Supporting Information

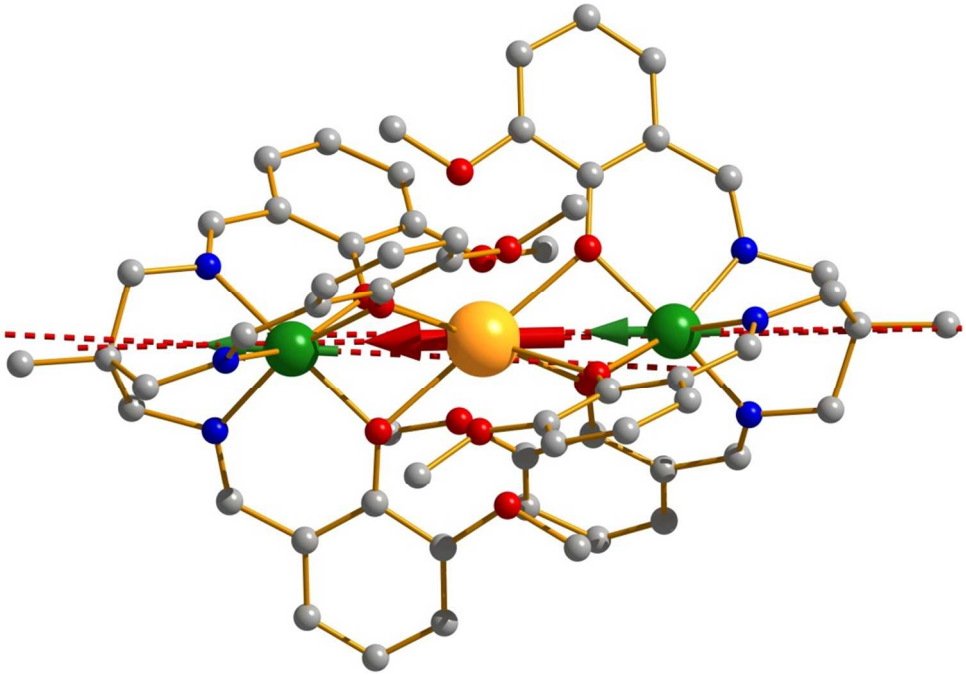


Figure S1. Structure of the CoTbCo complex (**2**).

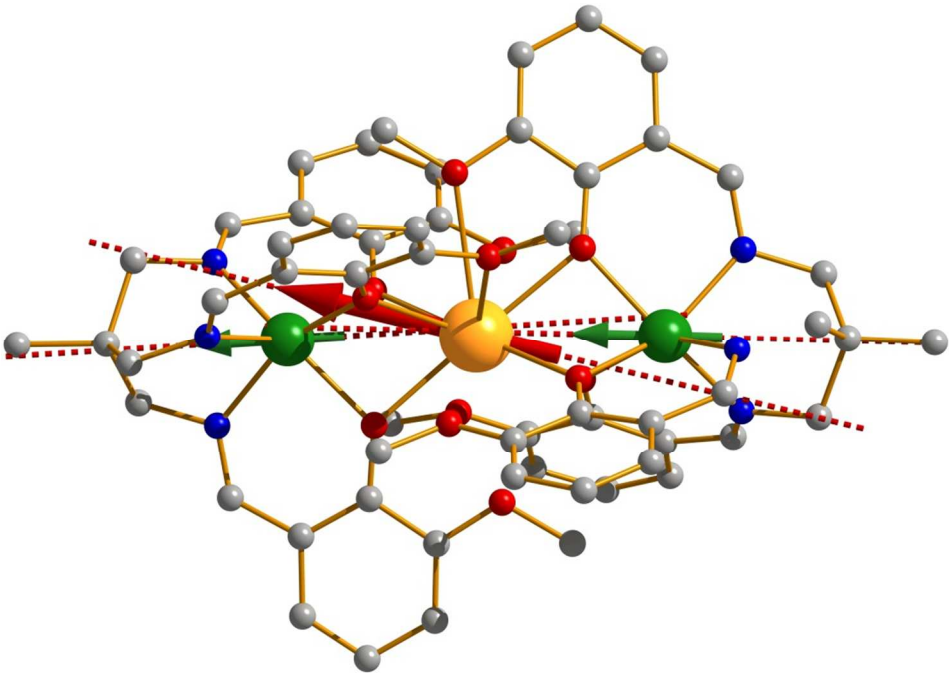


Figure S2. Structure of the CoDyCo complex (**3**).

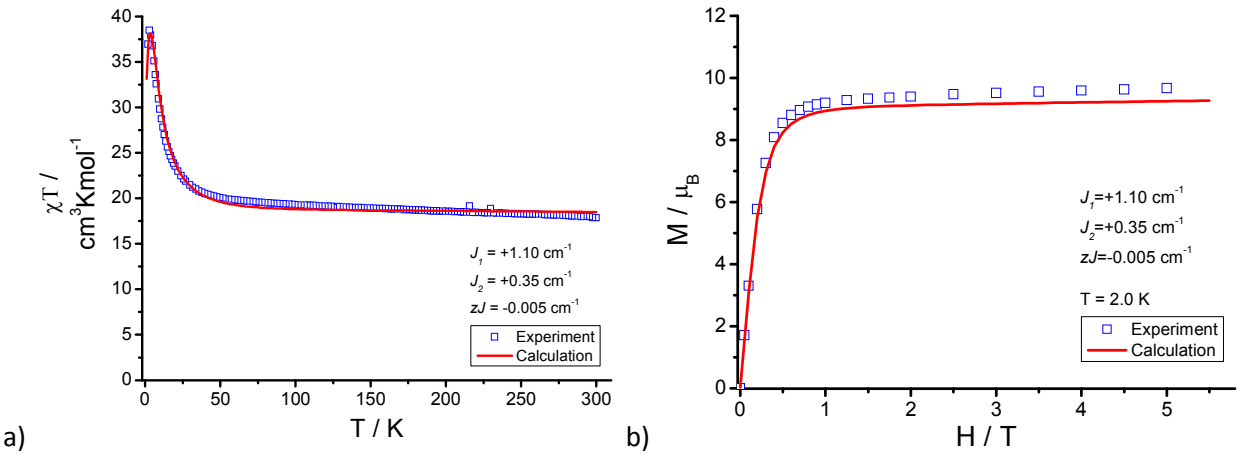


Figure S3. Magnetism of the CoTbCo complex (**2**)

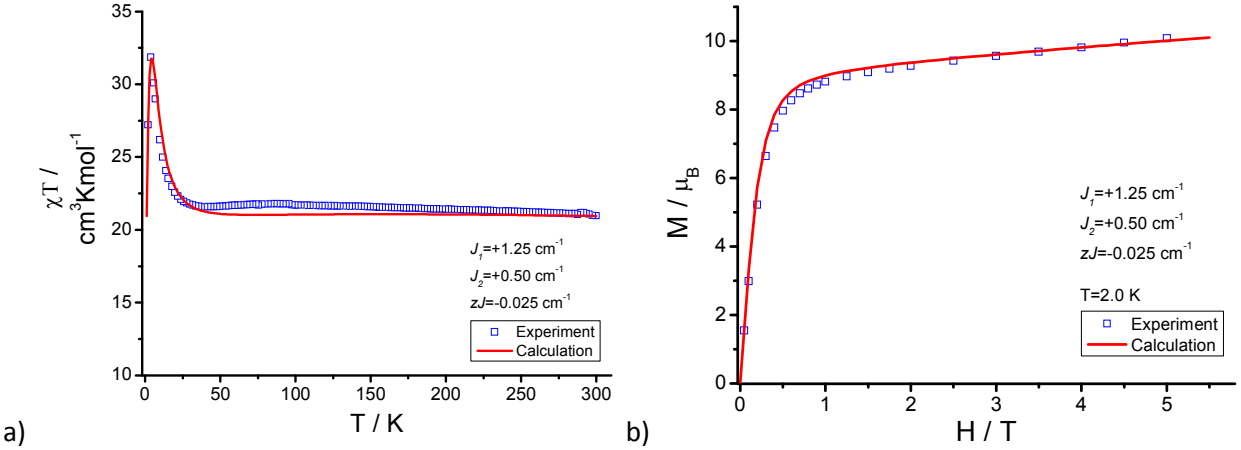


Figure S4. Magnetism of the CoDyCo complex (**3**)

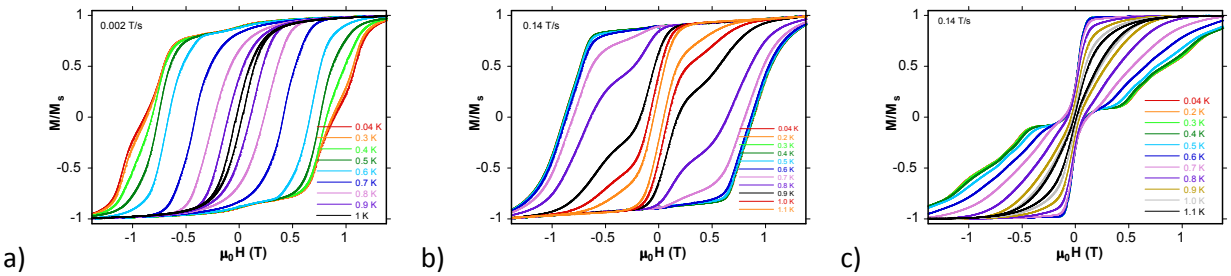


Figure S5. Magnetization M versus applied dc field H hysteresis loops for single crystals of **1** [LCoGdCoL]NO_3 (a), **2** [LCoTbCoL]NO_3 (b), and **3** [LCoDyCoL]$NO_3 \cdot CH_3OH$ (c), at the indicated temperatures. The magnetizations are normalized to their saturation values M_S at 1.4 T.

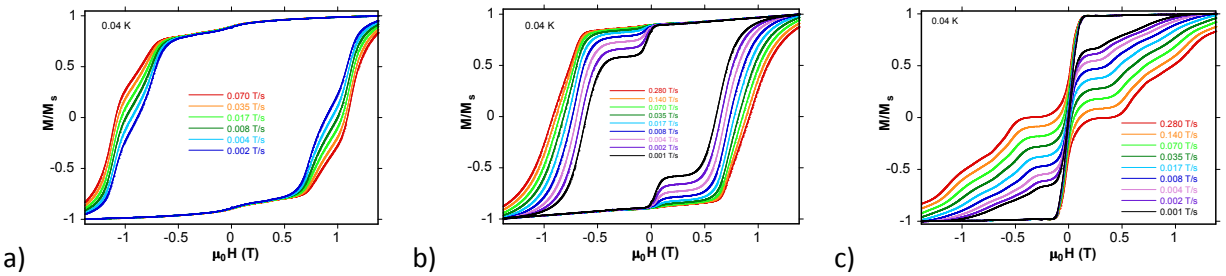


Figure S6. Magnetization M versus applied DC field H hysteresis loops for single crystals of **1** LCoGdCoL]NO_3 (a), **2** [LCoTbCoL]NO_3 (b), **3** [LCoDyCoL]$NO_3 \cdot CH_3OH$ (c) at the indicated field sweep rates. The magnetization is normalized to its saturation value M_S at 1.4 T.

Calculation of local electronic structure of metal ions and the magnetic properties of 1, 2 and 3

1. Computational details

Model fragments containing one single magnetic center were built by substituting the remaining centers by diamagnetic ions. The Co was computationally modeled by Zn, while the Tb, Dy and Gd ions were modeled by La. For example, calculation on center Co1 from Co1_Dy_Co2 was actually performed on Co1_La_Zn model fragment. All other atoms were kept as in the crystal structure, and no geometry optimization was employed.

Basis Sets: All employed basis sets were taken from the standard ANO-RCC basis set library from MOLCAS. The following contractions were used for the atoms:
Dy – 8s7p5d4f2g1h.
Co – 6s5p3d2f1g.
Zn – 5s4p2d.
La – 7s6p4d2f.
N, O – 3s2p1d. (only for the first coordinated atoms, which make a bond with the main magnetic ion Co or Dy).
N, O, C – 2s1p. (for distant atoms)
H – 1s.
For **Co fragments**, the active space of the CASSCF method included 7 electrons in 10 (3d +3d') orbitals. The spin orbit interaction was computed by mixing of 10 quartets and 40 doublet spin free states.

For **Ln fragments** the active space of the CASSCF method included all electrons from the last shell electrons in 7 orbitals of the 4f type. The spin orbit interaction was computed by mixing the maximal

number of spin states allowed by the hardware: 279 spin free states (SFS) for Dy, 322 SFS for Tb and 252 SFS for Gd.

2. Results of the ab initio calculations

Table S1. Energies (cm^{-1}) of the spin-free (CASSCF) and spin-orbit (RASSI) states of the individual magnetic centers in **1**.

2S+1	spin free states (CASSCF)			spin-orbit states (RASSI)		
	Co1	Gd	Co2	Co1	Gd	Co2
8	--	0.000	--	0.000	0.000	0.000
6	--	40951.796	--	248.686	0.459	242.221
		40955.243		536.549	0.754	549.084
		40959.320		852.041	0.904	856.123
		43709.677		3771.567	39657.874	3880.779
		43712.877		3847.394	39741.772	3954.752
		43749.287		8240.171	39793.460	8646.415
		43749.510		8303.550	39817.743	8749.443
		43763.174		8612.589	40134.377	8856.828
		43764.276		8676.778	40192.575	8967.140
		43767.619		9398.198	40223.903	9767.685
		43797.535		9426.755	40694.410	9794.451
		43798.271		15004.923	40755.396	14741.205
		43815.068		15222.244	43181.351	14904.096
		43817.852		16553.154	43244.905	17206.024
		43855.984		16559.354	43285.694	17212.782
		...		20009.709	43295.628	20003.457
4	0.000	66933.203	0.000	20420.362	43474.988	20408.288
	49.612	66935.731	120.039	20823.988	43544.634	20865.872
	3410.215	66941.413	3551.690	21435.022	43567.710	21478.728
	7868.361	66952.636	8384.093	21721.030	43574.592	21749.946
	8167.969	66954.863	8417.110	22141.505	43584.134	22174.669
	8959.178	67076.574	9364.858	23802.246	43685.905	24171.359
	16091.098	67077.589	16784.345	23841.614	43713.558	24213.464
	23555.847	67080.963	23965.211	23954.783	43736.591	24320.718
	23655.956	67082.068	24108.922	24036.957	43740.327	24363.784
	23980.663	67092.301	24166.414	24268.559	43747.728	24429.783
		67094.738		24524.293	43753.764	24769.650
		67106.642		26197.380	43761.884	26464.735
		67106.905		26573.846	43783.338	26694.558
		67107.376		26832.251	43789.411	26911.157
		67108.579		27198.656	43794.987	27333.714
		...		29459.037	43808.830	29727.542
2	14594.116	78203.219	14367.833	29544.610	43827.734	29778.513
	14783.778	78203.260	14488.875	30044.771	43840.335	30315.766
	19775.691	78210.062	19798.075	30374.856	43848.458	30646.485
	19854.312	78210.140	19873.036	30538.111	43856.804	30835.040
	20396.084	78223.390	20473.729	31233.164	43914.202	31528.826
	21012.205	78223.732	21125.938	32850.517	43920.393	33276.486
	21134.374	78225.307	21161.332	33083.124	43964.607	33368.590
	21643.792	78225.330	21710.810	34076.453	43971.254	34458.339
	25940.333	78230.032	26268.223	34556.362	43989.310	34928.957
	26112.080	78230.332	26282.448	35830.063	43993.645	36286.992
	26187.801	78233.656	26310.039	36626.387	44002.887	37055.124

	26297.678	78234.046	26358.024	37474.830	44004.834	38058.994
	28926.764	78246.495	29230.434	37613.908	44014.227	38187.232
	29014.533	78247.047	29281.736	38257.121	44029.273	38835.442
	29606.825	78248.072	29912.683	38977.723	44033.757	39541.646
	...	...	...	...	...	...

Table S2. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets on individual magnetic centers in **1.**

KD		Co1		Gd		Co2	
		energy	g	energy	g	energy	g
1	g_X	0.000	0.4197	0.000	0.0003	0.000	0.4066
	g_Y		0.4233		0.0003		0.4155
	g_Z		9.2928		13.9720		9.2570
2	g_X	248.686	0.5064	0.459	0.0406	242.221	1.4578
	g_Y		0.9614		0.0429		1.9117
	g_Z		5.2042		9.9720		4.9886
3	g_X	536.549	0.6653	0.754	1.7192	549.084	0.9821
	g_Y		0.8109		1.7578		1.6751
	g_Z		1.2123		5.8877		1.7170
4	g_X	852.041	0.0425	0.904	1.9027	856.123	0.0063
	g_Y		0.0639		6.1866		0.0258
	g_Z		2.7922		9.6652		2.8266
5	g_X	3771.567	0.0909	39657.874	0.0028	3880.779	0.0670
	g_Y		0.0931		0.0029		0.0680
	g_Z		6.8234		11.8221		6.7833
6	g_X	3847.394	2.2708	39741.772	0.0276	3954.752	2.2580
	g_Y		3.8139		0.0285		3.8447
	g_Z		3.9902		8.3060		3.9622
7	g_X	8240.171	0.4635	39793.460	0.3703	8646.415	0.0612
	g_Y		0.5256		0.4291		0.0680
	g_Z		6.8985		4.9302		7.3284
8	g_X	8303.550	2.3929	39817.743	1.6252	8749.443	1.1093
	g_Y		3.1541		6.3032		1.2206
	g_Z		4.0362		7.1009		3.3525

Table S3. Energies (cm^{-1}) of the spin-free (CASSCF) and spin-orbit (RASSI) states of the individual magnetic centers in **2**.

2S+1	spin free states (CASSCF)				spin-orbit states (RASSI)		
	Co1	Co2	2S+1	Tb	Co1	Tb	Co2
4	0.000	0.000	**7**	0.000	0.000	0.000	0.000
	170.680	89.086		69.118	235.888	0.024	246.556
	3477.294	3412.461		406.657	565.842	242.230	544.115
	8153.958	7985.379		439.089	868.098	242.657	857.361
	8175.965	8224.826		461.098	3786.448	396.648	3756.835
	9082.558	8994.548		977.241	3862.058	401.120	3832.869
	16287.786	16157.612		1041.032	8393.323	446.753	8328.248
	23691.650	23732.340			8498.022	534.325	8400.194
	23814.088	23784.322			8602.796	543.750	8654.123
	24083.132	23893.276			8713.271	562.471	8726.525
2	14594.992	14592.066	**5**	47263.102	9469.389	596.330	9415.464
	14751.386	14723.292		47264.547	9495.766	622.897	9445.901
	19790.991	19828.538		47279.358	14951.091	647.061	14979.082
	19956.579	19864.499		48244.755	15140.960	2320.666	15151.970
	20475.649	20409.407		48272.552	16695.719	2374.257	16601.467

	21105.990	21036.666		48282.494	16702.071	2385.078	16608.198
	21159.106	21152.195		48340.525	20005.744	2395.835	20027.448
	21699.453	21648.448		48349.346	20436.962	2417.300	20429.737
	26080.723	26015.921		48367.789	20849.458	2425.417	20821.782
	26201.606	26129.213		48432.332	21451.345	2511.114	21437.352
	26255.783	26221.974		48435.498	21720.790	2514.505	21726.978
	26333.177	26255.595		48456.076	22144.589	2647.967	22130.756
	29053.765	29005.653		48488.619	23891.101	2662.383	23948.564
	29132.110	29071.853		48508.718	23924.945	2756.147	23970.708
	29727.809	29651.073		48511.406	24051.129	3691.000	24028.855
	...	...		...	24121.061	3722.748	24101.146
			3	50026.880	24316.607	3743.962	24181.693
				50028.472	24586.948	3749.385	24517.985
				50058.346	26270.849	3856.764	26239.229
				50058.444	26603.123	3860.358	26580.564
				50122.068	26836.502	3883.087	26806.021
				50128.044	27228.847	4094.493	27203.854
				50129.730	29532.424	4105.904	29520.861
				50163.464	29610.702	4799.971	29584.549
				50164.673	30112.890	4810.257	30071.361
				50182.721	30437.182	4828.525	30478.299
				50218.614	30646.924	4950.477	30641.798
				50222.667	31297.511	4960.076	31272.245
				50373.167	33000.773	4980.612	32901.672
				50379.184	33075.231	5014.769	33061.059
				50421.797	34184.826	5420.497	34169.121
				...	34662.992	5667.867	34635.804
			1	56893.724	35930.587	5698.925	35863.206
				57476.564	36724.674	5784.702	36689.536
				57504.992	37650.618	5803.963	37619.218
				57542.207	37761.376	6002.824	37732.840
				57547.276	38366.195	6248.309	38282.212
				57596.769	39087.199	6265.009	39004.334
				57608.981	45964.627	6428.050	45950.114
				57617.543	46301.768	23712.104	46279.079
				57744.909	47127.081	23712.120	47125.886
				57749.687	47584.436	23750.299	47601.420
				57756.398	47722.235	23752.124	47632.412
				57760.157	48376.461	23823.998	48358.697
				57801.207	49412.477	23824.412	49395.306
				57807.331	69801.696	23872.799	69735.227
				57822.964	70405.104	23879.336	70457.800
				...	70679.522	...	70566.408
					70995.791		71000.096
					71466.066		71472.192

Table S4. Energies (cm^{-1}) and *g* tensors of the lowest doublets on individual magnetic centers in **2.**

KD		Co1		Tb		Co2	
		energy	g	energy	g	energy	g
1	g_X	0.000	0.4224	0.000	0.0000	0.000	0.2783
	g_Y		0.4380	0.024	0.0000		0.2805
	g_Z		9.2363		17.9155		9.4461
2	g_X	235.888	1.9734	242.230	0.0000	246.556	0.6594
	g_Y		2.4604	242.657	0.0000		0.9509
	g_Z		4.7973		14.3663		5.3598
3	g_X	565.842	0.7942	396.648	0.0000	544.115	0.7881

	g_Y		2.1865	401.120	0.0000		0.8313
	g_Z		2.2911		9.5708		1.3492
4	g_X	868.098	0.0244	446.753	---	857.361	0.0088
	g_Y		0.0455				0.0286
	g_Z		2.8456				2.6436
5	g_X	3786.448	0.0502	534.325	0.0000	3756.835	0.0557
	g_Y		0.0506	543.750	0.0000		0.0568
	g_Z		6.8164		12.0181		7.0505
6	g_X	3862.058	2.2692	562.471	0.0000	3832.869	2.3468
	g_Y		3.8560	596.330	0.0000		3.9706
	g_Z		3.9460		11.1690		4.0720
7	g_X	8393.323	0.0969	622.897	0.0000	8328.248	0.0157
	g_Y		0.1050	647.061	0.0000		0.0210
	g_Z		7.3342		14.3461		7.4539

Table S5. Energies (cm^{-1}) of the spin-free (CASSCF) and spin-orbit (RASSI) states of the individual magnetic centers in **3**.

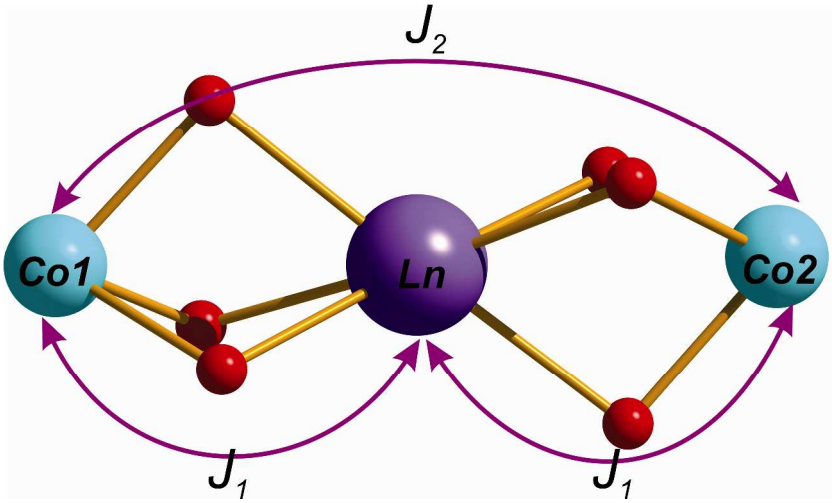
2S+1	spin free states (CASSCF)			spin-orbit states (RASSI)		
	Co1	Dy	Co2	Co1	Dy	Co2
6	---	0.000	---	0.000	0.000	0.000
		93.230		257.856	31.745	258.692
		109.652		570.629	66.329	558.883
		161.805		896.087	96.717	883.897
		185.444		4467.143	139.925	4381.742
		201.687		4549.273	314.305	4460.845
		385.061		7528.764	451.885	7815.047
		395.837		7626.498	546.634	7931.218
		670.791		7842.744	3549.784	8059.143
		708.769		7932.645	3566.922	8171.572
		841.709		8712.609	3671.714	8976.709
		7638.680		8732.960	3792.008	8988.859
		7653.085		14438.177	3838.247	15077.114
		7832.169		14443.035	3870.965	15081.226
		7845.399		16248.013	3891.168	15928.259
		7853.971		16455.807	6069.039	16102.419
		7953.477		20109.259	6140.730	20087.808
		7997.977		20548.374	6251.209	20524.841
		34833.235		20816.648	6321.362	20839.041
		35316.681		21400.456	6357.901	21429.213
		35359.084		21692.744	6397.654	21719.777
4	0.000	24870.581	0.000	22569.952	8031.511	22502.496
	95.262	24871.030	56.659	23257.728	8130.189	23448.743
	4142.043	24912.820	4033.881	23300.470	8195.031	23482.474
	7195.527	24915.310	7510.562	23373.499	8314.125	23645.298
	7381.008	24932.816	7567.419	23494.250	8344.373	23746.057
	8262.260	24934.547	8512.838	23665.211	9555.838	23852.721
	13963.905	25027.237	14595.893	23923.772	9664.837	24136.494
	23018.017	25033.645	23165.021	25611.554	9819.530	25836.557
	23083.259	25086.920	23382.759	26376.481	9840.929	26462.527
	23314.746	25103.730	23497.595	26743.357	10053.278	26793.366
		...		26947.292	10060.055	27040.367
2	15865.577	37255.859	15530.848	28978.711	10080.746	29165.768
	16017.137	37256.050	15640.990	29093.412	10140.767	29270.725
	19925.223	37303.304	19861.066	29462.950	10161.540	29656.225
	19946.667	37312.363	19933.868	29683.878	10297.158	29898.777

	20382.578	37341.984	20395.827	29900.380	10731.369	30099.354
	21020.605	37342.623	21039.299	30907.387	10901.342	31073.243
	21063.347	37509.654	21074.857	31848.257	11075.482	32212.410
	22124.414	37534.522	22031.249	32184.918	11482.672	32482.868
	25266.880	37538.498	25498.393	33025.685	11529.089	33318.039
	26035.919	37565.259	26105.250	33313.352	11578.908	33651.772
	26094.697	37570.501	26150.486	34398.811	11596.556	34843.436
	26193.640	37586.938	26196.741	35624.146	11603.260	35958.427
	28460.334	37664.426	28630.188	36270.200	13407.009	36718.911
	28545.959	37667.321	28715.923	36340.373	13471.025	36791.802
	29034.714	37691.691	29210.176	37189.729	13521.430	37604.712
	...	...	...	...	...	...

Table S6. Energies (cm^{-1}) and *g* tensors of the lowest Kramers doublets on individual magnetic centers in **3.**

KD		Co1		Dy		Co2	
		energy	g	energy	g	energy	g
1	g_X	0.000	0.2535	0.000	0.0565	0.000	0.2783
	g_Y		0.2561		0.1363		0.2805
	g_Z		9.4737		16.9671		9.4461
2	g_X	257.856	1.1901	31.745	0.0687	258.692	0.6594
	g_Y		1.4575		0.3045		0.9509
	g_Z		5.2998		15.3855		5.3598
3	g_X	570.629	1.2442	66.329	0.2247	558.883	0.7881
	g_Y		1.2968		0.2716		0.8313
	g_Z		1.3946		17.0384		1.3492
4	g_X	896.087	0.0259	96.717	0.4384	883.897	0.0088
	g_Y		0.0464		0.6655		0.0286
	g_Z		2.6141		15.0624		2.6436
5	g_X	4467.143	0.0783	139.925	4.2353	4381.742	0.0557
	g_Y		0.0793		5.4988		0.0568
	g_Z		7.1531		7.6723		7.0505
6	g_X	4549.273	2.3804	314.305	4.7545	4460.845	2.3468
	g_Y		3.9861		4.9606		3.9706
	g_Z		4.1244		5.6174		4.0720
7	g_X	7528.764	0.0720	451.885	2.0222	7815.047	0.0157
	g_Y		0.0742		3.6808		0.0210
	g_Z		7.3264		4.7296		7.4539
8	g_X	7626.498	2.8331	546.634	1.0715	7931.218	1.6012
	g_Y		3.1057		7.0674		1.6424
	g_Z		3.2513		13.4565		3.4225

3. Model for the exchange coupling



Scheme 1. Exchange model employed for CoLnCo series.

$$\hat{H}_{exch} = -J_1\left(\hat{\tilde{S}}_{Co1}\cdot\hat{\tilde{S}}_{Ln} + \hat{\tilde{S}}_{Co2}\cdot\hat{\tilde{S}}_{Ln}\right) - J_2\hat{\tilde{S}}_{Co1}\cdot\hat{\tilde{S}}_{Co2}$$

The exchange matrix was written on the basis of lowest spin-orbit multiplets on sites.

CoGdCo:

Magnetic properties are quite well reproduced by the following set of Lines exchange coupling constants:

J_1 = +0.90 cm^{-1}

J_2 = +0.60 cm^{-1}

zJ = -0.0005 cm^{-1}

The calculated exchange spectrum and the comparison of the measured and calculated magnetic properties are further shown.

Table S7. Energies (cm^{-1}) and *g* tensors of the lowest exchange Kramers doublets of the CoGdCo complex (**1**)

KD	Ab Initio Calculation			*Ising -1 (*)*			*Ising-2 (**)*		
	energy (cm^{-1})	*g* tensor		energy (cm^{-1})	*g* tensor		energy (cm^{-1})	*g* tensor	
1	0.000000	g_X g_Y g_Z	0.0000 0.0000 32.5280	0.000000	g_X g_Y g_Z	0.0000 0.0000 32.5280	0.000000	g_X g_Y g_Z	0.0000 0.0000 32.5284
2	3.075113	g_X g_Y g_Z	0.0000 0.0000 28.5158	3.086711	g_X g_Y g_Z	0.0000 0.0000 28.5348	2.628584	g_X g_Y g_Z	0.0000 0.0000 28.5348
3	5.991168	g_X g_Y g_Z	0.0000 0.0000 24.4785	6.018829	g_X g_Y g_Z	0.0000 0.0000 24.5415	5.266426	g_X g_Y g_Z	0.0000 0.0000 24.5411
4	8.752611	g_X g_Y	0.0091 0.0092	8.809533	g_X g_Y	0.0000 0.0000	7.913607	g_X g_Y	0.0000 0.0000

		g_Z	20.3355		g_Z	20.5479		g_Z	20.5474
5	11.297845	g_X g_Y g_Z	2.0647 2.0796 14.8986	11.465922	g_X g_Y g_Z	0.0000 0.0000 16.5539	10.570209	g_X g_Y g_Z	0.0000 0.0000 16.5537
6	11.947111	g_X g_Y g_Z	0.0004 0.0006 13.9691	11.944037	g_X g_Y g_Z	0.0000 0.0000 13.9534	11.828782	g_X g_Y g_Z	0.0001 0.0002 14.0374
7	11.959513	g_X g_Y g_Z	0.0001 0.0004 13.9874	11.951207	g_X g_Y g_Z	0.0000 0.0000 14.0172	11.860694	g_X g_Y g_Z	0.0022 0.0025 9.6008
8	12.378298	g_X g_Y g_Z	0.0261 0.0633 9.9506	12.375643	g_X g_Y g_Z	0.0003 0.0012 9.9458	11.890140	g_X g_Y g_Z	0.0074 0.0103 5.3525
9	12.389451	g_X g_Y g_Z	0.0091 0.0513 9.9388	12.380981	g_X g_Y g_Z	0.0001 0.0008 10.0054	11.916831	g_X g_Y g_Z	0.0021 0.0156 1.2946
10	12.647814	g_X g_Y g_Z	0.9698 3.2386 3.5302	12.642731	g_X g_Y g_Z	0.0050 0.0138 4.3487	11.940404	g_X g_Y g_Z	0.0038 0.0184 2.5595
11	12.665825	g_X g_Y g_Z	0.2854 1.5876 3.2201	12.659567	g_X g_Y g_Z	0.0020 0.0117 1.9608	11.959929	g_X g_Y g_Z	0.0045 0.0151 6.6608
12	12.766155	g_X g_Y g_Z	0.2793 0.7785 2.5303	12.765863	g_X g_Y g_Z	0.0014 0.0014 4.4080	11.977252	g_X g_Y g_Z	0.0037 0.0083 9.0710
13	12.845484	g_X g_Y g_Z	0.8158 3.1351 10.0399	12.850572	g_X g_Y g_Z	0.0010 0.0031 11.4657	11.983055	g_X g_Y g_Z	0.0034 0.0105 12.1828
14	14.159214	g_X g_Y g_Z	1.8149 1.8253 10.7485	13.988301	g_X g_Y g_Z	0.0000 0.0000 12.5596	13.236329	g_X g_Y g_Z	0.0000 0.0000 12.5599
15	16.417228	g_X g_Y g_Z	0.0056 0.0056 8.3834	16.370121	g_X g_Y g_Z	0.0000 0.0000 8.5659	15.912043	g_X g_Y g_Z	0.0000 0.0000 8.5662
16	18.615243	g_X g_Y g_Z	0.0000 0.0000 4.5390	18.598739	g_X g_Y g_Z	0.0000 0.0000 4.5775	18.597443	g_X g_Y g_Z	0.0000 0.0000 4.5724

(*) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), while the ab initio obtained zero field splitting (ZFS) of the Gd^{3+} was kept in the exchange calculation (see Table S1).

(**) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), the zero-field splitting on Gd^{3+} was not taken into account: ZFS of the ground S=7/2 = 0.

CoTbCo:

Magnetic properties are best reproduced by the following Lines exchange coupling constants:

J_1 = +1.10 cm^{-1}

J_2 = +0.35 cm^{-1}

zJ = -0.005 cm^{-1}

The calculated exchange spectrum and the comparison of the measured and calculated magnetic properties are further shown.

Table S8. Energies (cm^{-1}) and *g* tensors of the lowest exchange Ising doublets of the CoTbCo complex (**2**)

KD	Ab Initio Calculation			*Ising -1 (*)*			*Ising-2 (**)*		
	energy (cm^{-1})		*g* tensor	energy (cm^{-1})			energy (cm^{-1})		*g* tensor
1	0.000000000	Δ_{tun}	3.51E-07	0.000000000	Δ_{tun}	3.11E-07	0.000000000	Δ_{tun}	1.39E-07
	0.000000351	g_z	36.4329	0.000000311	g_z	36.4330	0.000000138	g_z	36.4330
2	11.196736326	Δ_{tun}	9.52E-03	11.202534139	Δ_{tun}	1.35E-05	11.207884462	Δ_{tun}	1.52E-07
	11.206259546	g_z	13.4639	11.202547596	g_z	12.4564	11.207884614	g_z	18.0034
3	11.232781940	Δ_{tun}	9.52E-03	11.237094407	Δ_{tun}	1.35E-05	11.231741474	Δ_{tun}	8.79E-08
	11.242304834	g_z	13.3190	11.237107865	g_z	12.3052	11.231741562	g_z	17.8522
4	19.347782065	Δ_{tun}	7.89E-07	19.348283883	Δ_{tun}	3.49E-07	19.348268157	Δ_{tun}	1.01E-07
	19.347782854	g_z	1.0116	19.348284233	g_z	1.0141	19.348268258	g_z	1.0141

(*) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), while the ab initio obtained Δ_{tun} of the Tb^{3+} center for the ground doublet (0.024 cm^{-1}) was kept in the exchange calculation (see Table S3).

(**) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), while the ab initio obtained Δ_{tun} of the Tb^{3+} of the ground doublet was not taken into account: Δ_{tun} of the Tb^{3+} center of the ground doublet = 0.

CoDyCo:

Magnetic properties are best reproduced by the following Lines exchange coupling constants:

J_1 = +1.25 cm^{-1}

J_2 = +0.50 cm^{-1}

zJ = -0.025 cm^{-1}

The calculated exchange spectrum and the comparison of the measured and calculated magnetic properties are further shown.

Table S9. Energies (cm^{-1}) and *g* tensors of the lowest exchange Kramers doublets of the CoDyCo complex (**3**)

KD	Ab Initio Calculation			*Ising -1 (*)*			*Ising-2 (**)*		
	energy (cm^{-1})	*g* tensor		energy (cm^{-1})	*g* tensor		energy (cm^{-1})	*g* tensor	
1	0.000000	g_X g_Y g_Z	0.0000 0.0000 35.7500	0.000000	g_X g_Y g_Z	0.0000 0.0000 35.7504	0.000000	g_X g_Y g_Z	0.0000 0.0000 35.7504
2	9.758455	g_X g_Y g_Z	0.0057 0.0132 17.1455	9.758084	g_X g_Y g_Z	0.0000 0.0000 17.1466	9.758039	g_X g_Y g_Z	0.0000 0.0000 17.1575
3	9.863980	g_X g_Y g_Z	0.0034 0.0100 16.8240	9.863500	g_X g_Y g_Z	0.0000 0.0000 16.8237	9.863452	g_X g_Y g_Z	0.0000 0.0000 16.8351
4	15.101509	g_X g_Y g_Z	0.0000 0.0004 5.1933	15.099948	g_X g_Y g_Z	0.0000 0.0000 5.2027	15.099857	g_X g_Y g_Z	0.0000 0.0000 5.2028

(*) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), while the ab initio obtained g_X and g_Y of the Dy^{3+} was kept in the exchange calculation (see Table S6).

(**) -- The Co^{II} centers were considered perfectly Ising (for the ground KD $g_X = g_Y = 0$), the ab initio obtained g_X and g_Y of the Dy^{3+} were not taken into account: g_X and g_Y of the Dy^{3+} of the ground Kramers doublet = 0.