Two Polymorphic Modifications of Dibromo-bis(acetonitrile-N)-zinc(II)

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

Two polymorphic modifications of dibromo-bis(acetonitrile-N)-zinc(II) have been characterized by single crystal structure analysis and X-ray powder measurements. Form **I** cyrstallizes in the orthorhombic space group *Pnma* with $a = 13.101(2)$, $b = 10.210(1)$, $c = 6.8078(7)$ Å and $Z = 4$. The structure is composed of discrete molecular complexes in which each zinc cation is coordinated by two bromide anions and two acetonitrile ligands within distorted tetrahedra. Form **II** crystallizes in the orthorhombic space group *Cmcm* with $a = 8.0734(8)$, $b = 11.012(1)$, $c = 10.204(1)$ Å and $Z = 4$. In this compound also discrete complexes are found and the coordination of the zinc atoms is identical to that of form **I**. Two bromide atoms and two acetonitrile ligands coordinate to the zinc cations within distorted tetrahedra. The packing of the discrete molecular complexes in form **II** is completely different form that in form **I**. Form **I** was originally prepared in the presence of 2-chloropyrazine but can also be synthesized phase pure by crystallization from acetonitrile alone. In contrast, form **II** was only obtained in the presence of 2-chloropyrazine if the crystallization is performed under kinetic control but it immediately transforms into form **I**. Crystallization experiments reveal that form **I** is the thermodynamically most stable form between −40 °C and the boiling point of acetonitrile of 80 °C, whereas form **II** is metastable. On storing, the thermodynamically stable form **I** at room temperature decomposes into zinc(II) bromide within a few hours, but in a saturated acetonitrile atmosphere it is stable over a long period. On heating form **I** all ligands are liberated in one step leading to zinc bromide.

Key words: Polymorphism, Coordination Compounds, Zinc Bromide, Crystal Structures

Introduction

For several years we have been interested in the synthesis, crystal structures and properties of inorganic-organic coordination polymers based on copper(I) halides or pseudo halides Cu*X* and nitrogen donor ligands. For a certain copper(I) halide or pseudohalide and a specific nitrogen donor ligand frequently several compounds are found, which differ in the ratio between the inorganic and organic part. During our investigations we have found that most of the ligand richer compounds loose their ligands stepwise on heating, forming ligand poorer intermediate compounds [1 – 8]. In most cases these intermediates can be isolated in a very pure form and in almost 100% yield. Hence, the thermal decomposition of suitable Cu*X* precursor compounds is an alternative route for the preparation of new Cu*X* coordination polymers which cannot be prepared in solution or which are otherwise only obtained as mixtures.

Starting from these findings we have investigated if the preparation of ligand poorer coordination compounds is limited to copper(I) halide coordination polymers or if it can be expanded to other classes of coordination compounds. Because in the ligand rich and ligand poor copper(I) halide coordination polymers in most cases different CuX substructures like *e. g.* monomers, or single and double chains are found, ligand rich and ligand poor compounds can be expected for those metal halides, which shows a similar structural behaviour. Since metal halide substructures are also found in compounds on the basis of zinc(II) halides and donor ligands, these compounds should be good candidates for further investigations [9 – 13]. Therefore, we have started systematic investigations on the preparation, structures and thermal properties of zinc(II) halide coordination compounds. In the beginning we tried to prepare compounds with some pyrazine derivatives as ligand like *e. g.* 2-chloropyrazine, which we have also used in

the preparation of the copper(I) coordination polymers. During these investigations we have synthesized and structurally characterized the coordination compounds ZnX_2(2-chloropyrazine)$_2$ (X = Cl, Br, I) [14]. In order to prove if there are several compounds of different stoichiometry we reacted different amounts of the zinc halides in acetonitrile. In one of these batches we obtained a mixture of the 1 : 2 compound $ZnBr_2$(2-chloropyrazine)$_2$ and two polymorphic modifications of $ZnBr_2$(acetonitrile)$_2$. The phenomenon of polymorphism is of interest from several points of view. First of all the structural aspects of polymorphism provide information on intermolecular interactions in crystals, and therefore, can be used for a more rational crystal design [15]. Because the structure is different while the chemical composition is identical, structure property relationships can be investigated [16]. Moreover, investigations on the thermodynamic and kinetic aspects of polymorphism provide important information on the stability of the modifications and their transformation behavior [17]. In addition, even though some examples of polymorphic modifications of coordination compounds have been reported in literature, this is a very rare phenomenon in this area [18–21]. Therefore, we have structurally characterized and investigated both forms.

Results and Discussion

Crystal structures

Form **I** of dibromo-bis(acetonitrile-N) zinc(II) crystallizes in the orthorhombic primitive space group *Pnma* with four formula units in the unit cell (Table 2). The asymmetric unit consists of one zinc cation and two bromide anions which are located on a crystallographic mirror plane, and one acetonitrile ligand which occupies a general position. Each zinc cation is coordinated by two bromide anions and two nitrogen atoms of symmetry related acetonitrile ligands within a distorted tetrahedron forming discrete complexes (Fig. 1). The Zn-Br distances of 2.336 and 2.338 Å as well as the Zn-N distance of 2.046 Å are comparable to distances retrieved from the CSD data base (Conquest; Version 1.6, 2005) (Table 1) [22]. The N-Zn-N angles of 95.9° as well as the Br-Zn-Br angles of 119.85° deviate strongly from the ideal tetrahedral values, whereas the N-Zn-Br angles are close to 109° (Table 1).

Form **II** of dibromo-bis(acetonitrile-N)-zinc(II) crystallizes in the orthorhombic *C*-centered space group C*mcm* with four formula units in the unit cell (Table 2). The asymmetric unit consists of one zinc cation located on a position with site symmetry *m*2*m* as well as one bromide anion and one acetonitrile ligand which are located on a crystallographic mirror plane. Because of symmetry, the hydrogen atoms of the acetonitrile ligand are disordered in two orientations. The zinc cations are each coordinated by two symmetry related bromide anions and the nitrogen atoms of two symmetry related acetonitrile ligands within a distorted tetrahedron (Fig. 2). As in form **I**, discrete molecular complexes are formed. The Zn-Br distance of 2.336 Å and the Zn-N distance of 2.034 Å are comparable to those in form **I** and agree well with those retrieved

Table 1. Selected bond lengths (Å) and angles (°) for form **I** and form **II**.

Form **I**		Form **II**	
Zn1-Br1	2.338(1)	Zn1-Br1	2.336(1)
Zn1-Br2	2.336(1)	Zn1-Br1^{i}	2.336(1)
Zn1-N1	2.036(5)	Zn1-N1	2.034(6)
Zn1-N1^{i}	2.036(5)	Zn1-N1^{ii}	2.034(6)
N1-Zn1-N1^{i}	95.9(3)	N1^{ii}-Zn1-N1	96.0(4)
N1-Zn1-Br2	109.6(2)	N1^{ii}-Zn1-Br1^{i}	109.5(1)
N1^{i}-Zn1-Br2	109.6(2)	N1-Zn1-Br1^{i}	109.5(1)
N1-Zn1-Br1	109.6(2)	N1^{ii}-Zn1-Br1	109.5(1)
N1^{i}-Zn1-Br1	109.6(2)	N1-Zn1-Br1	109.5(1)
Br2-Zn1-Br1	119.85(4)	Br1^{i}-Zn1-Br1	120.2(1)
C1-N1-Zn1	171.7(5)	C1-N1-Zn1	172.0(6)

Symmetry transformations used to generate equivalent atoms for form **I** (^{i} x, $-y+1/2$, z) and form **II** (^{i} $-x$, y, $-z+1/2$, ^{ii} x, y, $-z+1/2$).

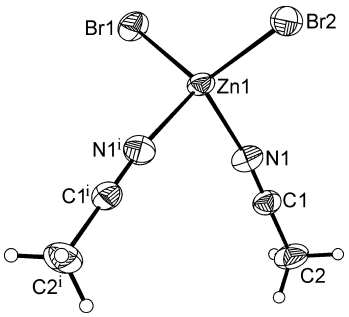

Fig. 1. Crystal structure of form **I** with labelling and displacement ellipsoids drawn at the 50% probability level (symmetry codes: ^{i} x, $-y+1/2$, z).

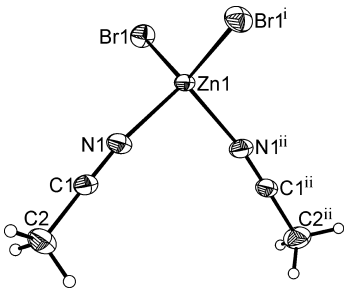

Fig. 2. Crystal structure of form **II** with labelling and displacement ellipsoids drawn at the 50% probability level (the disorder of the hydrogen atoms is not shown for clarity; symmetry codes: ^{i} $-x$, y, $-z+1/2$; ^{ii} x, y, $-z+1/2$).

Table 2. Selected crystal data and results of the structure refinements for form **I** and **II**.

Compound	Form I	Form II
Formula	$C_4H_6Br_2N_2Zn$	$C_4H_6Br_2N_2Zn$
MW [g·mol^{-1}]	307.30	307.30
Crystal colour	colourless	colourless
Crystal size [mm^{-1}]	$0.40 \times 0.35 \times 0.30$	$0.45 \times 0.30 \times 0.25$
Crystal system	orthorhombic	orthorhombic
Space group	*Pnma*	*Cmcm*
a [Å]	13.101(2)	8.0734(8)
b [Å]	10.210(1)	11.012(1)
c [Å]	6.8078(7)	10.204(1)
V [Å^3]	910.6(2)	907.2(3)
Temperature [K]	200	200
Z	4	4
$D_{calc.}$ g·cm^{-3}	2.241	2.250
2θ-Range [°]	3–56	3–56
h/*k*/*l* Ranges	−17/17	−10/10
	−13/10	−14/13
	−8/7	−13/13
μ(Mo-K$_\alpha$) [mm^{-1}]	11.4	11.4
Min./max. transm.	0.110/0.205	0.104/0.380
Measured reflections	4746	4265
$R_{int.}$	0.0794	0.1294
Independent refl.	1137	614
Refl. with $I > 2\sigma(I)$	828	548
Parameters	48	31
R_1 $[I > 2\sigma(I)]$	0.0437	0.0447
wR_2 [all data]	0.1103	0.1275
Goof	0.993	1.036
Residual electron density [e·Å^{-3}]	1.51/−1.14	1.34/−0.84

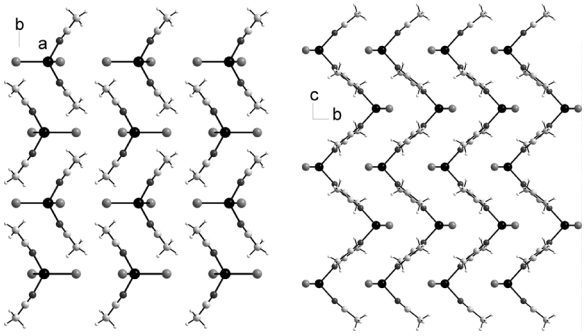

Fig. 3. Crystal structure of form **I** with view along the crystallographic *c*-axis (left) and of form **II** with view along the crystallographic *a*-axis (right).

from the CSD data base (Table 1) [22]. The distortion of the polyhedra is comparable to that in form **I** (N-Zn-N angles = 96.0°; Br-Zn-Br angles = 120.2°) (Table 1).

The crystal structures of both forms are completely different. In form **I** the discrete complexes are stacked in the direction of the *c*-axis, with the bromide anions pointing in the direction of the *a*-axis, the neighbouring stacks being related by inversion symmetry in the direction of the *b*-axis (Fig. 3: left). The stacks are packed in a way that one stack fits perfectly into the aperture formed by the surrounding stacks. The organic ligands as well as the $ZnBr_2$ units are arranged in layers, which are stacked perpendicular to the *b*-axis (Fig. 4: left). The shortest intermolecular Br···Br distances amount to 3.947 and 4.045 Å. There is one short intermolecular C-H···Br contact with an H···Br distance of 3.145 Å and a C-H···Br angle of 166.0° indicative of weak hydrogen bonding.

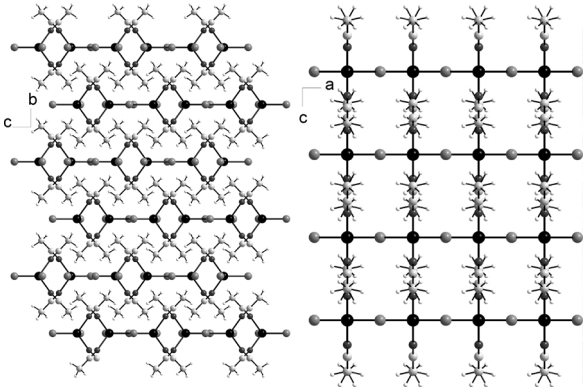

Fig. 4. Crystal structure of form **I** with view along the crystallographic *a*-axis (left) and of form **II** with view along the crystallographic *b*-axis (right).

In contrast to form **I**, in the crystal structure of form **II** the discrete complexes are shifted in the *b*-*c*-plane and therefore, no stacks are found (Fig. 3: right). Additionally, the methyl groups are not arranged in separate layers as in form **I** (Fig. 4: right). The shortest intermolecular Br···Br distances of 4.024 and 4.049 Å are slightly longer that in form **I**. The shortest intermolecular H···Br contact amounts to 3.131 Å but the angle C-H···Br of 137.5° deviates strongly from linearity and therefore, this should not correspond to any significant stabilizing interaction. This could be the reason for the disorder of the methyl hydrogen atoms and besides other reasons for the lower stability of this form.

Crystallization experiments

As mentioned in the experimental part, both forms were isolated for the first time by serendipity in one batch which contained 2-chloropyrazine as a ligand. Therefore, we tried to prepare both forms from acetonitrile. However, all crystals investigated consists only of form **I**. In the following we determined which of

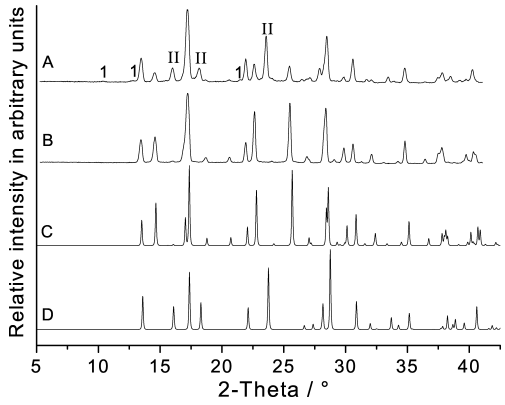

Fig. 5. Experimental X-ray powder pattern of a residue obtained by fast crystallization of a mixture of $ZnBr_2$ with 2-chloropyrazine in acetonitrile (A), after stirring a suspension of crystalline $ZnBr_2$ in acetonitrile for 2 d leading to the thermodynamically most stable form **II** (B), and theoretical X-ray powder patterns calculated for form **I** (C) and form **II** (D) from single crystal data (II indicates reflections which originate from modification II and 1 indicates reflections which originates from the 1 : 2 compound $ZnBr_2$(2-chloropyrazine)$_2$.

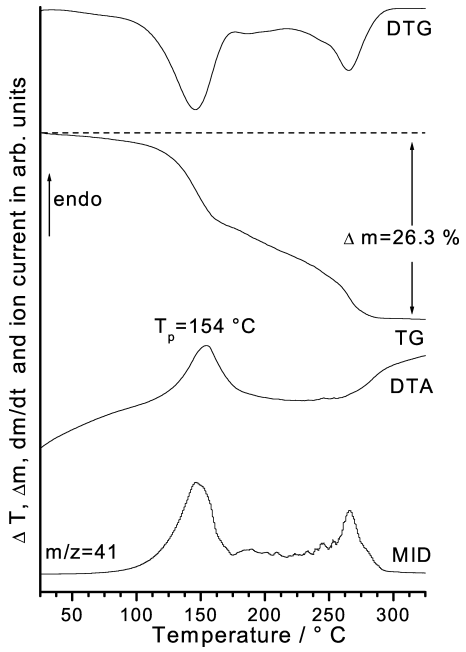

Fig. 6. DTA-, TG-, DTG and MS trend scan curve for form **I** (T_p = peak temperature; $m/z = 41$ corresponds to acetonitrile).

the two forms represents the thermodynamically most stable form at r. t. Therefore, we stirred suspensions of crystalline zinc(II) bromide in acetonitrile for two days and investigated the residue obtained by X-ray powder measurements. By comparing the experimental pattern with those calculated for forms **I** and **II** from single crystal data, it was obvious that only modification **I** had formed phase pure (Fig. 5: B – D). Therefore, this form represents the thermodynamically most stable form at r. t. To investigate the stability range of form **I**, we have performed additional experiments, in which suspensions were stirred at −40 and 80 °C and the residues were immediately investigated by X-ray powder diffraction. In all of these experiments we obtained only form **I** as a phase pure compound and therefore, this modification represents the thermodynamically most stable forms within this temperature range. However, these experiments indicated that modification **II** was formed only by kinetic control. Therefore, we have added clear solutions of zinc(II) bromide in acetonitrile to tetrachloromethane in which this compound is insoluble. The precipitates formed were isolated immediately and investigated by X-ray powder measurements. However, the powder pattern can be explained successfully only with the presence of the stable form **I**. Because the crystals of modification **II** were formed in the presence of 2-chloropyrazine (see Experimental Section), we assumed that this ligand is needed for the crystallization of the metastable form. It is well known that in different solvents or in the presence of some additives crystal growth of some thermodynamically stable forms is prevented and a metastable form may be observed. Therefore, we have performed crystallization experiments in the presence of 2-chloropyrazine and we have found in some batches mixtures which consisted of large amounts of the stable form **I** and small amounts of $ZnBr_2$(2-chloropyrazine)$_2$ as well as of form **II** (Fig. 5: A), but we have to mention that in some batches only form **I** appeared. Therefore, the preparation of form **II** is difficult to reproduce and depends on the experimental conditions. This is not an unusual phenomenon and several of such observations have been described in the literature [23].

Form **I** was additionally investigated by simultaneous differential thermoanalysis and thermogravimetry coupled to mass spectroscopy in order to investigate if the decomposition of this compound directly leads to the formation of zinc bromide or if some ligand poor intermediate compound can be observed (Fig. 6). During the thermogravimetric analysis of form **I** only a single mass loss is observed in the TG curve which is accompanied by an endothermic event at 154 °C in the DTA curve. This mass loss is finished at about 300 °C and the MS measurements show clearly that only ace-

Table 3. Atomic coordinates $[\cdot 10^4]$ and equivalent isotropic displacement parameters $[\text{Å}^2 \cdot 10^3]$ for form **I**.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}
Zn(1)	4*c*	5109(1)	2500	5388(1)	27(1)
Br(1)	4*c*	5782(1)	2500	2207(1)	38(1)
Br(2)	4*c*	3342(1)	2500	5848(1)	36(1)
N(1)	8*d*	5746(3)	3981(6)	6972(7)	36(1)
C(1)	8*d*	6157(4)	4688(6)	7977(7)	31(1)
C(2)	8*d*	6677(5)	5598(7)	9276(9)	45(2)

Equivalent isotropic U_{eq} calculated as a third of the trace of the orthogonalized U_{ij} tensors.

Table 4. Atomic coordinates $[\cdot 10^4]$ and equivalent isotropic displacement parameters $[\text{Å}^2 \cdot 10^3]$ for form **II**.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}
Zn(1)	4*c*	0	4764(1)	2500	18(1)
Br(1)	8*g*	−2508(1)	5822(1)	2500	29(1)
N(1)	8*f*	0	3528(5)	3981(6)	26(1)
C(1)	8*f*	0	2743(6)	4692(7)	24(1)
C(2)	8*f*	0	1715(7)	5582(8)	39(2)

Equivalent isotropic U_{eq} calculated as a third of the trace of the orthogonalized U_{ij} tensors.

tonitrile $(m/z = 41)$ is emitted. In addition, the experimental mass loss of 26.3% is in very good agreement with that calculated for the removal of all ligands $(\Delta m_{\text{theo}} = -26.7\%)$. From the nature of the TG curve there is some hint for the formation of a ligand poor intermediate phase at about 150 °C. Therefore, we performed further DTA-TG measurements in which the reaction was stopped at about 150 °C, where the DTG curve exhibits a minimum. The residue isolated at this temperature was investigated later by X-ray powder measurements. The experimental powder pattern was in perfect agreement with that calculated for form **I** and therefore, the presence of a ligand poor compound can be excluded.

Conclusion

In the present work two polymorphic modifications of dibromo-bis(acetonitrile-N)-zinc(II) were found by serendipity. Both forms consists of discrete complexes built up of zinc cations which are coordinated by two bromide anions and two acetonitrile ligands within distorted tetrahedra. The crystallization experiments have shown that form **I** represents the thermodynamically most stable form at r. t., whereas form **II** must be metastable. The reason for the higher stability of form **I** compared to form **II** is difficult to analyze. However, in contrast to form **II**, intermolecular C-H···Br and Br···Br interactions are observed in the stable modification **I**. In addition, in the stable form the methyl groups of the acetonitrile ligands are arranged in layers and therefore, van der Waals interactions might also contribute to the stabilization of this form. Additionally, crystallization expriments reveal that form **I** should also be the thermodynamically most stable form between −40 and 80 °C. However, it might be that both forms behave monotropically and that form **I** is the thermodynamically most stable form over the complete temperature range. It might also be that they behave enantiotropically, but in this case form **II** must be the most stable form at lower temperatures which would be in accordance with the higher density of this form.

Finally, our investigations have shown that the phenomenon of polymorphism is sometimes hard to investigate and especially the preparation of metastable forms is very often difficult to reproduce.

Experimental Section

Preparation of form **I**

Forms **I** and **II** were originally prepared by the reaction of equivalent amounts of zinc(II) bromide with 2-chloropyrazine in an large excess of non-dried commercial available acetonitrile, which leads to a mixture of both forms and of $ZnBr_2$(2-chloropyrazine)$_2$. However, form **I** can simply be prepared by stirring suspensions of crystalline zinc(II) bromide in acetonitrile at r. t. Single crystals of form **I** were prepared by slow evaporation of the solvent from a solution of zinc(II) bromide in acetonitrile. In this case very brittle colorless crystals of irregular shape were obtained. Most of them were grown together and decomposed on storage. $C_4H_6Br_2N_2Zn$ (307.30): calcd. C 15.63, H 1.97, N 9.12; found C 15.45, H 1.89, N 9.01.

Crystals of form **II** were initially obtained in a batch where 2-chloropyrazine was present. Small amounts could also be prepared as the crystallization was performed in the presence of 2-chloropyrazine under kinetic control, but it was not possible to obtain form **II** as a phase pure product.

Single crystal structure analysis

All data were measured using an Imaging Plate Diffraction System from STOE & CIE. Structure solutions were performed with direct methods using SHELXS-97 [24]. Structure refinement was carried out against F^2 using SHELXL-97 [24]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealised geometry, allowed to rotate but not tip, and refined with isotropic displacement

parameters using the riding model. For both forms a numerical absorption correction was performed using X-RED and X-SHAPE [25]. In form **II** the methyl hydrogen atoms are disordered in two orientations with equal s.o.f.'s due to symmetry. The low reliability factors for both structure determinations originate from very low crystal quality. Selected crystal data and results of the structure refinements are shown in Table 2, atomic coordinates and equivalent isotropic displacement parameters are given in Tables 3 and 4.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-600157 (form **I**), CCDC-600158 (form **II**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

X-ray powder diffraction

X-ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer equipped with a 4° PSD (position sensitive detector) using Cu-K_α radiation ($\lambda = 1.540598$ Å).

Differential thermal analysis, thermogravimetry and mass spectrometry

DTA-TG-MS measurements were performed using the STA-409CD instrument with heating rates of 4 °C/min in flowing nitrogen atmosphere (purity: 5.0), which is connected to a mass spectrometer from Balzers by skimmer coupling from Netzsch. All measurements were performed with a flow rate of 75 ml/min and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Acknowledgements

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