Liquid coordination complexes of Lewis acidic metal chlorides: Lewis acidity and insights into speciation

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SUPPLEMENTARY INFORMATION

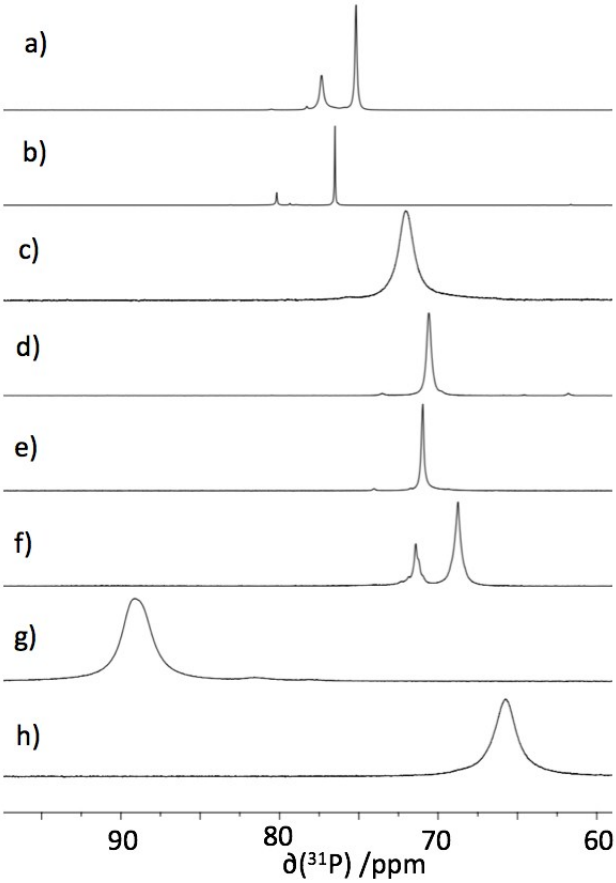

Figure 1 SI. ^{31}P NMR spectra of $P_{888}O\text{-}MCl_x$, χ_{MClx} = 0.50, where M is a) Al, b) Ga, c) In, d) Sb, e) Sn^{II}, f) Sn^{IV}, g) Ti, h) Zn

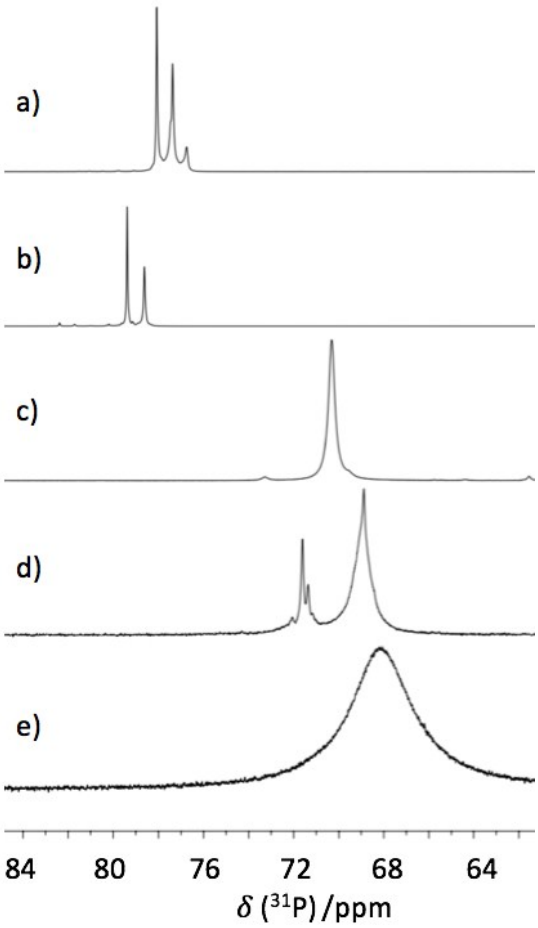

Figure 2 SI. ^{31}P NMR spectra of $P_{888}O\text{-}MCl_x$, χ_{MClx} = 0.60, where M is a) Al, b) Ga, c) Sb, d) Sn^{IV}, e) Zn.

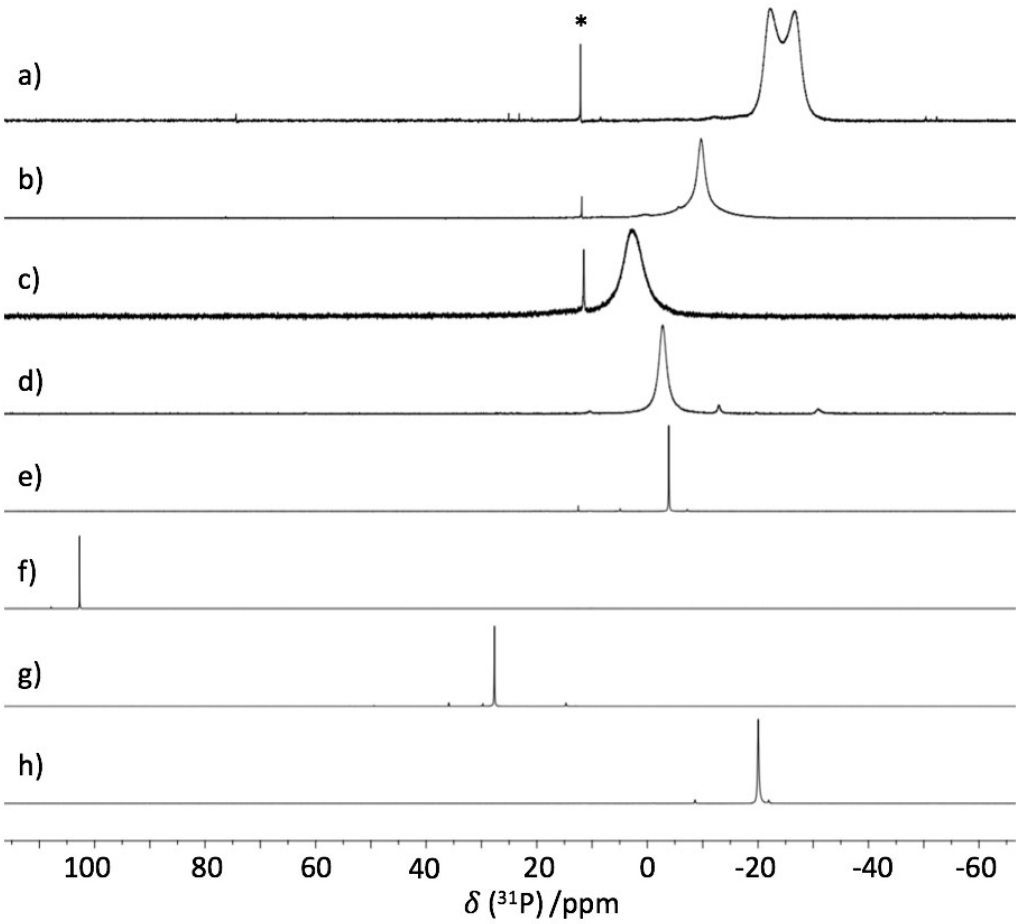

Figure 3 SI. ^{31}P NMR spectra of P_{888}-MCl_x, χ_{MClx} = 0.50, where M is a) Al, b) Ga, c) In, d) Sb, e) Sn^{II}, f) Sn^{IV}, g) Ti, h) Zn (*- artefact).

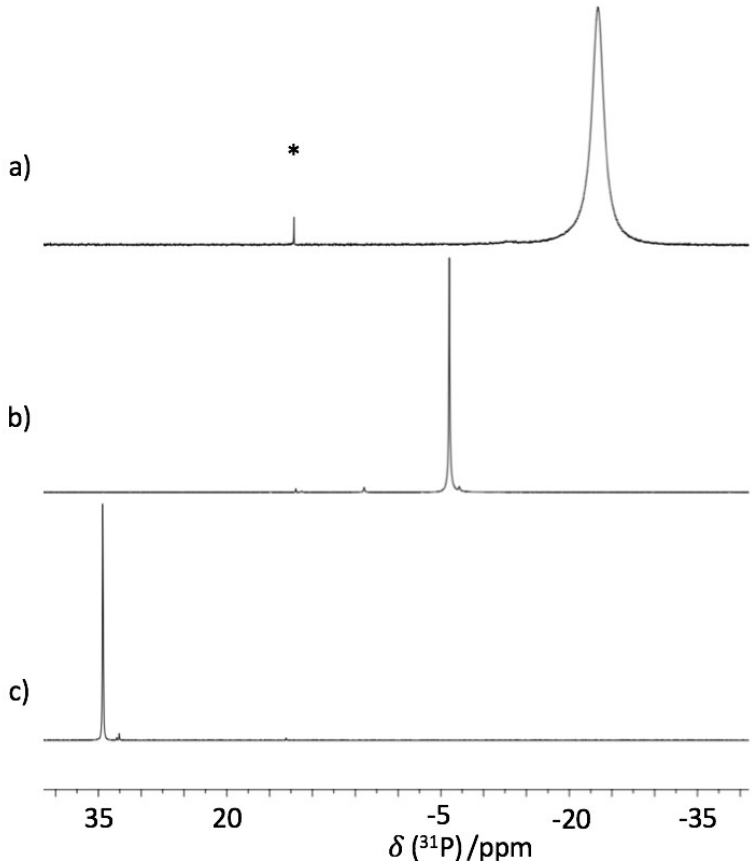

Figure 4 SI. ^{31}P NMR spectra of P_{888}-MCl_x, χ_{MClx} = 0.60, where M is a) Al, b) Ga, c) Ti (*-artefact).

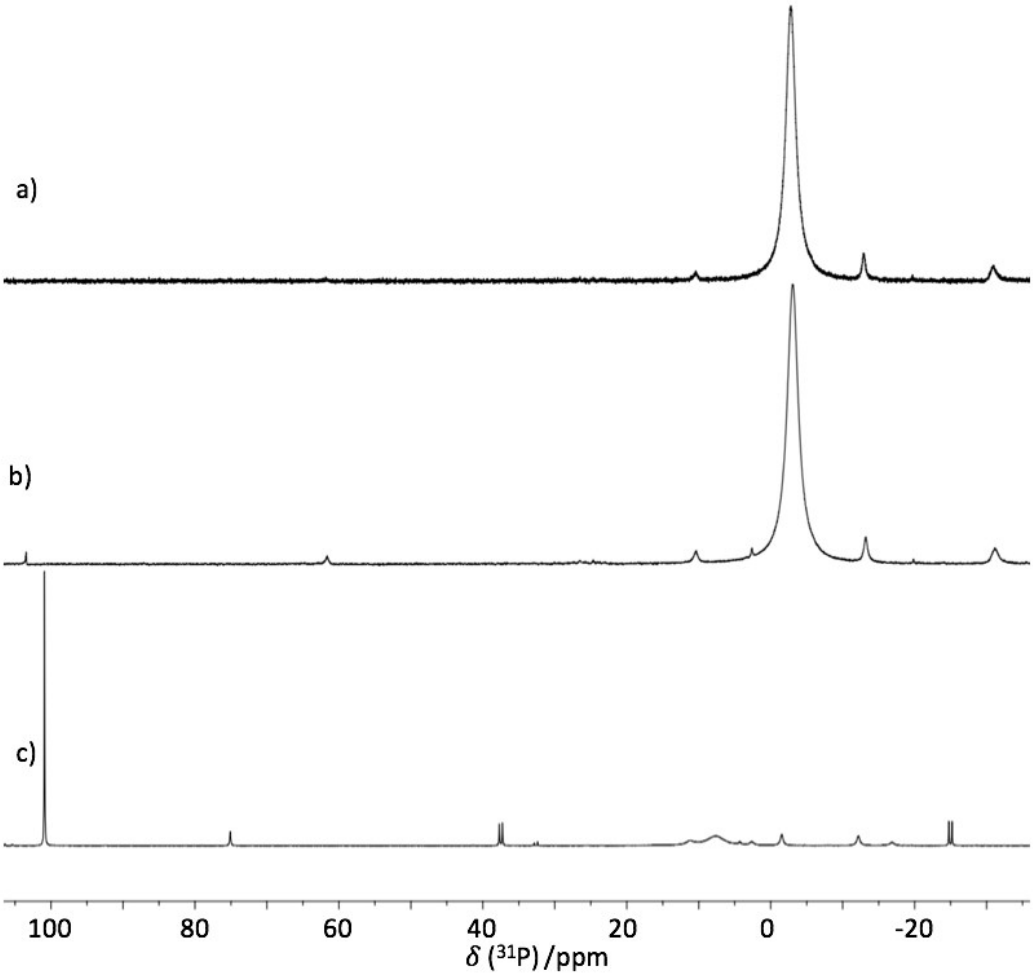

Figure 5 SI. ^{31}P NMR spectra of P_{888}-$SbCl_3$, χ_{SbCl3} = 0.50, a) fresh sample, b) after 2 days, c) spectra taken after six months.

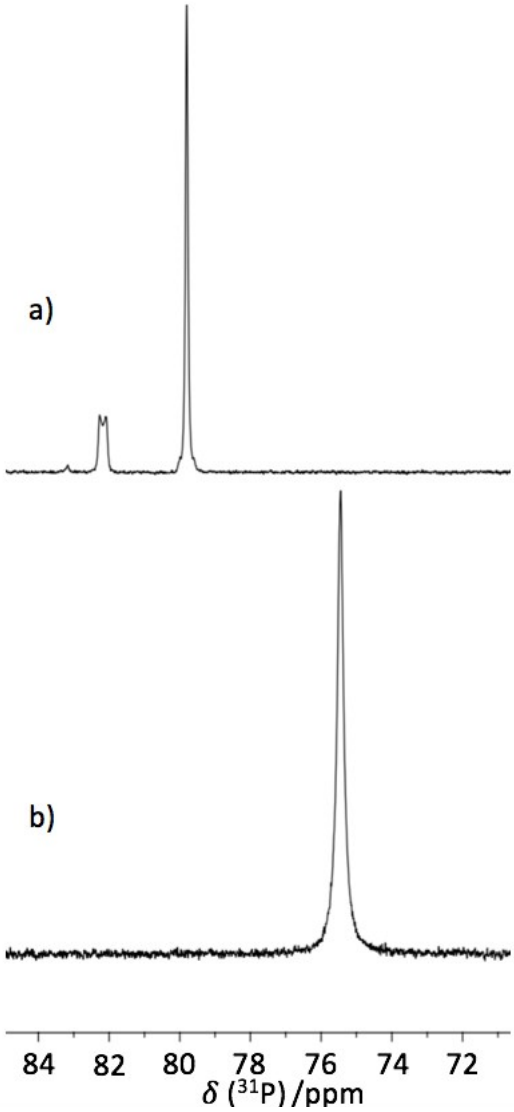

Figure 6 SI. ^{31}P NMR spectra of: a) $P_{222}O$ and $AlCl_3$ as 0.375 mol dm^{-3} solution in 1,2-dichoroethane, b) $P_{222}O$ and $GaCl_3$ as 0.375 mol dm^{-3} solution in 1,2-dichoroethane.

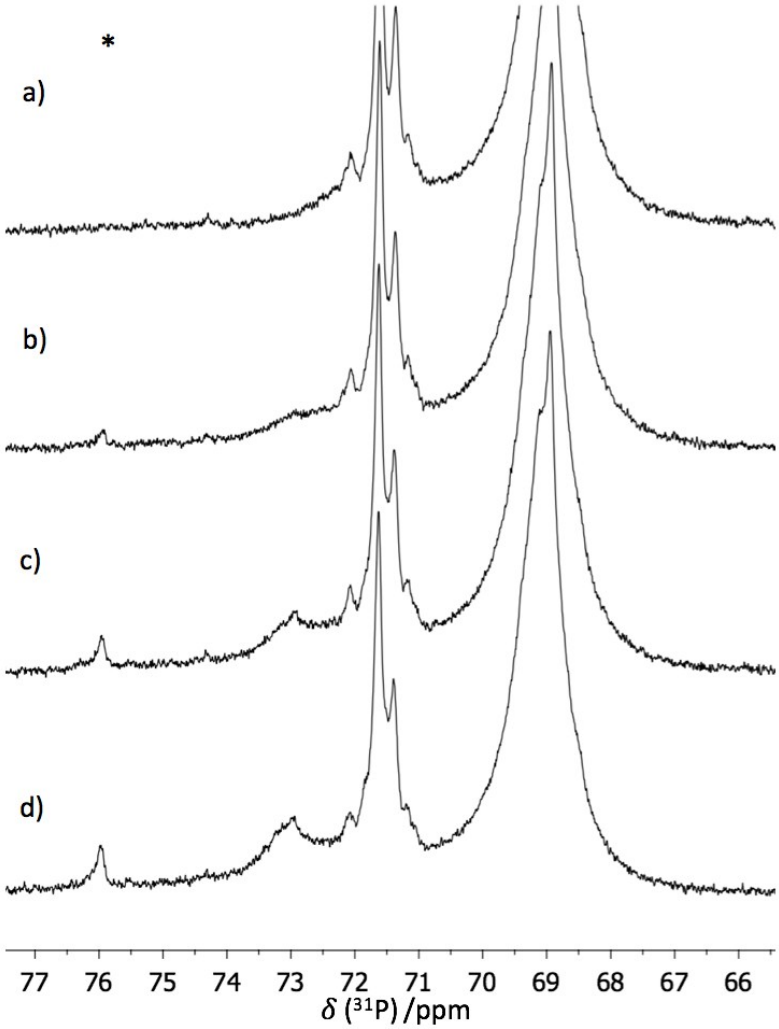

Figure 7 SI. ^{31}P NMR spectra of the $P_{888}O$-$SnCl_4$, χ_{SnCl4} = 0.60, a) neat, b) with 1 wt % of $P_{222}O$, c) with 2 wt % of $P_{222}O$, d) with 3 wt % of $P_{222}O$. The asterisk denotes the signal attributed to $P_{222}O$.

Table 1 SI. ^{31}P NMR chemical shifts of the $P_{222}O$ probe, recorded for metal chlorides (studied as 1,2-dicholoethane solution) and LCCs (studied neat). The asterisk denotes the samples with multiple signals, where the signal of the largest area was selected.

MCl_x	χ_{MClx}	**$P_{222}O$ content /wt %**	**δ ^{31}P originating from $P_{222}O$ /ppm**		
			-	**$P_{888}O$**	**P_{888}**
$AlCl_3$	0.50	1%		79.43*	78.48*
		2%		79.30*	78.55*
		3%		79.22*	78.56*
	0.60	1%		82.95	86.34
		2%		82.59	86.30
		3%		82.30	86.08
	1.00	1%	79.8*		
		2%	79.7*		
		3%	79.6*		
$GaCl_3$	0.50	1%		80.49	80.23
		2%		80.50	80.24
		3%		80.53	80.25
	0.60	1%		83.24	83.29*
		2%		83.01	82.92*
		3%		82.69	82.51*
	0.67	1%		87.38*	86.39*
		2%		87.12*	86.10*
		3%		86.71*	86.00*
	0.75	1%		88.60	87.62
		2%		88.53	87.61
		3%		88.41	87.47
	1.00	1%	75.45		
		2%	75.42		
		3%	75.37		
$InCl_3$	0.50	1%		74.91	71.43
		2%		74.85	70.94
		3%		74.63	70.75
	1.00	1%	72.67		
		2%	73.28		
		3%	73.67		
$SbCl_3$	0.50	1%		72.01	67.73
		2%		71.41	67.46
		3%		71.00	67.44
	0.60	1%		73.97	
		2%		73.99	
		3%		73.66	
	1.00	1%	70.87		
		2%	70.45		
		3%	69.94		
$SnCl_2$	0.50	1%		74.29	75.77
		2%		73.44	75.59
		3%		73.00	75.43
	1.00	1%	75.10		
		2%	75.07		
		3%	75.05		

$SnCl_4$	0.50	1%		76.92	-
		2%		76.99	
		3%		76.98	
	0.60	1%		75.94*	-
		2%		75.96*	
		3%		75.97*	
	1.00	1%	73.61*		
		2%	73.59*		
		3%	73.66*		
$TiCl_4$	0.50	1%		89.72	94.87
		2%		89.88	94.87
		3%		89.74	94.74*
	0.60	1%			100.88*
		2%			100.87*
		3%			100.89*
	1.00	1%	89.13*		
		2%	88.65*		
		3%	88.32*		
$ZnCl_2$	0.50	1%		68.96	70.27
		2%		68.76	69.94
		3%		68.55	69.78
	0.60	1%		71.16	
		2%		71.23	
		3%		71.38	
	1.00	1%	71.02		
		2%	71.04		
		3%	71.06		