Computational Results

General Information and Methodical Details

As the first and basic aspect, the individual energies of the two types of dimeric aggregation motifs present in (*meso*)-[(norcamphor oximato)$GaMe_2$]$_2$ (**1**) and [{(*meso*)-[(norcamphor oximato)$InMe_2$]$_2$}$_2$]$_\infty$ (**2**) had to be obtained, being the six-membered $M_2O_2N_2$ and the four-membered M_2O_2 heteroatom ring motif. As the starting points for these calculations, the molecular geometries of the single $M_2O_2N_2$ and M_2O_2 rings as yielded by the X-ray experiments on (*meso*)-[(norcamphor oximato)$GaMe_2$]$_2$ (**1**) and [{(*meso*)-[(norcamphor oximato)$InMe_2$]$_2$}$_2$]$_\infty$ (**2**) were used. In order to reduce computational complexity and to exclude affections by substituent conformations, the formoximato unit was used as a simplified model of the norcamphor oximato ligand. Since the bicyclo[2.2.1]hept-2-ylidene skeleton does not play any role in **1** or **2** with respect to arguments like steric congestion (as judged from their crystal structures), replacing it by a mere methylene group was considered adequate. Combining these prerequisites, the four basic molecules to be calculated were the dimethylgallium and -indium formoximates [$Me_2M(O{-}N{=}CH_2)$]$_2$ (M = Ga, In), both as a six-membered (μ^1-O,μ^1-N)-bridged ($M_2O_2N_2$ motif; molecules **A** and **D**) and a four-membered (μ^2-O)-bridged (M_2O_2 motif; molecules **B** and **E**) cyclic dimer. From the single energy values thus obtained, the energetics of the transformation $M_2O_2N_2$ → M_2O_2 [(μ^1-O,μ^1-N)- → (μ^2-O)-coordination; Ga: **A** → **B**; In: **D** → **E**] were at hand for both Ga and In, since this apparently is the initial step in the construction of the polymeric solid-state aggregation motif of **2** from the $In_2O_2N_2$ dimers present in solution.

The second and central issue to be scrutinized was the "dimerisation" of one $M_2O_2N_2$ molecule (Ga: **A**; In: **D**) with one of the type M_2O_2 (Ga: **B**; In: **E**) – thus the formation of the "new" M_2O_2N five-membered ring, or likewise the two "new" dative bonds (O→M' and N'→M). The $M_4O_4N_4$ "tetramers" ([{$Me_2M[(\mu^1$-O,μ^1-N)-(O−N=CH_2)]}$_2$-*O*]-[{$Me_2M'[(\mu^2$-O')-(O'−N'=CH_2)]}$_2$-*N'*]) obtained in that way (Ga: **C**; In: **F**) represent the minimum unit of a one-dimensional polymeric aggregate as found in the solid state for **2**. The calculations of the compounds **C** and **F** were launched based on the geometry data of **2** as determined by X-ray crystallography. Note that the tricyclic cores of **C** and **F** ($M_4N_4O_4$ motif; fused four-, five- and six-membered rings) were each dealt with as an *isolated molecule in the gas phase*, as is natural in computational chemistry. Therefore, the final geometries yielded cannot fully match the ones of an *aggregated polymer in the condensed phase* (like the In species **2**). Nevertheless, these deviations can be considered as minor enough not to blur the validity of the overall computational approach.

With all six optimisations leading to stably converging molecular structures (Ga: **A** to **C**; In: **D** to **F**), the energy balance between the formation of **C** (or **F**, resp.) and the first-mentioned transformation **A** → **B** (or **D** → **E**, resp.) now allowed to quote on the verge of tetracoordination in the present group 13 oximates in a reliable manner. Note that the values for the formation of **C** or **F** have to be included into their balance of concern *twice*, since the $\{M_4O_4N_4\}_\infty$ motif is of one-dimensional polymeric nature.

All calculations were carried out with the Turbomole program package, version 5.7.[1] Geometry optimizations were performed at the Density Functional Theory (DFT) level using Turbomole's DFT program deck,[2] with the PBE0[3] hybrid functional, default TZVP basis sets[4] [implying a quasi-relativistic electronic core potential (ECP-46-MWB)[5] and an additional d-function for the valence orbitals of indium] and a quadrature of m4 quality employed.[6] Redundant internal coordinates were used for the geometry optimization procedure.[7] In order to characterize each converged geometry as a local minimum on the Potential Energy Surface (PES), only the three lowest eigenvalues of the hessian were determined by the Lowest Eigenvalue Search (LES) procedure as it is implemented in Turbomoles Aoforce deck.[8, 9]

Coordinates in Bohr units

$\{Me_2Ga[(\mu^1\text{-}O,\mu^1\text{-}N)\text{-}(O{-}N{=}CH_2)]\}_2$

(**A**, $M_2O_2N_2$ motif):

absolute energy: E = −4347.0092690740 hartrees

0.54440849123171	2.46040265614262	−6.04635178859101	C
−0.40401168708582	−0.08676014117012	−3.49630613787486	Ga
2.76815760979201	−0.70521809705440	−1.25450624348791	N
2.37438134195763	−1.73721342735331	1.01410325452603	O
0.40580300283597	0.10120660269305	3.49940920786874	Ga
−0.51051481322405	−2.41285157119653	6.09358742015376	C
−1.83625041495165	−3.49926899269088	−3.95758025038732	C
−2.39104263112219	1.71770814997702	−1.00060645350710	O
−2.77905789440121	0.66790572976913	1.26130796919968	N
−5.04709094554950	0.41458613137499	2.01499685159922	C
5.03593612954518	−0.50477351876251	−2.02527905204092	C
1.83117704271252	3.52562827254567	3.88692035815124	C
1.45667893638084	4.09007920330964	−5.16752431466184	H
1.81754754706140	1.68613422593409	−7.47713254376867	H
−1.14085727518963	3.13918460863288	−7.02757915388070	H
−1.20491731128835	−4.15204154197234	5.22594719532850	H
−1.95685379733592	−1.70058587186422	7.38561681706753	H
1.14252927002309	−2.89376982081130	7.23352626605473	H
−2.10953116535029	−4.43287108038992	−2.13712997040382	H
−3.66020905180720	−3.40838308227028	−4.92134984211190	H
−0.58083297270263	−4.68241881012111	−5.09277441168068	H
6.59532608235446	−1.09259586850081	−0.82721400931392	H
5.34252114599731	0.26236096188334	−3.89753943333422	H
−5.34967958473274	−0.36513607002471	3.88261857496721	H
−6.61086325341551	0.97122899349733	0.80767293742765	H
0.87294376884639	4.56696248070420	5.39053107959823	H
3.83836122483048	3.43454251514899	4.36440189951675	H
1.62936095076191	4.60012167326043	2.13619599125068	H

$\{Me_2Ga[(\mu^2\text{-}O)\text{-}(O{-}N{=}CH_2)]\}_2$

(**B**, M_2O_2 motif):

absolute energy: E = −4346.9979457670 hartrees

−3.11983028432903	4.06301427861081	−2.39691167785717	C
0.05083744554064	2.84742965218496	−0.89644587777120	Ga
−0.75576468730376	0.61968373635564	2.12288671615823	O
−0.41793779675629	0.99528886525539	4.66615805882070	N
−0.67785784584977	3.25706863479204	5.39364277376475	C
3.28093753485360	4.56651566325877	−0.22856153900348	C
−0.04807373376217	−2.84744920533832	0.89703346551625	Ga
3.12918223421157	−4.05317259153830	2.39164464351272	C
0.74928140991462	−0.62039068224449	−2.12511493418178	O
0.41210833589279	−0.99362343026791	−4.66818853547551	N
0.66039608934396	−3.25647345448288	−5.39643135836848	C
−3.27421315957683	−4.57747860219883	0.23792690391019	C
3.01777149569148	6.36495954618019	0.74970465906051	H
4.52273069884720	3.37780444804281	0.91221499510515	H
4.23653350327241	4.96122532169280	−2.01678248675915	H
−3.70119131103315	5.86928927309477	−1.58342206176291	H
−4.63268462019315	2.69373137824473	−2.09352189170566	H
−2.88555517642064	4.32194476994350	−4.43133382534678	H
−4.50087083137831	−3.41830373863169	−0.94878040259189	H
−3.00414075797458	−6.40302408907342	−0.68672636048285	H
−4.25050242701700	−4.91992919126032	2.02572957313139	H
3.74248614586301	−5.82935940652628	1.53624265291467	H
4.62390010295742	−2.65508120780657	2.13339807963287	H
2.88597743047854	−4.36786754745214	4.41708641620936	H
0.42297619966001	−3.60350279504671	−7.40056711451185	H
1.10222269745209	−4.82187399037811	−4.12933732204827	H
−0.44029796235689	3.60655395470753	7.39736183281147	H
−1.13009430085823	4.81913297968230	4.12606706196508	H

([{$Me_2Ga[(\mu^1$-O,μ^1-N)-(O−N=CH_2)]}$_2$-*O*][{$Me_2Ga'[(\mu^2$-O')-(O'−N'=CH_2)]}$_2$-*N′*])

(**C**, $M_4O_4N_4$ motif):

absolute energy: E = −8694.0105330520 hartrees

−2.61499751713766	5.04928518902785	−3.71636383283524	C
0.52245025875659	3.35362273872042	−2.58781018942241	Ga
1.95417931661632	2.31726305582272	−6.27724113923521	N
0.44360601467529	1.02955843709447	−7.84810770716132	O
−0.70153995867337	−2.30363447033931	−6.94460341759921	Ga
−3.77799049785352	−2.90750111560427	−8.96497148730306	C
3.64496429295857	4.70386561178584	−1.04466830017372	C
−0.11648878374728	−0.29054262840475	−1.84371483028133	O
0.97356971707575	−1.97888538809635	2.08040236591270	Ga
−1.25816590018488	−4.95614658919083	1.78963203255022	C
−1.93955665817648	−1.28755657791169	−3.33778952374372	N
−4.13766557951439	−1.56513492666659	−2.42473564475774	C
3.95659220954277	3.25346702245525	−7.21969710509082	C
4.58822906404738	−1.39728330144443	1.42484807786219	C
−0.81106608523742	0.88728286812183	7.25960440822640	Ga
1.38727321723431	3.68211729180282	8.38037166043473	C
−0.93271987018262	1.07785849707666	3.39179151233987	O
−1.45924434797307	3.11315378159175	1.92522757968841	N
−2.84927285371858	4.79582820121423	2.91055374650065	C
1.19756723613058	−1.97639042956399	6.20924498638884	O
1.20931970445544	−3.90410262851671	7.94046275015254	N
2.65764484685184	−5.72807810788957	7.38953378550506	C
−4.14520376155451	−0.17415825013154	8.53104867059928	C
2.18990029109227	−4.56753557063572	−6.30575481956190	C
5.29011204869565	3.52248604777411	−1.43321334249022	H
3.44752191037860	4.86142216511501	1.00041779671517	H
4.01842888659083	6.59866257947470	−1.78408764579755	H
−1.30615683402560	−5.71350254208122	−0.12860163283254	H
−3.18899388982325	−4.52545279199619	2.38017997303353	H
−0.56446658691444	−6.44438927747280	3.04023050697526	H
5.66378253944460	−3.02736943865811	2.09970623581439	H

5.26450012500171	0.26217634746240	2.44512280260783	H
4.97871719981259	−1.15485453265638	−0.58367700743096	H
1.51736949921315	3.71878714414869	10.44080334373506	H
3.28892272254602	3.43498852366076	7.61847152657969	H
0.68330462047637	5.52404394280541	7.76743266551844	H
−5.34555759870748	1.43362196186576	9.01944401496048	H
−5.12902033297378	−1.32886737027857	7.13174059059925	H
−3.89556757684890	−1.32121242856554	10.22940461481424	H
−5.06388122623720	−1.29542566250595	−8.86552753057007	H
−4.79083653929520	−4.60159095493369	−8.35443250062163	H
−3.27455697055573	−3.17946216254926	−10.94916771259286	H
−3.28323147750328	6.42405954212781	1.74794503762530	H
−3.61382682059187	4.65724829565273	4.81747107089054	H
2.72399413985240	−7.27832746961207	8.72678281971467	H
3.81636247818417	−5.77822977656827	5.68778726506811	H
4.42955442029819	2.93055967494626	−9.19170085790007	H
5.15185778465465	4.37550785346554	−5.99644022562401	H
1.55736373983996	−6.43314474001030	−5.68552165609143	H
3.30678318853374	−4.82241804806840	−8.02378308927383	H
3.42314483231432	−3.78890852172860	−4.84581735832255	H
−5.56054792934536	−2.39576271730133	−3.64115073501695	H
−4.56868356220536	−0.99622964875840	−0.50190314902492	H
−4.30485277129087	4.15787559268540	−2.93533488719608	H
−2.61884337459450	7.03001566816675	−3.12713770938510	H
−2.75766575482198	4.99742979683637	−5.77373678318031	H

$\{Me_2In[(\mu^1\text{-}O,\mu^1\text{-}N)\text{-}(O{-}N{=}CH_2)]\}_2$

(**D**, $M_2O_2N_2$ motif):

absolute energy: E = −501.5677295148 hartrees

1.06459946955752	2.82797670186327	−6.26723500699756	C
−0.26785858821412	−0.05311233269445	−3.75501731938146	In
2.95993643161601	−0.90198562083498	−1.17618611806679	N
2.31447211756664	−1.84174526207189	1.06909075355846	O
0.27100960490699	0.07404800049561	3.76073066231696	In
−1.00489846502026	−2.75584472853259	6.35889007968215	C
−1.96386846823225	−3.67408824505619	−4.38764102071997	C
−2.34157308907369	1.80555303278235	−1.04741761579867	O
−2.98255411607343	0.82924700832040	1.18445575079254	N
−5.32119504706889	0.67950692561165	1.72818385119339	C
5.29398636724959	−0.86135568220031	−1.75849920420913	C
1.95346557978905	3.72189494814228	4.25472513179560	C
1.96019573292665	4.34834118670285	−5.19716983127621	H
2.42889765619647	2.09424069054159	−7.63215047016191	H
−0.50544830752903	3.64306124659567	−7.33037888674248	H
−1.42368314621181	−4.50305316724140	5.34401349181506	H
−2.70702352673922	−2.16404539402192	7.36788511820719	H
0.44143050438919	−3.16774059773045	7.77201324667280	H
−2.68156880153669	−4.43853538590720	−2.61002137457338	H
−3.53294289976527	−3.54764506839370	−5.72200443923693	H
−0.58780983153237	−5.01394482736615	−5.14379875207279	H
6.71599398960554	−1.51690132137421	−0.43012469400678	H
5.80455717178532	−0.15474304265854	−3.61087760535543	H
−5.82874810724056	−0.05700060412859	3.56952699312907	H
−6.75010279355418	1.27755912505770	0.38015488215197	H
1.25271622536255	4.67241127624121	5.94658456777834	H
4.00485946127187	3.55748726564824	4.41948659997212	H
1.53098104197976	4.90866130088322	2.62002672859268	H

$\{Me_2In[(\mu^2\text{-}O)\text{-}(O{-}N{=}CH_2)]\}_2$

(**E**, M_2O_2 motif):

absolute energy: E = −501.5642448049 hartrees

−3.64810573056899	4.81491497215506	−0.89383561499542	C
0.01524911158263	3.21886858822644	−0.31356724261118	In
−0.28999919194839	0.18308816905274	2.34903290444070	O
−0.19431171367228	−0.10185265465557	4.91081239711491	N
−0.35125421262268	1.91481868126836	6.18461342719570	C
3.70955789589432	4.81186494820503	0.06686178841410	C
−0.01581400858617	−3.21622854971400	0.31425939630362	In
3.65692684490633	−4.79334909583170	0.88689464428454	C
0.27408843545605	−0.17972206694054	−2.34959972129569	O
0.20020214909582	0.10233374784841	−4.91225296889661	N
0.33896103326100	−1.91814292791403	−6.18208723464496	C
−3.69157230958155	−4.85227855423745	−0.06512601709329	C
3.82653738604342	6.09511824071534	1.67921741812974	H
5.09318372696191	3.30507460241363	0.33520014592464	H
4.22636490416448	5.87193623410977	−1.62673256247521	H
−4.03738911830032	6.35048307000094	0.42876651372192	H
−5.09098024371812	3.36048150410168	−0.65054915415202	H
−3.80631467481245	5.56562012855210	−2.80978605773294	H
−5.09026615650044	−3.37632597518041	−0.41228138797560	H
−3.76426515746361	−6.19697977941171	−1.62982534720757	H
−4.22164657511796	−5.85827973819602	1.65723914649117	H
4.07830445547689	−6.27538801543631	−0.48614703184554	H
5.08666201550000	−3.31618482849488	0.71301343333867	H
3.80155846775676	−5.61187966146081	2.77581569251062	H
0.28826434995691	−1.73420029684111	−8.22033397234702	H
0.50878007287406	−3.79006612726981	−5.32839439325688	H
−0.28392079152096	1.72865377363529	8.22219743921064	H
−0.55277320566244	3.78529467667083	5.33469408117249	H

([{$Me_2In[(\mu^1$-O,μ^1-N)-(O−N=CH_2)]}$_2$-*O*][{$Me_2In'[(\mu^2$-O')-(O'−N'=CH_2)]}$_2$-*N'*])

(**F**, $M_4O_4N_4$ motif):

absolute energy: E = −1003.1537457060 hartrees

−2.76033884051874	5.70542932018942	−3.52939173023808	C
0.47477851814239	3.67995032631438	−2.14597588345848	In
−1.57928256618580	3.05619097904755	2.05518886808575	N
−3.07478333871140	4.63270230689039	3.06720281201669	C
2.19298440220980	2.72029881291013	−6.06073332212336	N
4.26423946403611	3.66813436981422	−6.83348873138935	C
3.93350652073675	4.77348858961148	−0.32884711291368	C
−0.37450999624767	−0.26016824243910	−1.87415801200048	O
−2.17347505500595	−1.14493697223638	−3.47172152596651	N
−4.40395486572003	−1.39774622732141	−2.63166472583282	C
0.76937504192091	1.51977167386119	−7.76793649965988	O
−0.61390680866748	−2.04232338681007	−7.31465667218666	In
2.38385125873174	−4.63685299790731	−6.50536077803708	C
−3.87176625302358	−2.30676931840283	−9.70510039669143	C
0.83464372834824	−2.33749694349745	1.81416595407221	In
1.11033447156186	−2.41587063889295	6.04864267219835	O
1.55332784538622	−4.23683007100438	7.82817475343557	N
2.83148020384550	−6.11597581916415	7.07910538039724	C
−1.86707064429186	−5.35252894578390	1.51600559398721	C
4.76993121566560	−1.91641200237852	0.98360970168274	C
−0.73762585904890	0.65710924889997	7.52917530183308	In
−4.41200723061687	−0.38583707326188	8.86571975391864	C
−0.89830282790040	1.02831883959607	3.44082607841022	O
1.87381316906608	3.48742076441950	8.76282766244679	C
5.49681927821715	3.52364668557225	−0.82707657451430	H
3.72044220160103	4.72663166432500	1.72262394307025	H
4.45166736010506	6.70244510908910	−0.86008053329818	H
−2.02692376743755	−6.09953146195248	−0.40125125700493	H
−3.74155485998469	−4.75129542718123	2.14200071456886	H
−1.28766163447304	−6.90099314138766	2.75322502744140	H
5.72774810981023	−3.73984364595961	1.15242939780566	H

5.65049302383667	−0.61404931148079	2.31953612432471	H
5.07906312813973	−1.21158232798860	−0.92893747405852	H
2.66643712927149	2.98095611339003	10.60030208713969	H
3.42743978964253	3.63853344841322	7.41364047683840	H
0.98285331461678	5.33976492968748	8.94803922238520	H
−5.51253037238277	1.23515296465356	9.51499371097497	H
−5.46539160345232	−1.34653412524350	7.37336132865140	H
−4.22145269572244	−1.69957318151450	10.44657060269879	H
−4.98104464412799	−0.56959672102085	−9.59369546454126	H
−5.08326598883425	−3.89880204372551	−9.19199757684707	H
−3.30904106555991	−2.56772758419266	−11.67385629596056	H
−3.60410403557487	6.26127849388233	1.94614607769718	H
−3.83870754976423	4.39128192962653	4.96523691194485	H
3.20940058444741	−7.57880120489615	8.46121615994020	H
3.55970660152143	−6.29812283157483	5.16025661251031	H
4.86128284717984	3.44016042506601	−8.78595092027140	H
5.39789599077374	4.70541120359878	−5.48136730315630	H
1.68967451078455	−6.56956798072940	−6.30184595337251	H
3.78345391651836	−4.62053277433232	−8.02270701937197	H
3.33395621038643	−4.09662885706074	−4.75481505447789	H
−5.81824950096084	−2.12603079646897	−3.92237206385328	H
−4.88489666422124	−0.90814384109185	−0.69727345424405	H
−4.51125165610202	4.66064141019467	−3.19742605888725	H
−2.94637459575390	7.55779796675456	−2.63352755077915	H
−2.58336658581018	6.00284789675448	−5.56342448682465	H

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