Russian Journal of Coordination Chemistry, Vol. 27, No. 1, 2001, pp. 38–40. Translated from Koordinatsionnaya Khimiya, Vol. 27, No. 1, 2001, pp. 42–45.
Original Russian Text Copyright © 2001 by Popova, Smotrina, Denisova, Aksenova.

Chromium(II) Complexes with Hydroxyethylidenediphosphonic Acid

T. V. Popova, T. V. Smotrina, O. N. Denisova, and N. V. Aksenova
Mari State University, pl. Lenina 1, Ioshkar Ola, Russia

Received April 13, 2000

Abstract—The complex formation of chromium(II) with hydroxyethylidenediphosphonic acid (HEDP, H_5L) in an aqueous solution is studied by spectrophotometry. The pH region is determined where the HEDP complexonates of chromium(II) are stable. The effect of pH on the complexation and the composition of the coordination sphere of the complex ions is shown. The optimum conditions for the practical application of HEDP as a stabilizing ligand are chosen. The instability constants for tetra-, tri-, di-, and monoprotonated and neutral chromium(II) hydroxyethylidenediphosphonate complexes were calculated, whose p*K* were found to be 1.21, 2.43, 6.87, 12.60, 19.40, respectively. A new complex of chromium(II), $Na_4[Cr(H_2L)_2 \cdot 2H_2O] \cdot 4H_2O$, was isolated from a solution and characterized using elemental, IR spectroscopic, and thermographic analyses.

INTRODUCTION

Study into coordination compounds of metals with unstable oxidation states is always of topical interest. The search for information on these compounds makes it possible to assert that this interest does not wane with time. The chromium(II) complexes with ligands of a number of aliphatic amines, amino acids, aliphatic and aromatic mono- and dicarboxylic acids and their derivatives, complexones of polyamino- and polythiocarboxylic acids, thiophene and pyridine derivatives, and macrocyclic ligands are described in [1–9]. The authors of these papers report on the instability of the chromium(II) complexes in aqueous solutions; on their increasing stability in noncoordinating solvents; and on the high stability of some solid chromium(II) complexes, which were synthesized in an inert gas atmosphere. Data on compounds of chromium(II) with phosphorus-containing ligands, in particular, with hydroxyethylidenediphosphonic acid (HEDP, H_5L), are unavailable.

The purpose of this work was to study the complexation reaction between Cr^{2+} ions and hydroxyethylidenediphosphonic acid and to confirm this through comparative analysis of similar complexation processes involving Cr^{3+} and Cr^{2+} ions. We also attempted to establish the conditions under which the chromium(II) complexonates with HEDP exist in an aqueous solution and in a solid state and to make a conclusion on the possibility of stabilizing the unstable oxidation state of chromium via complexation with HEDP.

RESULTS AND DISCUSSION

The chromium(II) acetate used as a starting compound was prepared by the reduction of chromium(III) chloride with zinc dust in an inert gas atmosphere followed by the addition of sodium acetate [10].

The electronic absorption spectra (EAS) of solutions of the chromium(II) acetate without HEDP and with a complexone added during the synthesis of the acetate in an inert atmosphere were recorded on a Specord UV VIS spectrophotometer. They are presented in Fig. 1. After HEDP was introduced into the chromium(II) acetate solution, the red color of the solutions immediately changed to violet. The EAS of the chromium(II) acetate with HEDP exhibits a high hyperchromic effect ($\Delta A = 0.4$) and changes its shape in the short-wave visible region. When the solution is

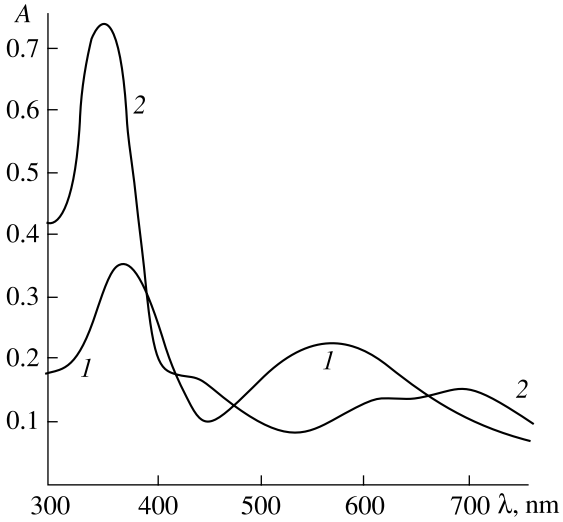

Fig. 1. Electronic absorption spectra of chromium(II) acetate (*1*) without and (*2*) with HEDP at $c_{Cr^{2+}} = 5 \times 10^{-3}$ mol/l.

kept in air, its color gradually changes from violet through blue to green and absorption bands appear in its spectrum with maxima at 460 and 660 nm. These bands are characteristic of the HEDP complexonates of chromium(II) [11], which is evidence of an oxidation reaction.

In weak acid or weak alkaline media, with no exposure to mechanical forces, the violet solutions of the chromium(II) HEDP complexonates remain stable in air over the course of 2 to 3 h. The EAS of the chromium(II) HEDP complexonates measured at different intervals starting from the time of their preparation at constant pH and concentration of Cr^{2+} are presented in Fig. 2. The mechanical stirring of the solutions considerably increases the rate of the chromium (II) oxidation. Even with an optimum pH 6–7, continuous stirring of the solution reduced the time interval within which the complex is stable to 3–5 min.

The stability of solutions of the chromium(II) HEDP complexonates stored in an atmosphere of CO_2 was found to be 25–30 times lower than that in air, though the initial solutions of chromium(II) acetate are more stable in CO_2.

The solution concentration and pH of a medium also produce a substantial effect on the stability of the chromium(II) HEDP complexonates. A decrease in the concentration and pH makes the solutions of chromium(II) with HEDP unstable, which is undoubtedly due to hydrolytic processes and the increasing lability of the coordination sphere of the protonated complexes.

Study of the optical density of the solutions as a function of pH at the unchanged concentration of the Cr^{2+} ions shows that the reaction between chromium(II) acetate and HEDP starts at pH 2 and is complete at pH 5.5 with the formation of the neutral HEDP complexonate. The composition and pK_{inst} of the expected Cr(II) HEDP complexonates were calculated from the $A = f(pH)$ dependence using the Rossotti method. For tetra-, tri-, di-, and monoprotonated and neutral Cr(II) HEDP complexonates, the pK_{inst} are equal to 1.21 ± 0.10, 1.43 ± 0.10, 5.84 ± 0.20, 10.68 ± 0.30, and 19.40 ± 0.20, respectively. The reduction of the chromium(II) chloride with zinc dust in a solution affords zinc chloride, which at pH 2–5 forms a complex with HEDP with a ratio of Zn : HEDP = 1 : 1 that does not absorb in the visible spectral region [12]. Therefore, the reaction of the complex formation of chromium(II) with HEDP was run with a ligand excess.

By making use of the data on complexation in the Cr(III)–HEDP–H_2O system [11], one can distinguish several specific features of the complex formation of chromium(II) with HEDP as compared to similar reactions of chromium(III). The chromium(II) hydroxyethylidenediphosphonate complexes were formed at a high rate, whereas complexation in the Cr(III)–HEDP system was very slow as a result of the inertness of the starting chromium(III) aqua complexes, which correlates well with the published data on the kinetics of the complex formation of chromium(II) and chromium(III) in aqueous solutions [8, 11, 13–15].

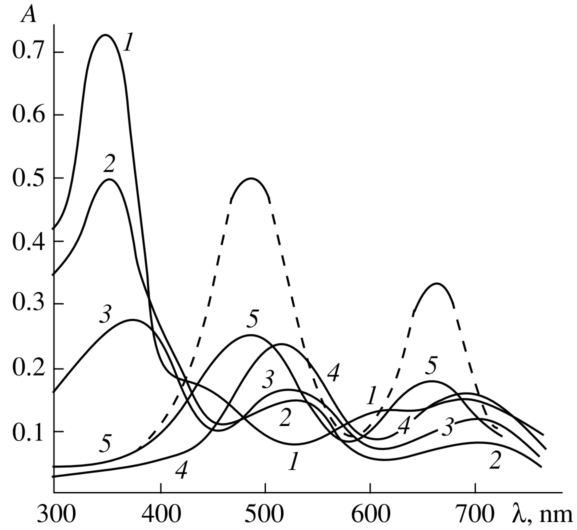

Fig. 2. Electronic absorption spectra of solutions of the chromium(II) complex with HEDP recorded (*1*) 1, (*2*) 4, (*3*) 5, (*4*) 8, and (*5*) 12 h after their preparation; $c_{Cr^{2+}} = 5 \times 10^{-3}$ mol/l, pH 6.0. The spectrum of the solution of the chromium(III) HEDP complex at $c_{Cr^{3+}} = 1.3 \times 10^{-2}$ mol/l (pH 5.0) is indicated by the dotted line.

The EAS of the chromium(II) complex differs substantially from that of a similar chromium(III) HEDP complexonate and has a doublet band with maxima at 320 and 350 nm. Complex formation is accompanied by hypsochromic effects in addition to the hyperchromic effect (Δλ = 40 and 10 nm), although the bathochromic shift is registered for similar reactions of chromium(III). This is undoubtedly the result of the different electronic configurations and energy states of the chromium atom with different oxidation states.

The complexes were isolated in the solid state by salting out with ethanol from concentrated aqueous solutions with the initial component ratios Cr(II) : HEDP = 1 : 1 and 1 : 2 at pH 7. For this purpose, the chromium(II) acetate was prepared in the solid state and repeatedly washed with water saturated with CO_2 (to remove zinc compounds) and ethanol. Then, HEDP and alkali were added to provide the required pH of the medium.

The synthesized complexes are fine bright lilac (1 : 2) and blue (1 : 1) powders (the chromium(III) complexes with a similar composition are green). We found that the reducing properties of the solid chromium(II) HEDP complexonates are far less substantial than those of aqueous solutions. These powders are stable in air in the absence of moisture, whereas minor amounts of moisture change the color to green.

A nonstoichiometric mixture of the Cr(II) compounds was isolated from a solution with an initial 1 : 1 ratio of components. We failed to identify these compounds. A single complex $Na_4[Cr(H_2L)_2(H_2O)_2] \cdot 4H_2O$ was isolated from a solution with a ratio of Cr(II) : HEDP = 1 : 2. Its composition was found from elemental, IR spectroscopic, and thermographic analyses.

For $Na_4[Cr(C_2P_2O_7H_5)_2(H_2O)_2] \cdot 4H_2O$

anal. calcd. (%): Cr, 7.9; P, 18.84; H_2O(cryst.), 10.94.

Found (%): Cr, 7.74; P, 18.86; H_2O(cryst.), 10.92.

The thermolysis of the isolated chromium(II) complex proceeds in several stages. In the 70–210°C temperature interval, the sample mass loss (11.00%) was accompanied by the endoeffect (T_{max} = 137°C), which was due to the removal of 4 moles of water of crystallization and agrees well with the theoretical value (10.94%). Further increase in temperature to 380°C resulted in an additional mass loss of 6.00% (Δm_{theor} = 6.14%), caused by the removal of two moles of water from the coordination sphere. In the interval from 380 to 470°C, the mass increased by 1.25%, which in our opinion, was the result of the oxidation of Cr(II) to Cr(III). However, the decomposition of the organic part of the complex begins at the same time which is registered on a derivatogram as a high exothermic effect (T_{max} = 440°C). Therefore, the increase in the sample mass noticeably differs from the expected value (Δm_{theor} = 2.90%). At temperatures from 470 to 1000°C, the mass decreases smoothly by 6.25% and a low exothermic effect (T_{max} = 720°C) is observed, which is due to the gradual decomposition of the Cr(III) HEDP complexonate, the removal of volatile decomposition products, and to the formation of thermally stable chromium(III) and sodium pyrophosphates at a molar ratio of 1 : 4. The total mass loss (22.00%) agrees well with the suggested mechanism (total Δm_{theor} = 20.76%).

The thermolysis of protonated Cr(III) biscomplexonate of similar composition is described in [16]. Its derivatogram differs from that of the chromium(II) complex in the absence of the mass increase stage due to chromium(II) oxidation, which undoubtedly confirms the oxidation state of the chromium in the complex prepared.

Some conclusions about the structure of the isolated chromium(II) complex were drawn from the analysis of the IR spectra recorded on an IKS-29 spectrophotometer in vaseline oil. The IR spectra were examined using the published data in [17–19].

The IR spectrum of the Cr(II) complex contains bands due to stretching vibrations of the nonionized phosphonic groups at 915 and 960 cm^{-1}, which indicates that the complex is protonated. However, the sharp decrease in the intensity of these bands, as compared to those in the spectrum of HEDP, points to the partial deprotonation of HEDP in the complex. This conclusion is also confirmed by the appearance of distinct bands due to the stretching vibrations of the ionized phosphonic groups in the spectrum of the Cr(II) complexonate: $\nu_d(PO_3) = 1000$ cm^{-1}, $\nu_s(PO_2) = 1065$ cm^{-1}, and $\nu_{as}(PO_2) = 1110$ cm^{-1}.

The bands within 640–650 cm^{-1} were assigned to the stretching vibrations of the Cr–O bonds. The spectrum of the Cr(II) complex also contains a broad band at 1180 cm^{-1}, which is absent in that of the Cr(III) HEDP complexonate. This band is assigned to the vibration ν(P=O). This suggests that the coordination of the PO_3 group by the Cr(II) atom occurs with the retention of the localized π(P=O) bond. In the IR spectrum of HEDP, the band of π(P=O) lies at 1200 cm^{-1}. The coordination of the PO_3 group in the Cr(III) complexonate is accompanied by the alignment of all PO bonds, and the band of ν(P=O) in its IR spectrum disappears. In our opinion, this difference in the IR spectra also confirms the oxidation state of chromium(II) in the synthesized compound.

REFERENCES

1. Dei, A. and Mani, F., *J. Chem. Res., Synop.*, 1981, no. 11, p. 358.
2. Jubb, J., Larkworthy, L.F., Leonard, G.A., *et al.*, *J. Chem. Soc., Dalton Trans.*, 1989, no. 8, p. 1631.
3. Mani, F., *Inorg. Chim. Acta*, 1982, vol. 60, p. 184.
4. Shakir, M., Kumar, D., and Siddiqui, Z.A., *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 1990, vol. 29, no. 9, p. 919.
5. Dei, A. and Mani, F., *Inorg. Chem.*, 1979, vol. 18, no. 10, p. 2574.
6. Asato, E., Kida, S., and Murase, I., *Inorg. Chem.*, 1989, vol. 28, no. 4, p. 800.
7. Edema, J.J., Smeets, W.J.J., and Spek, A.L., *Inorg. Chem.*, 1989, vol. 28, no. 7, vol. 1407.
8. Mickei, K., Debrezeni, F., and Nagypal, I., *J. Chem. Soc., Dalton Trans.*, 1983, no. 7, p. 1335.
9. Segal, M.G., *J. Chem. Soc., Dalton Trans.*, 1987, no. 10, p. 2485.
10. *Hanbuch der präparativen anorganische Chemie*, Brauer, G.T., Ed., Stuttgart: Ferdinand Enke, 1981.
11. Zakharova, D.V. and Popova, T.V., Abstracts of Papers, *3 Vsesoyuznoe soveshchanie po khimii i primeneniyu kompleksonov i kompleksonatov metallov* (3rd All-Union Conf. on the Chemistry and Application of Complexones and Metal Complexonates), Chelyabinsk, 1988, p. 96.
12. Urinovich, E.M., Bikhman, B.I., Smirnova, V.A., *et al.*, *Zh. Neorg. Khim.*, 1977, vol. 22, no. 10, p. 2679.
13. Popova, T.V., Mel'nikova, O.L., and Al Ansari, S.V., *Koord. Khim.*, 1998, vol. 24, no. 10, p. 741.
14. Koch, S., *Z. Chem.*, 1990, vol. 30, no. 8, p. 300.
15. Koch, S., *Z. Chem.*, 1990, vol. 30. no. 8, p. 301.
16. Domracheva, T.M. and Popova, T.V., *Koord. Khim.*, 1999, vol. 25, no. 3, p. 198.
17. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1988.
18. Nakanisi, K., *Infrared Absorption Spectroscopy: Practical*, San Francisco: Holden-Day, 1962.
19. Kushikbaeva, B.Kh., Mitrofanova, N.D., and Martynenko, L.I., *Khimiya kompleksonov i ikh primenenie* (The Chemistry and Applications of Complexones), Mezhvuz. Sb. Nauch. Trudov, Kalinin, 1986, p. 85.