Inorganica Chimica Acta, 61 (1982) 109–113

NMR Relaxation Studies in Solution of Transition Metal Complexes. V. Proton Exchange Reactions in Aqueous Solutions of VO^{2+}–Oxalic Acid, –Malonic Acid Systems

ISTVÁN NAGYPÁL and ISTVÁN FÁBIÁN*

Institute of Inorganic and Analytical Chemistry, L. Kossuth University, H-4010 Debrecen, Hungary

Received October 31, 1981

The equilibria existing in the VO^{2+}–oxalic acid and –malonic acid systems have been studied pH-metrically and the proton exchanges between the bulk water and the different paramagnetic species have been investigated by measuring the T_2 relaxation time of water protons at 298 K, $I = 1.0$ M $NaClO_4$.

Mainly VOL and VOL_2^{2-} type complexes are formed in both systems, the relative amounts of the protonated and mixed hydroxo complexes being very small up to pH 5.

The first order rate constants of the proton exchange between the bulk water and the paramagnetic species are given. The surprisingly high value for the VOL_2^{2-} type complexes is interpreted by a continuous intramolecular rearrangement of the ligands from two equatorial positions to axial–equatorial position and vice versa. *The unexpectedly high rate constant for the protonated complex $VOmalH^+$ is interpreted by its fast acid dissociation process.*

Introduction

It was shown in the previous parts of the series [1] that the pre-requisite of the proton relaxation studies in solution of transition metal complexes is to know the composition and stability of the complexes formed under the condition used for NMR studies. The vanadyl ion and its complexes formed with some organic [2] and inorganic [3–5] ligands have been extensively studied by the NMR relaxation method. The equilibrium studies, however, are rather limited and led to contradictory results even in case of the simple VO^{2+}–malonic acid system.

Wüthrich [6] indicated the formation of VOL and VOL_2 type complexes from ESR measurements, and Ivakin *et al.* [7] determined spectrophotometrically the appropriate stability constants. Ohtaki *et al.*, however, interpreted the pH-titration curves by the formation of protonated VOLH complex only [8]. The acidity of the complex was found to be less than that of the HL^- form of the ligand, which is a unique relation among the protonated complexes. These workers assumed that one of the carboxylate groups is coordinated to one of the equatorial positions of the vanadyl ion, while the other carboxyl group is hydrogen-bonded to the vanadyl oxygen. For the interpretation of the NMR relaxation results, however, it had to be assumed that the complex VOL_2 is the dominating one in high ligand excess [9].

The aim of the present work was to investigate the VO^{2+}–malonic acid system pH-metrically and to interpret the results of the relaxation studies in solutions which are known exactly from the equilibrium point of view. For comparison, pH-metric and relaxation measurements have been carried out and interpreted in the VO^{2+}–oxalic acid system.

Experimental

The $VO(ClO_4)_2$ stock solution was prepared from NH_4VO_3. Its ammonia content was eliminated by heating in alkaline solution. The reduction was carried out mainly by HCl and was finished by KI in acidic solution. The I_2 formed was filtered off, together with an appropriate amount of charcoal. The halide content was separated by precipitation with $AgClO_4$ solution prepared from Ag_2O and $HClO_4$. The stock solution does not precipitate with $AgClO_4$ or with HCl solution. The VO^{2+} concentration was determined spectrophotometrically. For this, a standard solution was prepared from spectral-pure vanadium. The $HClO_4$ concentration in the stock solution was determined pH-metrically, using the appropriate Gran function. $NaClO_4$ was prepared from *p.a.* Merck NaOH and $HClO_4$. The inonic strength of all of the solutions studied was adjusted to 1 *M* $NaClO_4$. The ligands were purified by recrystallization.

---

*Present address: Institute of Physical Chemistry, L. Kossuth University, H-4010 Debrecen, Hungary.

0020-1693/82/0000-0000/$02.75

A radiometer PHM-52 type pH-meter, GK-2301 electrode (filled with saturated NaCl) was used for pH-measurements, and was calibrated for $-\log[H^+]$ according to Irving *et al.* [21]. A Newport N20 pulse spectrometer working at 2.5 MHz frequency was used to measure the T_2 relaxation time of the water protons. All of the experiments were carried out as titration at 25.0 ± 0.1 °C. The composition of the initial solutions used for the different titrations are given in Tables I–II.

Although the hydrolysis of the vanadyl ion has been extensively studied, to get the constants in 1 *M* $NaClO_4$ we made pH-measurements in separate samples in the 0.006–0.016 $T_{VO^{2+}}$ concentration and in the 3.4–3.8 pH-range. Because of the slow hydrolytic reactions, it took about 1–1.5 hour to reach the equilibrium.

All of the experiments were carried out under purified argon atmosphere.

Results and Discussion

Equilibrium Studies

The logarithm of the equilibrium constants for the

$$VO^{2+} + H_2O \rightleftharpoons VO(OH)^+ + H^+;\ \beta_{11} = \frac{[VO(OH)^+]\,[H^+]}{[VO^{2+}]}$$

and

$$2VO^{2+} + 2H_2O \rightleftharpoons (VO)_2(OH)_2^{2+} + 2H^+;$$

$$\beta_{22} = \frac{[(VO)_2(OH)_2^{2+}]\,[H^+]^2}{[VO^{2+}]^2}$$

reactions are in good agreement with the earlier results [10–12].

The formation curves for the VO^{2+}–oxalic acid system could not be calculated from the pH-metric titration curves, because of the high stability of the complexes compared to the protonation constants. This finding is qualitatively in agreement with Ivakin's results ($\log K_1 = 6.45$, $\log K_2 = 5.33$ [7]).

Some of the formation curves calculated for the VO^{2+}–malonic acid system (in the usual way [13] without taking into account the hydrolysis of the vanadyl ion) are seen in Fig. 1. From the shape of the curves the following conclusions could be drawn:

– The coincidence of the four curves in a wide pL range indicates that mainly VOmal and $VOmal_2^{2-}$ complexes are formed in the system.

– The small deviation of the curves at the beginning, at low pH, indicates the formation of a protonated complex.

– The sharp increase of the calculated $\bar{n}$ values at the end of the titration curves, *i.e.* at pH > 5, may be interpreted by the formation of $VOmal(OH)^-$ and $VOmal_2(OH)^{3-}$ hydroxo complexes.

TABLE I. Composition of the Solutions Used for pH-titrations.[a]

No.	T_H^o	$T_{mal^{2-}}^o$	$T_{VO^{2+}}^o$	Number of exp. points
VO^{2+}–malonic acid system				
1	0.0159	0.00795	–	32
2	0.0398	0.0199	–	36
3	0.0557	0.0278	–	34
4	0.0795	0.0398	–	40
5	0.1193	0.0597	–	42
6	0.0183	0.00795	0.00324	27
7	0.0342	0.0159	0.00324	35
8	0.0581	0.0278	0.00324	32
9	0.0219	0.00795	0.00810	14
10	0.0457	0.0199	0.00810	22
11	0.0855	0.0398	0.00810	35
12	0.1253	0.0598	0.00810	36
13	0.0438	0.0159	0.0162	18
14	0.0676	0.0278	0.0162	29
15	0.1313	0.0597	0.0162	32
VO^{2+}–oxalic acid system				
1	0.0411	0.0205	–	20
2	0.0288	0.0144	–	13
3	0.0164	0.0082	–	15
4	0.0560	0.0205	0.0203	25
5	0.0280	0.0103	0.0101	15
6	0.0235	0.0103	0.0040	12
7	0.0470	0.0205	0.0081	20
8	0.0485	0.0205	0.0101	22

[a]The solutions were titrated by 1.007 *M* NaOH.

TABLE II. Composition of the Solutions Used for NMR-titration of the VO^{2+}–Malonic Acid System.[a]

No.	T_H^o	$T_{mal^{2-}}^o$	$T_{VO^{2+}}^o$	Number of exp. points
1	0.0219	0.00795	0.0081	16
2	0.0412	0.0142	0.0174	20
3	0.0980	0.0426	0.0174	47
4	0.0676	0.0278	0.0162	27
5	0.1313	0.0597	0.0162	44

[a]The solutions were titrated by 1.007 *M* NaOH.

The evaluation of the titration curves was carried out with our own computer program [14]. The results of the equilibrium calculations are collected in Table III, together with the comparable data from the literature.

The concentration distribution of the complexes formed in the VO^{2+}–malonic acid system is illustrated in Fig. 2. The presence of the $VO(OH)^+$ and $(VO)_2(OH)_2^{2+}$ hydroxo complexes was taken into account during the computer calculation, but their concentration remained below 1% of the total

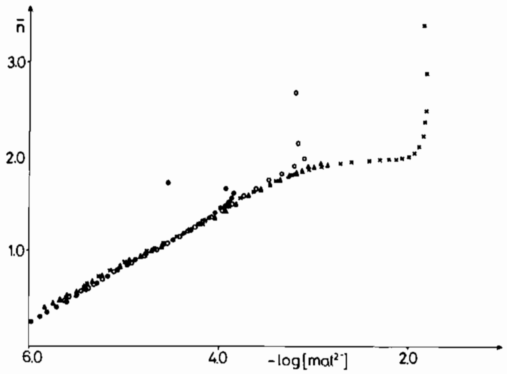


Fig. 1. Some of the calculated formation curves of the VO^{2+}–malonic acid system. o titration No. 6 in Table I. X titration No. 8 in Table I. ● titration No. 14 in Table I. ▲ titration No. 15 in Table I.

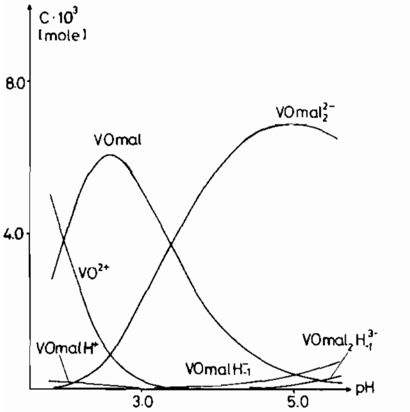


Fig. 2. Concentration distribution of the complexes formed in the VO^{2+}–malonic acid system. Titration No. 10 in Table I.

TABLE III. Logarithm of the Formation Constants of the Species Formed in the VO^{2+}–Malonic Acid System:

$$\beta_{(VO)_x mal_y H_z} = \frac{[(VO)_x mal_y H_z]}{[VO^{2+}]^x [mal^{2-}]^y [H^+]^z}$$

Species	This work	[7] I = 1 *M* $NaClO_4$ 20 ℃	[8] I = 3 *M* $NaClO_4$ 25 ℃
$Hmal^-$	5.020 ± 0.002	4.96	5.78
H_2mal	7.583 ± 0.003	7.44	8.60
VOH_{-1}^-	−6.07 ± 0.20	–	−6.00*
$(VO)_2H_{-2}^{2-}$	−6.59 ± 0.02	–	−6.88*
VOmal	5.594 ± 0.004	5.23	–
$VOmal_2^{2-}$	9.480 ± 0.007	8.85	–
$VOmalH^+$	6.20 ± 0.12	–	7.41 ± 0.02
$VOmalH_{-1}^-$	0.52 ± 0.10	–	–
$VOmal_2H_{-1}^{3-}$	2.56 ± 0.13	–	–

*Accepted from ref. [10].

vanadyl ion concentration in the whole pH range, thus they are not seen in Fig. 2. The computer calculation justified the conclusions drawn from the shape of the formation curves—mainly complexes VOmal and $VOmal_2^{2-}$ are formed in the system. This is in agreement with Wüthrich's ESR and with Ivakin's spectrophotometric result [6, 7], but is in complete disagreement with Ohtaki's finding [8].

A carefull study of Ohtaki's paper revealed that the authors did not use the mass-balance equation for the hydrogen ion in their iteration procedure. This mistake explains why they found the formation of the $VOmalH^+$ complex only.

Relaxation Studies

The equilibria existing in the VO^{2+}–oxalic acid system between $1.5 < pH < 4.5$ are very simple, $\bar{n} \approx T_{ox^{2-}}/T_{VO^{2+}}$ if $T_{ox^{2-}}/T_{VO^{2+}} < 2$ and $\bar{n} = 2$ if $T_{ox^{2-}}/T_{VO^{2+}} > 2$. Moreover, the oxalate ligand does not contain labile protons, thus only the proton (water) exchange between the bulk water and the different paramagnetic species should be taken into account for the evaluation of the relaxation results. Because of these simple relations only one relaxation titration was carried out: 2.03×10^{-2} *M* $VO(ClO_4)_2$ at pH ~ 2.5 was titrated with a pH ~ 2.5 solution containing the same vanadyl concentration and 6.00 $\times 10^{-2}$ *M* oxalate. The normalized paramagnetic relaxation rate as a function of $T_{ox^{2-}}/T_{VO^{2+}}$ is seen in Fig. 3. Figure 3 suggests that the measured relaxation rate is a linear function of the VO^{2+}, VOox and $VOox_2^{2-}$ concentrations:

$$T_{2p}^{-1} = T_2^{-1} - T_{20}^{-1} = r_{VO^{2+}}\{VO^{2+}] + r_{VOox}[VOox] + \\ + r_{VOox_2^{2-}}[VOox_2^{2-}] \qquad (1)$$

where:
T_{2p}^{-1} = paramagnetic contribution to the relaxation rate. T_2 = the measured relaxation time. T_{20} = relaxation time in absence of vanadyl complexes. r_i = molar relaxation coefficient of the i-th species.

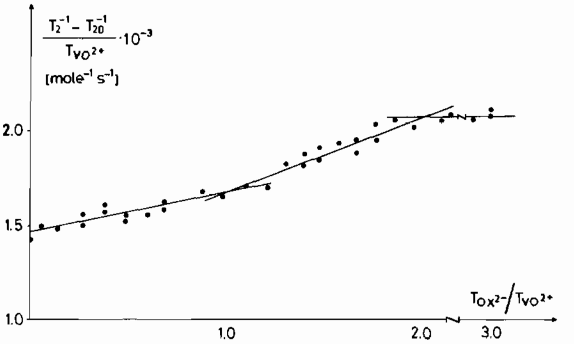


Fig. 3. The normalized relaxation rate as a function of $T_{ox^{2-}}/T_{VO^{2+}}$ concentration ratio in the VO^{2+}–oxalic acid system.

The linear least squares treatment of equation (1), written for all of the experimental points, led to the following results: $r_{VO^{2+}} = (1.5 \pm 0.1)10^3 \, M^{-1} \, s^{-1}$, $r_{VOox} = (1.7 \pm 0.1)10^3 \, M^{-1} \, s^{-1}$, $r_{VOox_2^{2-}} = (2.1 \pm 0.1)10^3 \, M^{-1} \, s^{-1}$.

For the illustration of the relaxation measurements in the VO^{2+}–malonic acid system, the result of titration No. 4 in Table II is seen in Fig. 4, together with the concentration distribution of the complexes. The difference of the 'intercepts' in Fig. 3 and 4 indicates that the protonated complex $VOmalH^+$ has a significant role in the measured relaxation rate, thus the data were evaluated by taking into account the $r_{VOmalH^+}[VOmalH^+]$ term beside the terms similar to that of equation (1). The linear least squares treatment of the five titration curves simultaneously led to the following data: $r_{VO^{2+}} = (1.6 \pm 0.1)10^3 \, M^{-1} \, s^{-1}$, $r_{VOmal} = (1.70 \pm 0.07)10^3 \, M^{-1} \, s^{-1}$, $r_{VOmal_2^{2-}} = (1.42 \pm 0.04)10^3 \, M^{-1} \, s^{-1}$, $r_{VOmalH^+} = (1.31 \pm 0.11)10^4 \, M^{-1} \, s^{-1}$.

The inclusion of VOmal(OH) and/or $VOmal_2(OH)$ hydroxo complexes into the calculation did not significantly improve the average fit of the experimental data, and in some cases gave a negative value for the appropriate r_i.

For the interpretation of the molar relaxation coefficients, one has to decide if the measured relaxation rate is exchange or paramagnetic relaxation controlled. Exchange control is supported by the earlier results in the literature [2, 3, 4, 14–16] and by the increase of the relaxation rate with increasing temperature, which we experienced in some separate samples. A further evidence of exchange control is that in the case of relaxation control the rate would decrease with decreasing number of water molecules remaining in the first coordination sphere, as was found in case of the copper(II) complexes [18].

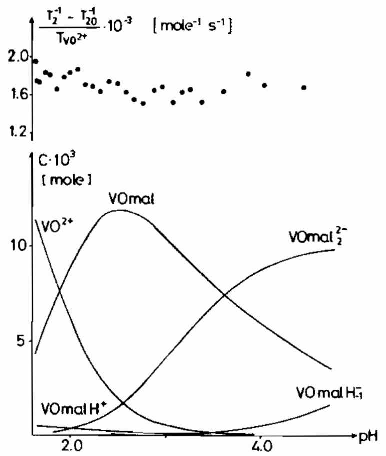


Fig. 4. The normalized relaxation rate as a function of pH in the VO^{2+}–malonic acid system, together with the distribution of the complexes. Titration No. 4 in Table II.

Thus the molar relaxation coefficients can be transformed into the appropriate first order rate constants of the reactions.

$$VOmal_xH_y(HOH) + \overset{*}{H}OH \rightleftharpoons VOL_xH_y(HO\overset{*}{H}) + HOH$$

$$k_i = 2[H_2O]\, r_i = 108 r_i$$

(The water concentration in 1 *M* $NaClO_4$ is 54 *M*). The rate constants calculated are collected in Table IV.

TABLE IV. First Order Rate Constants of the Proton Exchange between the Bulk Water and the Different Paramagnetic Species.

Species	$k(s^{-1})$*
VO^{2+}	$(1.70 \pm 0.10)10^5$
VOox	$(1.85 \pm 0.15)10^5$
$VOox_2^{2-}$	$(2.30 \pm 0.12)10^5$
VOmal	$(1.85 \pm 0.10)10^5$
$VOmal_2^{2-}$	$(1.55 \pm 0.05)10^5$
$VOmalH^+$	$(1.43 \pm 0.12)10^6$

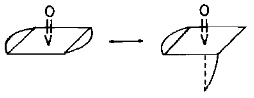
*The rate constants are sometimes normalized for the number of protons found in the paramagnetic species. We do not follow this, because the number of protons are not always known.

From the data of Table IV the following conclusions can be drawn:

– The rate constant for the proton exchange of the free vanadyl ion is in good agreement with the earlier results in the literature: $k = 6.2 \times 10^4 \, s^{-1}$ [17], $k = 8 \times 10^4 \, s^{-1}$ [15], $k = 1.8 \times 10^5 \, s^{-1}$ [2].

– In spite of the decreasing number of water molecules remaining in the VOL complexes compared to that of the free vanadyl ion, the rate constants are higher, and they have the same value in the VOox and VOmal complexes. Similar increase of the exchange rate was found by other authors [2, 3]. This may probably be explained by the fact that the coordination of the L^{2-} ligands weakens the $VO–OH_2$ bond, thus increases the exchange rate of the water molecule, which is also reflected in the proton exchange rate constant.

– The proton exchange rate constants for the VOL_2^{2-} complexes are surprisingly high. Wüthrich and Connick [2] as well as Reuben and Fiat [17] stated earlier that the exchange of the water molecules in the fifth axial position did not influence the relaxation rate, because of the very weak coupling between the protons of the axial water molecule and the unpaired electron of the vanadyl ion. In the light of their finding, it must be assumed that the exchange of an equatorially-bound water molecule is taking place from the VOL_2^{2-} complexes. The most probable way of this process is a continuous intramolecular rearrangement of the ligands from two equatorial positions to an axial–equatorial position illustrated below:



– The first order proton exchange rate constant for the protonated complex $\mathrm{VOmalH^+}$ is also surprisingly high. For the interpretation of this it should be taken into account that beside the direct proton exchange between the bulk water and the water molecules remaining in the first coordination sphere of $\mathrm{VOmalH^+}$:

$$\mathrm{VOmalH(HOH)^+ + \overset{*}{H}OH \underset{}{\overset{k_a}{\rightleftharpoons}} VOmalH(HO\overset{*}{H})^+ + HOH} \tag{a}$$

there may be three different processes responsible for this datum:

$$\mathrm{VO(HOH)^{2+} + \overset{*}{H}mal^- \overset{k_b}{\rightleftharpoons} VO(HO\overset{*}{H})^{2+} + Hmal^-} \tag{b}$$

$$\mathrm{VO^{2+} + Hmal^- \overset{k_c}{\rightleftharpoons} VOmalH^+} \tag{c}$$

$$\mathrm{VOmalH^+ \overset{k_d}{\rightleftharpoons} VOmal + H^+} \tag{d}$$

i.e.

$$108r_{\mathrm{VOmalH^+}} = k_a + (k_b + k_c)\,\frac{1}{K_{\mathrm{VOmalH^+}}} + k_d$$

where:

$$K_{\mathrm{VOmalH^+}} = \frac{[\mathrm{VOmalH^+}]}{[\mathrm{VO^{2+}}]\,[\mathrm{malH^-}]}$$

Equation (b) means an acid-catalyzed proton exchange from the vanadyl ion. Its second order rate constant would be about $2 \times 10^7\ M^{-1}\ s^{-1}$, much higher than the second order rate constant for the $\mathrm{VO(HOH)^{2+} + \overset{*}{H}OH_2^+ \rightleftharpoons VO(HO\overset{*}{H})^{2+} + HOH_2^+}$ process ($k = 4 \times 10^6\ M^{-1}\ s^{-1}$ [19]). This explanation is thus not probable.

Equation (c) is the formation of the protonated complex $\mathrm{VOmalH^+}$. The rate of this process would be much higher than the rate of elimination of water molecules from the aquated vanadyl ion. A similar process, $\mathrm{VO^{2+} + glycineH^{\pm} \rightleftharpoons VOglycineH^{2+}}$ was studied by Tomiyasu *et al.* [20] who found a much lower value ($1.3 \times 10^3\ M^{-1}\ s^{-1}$) for the formation rate constant than would be calculated from our measurements. Thus this explanation is not probable either.

The most probable explanation is therefore a fast dissociation of the proton from the protonated complex $\mathrm{VOmalH^+}$ (equation (d)). It cannot be excluded, however, that this process is in fact relaxation controlled, but because of the complete overlap of the different processes it cannot be proved directly.

References

1 I. Nagypál, F. Debreczeni and R. E. Connick, *Inorg. Chim. Acta, 48*, 225 (1981). I. Nagypál, F. Debreczeni and F. Erdödi, *Inorg. Chim. Acta, 57*, 125 (1982). F. Debreczeni and I. Nagypál, *Inorg. Chim. Acta, 57*, 135 (1982).

2 K. Wüthrich and R. E. Connick, *Inorg. Chem., 7*, 1377 (1968).

3 A. H. Zeltmann and L. O. Morgan, *Inorg. Chem., 10*, 2739 (1971).

4 W. C. Copenhafer and D. H. Rieger, *Inorg. Chem., 16*, 2431 (1977).

5 M. W. Kending and D. H. Rieger, *Inorg. Chim. Acta, 17*, 175 (1976).

6 K. Wüthrich, *Helv. Chim. Acta, 48*, 779 (1965).

7 A. A. Ivakin, E. M. Voronova and L. V. Chaschina, *J. Inorg. Chem., Moscow, 15*, 1839 (1970).

8 S. Ito, H. Tomiyasu and H. Ohtaki, *Bull. Chem. Soc. Japan, 46*, 2238 (1973).

9 H. Tomiyasu, S. Ito and S. Tagami, *Bull. Chem. Soc. Japan, 47*, 2843 (1974).

10 F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand., 9*, 1177 (1955).

11 A. Komura, M. Hayasi and H. Imaga, *Bull. Chem. Soc. Japan, 50*, 2927 (1977).

12 M. M. Khan and A. E. Martell, *J. Am. Chem. Soc., 90*, 6011 (1968).

13 M. T. Beck, 'Chemistry of Complex Equilibria', Van Nostrand, London (1969).

14 I. Nagypál, I. Páka and L. Zékány, *Talanta, 25*, 549 (1978).

15 T. J. Swift, T. A. Stephenson and G. R. Stein, *J. Am. Chem. Soc., 89*, 1611 (1967).

16 K. Wüthrich and R. E. Connick, *Inorg. Chem., 6*, 583 (1967).

17 J. Reuben and D. Fiat, *Inorg. Chem., 6*, 579 (1967); *8*, 1821 (1969); *J. Am. Chem. Soc., 91*, 4652 (1969).

18 F. J. C. Rossotti and H. Sunshine, *Chem. Comm.*, 447 (1968).

19 I. Nagypál, I. Fábián and R. E. Connick, *Acta Chim. Acad. Sci. Hung.*, accepted for publication.

20 H. Tomiyasu, K. Dreyer and G. Gordon, *Inorg. Chem., 11*, 2409 (1972).

21 H. Irving, M. G. Miles, L. D Pettit, *Anal. Chim. Acta, 38*, 475 (1967).