BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 680—683 (1975)

Polarographic Studies of Bis(2,2′,2″-terpyridine) Complexes of Manganese(II), Cobalt(II), Nickel(II) and Europium(III) in Acetonitrile

Makoto Aihara,* Hirofumi Kishita, and Seizo Misumi**
Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Fukuoka 812

(Received June 8, 1974)

The reduction mechanism of bis 2,2′,2″-terpyridine complexes of manganese(II), cobalt(II), nickel(II) and europium(III) were investigated in acetonitrile by means of DC and AC polarograph and Kalousek polarograph at DME and cyclic voltammetry at an HDME. It was found that univalent metal complex anions, such as $[\mathrm{M(terpy)_2}]^-$ (M=manganese and nickel), were formed at the electrode surface in acetonitrile. For the europium(III) complex, the standard rate constant of the second reduction step was estimated.

It is well-known that ligands such as 2,2′-bipyridine and 1,10-phenanthroline which have available acceptor orbitals for π electrons stabilize low valency states of these metal complexes.[1] Acetonitrile is a more inert solvent than water in the reduction of metal complexes. Formation of univalent tris(2,2′-bipyridine)metal complex anions in acetonitrile has been reported in polarographic studies.[2-4]

In this work, the electrode processes of bis(2,2′,2″-terpyridine)metal(II, III) complexes (metal ions; manganese(II), cobalt(II), nickel(II) and europium(III)) in acetonitrile were investigated by polarography.

Experimental

Materials. Bis(2,2′,2″-terpyridine)metal(II, III) perchlorates were prepared by the methods of Morgan and Burstall,[5] Hogg and Wilkins[6] and Sinha.[7] The compositions were identified by elementary analysis. Acetonitrile (AN) was purified[8] and water content was determined to be 5 mM by Karl Fischer titration. $\mathrm{Et_4NClO_4}$(TEAP) was used as a supporting electrolyte.

Apparatus. The electrolysis cell and reference electrode were the same as previously reported.[9] Cyclic voltammograms were recorded by a Rikendenshi X-Y recorder. Triangular potential signals were obtained from the Yokogawa-Hewlett-Packard 3300 A Function Generator. The DME had the following characteristics: $m=0.706$ mg/s, $t=6.17$ s in 0.1 M TEAP-AN medium at -1.4 V *vs.* SCE. The HDME(surface area of HDME; 0.031 cm^2) was used for cyclic voltammetry as a working electrode.

Procedure. A sample solution was prepared by dissolving 0.1—1.0 mM bis (terpyridine) metal(II, III) perchlorate and 0.1 M TEAP in AN. Triton X-100 was used as a maximum suppressor. The dissolved oxygen in the solution was removed by bubbling pure nitrogen presaturated with acetonitrile vapour for 20 min. All the experiments were carried out at 25.0±0.1 °C. Other procedures were the same as previously described.[9]

Results and Discussion

Bis(2,2′,2″-terpyridine)manganese(II) Complex. DC polarograms of 0.5 mM $[\mathrm{Mn(terpy)_2}](\mathrm{ClO_4})_2$ complex in acetonitrile are shown in Fig. 1. The complex gave a six-step reduction wave. The maximum (2B) at the second step was not suppressed by the addition of

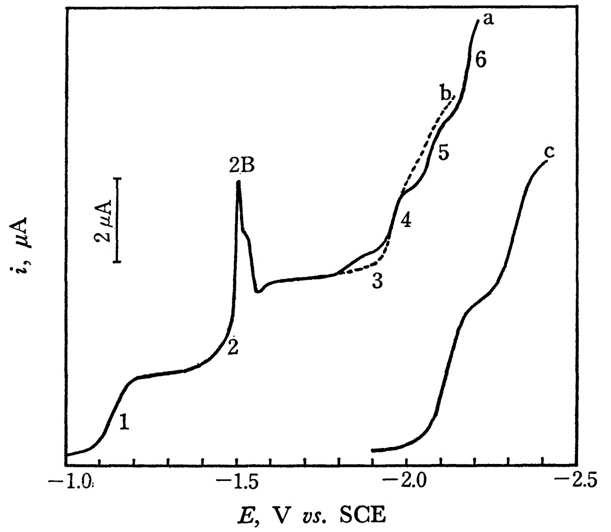


Fig. 1. DC polarograms of $[\mathrm{Mn(terpy)_2}](\mathrm{ClO_4})_2$ in 0.1 M TEAP-AN.
a: 0.5 mM $[\mathrm{Mn(terpy)_2}](\mathrm{ClO_4})_2$, b: a) +5 mM 2,2′,2″-terpyridine, c: 0.5 mM 2,2′,2″-terpyridine.

Table 1. Half-wave potentials and reciprocal slopes of 0.5 mM bis(2,2′,2″-terpyridine)metal(ii, iii) perchlorates in 0.1 M TEAP-AN

	$E_{1/2}$ V *vs.* SCE	Slope mV
Mn(II) complex		
1st wave	−1.155	58
2nd wave	−1.506	80
3rd wave	*ca.* −1.85	—
4th wave	−1.962	—
Co(II) complex		
1st wave	−0.789	57
2nd wave	−1.725	56
Ni(II) complex		
1st wave	−1.246 (−1.249)[a]	60 (47)[a]
2nd wave	−1.479 (−1.485)[a]	47 (47)[a]
3rd ware	−1.919	—
Eu(III) complex		
1st wave	−0.258	88
2nd wave	−1.595	64

a) In the presence of 5.0 mM 2,2′,2″-terpyridine

---

* Present address: Fukuoka Women's University, Kasumigaoka, Higashi-ku, Fukuoka 813.

** Present address: Kyushu Sangyo University, Matsugadai, Higashi-ku, Fukuoka 812.

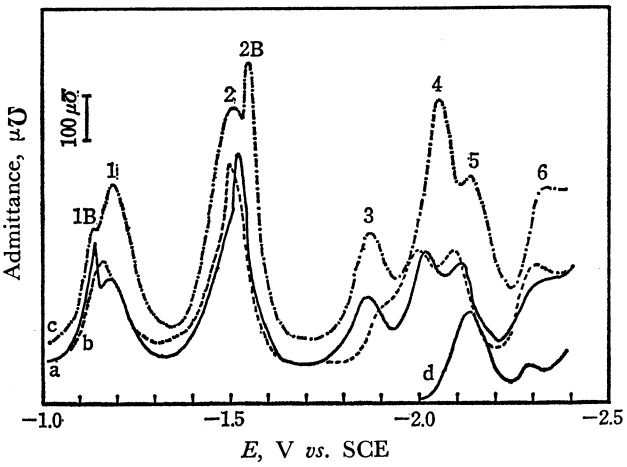
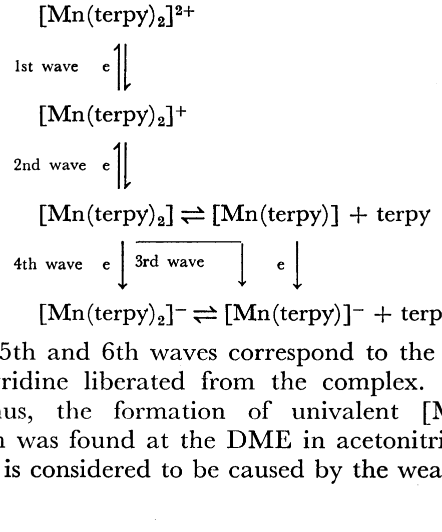


Fig. 2. AC polarograms of $[Mn(terpy)_2](ClO_4)_2$ in 0.1 M TEAP-AN.
a: 0.5 mM $[Mn(terpy)_2](ClO_4)_2$, b: a) + Triton X-100, c: 1.0 mM $[Mn(terpy)_2](ClO_4)_2$, d: 0.5 mM 2,2′,2″-terpyridine.

Triton X-100. The third and fourth waves were close to each other, making it difficult to analyze them. The electrode reactions of the first and second waves were found to be diffusion-controlled. The polarographic data are given in Table 1. The ratio of wave heights for the first four waves was 1.00 : 1.07 : 0.30 : 0.71. The diffusion current constant at the first step was 2.05, which is nearly equal to the value of one-electron reduction of various metal ions[10] and tris(2,2′-bipyridine)manganese(II).[3] From log-plot analysis and Kalousek polarogram, the first and second steps were found to be due to reversible one-electron and quasi-reversible one electron reductions, respectively. The first and second waves were not affected by the addition of free 2,2′,2″-terpyridine, but the third wave was suppressed and the fourth wave showed no distinct diffusion plateau (Fig. 1). AC polarograms of the complex are shown in Fig. 2. The main peak admittance increased with the increase in concentration of the complex, sharp peaks (1B and 2B) being observed at the first and second steps. The 1B peak was suppressed by the addition of triton X-100 but the 2B peak remained unchanged. The electrocapillary curve of manganese(II) complex, shown in Fig. 3, shows a depression in the cathodic potential range. The depression was observed at the potentials whose maximum appeared in AC polarography. This shows that the adsorption of the complex occurs on the electrode surface.

Cyclic voltammograms of manganese(II) complex are shown in Fig. 4. Sharp peaks corresponding to the 1B and 2B peaks appeared at 0.5 mM $[Mn(terpy)_2](ClO_4)_2$ but not at 0.1 mM $[Mn(terpy)_2](ClO_4)_2$. The values of ΔE_{peak} (the difference in peak potentials at the anodic and cathodic sides) are 74 and 51 mV for the first and second waves, respectively. No anodic peak of the third step was observed because of irreversibility of the electrode reaction.

It was found that: 1) the reduction potentials of the third and fourth waves differ from those of 2,2′,2″-terpyridine; 2) the total diffusion current constant (2.07) of the third and fourth waves is nearly equal to the value of one electron reduction of various metal ions; and 3) the third wave was suppressed by the addition of 2,2′,2″-terpyridine. From these results and those for the first and second waves, the electrode processes are estimated as follows:


$[Mn(terpy)_2]^{2+}$
1st wave e ⇅
$[Mn(terpy)_2]^{+}$
2nd wave e ⇅
$[Mn(terpy)_2] \rightleftharpoons [Mn(terpy)] + terpy$
4th wave e ↓ 3rd wave ↓ e ↓
$[Mn(terpy)_2]^{-} \rightleftharpoons [Mn(terpy)]^{-} + terpy$

The 5th and 6th waves correspond to the reduction of terpyridine liberated from the complex.

Thus, the formation of univalent $[Mn(terpy)_2]^{-}$ anion was found at the DME in acetonitrile. The 1B peak is considered to be caused by the weak adsorption

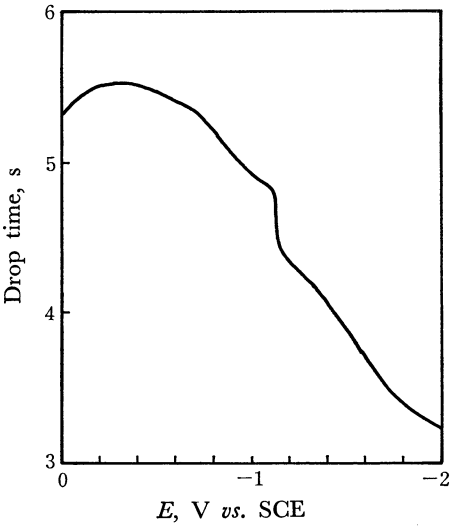


Fig. 3. The electrocapillary curve for $[Mn(terpy)_2](ClO_4)_2$ in 0.1 M TEAP-AN.

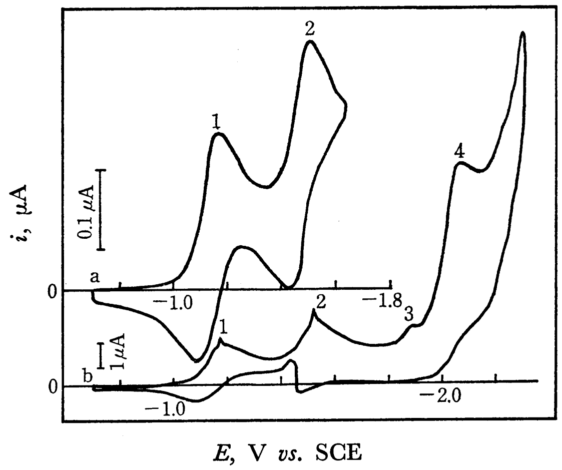


Fig. 4. Cyclic voltammograms of a) 0.1 mM $[Mn(terpy)_2](ClO_4)_2$ at 0.04 V/s, b) 0.5 mM $[Mn(terpy)_2](ClO_4)_2$ at 0.26 V/s in 0.1 M TEAP-AN.

of product, from the fact that the maximum did not interfere with the DC polarogram of the first wave, and the peak at cyclic voltammogram was suppressed by the addition of Triton X-100. On the other hand, the second wave was affected appreciably by the maximum and was not suppressed by the addition of Triton X-100.

Bis(2,2′,2″-terpyridine)cobalt(II) Complex. The DC polarogram of 0.5 mM $[Co(terpy)_2](ClO_4)_2$ in acetonitrile is shown in Fig. 5. A four-step reduction wave was observed and the electrode reactions of the first three steps found to be diffusion-controlled (Table 1). The ratio of the first and second wave heights was 1 : 1. The diffusion current constant for the first wave was 1.96, nearly equal to the value of a one-electron reduction of tris(2,2′-bipyridine)cobalt(II) complex.[2] The value of the reciprocal slope for the first and second waves was close to the theoretical value of 0.059 V, while the log-plot of the third wave gave a curve with two linear parts. The AC polarogram of the complex is also shown in Fig. 5. AC peaks corresponding to the first and second steps were observed, but the peak potential of the third did not coincide with that of the ligand.

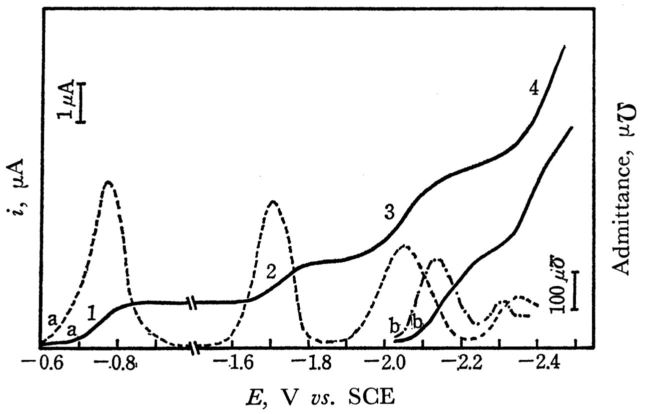


Fig. 5. DC and AC polarograms of 0.5 mM $[Co(terpy)_2](ClO_4)_2$ (curve a) and 0.5 mM 2,2′,2″-terpyridine (curve b) in 0.1 M TEAP-AN.

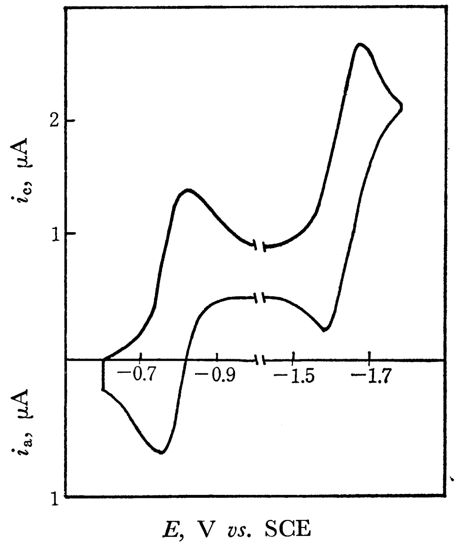


Fig. 6. Cyclic voltammograms of 0.5 mM $[Co(terpy)_2](ClO_4)_2$ in 0.1 M TEAP-AN. Scan rate: 0.03 V/s.

The effect of free 2,2′,2″-terpyridine upon the reduction wave was investigated. No effect was observed upon the first and second waves, but the third and fourth waves increased in height with increase in the concentration of 2,2′,2″-terpyridine.

Cyclic voltammograms of 0.5 mM cobalt(II) complex are shown in Fig. 6. The values of ΔE_{peak} for the first and second steps are close to the theoretical value of reversible one-electron reduction.

Thus, the electrode reactions are written as,

$$[Co(terpy)_2]^{2+} + e \rightleftharpoons [Co(terpy)_2]^+$$

$$[Co(terpy)_2]^+ + e \rightleftharpoons [Co(terpy)_2]$$

The formation of $[Co(terpy)_2]^+$ and $[Co(terpy)_2]$ was found in the same way as in the case of bis(2,2′,2″-terpyridine) iron(II) complex,[11] but that of $[Co(terpy)_2]^-$ could not be confirmed by DC or AC polarography.

Bis(2,2′,2″-terpyridine)nickel(II) Complex. DC and AC polarograms of the nickel(II) complex are shown in Fig. 7. It gave a five-step reduction wave. A small maximum appeared at the positive side of the third wave in DC polarograms. The electrode reactions for the first three waves were found to be diffusion-controlled (Table 1). By the addition of free 2,2′,2″-terpyridine to the solution of 0.5 mM complex, the first wave increased and the second wave decreased. The reciprocal slope of the first wave approached the value of a reversible two-electron reduction. The diffusion current constant for the third step is 2.23, which nearly equals the value of one-electron reduction of various metal ions.[10] The total height of the first and second waves was about twice as much as that of the third wave. The 1B peak in AC polarogram was suppressed but the 3B peak remained with the addition of Triton X-100 (Fig. 7). Cyclic voltammetry of the nickel(II) complex was investigated. The sharp peaks corresponding to the 1B and 3B waves also appeared in the cyclic voltammogram. The 1B peak was significantly large at the anodic and cathodic sides. The clear anodic and cathodic peaks of the first and the second steps were observed and the cathodic peak of the third step was observed as a shoulder at −1.9 V *vs.* SCE.

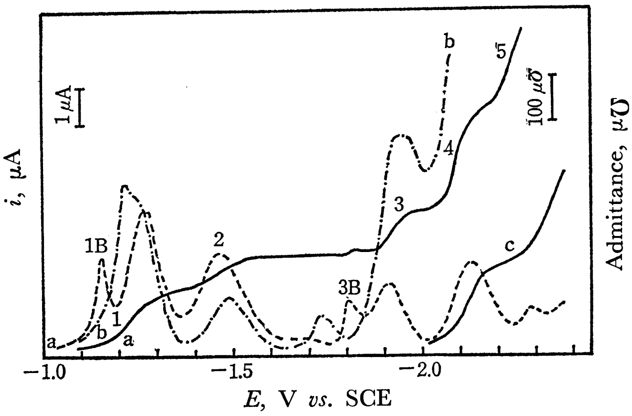


Fig. 7. DC and AC polarograms of $[Ni(terpy)_2](ClO_4)_2$ in 0.1 M TEAP-AN.
a: 0.5 mM $[Ni(terpy)_2](ClO_4)_2$, b: a) +5 mM 2,2′,2″-terpyridine, c: 0.5 mM 2,2′,2″-terpyridine.

The electrode reactions for the first and third waves are estimated as follows.

$$[\mathrm{Ni(terpy)_2}]^{2+} + 2e \rightleftharpoons [\mathrm{Ni(terpy)_2}]$$

$$[\mathrm{Ni(terpy)_2}] + e \rightleftharpoons [\mathrm{Ni(terpy)_2}]^-$$

The univalent $[\mathrm{Ni(terpy)_2}]^-$ anions are formed at the electrode surface. From the fact that the second wave decreased with the addition of 2,2′,2″-terpyridine, the second wave might correspond to the irreversible two electron reduction of dissociated complex species, *e.g.* $[\mathrm{Ni(terpy)}]^{2+}$.

Bis(2,2′,2″-terpyridine)europium(III) Complex. DC and AC polarograms of 0.5 mM $\mathrm{Eu(terpy)_2(ClO_4)_3}$ are shown in Fig. 8. The europium complex gave a four-step reduction wave, the electrode reactions of the first and second waves being found to be diffusion-controlled (Table 1). The diffusion current constant of the first step was 2.05, which is nearly equal to the value of one-electron reduction. The ratio of the wave heights of the first and second steps is 1 : 1.9. It was concluded that the first and second waves were one- and two-electron reduction waves, respectively. The third and fourth waves are due to the reduction of the ligand.

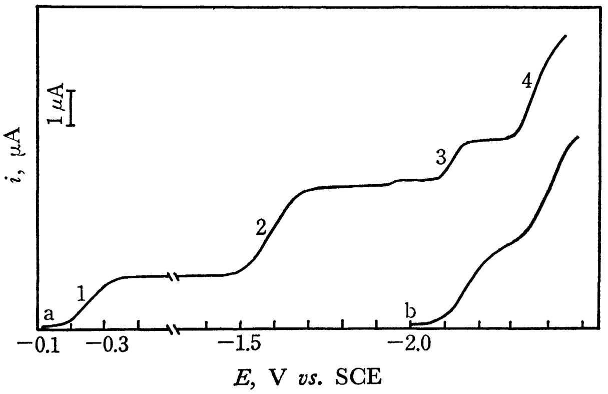


Fig. 8. DC polarograms of 0.5 mM $[\mathrm{Eu(terpy)_2}](\mathrm{ClO_4})_3$ (curve a) and 0.5 mM 2,2′,2″-terpyridine (curve b) in 0.1 M TEAP-AN.

With the addition of free 2,2′,2″-terpyridine, the first wave was shifted to a more negative potential and the value of the reciprocal slope became equal to that of a reversible one-electron reduction. The reversibility of the second wave decreased with an increase in concentration of the ligand reagent.

A cyclic voltammogram of the complex is shown in Fig. 9. Peaks of the first and second steps were observed, the peak potential of the second wave shifting to a more negative potential with increasing scan rate. This indicates the irreversibility of the second step, also. The electrode reaction scheme is shown to be as follows.

$$[\mathrm{Eu(terpy)_2}]^{3+} + e \rightleftharpoons [\mathrm{Eu(terpy)_2}]^{2+}$$

$$[\mathrm{Eu(terpy)_2}]^{2+} + 2e \rightleftharpoons \mathrm{Eu^0} + 2\mathrm{terpy}$$

The standard rate constant (k_s) for the second step was determined to be 6.7×10^{-4} cm/s by the single sweep method.

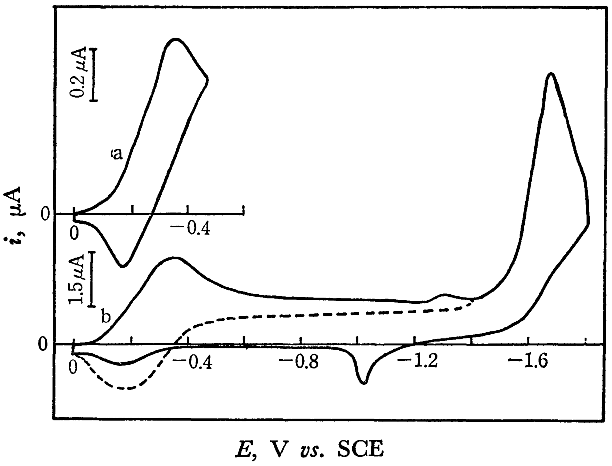


Fig. 9. Cyclic voltammograms of $[\mathrm{Eu(terpy)_2}](\mathrm{ClO_4})_3$ in 0.1 M TEAP-AN.
a: 0.5 mM $[\mathrm{Eu(terpy)_2}](\mathrm{ClO_4})_3$ at 0.038 V/s, b: 0.7 mM $[\mathrm{Eu(terpy)_2}](\mathrm{ClO_4})_3$ at 0.285 V/s.

The waves corresponding to the formation of $[\mathrm{M(terpy)_2}]^-$ (M=Mn and Ni) were observed in DC polarograms. In the case of the Co(II) complex, the formation of $[\mathrm{Co(terpy)_2}]^-$ was not confirmed since the wave overlapped with that of the free 2,2′,2″-terpyridine.

On the other hand, bis(2,2′,2″-terpyridine)europium (III) complex was not reduced to the univalent complex anion but decomposed into metal amalgam and ligands after reduction at the potential of the second wave. This indicates that there is a more stable and stronger tendency of complex formation of d-element than that of f-element in bisterpyridine complexes of metal(0).

The work was carried out with financial support from the Ministry of Education.

References

1) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).
2) N. Tanaka and T. Sato, This Bulletin, **41**, 2059 (1968).
3) Y. Sato and N. Tanaka, *ibid.*, **41**, 2064 (1968).
4) N. Tanaka and T. Sato, *Inorg. Nucl. Chem. Letters.*, **4**, 487 (1968).
5) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, **1937**, 1649.
6) R. Hogg and R. G. Wilkins, *ibid.*, **1962**, 341.
7) S. P. Sinha, *Z. Naturforschg.* **20a**, 552 (1965).
8) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).
9) S. Misumi and M. Aihara, *Talanta*, **19**, 549 (1972).
10) I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 1852 (1957).
11) S. Musumeci, E. Rizzareili, S. Sammartano, and R. P. Bonomo, *J. Inorg. Nucl. Chem.*, **36**, 853 (1974).