Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Ringing the Changes in Fe^{III}/4f Molecules: Cyclic Coordination Clusters

Amer Baniodeh[1], Christopher E. Anson[1], Annie K. Powell[1,2]

[1]Institut für Anorganische Chemie, Karlsruher Institut für Technologie, Engesserstrasse 15, D-76131, Karlsruhe, Germany.

[2]Institut für Nanotechnologie, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany.

Table S1. Crystallographic data for the compounds **1-7**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{60}H_{67}Fe_2N_5O_{20}Yb_2$	$C_{119}H_{162}F_3Fe_5N_{17}O_{41}SYb_3$	$C_{85}H_{111}Fe_4N_7O_{29}Yb_2$	$C_{72}H_{94}Fe_3N_5O_{25}Yb_2$
FW (g mol^{-1})	1635.97	3374.09	2264.29	1943.15
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	18.8025(14)	16.4830(8)	14.2113(9)	19.9227(15)
b (Å)	15.9088(9)	19.8976(9)	18.5580(13)	19.6790(12)
c (Å)	21.9072(15)	20.2276(9)	19.2000(12)	22.0382(15)
α (°)	90	76.119(1)	84.231(5)	90
β (°)	109.900(6)	74.622(1)	70.788(5)	108.184(8)
γ (°)	90	81.570(1)	83.144(5)	90
V (Å^3)	6161.7(7)	6185.3(5)	4737.3 (5)	8208.8(10)
Z	4	2	2	4
T (K)	150(2)	100(2)	150(2)	200(2)
F(000)	3256	3412	2292	3916
ρ_{calc} (g/cm^{-3})	1.764	1.812	1.587	1.572
μ (mm^{-1})	3.548	2.929	2.630	2.849
Crystal size (mm)	0.24×0.22×0.19	0.28×0.24×0.22	0.31×0.26×0.18	0.32×0.27×0.23
Data measured	20471	49751	76472	47608
Unique data	6061	25848	21770	15902
R(int)	0.0339	0.0217	0.0568	0.0847
Data with I>2σ(I)	5185	21874	15906	9349
Parameters	410	1526	1014	971
wR_2 (all data)	0.1426	0.0781	0.1851	0.1534
S (all data)	1.070	1.042	1.031	0.981
R_1 (I > 2σ(I))	0.0520	0.0278	0.0686	0.0547
Largest diff. peak / hole (e Å^{-3})	+0.63 / -2.68	+1.22 / -0.55	+1.14 / -4.21	+0.72 / -2.45

Table S1: (continued)

Compound	**5**	**6**	**7**
Formula	$C_{61}H_{115}Fe_4N_7O_{27}S_2Yb_2$	$C_{182}H_{353}Fe_{10}N_{51}O_{90}Yb_{10}$	$C_{46}H_{60}N_2O_{14}Yb_2$
FW (g mol^{-1})	2012.20	6985.05	1211.04
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	14.449(2)	16.5530(12)	9.8980(15)
b (Å)	24.951(4)	20.5964(13)	14.2365(15)
c (Å)	23.760(4)	21.1312(16)	17.039(3)
α (°)	90	108.791(5)	90
β (°)	101.820(2)	101.118(6)	94.369(13)
γ (°)	90	95.993(5)	90
V ($Å^3$)	8384(2)	6583.9(8)	2394.0(6)
Z	4	1	2
T (K)	150(2)	150(2)	150(2)
F(000)	4088	3482	1204
ρ_{calc} (g/cm^{-3})	1.594	1.762	1.680
μ (mm^{-1})	4.063	4.133	3.948
Crystal size (mm)	0.15×0.04×0.02	0.31×0.24×0.20	0.17×0.13×0.09
λ (Å)	0.80000	0.71073	0.71073
Data measured	30732	62927	15933
Unique data	11932	25727	4544
R(int)	0.0675	0.0528	0.0818
Data with I>2σ(I)	9576	15716	2870
Parameters	847	1276	289
wR_2 (all data)	0.2858	0.1101	0.1104
S (all data)	1.293	0.959	0.983
R_1 (I > 2σ(I))	0.0974	0.0474	0.0484
Largest diff. peak / hole (e $Å^{-3}$)	+3.39 / -2.95	+0.95 / -1.53	+0.72 / -2.12

Data for **1**-**4**, **6** and **7** were measured on Bruker SMART Apex (**2**), Stoe IPDS II (**1**, **3**, **6**, **7**) or Stoe IPDS I (**4**) diffractometers using graphite-monochromated Mo-Kα radiation. Data for **5** were measured at the ANKA synchrotron source, Karlsruhe, on a Bruker SMART Apex diffractometer uisng Si-monochromated radiation of wavelength 0.80000 Å. Data were corrected for polarisation and absorption effects (and for primary beam decay in the case of **5**).[x1] For compound **5**, decomposition of the crystal in the synchrotron beam was observed during the latter stages of data collection, and for this reason the dataset is only 77.7% complete out to (sin θ)/λ =

0.60; however the data are clearly sufficient to establish the connectivity of the structure, with the data:parameter ratio still over 10:1.

Structures were solved using direct methods and refined by full-matrix least-squares refinement against F^2 (all data) using the SHELXTL software package.[x1] Ordered non-H atoms were refined using anisotropic thermal parameters. H atoms bonded to C were placed in calculated positions; the coordinates of H atoms bonded to O or N were refined, with restrained N-H or O-H bond lengths.

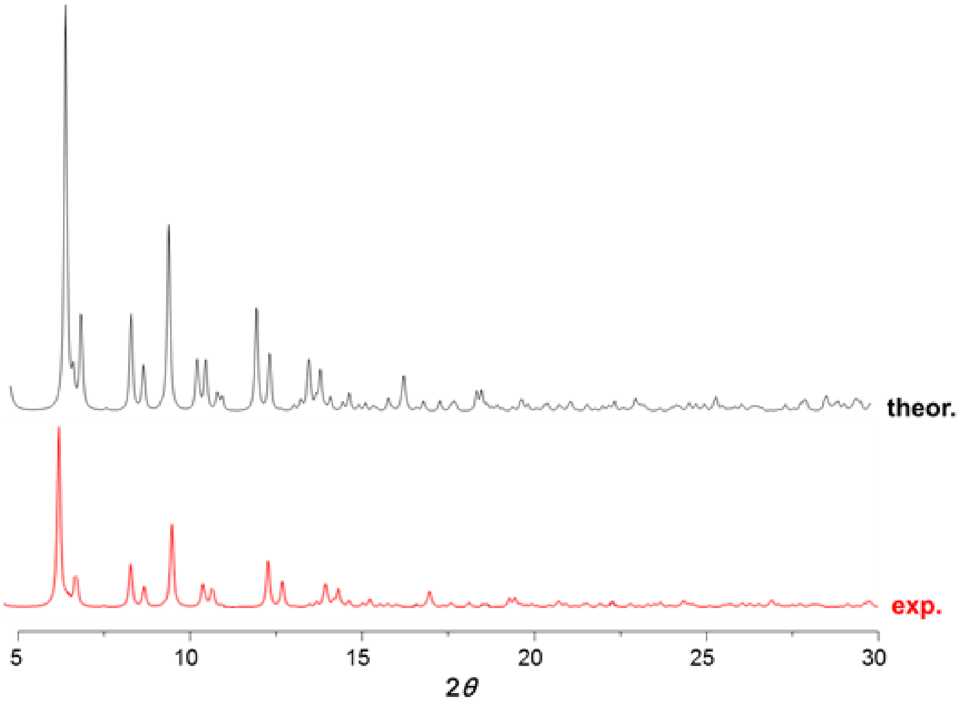
Disordered groups were modelled using isotropic partial occupancy atoms, with geometrical similarity restraints (or refinement as rigid hexagons for disordered benzoates) as appropriate. This mostly affected the ligands, but in **2** a triflate anion and an MeCN were disordered over an inversion centre (i.e. half an anion and half a MeCN per cluster, which is on a general position).

In the structures of 2, 3, 5 and 6, some or all of the lattice solvent was badly disordered, and could not be refined satisfactorily, and the data were treated using the SQUEEZE option in the PLATON package.[x2] For further details, see the individual cifs.

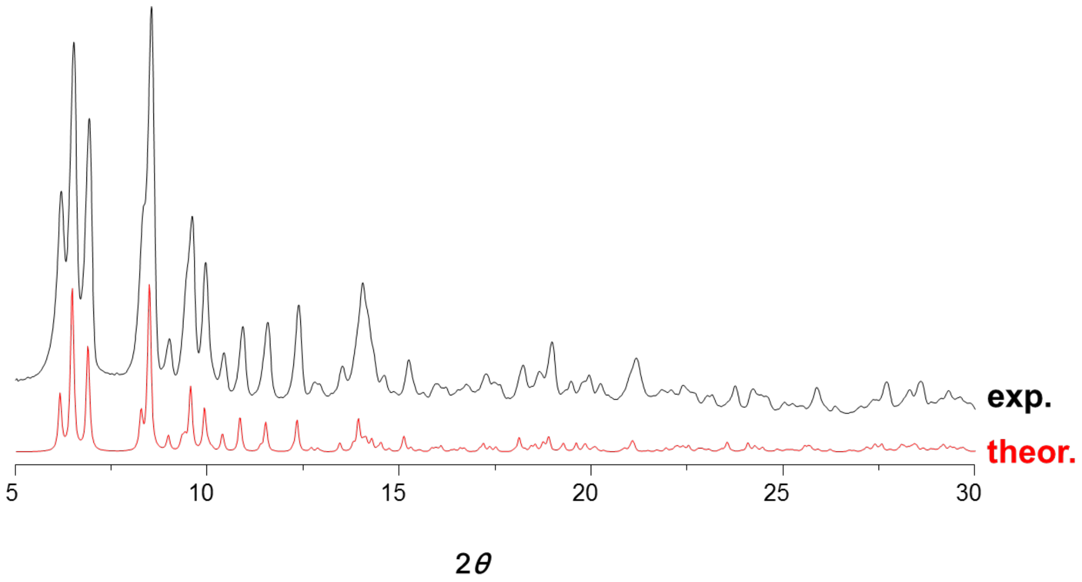
Further analytical data for the compounds 2, 3, 4, 6 and 7

Note that compound **1** has already been published and the yield of compound **5** was too low to perform further analyses.

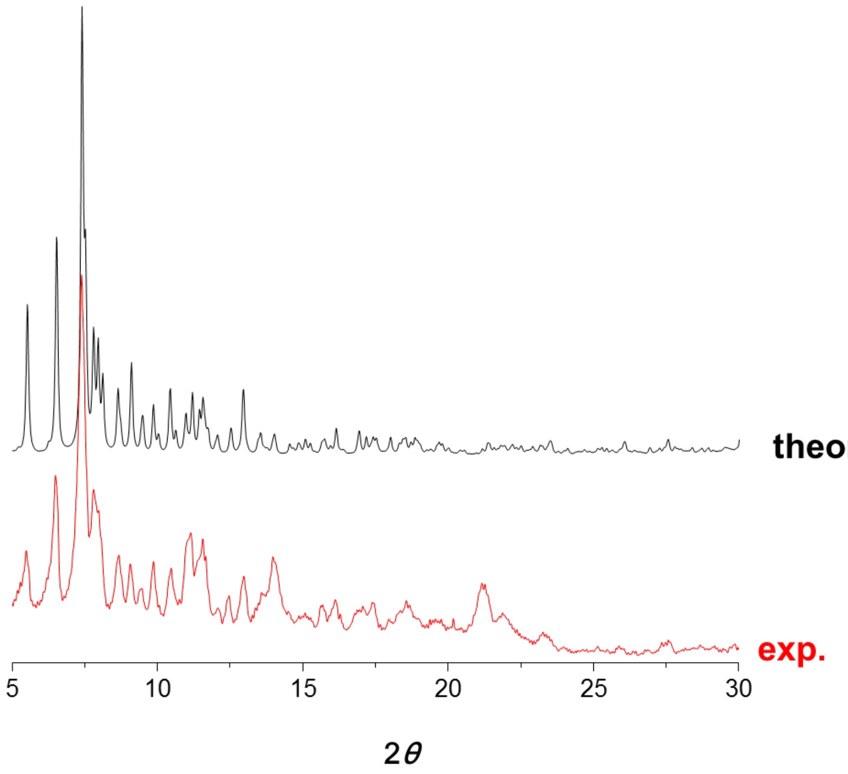
Powder X-ray Diffraction Data



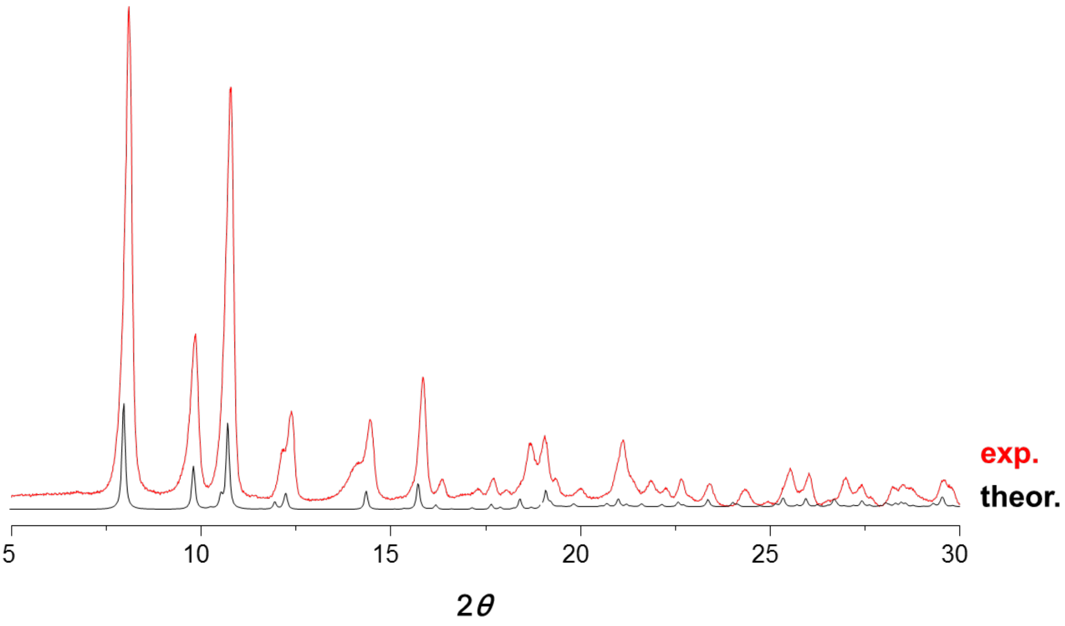
Theoretical (black) and experimental (red) powder pattern for compound **3**.



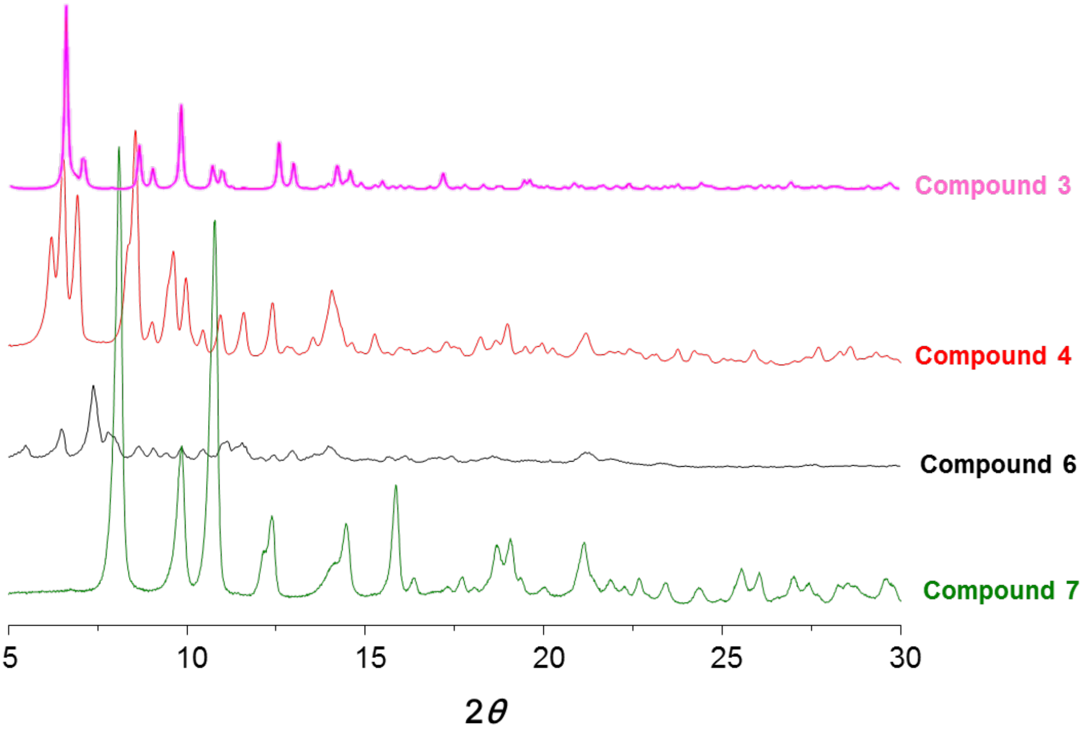
Theoretical (red) and experimental (black) powder pattern for compound **4**.



Theoretical (black) and experimental (red) powder pattern for compound **6**.

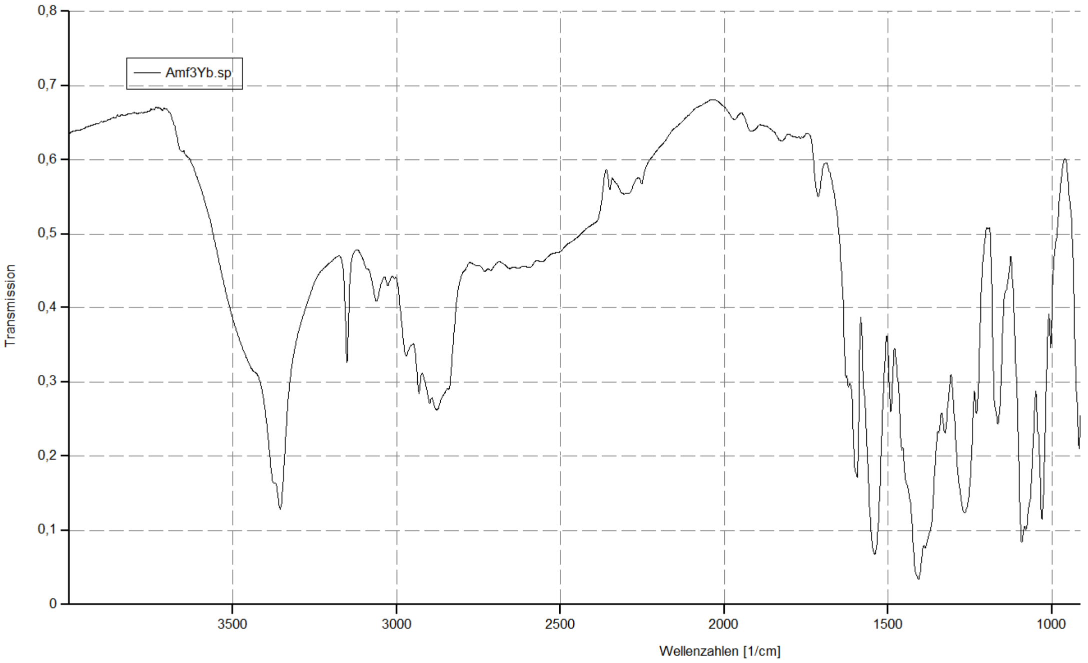


Theoretical (black) and experimental (red) powder pattern for compound **7**.

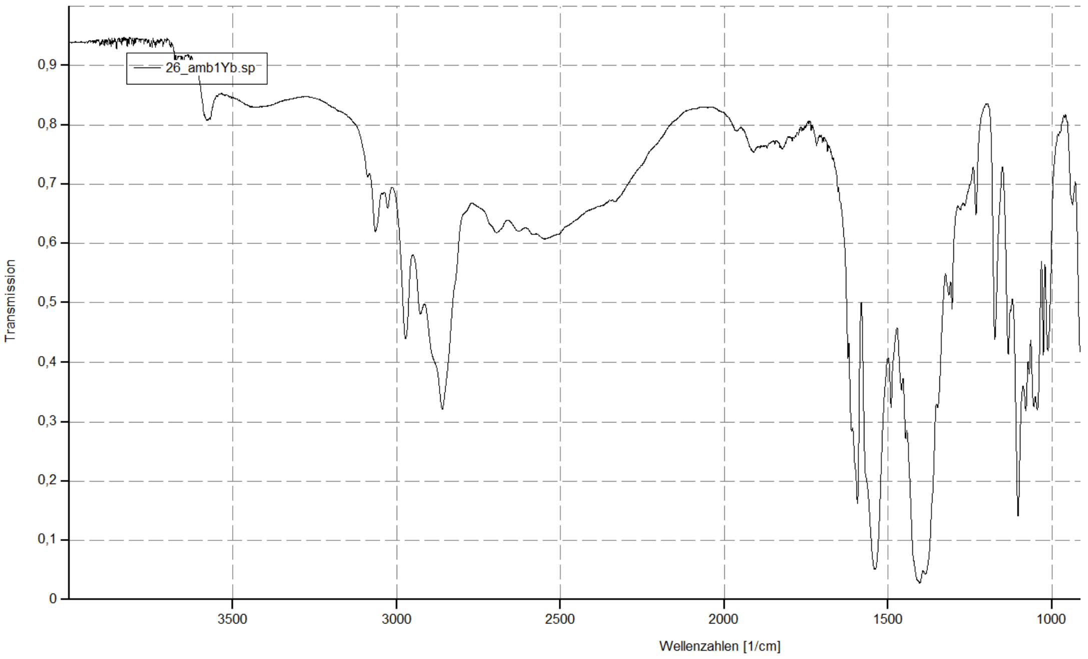


Comparison between the powder patterns of compounds **3,** ***4***, ***6*** and *7*.

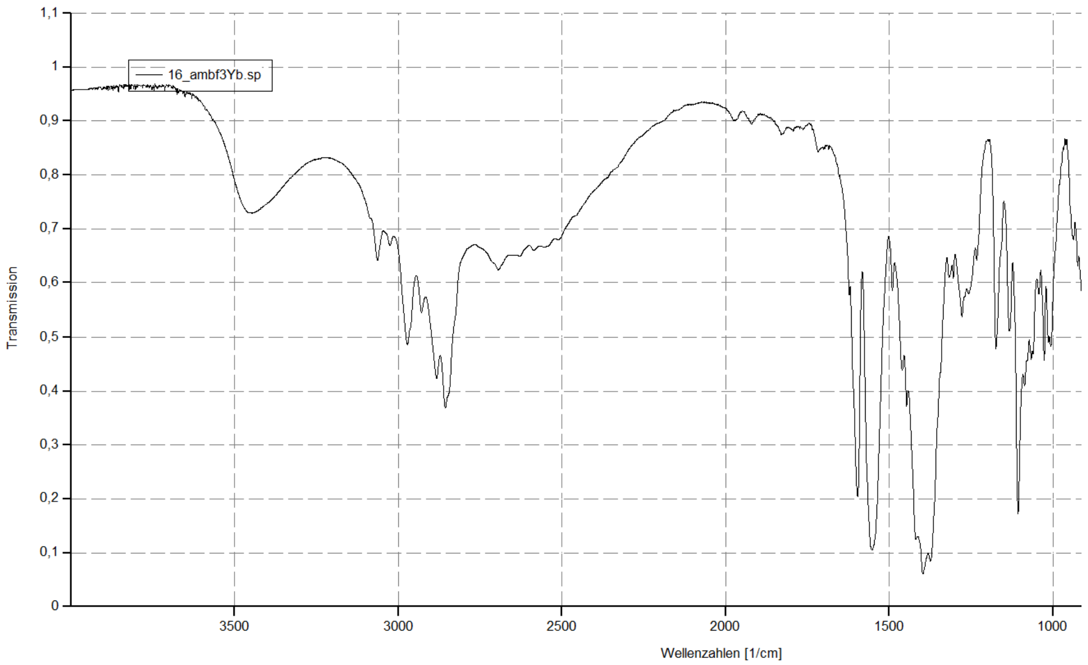
Infra-red spectra



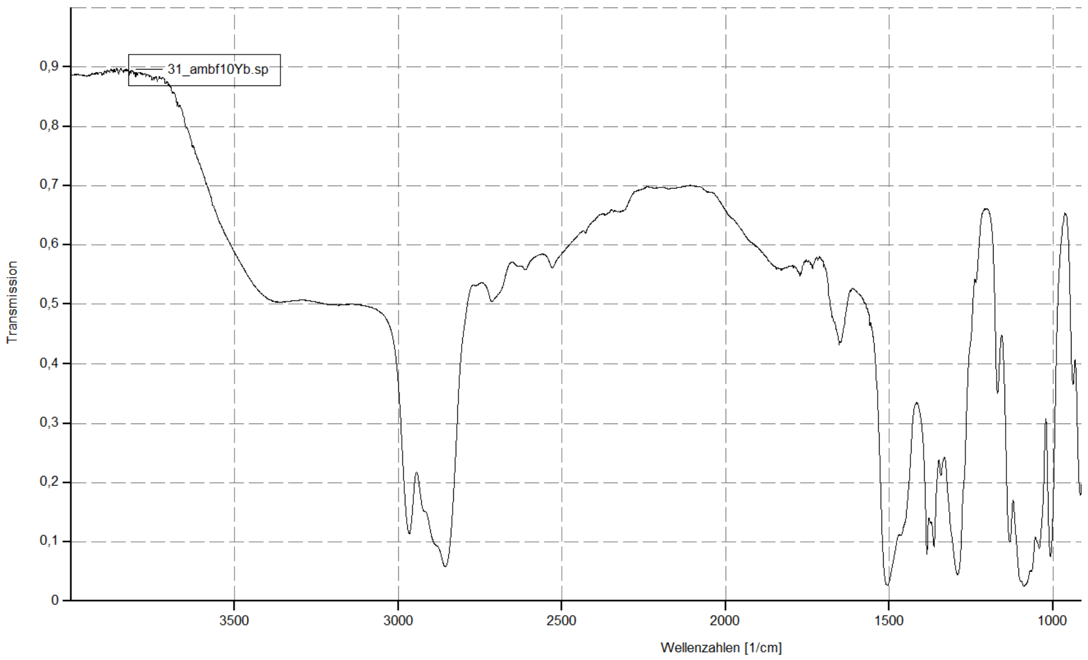
Fe5Yb3 compound 2



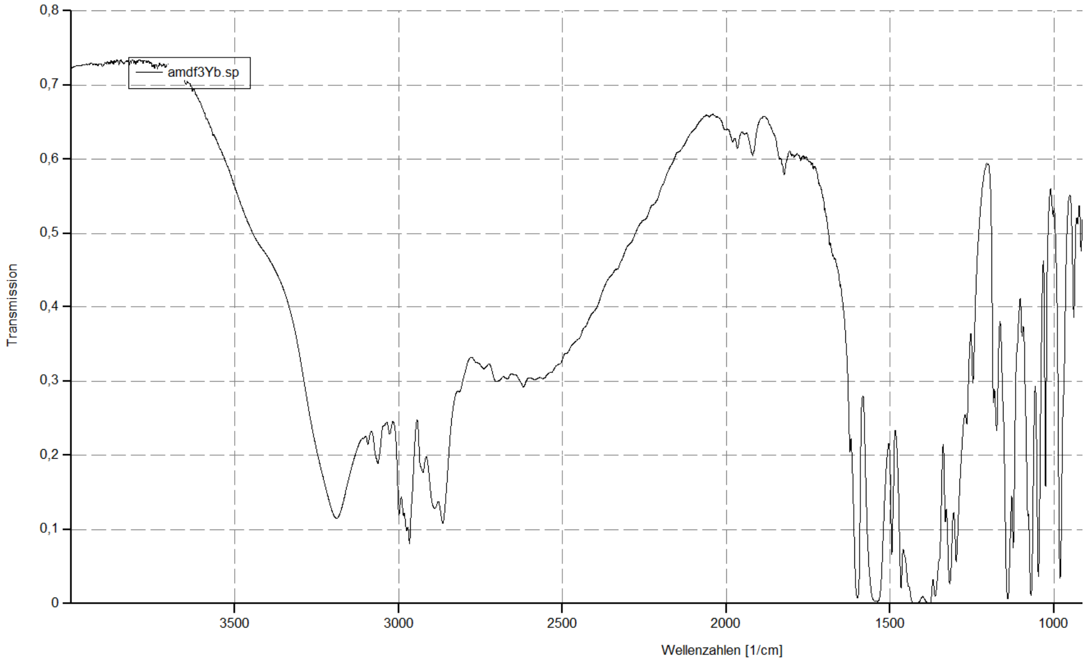
Fe4Yb2 compound 3



Fe3Yb2 compound 4



ambf10Yb= Fe10Yb10 = compound 6



Yb2 = compound 7