ELECTROANALYTICAL CHEMISTRY OF VANADIUM COMPLEXES. COMPARISON OF THE VOLTAMMETRIC FEATURES OF AMAVADINE WITH THOSE OF THE VANADIUM COMPLEXES WITH IMINODIACETIC ACID AND METHYLIMINODIACETIC ACID

Roland MEIER[a], Harald FRANK[b], Reinhard KIRMSE[b], Reiner SALZER[b], Joachim STACH[b], Gerhard WERNER[b] and Matthias OTTO[c]

[a] *Department of Natural Sciences, Technical University of Leipzig, P.O. Box 66, 7030 Leipzig, G.D.R.*

[b] *Department of Chemistry, Karl Marx University Leipzig, 70 10 Leipzig, G.D.R. and*

[c] *Department of Chemistry, Bergakademie Freiberg, 9200 Freiberg, G.D.R.*

The voltammetric behaviour of amavadine (AV) was found to be considerably different from that of the complexes of VO^{2+} with methyliminodiacetic acid (MIDA) and iminodiacetic acid (IDA). To get an insight in the rather complicated reduction mechanism of the latter complexes the reductions of V(III) (MIDA) and V(III) (IDA) have been studied for comparison. The species V(III) (MIDA)$_2$ and V(III) (IDA)$_2$ are reduced to the appropriate V(II) complexes in a chemically reversible process. VO(MIDA)$_2$ and VO(IDA)$_2$ are reduced to the same complexes via an ECE mechanism. The investigation of the electroreduction of AV shows that this process is not reversible in the chemical sense. As a probable explanation, the conclusion was drawn that AV and the usual V(IV)O-iminocarboxylato complexes differ in their structures.

Amavadine (AV) is a naturally occuring vanadium complex which can be isolated from the toadstool *Amanita muscaria*[1].

The results presented in a recent review have shown that AV is a complex of the VO^{2+}-unit with two molecules of N-hydroxy-imino-α,α'-dipropionic acid $(HIDPA)$ (ref.[2]).

Whereas different spectroscopic methods were applied to study the solution chemistry of AV and related complexes[2], a report on the electrochemical properties of AV did not yet appear in the literature. Only, Nawi and Riechel investigated the VO^{2+} complexes with iminodiacetic acid (IDA), α,α'-iminodipropionic acid and β,β'-iminodipropionic acid by means of cyclic voltammetry[3].

We have isolated AV from collected mushrooms and studied its electrochemistry with cyclic voltammetry (CV) and differential pulse polarography (DPP).

For comparison, the V(IV) and V(III) complexes with IDA and methyliminodiacetic acid (MIDA) *II* were investigated in order to verify whether the electrochemical

properties of the VO^{2+}-iminocarboxylato complexes are comparable with those of their N-hydroxy analogues (*I*), as suggested by Nawi and Riechel[3].
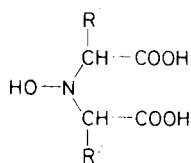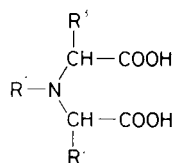
I, $R' = R^2 = H$, CH_3 *II*, $R' = R^2 = R^3 = H$, CH_3

EXPERIMENTAL

Spectroscopic Measurements

IR spectra were recorded with the FTIR-spectrometer IRF 180 (Center of Scientific Instruments, Berlin-Adlershof, G.D.R.) using the KBr-pellet technique. The UV/VIS-spectra were recorded with a specord M 40 double channel spectrophotometer (VEB Carl Zeiss Jena, G.D.R.). The EPR-spectra were obtained with a Varian E 112 spectrometer working at room temperature.

Electrochemical and pH Measurements

All measurements were done in a standard three compartment cell. Mercury electrodes were used throughout the work. Cyclic voltammograms were obtained with the static mercury drop electrode SMDE 1 working in the hanging mercury drop mode. This device is part of the polarographic analyzer PA 3 (Laboratorní přístroje, Prague, Czechoslovakia) A classical dropping mercury electrode was used to record the differential pulse polarograms. The drop time was controlled with a mechanical drop knocker. All solutions were degassed with prepurified argon (10 min) before each measurement. The potentials given in this work refer to the $Ag/AgCl/KCl_{sat}$ reference electrode, unless otherwise stated.

The pH-values were measured with an EGA 801N combination electrode (FI "Kurt Schwabe" Meinsberg, G.D.R.) coupled to a MV 88 pH-meter (VEB Praecitronik, Dresden, G.D.R.).

Materials and Solutions

MIDA and the disodium salt of IDA were commercial products and used as received. The V(III) complexes of IDA and MIDA were prepared in solution by adding an aliquot of V(III) from a stock solution to an exhaustively degassed solution which contained the appropriate amount of the ligand. The pH was adjusted by addition of small amounts of degassed concentrated NaOH or H_2SO_4. In the same way, the VO^{2+} complexes of MIDA and IDA were generated. The V(III) stock solution was prepared from VCl_3 (Riedel–de Haen) in 0·5M HCl. The VO^{2+} stock solution was made from $VOSO_4.5 H_2O$ (Merck). Both solutions were standardized spectrophotometrically[4,5]. The isolated AV (see below) was added to the sample solution as a precisely weighed solid aliquot.

Isolation and Identification of AV

The mushrooms were collected in the Colbitz forest near Klitzschen, Kreis Torgau, G.D.R. The same isolation procedure as given in ref.[1] was used. A somewhat lower yield (30 mg AV per 5 kg fresh mushrooms) was obtained.

The purity of the isolated substance was controlled by comparison of its spectral data with those given in the literature.

Parameters of the visible absorption spectrum are listed in Table I together with the values reported earlier. The slight differences in the band locations and the ε-values, respectively, might be caused by the pH-dependence of these values. The IR-spectra of our isolated product have been found to be identical with that given in ref.[6] for the natural AV. The determined EPR-parameters are given in Table II together with previous determinations. The deviations of the values from different sources should have the same reason as mentioned for the data of the visible absorption spectra.

RESULTS AND DISCUSSION

The V(III)/V(II) *Couple Complexed with* MIDA *and* IDA

Previous electrochemical studies have shown that V(III)EDTA$^-$ undergoes a simple, one-electron, reversible reduction to V(II)EDTA^{2-} without significant changes in the coordination environment of the vanadium center[7-9].

TABLE I

Comparison of VIS-parameters of AV from different sources; values in parantheses are ε-values (molar absorptivity, $mol^{-1} \, l \, cm^{-1}$)

	Ref.[1]	Ref.[2]	This work
	565 nm (23·5)	560 nm (29·0)	570 nm (23·0)
	715 nm (18·9)	700 nm (23·0)	720 nm (19·0)
	775 nm (19·3)	790 nm (23·8)	780 nm (19·5)

TABLE II

Room temperature EPR-parameters of the AV from this work in comparison to literature data

Parameter	Ref.[2]	Ref.[23]	This work
$A_0 . 10^4, cm^{-1}$	83·0	79·6	81·4
g_0	1·962	1·970	1·968

For the V(III)EDTA$^-$ complex one can assume a hexadentate coordination of the ligand in solution[10,11]. That means the first coordination sphere being formed by two nitrogens and four carboxylato-oxygen atoms. An identical coordination environment should be found for the V(III) ion in its bis complexes with IDA and MIDA, respectively. To our knowledge, the existence of these complexes was not yet mentioned in the literature. Nevertheless, it should be possible to generate both species in solution. This was achieved by the use of a sufficient ligand excess and by adjustment of an appropriate pH-value. Solutions in which the existence of both V(III)(MIDA)$_2$ and V(III)(IDA)$_2$ can be assumed gave a typical CV-pattern. In Table III the data for a series of CV's recorded under these conditions at different scan rates are summarized. The peak potential separation (ΔE_p) of anodic and cathodic peak positions is somewhat larger than expected for a fully Nernstian couple. But, the ratio of the anodic to cathodic peak currents (i_{pa}/i_{pc}) is essentially unity which indicates that chemical reversibility is given.

To establish the electrode reactions, the pH-dependence of the half-wave potentials ($E_{1/2}$) for the reduction of both V(III)(IDA)$_2$ and V(III)(MIDA)$_2$ was evaluated. Both $E_{1/2}$-values did not show any significant change in the pH-range 6 to 9. This led us to formulate the electrode reactions for the V(III)(IDA)$_2$/V(II)(IDA)$_2$ and V(III)(MIDA)$_2$/V(II)(MIDA)$_2$ couples, respectively, as follows:

$$V(III)L_2^- + e \rightleftharpoons V(II)L_2^{2-} \quad (L\ MIDA^{2-}, IDA^{2-}) . \qquad (1)$$

The difference between both couples is the more negative located $E_{1/2}$-value of the IDA-couple ($-1\cdot1$ V vs Ag/AgCl/KCl$_{sat}^-$) in comparison to that of the MIDA-couple ($-1\cdot0$ V vs Ag/AgCl/KCl$_{sat}^-$). The separation between the peak potentials is also somewhat larger for the latter couple, indicating a smaller rate of electron transfer

TABLE III

CV-data for the reduction of V(MIDA)$_2^-$. 1 mM V(III) in 0·1M Na$_2$SO$_4$, 0·1M MIDA, pH 7·8

v mV s^{-1}	E_{pc} mV	E_{pa} mV	ΔE_p mV	$E_{1/2}$^{a} mV	$E_{pc} - E_{pc/2}$ mV	$i_{pc}v^{-1/2}$ $\mu A\ mV^{-1/2}\ s^{1/2}$	i_{pa}/i_{pc}^{b}
200	$-1\,053$	-947	106	$-1\,000$	83	0·43	1·03
100	$-1\,050$	-943	106	-997	80	0·46	1·10
50	$-1\,048$	-945	101	-997	78	0·48	1·07
20	$-1\,045$	-945	100	-995	75	0·53	1·02

^{a} $E_{1/2} = (E_{pc} + E_{pa})/2$; ^{b} determined by Nicholson's semiempirical method[24].

compared to the former couple. This raises the question whether the coordination environments for V(III)(IDA)$_2$ and V(III)(MIDA)$_2$ are really identical.

In this regard, a comparison with the analogues Cr(III) complexes is useful[12]. Weyh and Hamm suggested a *cis*-configuration for Cr(III)(IDA)$_2$ (two nitrogens on neighbouring positions in the basal plane of the octahedron) while Cr(III). .(MIDA)$_2$ should occur as the *trans*-meridional isomer (two nitrogens at opposite positions in the basal plane). It might then be possible that the same is true for V(III)(MIDA)$_2$ and V(III)(IDA)$_2$, whereas the latter should be more similar to V(III)EDTA than the former one.
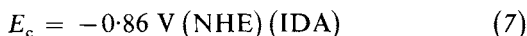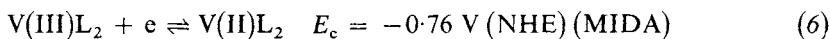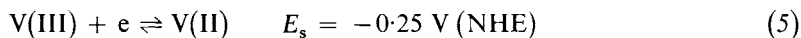
In this connection, the knowledge of the stability constants of both V(III) complexes would be useful. But with the formal potentials ($E_{1/2}$ can be taken as E_c is formal potential of the complexed couple), only the stability constant ratio of the oxidized form to that of the reduced form $\log \beta_{III}/\log\beta_{II}$ is accessible. This ratio was evaluated as follows[13]:

$$E_c - E_s = (-0.059/n) \log (\beta_{III}/\beta_{II}),\qquad (2)$$

where β_{II} and β_{III} are the stability constants for the reactions as defined in Eqs (*3*) and (*4*), respectively,

$$V(II) \; + 2\,L \rightleftharpoons V(II)L_2 \quad (L\;MIDA^{2-}, IDA^{2-}) \qquad (3)$$

$$V(III) + 2\,L \rightleftharpoons V(III)L_2 \qquad (4)$$

and E_c and E_s are the potentials for the complex ion and aqueous ion half-cells (Eqs (*5*) and (*6*))

$$V(III) + e \rightleftharpoons V(II) \qquad E_s = -0.25 \text{ V (NHE)} \qquad (5)$$

$$V(III)L_2 + e \rightleftharpoons V(II)L_2 \quad E_c = -0.76 \text{ V (NHE) (MIDA)} \qquad (6)$$

$$E_c = -0.86 \text{ V (NHE) (IDA)} \qquad (7)$$

with one electron involved in the redox system. The observed potential shift corresponds to a ratio of the formation constants $\beta_{III}/\beta_{II} = 4.4 \cdot 10^8$ (MIDA) and $2.2 \cdot 10^{10}$ (IDA). This agrees well with the observed strong stabilization of the M(III)EDTA complexes (M is a first-row transition metal) over their M(II)EDTA- -partners[14].

Reduction of V(IV)O(MIDA)$_2$ *and* V(IV)O(IDA)$_2$

Until now, no equilibrium data were reported on the formation of V(IV)O^{2+} bis- -complexes with IDA and MIDA. In a paer of Napoli only the existence of the

mono-complex of $V(IV)O^{2+}$ and IDA was described[15]. On the other hand, a complex with the composition $VO(IDA)_2.2\,H_2O$ was isolated in the solid form[3].

Our room temperature EPR measurements in solutions of VO^{2+} with varying ligand concentrations and increasing pH-values have shown that under proper conditions the VOL_2-form (L MIDA, IDA) predominates[16].

A CV recorded in such a solution is shown in Fig. 1 for the reduction of $VO(MIDA)_2$ (the reduction observed in solutions of $VO(IDA)_2$ gave identical CV's).

Usually, the electrochemical reduction of $V(IV)O^{2+}$ complexes is an irreversible process[17]. The rupture of the double bond between the yl-oxygen and the $V(IV)$--center causes a high overpotential. Therefore, the $V(IV)$ reduction occurs at potentials more negative than the $E_{1/2}$-value of the appropriate $V(III)/V(II)$ couple and leads directly to $V(II)$. The result is a rather complicated mechanistic pattern for the whole electrode process (a distinct type of an ECE-mechanism, for analogy see e.g. ref.[18]).
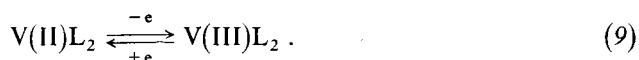
At first, the waves shown in Fig. 1 were interpreted qualitatively. In the first scan (curve 1), VOL_2 is directly reduced to $V(II)L_2$. In the potential range of interest, the $V(II)L_2$ can be reoxidized only to $V(III)L_2$ (anodic part of scan 1).

That this is true shows scan 2 which was recorded immediately after 1 at the same mercury drop. In this way, the reduction wave for the electrogenerated $V(III)L_2$ complex becomes visible. Regarding the $E_{1/2}$ and ΔE_p-values the so produced $V(III)L_2/V(II)L_2$ couple is identical with that described in the previous section. The observed reaction sequence can be formulated as follows

First cathodic scan:

$$V(IV)OL_2 + 2\,H^+ + 2\,e \rightleftharpoons V(II)L_2 , \tag{8}$$
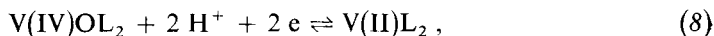
Return scan and second scan:

$$V(II)L_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} V(III)L_2 . \tag{9}$$

A more quantitative elucidation of the mechanistic details of the reduction of $V(IV)OL_2$ complexes is in progress and will be reported elsewhere.

Electrochemistry of Isolated AV

The suggestions made by Nawi and Riechel[3] and, very recently, by Kneifel and Bayer[6] let us await a very similar electrochemistry of AV compared to $VO(IDA)_2$ and $VO(MIDA)_2$. The stability constant of AV was estimated to be higher than that of $VO(EDTA)$ (ref.[6]) ($\log K_{VOEDTA} = 18\cdot35$ (ref.[10])). So, electrochemical measurements should be possible over a wide pH-range without appreciable hydrolytic decay of AV. For the case of $VO(EDTA)$ this was demonstrated by us earlier[9].

Therefore, in adaptation to $VO(MIDA)_2$ and $VO(IDA)_2$, our measurements were started in unbuffered Na_2SO_4-solution in the pH-range 6—9. But, in the course of the CV-measurements, neither reduction nor oxidation waves of AV could be observed.

The DPP-measurements did show no peak but only a very drawn out wave (not shown) superimposed with the final current rise. As a conclusion, measurements were made in Na_2SO_4-solutions with lower pH-values. The results of a series of DPP-measurements in Na_2SO_4 with pH-values ranging from 2·5 to 3·5 are shown in Fig. 2. The presence of different species, apparently in equilibrium with each other, is obvious. The potential for the peak (E_{pc}) at pH 2·5 (solid line in Fig. 2) is shifted in the negative direction with increasing pH. A plot of E_{pc} versus pH gave a slope of 120 mV/pH in the range 2 < pH < 4. If one assumes $n = 1$, two protons should participate in the electrode reaction. This assignment is only tentative because n was not determined directly.

Parallelly with the potential shift, the current of this peak increases, reaches a maximum and decreases drastically at pH > 3·0. While the current of the first peak decreases, two peaks at more negative potentials grow up (see Fig. 2). These peaks suffer also a cathodic shift when the pH-value is raised. At least now, a comparison should be made with the statements in ref.[6] and the equilibrium data in paper[2]. The stability constant for AV should be the same as for $VO(HIDPA)_2$, its synthetic analogue. For the latter complex a brutto constant with the value $\log \beta_2 = 12·85$ was determined[2]. This is about six orders of magnitude lower than $\log K$
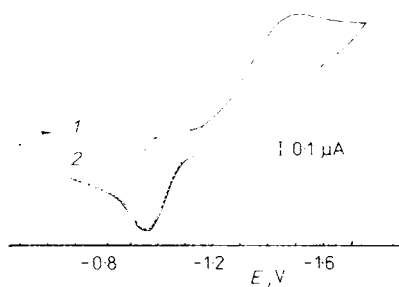

FIG. 1

Cyclic voltammogram of 0·5mM VO^{2+} in 0·1M Na_2SO_4, 0·05M MIDA. pH 8·1, scan rate 0·2 V s^{-1}. *1* first scan; *2* second scan at the same Hg-drop
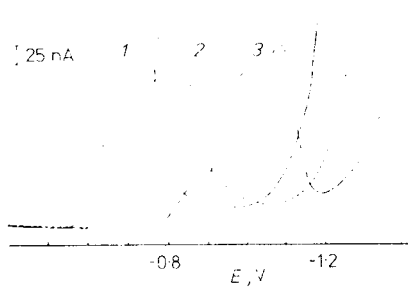
FIG. 2

Differential pulse polarograms of 0·4 mM AV in 0·1M Na_2SO_4. Drop time 1 s, scan rate 2 mV s^{-1}, pulse amplitude −25 mV; pH: *1* 2·45; *2* 3·0; *3* 3·5

for the formation of VO(EDTA). Thus, it is not surprising that a mixture of several V(IV) species was found in our DPP-measurements.

A distribution-pH diagram for the different complexed species in the system VO^{2+}–HIDPA with an assumed metal to ligand ratio of 1 : 5 is given in Fig. 2 of ref.[2]. On the basis of this diagram, a tentative assignment of the species causing the DPP-peaks in Fig. 2 is possible.

One can assume that the more anodic peak is the result of the reduction of VO(HIDPA) whereas the second and third peak appear due to the reduction of $VO(HIDPA)_2$ and $V_2O_2(HIDPA)_2(OH)_2$, respectively.

The reduction product is consumed by a chemical reaction. This becomes clearly visible on the CV's in Fig. 3 which were recorded under identical conditions like the DPP's in Fig. 2. No anodic waves could be detected with scan rates up to 500 mV s^{-1}. One can also see that the cathodic peaks are shifted to the negative direction with increasing pH.

To answer the question on the nature of the reduction products, a controlled potential coulometric study with subsequent investigation of the reduced species formed in the bulk of the solution would be necessary. This was impossible because the amount of isolated AV was too low for that purpose.

So, in view of the electrode mechanism and the nature of the products, only preliminary suggestions are possible. We have to add some observations found in the CV-investigation of the reduction of VO–MIDA and VO–IDA complexes under
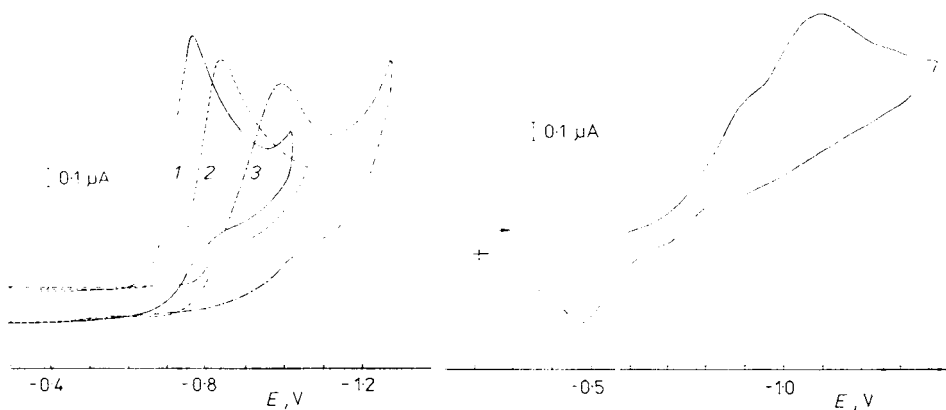

FIG. 3

Cyclic voltammograms of 0·4 mM AV in 0·1M Na_2SO_4 at different pH-values. Scan rate 0·2 V s^{-1}; pH: *1* 2·45; *2* 3·0; *3* 3·5

FIG. 4

Cyclic voltammogram of 1 mM VO^{2+} in 0·1M Na_2SO_4, 3 mM MIDA. pH 4·0, scan rate 0·1 V s^{-1}

conditions which are comparable with those of the AV investigation (lower pH, no ligand excess).

A CV for the reduction of VO–MIDA in 0·1M Na_2SO_4 at pH 4·0 is shown in Fig. 4. A double wave is seen in the cathodic scan whereas a single wave is produced in the anodic scan. The separation between cathodic and anodic peak potentials (about 500 mV) shows that no reversible redox couple is found. We assume that the double wave is caused by the reduction of VO(MIDA) and VO(MIDA)$_2$, respectively. Both are reduced to the same V(II)–MIDA complex. This complex is so unstable at this pH that it decays in the time scale of CV to uncomplexed V(II) and free ligand.

The suggestion is based on the different complexing properties of the three vanadium oxidation states under study. For example, the formation constants with EDTA differ drastically[10]: $\log K_{V(II)EDTA} = 12·7$, $\log K_{V(III)EDTA} = 25·7$ and $\log K_{VOEDTA} = 18·35$.

As a consequence, V(II)-aminocarboxylato complexes are very susceptible to hydrolytic decay under conditions where their corresponding partners in the V(IV)- and V(III)-state are still stable[9].

The assignment of the anodic peak in Fig. 4 to the oxidation of the free V(II) to V(III) is based on the comparison of its peak potential ($E_{pa} = -0·47$ V) with the formal potential of the uncomplexed V(III)/V(II)-couple ($E° = -0·45$ V) (ref.[17]).

We mention these facts because under the condition that AV behaves like a typical VO^{2+}-aminocarboxylato complex the CV responses should be identical but the reoxidation wave for the uncomplexed V(II) is missed in the case of the AV reduction.

Our preliminary interpretation of the AV reduction is based on the following observations:

The difference $E_{pc} - E_{pc/2}$ (cathodic peak potential minus potential at half peak height) for the CV's recorded with different scan rates at pH 2·45 (data see Table IV) is close to the value for an one-electron reduction (59 mV).

On the other hand, a plot of the E_{pc}-values from Table IV versus the logarithm of the scan rate ($\log v$) gave a slope of 31 mV. This is very close to the value (29·6 mV)

TABLE IV
CV-data for the reduction of AV at pH 2·45 . 0·4 mM AV in 0·1M Na_2SO_4

v mV s^{-1}	E_{pc} mV	$E_{pc} - E_{pc/2}$ mV	$i_{pc}v^{-1/2}$ μA mV$^{-1/2}$ s$^{1/2}$
200	−780	60	0·087
100	−775	58	0·091
50	−760	57	0·090
20	−755	59	0·093

that is found when the electron transfer reaction is followed by a very fast chemical reaction and an EC_{irr}-mechanism is operative[20].

Thus, the conclusion can be drawn that AV is reduced to a V(III)-product which reacts immediately further.

We suspect, that it is the reactivity of the HIDPA-ligand itself which is responsible for this irreversible following reaction. HIDPA is a derivative of hydroxyl amine II in which the nitrogen bears the formal oxidation number -1 (in IDA and its derivatives it has the oxidation number -3). So, HIDPA should be oxidizable and reducible, as well. From the literature it is known, that V(III) and V(III)-aminocarboxylato complexes can reduce hydroxyl amine to ammonia under generation of V(IV) (refs[21,22]).

It seems possible that in the case of the AV reduction, the generated V(III) product should also be able to react in an intramolecular redox pathway with HIDPA. However we were unable to detect the products of this step in the course of our CV-measurements. (These might be V(IV), NH_3 and propionic acid). To bring clarity to these questions it is necessary to prepare HIDPA in a pure form and to investigate its reactivity towards V(III). Such attempts are now in progress in this laboratory.

CONCLUSIONS

The mechanistic study for the electroreduction of AV reveals that AV behaves quite differently compared to common V(IV) iminocarboxylato complexes. The differences in the redox behaviour might, among others, be the result of different structures for both classes of complexes. This suggestion is supported, e.g., by the drastically different EPR parameter of the VO^{2+} complexes with the N-hydroxy IDA-derivatives, on the one hand, and those of the VO^{2+} complexes with the common IDA--derivatives, on the other hand[2].

REFERENCES

1. Bayer E., Kneifel H.: Z. Naturforsch., B 27, 207 (1972).
2. Bemsky G., Felcam J., Frausto de Silva J. J. R., Moura I., Moura J. J. G., Candida Vaz M., Vilas Boaz L. F. in: *Frontiers in Bioinorganic Chemistry* (A. V. Xavier, Ed.), p. 97. VCH Publishers, Weinheim 1986.
3. Nawi M. A., Riechel T. L.: Inorg. Chim. Acta 93, 131 (1984).
4. Martin E. L., Bentley K. E.: Anal. Chem. 34, 354 (1962).
5. Chasteen N. D. in: *Biological Magnetic Resonance* (L. Berliner and J. Reuben, Eds), Vol. 3, p. 53. Plenum, New York 1981.
6. Kneifel H., Bayer E.: J. Am. Chem. Soc. 108, 3075 (1986).
7. Pecsok R. L., Juvet R. S.: J. Am. Chem. Soc. 75, 1202 (1953).
8. Kato N., Nakano K., Tanaka K.: J. Electroanal. Chem. 149, 83 (1983).
9. Meier R.: *Thesis*. Karl Marx University, Leipzig 1985.

10. Schwarzenbach G., Sandera J.: Helv. Chim. Acta *36*, 1089 (1953).
11. Ahmad J. A. M., Higginson W. C. E.: J. Chem. Soc., Dalton Trans. *1983*, 1449.
12. Weyh J. A., Hamm R. E.: Inorg. Chem. *7*, 2431 (1968).
13. Meites L.: *Polarographic Techniques*, 2nd ed., p. 279. J. Wiley, New York 1965.
14. Garven F. L. in: *Chelating Agents and Metal Chelates* (F. P. Dwyer and D. P. Mellor, Eds), p. 283. Academic Press, New York 1964.
15. Napoli A., Pontelli L.: Gazz. Chim. Ital. *103*, 1219 (1973).
16. Meier R., Kirmse R., Stach J.: Unpublished results.
17. Israel Y., Meites L.: Vanadium, in: *Encyclopedia of Electrochemistry of the Elements* (A. J. Bard, Ed.), Vol. 7, p. 293. Dekker, New York 1976.
18. Gaudiello J. G., Wright T. C., Jones R. Y., Bard A. J.: J. Am. Chem. Soc. *107*, 888 (1985).
19. Meier R., Werner G., Otto M.: Unpublished results.
20. Nadjo L., Saveant J. M.: J. Electroanal. Chem. *48*, 113 (1973).
21. Tomat R., Rigo A.: J. Inorg. Nucl. Chem. *36*, 611 (1974).
22. Tomat R., Rigo A.: J. Electroanal. Chem. *50*, 345 (1974).
23. Krauss P., Bayer E., Kneifel H.: Z. Naturforsch., B *39*, 829 (1984).
24. Nicholson R. S.: Anal. Chem. *37*, 1351 (1965).