INORGANICA CHIMICA ACTA

Volume 5, Number 4 December 1971

Contribution from the Jaroslav Heyrovsky Institute of Polarography,
Czechoslovak Academy of Sciences, Vlašská 9, Prague 1, Czechoslovakia

Nitrosyl Compounds. IX. The Purported Existence of the $[V(CN)_5NO]^{5-}$ Ion

J. Masek and R. Pribil, Jr.

Received February 12, 1971

In the light of recent studies the existence of the $[V(CN)_5NO]^{5-}$ ion seems to be not fully established. Our results suggest that the only preparation method described in the literature yields polyvanadate-type compounds containing no NO and CN groups. The analysis of the preparation method used explains its inapplicability for the given case.

Introduction

The complex anion $[V(CN)_5NO]^{5-}$ is the last member of the isoelectronic series of pentacyanonitrosyl complexes $M(CN)_5NO^{n-}$ where M is Fe (n=2), Mn (n=3), Cr (n=4), V (n=5). The complex $K_5[V(CN)_5NO]$ was first described and prepared by Griffith, Lewis, and Wilkinson[1] who used the so-called hydroxylamine method of introducing the nitrosyl group into the complex. The resulting substance was identified on the basis of potassium and vanadium determination. The found IR bands 1575 cm^{-1} and 2095 cm^{-1} were assigned as corresponding to NO and CN stretching vibrations, respectively.

Manoharan and Gray[2] calculated the electronic structure of the complex and compared the theoretical results with experimental spectroscopic data obtained with a compound which they prepared according to the original procedure.[1] Some discrepancies between the predicted and observed energies were accounted for by the neglect of the effect of the coulomb integrals in the calculation.

The X-ray analysis of the compound was studied recently by Jagner and Vannerberg[3] who came to the conclusion that the substance obtained by the mentioned method[1] contains either two different species or a single species $K_3[V(CN)_5NO]$. Their IR spectra show deviations from those obtained in the original paper[1] (1530 cm^{-1} assigned as ν_{NO}, and 2080 cm^{-1} and 2110 cm^{-1} assigned as ν_{CN}).

Within our systematic studies of nitrosyl complexes we examined the polarographic behaviour of the compound prepared by the procedure[1] and followed also polarographically the intermediates of the preparation. On the basis of these results, those of the elemental analysis and analysis of the preparation method we came to the conclusion that this method does not lead to the desired complex.

Experimental Section and Results

The compound was prepared according to the procedure described by Griffith *et. al.*[1] Since the product yields a relatively complicated polarographic pattern we tried to exclude the possible influence of impurities and to ascertain that the substance is chemically homogeneous. It was found that a repeated dissolution and separation of the product from the aqueous solution by means of ethylalcohol does not influence the polarographic pattern of the product.

When the orange oil obtained after separation by ethanol was dissolved in water and transferred into the methylalcohol a fine precipitate was obtained which after separation and drying in vacuo yielded a yellow powder. This substance showed identical polarographic behaviour as the orange substance prepared by the original procedure, *i.e.* by trituration of the orange oil with a mixture of ethanol and ether. A typical polarographic curve is shown in Figure 1.

In view of this result we followed the reaction course of the preparation polarographically. In different stages of the preparation samples of the reaction mixture were taken and examined in the Britton-Robinson buffer of pH 7.00. It appeared that the product does not differ polarographically from the metavanadate in the given medium. It was found that during the preparation no new polarographically active products were formed and that the development of the deeply red colour was accompanied only by a

---

* Part VIII: *Inorg. Chim. Acta*, in press.

(1) W.P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1632 (1959).

(2) P.T. Manoharan and H.B. Gray, *Inorg.Chem.*, 5, 823 (1966).

(3) S. Jagner and N.G. Vannerberg, *Acta Chem. Scand*, 22, 3330 (1968).

slight lowering of the original waves corresponding to the metavanadate. The polarographic pattern observed is in accord with that obtained by Filipovič *et. al.*[4] who studied the polarographic behaviour of metavanadate in neutral phosphate buffer media. These results showed unambiguously that the reaction product is not a single vanadium pentacyanonitrosyl complex whereas the colouration of the reaction mixture and of the product indicates the formation of polyvanadates.[5,6]

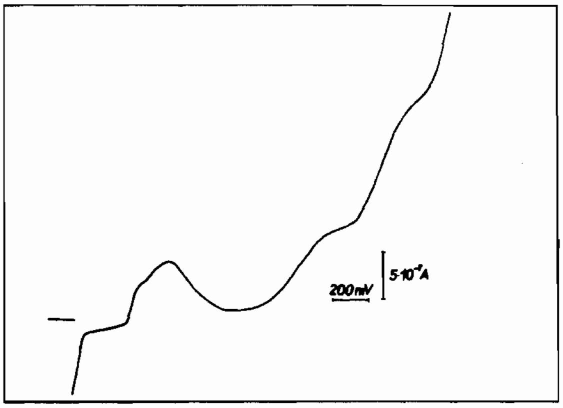

Figure 1. Polarographic Curve of the Substance Prepared according to Griffith *et al.*[1]
Supporting electrolyte: Britton-Robinson buffer pH 7.12. Start from +0.3 V vs. NCE.

The elemental analysis of the resulting products were carried out with the following results. The orange powder prepared by the original trituration procedure,[1] found: C, 1.87, 1.95; N, 1.27, 1.00; H, 1.12, 0.98; K, 40; V, 21. Light yellow powder precipitated by methylalcohol, found: C, 1.67, 1.86; N, less than 0.50; H, 0.68, 0.79; K, 34; V, 21. For $K_5[V(CN)_5NO] \cdot H_2O$ calculated: C, 14.17; N, 19.70; H, 0.47; K, 46.11; V, 12.01. From these results it is seen that the carbon and nitrogen content in the prepared substances ranges on the level of impurities and consequently the compounds do not contain CN and NO as ligands.

The IR spectra contained several strong absorption bands in the region 650-1200 cm^{-1} and another one at 1660 cm^{-1} found with both products. In addition, with the orange product absorption was found in the region 1400-1480 cm^{-1}. In the region of the stretching vibrations of the CN group both substances showed only a very weak absorption.

The preparation of the substance was carried out very carefully and was repeated many times. Even so we did not succeed in preparing a substance which could be identified as a vanadium cyanonitrosyl compound although the substance agreed well with the visual description given in the literature.

Discussion

The hydroxylamine method used for the preparation of the complex is one of the general methods for preparanig transition metal nitrosyl complexes. The fundamental step in this procedure is the substitution of one CN^- group in the hexacyano complex formed as an intermediate, for the NO^- group.[7,8] This substitution is accompanied immediately by an electron density redistribution in form of an internal redox process (the NO^- group is oxidized formally to NO^+ and the central ion is reduced by two oxidation numbers lower). The source of the NO^- group is hydroxylamine which undergoes a spontaneous disproportionation in alkaline media:

$$2NH_2OH + OH^- \rightarrow NH_3 + NO^- + 2H_2O$$

In addition, the hydroxylamine plays in some cases a role of a reducing agent. E.g. in the preparation of $K_3[Cr(CN)_5NO]$ the starting material is chromate[8] which is reduced to Cr^{3+}. In the intermediate $[Cr^{III}(CN)_6]^{3-}$ one of the CN^- groups is substituted for the NO^- group and the subsequent internal redox process leads formally to $[Cr^I(CN)_5NO^+]^{3-}$.

Assuming that the formation of the vanadium pentacyanonitrosyl complex should proceed with the same mechanism then hydroxylamine had to be able to reduce V^V to V^I which is highly improbable for thermodynamic reasons. Although exact standard potential values for the lower valent vanadium systems in alkaline media are not available, from analytical applications it can be deduced that lower valent vanadium species are in alkaline media strong reducing agents. The potential of equimolar 0.1 M VO^{2+}/VO_3^- system in 2.5 M NaOH amounts to −0.60 V (vs. standard hydrogen electrode, Europian convention of potential sign) and thus already VO^{2-} is in alkaline media a fairly strong reducing agent, comparable with the hydroxylamine couple $NH_2OH/N_2O_2^{2-}$ in alkaline media[11] ($E = -0.76$ V). The resistance of the trivalent vanadium species towards reduction in alkaline media is demonstrated by the fact that the reduction of vanadic acetate for the purpose of preparation of $K_4[V^{II}(CN)_6]$ must be carried out by means of a reducing agent as strong as potassium amalgam.[12]

For these reasons it is highly improbable that the hydroxylamine method could lead even theoretically to the formation of the complex $K_5[V(CN)_5NO]$ since hydroxylamine is not able to reduce the metavanadate in alkaline medium to lower oxidation states. Under these circumstances the formation of cyanide or nitrosyl complexes cannot be expected which is in agreement with the results of elemental analysis of the product in which carbon and nitrogen was found only in trace amounts. In view of our polarographic results and kind of the colouration it seems probable that the substance hitherto considered as $K_5[V(CN)_5NO]$ is a mixed compound of a polyvanadate type.

---

[4] I. Filipovic, Z. Hall, Z. Gasparac and V. Klemencic, *J. Am. Chem. Soc.*, *76*, 2074 (1954).
[5] O.W. Howarth and R.E. Richards, *J. Chem. Soc.*, 864 (1965).
[6] V. Koncel, private communication.
[7] W. Hieber, R. Nast, G. Gehring, *Z. Anorg. Chem.*, *256*, 169 (1948).
[8] W.P. Griffith, J. Lewis, G. Wilkinson, *J. Cem. Soc.*, 872 (1959).
[9] O. Tomicek, *Chem. Listy*, *32*, 442 (1938).
[10] H.H. Willard, G.D. Manolo, *Ind. Eng. Chem. An. Ed.*, *19*, 462 (1947).
[11] W.M. Latimer, « The Oxidation States of the Elements and Their Potentials in Aqueous Solutions », p. 104. Prentice-Hall, New York 1952.
[12] P.J. Durrant and B. Durrant, « Introduction to Advances Inorganic Chemistry », p. 968, Longmans, London 1962.