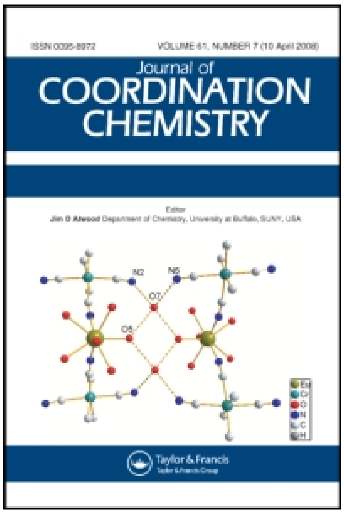

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Reaction of Trimethylaluminum with 3-Amino-5,6-Dimethyl-l,2,4-Triazine. Synthesis and Molecular Structure of $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][AI(CH_3)31$; a Highly Aggregated Al-N System

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REACTION OF TRIMETHYLALUMINUM WITH 3-AMINO-5,6-DIMETHYL-1,2,4-TRIAZINE. SYNTHESIS AND MOLECULAR STRUCTURE OF $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$; A HIGHLY AGGREGATED Al–N SYSTEM.

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Reaction of trimethylaluminum with 3-amino-5,6-dimethyl-1,2,4-triazine in toluene affords the crystalline product $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$ (I). (I) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with unit cell parameters a = 11.081(4), b = 12.807(4), c = 16.519(5) Å, α = 91.95(3), β = 104.86(3), γ = 101.89(3)°, V = 2208(1) Å^3, and ρ = 1.07 g cm^{-3} for $Z = 2$. Full-matrix least-squares refinement based on 3217 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50 \leqslant 2\theta \leqslant 45.0°$ converged at R = 0.066, R_w = 0.085. The mean Al–N bond length is 1.957(6) Å. The core of the molecule contains an eight-membered $Al_2N_4C_2$ ring bisected by a bridging dimethylaluminum unit.

Keywords: Aluminum alkyl, amine, X-ray structure

INTRODUCTION

The interaction of aluminum alkyls with amine systems is arguably one of the most extensively studied aspects of organoaluminum chemistry.[1] Smith *et al.*[2,3,4] have shown that the room-temperature reaction of organoaluminum species with primary or secondary amines results in the formation of $R_3Al:NR'_3$ adducts (where R' = H or alkyl). At higher temperatures these products were shown to undergo intermolecular condensation involving alkane elimination resulting in organoaluminum compounds containing Al_2N_2 fragments. For the past several years, this laboratory has studied the reactivity of various organoaluminum reagents with macrocyclic and open-chain multidentate amines.[5,6,7] These studies have proven fruitful as several five- and six-coordinate aluminum complexes were isolated, possessing extensive Al–N interactions.[8,9,10] The corresponding organoaluminum chemistry of amine systems possessing conjugated ring systems has not been developed to a comparable extent. Herein, we report the synthesis and molecular structure of $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$ (I) isolated from the reaction of 3-amino-5,6-dimethyl-1,2,4-triazine (Figure 1) with trimethylaluminum in toluene.

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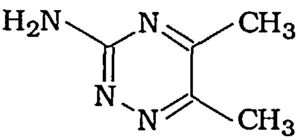

FIGURE 1 3-amino-5,6-dimethyl-1,2,4-triazine.

EXPERIMENTAL

General

Due to the extreme air sensitivity of trimethylaluminum and the resulting reaction product all manipulations were carried out using standard Schlenk and glovebox techniques. Toluene was distilled over sodium/benzophenone under an atmosphere of argon prior to use. 3-Amino-5,6-dimethyl-1,2,4-triazine was purchased from the Aldrich Chemical Co. and used as received. Trimethylaluminum was generously donated by the Ethyl Corporation and used without further purification. Single crystal X-ray data were collected on a Nicolet R3m/V diffractometer. ^{1}H NMR spectra were recorded on a Bruker AC300 FT-NMR. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$

A reaction vessel was charged with toluene (10 cm^3) and 3-amino-5,6-dimethyl-1,2,4-triazine (5.59 mmol) inside the dry box. Trimethylaluminum (22.0 mmol) was slowly added drop-wise, *via* a syringe, to the brownish mixture. Reaction was immediate and vigorous. The reaction vessel was removed from the dry box and stirred at room temperature for 48 hours. A clear brown solution resulted. The solution was transferred *via cannula* to a 150 cm^3 Schlenk flask where approximately half the solvent was removed *in vacuo*. Upon cooling to −4°C, a multitude of slightly yellow, extremely air sensitive crystals resulted (84% yield); mp = 210°C (dec.). *Anal.* Calcd for $C_{25}H_{54}N_8Al_6$: C, 46.70; H, 8.67%. Found: C, 46.02; H, 7.99%. ^{1}H NMR: δ -0.490– -1.159 (m, 39 H, (CH_3)Al), 2.220 (s, 3 H, CH_3), 2.263 (s, 6 H, 2CH_3), 2.627 (s, 3 H, CH_3), 2.662 (s, 3 H, CH_3).

Structural solution and refinement

A single crystal of (I) was mounted in a thin-walled glass capillary under argon. Cell parameters and an orientation matrix from the setting angles of 50 carefully centred reflections in the range $24.01 < 2\theta < 31.02°$ corresponded to a triclinic cell. The space group was determined to be $P\bar{1}$ (No. 2) with unit cell parameters $a = 11.081(4)$, $b = 12.807(4)$, $c = 16.519(5)$ Å, $\alpha = 91.95(3)$, $\beta = 104.86(3)$, $\gamma = 101.89(3)°$, $V = 2208(1)$ Å^3, and $\rho = 1.07$ g cm^{-3} for $Z = 2$. Full-matrix least-squares refinement based on 3217 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50 \leqslant 2\theta \leqslant 45.0°$, using SHELXTL,[11] converged at $R = 0.067$, $R_w = 0.085$. Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at optimized positions ($d_{C-H} = 0.96$ Å), and were allowed to ride on the atom to which they were bonded. An isotropic group thermal parameter ($U_{iso} = 0.156(6)\,Å^2$) was refined for all of the hydrogen atoms. The weighting scheme was based on counting statistics and included a factor ($p = 0.00075$) to downweight the intense reflections. In addition to the title compound, the unit cell contains one disordered toluene solvent molecule. This disorder was modelled by refining a major and minor component molecule, each constrained as idealized toluene molecules ($ring_{c-c} = 1.395$ A°; C–Me = 1.500 A°), and refined as rigid groups. A single group thermal parameter ($U_{toluene} = 0.161(3)\,Å^2$) was refined for all of the major and minor component atoms. Relevant crystallographic data are given in Table I.

TABLE I
Summary of the crystallographic data for $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]\cdot C_7H_8$.

Empirical formula	$C_{25}H_{54}N_8Al_6$
Molecular weight	708.9
Colour; habit	colourless; parallelepiped
Space group	triclinic; $P\bar{1}$ (No. 2)
a, Å	11.081(4)
b, Å	12.807(4)
c, Å	16.519(5)
α (deg)	91.95(3)
β (deg)	104.86(3)
γ (deg)	101.89(3)
Cell volume, $Å^3$	2208(1)
Z	2
ρ/g cm^{-3}	1.07
Diffractometer	Nicolet R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature	21°C
2θ range	3.50° to 45.0°
Reflections collected	6143
Reflections observed	3217
GOF	1.73
R	0.066
R_w	0.085

RESULTS AND DISCUSSION

Recently, there has been renewed interest in the organometallic chemistry of Group 13–15 (III–V) compounds. The interest in this chemistry is due in large measure to the potential of these compounds in electronic devices.[12,13,14] While the initial efforts of this laboratory concerned macrocyclic multidentate amines, recent studies have focused on the organo main group chemistry of multidentate open-chain amines. The inclusion of heterocyclic aromatic systems represents a logical extension. The title compound $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$ (I) was isolated from the reaction of 3-amino-5,6-dimethyl-1,2,4-triazine with trimethylaluminum in toluene. The X-ray crystal structure of (I) is given in Figure 2. Final atomic coordinates are given in Table II while selected bond distances and angles are provided in Tables III and IV, respectively.

TABLE II
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[(Al(CH_3)_2)]_5[C_{11}N_8][Al(CH_3)_3]$.

Atoms	*x/a*	*y/b*	*z/c*	*U*(eq)*
Al(1)	3033(2)	3151(2)	3030(1)	63(1)
Al(2)	5732(2)	4343(2)	2759(2)	65(1)
Al(3)	2174(2)	4162(2)	1264(1)	65(1)
Al(4)	5173(2)	1757(2)	2687(1)	71(1)
Al(5)	1244(2)	5102(2)	2789(2)	75(1)
Al(6)	3327(2)	−620(2)	1000(2)	83(1)
N(1)	4408(5)	3063(4)	2505(3)	53(2)
N(2)	4096(5)	1669(4)	1552(3)	61(2)
N(3)	3363(5)	975(4)	852(4)	65(2)
N(4)	3114(5)	3087(4)	1072(3)	59(2)
N(5)	2573(5)	4436(4)	2497(3)	59(2)
N(6)	4743(5)	5445(4)	2944(3)	56(2)
N(7)	5564(5)	6400(4)	3300(4)	66(2)
N(8)	3038(5)	6091(4)	3204(4)	64(2)
C(1)	3836(6)	2646(5)	1665(4)	56(3)
C(2)	2772(7)	1401(6)	230(5)	74(3)
C(3)	2989(7)	2603(6)	204(5)	74(3)
C(4)	1850(9)	688(7)	−516(6)	126(5)
C(5)	1939(9)	2978(7)	−436(5)	110(5)
C(6)	4251(9)	2987(7)	−9(5)	99(4)
C(7)	3507(6)	5319(5)	2867(4)	58(3)
C(8)	5120(7)	7162(5)	3571(5)	68(3)
C(9)	3798(7)	7003(6)	3553(5)	70(3)
C(10)	6056(7)	8190(5)	3938(5)	85(4)
C(11)	3252(8)	7822(6)	3916(6)	105(5)
C(12)	1568(7)	1938(5)	2630(5)	89(4)
C(13)	3742(8)	3561(6)	4245(5)	88(4)
C(14)	6438(7)	4798(6)	1830(6)	98(4)
C(15)	6862(7)	4357(6)	3896(5)	94(4)
C(16)	2871(8)	5511(6)	852(5)	91(4)
C(17)	339(7)	3493(7)	934(6)	101(4)
C(18)	4596(10)	949(6)	3551(5)	109(5)
C(19)	6970(7)	2038(7)	2689(6)	100(4)
C(20)	618(9)	4479(7)	3684(6)	114(5)
C(21)	269(8)	5875(7)	1957(6)	109(5)
C(22)	1869(10)	−1019(8)	1459(8)	149(7)
C(23)	4996(8)	−631(6)	1784(6)	104(4)
C(24)	3228(10)	−1363(7)	−71(6)	122(5)
C(25)	9600(13)	8611(11)	3446(8)	161(3)
C(26)	10555	9245	4100	161(3)
C(27)	10996	8817	4857	161(3)
C(28)	10480	7757	4960	161(3)
C(29)	9525	7123	4306	161(3)
C(30)	9085	7551	3549	161(3)
C(31)	9048	8917	2583	161(3)
C(25A)	9581(18)	8153(16)	3734(12)	161(3)
C(26A)	10270	9187	3704	161(3)
C(27A)	11214	9712	4413	161(3)
C(28A)	11468	9204	5152	161(3)
C(29A)	10778	8171	5182	161(3)
C(30A)	9834	7645	4473	161(3)
C(31A)	8682	7960	2862	161(3)

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* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *Uij* tensor. Atoms C(25) through C(31) represent the major component of a disordered toluene molecule, treated as a rigid group, while C(31A) represents the minor component.

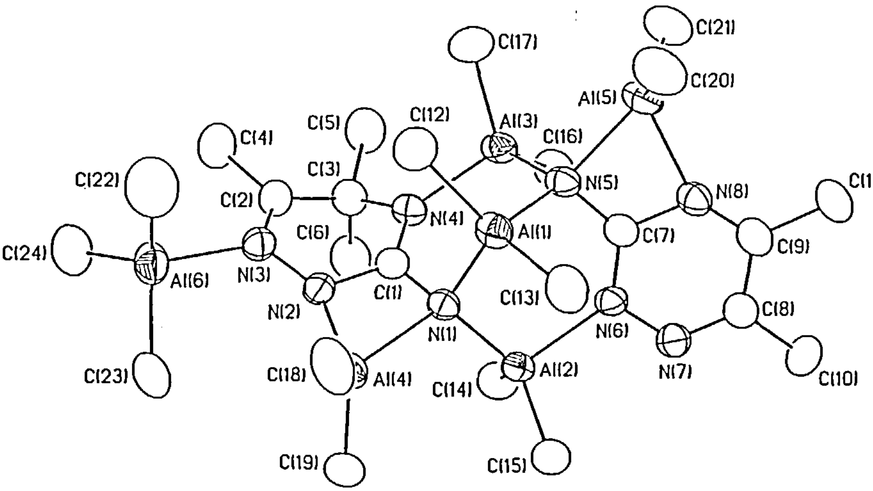

FIGURE 2 A view of the $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$ molecule showing the atom labelling scheme. Thermal ellipsoids for aluminum and nitrogen atoms show 30% probability levels; hydrogen atoms have been omitted.

TABLE III

Bond lengths (Å) for $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$.

Atoms	Distances	Atoms	Distances
Al(1)-N(1)	1.957(6)	Al(1)-N(5)	1.990(6)
Al(1)-C(12)	1.957(7)	Al(1)-C(13)	1.967(7)
Al(2)-N(1)	1.914(5)	Al(2)-N(6)	2.016(6)
Al(2)-C(14)	1.948(10)	Al(2)-C(15)	1.969(8)
Al(3)-N(4)	1.952(6)	Al(3)-N(5)	1.972(6)
Al(3)-C(16)	1.961(8)	Al(3)-C(17)	1.962(7)
Al(4)-N(1)	2.023(6)	Al(4)-N(2)	1.933(5)
Al(4)-C(18)	1.953(10)	Al(4)-C(19)	1.949(8)
Al(5)-N(5)	1.996(7)	Al(5)-N(8)	2.056(5)
Al(5)-C(20)	1.919(11)	Al(5)-C(21)	1.950(10)
Al(6)-N(3)	2.060(6)	Al(6)-C(22)	1.938(13)
Al(6)-C(23)	1.970(9)	Al(6)-C(24)	1.947(10)
N(1)-C(1)	1.404(8)	N(2)-N(3)	1.392(7)
N(2)-C(1)	1.358(9)	N(3)-C(2)	1.274(9)
N(4)-C(1)	1.319(8)	N(4)-C(3)	1.503(10)
N(5)-C(7)	1.368(7)	N(6)-N(7)	1.373(6)
N(6)-C(7)	1.318(9)	N(7)-C(8)	1.295(10)
N(8)-C(7)	1.371(10)	N(8)-C(9)	1.307(8)
C(2)-C(3)	1.512(10)	C(2)-C(4)	1.513(10)
C(3)-C(5)	1.529(12)	C(3)-C(6)	1.518(13)
C(8)-C(9)	1.429(11)	C(8)-C(10)	1.496(8)
C(9)-C(11)	1.495(13)		

TABLE IV
Bond angles (°) for $[(Al(CH_3)_2)]_5[C_{11}H_{15}N_8][Al(CH_3)_3]$.

Atoms	Angles	Atoms	Angles
N(1)-Al(1)-N(5)	96.6(2)	N(1)-Al(1)-C(12)	111.9(3)
N(5)-Al(1)-C(12)	108.3(3)	N(1)-Al(1)-C(13)	110.3(3)
N(5)-Al(1)-C(13)	107.5(3)	C(12)-Al(1)-C(13)	119.7(4)
N(1)-Al(2)-N(6)	101.1(2)	N(1)-Al(2)-C(14)	115.2(3)
N(6)-Al(2)-C(14)	105.1(3)	N(1)-Al(2)-C(15)	109.9(3)
N(6)-Al(2)-C(15)	101.5(3)	C(14)-Al(2)-C(15)	120.8(3)
N(4)-Al(3)-N(5)	105.5(2)	N(4)-Al(3)-C(16)	109.5(3)
N(5)-Al(3)-C(16)	106.4(3)	N(4)-Al(3)-C(17)	108.5(3)
N(5)-Al(3)-C(17)	103.3(3)	C(16)-Al(3)-C(17)	122.3(4)
N(1)-Al(4)-N(2)	69.3(2)	N(1)-Al(4)-C(18)	111.0(4)
N(2)-Al(4)-C(18)	121.9(3)	N(1)-Al(4)-C(19)	113.2(3)
N(2)-Al(4)-C(19)	110.3(3)	C(18)-Al(4)-C(19)	120.2(4)
N(5)-Al(5)-N(8)	68.4(2)	N(5)-Al(5)-C(20)	113.8(4)
N(8)-Al(5)-C(20)	113.0(3)	N(5)-Al(5)-C(21)	119.2(4)
N(8)-Al(5)-C(21)	104.9(3)	C(20)-Al(5)-C(21)	122.8(4)
N(3)-Al(6)-C(22)	101.2(4)	N(3)-Al(6)-C(23)	104.8(3)
C(22)-Al(6)-C(23)	114.9(5)	N(3)-Al(6)-C(24)	109.4(3)
C(22)-Al(6)-C(24)	117.2(4)	C(23)-Al(6)-C(24)	108.3(4)
Al(1)-N(1)-Al(2)	112.2(3)	Al(1)-N(1)-Al(4)	116.8(3)
Al(2)-N(1)-Al(4)	110.4(3)	Al(1)-N(1)-C(1)	107.6(4)
Al(2)-N(1)-C(1)	119.8(4)	Al(4)-N(1)-C(1)	88.2(4)
Al(4)-N(2)-N(3)	144.7(4)	Al(4)-N(2)-C(1)	93.3(4)
N(3)-N(2)-C(1)	119.5(5)	Al(6)-N(3)-N(2)	114.4(4)
Al(6)-N(3)-C(2)	129.1(4)	N(2)-N(3)-C(2)	116.4(5)
Al(3)-N(4)-C(1)	125.4(5)	Al(3)-N(4)-C(3)	122.0(4)
C(1)-N(4)-C(3)	112.4(6)	Al(1)-N(5)-Al(3)	109.2(3)
Al(1)-N(5)-Al(5)	121.0(3)	Al(3)-N(5)-Al(5)	109.4(3)
Al(1)-N(5)-C(7)	108.8(4)	Al(3)-N(5)-C(7)	117.0(5)
Al(5)-N(5)-C(7)	90.7(4)	Al(2)-N(6)-N(7)	110.6(4)
Al(2)-N(6)-C(7)	129.1(4)	N(7)-N(6)-C(7)	119.7(6)
N(6)-N(7)-C(8)	119.8(6)	Al(5)-N(8)-C(7)	88.1(4)
Al(5)-N(8)-C(9)	151.3(6)	C(7)-N(8)-C(9)	120.4(6)
N(1)-C(1)-N(2)	109.0(5)	N(1)-C(1)-N(4)	127.0(6)
N(2)-C(1)-N(4)	123.9(6)	N(3)-C(2)-C(3)	121.9(6)
N(3)-C(2)-C(4)	119.3(7)	C(3)-C(2)-C(4)	118.7(6)
N(4)-C(3)-C(2)	107.7(6)	N(4)-C(3)-C(5)	109.8(7)
C(2)-C(3)-C(5)	114.5(6)	N(4)-C(3)-C(6)	108.3(5)
C(2)-C(3)-C(6)	107.7(7)	C(5)-C(3)-C(6)	108.6(7)
N(5)-C(7)-N(6)	126.3(6)	N(5)-C(7)-N(8)	112.7(6)
N(6)-C(7)-N(8)	120.9(5)	N(7)-C(8)-C(9)	120.9(6)
N(7)-C(8)-C(10)	117.3(7)	C(9)-C(8)-C(10)	121.7(7)
N(8)-C(9)-C(8)	117.9(7)	N(8)-C(9)-C(11)	118.8(7)
C(8)-C(9)-C(11)	123.3(6)		

Several points are worthy of note concerning structure and bonding in the title compound. While the formation of Al_2N_2 units is common in Al–N compounds it is interesting to note that such formation did not occur even as considerable Al–R and N–H bond cleavage took place. Moreover, there is a high Al–N association in (I) as it contains six aluminum atoms. The core of the molecule is occupied by an eight-membered $Al_2N_4C_2$ ring. The ring strain present in (I) gives rise to distorted tetrahedral geometries for some of the aluminum atoms. For example, the N(2)–Al(4)–N(1) and mean C–Al–C bond angles for the Al(4)–N(2)–C(1)–N(1) ring are 69.3(2) and 121.35(4)°, respectively. Likewise, for the Al(5)–N(5)–C(7)–N(8) ring, the N(8)–Al(5)–N(5) and mean C–Al–C bond angles are 68.4(2) and 121.35(4)°, respectively. The mean Al–N distance for the molecule is 1.957(6) Å.

Another interesting point is the fact that one of the triazine units in the product has been methylated at the C(3) position. The methylation of C(3) results in a loss of aromaticity in the heterocyclic ring. This loss of aromaticity is reflected in bond distances: N(2)–C(1) = 1.358(9), C(1)–N(4) = 1.319(8), and N(4)–C(3) = 1.503(10) Å compared to corresponding counterparts in the conjugated ring, N(6)–C(7) = 1.318(9), C(7)–N(8) = 1.371(10), and N(8)–C(9) = 1.307(8) Å, respectively.

Though the precise mechanism for this alkylation is not known, a possible approach is presented. Addition of trimethylaluminum to N(2) could result in the loss of the N(2)–C(1) double bond and a positive charge on C(1). This charge could then be located on C(3) by bond rearrangement about the heterocyclic ring, where C(1)–N(4) assume double bond character. Alkylation of C(3) by trimethylaluminum would afford the methylated species. This new methylated species could then undergo further reaction with four moles of trimethylaluminum and one 3-amino-5,6-dimethyl-1,2,4-triazine unit to provide four moles of methane and (I). While the methylation of the heterocycle is unusual, the elimination of alkane from Al–R/N–H systems is quite common and has been extensively studied by Smith *et al*,[15,16] It is interesting to note that in the related dimethylaluminum hydride-*N*-methylaniline system, hydrogen, not methane, is the elimination product.[17]

This initial study into the reactivity of conjugated heterocyclic systems towards aluminum alkyls has proven quite interesting. Forthcoming contributions will address this and other aspects of organoaluminum chemistry with conjugated heterocyclic ligands.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

Summary of data collection and refinement, molecular plots, tables of bond distances and angles, final fractional coordinates, and thermal parameters (10 pages) and a listing of observed and calculated structure factors (21 pages) are available from G.H.R.

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