Supporting Information

Functional Polyoxometalates from Solvothermal Reactions of $VOSO_4$ with Tripodal Alkoxides – A Study on the Reactivity of Different "Tris" Derivatives

Olaf Nachtigall,[a] Adelheid Hagenbach,[a] Jelena Wiecko,[a] Dieter Lentz,[a] Ulrich Abram,[a] and Johann Spandl*[a]

a Freie Universität Berlin, Institut für Chemie und Biochemie, Fabeckstr. 34-36, 14195 Berlin, Germany
* jspandl@chemie.fu-berlin.de

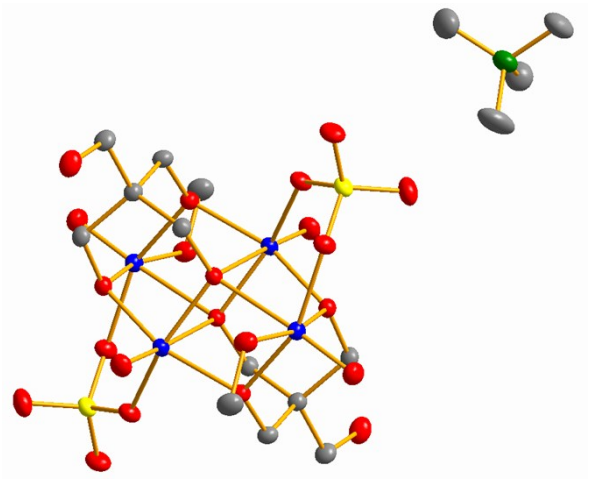
Table of Contents

1. Crystallographic Data

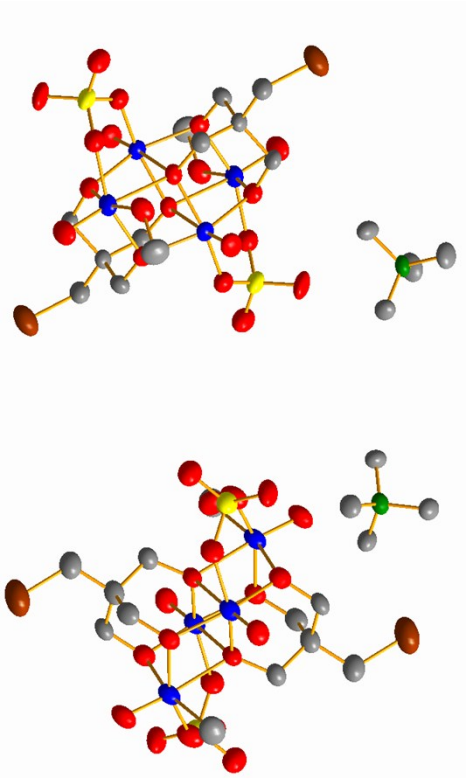
The intensities for the X-ray determinations for **I**, **II**, and **III** were collected on a STOE IPDS 2T instrument. The crystallographic experiments for compounds **IV**, **V**, **VI**, and **VII** were performed on a Bruker X8 Kappa APEX II diffractometer with a CCD-based detector. Mo K_α radiation (λ = 0.71073 Å) was used in all experiments but for compound **V**. The crystal structure of **V** was determined using Cu radition (λ = 1.54178 Å). Standard procedures were applied for data reduction and absorption correction. All structures were solved by intrinsic or direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL and WinGX program packages.[1,2] Disordered water molecules in the crystal structures of II, IV, V, and VI were treated with PLATON SQUEEZE software.[3] A twin matrix for compound II was determined with TwinRotMat.[4]

Compound	**I**	**II**	**III**	**IV**
M / g·mol^{-1}	954.52 (**I** · $\frac{1}{2}$ CH_3OH)	1064.30	1196.82 (**III** · 4 CH_3OH · 2 H_2O)	1052.62 (**IV** · CH_3OH)
Crystal colour	blue	blue	blue	green
Crystal shape	prism	platelet	block	block
Crystal size / mm^3	0.60 × 0.40 × 0.30	0.32 × 0.18 × 0.04	0.30 × 0.20 × 0.20	0.40 × 0.19 × 0.15
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	P $\bar{1}$	P 2_1 / c	P $\bar{1}$	P c c n
***a* / Å**	8.713	22.978	10.670	17.862
***b* / Å**	10.012	18.463	11.411	23.031
***c* / Å**	11.959	10.571	11.905	10.466
***α* / °**	69.32	90	92.03	90
***β* / °**	82.13	91.74	110.13	90
***γ* / °**	73.57	90	107.54	90
***V* / Å^3**	936.57	4482.96	1281.94	4305.34
Z	1	4	1	4
***T* / K**	210	210	210	100
***D$_{calc}$* / g·cm^{-3}**	1.692	1.743	1.550	1.670
***μ*(Mo K$_α$) / mm^{-1}**	1.166	2.765	0.874	1.030
***T*$_{min}$ / *T*$_{max}$**	0.546 / 0.737	0.546 / 0.737	0.589 / 0.868	0.692 / 0.745
***Θ*$_{max}$ / °**	29.21	29.35	29.29	26.372
Total reflections	4989	11652	6854	4398
Unique reflections	4236	6007	3476	3350
Refined Parameters	240	498	323	277
GooF	1.061	0.925	0.909	1.025
***R*$_1$ [*I* ≥ 2*σ*(*I*)]**	0.0390	0.0923	0.0605	0.0461
***R*$_1$ (all data)**	0.0467	0.1467	0.1316	0.0754
***wR*$_2$ [*I* ≥ 2*σ*(*I*)]**	0.1165	0.2437	0.1190	0.1044
***wR*$_2$ (all data)**	0.1202	0.2776	0.1448	0.1143
Δ*ρ*$_{max / min}$ / e·Å^{-3}	+1.348 / -0.964	+1.640 / -1.751	+0.456 / -0.598	+0.876 / -0.465

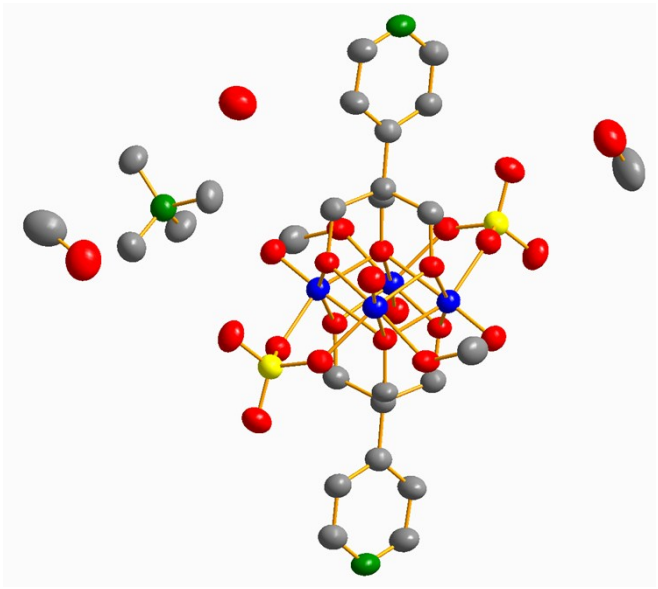
Compound	**V**	**VI**	**VII**
M / g·mol^{-1}	1320.64	1424.66	890.37 (**VII** · 4 CH_3OH)
Crystal colour	grey	violet	blue
Crystal shape	platelet	platelet	hexagon
Crystal size / mm^3	0.37 × 0.21 × 0.04	0.62 × 0.29 × 0.04	0.13 × 0.07 × 0.05
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	P 2_1 / c	I b a m	P 2_1 / n
***a* / Å**	11.288	22.024	10.917
***b* / Å**	13.407	43.315	8.536
***c* / Å**	33.968	13.807	17.170
***α* / °**	90	90	90
***β* / °**	92.67	90	97.22
***γ* / °**	90	90	90
***V* / Å^3**	5135.24	13171.32	1587.36
Z	4	4	2
***T* / K**	100	100	100
***D$_{calc}$* / g·cm^{-3}**	1.750	1.518	1.863
***μ*(Mo K$_α$) / mm^{-1}**	***μ*(Cu K$_α$) / mm^{-1}:** 10.818	1.131	1.370
***T*$_{min}$ / *T*$_{max}$**	0.493 / 0.754	0.577 / 0.746	0.692 / 0.745
***Θ*$_{max}$ / °**	72.27	26.00	27.12
Total reflections	9760	6741	3483
Unique reflections	7512	5577	3033
Refined Parameters	676	398	220
GooF	1.158	1.139	1.074
***R*$_1$ [*I* ≥ 2*σ*(*I*)]**	0.0850	0.0792	0.0377
***R*$_1$ (all data)**	0.1093	0.1044	0.0457
***wR*$_2$ [*I* ≥ 2*σ*(*I*)]**	0.1735	0.1673	0.0931
***wR*$_2$ (all data)**	0.1843	0.1767	0.0978
Δ*ρ*$_{max / min}$ / e·Å^{-3}	+1.047 / -0.737	+2.245 / -1.534	+1.384 / -1.733



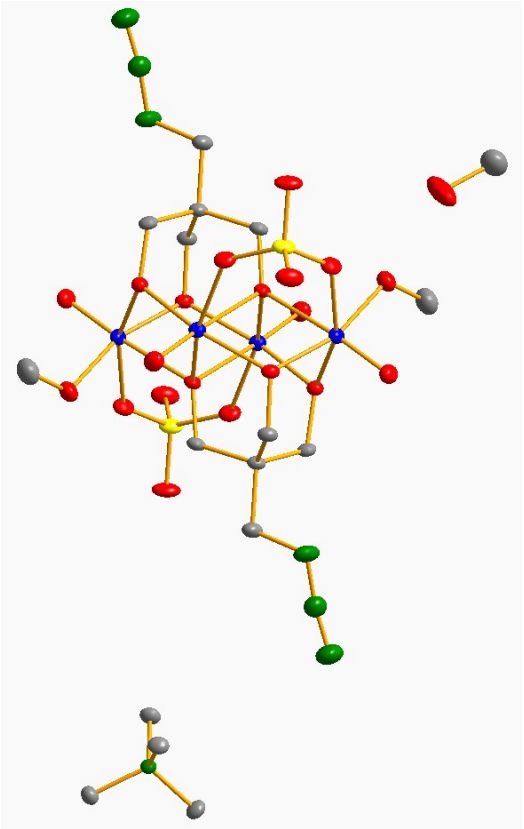
Ellipsoid (50% prob.) plot of **I**.



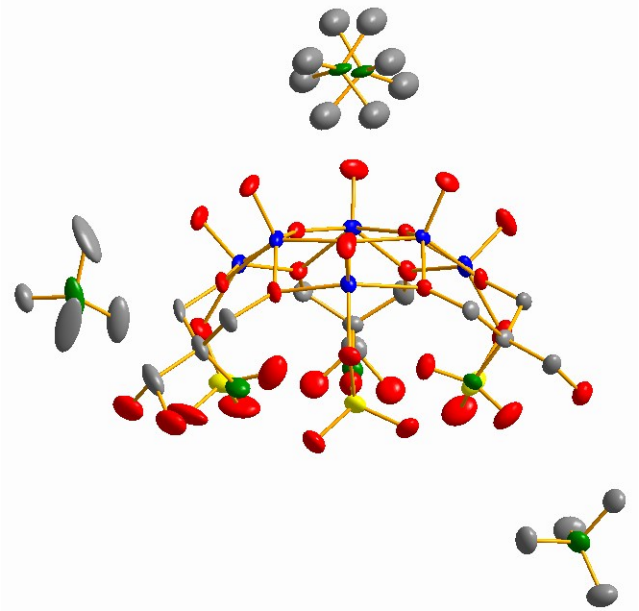
Ellipsoid (50% prob.) plot of **II**.



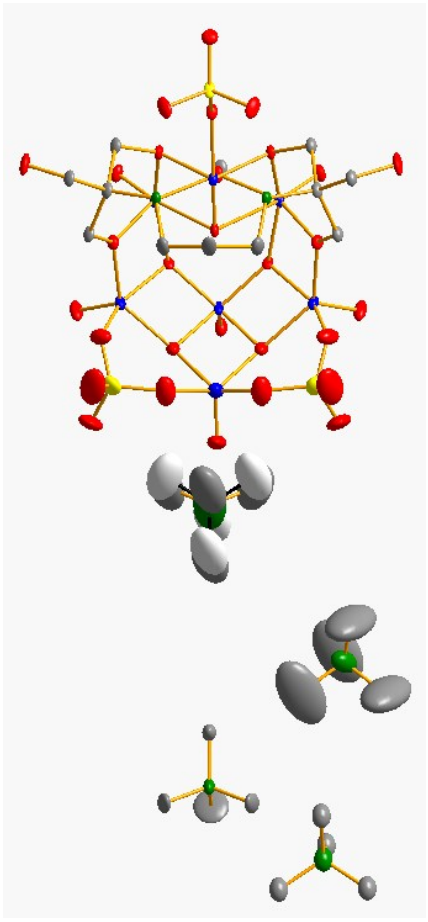
Ellipsoid (50% prob.) plot of **III**.



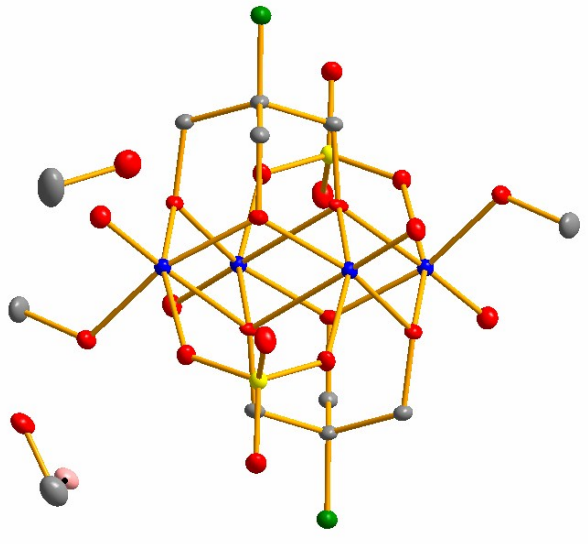
Ellipsoid (50% prob.) plot of **IV**.



Ellipsoid (50% prob.) plot of **V**.
(Disordered NMe_4^+ (top) plotted in two positions)



Ellipsoid (50% prob.) plot of **VI**.
(Disordered NMe_4^+ (middle) plotted in two positions for carbon (grey vs. white))



Legend

Blue:	Vanadium
Red:	Oxygen
Grey:	Carbon
Green:	Nitrogen
Yellow:	Sulphur
Brown:	Bromine

Ellipsoid (50% prob.) plot of **VII**.
(Disordered methanol (bottom left) plotted in two positions for oxygen (red vs. pink))

2. Valence Sum Calculations[5]

Valence sums were calculated using $\Sigma_i[d(V\text{-}O_i)/1.770]^{-5.2}$ for V(IV) and $\Sigma_i[d(V\text{-}O_i)/1.791]^{-5.1}$ for V(V).

Compound **I**	V1	V2	(V3)	(V4)
V(IV)	3.962	4.017	(3.962)	(4.017)
V(V)	4.225	4.284	(4.225)	(4.284)

Compound **II**	V1	V2	(V3)	(V4)
V(IV)	4,009	4,036	(4,009)	(4,036)
V(V)	4,366	4,303	(4,366)	(4,303)

Compound **III**	V1	V2	(V3)	(V4)
V(IV)	4,088	4,067	(4,088)	(4,067)
V(V)	4,358	4,336	(4,358)	(4,336)

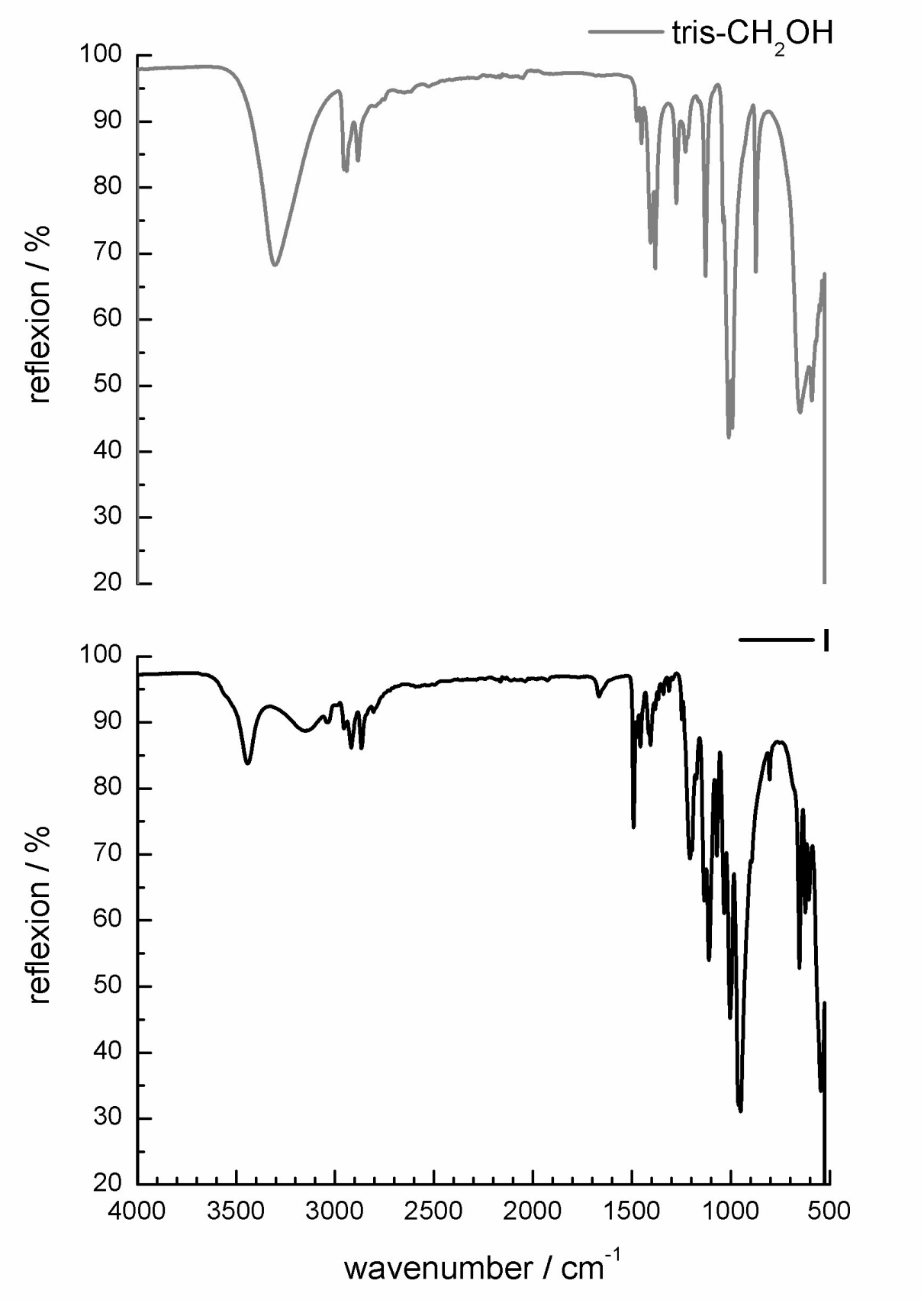
Compound **IV**	V1	V2	(V3)	(V4)
V(IV)	4,058	4,062	(4,058)	(4,062)
V(V)	4,326	4,331	(4,326)	(4,331)

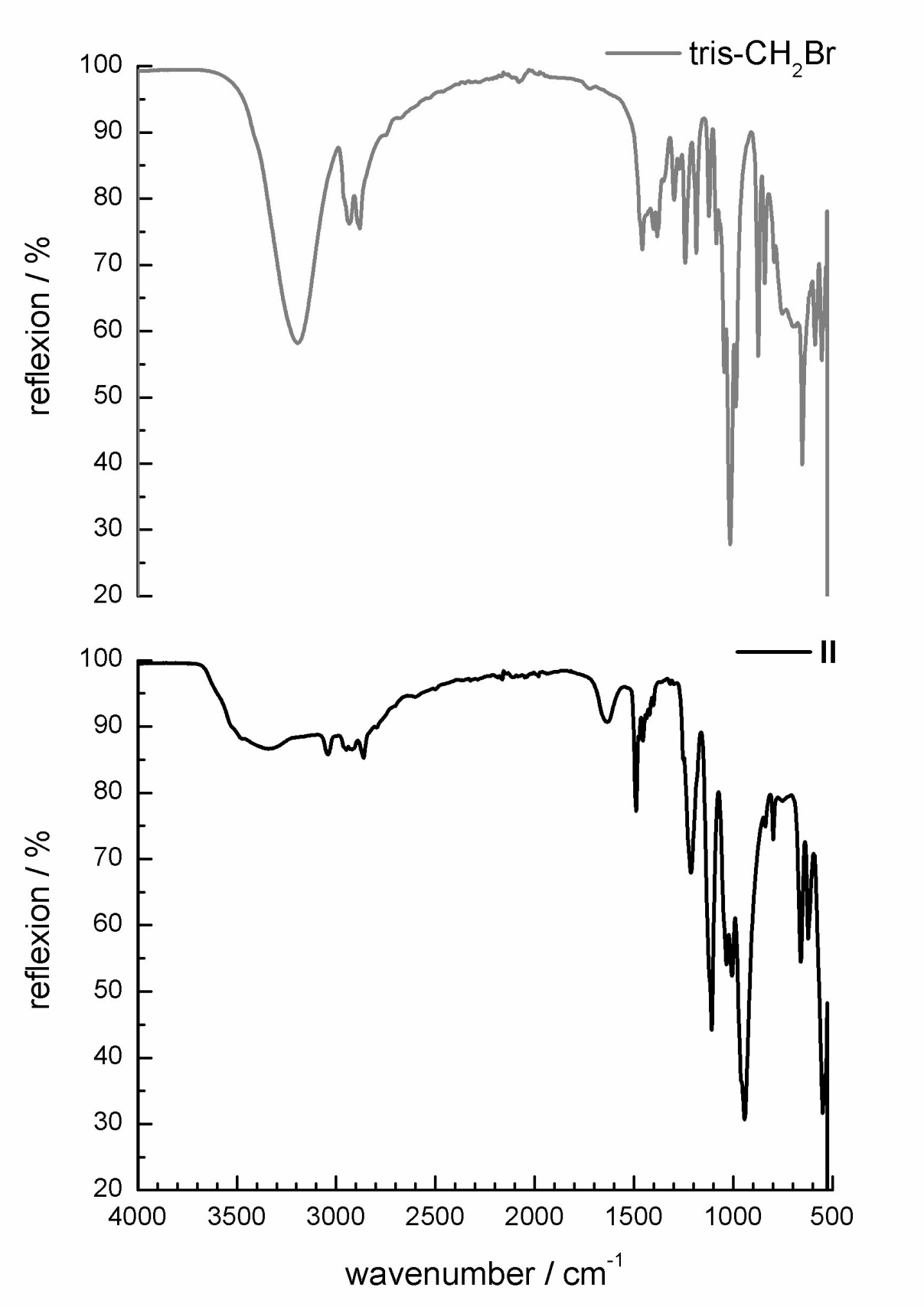
Compound **V**	V1	V2	V3	V4	V5	V6
V(IV)	4.141	3.861	3.729	4.079	4.179	3.965
V(V)	4.403	4.108	3.971	4.336	4.443	4.220

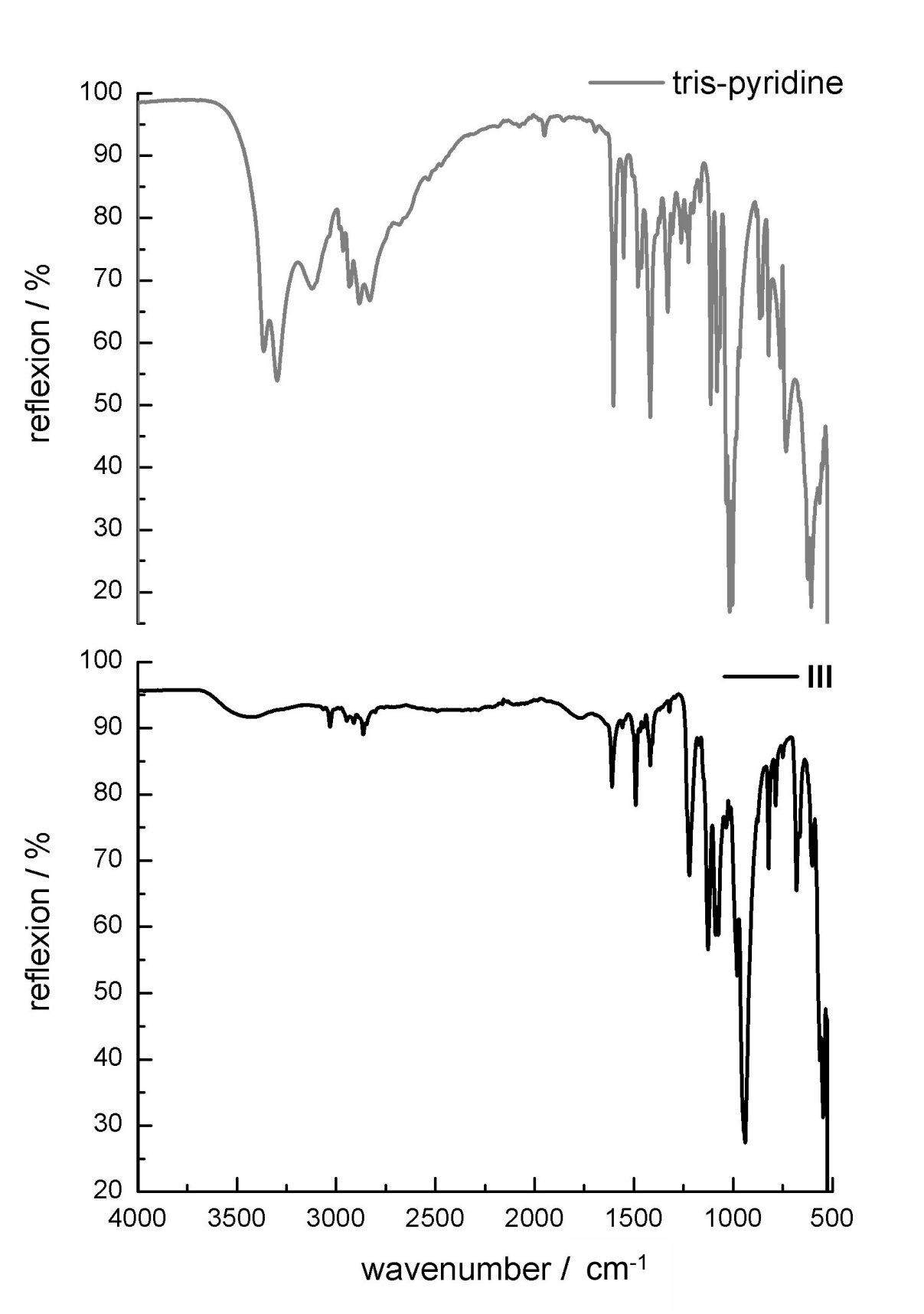
Compound **VI**	V1	V2	V3	V4	(V5)	(V6)	V7
V(IV)	4.136	4.113	3.835	4.016	(4.113)	(3.835)	4.802
V(V)	4.397	4.381	4.015	4.273	(4.381)	(4.015)	4.995

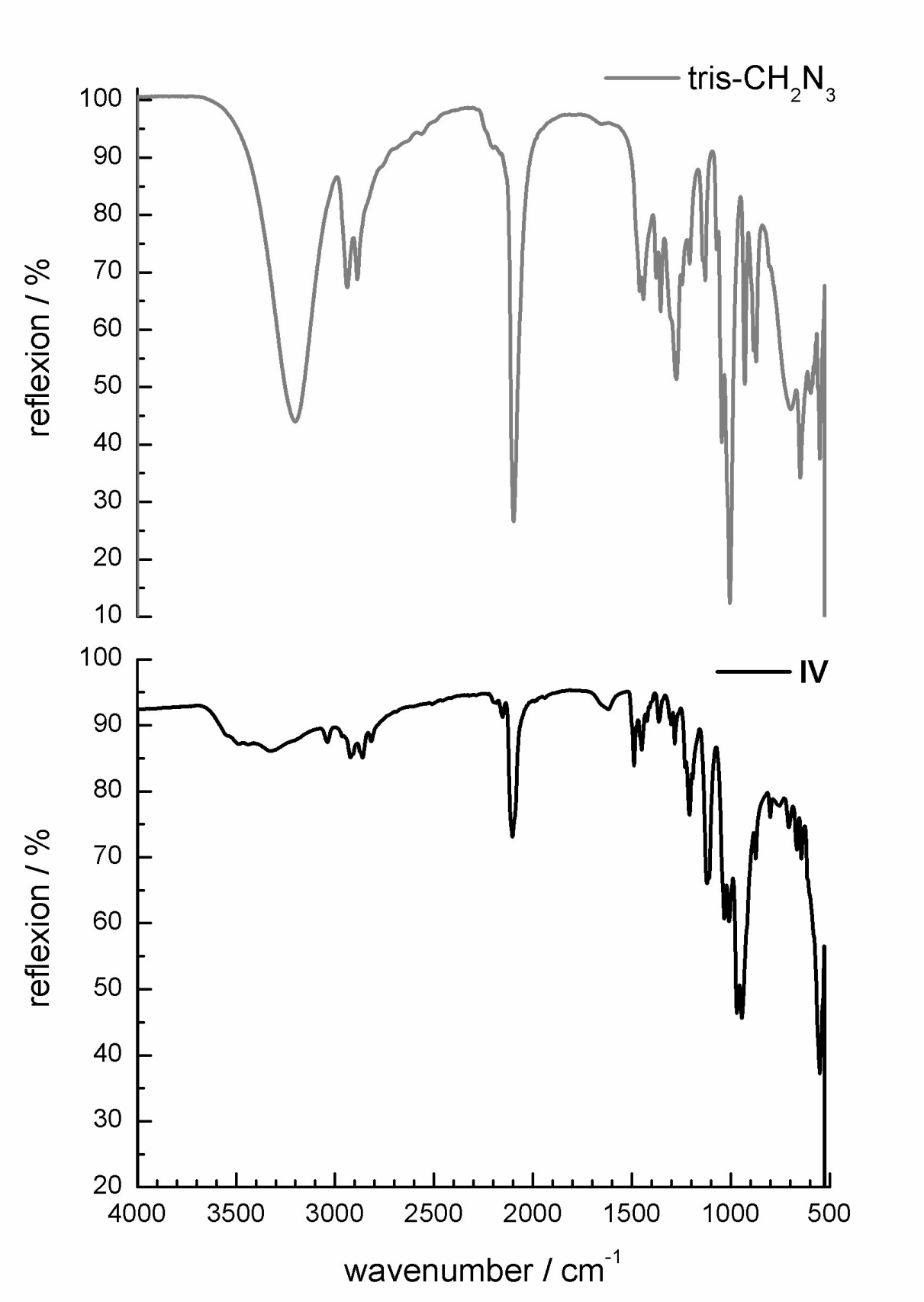
Compound **VII**	V1	V2	(V3)	(V4)
V(IV)	4,053	4,048	(4,053)	(4,048)
V(V)	4,321	4,316	(4,321)	(4,316)

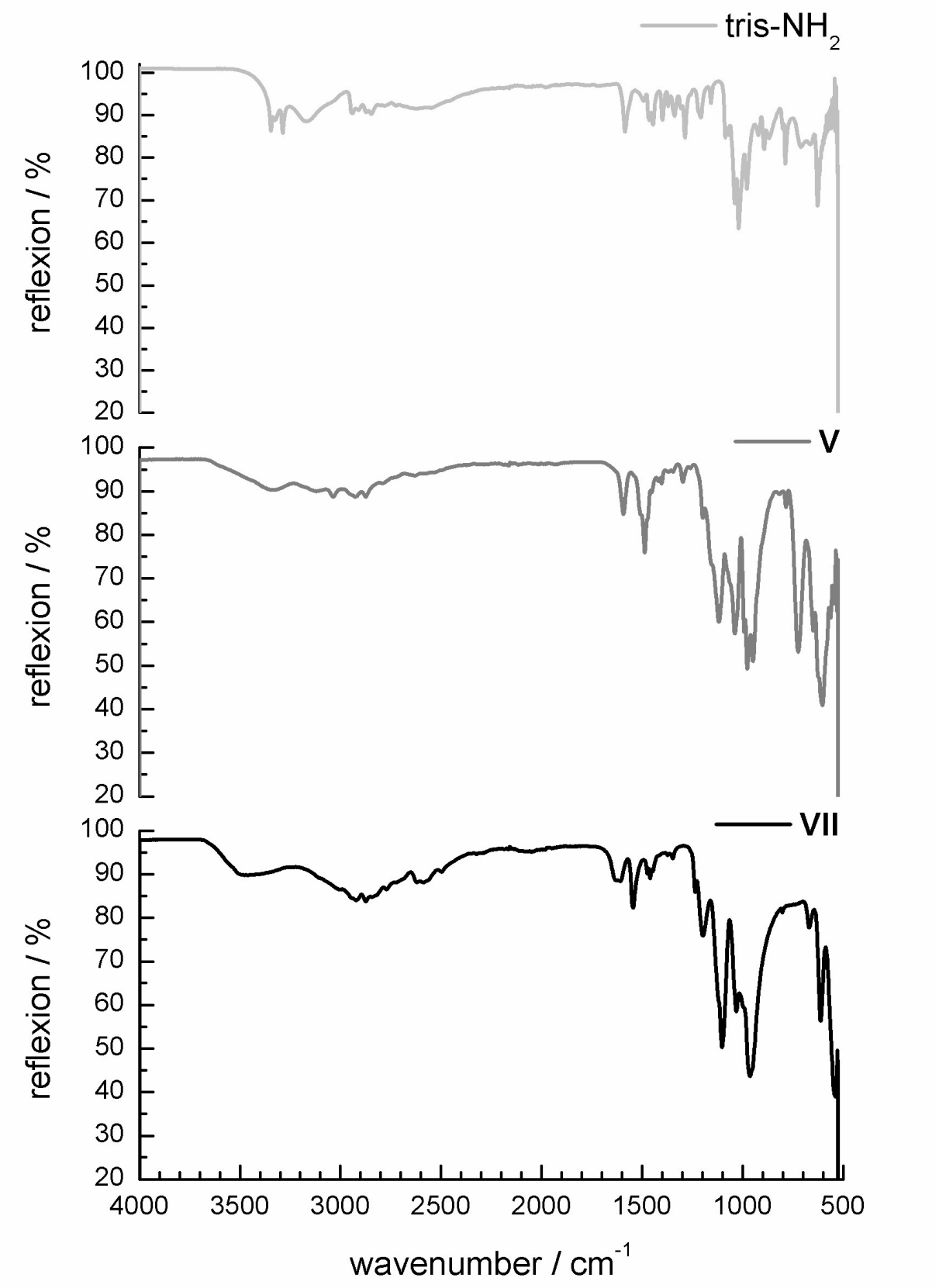
3. Infrared Spectroscopy

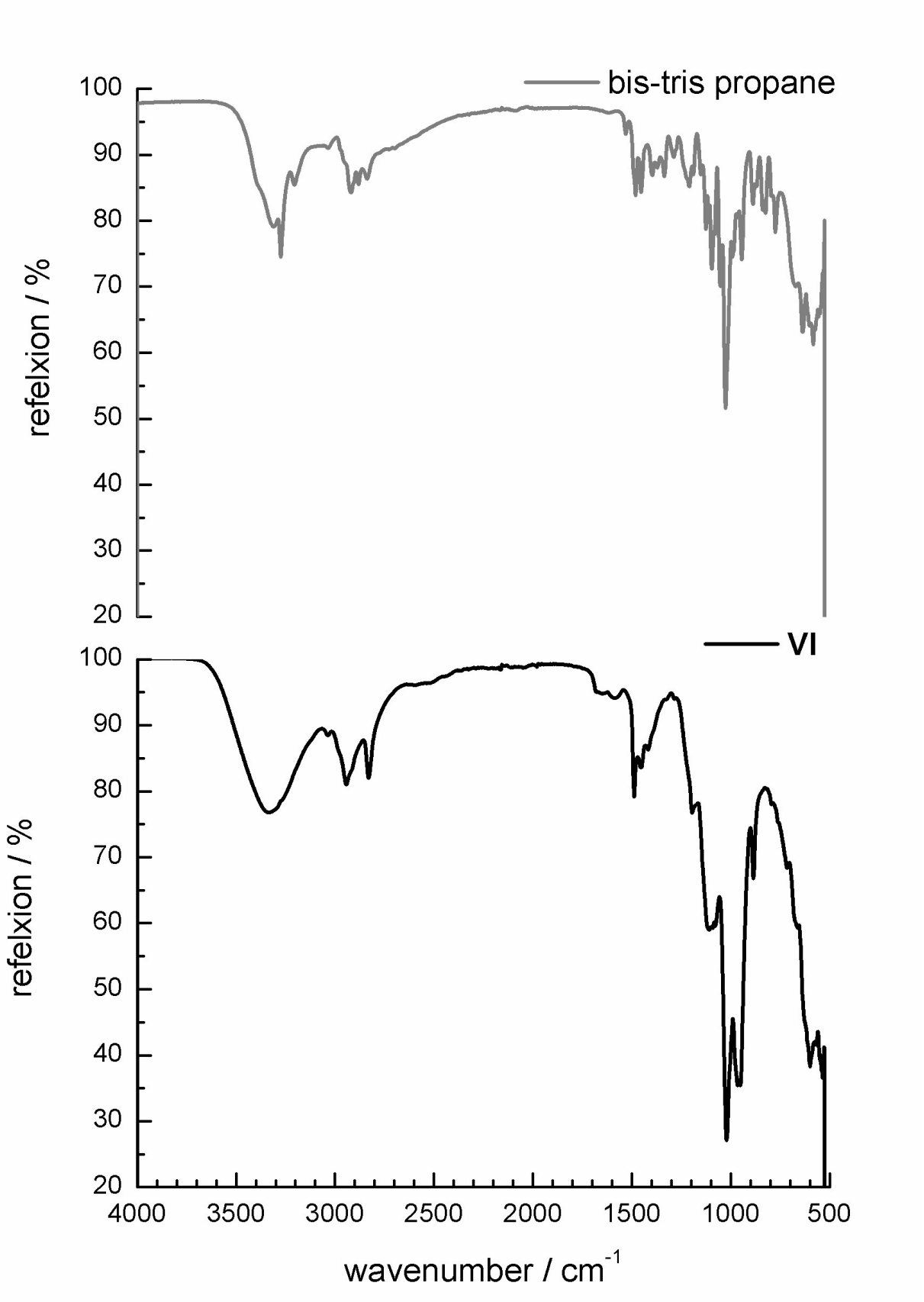



tris-CH2Br
II
reflexion / %
reflexion / %
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
wavenumber / cm-1


tris-pyridine
III
reflexion / %
reflexion / %
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
wavenumber / cm-1


tris-CH2N3
IV
reflexion / %
reflexion / %
100
90
80
70
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
wavenumber / cm-1


tris-NH2
V
VII
reflexion / %
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
wavenumber / cm-1


bis-tris propane
VI
refelxion / %
refelxion / %
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
wavenumber / cm-1

Selected characteristic vibrational frequencies for compounds **I-VII**.

The assignment of the vibration modes was tentatively conducted by adjustment of the IR-data of our compounds with the IR-data of ligands and Vanadyl sulfate[6] and comparison with IR-data from related alkoxo-oxovanadates.[7-9]

	V_4					V_6	V_7
	I	**II**	**III**	**IV**	**VII**	**V**	**VI**
ν(OH, NH)	3450(w, br)				3500(w, br)	3350(w, br)	3450(w, br)
$\nu(N_3)$				2099(s) 2080(s,sh)			
$\delta(NH_2)$					1546(w)	1584 (w)	
$\nu(S\text{-}O)^*$	1110(m)	1120(m, sh) 1106(m)	1122(m)	1121(m) 1106(m)	1120(m) 1098(s)	1119(m)	1110(m)
ν(C-O)	1032(m) 1002(s)	1034(m) 1001(m) 990(m, sh)	1026(m) 1002(m)	1029(m) 1005(m)	1031(m) 996(m)	1032(s) 991(s)	1021(vs) 1000(s, sh)
$\nu(V\text{-}O_t)$	959(vs) 947(vs)	957(vs) 944(vs)	956(vs) 939(vs)	968(vs) 944(vs)	967(vs) 949(vs)	976(vs) 945(vs)	965(vs) 949(vs)
$\delta(SO_3)^*$						722(s)	708(m)
ν(C-Br)		659(s)					
$\nu(V_2\text{-}OR)$ / $\delta(SO_2)^*$	622(m) 604(m)	622(m) 615(m)	609(m)	610(m,sh)	608(m)	600 (vs, br)	600(s, br)
$\nu(V_3\text{-}OR)^*$	544(vs)	544(vs)	546(vs)	546(vs)	543(vs)		

br: broad, sh: shoulder

*The stretching and bending modes of the sulfato ligand as well as the stretching modes of the μ_2 and μ_3 bridging oxo or alkoxogroups ($\nu(V_2O)$ or $\nu(V_3O)$) cannot be exactly assigned because of the overlap with the CH_2 bending and other deformation modes of the tris-alkoxo ligands.

4. References

1. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
2. G. M. Sheldrick, *Acta Cryst.*, 2008. **A64**, 112-122.
3. A. L. Spek, *ActaCryst.*, 2015, **C71**, 9-18.
4. A. L. Spek, *J.Appl.Cryst.*, 2003, **36**, 7-13
5. I. D. Brown, K. K. Wu, *Acta Cryst.,* 1976, **B32**, 1957-1959.
6. C. Evans, *Inorg. Chem.*, 1962, *2*, 372-375.
7. C. C. Debbie, J. C. Feilong, P. Oren, *Inorg. Chem.,* 1997, **36**, 1038-1047.
8. H. Hartl, C. Daniel, *J. Am. Chem. Soc.*, 2005, **127**, 13978–13987.
7. K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, 5th ed; Wiley-Intersience: New York 1997.