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Mendeleev Commun., 2022, **32**, 74–77
Mendeleev Communications

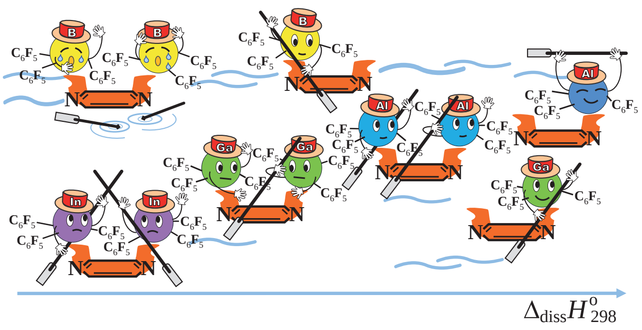
Molecular complexes of non-chelating polydentate Lewis bases with group 13 Lewis acids: crystal structure and computed energy of stepwise donor–acceptor bond formation

Nadezhda A. Shcherbina,[a] Igor V. Kazakov,[a] Anna S. Lisovenko,[a] Mariya A. Kryukova,[a] Irina S. Krasnova,[a] Michael Bodensteiner[b] and Alexey Y. Timoshkin*[a]

[a] *Institute of Chemistry, St. Petersburg State University, 199034 St. Petersburg, Russian Federation. E-mail: a.y.timoshkin@spbu.ru*
[b] *X-Ray Crystallography Department, Faculty of Chemistry and Pharmacy, University of Regensburg, 93053 Regensburg, Germany*

DOI: 10.1016/j.mencom.2022.01.024

The crystal structures of five donor–acceptor (DA) complexes of 1 : 1 and 2 : 1 composition between $E(C_6F_5)_3$ (E = B, Al, Ga and In) and pyrazine (pyz) as a non-chelating bidentate nitrogen-containing donor, as well as the $GaI_3{\cdot}pyz{\cdot}GaI_3$ complex have been established for the first time. A joint analysis of the experimental structural data and the results of computations at the M06-2X/def2-TZVP level of theory reveals that with an increase in the number of acceptor molecules in the DA complex, the DA bond distances increase, while the DA bond energies and Wiberg bond indexes decrease, indicating a weaker bonding. The previously reported 'inverse' relationship between the Lewis acidity and the capacity of a polydentate donor to complex with multiple Lewis acids is not confirmed.



Keywords: donor–acceptor interaction, group 13 Lewis acids, pyrazine, hexamethylenetetramine, structural study, DFT computations.

Donor-acceptor interactions play a significant role in modern chemistry.[1] Molecular complexes of 1:1 composition with monodentate ligands are extensively studied in the solid, liquid and gas phases.[2,3] However, molecular complexes formed by non-chelating polydentate Lewis bases with several Lewis acids are much less studied, partly due to the preference for ionic complexes or coordination polymers.[4–11] Rare examples of molecular complexes of different compositions with polydentate Lewis acids are the complexes of trimethylgallium with hexamethylenetetramine (hmta), $(GaMe_3)_n{\cdot}hmta$ (n = 1, 2 and 4).[12,13] Based on the existence of the 4:1 complex $(GaMe_3)_4{\cdot}hmta$, but the absence of its aluminum analog (even when an 8-fold excess of $AlMe_3$ was employed, only the 3:1 complex $(AlMe_3)_3{\cdot}hmta$ was formed), Robinson suggested that the capacity of hmta 'to accommodate MMe_3 units is inversely proportional to the relative Lewis acid strength of the metal alkyl'.[13] The question of how the number and nature of Lewis acids affect the stability of molecular complexes of non-chelating polydentate ligands with multiple Lewis acids remains open. Unfortunately, there are no structurally characterized series of molecular complexes of different compositions formed by strong Lewis acids of group 13 elements with polydentate donors. Here we report the structural data for six molecular complexes of 1:1 composition, $B(C_6F_5)_3{\cdot}pyz$ **1**, $Al(C_6F_5)_3{\cdot}pyz$ **3** and $Ga(C_6F_5)_3{\cdot}pyz$ **4**, and 2:1 composition, $\{B(C_6F_5)_3\}_2{\cdot}pyz$ **2**, $\{Ga(C_6F_5)_3\}_2{\cdot}pyz$ **5** and $\{In(C_6F_5)_3\}_2{\cdot}pyz$ **6**, between perfluorophenyl compounds of group 13 elements, $E(C_6F_5)_3$ (E = B, Al, Ga and In), and the non-chelating bidentate donor, pyrazine (pyz), as well as the structure of $(GaI_3)_2{\cdot}pyz$ **7**, along with the results of computational studies of complexes of group 13 Lewis acids with polydentate ligands pyz and hmta (Figure 1).

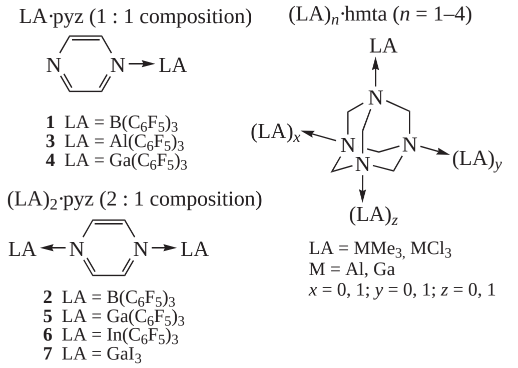


Figure 1 Compounds considered in this work: complexes $(LA)_n{\cdot}pyz$ (LA = Lewis acid; n = 1, 2) and $(LA)_n{\cdot}hmta$ (n = 1–4).

Complexes **1–5** were synthesized by the reaction of $B(C_6F_5)_3$ or $M(C_6F_5)_3{\cdot}Et_2O$ (M = Al, Ga, In)[14] with equivalent amounts of pyrazine in dichloromethane (complexes **2**, **3** and **4**) or toluene (complexes **1** and **5**) solutions. Compound **6** was obtained by vacuum sublimation of an insoluble precipitate formed after the reaction of $In(C_6F_5)_3{\cdot}Et_2O$ with an equimolar amount of pyrazine in dichloromethane.† Molecular complex **7** was obtained by a

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† *Caution!* Heating complexes of $M(C_6F_5)_3$ (M = Al, Ga and In) with Et_2O and pyrazine may result in an explosion!

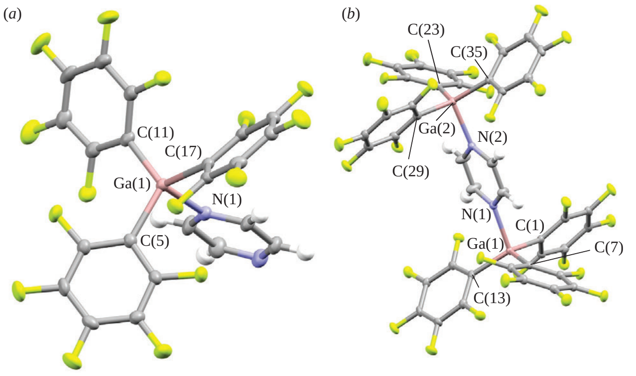

Figure 2 Molecular structures of complexes of 1 : 1 and 2 : 1 composition as exemplified by (*a*) $Ga(C_6F_5)_3{\cdot}pyz$ and (*b*) $\{Ga(C_6F_5)_3\}_2{\cdot}pyz$ (only one of four independent molecules is shown). Atoms are shown as thermal ellipsoids at 50% probability level.

direct reaction between the components with a slight excess of GaI_3 in the whole glass system under vacuum. The structures of the compounds were determined using single crystal X-ray diffraction analysis (for details, see Online Supplementary Materials). The structural data for compounds **1**–**7** are deposited in the CCDC database under deposit numbers 2105697–2105703.[‡]

The structural data reveal that both the 1 : 1 complexes $E(C_6F_5)_3{\cdot}pyz$ and the 2 : 1 complexes $\{E(C_6F_5)_3\}_2{\cdot}pyz$ adopt a molecular structure with the expected tetrahedral coordination geometry of the central atom (Figure 2). The structure of solvate $\mathbf{2}{\cdot}2CH_2Cl_2$ is in good agreement with previously reported data.[15] Complex $(GaI_3)_2{\cdot}pyz$ **7** crystallizes in the triclinic space group $P\bar{1}$ and is not isostructural to its monoclinic $P2_1/c$ analogs $(GaCl_3)_2{\cdot}pyz$ and $(AlBr_3)_2{\cdot}pyz$, which have the same molecular structure.[6] There are two short C–H···F–C contacts in the solid state structures of complexes **3** (2.29 and 2.32 Å) and **5** (2.26 and 2.35 Å), and as a result, the pyrazine ligand in these complexes is disordered over two positions (rotation along the M–N bond makes it possible to form a C–H···F–C contact with one or the other C_6F_5 group).

Computational studies at the M06-2X/def2-TZVP[16,17] level of theory were performed to obtain the structural and thermodynamic characteristics of the complexes. The structures of all compounds were fully optimized and correspond to minima on the potential energy surface, as verified by vibrational analysis. The basis set superposition error (BSSE) computed using the counterpoise method[18] is small (3–4 kJ mol^{-1} per one DA bond), and since the counterpoise method overestimates the BSSE,[19] in the following, we will report and discuss values uncorrected for the BSSE. The Wiberg bond indexes (WBI) were obtained from the natural bond orbital analysis[20] implemented in the Gaussian 16 program package.[21]

It should be noted that the interaction of equimolar amounts of $In(C_6F_5)_3$ with pyrazine in dichloromethane repeatedly leads to a precipitate insoluble in benzene, toluene, chloroform and dichloromethane. Sublimation of this solid leads to the formation of crystals of a volatile complex of 2 : 1 composition, $\{In(C_6F_5)_3\}_2{\cdot}pyz$ **6**. The X-ray diffraction pattern of the precipitate differs from that calculated for complex **6** (see Online Supplementary Materials). In contrast to the molecular complexes of B, Al and Ga analogs, the indium complex of 1 : 1 composition presumably exists as a 1D coordination polymer $[In(C_6F_5)_3{\cdot}pyz]_n$, like the previously characterized polymer complexes $(GaCl_3{\cdot}pyz)_n$ and $(AlBr_3{\cdot}pyz)_n$ with trigonal bipyramidal geometry[4,6] or as a 1D coordination polymer $(InCl_3{\cdot}1.5pyz)_n$ featuring two polymer chains interlinked through pyrazine molecules with six-coordinated octahedral indium centers.[10] Note also that the 1 : 1 gallium triiodide complex, $GaI_3{\cdot}pyz$, is monomeric in the solid state[6] with tetrahedral geometry around the gallium atom. To understand the difference in coordination behavior, we computed the model complex $LA{\cdot}(pyz)_2$, in which the central atom has trigonal bipyramidal environment with a coordination number of 5. This complex is the simplest model for the 1D polymer $(LA{\cdot}pyz)_n$. In the case of the $B(C_6F_5)_3{\cdot}(pyz)_2$ complex, geometry optimization results in the dissociation of one pyrazine molecule in line with the known preference of the boron atom to form complexes with a coordination number of 4. The values of the change in the standard Gibbs free energy for the formation of the model complexes $LA{\cdot}(pyz)_2$ in the gas phase [reaction (1)] are given in Table 1.

$$LA{\cdot}pyz + pyz = LA{\cdot}(pyz)_2 \qquad (1)$$

For $Al(C_6F_5)_3$, $Ga(C_6F_5)_3$ and GaI_3, the formation of the $LA{\cdot}(pyz)_2$ complex is slightly endergonic, in line with the experimentally observed molecular structures of 1 : 1 complexes

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[‡] *Crystal data for* $\mathbf{1}{\cdot}$*toluene*. $C_{29}H_{12}BF_{15}N_2$, M = 684.21, monoclinic, space group *Cc*, a = 14.3783(1), b = 11.0646(1) and c = 16.7682(1) Å, β = 96.031(1)°, V = 2652.89(3) Å^3, T = 100.0(3) K, Z = 4, d_{calc} = 1.713 g cm^{-3}, μ = 1.579 mm^{-1}. A total of 36201 reflections were collected (5151 independent, R_{int} = 0.0352) and used in the refinement, which converged to wR_2 = 0.0580 for all data [R_1 = 0.0218 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for $\mathbf{2}{\cdot}2CH_2Cl_2$. $C_{42}H_8B_2Cl_4F_{30}N_2$, M = 1273.91, monoclinic, space group $P2_1/n$, a = 14.1392(1), b = 15.8913(2) and c = 19.9879(2) Å, β = 100.099(1)°, V = 4421.50(8) Å^3, T = 99.9(8) K, Z = 4, d_{calc} = 1.914 g cm^{-3}, μ = 3.990 mm^{-1}. A total of 76953 reflections were collected (8398 independent, R_{int} = 0.0481) and used in the refinement, which converged to wR_2 = 0.1373 for all data [R_1 = 0.0515 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for **3**. $C_{22}H_4AlF_{15}N_2$, M = 608.24, monoclinic, space group $P2_1/c$, a = 12.6505(1), b = 8.0408(1) and c = 21.2853(2) Å, β = 96.201(1)°, V = 2152.49(4) Å^3, T = 99.9(3) K, Z = 4, d_{calc} = 1.877 g cm^{-3}, μ = 2.233 mm^{-1}. A total of 17013 reflections were collected (4376 independent, R_{int} = 0.0347) and used in the refinement, which converged to wR_2 = 0.0788 for all data [R_1 = 0.0286 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for **4**. $C_{22}H_4F_{15}GaN_2$, M = 650.98, monoclinic, space group $P2_1/c$, a = 12.5970(2), b = 8.1516(1) and c = 21.2344(4) Å, β = 96.133(2)°, V = 2167.99(6) Å^3, T = 100.0(2) K, Z = 4, d_{calc} = 1.995 g cm^{-3}, μ = 3.134 mm^{-1}. A total of 25345 reflections were collected (4401 independent, R_{int} = 0.0846) and used in the refinement, which converged to wR_2 = 0.1385 for all data [R_1 = 0.0503 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for **5**. $C_{40}H_4F_{30}Ga_2N_2$, M = 1221.87, triclinic, space group $P\bar{1}$, a = 12.6496(1), b = 16.2893(1) and c = 28.0758(2) Å, α = 89.907(1), β = 89.156(1) and γ = 89.953(1)°, V = 5784.47(7) Å^3, T = 100.0(2) K, Z = 6, d_{calc} = 2.105 g cm^{-3}, μ = 3.450 mm^{-1}. A total of 81534 reflections were collected (19660 independent, R_{int} = 0.0380) and used in the refinement, which converged to wR_2 = 0.0935 for all data [R_1 = 0.0341 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for **6**. $C_{40}H_4F_{30}In_2N_2$, M = 1312.06, triclinic, space group $P\bar{1}$, a = 12.78749(8), b = 16.56864(9) and c = 28.47470(16) Å, α = 90.0894(4), β = 90.5622(5) and γ = 90.1349(5)°, V = 6032.66(6) Å^3, T = 99.96(14) K, Z = 6, d_{calc} = 2.167 g cm^{-3}, μ = 10.830 mm^{-1}. A total of 93995 reflections were collected (21820 independent, R_{int} = 0.0452) and used in the refinement, which converged to wR_2 = 0.0839 for all data [R_1 = 0.0331 was calculated for reflections with $I \geqslant 2\sigma(I)$].

Crystal data for **7**. $C_4H_4Ga_2I_6N_2$, M = 980.93, triclinic, space group $P\bar{1}$, a = 6.4268(4), b = 7.3619(4) and c = 9.7451(7) Å, α = 81.465(5), β = 84.767(6) and γ = 69.644(5)°, V = 427.11(5) Å^3, T = 123.05(10) K, Z = 1, d_{calc} = 3.814 g cm^{-3}, μ = 13.970 mm^{-1}. A total of 4498 reflections were collected (1736 independent, R_{int} = 0.0457) and used in the refinement, which converged to wR_2 = 0.0766 for all data [R_1 = 0.0333 was calculated for reflections with $I \geqslant 2\sigma(I)$].

CCDC 2105697–2105703 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 1 Computed changes in the standard Gibbs free energy for the addition of the second pyrazine molecule to the LA·pyz complex in the gas phase [reaction (1)] and experimentally observed structural types of the LA·pyz complexes.

Lewis acid	$\Delta_{(1)}G^{\circ}_{298}$/kJ mol^{-1}	Structural type	Coordination number
$B(C_6F_5)_3$	–[a]	molecular	4
$Al(C_6F_5)_3$	2.5	molecular	4
$Ga(C_6F_5)_3$	5.3	molecular	4
$In(C_6F_5)_3$	–16.0	–	–
GaI_3	5.5	molecular[6]	4
$GaCl_3$	–12.2	1D polymer[6]	5
$AlBr_3$	–12.4	1D polymer[6]	5

[a] Complex $B(C_6F_5)_3{\cdot}(pyz)_2$ dissociates into $B(C_6F_5)_3{\cdot}pyz$ and pyrazine upon geometry optimization.

3, **4** and $GaI_3{\cdot}pyz$.[6] However, in the case of $In(C_6F_5)_3$, reaction (1) is exergonic by 16 kJ mol^{-1}.

Note also that in the case of $GaCl_3$ and $AlBr_3$, which form 1D coordination polymers in the solid state,[4,6] reaction (1) is also exergonic (see Table 1). Thus, the computational results indicate that, in the case of $In(C_6F_5)_3$, the addition of a second pyrazine molecule is thermodynamically favorable, which supports our assumption about the formation of the 1D coordination polymer $[In(C_6F_5)_3{\cdot}pyz]_n$.

Pyramidalization of the group 13 acceptor moiety upon the complex formation is accompanied by the E–R bond elongation. The relative elongation of E–C bond lengths upon the formation of the $E(C_6F_5)_3{\cdot}pyz$ complex decreases in the order B (4.1–4.3%) > > Al (1.7–2.0%) > Ga (1.5–1.8%) > In (1.0–1.2%). Greater In–C distance results in less bond elongation and less reorganization energy. This reorganization can, in part, affect the possibility of 1D polymer formation, decreasing the steric bulkiness of the C_6F_5 groups.

Mass spectrometric study of complexes **1**–**6** in the temperature range 313–573 K indicates that upon heating, complexes of 1:1 composition dissociate with the evolution of gaseous pyrazine. In contrast, complexes of 2:1 composition undergo evaporation and dissociation processes in the same temperature range (see Online Supplementary Materials). It should be noted that the $C_6F_5H^+$ ion is observed in the mass spectra of complexes **1**–**6**, indicating partial thermal decomposition with the formation of pentafluorobenzene, as previously reported for the $E(C_6F_5)_3{\cdot}Py$ complexes.[22]

An analysis of the available experimental and computational structural data makes it possible to compare the changes in the donor–acceptor bond distances Δr(DA) when increasing the number of Lewis acids from one to two (Table 2). The donor–acceptor bond length increases with the addition of a second Lewis acid to the complex of 1:1 composition. This increase may indicate a weaker interaction. However, DA distances in the solid state should be used with caution when discussing Lewis acidity trends.[23]

Computed data indicate the same trend in bond distances (see Table 2). Stepwise dissociation enthalpies, donor–acceptor bond energies and WBI (see Online Supplementary Materials) decrease when going from 1:1 to 2:1 complexes, indicating a weaker bonding of pyrazine with the second $E(C_6F_5)_3$ molecule.

Finally, to test Robinson's statement about the 'inverse' relationship between the Lewis acidity and the capacity to form multi-Lewis acid complexes,[13] we have performed computations of complexes $(LA)_n{\cdot}$hmta (n = 1–4; LA = MMe_3, MCl_3; M = Al, Ga). The Lewis acidity of the indicated Lewis acids decreases in the series $AlCl_3 > GaCl_3 >> AlMe_3 > GaMe_3$, consistent with both the fluorine ion affinity scale[24] and the ammonia affinity scale.[25] The results obtained indicate that stronger Lewis acids form stronger bound complexes, in contrast to the trend described by Robinson.[13] The stepwise dissociation energies of the complexes decrease with an increase in the number of Lewis acids (Figure 3); a more significant decrease is observed for the stronger Lewis acids. The same trend is also found for the studied complexes of $E(C_6F_5)_3$ with pyrazine. Interestingly, for group 13 metal Lewis acids, there is a good correlation between the WBI of DA bonds and the dissociation enthalpy of the complex, $\Delta_{diss}H^{\circ}_{298}$ (Figure 4). The amount of charge transferred to each Lewis acid decreases with increasing n (see Online Supplementary Materials) as several Lewis acids compete with each other.

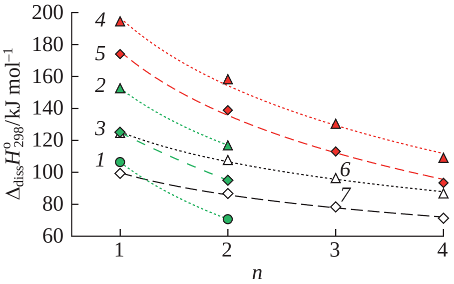

Figure 3 Standard enthalpy changes of stepwise dissociation of complexes $(LA)_n{\cdot}$LB (LB = Lewis base): (*1*) $\{B(C_6F_5)_3\}_n{\cdot}$pyz, (*2*) $\{Al(C_6F_5)_3\}_n{\cdot}$pyz, (*3*) $\{Ga(C_6F_5)_3\}_n{\cdot}$pyz, ($n$ = 1 or 2), (*4*) $(AlCl_3)_n{\cdot}$hmta, (*5*) $(GaCl_3)_n{\cdot}$hmta, (*6*) $(AlMe_3)_n{\cdot}$hmta, (*7*) $(GaMe_3)_n{\cdot}$hmta (n = 1–4). Lines are drawn for viewing direction only.

Table 2 Experimental and computed donor–acceptor bond lengths (R_{DA}) in the studied complexes $(LA)_n{\cdot}$pyz (n = 1, 2) and the difference in bond lengths (ΔR_{DA}) between the 2:1 and 1:1 complexes with a coordination number of 4 for the central atom.

Lewis acid	X-Ray crystallography			M06-2X/def2-TZVP computation		
	R_{DA}(LA·pyz)/Å	R_{DA}[(LA)$_2$·pyz]/Å	$\Delta_{exp}R_{DA}$/Å	R_{DA}(LA·pyz)/Å	R_{DA}[(LA)$_2$·pyz]/Å	$\Delta_{comp}R_{DA}$/Å
$AlBr_3$	2.133(2)[a,6]	1.999(6)[6]	–	1.996	2.029	0.033
$GaCl_3$	2.203(5),[a,6] 2.2112(15)[a,4]	2.044(7)[6]	–	2.073	2.111	0.038
GaI_3	2.027(6)[6]	2.092(6)	0.065(9)	2.098	2.141	0.043
$B(C_6F_5)_3$	1.637(3)	1.654(3), 1.661(3) mean 1.658 1.645(2), 1.652(2)[15] mean 1.649	0.021(4) 0.012(4)	1.639	1.653	0.014
$Al(C_6F_5)_3$	2.025(1)	–	–	2.018	2.053	0.035
$Ga(C_6F_5)_3$	2.097(2)	2.091(2)–2.122(2) mean 2.106	0.009(3)	2.114	2.155	0.041
$In(C_6F_5)_3$	–	2.298(3)–2.322(3) mean 2.310	–	2.339	2.385	0.046

[a] 1D polymer.

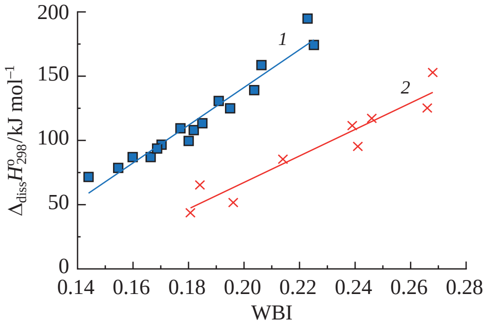

Figure 4 Correlation between WBI and dissociation enthalpy of (*1*) complexes $(MR_3)_n\cdot$hmta (M = Al, Ga; R = Me, Cl; $n = 1–4$) ($R_2 = 0.94$) and (*2*) complexes $\{M(C_6F_5)_3\}_n\cdot$pyz and $M(C_6F_5)_3\cdot(pyz)_2$ (M = Al, Ga, In; $n = 1, 2$) ($R_2 = 0.91$).

Thus, joint experimental and computational studies show that the complexation of a rigid non-chelating polydentate ligand with the second and subsequent Lewis acids is less energetically favorable than with the previous one. Stronger Lewis acids form stronger complexes, and the previously noted ‘inverse’ relationship[13] between the Lewis acidity and the capacity to form complexes is not confirmed.

This work was supported by the Russian Science Foundation (grant no. 18-13-00196) with the involvement of the research centers ‘Computing Centre’, ‘Centre for X-ray Diffraction Studies’, ‘Chemical Analysis and Materials Research Centre’, ‘Magnetic Resonance Research Centre’ of the Research Park of St. Petersburg State University.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.024.

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Received: 27th August 2021; Com. 21/6662