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Mercury(II) Halide Complexes of Tertiary Phosphines. Part III.* The Crystal Structure and Vibrational Spectra of the Discrete Dimer β-$HgCl_2(PBu_3)$, and a Comparison with the 'Tetrameric' α-Form

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A discrete dimeric form of the 1:1 adduct of mercury(II) chloride with tributylphosphine, β-$HgCl_2(PBu_3)$, has been characterised by full single-crystal X-ray diffraction analysis. In contrast to the previously reported α-form, which has been described as 'tetrameric', β-$HgCl_2(PBu_3)$ consists of centrosymmetric halogen-bridged dimers with no indication of any further association; the far-i.r. and Raman spectra may readily be assigned on this basis. The spectra of the α-form are markedly different to those of the β-isomer, yet these too are best interpreted in terms of a dimeric structure, albeit one significantly distorted by weak inter-dimer interactions, rather than the 'tetrameric' structure previously advocated.

Introduction

Reaction of equimolar amounts of mercury(II) chloride and tributylphosphine can give rise to one of two forms (α- or β-) of the 1:1 complex $HgCl_2(PBu_3)$, depending on the conditions used [1, 2]. The two compounds are found to have very different far-i.r. spectra in the solid state (Fig. 1), and in order to understand these differences we have determined the crystal and molecular structures of both complexes. In α-$HgCl_2(PBu_3)$, dimeric units are found to be linked together by long Hg–Cl bridges to give a tetrameric arrangement [1]. In the present paper we report the structure and vibrational spectra of β-$HgCl_2(PBu_3)$, and compare the nature of the two forms.

Experimental

Preparation of the Complexes

Dropwise addition of a concentrated ethanolic solution of tributylphosphine to a similar solution of mercury(II) chloride resulted in immediate formation of a fine white precipitate. When approximately half a mol equivalent of the phosphine had been

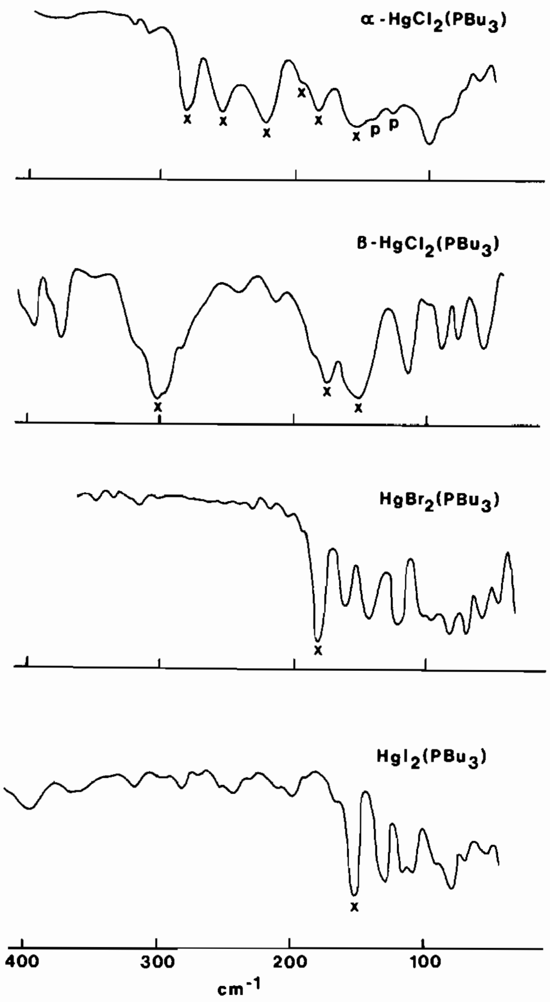

Fig. 1. Far-i.r. spectra (*ca.* 30 K) of 1:1 adducts of mercury(II) halides with tributylphosphine. Bands marked x are assigned as $\nu(HgX)$, while those marked p are attributed to $\nu(HgP)$ modes (see Tables III and IV).

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*Part II: see reference [5].

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TABLE I. Final Fractional Co-ordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses.

	x	y	z
Hg	158(1)	1200(1)	764(1)
Cl(1)	−2257(8)	1302(8)	1151(6)
Cl(2)	−829(8)	807(6)	−1041(4)
P	2762(7)	1704(4)	977(4)
C11	3834(30)	1109(22)	1977(19)
C12	3356(34)	1436(23)	2859(18)
C13	4267(40)	915(23)	3694(22)
C14	3798(54)	1285(35)	4551(25)
C21	3082(26)	3051(15)	1139(15)
C22	4658(33)	3440(23)	1240(21)
C23	4792(37)	4549(17)	1311(20)
C24	6502(45)	4918(26)	1446(25)
C31	3639(33)	1265(21)	30(21)
C32	3067(40)	1914(25)	−852(22)
C33	3886(54)	1600(33)	−1614(27)
C34	4969(60)	1908(36)	−1795(30)
H111	5026	1297	2029
H112	3686	301	1903
H121	2158	1265	2805
H122	3532	2241	2946
H131	5468	1076	3750
H132	4079	110	3619
H141	4459	894	5132
H142	2598	1123	4501
H143	3987	2089	4632
H211	2704	3256	1755
H212	2381	3430	564
H221	5080	3208	645
H222	5361	3111	1842
H231	4142	4884	696
H232	4328	4792	1888
H241	6537	5732	1498
H242	6976	4685	870
H243	7163	4593	2062
H311	3349	480	−109
H312	4866	1342	228
H321	3286	2706	−709
H322	1854	1796	−1085
H331	3079	1692	−2251
H332	4117	806	−1488
H341	5310	1525	−2358
H342	5847	1817	−1188
H343	4808	2702	−1951

added, the precipitate then obtained was collected, washed in ethanol then ether, dried *in vacuo*, and recrystallised from benzene/heptane to afford α-$HgCl_2(PBu_3)$. In a separate experiment, on continued addition of the tributylphosphine solution the precipitate first formed redissolved; when a full mol equivalent of the phosphine had been added a clear solution resulted, from which β-$HgCl_2(PBu_3)$ was isolated on addition of ether [2].

The complexes $HgBr_2(PBu_3)$ and $HgI_2(PBu_3)$ were prepared by dropwise addition of the phosphine to the mercury(II) halide, each dissolved in minimal quantities of ethanol, in equimolar proportions. The precipitates which formed on standing were collected, recrystallised from ethanol, and dried *in vacuo*.

All compounds subsequently studied gave satisfactory elemental analyses.

Vibrational Spectra

Far-infrared data were obtained using a Beckman-RIIC FS-720 interferometer. The solid samples were studied as pressed discs in polyethene (BDH), cooled to *ca.* 30 K using a CTi Model 20 closed cycle helium cryostat. For solutions, an RIIC FS-100 cell was used with 3 mm thick high density polythene windows. Raman spectra were recorded on a Coderg T-800 triple monochromator spectrometer using Ar^+ (488.0 nm) laser excitation.

Crystal Data

The crystal of β-$HgCl_2(PBu_3)$ used in this study was kindly provided by Dr. P. L. Goggin (University of Bristol). $C_{12}H_{27}Cl_2HgP$, M_r = 473.75, monoclinic, a = 8.930(9), b = 13.235(13), c = 14.980(14) Å, β = 101.70(5)°, U = 1733.6 Å^3, D_m 1.84, D_c 1.82 g cm^{-3}, Z = 4, space group $P2_1/n$, μ(Mo-K$_\alpha$) 89.04 cm^{-1}, $F(000)$ 912.

X-Ray Intensity Measurements

A crystal of approximate dimensions 0.16 × 0.16 × 0.48 mm was mounted with its a axis coincident with the ω-axis of a Stoë Stadi-2 two-circle diffractometer. Data were collected using the background-ω scan-background technique and with graphite monochromated Mo-K$_\alpha$ radiation. 3354 unique reflections were collected of which 1824 had $I/\sigma(I) \geqslant 2.0$ and were considered to be observed. Lorentz, polarisation and absorption corrections were applied.

Structure Determination and Refinement

The position of the mercury atom was readily located from the three-dimensional Patterson function, while remaining atoms were located from successive difference electron-density maps. Hydrogen atoms were located but included in the F_c calculations with an idealised position (C–H, 1.08 Å). Scattering factors were calculated using an analytical approximation [3]. Full matrix refinement was used with anisotropic temperature factors applied to all non-hydrogen atoms. Hydrogen atoms were given common isotropic temperature factors which refined to final values of U = 0.081(75), 0.093(40), 0.092(37) and 0.271(150) Å^2 for Hn11 Hn12, Hn21 Hn22, Hn31 Hn32, Hn41 Hn42 Hn43 (n = 1, 2, 3) respectively. The weighting scheme $w = 0.5015/[\sigma^2(F_o) + 0.0122\,(F_o)^2]$ was adopted and final reliability factors R = 0.067, R' = 0.076 were obtained. Final atomic parameters are listed in Table I; bond

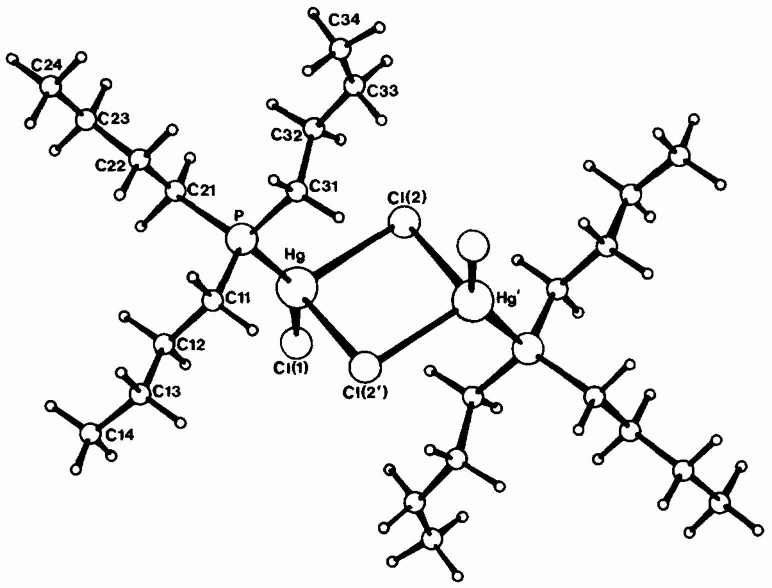


Fig. 2. Molecular structure of β-HgCl$_2$(PBu$_3$).

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Symmetry Code			
none x, y, z		(′) $-x, -y, -z$	
Distances (Å)			
Hg–Cl(1)	2.348(8)	P–C11	1.79(3)
Hg–Cl(2)	2.720(6)	P–C21	1.81(2)
Hg–Cl(2′)	2.736(6)	P–C31	1.85(3)
Hg–P	2.377(6)		
Hg–Hg′	3.893(2)	C–C	1.48*
Angles (°)			
Cl(2)–Hg–Cl(1)	97.3(3)	C31–P–C11	105.4(13)
Cl(2′)–Hg–Cl(1)	101.7(3)	Hg–P–C21	114.6(8)
P–Hg–Cl(1)	150.9(3)	C31–P–C21	109.4(12)
Cl(2′)–Hg–Cl(2)	89.0(3)	Hg–P–C31	111.4(9)
P–Hg–Cl(2)	107.3(2)	P–C11–C12	114(2)
P–Hg–Cl(2′)	94.2(3)	P–C21–C22	119(2)
Hg′–Cl(2)–Hg	91.0(5)	P–C31–C32	111(2)
Hg–P–C11	109.4(10)	C–C–C	115.3*
C21–P–C11	106.1(12)		

*Average values.

distances and angles are in Table II. Observed structure factors and thermal parameters have been deposited and are available from the Editor.

Structure Calculations

All calculations, apart from preliminary processing, were carried out on an IBM370/165 computer using the SHELX computing package.

Results and Discussion

β-HgCl$_2$(PBu$_3$) is found to contain discrete centrosymmetric chlorine-bridged dimers (Fig. 2). In contrast to the α-form, where the dimer units appear to be associated into tetramers [1], the present complex shows no further association beyond the dimer stage, the closest inter-dimer Hg···Cl distance being 4.99(8) Å. While small differences can be noted in the geometry of the dimer units in the α- and β-complexes, the further association found in α-HgCl$_2$(PBu$_3$) would not seem to result in any major changes from the dimer geometry found in the β-complex (Fig. 3), although bond length changes are significant spectroscopically (see below). In particular, the P–Hg–Cl$_{\text{terminal}}$ angles of 150.9(3)° (α form) and 147.8(7), 150.6(7)° (β-form) are very similar and reflect a strong electronic interaction between the mercury and phosphorus atoms [5]. The average values for the Hg–Cl$_{\text{bridging}}$ distances, 2.724 (α-form) and 2.728 Å (β-form), do not differ significantly, and while the Hg–P and Hg–Cl$_{\text{terminal}}$ distances are shorter in the α-complex, the large errors associated with the latter preclude any detailed discussion about the differences.

Far-infrared Spectra

Identification of the skeletal stretching modes of β-HgCl$_2$(PBu$_3$) has been made by comparison of the infrared spectrum with that of the bromo and the iodo analogues (Fig. 1), which by inference are also dimeric [2]. This has enabled the halogen-sensitive bands to be located and internal modes of the ligand to be identified. The assignments which thereby

TABLE III. Far-infrared and Raman Spectral Data (cm^{-1}) for α- and β-$HgCl_2(PBu_3)$.

α-$HgCl_2(PBu_3)$		β-$HgCl_2(PBu_3)$		Description[a]	
I.r.	Raman	I.r.	Raman[b]		
278s	280s	301s 295sh [c]		ν$(HgCl)_t$	A_u
252s[d]	252s[d]		298s	ν$(HgCl)_t$	A_g
218s	222wbr		177mw	ν$(HgCl)_b$	A_g
190sh		173m		ν$(HgCl)_b$	A_u
179m	182sh	150s		ν$(HgCl)_b$	A_u
149mbr	156sbr		148mw	ν$(HgCl)_b$	A_g
138sh		(150s)		ν(HgP)	A_u
122w				ν(HgP)	A_g
96s		110ms		skeletal bending modes	
80brsh		85m			
68sh		71m			
58w		54ms			

[a] Symmetry species A_u and A_g relate to the centrosymmetric dimeric structure of C_i symmetry determined in the present work for β-$HgCl_2(PBu_3)$. For the α-form the interpretation given is in terms of a distorted dimer of C_1 point group, for which the corresponding symmetry labels are all A (see Text). [b] From ref. [2]. [c] See Table IV. [d] The particularly low wavenumber of this mode is due to extension of the Hg–Cl bond concerned by association effects (see Text).

TABLE IV. Skeletal Stretching Modes in the Infrared Spectra of Dimeric Complexes of Stoichiometry $HgCl_2(PR_3)$.

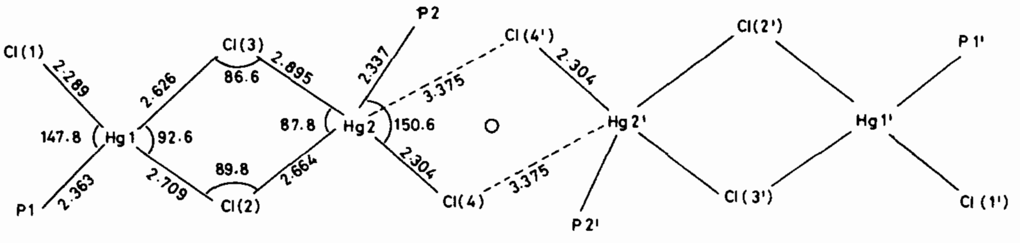
Complex	ν$(HgCl)_t/cm^{-1}$	ν$(HgCl)_b/cm^{-1}$	ν$(HgP)/cm^{-1}$	Reference
β-$HgCl_2(PBu_3)$[a]	301s, 295sh[b]	173m, 150s[b]		Present work[c]
$HgCl_2(PPh_3)$[a]	291s, 288sh	188s, 183s	157m	Present work[c,d]
$HgCl_2$(TPP)[a,e]	283s	219s, 156s		Present work[c]
$HgCl_2(PCy_3)$[e]	283s, 273sh	186m	140w	[6]
$HgCl_2(PBu^t_3)$	270s	175s, 169s	123[f]	[7]
$HgCl_2(PAr_3)$[c]	276vs	179s	138[f]	[7]

[a] Dimeric structure established by single-crystal X-ray study [this work and 5], otherwise by inference. [b] Alternative assignments discussed in text. [c] Data obtained at *ca.* 30 K, others at ambient. [d] Results in [6] are comparable. [e] TPP = 1,2,5-triphenylphosphole; Cy = cyclohexyl; Ar = *o*-$CH_3C_6H_4$. [f] Raman spectral value; the corresponding i.r. mode could not be identified.

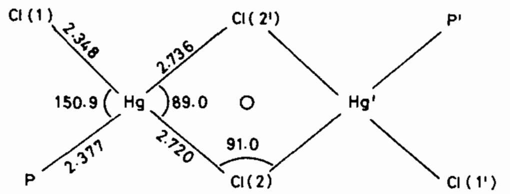
follow are shown in Table III, together with Raman data, and in comparison with those of other known (or very likely) dimers in Table IV [6, 7].

There are two aspects of the far-i.r. spectrum of β-$HgCl_2(PBu_3)$ which warrant comment. Firstly, only one ν$(HgCl)_t$ band is allowed in the infrared in terms of the centrosymmetric structure described above [A_g(Ra) + B_g(i.r.) under the approximate C_{2h} point group, or A_g(Ra) + A_u(i.r.) under strict C_i symmetry]. It is possible, therefore, that the shoulder observed at 295 cm^{-1} is actually an internal mode of the PBu_3 ligand (found in the spectrum of the α-form at 305 cm^{-1} but not consistently present in all the complexes studied, Fig. 1). The alternative interpretation, analogous to that suggested for $HgCl_2(PPh_3)$ [8], is that correlation field splitting occurs, but this is unlikely in the present case since the splitting of 6 cm^{-1} is not easily compatible with the large inter-dimer separation observed (*vide supra*).

Secondly, the assignment of the 150 cm^{-1} i.r. band to ν$(HgCl)_b$ rather than to ν(HgP) is preferred since in our experience and that of others [6, 7] the ν(HgP) modes are much weaker than the 150 cm^{-1} band is observed to be, and are not infrequently undetectable (Table IV). Two i.r.-active ν$(HgCl)_b$



α-HgCl$_2$(PBu$_3$)



β-HgCl$_2$(PBu$_3$)

Fig. 3. Comparison of the geometry of the dimer units in α- and β-HgCl$_2$(PBu$_3$). E.s.d.s in the α-complex are *ca.* 0.02 A and 0.7°, whereas those for the β-form are given in Table II.

modes are indeed expected (A_u + B_u under C_{2h}; $2A_u$ under C_i), and the separation of the 173 and 150 cm^{-1} bands (23 cm^{-1}) compared with that for HgCl$_2$(PPh$_3$) (5 cm^{-1}) and HgCl$_2$(TPP) (63 cm^{-1}) is compatible with the near symmetrical bridging structure demonstrated above [*cf.* 8, 9].

The most remarkable aspect of the i.r. spectrum of α-HgCl$_2$(PBu$_3$) is its gross dissimilarity to that of the β-form (Fig. 1), and it is clear that an exactly analogous interpretation is not appropriate or applicable. We first consider an interpretation of the spectral results in terms of a distorted dimeric arrangement, then in terms of a tetrameric structure; finally we discuss the extent to which the vibrational data can assist in distinguishing between these two models.

For the dimeric model, the asymmetry of the structure (C_1) gives rise to all skeletal modes being i.r.-active, with two $\nu(\mathrm{HgCl})_t$, four $\nu(\mathrm{HgCl})_b$ and two ν(HgP) modes predicted. The observation (Fig. 1) of eight i.r. bands in the region of ν(HgCl) and ν(HgP) [320–120 cm^{-1}, *cf.* Table IV] is thus in perfect agreement with this prediction. The band at 278 cm^{-1} is clearly assigned to stretching of the shorter HgCl terminal bond (2.289 Å), while that at 252 cm^{-1} is evidently associated with the other terminal Hg–Cl bond (in the dimer model), the notably and unusually lower wavenumber arising from the significant bond lengthening (to 2.304 Å) due to perturbation by the neighbouring dimer. The four i.r. bands in the 218–149 cm^{-1} range are logically attributed to 'stretching' (strictly, in-plane deformations) of the [HgCl$_2$Hg] four-membered ring; four such bands are indeed expected because of the asymmetry of the bridges, and the correspondence in band positions with other dimers *viz.* 219–150 cm^{-1} (Table IV) is striking. This leaves the 138 and 122 cm^{-1} bands as the candidates for ν(HgP), assignments which are again perfectly reasonable in comparison with other data (Table IV).

Thus although the far-i.r. spectra of the α- and β-forms of HgCl$_2$(PBu$_3$) are very different in appearance, an extremely consistent interpretation is possible in terms of similar dimeric structures but a somewhat distorted one in the case of the α-isomer due to the presence of further interaction.

An alternative treatment of the i.r. spectrum of the α-form may be given, based on a structural model in which the longer Hg–Cl contacts are considered significant enough to regard the structure as truly tetrameric. In this case, the C_i skeletal symmetry predicts:

$$\Gamma\nu(\mathrm{HgCl})_t = A_g(\mathrm{Ra}) + A_u(\mathrm{i.r.})$$

$$\Gamma\nu(\mathrm{HgCl})_b = 6A_g(\mathrm{Ra}) + 6A_u(\mathrm{i.r.})$$

$$\Gamma\nu(\mathrm{HgP}) = 2A_g(\mathrm{Ra}) + 2A_u(\mathrm{i.r.})$$

The two extra modes predicted by this model have their origin in $\nu(\mathrm{HgCl})_b$ motions derived from the very long inter-dimer contacts (3.375 Å), which in the dimeric model are translational lattice modes. The essential difference between spectral interpretation made in terms of the tetrameric structure rather than the distorted dimer model is that in the former case the assignments become antisymmetric i.r. components (A_u) of i.r./Raman pairs having their origin in A_1 modes of C_1 dimers. For example, in terms of a tetramer model the 278 cm^{-1} i.r. band is the antisymmetric (A_u) stretching mode of the two terminal Hg–Cl bonds (2.289 Å) at either end of the tetramer, rather than (as in the dimer model) the simple stretching of these unique bonds. No significance can be placed on the observation of only eight of the nine predicted i.r. skeletal modes, because there could easily be accidental coincidence (the 149 cm^{-1} band is notably broad), and moreover because motions substantially involving the very long (3.375 Å) inter-dimer contacts will be at particularly low and hitherto uncharacterised wavenumbers.

In other words, an interpretation of the i.r. spectrum of α-$HgCl_2(PBu_3)$ is possible which is equally plausible for both distorted dimer and centrosymmetric tetramer models. One approach in which the solid-state spectra might be used to determine which model is the more appropriate (and hence which structure is the best description) would be to compare the i.r. and Raman spectral band positions. For an isolated dimer of C_1 point group, there will be complete coincidence between all i.r. and Raman bands. For the centrosymmetric tetramer model (C_i), there will be mutual exclusion but the modes will occur as i.r.- and Raman-active pairs separated by amounts reflecting the extent of vibrational coupling across the centre of symmetry. The effect is analogous to that of correlation field splitting between two species related by a centre of symmetry, and it is not altogether surprising that the data do not allow a definitive conclusion to be drawn; the differences between the positions of the i.r. and Raman pairs of bands (Table III) are at the limit of reliability of the measurements.

There are, however, two quite distinct reasons to believe that the description of the structure of α-$HgCl_2(PBu_3)$ in terms of a dimeric arrangement is the more appropriate. Firstly, from a simple crystallographic point of view, the inter-dimer contacts of 3.375 Å must represent a weak interaction, and indeed there are no significant differences between the P–Hg–Cl angles (*vide supra*). Secondly, it must be significant that the inter-dimer bridges are readily disrupted by simple non-coordinating solvents, since the α-form (in benzene) and the β-form (in trichlorodeuteriomethane) give rise to the same far-i.r. and Raman spectra which are characteristic of a dimeric structure [2, 8].

We are thus led to the view that α-$HgCl_2(PBu_3)$, as the β-isomer, is essentially dimeric in the solid state, but that it is markedly perturbed by weak bridging interactions with an adjacent dimer species. The assignments given in Table III are made on this basis.

Acknowledgements

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