Eur. J. Inorg. Chem. **2006** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2006 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: Zinc Thiolate Complexes $[ZnL_n(SR)]^+$ with Azamacrocyclic Ligands, Part II: Mechanism of the Reaction with CS_2

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Ref. No.: I200500948

1 Kinetics — Data Analysis

Pseudo first-order rate constants k^* were determined by plotting $(\ln abs_{end} - \ln abs_t)$ as a function of time, where abs_{end} is the absorption after the complete reaction and abs_t is the absorption at a certain point of the reaction. According to

$$[\text{complex}] \sim \ln[A] - \ln[A]_0 = -k^* t \tag{1}$$

the pseudo first-order rate constants k^* were obtained from the slope of the linear fit, and the corresponding real rate constants k were calculated using the CS_2 concentration (390.6 mM) according to $k^* = k \cdot [CS_2]$. All determined rate constants are given in Table S1.

An ARRHENIUS plot (see Figure S1) of the obtained k-values yields the activation energy E_A from the slope of the linear fit and the pre-exponential constant A from the intersection with the ordinate. The values thus obtained are $A = 4.2 \pm 1.2\,\mathrm{M^{-1}\,s^{-1}}$ and $E_A = 67.8 \pm 0.8\,\mathrm{kJ\,mol^{-1}}$. In analogy to this, $\Delta H^\ddagger = 65.3 \pm 0.7\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\ddagger = -49.9 \pm 2.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$ were obtained from the EYRING plot ($\ln(k/T)$ was plotted as a function of the reciprocal absolute temperature, see figure S2). In case of linear regression parameters (i. e. k^*, E_A/R, $\ln A$, $\ln(k_B/h) + \Delta S^\ddagger/R$ and $\Delta H^\ddagger/R$), the asymptotic standard errors derived from the linear regression were used as errors. In case of the added CS_2 a volume error of $\pm 2\,\mu$L was assumed, resulting in a concentration error of $\pm 16\,\mu$M. For the error in temperature ± 0.1 K was assumed. The errors of the values for E_A, A, k, $\ln k$, $\Delta S^\ddagger$ and $\Delta H^\ddagger$ were calculated by summing up the contribution of each variable.

Table S1: Kinetical data and calculated values for k^* and k

T [°C]	abs_{end}	k^* [$10^{-3}\,\mathrm{s^{-1}}$]	k [$10^{-3}\,\mathrm{M^{-1}\,s^{-1}}$]
10.4	1.265	4.93±0.02	12.62±0.56
10.4	1.265	5.18±0.02	13.26±0.58
10.4	1.265	5.14±0.02	13.16±0.59
15.2	1.218	8.62±0.01	22.07±0.92
15.2	1.218	8.58±0.01	22.00±0.92
14.9	1.218	8.61±0.01	22.04±0.94
20.9	1.175	14.37±0.01	36.79±1.53
20.9	1.175	14.24±0.01	36.45±1.52
20.9	1.175	14.69±0.02	37.61±1.59
20.4	1.175	14.77±0.02	37.81±1.58
25.0	1.120	22.56±0.02	57.75±2.40
25.0	1.120	22.44±0.01	57.45±2.38
25.0	1.120	22.74±0.02	58.21±2.42
25.0	1.120	22.35±0.03	57.22±2.40
30.0	1.080	33.56±0.05	85.91±3.64
30.0	1.080	33.95±0.05	86.91±3.68
29.9	1.080	33.28±0.04	85.20±3.59
35.2	0.996	52.61±0.11	134.68±5.79
35.2	0.996	50.27±0.10	128.69±5.52
35.2	0.996	52.63±0.09	134.73±5.74

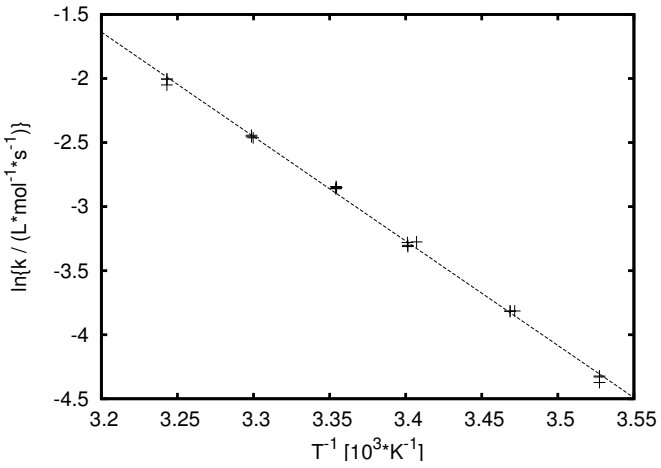


Figure S1: ARRHENIUS plot ($\ln k$ as a function of the reciprocal temperature T^{-1}).

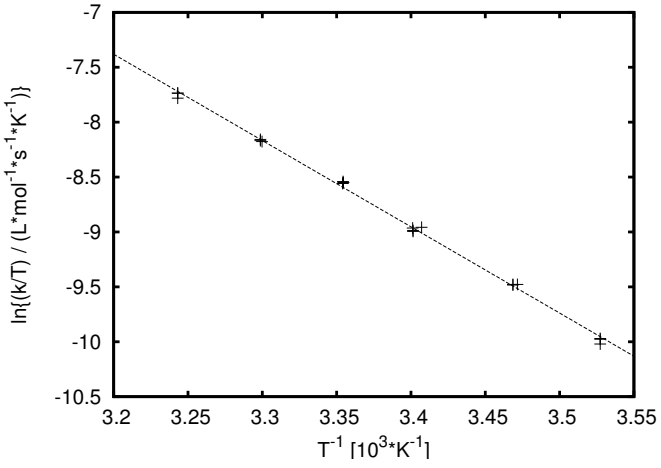


Figure S2: EYRING plot ($\ln(k/T)$ as a function of the reciprocal temperature T^{-1}).

2 Raman Spectra

As can be seen in Figure S3, compounds **1** and **1a** exhibit distinct differences in their Raman spectra. For **1**, the main bands are: N–H stretching modes at 3273 cm^{-1}; C–H stretching modes of the azamacrocycle and the thiolate with prominent signals at 2875, 2926 and 3054 cm^{-1}; benzene vibrations at 1598 and 995 cm^{-1} and vibrations of the azamacrocyclic ligand at 1467 cm^{-1}. The band assignment was done according to literature.[S1,S2] In both spectra, the symmetric stretching vibration of the ClO_4^- anion at 927 cm^{-1} was used for normalisation.[S3]

In the spectrum of **1a**, the main bands can be attributed to the N–H stretching modes at 3258 cm^{-1}, the C–H stretching modes at 2877, 2950 and 3059 cm^{-1}, benzene vibrations at 1597 and 999 cm^{-1} and macrocycle vibrations at 1470 cm^{-1}. The anion band can also be found at 927 cm^{-1}. It is evident that some bands change their shape and are shifted in comparison to the educt spectrum. In the fingerprint region below 1800 cm^{-1}, these shifts are small and lie within the spectral resolution. Larger shifts occur in the X–H stretching region (X=C, N). In this region, many normal vibrations are convoluted into one Raman signal. Rather small shifts in intensity and wavenumber of one normal mode may therefore result in large changes in the overall bandshape. This change in bandshape may lead to a seemingly high shift in the wavenumber.

(S1) F. R. Dollish, W. G. Fateley, F. F. Bentley, *Characteristic Raman Frequencies of Organic Compounds*, Wiley, New York, **1973**.

(S2) D. Lin-Vien, N. B. Colthup, W. G. Fately, J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, London, UK, **1991**.

(S3) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 3rd ed., **1978**.

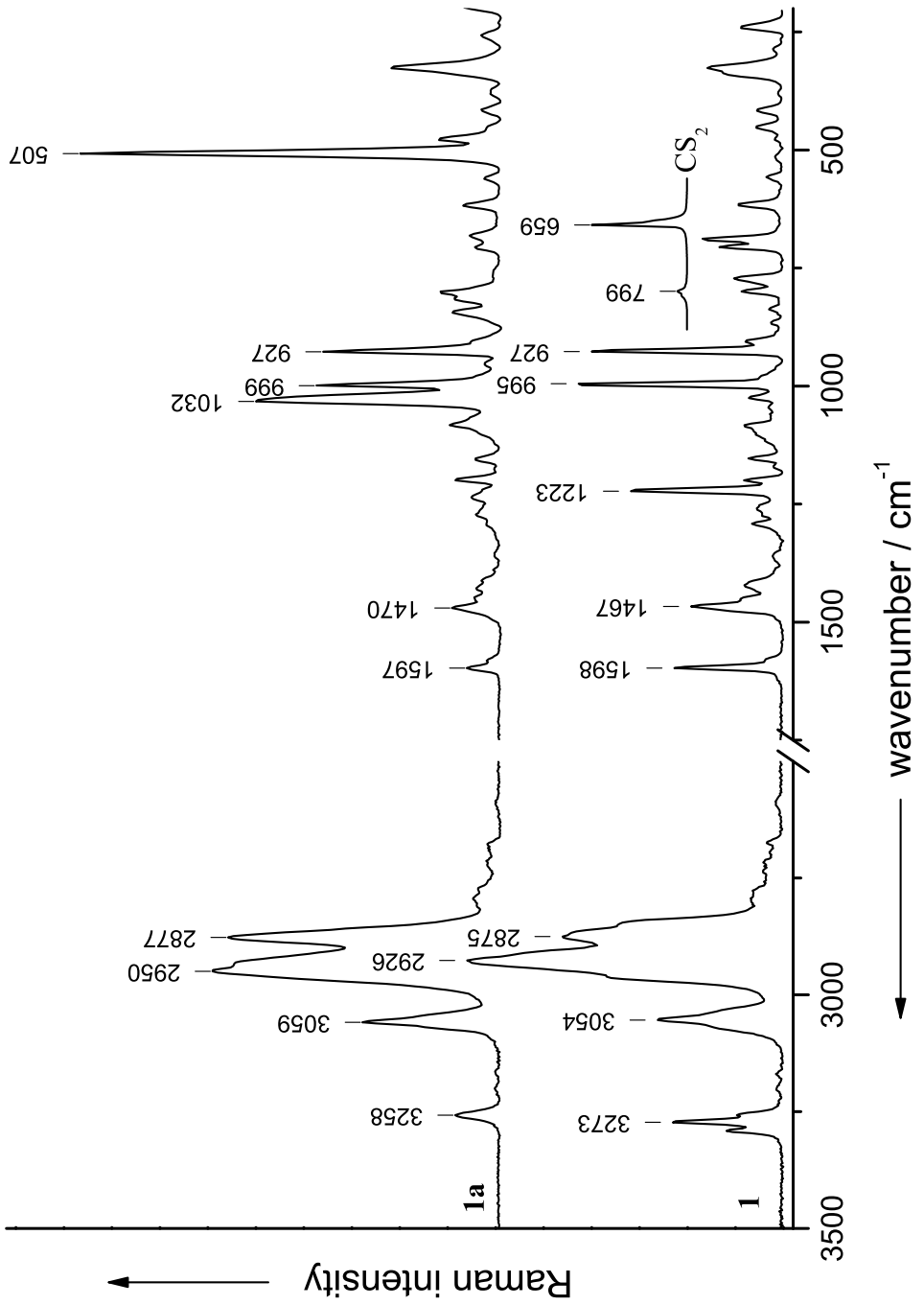


Figure S3: Raman spectra of **1** and **1a**

3 Absolute Energies of Calculated Structures

3.1 Gas Phase

All energies in the gas phase were calculated at the B3LYP/6-311+G(d) level of theory and corrected for zero point energy (ΔU) as well as thermodynamic effects (ΔG) using unscaled frequencies and standard temperature (298.15 K) and pressure (1 atm). N_{imag} denotes the number of imaginary frequencies.

Table S2: Absolute energies in the gas phase [a. u., B3LYP/6-311+G(d)]

Compound	E_{SCF}	ΔU	ΔG	N_{imag}
$C_7H_7S^-$	−669.275676459	−669.158354	−669.190949	0
$C_8H_7S_3^-$	−1503.85092228	−1503.736115	−1503.776529	0
CS_2	−834.552543203	−834.545660	−834.568599	0
educt	−3102.46042937	−3101.949506	−3102.005121	0
product	−3937.01610621	−3936.496738	−3936.559912	0
ts	−3936.97640191	−3936.457494	−3936.516535	1
$[Zn(15aneN_4)]^{2+}$	−2432.86247682	−2432.470444	−2432.513981	0

3.2 Solution

Solvent effects were incorporated through the C-PCM model by single point calculations on the gas phase geometries using chloroform ($\varepsilon = 4.9$) as the solvent. These calculations use a larger basis set and were performed at the C-PCM(B98/G3MP2Large)//B3LYP/6-311+G(d) level of theory. For zinc the 6-311+G(3df) basis set as implemented in GAUSSIAN was employed for the single point calculation. In the table ΔG_{solv} denotes the free energy in solution including all electrostatic and non-electrostatic terms. To obtain the total free energy the gas phase correction ($\Delta G - E_{SCF}$, Table S2) must be added to the ΔG_{solv} value in Table S3.

Table S3: Absolute single point energies in solution [a. u., B98/G3MP2Large]

Compound	E_{gas}	ΔG_{solv}
$C_7H_7S^-$	−669.128220	−669.213641
$C_8H_7S_3^-$	−1503.609338	−1503.680902
CS_2	−834.439462	−834.439692
educt	−3102.080013	−3102.137983
product	−3936.527472	−3936.588057
ts	−3936.485500	−3936.554750
$[Zn(15aneN_4)]^{2+}$	−2432.617734	−2432.829274

4 Cartesian Coordinates of Calculated Structures

All cartesian coordinates are given in Ångström. For convenience, coordinates of all compounds are also available in xyz-format packed together into a single ZIP-archive. All structures were fully optimized at the B3LYP/6-311+G(d,p) level of theory.

$C_7H_7S^-$

15

S	2.669269	−0.000124	−0.579193
C	1.517174	0.000276	0.869849
C	0.073345	0.000123	0.452037
C	−2.638671	−0.000142	−0.360307
C	−1.959633	1.203078	−0.156805
C	−1.959459	−1.203226	−0.156587
C	−0.624732	1.199059	0.243603
C	−0.624557	−1.198944	0.243822
H	1.705224	−0.881077	1.495780
H	1.705182	0.882005	1.495254
H	−3.679404	−0.000241	−0.674411
H	−2.473356	2.149202	−0.313376
H	−2.473039	−2.149457	−0.312974
H	−0.097009	2.139011	0.381388
H	−0.096696	−2.138797	0.381753

$C_8H_7S_3^-$

18

S	−3.611586	−1.255867	0.385605
S	−2.822401	1.604546	−0.182681
S	−0.861638	−0.715636	−0.070556
C	4.449785	−0.284340	0.302759
C	3.894906	−0.526705	−0.954902
C	3.656841	0.250007	1.314399
C	2.556117	−0.236077	−1.197785
C	2.314947	0.540616	1.069575
C	1.752550	0.303492	−0.187025
C	0.309587	0.658044	−0.446600
C	−2.483745	−0.034450	−0.150346
H	5.479592	−0.507980	0.488057
H	4.500890	−0.935042	−1.736993

H	4.073485	0.438521	2.281893
H	2.138103	−0.422928	−2.165770
H	1.711864	0.951692	1.853384
H	0.114675	0.822337	−1.498916
H	0.005461	1.501188	0.159990

CS_2

3

S	0.000000	0.000000	1.560902
S	0.000000	0.000000	−1.560902
C	0.000000	0.000000	0.000000

educt

57

Zn	−0.753034	0.057176	0.057842
S	−0.056258	−0.621224	−2.015302
N	0.814777	1.386461	1.036309
N	−2.616784	−1.386542	0.067665
N	−2.247655	1.680892	0.062850
N	−0.196212	−1.167024	1.838979
C	4.944827	−0.468039	0.137242
C	4.589519	0.821742	−0.247689
C	4.196190	−1.553397	−0.325976
C	3.486837	1.023128	−1.083557
C	3.094745	−1.348358	−1.152435
C	2.719047	−0.055070	−1.542633
C	1.554287	0.181825	−2.473760
C	1.073364	−0.635394	2.385611
C	1.034117	0.884222	2.407581
C	0.699471	2.862870	0.966017
C	−4.152796	0.323120	−0.918644
C	−3.532312	−1.063369	−1.053842
C	−3.201922	1.506584	−1.075392
C	−2.181974	−2.806194	0.008172
C	−1.682507	3.059959	0.020878
C	−1.462358	−3.260885	1.275695
C	−0.721546	3.384710	1.163507
C	−0.102573	−2.621643	1.538948

H	5.807624	−0.630892	0.774350
H	5.178317	1.671428	0.083071
H	4.483120	−2.563841	−0.052004
H	3.244830	2.030985	−1.412448
H	2.518925	−2.195617	−1.510758
H	1.966853	1.275674	2.831473
H	1.883444	−0.976724	1.735722
H	1.778672	−0.235712	−3.458282
H	1.635506	1.123651	0.489712
H	1.401686	1.252412	−2.618567
H	1.371811	3.325959	1.699080
H	1.271895	−1.031099	3.388146
H	1.055229	3.171239	−0.020698
H	0.545714	−2.730925	0.666562
H	0.381770	−3.137311	2.377807
H	0.219410	1.237958	3.048241
H	−4.916322	0.420245	−1.696477
H	−4.701866	0.402569	0.031150
H	−4.333806	−1.812221	−1.110289
H	−3.795064	2.423180	−1.179201
H	−3.152506	−1.274391	0.928789
H	−3.053502	−3.453439	−0.157543
H	−2.959389	−1.134087	−1.981213
H	−2.791825	1.615719	0.923008
H	−2.604682	1.397432	−1.983631
H	−2.511890	3.777417	0.023920
H	−2.115793	−3.126973	2.150271
H	−1.528457	−2.914422	−0.860284
H	−1.307505	−4.341396	1.199685
H	−1.177295	3.172837	−0.942599
H	−1.136577	3.047147	2.121554
H	−0.910918	−1.048312	2.555907
H	−0.661645	4.474413	1.246165

product

60

Zn	−2.035854	0.000568	−0.015057
S	2.896823	0.176403	−0.550665
S	1.104811	−0.881254	1.637699
S	0.072892	0.312073	−0.998251
N	−3.313798	−0.646025	−1.691181

N	−2.780918	2.148335	−0.409483
N	−2.677849	0.487299	2.055897
N	−2.006645	−2.004409	0.899123
C	8.101494	0.276289	−0.765630
C	7.455319	−0.928026	−1.040652
C	7.452605	1.254059	−0.013073
C	6.165437	−1.152260	−0.565611
C	6.162917	1.027791	0.461741
C	5.506505	−0.178336	0.192693
C	4.114985	−0.424763	0.710438
C	1.324576	−0.180072	0.131188
C	−3.551618	1.656681	−2.737777
C	−3.377177	−3.069770	−0.928431
C	−3.132674	−2.080903	−2.066671
C	−3.123159	0.201785	−2.906972
C	−2.822974	−1.975857	2.127431
C	−2.668379	2.519171	−1.841672
C	−2.494671	−0.711889	2.911431
C	−2.411744	2.980111	1.930090
C	−2.219721	−3.205440	0.059378
C	−2.036095	3.103130	0.454961
C	−2.000707	1.685880	2.625801
H	9.107503	0.450429	−1.132484
H	7.957272	−1.694694	−1.621493
H	7.952426	2.191215	0.208470
H	5.668721	−2.094003	−0.780731
H	5.664346	1.792075	1.051062
H	3.917171	0.111202	1.638206
H	3.916006	−1.482929	0.877653
H	−4.597491	1.708208	−2.402387
H	−4.314818	−2.833547	−0.409028
H	−4.287387	−0.540737	−1.405189
H	−3.883262	−2.000513	1.853704
H	−3.806765	−2.308957	−2.900979
H	−3.767586	2.227807	−0.162460
H	−3.689208	−0.240171	−3.735900
H	−3.676545	0.688429	2.022313
H	−3.551149	2.107885	−3.734649
H	−3.541450	−4.053217	−1.379840
H	−3.492030	3.144907	2.054415
H	−3.105460	−0.647826	3.818364
H	−2.938751	3.574829	−1.973222
H	−2.634404	−2.856127	2.753851
H	−2.375624	−4.083969	0.697207

H	−2.233984	4.130221	0.122527
H	−2.230850	1.764290	3.695488
H	−2.113092	−2.187662	−2.446260
H	−2.066117	0.144916	−3.178442
H	−1.934455	3.806153	2.465637
H	−1.618288	2.421430	−2.127699
H	−1.447721	−0.734065	3.217248
H	−1.293660	−3.379989	−0.494446
H	−1.021336	−1.977420	1.183838
H	−0.969345	2.917003	0.307978
H	−0.924528	1.520335	2.535961

ts

60

Zn	0.929252	−0.517678	0.178984
S	1.259983	3.177351	0.432563
S	−1.260030	4.009385	−1.067629
S	−0.165724	1.106603	−1.264218
N	3.090061	−0.222011	0.751887
N	1.921132	−1.658530	−1.509672
N	0.705947	0.298962	2.187692
N	−0.193254	−2.334889	0.653607
C	4.101647	−0.428291	−1.538549
C	3.926684	0.435926	−0.293455
C	3.145817	0.507881	2.043207
C	2.826184	−0.778164	−2.303104
C	1.972783	0.106273	2.926904
C	0.945335	−2.381850	−2.360118
C	0.230061	−3.485021	−1.584615
C	−5.009045	−0.652814	0.662143
C	−4.701480	−1.298045	−0.533265
C	−4.285260	0.480685	1.038226
C	−3.670360	−0.816384	−1.341530
C	−3.255284	0.958151	0.231549
C	−2.929131	0.310680	−0.968518
C	−1.884742	0.865906	−1.899012
C	−1.269684	−2.147306	1.679481
C	−0.790599	−1.557548	3.004084
C	−0.778295	−3.035018	−0.531929
C	−0.497083	−0.058843	2.977855
C	−0.089878	3.022819	−0.527128

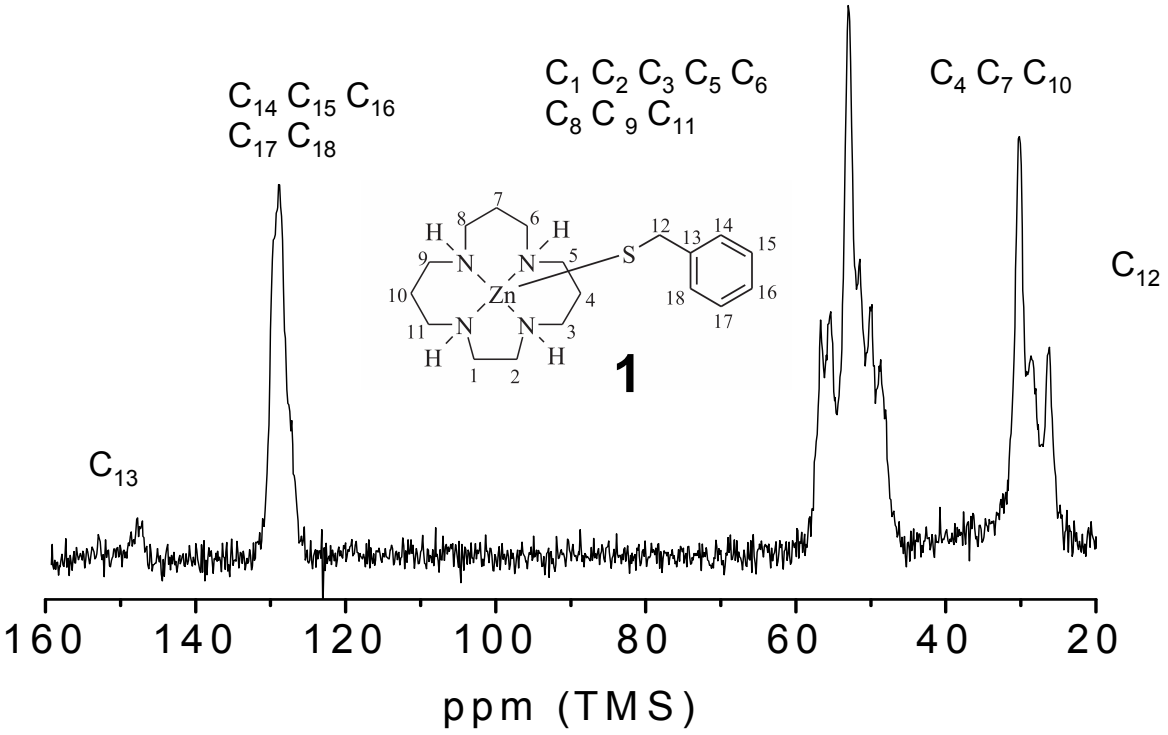
H	4.914545	0.671563	0.120799
H	4.764297	0.110731	−2.221890
H	4.642493	−1.351642	−1.283442
H	4.094751	0.327735	2.559626
H	3.481592	−1.149369	0.914078
H	3.441719	1.382591	−0.539818
H	3.099648	−1.285970	−3.236140
H	3.089496	1.572317	1.818446
H	2.512120	−2.373197	−1.085258
H	2.269561	0.121077	−2.574803
H	2.053804	−0.944325	3.223499
H	1.984638	0.700196	3.848213
H	1.460284	−2.820483	−3.224013
H	0.970212	−4.164629	−1.138362
H	0.650398	1.293038	1.941697
H	0.487419	−2.974993	1.064828
H	0.232893	−1.651969	−2.753848
H	0.065508	−2.123883	3.391691
H	−5.820525	−1.014192	1.284778
H	−5.274545	−2.163864	−0.848620
H	−4.542126	1.008854	1.950977
H	−3.466482	−1.304018	−2.291388
H	−2.724341	1.861508	0.512698
H	−2.137919	1.892607	−2.194155
H	−2.033023	−1.507341	1.233690
H	−1.805270	0.275927	−2.812842
H	−1.738637	−3.120637	1.865168
H	−1.590189	−1.720790	3.733260
H	−1.514168	−2.359386	−0.970326
H	−1.345119	0.466182	2.533045
H	−1.332892	−3.912350	−0.178077
H	−0.390614	0.316657	4.002621
H	−0.317962	−4.099969	−2.305059

$[Zn(15aneN_4)]^{2+}$

42

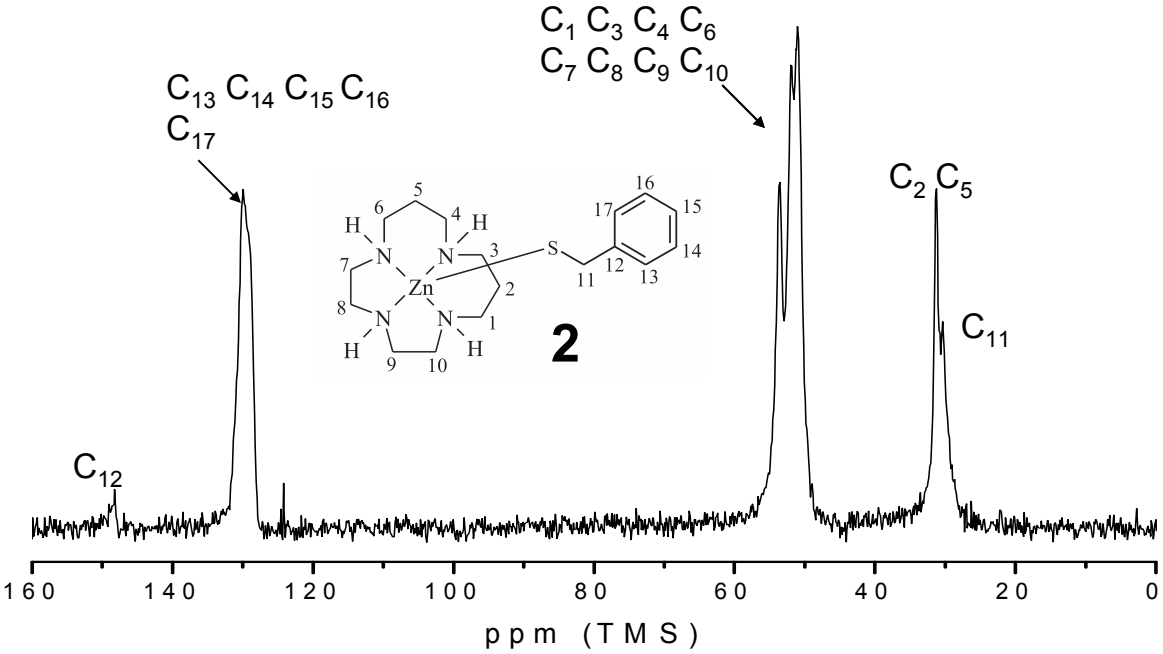
Zn	0.004190	−0.059866	0.026568
N	1.604117	1.304455	0.010321
N	1.236592	−1.733288	−0.592661
N	−1.458782	1.364214	−0.568271
N	−1.265532	−1.574208	0.793583

C	3.403805	−0.416699	−0.328683
C	2.927751	0.782538	0.488695
C	2.652353	−1.717786	−0.077063
C	1.290835	2.663001	0.566366
C	0.533969	−2.982430	−0.155624
C	0.145091	3.330718	−0.187566
C	−3.225488	−0.493258	−0.409082
C	−2.914627	0.997449	−0.373207
C	−2.739841	−1.269367	0.815166
C	−1.237320	2.730835	0.038460
C	−0.965899	−2.758125	−0.072977
H	4.450372	−0.597109	−0.066461
H	3.661938	1.590064	0.415368
H	3.421547	−0.170458	−1.398613
H	3.194514	−2.558034	−0.520432
H	2.834175	0.530602	1.548075
H	2.600603	−1.906291	0.998088
H	2.188524	3.284147	0.495577
H	1.728869	1.451690	−0.994028
H	1.293548	−1.753328	−1.610630
H	1.059569	2.553810	1.629064
H	0.922779	−3.254621	0.828218
H	0.759231	−3.815283	−0.825830
H	0.376405	3.391457	−1.259496
H	0.095092	4.371370	0.145872
H	−4.315111	−0.587479	−0.440855
H	−3.501852	1.527782	−1.127130
H	−3.283623	−2.213553	0.906441
H	−3.214149	1.402562	0.595353
H	−2.939899	−0.698834	1.725127
H	−2.881088	−0.949905	−1.343856
H	−1.998552	3.404863	−0.365044
H	−1.458358	−3.650810	0.322475
H	−1.434081	2.637526	1.109584
H	−1.387288	−2.570515	−1.062940
H	−1.331143	1.477362	−1.574748
H	−1.006275	−1.830504	1.746060



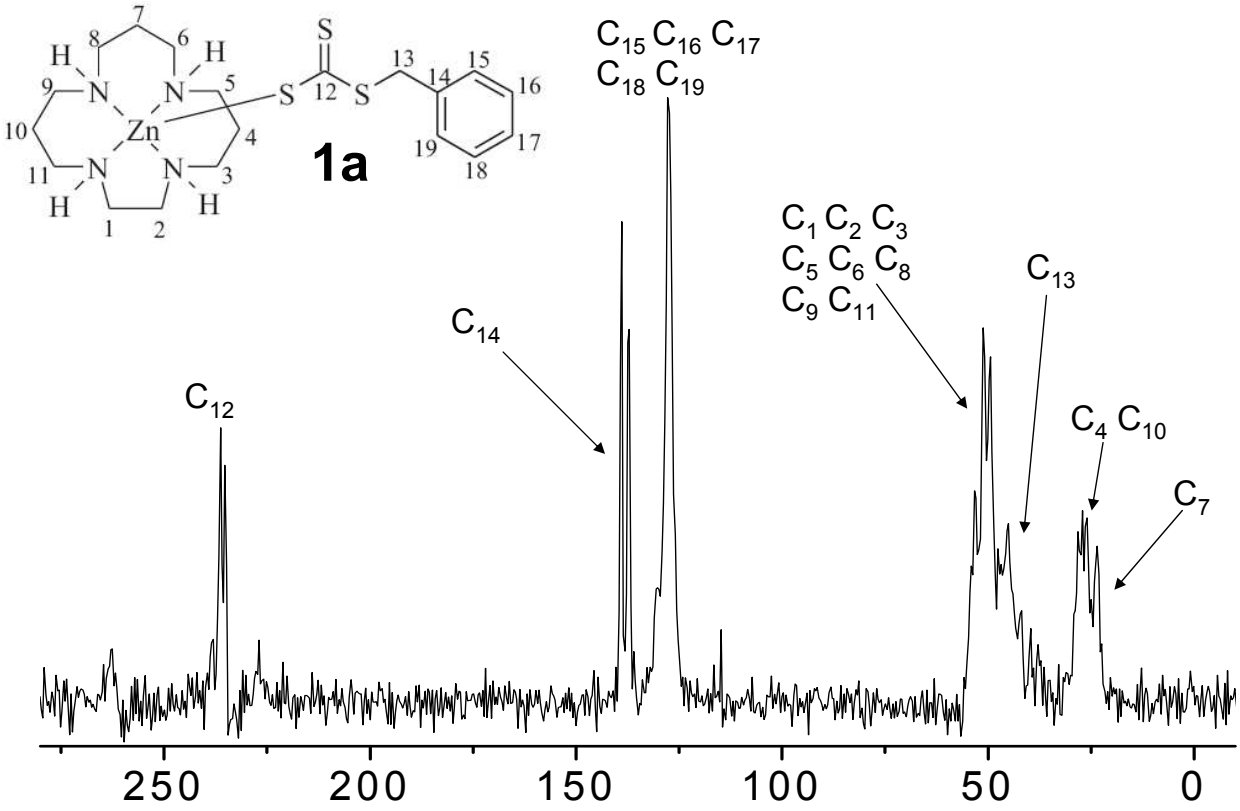
^{13}C-vaCP-MAS-NMR spectrum of compound **1** measured at **14T** at a MAS rotation frequency of 28kHz.

Contact time: 1.2msec; pulse delay 12sec

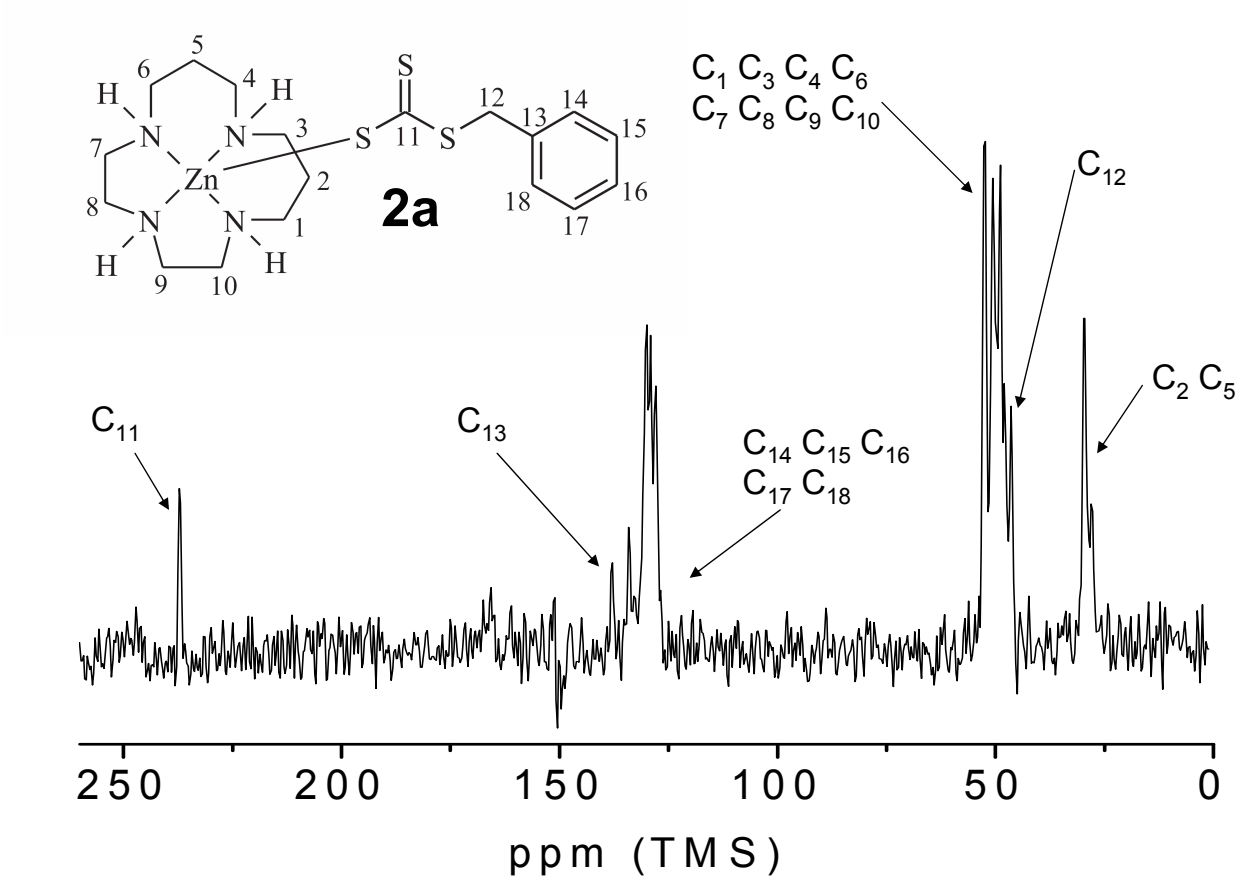


^{13}C-vaCP-MAS-NMR spectrum of compound **2** measured at **14T** at a MAS rotation frequency of 28kHz.

Contact time: 1.2msec; pulse delay 12sec



^{13}C-vaCP-MAS-NMR spectrum of compound **1a** measured at 9.4T. Note the splitting of C_{12} and C_{14}, indicating a conformational polymorphism.



^{13}C-{1H-BB}-NMR of compound **2a** measured at 11.7T at a rotation speed of 15kHz. 90°-degree pulse excitation, Pulse delay 100sec;