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On the Existence and Lifetime of the $Co(NH_3)_5{}^{3+}$ Intermediate in the Substitution Reactions of $(NH_3)_5CoX^{n+}$

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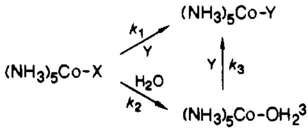
Anion competition data are reported for a wide range of spontaneous aquation reactions of complexes of the kind $(NH_3)_5CoX^{n+}$. Fourteen complexes with half-lives for acid hydrolysis ranging from ca. 1 h to less than 1 s have been examined, and included are data for three induced aquation processes. The thiocyanate ion competitor NCS^- has been used, and for 1.00 M NaNCS total anion capture ranges from 3% to 19%; it is strongly leaving-group-dependent. More significantly, both S and N of NCS^- are captured in every case and not only for the induced aquation processes as once believed. Although total NCS^- captures of the nitrosation reactions of $(NH_3)_5CoN_3{}^{2+}$ and $(NH_3)_5CoO_2CNH_2{}^{2+}$ are the same, as found previously for other competitors, the product ratios defined by $(NH_3)_5CoSCN^{2+}/(NH_3)_5CoNCS^{2+}$ are quite different. This result effectively dissolves the widely held case for a discrete $Co(NH_3)_5{}^{3+}$ intermediate in induced aquation. Indeed, the S/N product ratio varies substantially for all the hydrolysis reactions, contrasting with the constant S/N ratio reported recently for the base-catalyzed hydrolysis reactions of $(NH_3)_5CoX^{n+}$ covering a similar wide range of leaving groups. The detailed mechanistic implications of these results are discussed.

Introduction

The evidence for the existence of the transient $Co(NH_3)_5{}^{3+}$ intermediate rests largely with competition experiments directed to establishing properties independent of its source.[1,2] Thus the rapid induced aquation reactions of $(NH_3)_5CoX^{n+}$ yield $Co(NH_3)_5OH_2{}^{3+}$ together with significant amounts of $(NH_3)_5CoY^{2+}$ in Y^- media, and the competition ratio $[(NH_3)_5CoY^{2+}]/[Co(NH_3)_5OH_2{}^{3+}][Y^-]$ is essentially independent of the leaving group X.[2,3] In contrast, the spontaneous aquation reactions of $(NH_3)_5CoX^{n+}$ appear to give little or no anion competition.[4-8] However, few such experiments have been carried out because of the difficulty in separating the primary (k_1) and secondary (k_3) anion incorporation pathways:



Herein we describe the determination of NCS^- competition for the spontaneous aquation of $(NH_3)_5CoX^{n+}$ where this difficulty has been overcome. Moreover, a wide range of leaving groups has been examined to explore the possibility that the low and high anion competition for spontaneous (slow) and induced aquation (fast) respectively could simply be two well-spaced points on a continuum and that in general competition is leaving-group-dependent. The NCS^- ion is a particularly useful competitor with which to examine this problem since both the sulfur-bonded $(NH_3)_5CoSCN^{2+}$ and nitrogen-bonded $(NH_3)_5CoNCS^{2+}$ isomeric products can arise,[8-13] and they provide an additional handle on the leaving-group dependence of the product distribution. Moreover, they can be determined[10,11] with good accuracy at quite low levels (~0.5% of total cobalt).

We also report NCS^- competition data for the NO^+-induced aquation of $(NH_3)_5CoN_3{}^{2+}$,[3] $(NH_3)_5CoO_2CNH_2{}^{2+}$,[3] and $(NH_3)_5CoNCO^{2+}$ [14] and the H^+-induced hydrolysis of $(NH_3)_5CoNCO^{2+}$ [14] and some other[15,16] acid-sensitive pentaamminecobalt(III) complexes.

Experimental Section

The complexes $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$,[17] $[(NH_3)_5CoOClO_3](ClO_4)_2$,[18] $[(NH_3)_5CoO_3SCH_3](ClO_4)_2$,[6] $[(NH_3)_5CoOH_2](ClO_4)_3$,[6,17] $[(NH_3)_5CoOC(NH_2)NHC_6H_5]_2(S_2O_6)_3\cdot 3H_2O$,[18] $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3\cdot H_2O$,[12] $[(NH_3)_5CoOP(OCH_3)_3](ClO_4)_3\cdot H_2O$,[13,17,19] $[(NH_3)_5CoNHSO_2NH_2](ClO_4)_2$ and $[(NH_3)_5CoNHSO_2NH_2]BrClO_4$,[15,16] $[(NH_3)_5CoNHSO_2C_6H_4CH_3](ClO_4)_2$,[15,16] $[(NH_3)_5CoOC(NH_2)CH_2F]_2(S_2O_6)_3\cdot 3H_2O$,[16] $[(NH_3)_5CoN_3](ClO_4)_2$,[6] $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$,[3] and $[(NH_3)_5CoNCO](ClO_4)_2$[14,16] were synthesized by known methods and characterized fully according to previously recorded criteria. Many of the samples were from batches used in concurrent work.[10,11,16,18-21] All ^1H NMR spectra were measured on a Varian T60 spectrometer; Me_2SO-d_6 was the solvent and tetramethylsilane the reference. All chemicals were AnalaR grade or the equivalent. Visible absorption spectra were recorded with use of 1-cm or 1-dm silica cells and a Cary 210 spectrophotometer at 25 °C. Controlled-temperature (±0.05 °C) experiments utilized a Lauda thermostat bath and calibrated digital thermometer.[10] Ion-exchange chromatography was performed with use of SP-Sephadex C-25 (Na^+ form) cation-exchange resins, and light was routinely excluded in these experiments. Jacketed columns (5 °C) were employed for the product analyses of the incomplete reactions of the $(NH_3)_5CoOS(CH_3)_2{}^{3+}$ ion (vide infra), to avoid hydrolysis of recovered complex while on the column.

Thiocyanate Ion Competition. For the spontaneous aquation reactions, which were complete (>98%) in the designated times (Table I), the following general method was employed. Samples (0.1–0.3 g) of the appropriate $(NH_3)_5CoX^{n+}$ complex salt were dissolved directly in 1.00 M NaNCS (~25 mL, pH ~3) preequilibrated to 25.0 °C and allowed to hydrolyze in the dark for 5.0 min or more usually 5.0 h. For the reaction of the phenylurea species,[18] the acidity of the medium was preadjusted to pH ~2 ($HClO_4$) to block the parallel O- to N-linkage isomerization pathway. The product mixture was diluted to ~600 mL with ice water and sorbed on and eluted (0.25 M NaCl; 0.70 M NaCl) from Sephadex resin. The cobalt concentrations in the eluates for the two well-separated bands, first $(NH_3)_5Co(SCN)^{2+}$ (S- plus N-bonded isomers) and then $(NH_3)_5CoOH_2{}^{3+}$, were determined as described previously, as were the $(NH_3)_5CoSCN^{2+}/(NH_3)_5CoNCS^{2+}$ isomer ratios for the first band.[10,11] For the $PO(OCH_3)_3$ complex, an additional band ($(NH_3)_5CoO_2P(OCH_3)_2{}^{2+}$) was observed.[19] It elutes in front of and clear from the NCS^- complexes and was determined as described earlier.[19] All competition experiments were performed in triplicate, and the results

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Table I. Product Distributions, *R*, for the Aquation of $(NH_3)_5CoX^{n+}$ in 1.00 M NaNCS[a] at 25 °C for Leaving Groups X Yielding 3–19% NCS^- Capture

			% $(NH_3)_5Co(SCN)^{2+}$ and % $(NH_3)_5Co(NCS)^{2+}$								
			obsd[b]				corrected[c]				
X	$t_{1/2}$[e]	reacn time	% S	% N	S/N	% S + % N	% S	% N	S/N	% S + % N	*R*[d]
$CH_3SO_3^-$	58 min	5 h	1.8	2.3	0.78	4.1	1.5_4	1.5_6	0.99	3.1_0	0.032
$CF_3SO_3^-$	27 s	5 min	2.6	2.0	1.3_0	4.6	2.6	2.0	1.3_0	4.6	0.048
	27 s	5 h	3.0	3.3	0.91	6.3	2.6_1	2.2_2	1.1_8	4.8_3	0.051
ClO_4^-	7 s	5 min	2.5	2.6	0.96	5.1	2.5	2.6	0.96	5.1	0.054
Me_2SO	8.7_5 h	5 h	0.73_4	1.07	0.69	1.8	2.1_9	2.9_1	0.75	5.1	0.054
			(2.4_0)[i]	(3.4_8)[i]	0.69	(5.8_8)[i]					
$(MeO)_3PO$	34 min[g]	5 h	1.9	2.7	0.70	4.6	2.9_2	3.7_2	0.78	6.6	0.071
	(58 min)[f]		(3.2_2)[h]	(4.6_3)[h]	0.70	(7.8)[h]					
$NH_2CONHC_6H_5$	40 min	5 h[j]	3.2	4.2	0.76	7.4	2.9_1	3.3_9	0.86	6.3	0.067
NH_2COCH_2F	11 min	5 h[k]	4.0	5.6	0.71	9.6	3.6_3	4.5_7	0.79	8.2	0.089
$NH_2SO_2NH_2$	<1 s	5 h[k,l]	4.1	7.7	0.53	11.8	3.7_3	6.6_7	0.56	10.4	0.116
$NH_2SO_2C_6H_4{\cdot}CH_3$	<1 s	5 h[k,l]	4.9	7.8	0.63	12.7	4.5_3	6.7_7	0.67	11.3	0.127
H_2O	33 h[m]	5 h	0.40	1.17	0.36	1.53	3.3_5	9.3_5	0.36	12.7	0.145
$N_3^- + NO^+$	<1 s	5 min[n]	4.5	7.5	0.60	12.0[o]	4.5	7.5	0.60	12.0	0.273
	<1 s	5 min	7.3	11.8	0.62	19.1	7.3	11.8	0.62	19.1	0.236
$NCO^- + H^+$	~1 min	30 min	0.14_4	0.55	0.26	0.69[p]					ca. 0.44[q,r]
$NCO^- + H^+ + NO^+$	~1 min	30 min			0.24				0.24	ca. 22	ca. 0.2_8
$NH_2CO_2^- + NO^+$	~1 min	20 min[q]	3.0	7.5	0.41	10.5	≥3.0	≥7.5	0.41	≥19.0[q]	≥0.235[q]

[a] Note that two entries (see footnotes *o* and *r*) are for [NaNCS] = 0.5 M. [b] Apart from S- and N-bonded $(NH_3)_5Co(NCS)^{2+}$, the other product is $(NH_3)_5CoOH_2^{3+}$, except where noted otherwise. [c] Corrected for $(NH_3)_5Co(NCS)^{2+}$ arising from subsequent NCS^- anation of coformed $(NH_3)_5CoOH_2^{3+}$. Also corrected for side reaction not involving Co–X cleavage (i.e., $\sum(\%\ Co(NCS)^{2+} + \%\ CoOH_2^{3+}) = 100\%$), except where noted otherwise. [d] Conventional *R* factor for metal ion substitution path (Co–X cleavage): $R = [Co(NCS)^{2+}]/[CoOH_2^{3+}][NCS^-]$. [e] Kinetic data largely from: Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470. See also individual entries. [f] Jackson, W. G.; McGregor, B. C. *Inorg. Chim. Acta* **1984**, *83*, 115. [g] Reaction faster in NCS^- media because of parallel C–O cleavage leading to, inter alia, CH_3SCN. [h] Corrected for the parallel C–O cleavage reaction; i.e., the numbers are appropriate to the Co–O cleavage path. [i] Corrected for the incomplete reaction of the Me_2SO complex. [j] Fairlie, D. P.; Jackson, W. G., to be submitted for publication in *Inorg. Chem.* [k] Fairlie, D. P. Ph.D. Thesis, University of New South Wales, 1983. [l] Laird, J. L.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 855. [m] Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642. [n] Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199. See also: Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001. [o] [NaNCS] = 0.5 M; μ = 0.5 M. [p] Uncorrected for substantial side reaction leading to $Co(NH_3)_6^{3+}$ (refer to text and Table II). [q] Calculated by assuming that all $CoOH_2^{3+}$ arises from Co–X cleavage (hence the lower limit). [r] [NaNCS] = 0.5 M; μ = 1.0 M.

were averaged after normalization of cobalt recoveries (which were generally 100 ± 1.5%). Control experiments on the aqua complex in 1.00 M NaNCS were performed as described earlier.[11]

For the reaction of $(NH_3)_5CoOS(CH_3)_2^{3+}$ in 1.00 M NaNCS (pH ~3), reaction mixtures after 5.00 h were quenched by dilution with ice water. Chromatography as above but at 5 °C yielded three well-separated bands, $(NH_3)_5Co(SCN)^{2+}$, $(NH_3)_5CoOH_2^{3+}$, and unreacted $(NH_3)_5CoOS(CH_3)_2^{3+}$, eluted in this order. The last band was treated with sufficient 1 M NaOH to yield $[OH^-] \approx 0.1$ M and then left for 5 min at 20 °C to allow[13] quantitative conversion to $(NH_3)_5CoOH^{2+}$. Cobalt was determined as $(NH_3)_5CoOH_2^{3+}$ (ϵ_{492} 47.7) after reacidification (HCl) to pH ~1. The proportion of recovered Me_2SO complex was found to be 0.69_4, corresponding to $k = 2.0 \times 10^{-5}\ s^{-1}$ (cf. published values:[22] 1.8×10^{-5}, $2.2 \times 10^{-5}\ s^{-1}$).

Induced Hydrolysis. For the very fast acid-catalyzed reactions, solid complex (0.1–0.3 g) either was dissolved directly in the reaction mixture (ca. 25 mL, μ = 1.1 M) or was dissolved by the Y-tube mixing technique[23] described below. For the nitrosation reactions the latter method was used exclusively.

In a typical experiment, one arm of the Y-tube was charged with 5.0 mL of 1.00 M NaNCS and 5.0 mL of 2 M $HClO_4$. The other arm comprised a fresh solution of $[(NH_3)_5CoNCO](ClO_4)_2$ (0.12–0.14 g) in NaNCS (5.0 mL, 1.00 M), and $NaClO_4$ (5.0 mL, 0.40 M) was included to adjust the ionic strength to 1.1 M after mixing. Mixtures of acid and thiocyanate were always freshly prepared because of their instability, especially at high $[H^+]$ and $[NCS^-]$. Also, the concentrations of NCS^- in each arm were arranged to be the same, to avoid the possibility of significant reaction within the time of mixing and where the NCS^- may otherwise not have been uniform throughout the solution; conceivably this could have affected the NCS^- competition. After thermal equilibration at 25.0 °C for 10 min, the reagents were rapidly mixed and the reaction allowed to proceed at 25.0 °C for 30 min. The reaction was quenched by dilution to 600 mL with ice water, and then the mixture was sorbed on and eluted from Sephadex. The first band eluted (0.25 M $NaClO_4$, pH 3) comprised a mixture of $(NH_3)_5CoSCN^{2+}$ and $(NH_3)_5CoNCS^{2+}$, together with $(NH_3)_5CoO_2CNH_2^{2+}$. This was retained for further treatment below. The second band, $(NH_3)_5CoOH_2^{3+}$, was eluted rapidly in front of $Co(NH_3)_6^{3+}$ by adjusting the pH of the eluent (0.25 M $NaClO_4$) to 10; the eluate was acidified for the determination of cobalt as the aqua complex. Finally, the hexaammine was taken from the column with 0.5 M $NaClO_4$. The first band was rechromatographed on Dowex after first destroying the carbamato complex with excess NO^+ (10-fold molar excess of $NaNO_2$, $[H^+]$ = 0.1 M ($HClO_4$); 30 min reaction time followed by the addition of 15 equiv of NaN_3, which instantly destroys residual HNO_2). The S- plus N-linkage isomer mixture was eluted from the column with 1.5 M NaCl, and the aqua complex derived from the carbamate species was eluted with 3 M HCl. All complexes were determined spectrophotometrically, the SCN^- species as described previously,[10,11] the aqua ion from ϵ_{490} 47.7,[2,3] and the hexaammine from $\epsilon_{473.5}$ 56.9.[14]

The nitrosation experiments and product analysis for the reactions of the cyanate-*N* complex in NCS^- media were carried out similarly. One arm of the Y-tube was charged with a mixture of 1.00 M NaNCS and 2 M $HClO_4$ (10 mL) and the other with a mixture of cyanate complex (0.1–0.2 g) and aqueous NaNCS, $NaClO_4$, and $NaNO_2$ to a total volume of 10 mL. These experiments were carried out in duplicate for varied conditions of $[NO_2^-]$, $[NCS^-]$, and $[H^+]$, but always such that $[NCS^-]$ was the same in each arm of the Y-tube prior to mixing and also such that the final ionic strength was 1.1 M. The precise conditions are recorded in Table II; all reaction times were 30 min.

The nitrosation experiments on the carbamate-*O* complex were performed with the Y-tube containing NaNCS (1.0 M, 5.0 mL), $NaClO_4$ (1.6 M, 3.75 mL), and $HClO_4$ (2.0 M, 2.0 mL) in one arm and $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$ (0.1–0.15 g), NaNCS (1.0 M, 5.0 mL), 4.25 mL of H_2O, and $NaNO_2$ (0.080 g) in the other. A reaction time of 20 min (at 25.0 °C) was required to consume all the carbamato complex. In separate experiments the first band off the Sephadex column was treated with excess NO^+ (20 min), and after N_3^- quenching, it was rechromatographed on Dowex; no residual carbamate-*O* complex was detected.

The nitrosation experiments on the azido complex were carried out by using the Y-tube technique to effect mixing of equal volumes of aqueous solutions of complex (up to 1.0 g) and aqueous NaNCS (2.0 or 1.0 M) containing $HClO_4$ (0.1 or 0.05 M) under conditions of supersaturation. Aqueous $NaNO_2$ (2–5 equiv) in an NaNCS solution of the same con-

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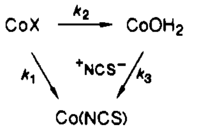
Table II. Observed Product Distributions, *R*, for the Nitrosation[a] of $(NH_3)_5CoNCO^{2+}$ in NaNCS Solution at Ionic Strength 1.1 M and 25.0 °C

entry no.	$[HClO_4]$,[b] M	[NaNCS], M	$[NaNO_2]$,[b] M	$[NaClO_4]$, M	% S[c]	% N[c]	% S + % N[c]	S/N[c]	% carb-*O*[d]	% aqua[e]	% hex[f]	*R*[g]
1	0.5	0.5	0.02	0.08	0.37_5	2.13	2.50	0.18	2.13	8.4	87.0	0.60
					0.49_3	2.08	2.57	0.24	2.17	8.5	86.7	
2	0.5	0.5	0.09	0.01	0.55_1	2.30	2.85	0.24	4.25	21.2	71.7	0.28
					0.57_3	2.41	2.98	0.25	4.37	21.0	71.7	
3	0.25	0.75	0.09	0.01	0.53_2	2.21	2.74	0.24	2.06	13.6	81.6	0.26
					0.53_2	2.18	2.71	0.24	2.10	14.0	81.3	
4	0.75	0.25	0.09	0.01	0.48_2	2.06	2.54	0.23	6.51	28.6	62.4	0.36
					0.51_1	2.09	2.60	0.24	6.51	28.8	62.1	
5	0.5	0.5	0	0	0.14_7	0.54_0	0.68_7	0.27	1.93	3.22	94.2	0.44
					0.13_9	0.56_5	0.70_4	0.25	1.93	3.15	94.2	

[a] Reaction time 30 min. Note that entry 5 refers to the H^+-induced reaction; i.e., there is no NO^+. [b] Initial concentration only. [c] The S- and N-bonded $(NH_3)_5Co(NCS)^{2+}$ isomers. [d] $(NH_3)_5CoO_2CNH_2^{2+}$. [e] $(NH_3)_5CoOH_2^{3+}$. [f] $Co(NH_3)_6^{3+}$. [g] $R = [(NH_3)_5Co(NCS)^{2+}]/[(NH_3)_5CoOH_2^{3+}][NCS^-]$.

centration (after mixing) was then rapidly injected into the mixture before the azido complex could crystallize; reaction (at $\mu = 0.5$ or 1.0 M) was complete in a few seconds. The NCS^- complexes were separated from the aqua complex by the usual chromatographic procedure[10,11] and analyzed as described above.

Data Analysis. The observed NCS^- competition for the relatively slow reactions of the $CH_3SO_3^-$, $PO(OCH_3)_3$, $NH_2CONHC_6H_5$, and CH_2FCONH_2 complexes required a small but significant correction for some $(NH_3)_5CoSCN^{2+}$ and $(NH_3)_5CoNCS^{2+}$ arising from subsequent SCN^- anation of coformed $(NH_3)_5CoOH_2^{3+}$ in the standard 5-h reaction time. The contribution to the observed NCS^- competition from the latter source was determined in control experiments on the aqua complex. For the reaction scheme



the observed competition, measured as [total NCS^- complex]/[total product] ($F_o = [Co(NCS)]/([Co(NCS)] + [CoOH_2])$), is related to the initial competition ($F_i = k_1/(k_1 + k_2)$) by the relation

$$F_i = [F_o(1 - r) + r(1 - e^{-k_0t}) - (1 - e^{-k_3t})]/[e^{-k_3t} - e^{-k_0t}]$$

where $r = k_3/(k_1 + k_2)$ and $k_0 = k_1 + k_2$. The difference between F_o and F_i gives the total thiocyanate complex (N- plus S-bonded forms) arising from the aqua species in the time to complete the reaction, and therefore corrections to the individual S- and N-isomer proportions could be made by knowing[11] that the NCS^- complex derived from $(NH_3)_5CoOH_2^{3+}$ and NCS^- is 26.5% $(NH_3)_5CoNCS^{2+}$ and 73.5% $(NH_3)_5CoSCN^{2+}$. The rate of the S- to N-rearrangement ($t_{1/2} = 9$ days at 25 °C, $k = 8.9 \times 10^{-7}$ s^{-1})[12] is such that it could be neglected. A similar but more complex relationship than the above was used to correct the SCN^- competition observed for the reaction of the $(NH_3)_5CoOP(OCH_3)_3^{3+}$ complex, which involves an additional and significant parallel pathway yielding $(NH_3)_5CoOPO(OCH_3)_2^{2+}$ (41% for 1.00 M NCS^{-19}). Finally, for the very reactive species X = $CF_3SO_3^-$ and ClO_4^-, $r = 0$ and $e^{-k_0t} = 0$, and the above expression simplifies to one where the correction is essentially that directly determined for the blank on the aqua complex. We chose to retain a standard reaction time of 5.0 h (sufficient for complete reaction of all the complexes, X = $(CH_3)_2SO$ excepted) and correct the competition data, rather than use several different reaction times, each sufficiently short so that no (or minimal) corrections were necessary. As can be seen for the $CF_3SO_3^-$ complex, the NCS^- competition data determined for the short reaction time and the corrected data for the long reaction time are the same, indicating the correctness of the analysis.

Results

Table I is a compilation of observed and corrected NCS^- competition data for eight spontaneous, three NO^+-induced, and three H^+-induced aquation reactions. It has been noted previously[32] that "spontaneous" and "induced" are labels that have been perpetuated only for historical[24,25] reasons; there is no fundamental distinction once it is understood that, e.g., the H^+-induced equation of $(NH_3)_5CoNHSO_2NH_2^{2+}$ is equivalent to spontaneous aquation of $(NH_3)_5CoNH_2SO_2NH_2^{3+}$ and the NO^+-induced aquation of $(NH_3)_5CoN_3^{2+}$ is believed[3,25] to involve the hydrolysis of the reactive species $(NH_3)_5Co(N_4O)^{3+}$. Generally speaking, the species involved in the induced aquation reactions are considerably more reactive than those of spontaneous aquation.

In some cases the nature of the reactive species and even the nature of the leaving group are uncertain, but for the purposes of this article this is unimportant. The H^+-induced hydrolysis of the sulfamide complex is a case in point. First, it is likely[15] but uncertain[16,26] that H^+ adds to the coordinated nitrogen rather than the exo oxygen of $(NH_3)_5CoNHSO_2NH_2^{2+}$ to generate the reactive species $(NH_3)_5CoNH_2SO_2NH_2^{3+}$. Second, this complex could first rearrange intramolecularly to the O-bonded linkage isomer,[16] as the closely related $(NH_3)_5CoNH_2SOCH_3^{3+}$ complex does,[27] before ultimately hydrolyzing. Even the slower of these two steps has a half-life shorter than 1 s,[14,26] and since we were concerned here with rapid Co–X cleavage reactions for varied X, the lack of information about the precise nature of Co–X in cases such as this is not of overwhelming concern.

The entry for X = H_2O serves two purposes. First, it was required as a correction for the competition data for the other complexes (see Experimental Section). Second, water can be treated as any other leaving group for the purpose of determining the relative effectiveness of H_2O and NCS^- as entering groups, i.e., determining the anion competition, providing leaving and entering H_2O can be distinguished. Taube[25] (and later others[3]) has done this kinetically, for a variety of entering groups, by comparing the anation and water-exchange rates, and we have performed a similar calculation for NCS^- (Table I). Strictly, the specific water-exchange rate used in this calculation[25] should be that measured for 1.00 M NaNCS, but only values for low- and high-ionic-strength media are available.[28-30] However, these numbers are unlikely to be very different, especially for a poorly ion pairing anion such as NCS^- and for a reaction involving a neutral leaving group. Indeed, for hydrolysis reactions involving neutral leaving groups similar to H_2O, it is *known* that the hydrolysis rates in H_2O and 1 M NaNCS are essentially identical.[31]

Where possible, the competition data have been corrected for side reaction not involving Co–X cleavage, and this is so noted

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(24) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1957**, *79*, 255.

(25) Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199.

(26) Jackson, W. G.; Jurisson, S. S.; Thompson, K. H., to be submitted for publication in *Inorg. Chem.*

(27) Fairlie, D. P.; Jackson, W. G.; Jurisson, S. S. Thompson, K. H., to be submitted for publication in *Inorg. Chem.*

(28) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.

(29) It has been shown that SO_4^{2-}, at quite high concentration levels, only slightly reduces the exchange rate.[30] However, the behavior at intermediate concentration levels remains unknown.

(30) Rutenberg, A. C.; Taube. H. *J. Chem. Phys.* **1952**, *20*, 823.

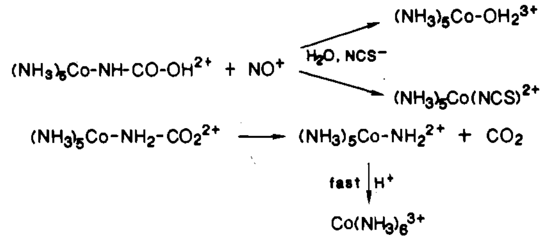
(31) McGregor, B. C. Honours Thesis, University of New South Wales, 1982.

(32) Jackson, W. G. In *The Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, pp 255–357.

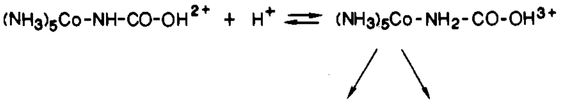
in Table I. The $PO(OCH_3)_3$ complex, for example, reacts partly (41%) by a path involving nucleophilic demethylation of the ligand.[19] The NCS^- competition results have been normalized to correct for this; i.e., the products of Co–X cleavage add up to 100%. The O-bonded phenylurea complex reacts in neutral solution by an intramolecular path leading to the production of some deprotonated N-bonded isomer.[18] This path has been totally suppressed by working in sufficiently acid solution (pH ≤ 2). Finally, mention is made of alternative reaction pathways for several of the O-bonded complexes, e.g., $(NH_3)_5CoOClO_3^{2+}$. It can hydrolyze to $(NH_3)_5CoOH_2^{3+}$ and ClO_4^- by normal Co–O cleavage or by Cl–O cleavage, and the latter route cannot lead to anion incorporation. To determine the site of bond rupture, the necessary ^{18}O-tracer work has been carried out for most[6] of the complexes falling in this category, and all except the carbamate-*O* complex–NO^+ [3] and cyanate–H^+ and –NO^+ reactions[14] behave normally; i.e., there is 100% Co–O cleavage in the product-determining step. For the nitrosation of $(NH_3)_5CoO_2CNH_2^{2+}$, there is 80% Co–O and 20% C–O cleavage in water,[3] but there is no guarantee that these figures pertain to other media such as 1 M NaNCS or HCl. The NCS^- competition (Table I) therefore remains uncorrected for the percent C–O cleavage. For the reactions of the $(NH_3)_5CoNCO^{2+}$ complex, it is known[14] that acid-catalyzed hydration occurs first, even in the presence of NO^+:

$$(NH_3)_5Co{-}NCO^{2+} \xrightarrow{H_2O,\ H^+} (NH_3)_5Co{-}NH{-}CO{-}OH^{2+} \rightarrow (NH_3)_5Co{-}NH_2{-}CO_2^{2+} \xrightarrow{H^+} Co(NH_3)_6^{3+} + CO_2$$

The reaction bifurcates at the second stage, with nitrosation of the N-bonded carbamate complex competing with its decarboxylation:



There is an additional secondary reaction that increases in importance as $[H^+]$ is raised:



Buckingham et al.[14] were able to unravel most of the details of these reactions, by examining the $[H^+]$ and $[HNO_2]$ dependences of both the rates and product distribution with Cl^- as the competitor, and also carried out some ^{18}O-tracer work which showed that the nitrosation of the $(NH_3)_5Co{-}NHCOOH^{2+}$ intermediate, like the protonation reaction, involved an intramolecular path leading first to an O-bonded rearranged species but ultimately to $(NH_3)_5CoOH_2^{3+}$—but without Co–O cleavage. We have attempted to likewise unravel the several possible pathways to products, in particular those paths involving Co–X cleavage and leading to anion (NCS^-) competition. Rate studies have not been carried out, but we have examined in a limited way the $[NCS^-]$, $[H^+]$, and $[HNO_2]$ dependence of the product distribution (Table II). Entries 5, 1, and 2 respectively indicate less $Co(NH_3)_6^{3+}$ and more $(NH_3)_5CoOH_2^{3+}$ as $[HNO_2]$ is raised, consistent with an increased contribution from NO^+ reaction (as opposed to H^+) with the monoprotonated carbamate-*N* complex $(NH_3)_5Co{-}NHCOOH^{2+}$, first formed from the cyanate complex under all conditions. Surprising, however, is the parallel *increase* in carbamate-*O* complex, which is known[14] to arise from the doubly protonated carbamate-*N* species, i.e., suggesting the opposite—an increased contribution from the H^+ rather than NO^+ path. However, it is possible that NO^+ like H^+ assists the N to O rearrangement and that the O-bonded carbamate product survives final degradation by NO^+ in our experiments because it is a fairly slow reaction (and also because HNO_2 reacts with free NCS^-, vide infra). This raises a general problem with slow nitrosation reactions in NCS^- media, namely that nitrosation of the complex could well be competitive with nitrosation of free NCS^-. This has been checked[9,31] for the nitrosation of $(NH_3)_5CoN_3^{2+}$, a relatively fast reaction, and it would appear from the result (Table II) that it is also not a problem even for the slow nitrosation reaction of the carbamate-*O* complex. For the latter reaction, it is our experience that the difficulty is not so much the diminution in the available NCS^- for competition, but rather the loss of HNO_2 so that not all the substrate is consumed. The experimental conditions have been devised to overcome this difficulty for the direct reaction of the carbamate-*O* species, but this could account for the surviving carbamate-*O* in the nitrosation experiments on the N-bonded cyanate.

The results recorded for varied $[H^+]$ at constant $[HNO_2]$ show a systematic decrease in the amount of hexaammine product, concomitant with an increase in the proportion of aqua complex and also the surviving O-bonded carbamate complex. Because of the possible (and variable) loss in carbamate-*O* as a result of subsequent nitrosation, the ratio aqua/carbamate-*O* could not be expected to change systematically with an increased contribution from the NO^+ pathway, and indeed it does not vary smoothly. The other major results recorded in Table II are, first, the essentially constant S/N isomer ratio for the NCS^- complex product, despite a change from the H^+-catalyzed path (entry 5) to conditions where the NO^+ pathway seems to contribute significantly. We do not fully understand the remaining point, namely the essential $[NCS^-]$ independence of the percent of $(NH_3)_5Co(NCS)^{2+}$. Normally this could be expected to vary according to the proportion of reaction via both the H^+ and NO^+ paths, and of course $(NH_3)_5Co(NCS)^{2+}/(NH_3)_5CoOH_2^{3+}$ should be linear in $[NCS^-]$ for each of these paths. This seems to be a compensation in effects in going from one pathway to another, and it appears that the H^+-catalyzed path entails higher NCS^- competition than the NO^+-induced route (Table II).

Discussion

The belief has been held for some time that anions compete much more effectively than solvent water for the so-called induced aquation as opposed to spontaneous aquation.[1,5-8] The first experiments of Pearson and Moore[5] are often quoted as the classic example. In their work NCS^- was used as the competitor for the spontaneous aquation of $(NH_3)_5COONO_2^{2+}$ and, in one case, $(NH_3)_5CoBr^{2+}$; these ions were about the fastest reacting species known at that time which permitted the experiments. For these reactions it was argued that NCS^- anation occurred as a subsequent rather than a concurrent process; however, the study did not admit the possibility of $(NH_3)_5CoSCN^{2+}$ formation in either the primary or secondary reaction, invalidating the basis for their conclusions. Nonetheless, the reexamination of this work has confirmed their claim that there is little direct competition product, and it is interesting to note that the acidato product that *is* formed (~1%) contains a significant amount of the S-bonded isomer.[11] In fairness, it need be noted that the Pearson and Moore experiments[5] predated the discovery[12] of the S-bonded NCS^- complex.

In the light of new data reported herein, the widely held belief that spontaneous aquation gives negligible anion competition compared to that of induced aquation[4-8] must now be challenged. The results of Table I show that the percent NCS^- capture is spread over the range 3–19% for 1 M NCS^- and that it is leaving-group-dependent. Especially interesting is the correlation obtained between the extent of anion capture and reactivity, i.e., the specific rate of hydrolysis (ROH complexes excepted[33]).

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(33) For the ROH complexes, a case can be made for enhanced ion pairing via H bonding localized adjacent to the leaving group. Given that the incoming anion enters adjacent to the leaving group in the pentaammines,[4] higher anion competition can then be coupled with ion pairing in the sense of an inherited ion atmosphere, as discussed in ref 13.

These new NCS^- competition results emphasize the artificiality[32] of the distinction between spontaneous and induced aquation and suggest a "continuum" based on leaving-group dependency rather than the former two discrete categories of reaction, the spontaneous (slow) and induced (fast) processes. Furthermore, it is tempting to suggest that NCS^- capture would be less than 3.1% (Table I) for a complex less reactive than $(NH_3)_5CoO_3SCH_3^{2+}$ and more than 19% for a complex more reactive than $(NH_3)_5Co(N_4O)^{3+}$.

The idea of a "continuum" in competition behavior needs qualification. The reactivity of the $(NH_3)_5CoX^{n+}$ species, and hence the observed anion competition, cannot be increased ad infinitum. Indeed, it has been reasoned that, for the nitrosation reaction of $(NH_3)_5CoN_3^{2+}$, the specific rate for the reactive species $(NH_3)_5Co(N_4O)^{3+}$ approaches the diffusion-controlled limit,[34] and therefore by our argument the ceiling for anion competition may have already been reached.

On the evidence presented here we adopt the view that the unique and discrete intermediate $Co(NH_3)_5^{3+}$ is *not* involved in any of the substitution reactions of $(NH_3)_5CoX^{n+}$ species, not even for the rapid induced aquation reactions typified by the nitrosations of $(NH_3)_5CoN_3^{2+}$ and $(NH_3)_5CoO_2CNH_2^{2+}$. Indeed, we now have justification for regarding the very similar competition ratios (*R* values)[1-3,14] exhibited for the several independent methods of generating the supposed common intermediate $Co(NH_3)_5^{3+}$ as coincidental. The previous data were very largely for NO_3^- and Cl^- as competitors, and the belief that their *R* values represented upper limits characteristic of a discrete $Co(NH_3)_5^{3+}$ intermediate was reached because the competition was apparently independent of the source of the intermediate. The NCS^- competition data (Table I) now dispel this belief. For competitors such as Cl^-, Br^-, and NO_3^- the competition has been argued to be the same for the two nitrosation reactions,[3] and while a similar case could be held for the total NCS^- competition (and note that the *R* value for the carbamate-*O* reaction is a *minimum* value[35]), the S/N product ratios are quite different (Table I). Furthermore, the S/N ratios vary significantly from one reaction to another and seem to defy rationalization.

The present data for NCS^- competition emphasize that the similarity in product distribution results for the less discriminating anions NO_3^-, Br^-, and Cl^- probably reflects similar rates for the generation of the "intermediate" by the induced routes. Indeed, differences in the extent of anion competition for some induced aquations previously existed;[1,2,36] anion competition accompanying the Cl_2 oxidation of bound dimethyl sulfoxide in $(NH_3)_5CoOS(CH_3)_2^{3+}$ is one notable example.[36] This anomaly would disappear if parallel "direct anion injection" paths were possible for some inducing agents; these would appear in the rate law and, accordingly, could be corrected for. Until complete rate law studies have been carried out, these reactions are candidates for inclusion in the "continuum" and are not necessarily anomalous. The difficulties in correctly deciphering the coupling of rate laws and product distributions have been exposed previously.[2]

For the hydrolysis reactions conducted in NCS^- media that we report here, some S-bonded NCS^- isomer is produced in every case, just as would be expected in dissociative substitution reactions. Previously[1,9,12] the capture of the S center was believed to be a feature of octahedral Co(III) substitution where reduced-coordination-number intermediates were involved, i.e., limiting dissociative reactions. Now it is apparent that it is the norm, not the exception, and is indicative of an intimate (d)[38] rather than stoichiometric (D)[38] mechanism. The capture of the S of NCS^- for spontaneous aquation has recently been exploited[39] in a convenient synthesis of $[(NH_3)_5CoSCN]Cl_2$, utilizing the reaction between $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ and 10 M aqueous NaNCS, albeit it is less efficient than published[10,12] methods.

How good a leaving group is required to generate a discrete $Co(NH_3)_5^{3+}$ intermediate? Can any of these reactions involve such a species? If they do not, why do better leaving groups lead to enhanced competition? The original notion[24,25] of the induced aquation reaction was that the lifetime of the intermediate could be extended by the very rapid loss of X from a $(NH_3)_5CoX^{n+}$ species, although it has never been clear how this might affect the energy barrier for the subsequent decay of the $Co(NH_3)_5^{3+}$ ion and, hence, its lifetime. Nonetheless, the present data very much strengthen this view, and there is a need now to consider the concept of a single intermediate but one which displays properties dependent upon its source. It has always been recognized[1] that the discrete reduced-coordination-number intermediate $Co(NH_3)_5^{3+}$, if indeed it existed, was so short-lived that its rate of decay was determined largely by abstraction of Y from its solvation sheath, rather than by bond making to incoming Y. The NCS^- competition data support this view, although the concept of a single reaction pathway via a common intermediate with unique properties must now be foregone. If the concept of a variable-lifetime intermediate is accepted, it seems reasonable that with more rapid generation the intermediate survives longer and in so doing becomes more discriminating; i.e., bond making with the incoming ligand becomes more important.

We have refrained from labeling the mechanism for any of these reactions as I_d, which by definition[38] they all surely are, because at least for the present series of reactions we regard these otherwise accepted mechanism classification schemes as inadequate. We are not alone in this view,[39] and the point is elaborated in a subsequent paper.

The leaving-group dependence for the competition data implies that the intermediate decays more rapidly than the leaving group diffuses to the bulk solution. By implication, it therefore cannot survive for the time required for the diffusion of ions in the bulk solution to the secondary solvation sheath, and certainly not for the time of equilibration with the bulk solution. This view appears to be tantamount to denying the existence of any sort of $Co(NH_3)_5^{3+}$ intermediate in all the $(NH_3)_5CoX^{n+}$ reactions studied, and further it implies that anion competition must arise from preassociation, i.e., an ion pair. However, it proves very difficult to account for the observed anion competition simply in terms of ion pairing. This problem has been discussed previously for the induced aquation reactions,[2,34,36] and we should note that there is a dichotomy of views. For the other reactions recorded in Table I there is no apparent correlation of total NCS^- competition with ion-pairing constants.[33] For example, the 3+ cations do not systematically give more anion competition than the 2+ species—the large spread amongst the 3+ ions themselves merges at the low-competition end with the (smaller) spread for the 2+ ions. More direct experimental evidence for the continued case of intermediate formation in $(NH_3)_5CoX^{n+}$ substitution reactions must await subsequent publications where we specifically attack the proposition of ion-paired reactants leading directly to competition product.

The evidence for the existence of energy minima (i.e., genuine intermediates) en route to products is very strong in at least some cases of base-catalyzed cobalt(III) substitution, but it is doubtful that a general case can be mounted.[1,4,32] Nonetheless the best evidence for such species exist there, and it seems that although they are still undoubtedly short-lived species, their lifetime is extended sufficiently to enable an experimental probe to detect their existence more readily. It has been seen that one such technique is the demonstration of competition properties independent of the source of the intermediate, and a very relevant observation is that the NCS^- competition results for the OH^--catalyzed substitution reactions of $(NH_3)_5CoX^{n+}$ ions display only a small leaving-group dependence.[10] More significantly, the S/N

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(34) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1982**, *21*, 3353.

(35) Presumably there is some reaction via C–O cleavage; in water the figure is 20%.[3]

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isomer ratios are absolutely constant[10] for some 11 leaving groups, a fact which contrasts sharply with the acid hydrolysis results reported in Table I. Indeed, the product ratios for the OH^--catalyzed reactions of pentaamminecobalt(III) species, defined not only by total anion competition[1] but also by ratios of linkage isomers[10,41,42] as well as geometric and optical isomers,[1,4,32] are generally less leaving-group sensitive compared to their "spontaneous" and "induced" aquation counterparts. In this light it does not seem unreasonable to discuss the substitution processes in terms of transient five-coordinate species that exist for lifetimes sometimes shorter and sometimes longer than the diffusion times associated with anion transferral (including the leaving group) between the solvation shell of the complex and the bulk solution.

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Preparation and Substitution Reactions of (Diphosphine)platinum(II) Carboxylate Complexes

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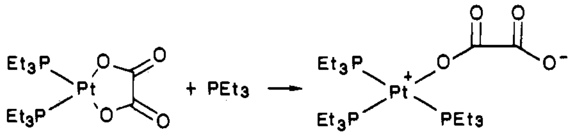
$[Pt(OCOPh)_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane), [Pt(mal)(dppe)] (mal = malonate), and [Pt(mal)(dppm)] (dppm = bis(diphenylphosphino)methane) are prepared by treatment of $[PtCl_2(dppe)]$ or $[PtCl_2(dppm)]$ with AgOCOPh or Ag_2(mal). $[Pt(OCOPh)_2(dppe)]$ reacts with P-*n*-Bu_3 to yield $[Pt(OCOPh)(P\text{-}n\text{-}Bu_3)(dppe)]^+$, which subsequently reacts with chlorinated solvents to produce $[PtCl(P\text{-}n\text{-}Bu_3)(dppe)]^+$. Analogously, [Pt(mal)(dppe)] gives $[PtCl(L)(dppe)]^+$ when treated with P-*n*-Bu_3, PEt_3, or $PMePh_2$. In the case of L = P-*n*-Bu_3 the intermediate $[Pt^+(OCOCH_2COO^-)(P\text{-}n\text{-}Bu_3)(dppe)]$ is observed spectroscopically at low temperature and may be protonated with $HClO_4$. The ease of substitution of dicarboxylate or diphosphine ligands is investigated by allowing $[Pt(\overset{\frown}{O\,O})(\overset{\frown}{P\,P})]$ ($\overset{\frown}{O\,O}$ = C_2O_4, mal; $\overset{\frown}{P\,P}$ = dppe, dppm) to react with P-*n*-Bu_3. [Pt(mal)(dppm)] reacts with 2 molar equiv of P-*n*-Bu_3 or $PMePh_2$ to give ion-paired species of the form $[Pt(L)_2(dppm)][mal]$.

Introduction

Halide substitutions by neutral ligands in complexes of the type $[PtCl_2(\overset{\frown}{P\,P})]$ ($\overset{\frown}{P\,P}$ = diphosphine) have been reported by Davies et al.,[1] and we have recently described a detailed spectroscopic study of the reactions of $[PtCl_2(\overset{\frown}{P\,P})]$ complexes with tertiary phosphines.[2] Information about the substitution chemistry of (diphosphine)platinum carboxylate complexes is scant, however. Many of the substitution reactions of platinum(II) carboxylate complexes containing monodentate ligands are presented in the literature in terms of their synthetic utility. Paonessa et al.,[3] for example, have reported that the triphenylphosphine ligands in $[Pt(C_2O_4)(PPh_3)_2]$ may be displaced by more nucleophilic ligands such as PMe_3, PEt_3 or P-*n*-Bu_3, (eq 1). Similarly, diethyl sulfide is readily displaced from $[Pt(C_2O_4)(SEt_2)_2]$ by treatment with PEt_3 or PPh_3,[3] and $[Pt(OCOMe)_2(SEt_2)_2]$ is converted to $[Pt(OCOMe)_2(PPh_3)_2]$ by treatment with triphenylphosphine.[4]

$$[Pt(C_2O_4)(PPh_3)_2] + 2L \rightarrow [Pt(C_2O_4)L_2] + 2PPh_3 \qquad L = PMe_3,\ PEt_3,\ P\text{-}n\text{-}Bu_3 \tag{1}$$

In each of the above examples it is the neutral ligand that is displaced, while the carboxylate ligand remains coordinated, but Paonessa et al. have described a reaction in which a carboxylate ligand is displaced from the platinum center.[3] When a CH_2Cl_2 solution of $[Pt(C_2O_4)(PEt_3)_2]$ is treated with excess PEt_3 an associative exchange of PEt_3 occurs, and a species of the form $[Pt(C_2O_4)(PEt_3)_3]$ is observed at low temperature (eq 2).



(2)

In this paper we report the preparation of some platinum(II) carboxylate complexes containing diphosphine ligands and their substitution reactions. The latter are complicated by reaction of the substitution products with chlorinated solvents, and these secondary reactions are discussed also. A preliminary account of part of this work has appeared.[5]

Results and Discussion

The platinum(II) oxalate and malonate complexes are prepared by the reaction of $[PtCl_2L_2]$ (L_2 = dppe, dppm) with 1 molar equiv of the appropriate silver(I) salt in CH_2Cl_2 solution, and they have been characterized by elemental analysis and infrared and $^{31}P\{^1H\}$ NMR spectroscopy. The data for the oxalate complexes have been reported previously.[6]

The infrared spectra of the oxalate complexes are characteristic of oxalate bound to the metal to form a five-membered ring.[3,7] The malonate complexes exhibit similar infrared spectra, for which band assignments are based on those reported previously.[8] Very broad absorptions appear at 1650 cm^{-1} for [Pt(mal)(dppe)] and 1640 cm^{-1} for [Pt(mal)(dppm)], and their shapes suggest that they are composites of several overlapping bands. These are

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