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Inorganica Chimica Acta 343 (2003) 347–350

Inorganica Chimica Acta

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Note

A convenient source of hexaaquacobalt(III)

Grant Wangila, R.B. Jordan *

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received 21 November 2001; accepted 12 July 2002

Abstract

A convenient preparation and full characterization, including a crystal structure, of green, crystalline $[Co(NH_3)_6][Co(CO_3)_3]$ is reported. This salt can be treated at 0 °C with aqueous solutions of $HClO_4$, HNO_3 or CF_3SO_3H to give $CO_2(g)$, the corresponding insoluble salt of $Co(NH_3)_6{}^{3+}$ and aqueous $Co(OH_2)_6{}^{3+}$. This reaction provides ready access to solutions of $Co(OH_2)_6{}^{3+}$ in a wide range of concentrations and acidities.

Keywords: Oxidation; Cobalt(III); Perchloric acid

1. Introduction

Studies of the chemistry of hexaaquacobalt(III) ion [1] have been severely limited by the lack of a convenient source for solutions of this species. This has hampered systematic studies on such fundamental properties as the hydrolysis constant, the state of oligimerization and the mechanism of ligand substitution. Early studies [2,3] indicated that $Co(OH_2)_6{}^{3+}$ is a far less reactive oxidant than predicted by Marcus theory, but there has been no further work to determine if this is a general feature that might provide insight into the electron-transfer process. In these ways, $Co(OH_2)_6{}^{3+}$ has fallen far behind its chromium(III) and iron(III) analogues.

There are two conventional preparative methods. Electrolysis of strongly acidic solutions of cobalt(II) salts [4] gives about 80% conversion to Co(III) in competition with water reduction. This method is tedious for routine work and yields rather modest concentrations of Co(III) in strongly acidic solution. The reaction of hydrogen peroxide with cobalt(II) in concentrated sodium or potassium bicarbonate solutions yields a green solution containing cobalt(III) species of moderate stability and uncertain composition [5]. These solutions can be acidified to obtain $Co(OH_2)_6{}^{3+}$, but the resultant solution contains large amounts of sodium or potassium ions and is of uncertain acidity because of the large amount of bicarbonate that must be neutralized. Solid sodium and potassium salts, formulated as $M_3[Co(CO_3)_3]\cdot 3H_2O$ or $M_3[Co(CO_3H)_3(OH)_3]$, have been prepared by Mori et al. [6] and Bauer and Drinkard [7]. However, these solids are of uncertain stability and purity and have not been used as sources of aquacobalt(III). In some early studies [8,9], solid $Co_2(SO_4)_3\cdot 18H_2O$ was treated with $Ba(ClO_4)_2$ in perchloric acid, but the solid is inconvenient to prepare and store. The same is true of the alum $CsCo(SO_4)_2\cdot 12H_2O$, although its crystal structure has been determined [10].

The ideal source of aquacobalt(III) would be a stable, easily prepared, well characterized solid that can be dissolved rapidly to give the hexaaquacobalt(III) ion. Such a source is described here.

2. Results and discussion

Although $[Co(NH_3)_6][Co(CO_3)_3]$ was prepared many years ago by McCutcheon and Schuele [11] by a somewhat circuitous route, its potential as a source of aquacobalt(III) seems to have gone unrecognized. The present study reports a convenient synthesis of the salt in crystalline form and its simple conversion to aqueous

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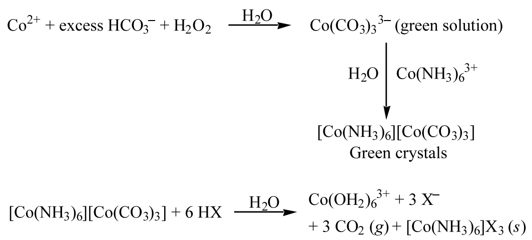
* Corresponding author. Tel.: +1-780-492 5551; fax: +1-780-492 8231

E-mail address: bob.jordan@ualberta.ca (R.B. Jordan).

PII: S0020-1693(02)01236-7



Scheme 1.

solutions of cobalt(III). The essence of the synthesis and conversion are described in Scheme 1.

The conditions for crystallization are given in Section 3. The composition of the green crystals has been determined from the content of $Co(NH_3)_6^{3+}$, the equivalent weight in the reaction with HX, and the X-ray structure. The material is quite stable and has been routinely stored under ambient conditions for several months without any sign of change in composition. It is insoluble in common organic solvents, and has very low solubility in water. The yield of crystalline material is rather modest, but, if too much $Co(NH_3)_6^{3+}$ is used in the preparation, the product is a green powder that gives substantially lower yields of $Co(OH_2)_6^{3+}$ when acidified.

The X-ray structure reveals that the crystalline solid contains the $Co(CO_3)_3^{3-}$ ion, with three chelated carbonato ligands. The essential features of the coordination and average bond lengths and angles are shown in Fig. 1. Full details are given in Section 4. The carbonato ligand is essentially planar with a dihedral angle of 179.2° at C. The structural parameters for $Co(CO_3)_3^{3-}$ are quite similar to those of the chelated mono-carbonatocobalt(III) complexes that have been reported [12]. It is a general feature of these structures that the O–Co–O and O–C–O angles are compressed to ~70° and ~110°, respectively, compared to the ideal values of 90° and 120°. It is noteworthy that the latter could be attained with normal bond lengths by compressing the Co–O–C angle from ~90° to ~75°.

The preparation of solutions of $Co(OH_2)_6^{3+}$ from $[Co(NH_3)_6][Co(CO_3)_3]$ is described in Section 3. Treatment with a strong acid HX ($X = ClO_4^-$, NO_3^-, $CF_3SO_3^-$) gives solid $[Co(NH_3)_6]X_3$, CO_2 and $Co(OH_2)_6^{3+}$. The solid is easily separated by centrifugation, and the final cobalt(III) and H^+ concentrations are controlled by the mass of $[Co(NH_3)_6][Co(CO_3)_3]$ used and the initial concentration of HX. Reproducible production of $Co(OH_2)_6^{3+}$ requires crystalline rather than powdered starting material.

The yield of cobalt(III) (~90%) is best if the reaction is done at low temperature, routinely 0 °C here, and with a final $[H^+] > 1.0$ M (before dilution). Despite numerous variations in the procedure for mixing the green crystals and the aqueous acid, a significantly better yield has not been achieved. Grinding the crystals, or using the powder gives lower and irreproducible yields of < 80%. It appears that there is some inevitable reduction of cobalt(III) during the dissolution/reaction of the solid. The final acidity is routinely within ±5% of that calculated from the stoichiometry in Scheme 1.

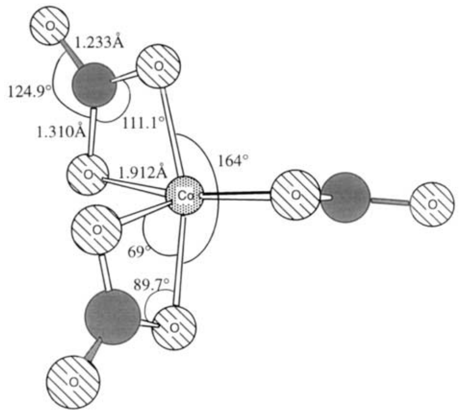


Fig. 1. Atom arrangement and average bond lengths and angles in $Co(CO_3)_3^{3-}$. Only one diastereoisomer is shown although the structure contains equal amounts of both.

There are several reports of the electronic spectrum of $Co(OH_2)_6^{3+}$ in strongly acidic solution [1,9,10,13,14] and in the solid $CsCo(SO_4)_2 \cdot 12H_2O$ [13]. The previous work is in agreement with the observations here that the main bands in solution are observed at 400 and 605 nm with extinction coefficients (ε) of 40.0 ± 0.5 and 35.0 ± 0.4 M^{-1} cm^{-1}. Because the present method allows the preparation of moderately concentrated solutions of $Co(OH_2)_6^{3+}$, it also has been possible to resolve a weak transition at 795 nm with ε of ~0.9 M^{-1} cm^{-1}, that was tentatively identified [15] in the alum at 800 nm. In order of decreasing energy, these are assigned to transitions from the ground state $^1A_{1g}$ to $^1T_{2g}$, $^1T_{1g}$, and $^3T_{2g}$, respectively. The crystal field analysis described by Johnson and Nelson [16] gives the parameters $\Delta = 16\,130$, $B = 740$ and $C = 3360$ cm^{-1}. Molecular orbital calculations of Zerner and coworkers [17] and Kai et al. [18] have shown modest success in calculating these transition energies.

A useful feature of the electronic spectrum is the absorbance at 325 nm, the minimum before the peak at 400 nm. At the minimum, $\varepsilon = 6.6$ M^{-1} cm^{-1} and any increase in this value is indicative of hydrolysis/oligomerization. Below this wavelength, the absorbance rises monotonically without any maximum down to 200 nm. The extinction coefficient also has been determined at 250 nm as 3.0×10^3 M^{-1} cm^{-1}, in agreement with earlier results [9,14].

3. Experimental

3.1. Materials

Hexaamminecobalt(III) chloride was prepared by a standard method [19]. Solutions containing $Co(CO_3)_3^{3-}$ were prepared by the method of Hoffman-Bang and Wulff [5] by mixing 2.9 g (1.0×10^{-2} mole) of cobalt(II) nitrate hexahydrate and 75.0 g (0.89 mole) of sodium bicarbonate in 250 ml of water. Then 2.0 ml of 30% hydrogen peroxide in 250 ml of water was added during 1 h, while stirring the mixture. The green solution was diluted to 1.0 l with water and stirred overnight to ensure dissolution of the $NaHCO_3$.

3.2. Preparation of $[Co(NH_3)_6][Co(CO_3)_3]$

A 3.1 g (1.15×10^{-2} mole) sample of hexaamminecobalt(III) chloride was dissolved in 200 ml of water and added to the 1.0 l of green solution described above. The solution was stirred and then stored in an ice bath in a refrigerator for ~24 h. The dark green crystalline product was collected by filtration, washed with water, and dried by drawing air through the sample. Yield 1.16 g, or 29% based on the initial cobalt(II) nitrate. *Anal*. Calc. for $[Co(NH_3)_6][Co(CO_3)_3]$: H, 4.5; N, 21.0; C, 9.0. Found: H, 4.5; N, 20.5; C, 9.2%.

3.3. Preparation of hexaaquacobalt(III)

For a typical procedure, 0.25 g of crystalline $[Co(NH_3)_6][Co(CO_3)_3]$ were added to 5.0 ml of 2.0 M $HClO_4$ in an ice-bath, and the mixture was stirred for ~60 min until all the green crystals had dissolved and evolution of CO_2 had stopped. The mixture was centrifuged and the supernatant blue solution was separated from the yellow solid with a pipet or eye-dropper and transferred to an appropriate container for dilution or direct use. For the example given, the concentrations before dilution should be 1.25 M H^+, and 0.125 M Co(III), however the latter actually will be ~0.11 M due to the ~90% yield. The Co(III) concentration can be determined, after dilution, from the absorbance at 605 nm.

The mass of crystals and the volume and concentration of acid can be varied, depending on the final concentrations of Co(III) and H^+ desired. Shorter reaction times are possible for final acidities >1.5 M. The $HClO_4$ can be replaced by any strong acid that will give an insoluble salt of $Co(NH_3)_6^{3+}$; nitric and trifluoromethanesulfonic acids were found to be suitable in this respect.

The $Co(NH_3)_6^{3+}$ content of the green crystals was determined by dissolving a known mass ($0.785–8.84 \times 10^{-2}$ g) in ~10 ml of 2.0 M HCl, boiling the solution to remove Cl_2 and CO_2, diluting to 25.0 ml and determining the absorbance at 472 nm. The amount of $Co(NH_3)_6^{3+}$ was calculated from the extinction coefficients of 56.7 and 3.24 $M^{-1}\ cm^{-1}$ for $Co(NH_3)_6^{3+}$ and $Co(OH_2)_6^{2+}$, respectively. Assuming 1 mole of $Co(NH_3)_6^{3+}$ per mole of material, the average of six determinations gave a molar mass of 400.3 ± 1.8, compared to the theoretical value of 400.09. The equivalent weight was determined similarly by reacting a known mass of sample with a known excess of HCl and titrating the remaining H^+ with standardized NaOH. The average of four determinations gave an equivalent weight of 66.7 ± 1.1, compared to the theoretical value of $400.09/6 = 66.7$.

The extinction coefficients were determined in 2.0 M $HClO_4$ by dissolving various masses of the green material as described and recording the spectrum on a Cary 219 spectrophotometer. The cobalt(III) concentration was determined by adding NaI to an aliquot of the solution and titrating the I_2 with standardized $Na_2S_2O_3$. The reported values are the average of four determinations.

4. Supplementary material

Tables listing crystal data, atomic coordinates, equivalent isotropic displacement parameters, selected interatomic distances and angles for $[Co(NH_3)_6][Co(CO_3)_3]$ are available from the author.

Acknowledgements

The authors are pleased to acknowledge the Natural Sciences and Engineering Research Council of Canada for financial support, and Dr. R. McDonald of the X-ray Crystallography Service Laboratory of the University of Alberta for the crystal structure.

References

[1] G. Davies, B. Warnqvist, Coord. Chem. Rev. 5 (1970) 349.
[2] R. Farina, R.G. Wilkins, Inorg. Chem. 7 (1968) 514.
[3] D.H. Mcartney, N. Sutin, Inorg. Chem. 24 (1985) 3403.
[4] (a) S. Swann, Jr., T.S. Xanthakos, J. Am. Chem. Soc. 53 (1931) 400;
(b) T.J. Conocchioli, G.H. Nancollas, N. Sutin, Inorg. Chem. 5 (1965) 1;
(c) C.F. Wells, Trans. Faraday Soc. 63 (1967) 156;
(d) J. Hill, A. McAuley, J. Chem. Soc. (A) (1968) 1169.
[5] N. Hofman-Bang, I. Wulff, Acta Chem. Scand. 9 (1955) 1230.
[6] M. Mori, M. Shibata, E. Kyuno, T. Adachi, Bull. Chem. Soc. Jpn. 28 (1956) 883.
[7] (a) H.F. Bauer, W.C. Drinkard, J. Am. Chem. Soc. 82 (1960) 5031;
(b) H.F. Bauer, W.C. Drinkard, Inorg. Synth. 8 (1966) 202.
[8] G. Hargreaves, L.H. Sutcliffe, Trans. Faraday Soc. 51 (1955) 786.
[9] J.H. Baxendale, C.F. Wells, Trans. Faraday Soc. 53 (1957) 800.

[10] J.K. Beattie, S.P. Best, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1981) 2105.
[11] T.P. McCutcheon, W.J. Schuele, J. Am. Chem. Soc. 75 (1953) 1845.
[12] (a) G.A. Barclay, B.F. Hoskins, J. Chem. Soc. (1962) 586;
(b) F. Bigoli, M. Lanfranchi, E. Leoprati, M.A. Pellinghelli, Cryst. Struct. Commun. 9 (1980) 1261;
(c) H. Masuda, C. Masuda, K. Jitsukawa, H. Eigana, Bull. Chem. Soc. Jpn. 67 (1994) 3000;
(d) T.J. Egan, D.A. Baldwin, L. Denner, Acta Crystallogr., C 51 (1995) 1994;
(e) S. Tsuboyama, J. Fujimoto, S. Hanabira, N. Yasuda, K. Kobayashi, T. Sakurai, K. Tsuboyama, J. Chem. Soc., Dalton Trans. (1996) 45;
(f) Z. Hai-Liang, C. Xiao-Ming, Acta Crystallogr., C 55 (1999) 2010.
[13] H.S. Habib, J.P. Hunt, J. Am. Chem. Soc. 88 (1966) 1668.
[14] D.W. Weiser, Ph. D. Thesis, University of Chicago, Chicago, IL, 1956.
[15] D.A. Johnson, A.G. Sharpe, J. Chem. Soc., A (1966) 798.
[16] D.A. Johnson, P.G. Nelson, Inorg. Chem. 38 (1999) 4949.
[17] W.P. Anderson, W.D. Edwards, M.C. Zerner, Inorg. Chem. 25 (1986) 2728.
[18] E. Kai, T. Arakawa, K. Nishimoto, Inorg. Chim. Acta 76 (1983) L287.
[19] G.G. Schlessinger, Inorganic Laboratory Preparations, Chemical Publishing, New York, 1962.