value of 3.1 Å for VO^{2+} in DMF,[24] or 3.2 Å for Co(*trans*-[14]diene)$^{2+}$.[25] The longer distance for $CuCR(DMF)^{2+}$ could be due to tetragonal distortion with elongation of the Cu–DMF bond.

A lower limit of 5×10^4 sec^{-1} at −60° is estimated for the solvent exchange rate constant in this system.

Discussion

For all the systems described here the solvent exchange rate appears to be larger than the solvent proton relaxation rate in the first coordination sphere of the metal ion ($\tau_M^{-1} > T_{2M}^{-1}$). The alternative, that exchange is slower, would require that the observed line broadening is entirely due to outer-sphere effects. This seems unlikely because it requires that the $(T_{2O})^{-1}$ values in Table I be increased by ~30%. The latter can only be done by making d_0 unreasonably short (by a factor of ~1.5), or by increasing the correlation times by about a factor of 3. Such a change is considered unlikely because the correlation times used here are consistent with the EPR spectral line widths of various vanadyl complexes[18] in various solvents, and have been used successfully in the interpretation of other NMR systems.[26–28]

The estimates of the lower limit of the solvent exchange rates do not indicate that these systems are very labile. However, the limits given are conservative in that they apply at the lowest temperature attained in the particular solvent. If a rather low activation energy for exchange of 5 kcal mol^{-1} is assumed, then the exchange rates at 25° for Co(*trans*-[14]diene)$^{2+}$ in methanol, acetonitrile, and DMF are calculated to be $>9 \times 10^5$ sec^{-1}, $>1.3 \times 10^5$ sec^{-1}, and $>3 \times 10^6$ sec^{-1}, respectively. These values are about an order of magnitude greater than those for high-spin, hexasolvated, cobalt(II) complexes. However, the estimates are too uncertain to permit any discussion of the effect of the Schiff base and the low-spin configuration on lability.

The results in water, methanol, and acetonitrile, at least, indicate that eq 12 and 13 can be used to describe the temperature dependence of $(T_{2P}P_M)^{-1}$ in the absence of exchange effects (i.e., T_{2M}^{-1}). The added $1/T$ factor in eq 13 does not affect the fitting of the results, but makes the exponential factor smaller, and in much better agreement with that predicted from the temperature dependence of the solvent viscosity. It would appear that ambiguities encountered in fitting previously studied systems[28,29] could be significantly reduced by the use of eq 13 with the temperature dependence of the viscosity ($f_T(\eta)$) treated as a known function.

Acknowledgment. Support for this research by the National Research Council of Canada is gratefully acknowledged. L.R. wishes to thank the National Research Council for support through a postgraduate scholarship.

Registry No. Co(*trans*-[14]diene)$(ClO_4)_2$, 15387-88-9; $CoCR(ClO_4)_2$, 57066-21-4; $CuCR(BF_4)_2$, 57066-22-5; H_2O, 7732-18-5; CH_3OH, 67-56-1; CH_3CN, 75-05-8; DMF, 68-12-2; Co(*trans*-[14]diene)$(BF_4)_2$, 57066-23-6.

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Aqueous Complexes of Gallium(III)

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The dilute aqueous coordination chemistry (25 °C, $\mu = 0.10$) of gallium(III) is described with 16 multidentate ligands which include various polyaminopolycarboxylic acids, hydroxyalkylaminocarboxylic acids, polycarboxylic acids, and phenolic aminocarboxylic acids. Quantitative interactions have been measured and equilibrium constants calculated through spectrophotometric determination of metal–metal competition, potentiometric measurement of hydrogen ion displacement, and ligand–ligand competition determined by potentiometric measurement of hydrogen ion concentration. Depending on the ligand and pH, the metal-containing species formed were found to fall within the bounds of the following stoichiometry: $Ga_a(OH)_bH_cL_d$, where $1 < a < 3$, $0 < b < 4$, $0 < c < 3$, $1 < d < 3$. The conditions and limitations for the applicability of each method are delineated and the results are discussed in terms of both internal consistency and relevance to previously published work.

Introduction

Since it has been reported that the gallium(III) ion exhibits considerable anticancer activity,[1,2] the possibility of using various ligands as metal carriers in chemotherapy has increased the need for a more extensive study of the aqueous coordination chemistry of gallium. The literature on this subject is very limited and in most cases inconsistent and contradictory. For these reasons the protonation, stability, and hydrolysis constants of the gallium chelates of the multidentate ligands *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED), ethylene-1,2-bis(*o*-hydroxyphenylglycine) (EHPG), triethylenetetraaminehexaacetic acid (TTHA), diethylenetriaminepentaacetic acid (DTPA), *N*-hydroxybenzyliminodiacetic acid (HBIDA), cyclohexanediaminetetraacetic acid (CDTA), ethylenediaminetetraacetic acid (EDTA), *N*-hydroxyethylethylenediamine-*N*,*N'*,*N'*-triacetic acid (HEDTA), *N*,*N'*-ethylenediaminediacetic acid (SEDDA), *N*,*N*-ethylenediaminediacetic acid (UEDDA), nitrilotriacetic acid (NTA), *N*,*N*-bis(2-aminoethyl)glycine (DTMA), *N*,*N'*-diglycylethylenediamine-*N''*,*N'''*-tetraacetic acid (DGENTA), *N*-hydroxyethyliminodiacetic acid (HIDA), iminodiacetic acid (IDA), and citric acid (CA) have been determined. Unlike the majority of previous studies of gallium, the hydrolysis of the unchelated metal ion has been taken into consideration in the calculation of the stability constants. These stability constants have been determined by three different techniques: 1, spectrophotometric metal–metal competition; 2, normal potentiometric titration; 3, a relatively new method of ligand–ligand potentiometric competition titrations of gallium with two ligands present. The stability constants of several complexes have been determined by two of the three methods, and the average results are reported.

Procedure

All titrations were carried out in a sealed, thermostated vessel (25.00 ± 0.05 °C) under a CO_2-free nitrogen atmosphere using CO_2-free standard 0.1 M KOH. Solutions were brought to 0.10 M ionic strength by the addition of KNO_3. The hydrogen ion concentration was measured using a Beckman Research model pH meter adjusted with standard HCl to read $-\log [H^+]$ directly.

HBED,[8] HBIDA,[3] DGENTA,[5] DTMA,[6] and UEDDA[7] were prepared in these laboratories while the remaining ligands were obtained commercially. The purity of each ligand was confirmed by potentiometric titration of the free ligand with standard KOH.

Standard solutions of $GaCl_3$ were prepared from solutions of weighed samples of 99.99% pure gallium metal in concentrated HCl, after evaporation to about 25% volume three times to remove most of the excess HCl. Some excess acid was always allowed to remain in order to prevent hydrolysis of the metal ion. The exact amount of acid was determined by titration of 1:1 ratios of gallium with EDTA or HBIDA. The amount of KOH consumed in excess of the amount needed to neutralize all of the ligand protons represents the excess HCl.

The electronic spectra were obtained on a Cary 14 spectrophotometer using 1-cm and 5-cm matched cells. Solutions were adjusted to 0.10 M ionic strength by the addition of KNO_3 except when ultraviolet spectra of solutions of HBIDA were measured, in which case KCl was used as the supporting electrolyte.

Results

Ligand protonation constants for TTHA, DTPA, triethylenetetramine (trien), CA, SEDDA, and HEDTA were calculated from potentiometric titration of the free ligand using an iterative protonation computer program described previously.[3] Protonation constants were expressed as

$$K_n = [H_nL]/[H_{n-1}L][H^+] \tag{1}$$

For HBED, CDTA, DGENTA, DTMA, EDTA, HBIDA, IDA, NTA, UEDDA, and HIDA the values of the ligand protonation constants were taken from the literature. The sets of protonation constants used in the calculation of the stability constants for each ligand are shown in Table I.

Protonated Chelates. The chelate protonation constants were expressed in the same form as the ligand protonation constants

$$K^H{}_{MH_nL} = [MH_nL]/[MH_{n-1}L][H^+] \tag{2}$$

In the cases where the protonated complexes were essentially 100% formed prior to the onset of the deprotonation reactions, $K^H{}_{MH_nL}$'s were calculated using the ligand protonation computer program. When the formation and deprotonation equilibria overlapped one another, the values of $K^H{}_{MH_nL}$ were chosen so that they minimized the average deviation in the calculation of the chelate stability constant. The final values of $K^H{}_{MH_nL}$ are listed in Table II.

Table I.[a] Logarithms of Protonation Constants of Ligands Used in This Study

Ligand	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	Ref
TTHA	10.63 (1)	9.58 (1)	6.17 (1)	4.07 (1)	2.78 (1)	2.20 (1)	This work
DTPA	10.56 (1)	8.64 (1)	4.29 (1)	2.74 (1)	2.11 (1)		This work
HBED	12.46	11.00	8.32	4.64			4
CDTA	12.30	6.12	3.53	2.42			4
EHPG	11.85	10.56	8.78	6.39			4
DGENTA	7.31	6.15	2.70	1.98			5
DTMA	10.81	9.59	3.24	2.42			6
EDTA	10.17	6.11	2.68	2.00			4
trien	9.85 (1)	9.23 (1)	6.82 (1)	3.77 (1)			This work
CA	5.74 (1)	4.36 (1)	2.91 (1)				This work
SEDDA	9.67 (1)	6.57 (2)	2.36 (2)				This work
HEDTA	9.92 (2)	5.41 (3)	2.51 (1)				This work
HBIDA	11.71	8.07	2.34				3
IDA	9.34	2.61	1.82				4
NTA	9.65	2.48	1.84				4
UEDDA	11.13	5.65					7
HIDA	8.66	2.20					4

[a] All values listed are for 25.0 °C and $\mu = 0.10$ M (KNO_3).

Table II. Logarithms of Chelate Protonation Constants[a,b]

Ligand	log $K^H{}_{MHL}$	log $K^H{}_{MH_2L}$	log $K^H{}_{MH_3L}$
TTHA	5.6 (1)	3.62 (5)	2.58 (2)
DTPA	4.16 (1)		
CDTA	2.7 (1)		
EDTA	1.7 (1)		
DGENTA	3.75 (5)		

[a] All values listed are for 25.0 °C and $\mu = 0.10$ M (KNO_3).
[b] Equation 2.

Hydrolysis Constants. Protonation constants of hydrolyzed chelates, hereafter referred to as hydrolysis constants, were expressed as shown in eq 3. In the cases where the chelate

$$K^n{}_{OH} = [M(OH)_{n-1}L]/[M(OH)_nL][H^+] \tag{3}$$

had a relatively low stability constant and two or more water-coordinated sites, the hydrolysis log *K* was found to be very low and, as with the chelate protonation constants, had to be determined by minimizing the average deviation in the stability constant.

In all cases where the hydrolysis log $K^n{}_{OH}$ was about 4.0 or higher, it was possible to calculate the constant separately. For these calculations the quantity T_{OH} was defined as the total concentration of base added in excess of the amount necessary for the complete formation of the normal 1:1 chelate. From charge balance one could then write

$$[MOHL] = T_{OH} + [H^+] - [OH^-] \tag{4}$$

and from mass balance, the concentration of ML was calculated as

$$[ML] = T_M - [MOHL] \tag{5}$$

where T_M represents the analytical concentration of metal. Values of $K^1{}_{OH}$ were obtained by plotting $\{T_{OH} + [H^+] - [OH^-]\}[H^+]$ vs. [ML], which yielded straight-line graphs of zero intercept with a slope equal to $1/K_{OH}$. Both the linearity of the plot and any deviations from a zero intercept were considered in evaluating the results. Values of $K^1{}_{OH}$ were also calculated using the ligand protonation constant program. In all cases the values from the two methods were found to be

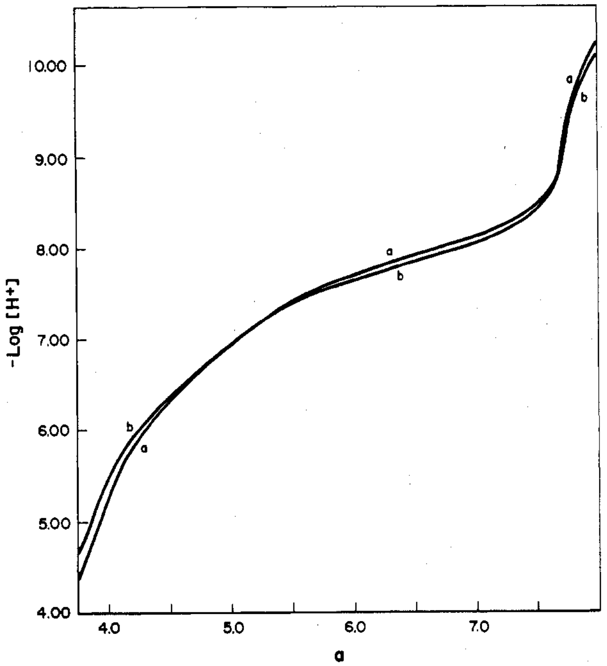

Figure 1. Potentiometric titration curves of 1:1 gallium (III)-diglycylethylenediaminetetraacetic acid indicating a complex polymerization reaction: curve a, $T_L = T_M = 2.50 \times 10^{-3}$ M; curve b, $T_L = T_M = 1.25 \times 10^{-3}$ M; $\mu = 0.100$ (KNO$_3$), $t = 25.0$ °C [a = moles of 0.10 M KOH added per mole of ligand present].

in excellent agreement. The dual calculation of the hydrolysis constants was designed to detect the formation of possible polynuclear species. Such species were detected only with the ligands DGENTA and citric acid.

In the case of DGENTA at two concentrations, the potentiometric titration curves shown in Figure 1 indicate a long buffer region from a = 4.0 to a = 7.75, where a is equal to the moles of base added per mole of ligand. The nonintegral break in the curve and the concentration dependence of the titration curve strongly suggest the formation of polynuclear species. However, it was not possible to determine exactly what species were present, since calculations using several models were done and yet would not adequately fit the experimental data.

The titration curves of 1:1 ratios of gallium to citric acid indicate polymerization at low pH and are described below. As shown in Figure 2, there is a buffer region at higher pH from a = 4.33 to a = 7.0, which apparently describes the breakdown of the polymer into smaller, more extensively hydrolyzed species, since the final break occurs at an integral a value and the curves display an inverse dependence on concentration compared to what one would expect to result from a polymerization reaction. As in the case of DGENTA, it was not possible to determine precisely what species were involved, and no definitive equilibrium constants could be calculated.

A serious problem in the determination of chelate hydrolysis constants is the amphoteric property of the gallium(III) ion. The dissociation of the metal ion from the complex at high pH was not marked by precipitation of the metal, as is the case with most transition elements. For this reason it was often unclear whether a particular upper pH buffer region was the result of continuing chelate hydrolysis or whether the complex was breaking apart with further hydrolysis of the metal ion. In the case of HBIDA, the strong similarity between the ultraviolet spectra of the chelate and the free ligand at high pH, as shown in Figure 3, seems to indicate the possible dissociation of the complex beginning as low as pH 9.5. Since this ligand formed one of the most stable gallium complexes studied, no hydrolysis constants for ligands of lower stability having a calculated value of log $K^n{}_{OH}$ greater than 9.5 have been reported. The chelates of HBED, EHPG, and TTHA showed no signs of hydrolysis over the entire pH range studied. The values for the chelate hydrolysis constants calculated at 25.0 °C and 0.10 M ionic strength are summarized in Table III.

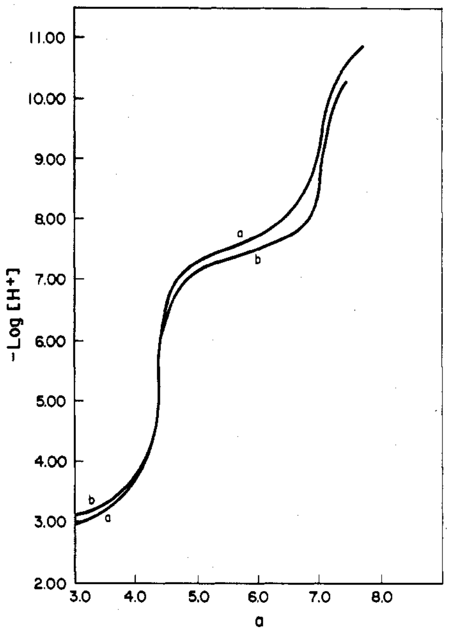

Figure 2. Potentiometric titration curve of the 1:1 gallium(III)-citrate system indicating difference in degree of formation at low pH and polymerization at higher pH: curve a, $T_L = T_M = 2.50 \times 10^{-3}$ M; curve b, $T_L = T_M = 1.25 \times 10^{-3}$ M; $\mu = 0.100$ (KNO$_3$), $t = 25.0$ °C [a = moles of 0.10 M KOH added per mole of ligand present].

Table III. Protonation Constants of Hydrolyzed Chelate for Gallium-Ligand Systems[a]

Ligand	log $K^1{}_{OH}$	log $K^2{}_{OH}$	Ligand	log $K^1{}_{OH}$	log $K^2{}_{OH}$
DTPA	7.51 (1)		NTA	4.27 (2)	7.64 (3)
CDTA	7.48 (1)		UEDDA	3.96 (2)	7.6 (1)
HBIDA	5.75 (2)	8.53 (2)	IDA	3.5 (1)	
EDTA	5.52 (5)		HIDA	3.25 (9)	5.48
SEDDA	4.70 (5)	7.6 (1)	CA	2.9 (1)	
HEDTA	4.38 (3)		DTMA	2.6 (1)	

[a] $K^n{}_{OH}$ defined in eq 3.

Stability Constants. The normal chelate stability constants were expressed as shown in eq 6. ML represents the normal

$$K_{ML} = [ML]/[M][L] \tag{6}$$

unprotonated, unhydrolyzed chelate, M represents the free, unhydrolyzed aquometal ion, and L represents the uncomplexed, totally deprotonated form of the ligand. Three different methods were used to determine chelate stability constants: metal–metal spectrophotometric competition, potentiometric titration of 1:1 metal–ligand solutions, and ligand–ligand potentiometric competition titrations.

a. Metal–Metal Spectrophotometric Competition. Because of the completely filled d shell of the gallium(III) ion, it was not possible to use spectrophotometric measurements to determine the degree of ligand–ligand competition. However, in the cases of HBED, EHPG, and HBIDA, it was possible to take advantage of the strong visible absorbance bands of the ferric chelates of these ligands. The extinction coefficients of the 485-nm band of FeHBED, the 418-nm band of FeHBIDA, and the 480-nm band of FeEHPG were found to be 3940, 1100, and 4660 cm^{-1} M^{-1}, respectively. In addition,

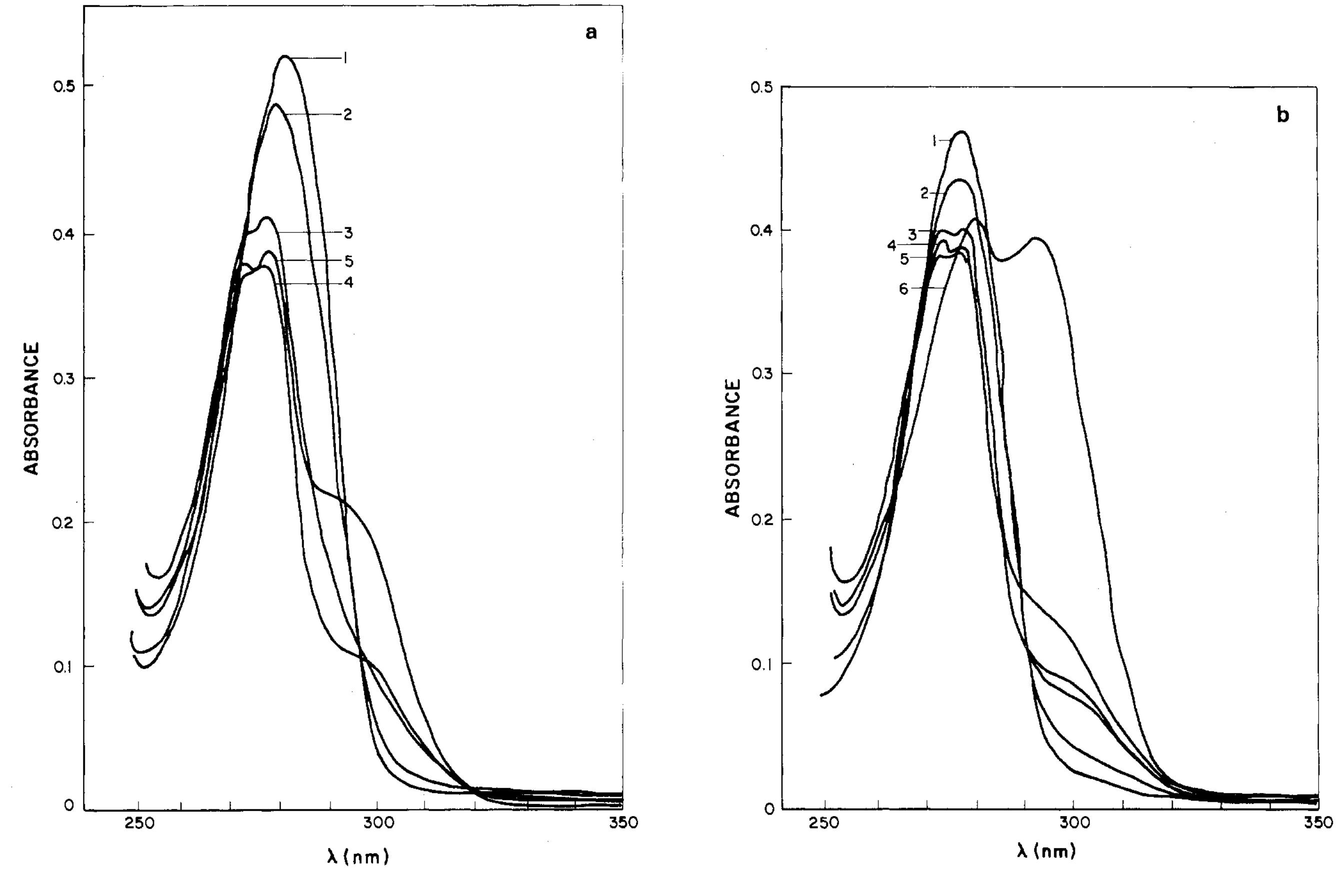

Figure 3. (a) Aqueous ultraviolet absorption uv spectra of Ga(III)–HBIDA (hydroxybenzyliminodiacetic acid) as a function of pH: 1, 7.00; 2, 8.40; 3, 9.62; 4, 10.70; 5, 11.54 pH units; t = 25.0 °C, μ = 0.100 M (KCl). (b) Aqueous uv absorption spectra of HBIDA at 25.0 °C, μ = 0.10 M, as a function of pH: 1, 7.63; 2, 8.16; 3, 9.09; 4, 10.01; 5, 11.06; 6, 12.03 pH units.

experiments were run using NTA with copper(II) as the competing metal ion. The extinction coefficients of the Cu–NTA chelate and the solvated copper ion at 740 nm were determined to be $\epsilon_{\text{Cu-NTA}} = 58.4$ and $\epsilon_{\text{Cu}^{2+}} = 9.8$ cm^{-1} M^{-1}. In no instance did the gallium(III) chelate or the free gallium(III) ion have an appreciable absorbance in the wavelength range studied. Literature values were used for the stability constants of the ferric chelates of HBED,[4] EHPG,[8] and HBIDA[3] and the cupric complex of NTA.[4]

The concentration of the absorbing chelate was readily calculated from the measured visible absorbance of solutions of 1:1 ratios of ligand and gallium with various ratios of competing metal ion. Using this information, the measured hydrogen ion concentration, and the gallium and ferric hydrolysis constants, it was possible to determine the concentrations of all of the other species GaL, Ga^{3+}, and M (where M = Fe^{3+} or Cu^{2+}) from the mass balance equations. It was assumed that the concentration of uncomplexed ligand was zero. To ensure that equilibrium was being reached, the order of mixing of the solutions was varied such that in some cases the competing metal was added to solutions of the gallium chelate, while in others the gallium was added to solutions of the chelate of the competing metal.

A displacement constant K_X was calculated as

$$K_X = \frac{[\text{GaL}][\text{M}^{n+}]}{[\text{ML}][\text{Ga}^{3+}]} = \frac{K_{\text{GaL}}}{K_{\text{ML}}} \qquad (7)$$

Both $[Ga^{3+}]$ and $[M^{n+}]$ represent the concentration of *unhydrolyzed* metal ion, not total unchelated metal. The metal hydrolysis constants used to calculated the concentration of free metal were expressed in the same form as the chelate hydrolysis constants already discussed. The values used for the hydrolysis constants of gallium were log K^1_{OH} = 2.91, log K^2_{OH} = 3.70, and log K^3_{OH} = 4.40.[9] The only iron(III) hydrolysis constant used was log K^1_{OH} = 2.63,[10] and it was assumed that in the pH range of 2.0–3.5 used in the study of CuNTA, the hydrolysis of free copper(II) ion was negligible. The results obtained by this method are shown in Table IV.

Table IV. Parameters and Results of Metal-Metal Competition Determinations of log K_{GaL}[a]

Ligand	M	−log [H⁺]	log K_X	log K_{ML}	log K_{GaL}
NTA	Cu^{2+}	2.0–2.5	3.30	12.94	16.20[b] (5)
HBIDA	Fe^{3+}	2.42	0.15	21.40	21.55 (3)
EHPG	Fe^{3+}	2.85	−0.30	31.91	31.61 (1)
HBED	Fe^{3+}	2.83	−0.11	39.68	39.57 (1)

[a] All values listed are for 25.0 °C and μ = 0.10 M (KNO_3).
[b] Value shown is the average of results obtained by two different methods.

b. Potentiometric Titrations. Whenever possible the K_{ML}'s as expressed in eq 6 were calculated directly from the potentiometric titration data of the 1:1 metal–ligand systems. The titration curves are shown in Figure 4. This was done by solving the simultaneous mass and charge balance equations to determine the concentrations of the three unknowns

$$T_{\text{L}} = A_1[\text{L}] + X_1[\text{ML}] \qquad (8)$$

$$T_{\text{M}} = Y_1[\text{M}] + X_1[\text{ML}] \qquad (9)$$

$$B = A_2[\text{L}] + Y_2[\text{M}] + X_2[\text{ML}] \qquad (10)$$

The quantity B in eq 10 was defined as

$$B = [\text{K}^+] + [\text{H}^+] - [\text{Cl}^-] - [\text{OH}^-] \qquad (11)$$

The coefficients A_n, X_n, and Y_n are the usual pH distribution functions of protonation and hydrolysis constants and hydrogen ion concentration. A list of stability constants determined by this direct procedure is shown in Table V. Included are the

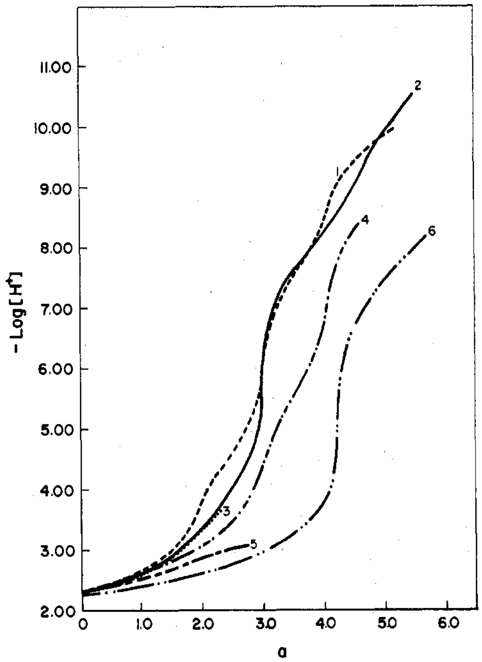

Figure 4. Potentiometric equilibrium curves of 1:1 systems of gallium (0.0025 M) with SEDDA (1), UEDDA (2), IDA (3), HIDA (4), DTMA (5), and citric acid (6) [a = moles of 0.1 M KOH added per mole of ligand present]; t = 25.0 °C, μ = 0.10 M (KNO_3).

Table V. Logarithms of Gallium-Ligand Stability Constants Determined by Direct Potentiometric Titration[a]

Ligand	$\log K_{ML}$	$\log K^{M}_{MHL}$	$\log K^{M}_{MH_2L}$
SEDDA	18.15[b] (6)		
HEDTA	17.2[b] (4)		
UEDDA	16.75 (5)		
DGENTA	13.26 (4)	9.70 (4)	
IDA	12.76 (4)		
HIDA	11.33 (3)		
DTMA			4.51 (2)
CA	10.02 (2)		

[a] All values listed are for 25.0 °C and μ = 0.10 M (KNO_3).
[b] Value listed is the average result from determination by two different methods.

stability constants of the protonated chelates, as defined by eq 12.

$$K^{M}_{MH_nL} = [MH_nL]/[M][H_nL] \tag{12}$$

The 1:1 gallium(III)–citric acid system had the unusual feature of a break in the titration curve at a = 4.33, indicating the formation of a polymer with an empirical formula of $(M^{3+}{}_3(OH)_4L^{3-}{}_3)_n$. As previously stated, the concentration dependence of the mid-pH buffer region indicates that the polymer dissociates over this pH range. These conclusions are supported by a recent report by Glickson et al.[11] that gallium citrate polymerizes at low pH, reaching a maximum degree of polymerization at pH 5, which corresponds to the first inflection in the gallium–citrate potentiometric equilibrium curve (see Figure 2), and then dissociating to a minimum degree of polymerization at pH 10, which corresponds to the second inflection in the potentiometric equilibrium curve. Since the second inflection occurred at a = 7.0, it is probable that at this point the complex has completely dissociated into free citrate and $Ga(OH)_4^-$.

For the purposes of calculations, it was assumed that at very low pH the degree of polymerization was negligible and that the primary equilibria were normal chelate formation and hydrolysis, as represented by eq 13 and 14. The equilibrium constants for these reactions are listed in Tables V and III, respectively ($pK_H = \log K^1{}_{OH}$).

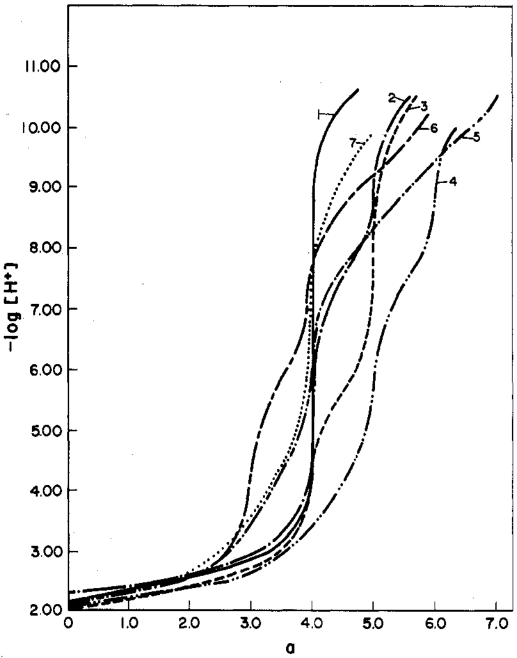

Figure 5. Potentiometric equilibrium curves of 1:1 metal-ligand (0.00250 M) systems of gallium with HBED (1), CDTA (2), EDTA (3), DTPA (4), NTA (5), HBIDA (6), and HEDTA (7); t = 25.0 °C, μ = 0.1 M (KNO_3) [a = moles of 0.10 M KOH added per mole of ligand present].

$$M + L \overset{K_{ML}}{\rightleftharpoons} ML \tag{13}$$

$$ML \overset{K_H}{\rightleftharpoons} M(OH)L + H^+ \tag{14}$$

It was impossible to determine the normal stability constant for the DTMA chelate due to precipitation of gallium hydroxide prior to deprotonation of either of the terminal amino groups.

c. Potentiometric Competition. The degree of formation of many gallium chelates, even at very low pH, was too high for the use of the normal potentiometric titration method just described. In such cases, in addition to the 1:1 metal–ligand system titrations shown in Figure 5, ligand–ligand competition titrations were also performed using various ratios (usually 1:1:1) of the ligand of unknown stability (L), gallium, and a reference ligand (L′), which had a known stability constant (K_R).

Such a system of one metal ion and two ligands was described by the following mass and charge balance equations, assuming the concentration of free metal to be zero

$$T_L = A_1[L] + X_1[ML] \tag{15}$$

$$T_{L'} = A'_1[L'] + X'_1[ML'] \tag{16}$$

$$T_M = X_1[ML] + X'_1[ML'] \tag{17}$$

$$B = A_2[L] + A'_2[L'] + X_2[ML] + X'_2[ML'] \tag{18}$$

where T_L and $T_{L'}$ are the analytical concentrations of ligand under consideration and of reference ligand, respectively, T_M is the analytical metal concentration, and the A_n's, X_n's, A'_n's, and X'_n's are functions of the known ligand and chelate protonation constants and of pH. These equations were solved by Newton–Raphson iteration for the concentrations of the four unknowns. A displacement constant K_X was then calculated in essentially the same form as that for the metal–metal competition

$$K_X = \frac{[ML][L']}{[ML'][L]} = \frac{K_{ML}}{K_{ML'}} \tag{19}$$

Since this procedure had not been widely used, the technique

Table VI. Parameters Used in Calculation of log K_{ML} for Cu(II) Ion Distributed between a Reference Ligand L′ and Unknown Ligand L

L	L′	log K_X	log $K_{ML'}$	log K_{ML} (exptl)	log K_{ML} (lit.)
trien	HBIDA	4.00	16.11	20.11 (4)	20.1[a]
EDTA	trien	−1.40	20.11	18.71 (6)	18.70[a]

[a] Reference 4.

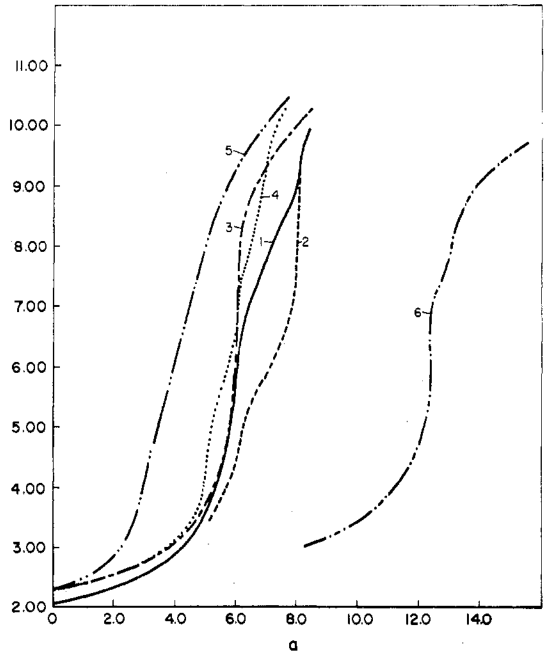

Figure 6. Potentiometric equilibrium curves of solutions of gallium with the ligand pairs DTPA–HBIDA (1), EDTA–CDTA (2), NTA–HEDTA (3), EDTA–HBIDA (4), SEDDA–HBIDA (5), and CDTA–NTA (6); $t = 25.0$ °C, $\mu = 0.10$ M (KNO_3), $[M]_0 = 0.0025$ M, $[L] = 0.0025$–0.0050 M.

was checked by running titrations of cupric ion with various combinations of EDTA, HBIDA, and trien. The stability constants for copper(II) with all three ligands are known.[3,4]

Since this method is capable of determining only the relative difference in the stability constants of any two ligands, it was necessary to choose the literature constant of one ligand as an absolute reference point. The ligand chosen was HBIDA, with a $K_{ML'} = 16.11$.[3] The calculated and literature values of K_{ML} for the other copper chelates are listed in Table VI.

The copper systems were also used to check the validity of the assumption of negligible free metal concentration. By using the stability constant of the reference ligand as a fifth equation describing the system, free metal ion concentration was included as a variable in the mass and charge balance equations. It was found that this addition produced no change in the calculated concentrations of the remaining four unknowns, and the concentration of free metal was indeed so small that the value calculated for that quantity was negligibly small, erratic, and unreliable. Therefore, free metal ion concentration was routinely disregarded in the following calculations.

The gallium competition titration curves are shown in Figure 6. It was assumed that no 2:1 or mixed-ligand complexes formed with any ligand containing five or more available donor groups. With the chelates of NTA and HBIDA, both of which contained two open coordination sites cis to one another, titrations of 2:1 ligand–metal systems were also run. In neither case was there any indication for the formation of a 2:1 complex. In the case of SEDDA the agreement between the values of log K_{ML} obtained by potentiometric competition (18.13) and by normal potentiometric titration (18.16) was taken as sufficient proof of the absence of a significant amount of either 2:1 or mixed-ligand complexes. The stability constants for the gallium complexes were based on the reference ligands NTA, CDTA, and HBIDA. The calculated constants for 25 °C and 0.10 M (KNO_3) ionic strength are reported in Table VII.

Table VII. Parameters Used in the Determination of log K_{ML} of Ga^{3+}–L Chelates by Potentiometric Ligand Competition[a]

L	L′	log K_x	log K_R	log K_{ML}
SEDDA	HBIDA	−3.40	21.55	18.15[b] (6)
DTPA	HBIDA	1.77	21.55	23.32 (6)
NTA	HBIDA	−5.41	21.55	16.19[b] (6)
HEDTA	HBIDA	−4.4	21.55	17.2[b] (4)
CDTA	NTA	6.15	16.19	22.3 (1)
EDTA	CDTA	−0.55	22.34	21.7 (1)

[a] All values listed are for 25.0 °C and $\mu = 0.10$ M (KNO_3).
[b] The value shown is the average of results obtained by two different methods.

Table VIII. A Comparison of Present Stability Constants with Available Literature Values[a]

Ligand	log K_{ML} (this work)	log K_{ML} (lit.)	Ref
NTA	16.19 (5)	13.6–14.0	12, 16
HEDTA	17.2 (4)	16.9	13
EDTA	21.7 (1)	20.3–21.7	12–15
DTPA	23.32 (6)	23.0–25.5	12, 13
CDTA	22.34 (1)	22.5–23.1	12–14

[a] log K_{ML} (this work) values are all measured at 25.0 °C and $\mu = 0.10$.

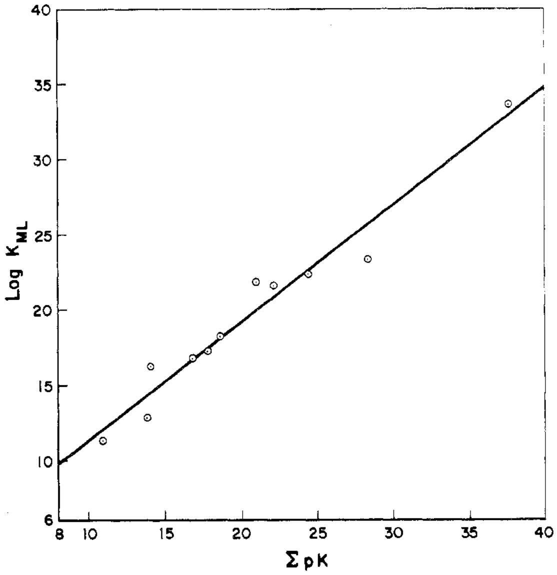

Figure 7. Regression of log K_{ML} on Σ_n log $K^H{}_n$'s for gallium ligand chelates in this work, $r = 0.98$.

Discussion

Comparisons of the stability constants reported here with published values are limited by the scarcity of previous work and in the cases where the stability constant of a ligand has been determined by more than one worker, by the wide variations in reported constants. Table VIII shows the constants determined in this work for the five ligands for which literature references were found and the range of values reported by other workers.

With the exception of those for NTA, the calculated stability constants fall in or near the range of literature values.

In an attempt to relate the gallium chelate stability constants to ligand basicity, in Figure 7 log K_{ML} was plotted against the sum of the logarithms of the protonation constants for each

Table IX. Comparison of Pearson *r* Correlation Coefficients for Published Trivalent Metal log K_{ML}'s vs. Σ log K^H's with Gallium(III) Values of This Study

Metal	No. of values used	Pearson *r*	Metal	No. of values used	Pearson *r*
Ga^{3+} [a]	11[a]	0.98[a]	Al^{3+}	8	0.95
Mn^{3+}	5	1.00	In^{3+}	5	0.97
Fe^{3+}	12	0.96			

[a] This study.

ligand except HBED, DGENTA, and CA. The result is a definite correlation with somewhat scattered points. The standard deviation in the slope of the least-squares-fitted line through these points was found to be 0.05. For finer refinement, factors such as the size and number of chelate rings in each complex would need to be taken into consideration, but as yet not enough data have been reported to allow for the subdivision of results into smaller, more closely related groups. The Pearson product–moment correlation coefficient[17] for the data plotted in Figure 7 is $r = 0.98$. This value of r was shown by a t test to be significant well below the $P = 0.001$ level. In order to establish a comparison base, the Pearson r was also calculated for the trivalent metal ions Mn^{3+}, Fe^{3+}, Al^{3+} and In^{3+}, using available published values[4] of constants for the ligands used in this study. The results as shown in Table IX indicate that the internal consistency of the gallium constants is as good as can be expected. The slightly higher value calculated for Mn^{3+} is probably due to the fact that the comparison is restricted to a smaller, more closely related group of ligands.

A correlation was also found to exist between the log K_{ML} and the log $K^1{}_{OH}$ for the series of ligands in this study. In Figure 8 r for these data was calculated to be 0.93. This value of r was also found to be significant below the $P = 0.001$ level. The scatter of the data plotted is reasonable considering that such factors as the number of available coordination sites and the charge of the chelate have not been taken into consideration.

The strong hydrolytic tendencies of gallium complexes severely hamper the study of gallium with small or weakly coordinated ligands. Precipitation normally restricts the pH range over which the complexes can be studied by normal potentiometric methods. In the IDA and DTMA systems, precipitation occurs at pH 3.5 and 3.0, respectively. In the case of DTMA, the two terminal amine groups are only weakly coordinated and apparently are not deprotonated prior to precipitation. For this reason only the protonated chelate stability constant is reported and not the normal K_{ML}.

The potentiometric competition method of determining equilibrium constants proved to be very useful in working with ligands of very high stability. The use of this technique was deliberately avoided with less stable ligands or ligands with less than four donor groups because of the strong possibility of mixed-ligand and 2:1 complexes. There was some problem in finding reference ligands which would give a reasonably even distribution of the metal between themselves and the competing ligands. In the one case of TTHA, a satisfactory reference ligand could not be found. Therefore no value for the K_{ML} of the Ga–TTHA complex is reported.

It now appears that the most important criterion for successful competition is that the two ligands must have very different protonation constants. This factor appears to be even more important than the difference in stability constants in determining whether or not two particular ligands can be successfully treated by this method. The strong dependence on ligand basicity is the result of competition from hydrogen ion on the metal-binding groups of the ligands. At low pH the hydrogen ions compete for the coordination sites more effectively on the more basic ligand, giving the more acidic ligand an advantage in the competition for the metal ion. This allows one to influence the distribution of the metal ion between the two ligands by adjusting the hydrogen ion concentration. Thus in a competition between a fairly acidic ligand such as NTA (log K's = 9.65, 2.48, and 1.84) and a more basic ligand such as HBIDA (log K's = 11.71, 8.07, and 2.34), the NTA is able to coordinate the larger proportion of metal ion at low pH, even though the stability constant of HBIDA is almost 4 log units higher. As the pH increases, the competition from hydrogen ion for the two basic groups of the HBIDA decreases, and the metal ion equilibrium shifts to the HBIDA. This results in a crossover region in which the metal is fairly evenly distributed between the competing ligands, and it is in this region where accurate calculations of K_X can best be performed.

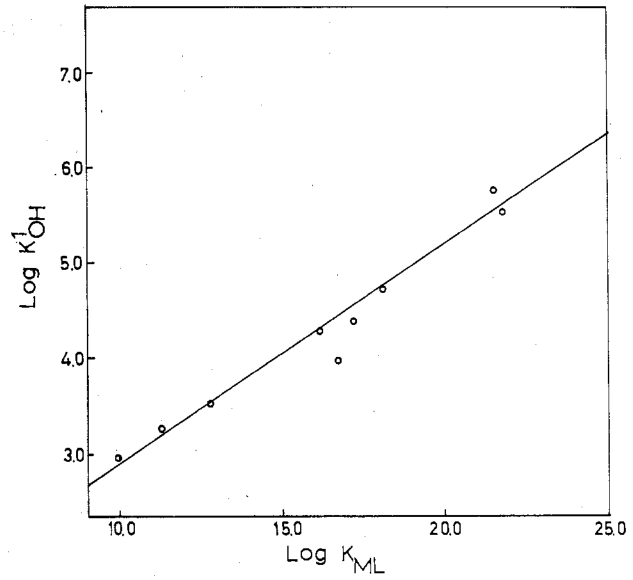

Figure 8. Regression of the normal stability constant for GaL formation upon log of the first hydrolysis constant, log $K^1{}_{OH}$, $r = 0.93$.

In some cases the strong competition from hydrogen ion for donor groups on the more basic ligand was not enough to overcome extremely large differences in stabilities between the two ligands. For example, none of the polyaminocarboxylic acids included in this study were able to compete effectively with HBED for the Fe(III) ion (log K_{ML} = 39.57), in the pH range available for experimental measurements.

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Registry No. HBED, 35998-29-9; EHPG, 10328-28-6; TTHA, 869-52-3; DTPA, 67-43-6; HBIDA, 7372-13-6; CDTA, 482-54-2; EDTA, 60-00-4; HEDTA, 150-39-0; SEDDA, 5657-17-0; UEDDA, 5835-29-0; NTA, 139-13-9; DTMA, 55682-20-7; DGENTA, 29725-86-8; HIDA, 93-62-9; IDA, 142-73-4; CA, 77-92-9; trien, 112-24-3; gallium, 7440-55-3.

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Notes

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Electronic Structure of the Tetracyanoplatinate(II) Anion

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The electronic absorption bands of compounds containing the square-planar $Pt(CN)_4^{2-}$ ion have received considerable experimental and theoretical study, since the anion is a model for planar complexes with strong-field ligands.[1-11] Of special interest has been the observation of spectral shifts in the ultraviolet electronic absorption spectra for various alkali and alkaline earth salts arising from an axial interaction between stacked complex ions in the solid state.[6,12]

Recent work on the metallic one-dimensional platinum compounds, $K_2Pt(CN)_4X_{0.3}\cdot 3H_2O$ (X = Cl, Br), in which planar tetracyanoplatinate units form linear chains of platinum atoms in one dimension,[13,14] has provided further impetus to determine the electronic structure of this ion.[11] The suggestions of a low-temperature transition to a Peierls insulator together with evidence for one-dimensional metallic properties at room temperature[14] has made the tetracyanoplatinates the subject of intense study recently.

Two theoretical MO calculations for $Pt(CN)_4^{2-}$ which included spin–orbit coupling implicitly[8,10] suggest a number of states for which spectroscopic transitions have not been observed. Self-consistent field, $X\alpha$ scattered-wave calculations also predict unobserved spectroscopic states.[11]

These results have prompted us to reinvestigate the ultraviolet electronic absorption spectrum of the $Pt(CN)_4^{2-}$ ion in aqueous and nonaqueous media using an interacting computer curve resolving program.

Experimental Section

Tetrabutylammonium tetracyanoplatinate(II), **1**, was prepared from commercially available $K_2Pt(CN)_4\cdot 3H_2O$, **2**, by a literature method.[5] Compounds **1** and **2** were purified prior to use by multiple recrystallizations.

Ultraviolet absorption spectra at 77 K were obtained on a Cary 15 recording spectrophotometer using a specially constructed low-temperature cell holder with a massive copper heat sink in contact with a liquid nitrogen reservoir. In this apparatus, 1-mm path length quartz absorption cells were filled with solutions in 9:1 (volume) methanol–water (a low-temperature glass) and cooled until the solutions solidified; the entire apparatus was evacuated to maintain constant temperature. Room-temperature absorption spectra were obtained in the usual manner.

Spectrophotometric data are presented via mechanical encoding to the analog inputs of a spectrophotometer interface (Data Graphics 9158) which provides analog to digital converted data at the output as parallel BCD (binary coded decimal) for further processing, serialization, and decoding by a programmable interface (Data Graphics 305). The programmable interface outputs the data in USASCII coding suitable for an automatic send–receive terminal (Texas Instruments ASR 733). This ASR terminal receives USASCII coded data for off-line storage on magnetic tape cassettes and transmits data to a Sigma 9 computer for processing and plotting.

An interactive Gaussian curve resolving program was used to deconvolute the observed spectral envelopes into a minimum number of Gaussian bands, which represent the various electronic absorption transitions for $Pt(CN)_4^{2-}$. This program performs successive interactions to obtain the best possible fit between the observed spectrum and the predicted spectrum, which is the sum of all Gaussian components. A standard deviation for the fits was generally $\sigma \approx 0.001$.

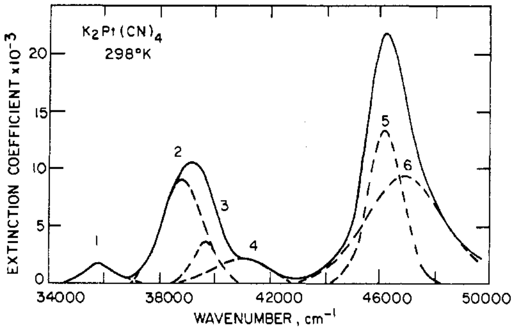

Figure 1. Deconvoluted electronic spectra for a 3.7×10^{-4} M solution of $K_2Pt(CN)_4$ in aqueous solution at room temperature.

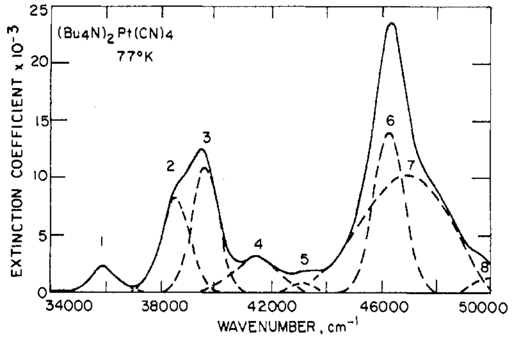

Figure 2. Deconvoluted electronic spectra for a 0.98×10^{-4} M solution of $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$ in 9:1 CH_3OH–H_2O at 77 K.

Results and Discussion

The solution electronic absorption spectra for $K_2Pt(CN)_4$ and $(Bu_4N)_2Pt(CN)_4$ are presented in Figures 1 and 2 and in Table I. The solid curve in Figure 1 represents the absorption envelope for a 3.7×10^{-4} M solution of $K_2Pt(CN)_4$ in water at 298 K. The spectrum is plotted as extinction coefficient (M^{-1} cm^{-1}) against energy (wavenumber). The dashed curves represent the Gaussian components from the curve fitting analyses. These may be correlated with individual electronic transitions between energy levels in $K_2Pt(CN)_4$.

The assumption that electronic transitions may be represented by Gaussian curves has been discussed by Siano and Metzler[15] and Siano.[16] This approximation is reasonable for bands which show no skewness. For skewed bands a log-normal approximation is preferred. The use of different functions does not alter the number of bands but may change relative positions slightly. From Figure 1 the absorption region between 37000 and 41000 cm^{-1} contains a band that clearly shows asymmetry. This has been resolved into two components identified as bands 2 and 3. Similarly, for the energy region between 44000 and 50000 cm^{-1} the asymmetric band has been