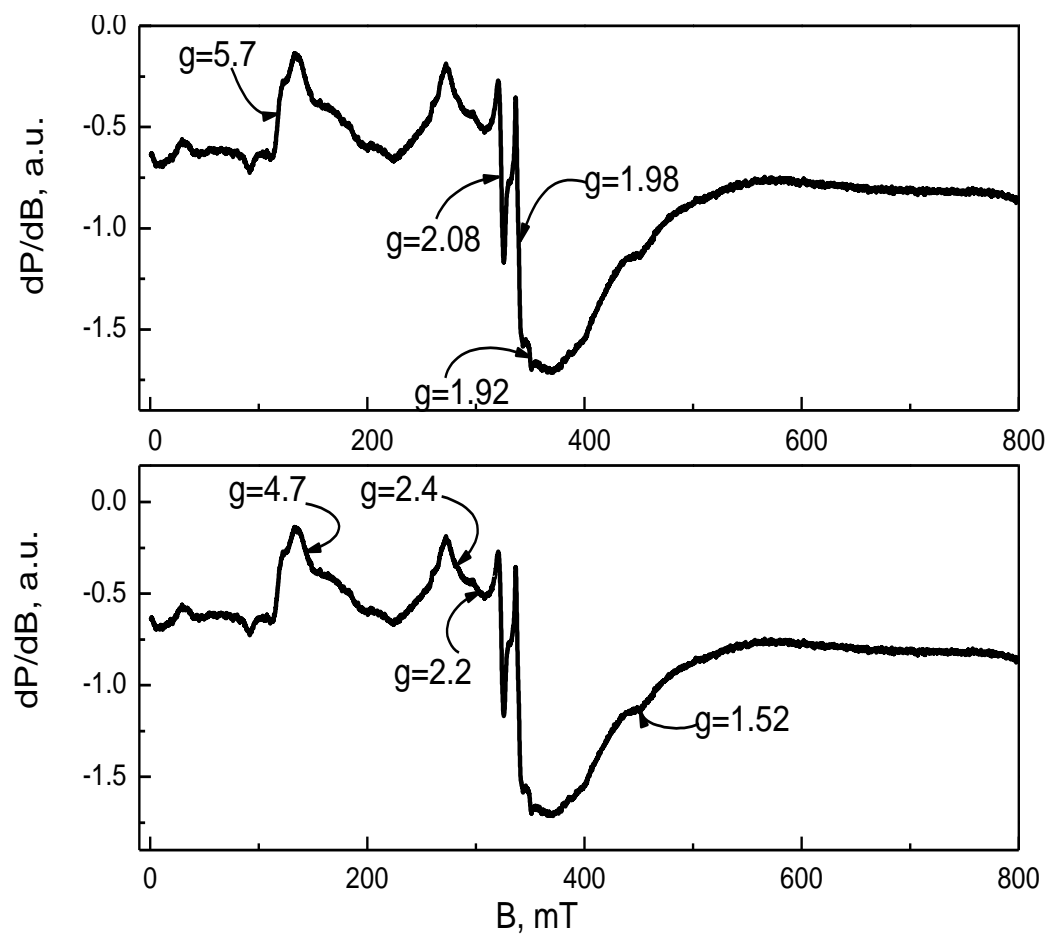


Fig. S7. EPR spectra of Cr^{3+} ion in ethylene glycol at room temperature and in the frozen state at 120 K: $[\text{Cr}^{3+}] = 3 \times 10^{-3} \text{ mol/dm}^3$. The Cr^{3+} concentration in the so called “standard sample” was found to be about $4 \times 10^{-4} \text{ mol/dm}^3$ (the spectra was integrated from 0 to 500 mT.)