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Determination of ε° and $d\varepsilon^\circ/dT$ for the Aqueous Tris(ethylenediamine)cobalt(II)–Tris(ethylenediamine)cobalt(III) Electrode in Cells without Liquid Junction

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The standard oxidation potential and its temperature coefficient of the $Co(en)_3{}^{2+,3+}$(aq) electrode has been determined in cells without liquid junction using cation-sensitive glass electrodes. The values obtained are +180 ± 2 mV and −1.07 ± 0.09 mV/deg, respectively. The results obtained are compared with the previously obtained experimental and estimated values of $\mathcal{E}^\circ$ for this electrode.

Introduction

It has been reported by Buckingham and Sargeson[2] that silver wool in the presence of chloride ion reduces tris(ethylenediamine)cobalt(III) to tris(ethylenediamine)cobalt(II) and on the basis of this observation these authors have suggested that the standard oxidation potential of the $Co(en)_3{}^{2+,3+}$ couple reported by Bjerrum[3] (+0.259 V at 30°) may be in error. That Bjerrum's value may not be reliable was also suggested by Rock[4] based on an estimate of the standard oxidation potential obtained from a semitheoretical procedure involving the use of ligand field theory parameters. We report here a determination, in cells without liquid junction, of the standard oxidation potential and its temperature coefficient for the $Co(en)_3{}^{2+,3+}$(aq) electrode. The value obtained differs significantly from the accepted value but is closer to the accepted value than the independently estimated value.[4] Possible reasons for these discrepancies are discussed.

Experimental Section

All solutions were prepared on a molality basis using distilled, deionized, and deoxygenated water. Reagent grade NaCl(s) (assay 99.5%) was dried at 165° for several days and stored in a desiccator. Reagent grade $Co(OH_2)_6Cl_2$(s) (assay 99.2%) and ethylenediamine (assay 99.3%) were used without further purification. The $Co(en)_3Cl_3$ was prepared and purified according to the prescription of Work.[5]

All measurements were carried out in a sealed, controlled-atmosphere, controlled-temperature, 2-ft³ "wetbox" constructed from 0.25-in. sheets of Plexiglas. Two 4.5-in. diameter holes were cut in one side of the box and a pair of flanged rubber gloves was securely taped to the outside of the box using Scotch electrical tape. Electrical and gas leads were run out through appropriately sized holes drilled in a removable top. The box was filled to a depth of *ca.* 10 in. with water. Cells, stirrers, heaters, etc., were mounted on a removable aluminum frame. Bath temperature control was ±0.01°.

Voltage measurements were made on a Beckman Instruments Research pH meter, Model 1019. The meter calibration was checked by feeding known voltages to the pH meter from a certified Leeds and Northrup K-3 potentiometer. The cells used were[6]

$$Au(s)|Co(en)_3Cl_3(m_1), Co(en)_3Cl_2(m_2), NaCl(m_3), H_2NCH_2CH_2NH_2(M)|\text{glass} \quad (1)$$

$$Hg(l)|Hg_2Cl_2(s)|NaCl(m_4)|\text{glass} \quad (2)$$

In cell 1 Au(s) represents a gold coil with the end submerged in wax to avoid any sharp points that might give rise to spurious emf values and glass represents a Beckman No. 39278 sodium ion glass electrode. The glass electrode in cell 2 is the same as in cell 1; *i.e.*, voltage measurements are made on both cells using the same glass electrode.[6] The calomel reference electrode was prepared according to the prescription of Hills and Ives.[7]

The method of preparation of the solution for cell 1 follows. Distilled, deionized, and deoxygenated water was weighed out into a 500-ml three-necked flask and the desired weighed amounts of NaCl(s), $Co(OH_2)_6Cl_2$(s), and $Co(en)_3Cl_3$(s) were dissolved (in the above order) in the water.[8] The flask was then sealed with rubber serum caps. One of the serum caps was equipped with a glass nitrogen gas inlet tube. Tank nitrogen was passed first through a chromous bubbler and then was bubbled vigorously through the solution. Two 1-in. syringe needles were used as gas exits. The flask and the cell vessels (which were equipped with presaturators so that nitrogen could be bubbled continuously through them) were then mounted in the wetbox. The calomel reference electrode was set up and the glass electrode was placed in the 0.1 *m* NaCl(aq) calomel electrode solution. The box was then sealed and the entire apparatus was deoxygenated for over 1 hr (a separate nitrogen supply was used for the box itself). At this point a glass syringe equipped with a platinum needle was flushed with nitrogen (using the vapor space over the flask solution as a nitrogen supply). The syringe was then filled with approximately 10 ml of ethylenediamine and discharged into the 500-ml flask through a hole punched in the serum cap with the syringe needle. The nitrogen bubbling through the solution served to stir the solution. After about 15 min a sample of the solution was removed with a separate platinum-needled syringe through a serum cap and discharged into the nitrogen-filled cell compartment. The cell was fitted with a Nalgene plastic stopper. The voltage measurements on cell 2 were then begun. After it was established that the voltage of cell 2 was stable with time, the glass electrode (which was fitted with a machined Teflon 19/38 flanged male sleeve to facilitate mounting in the cells without disturbing the glass electrode tip) was removed from cell 2 which was then capped. The glass electrode was then rinsed with cell electrolyte obtained from the 500-ml flask using a syringe. The glass electrode was then placed in cell 1 and readings were taken. To transfer back to cell 2 the glass electrode was removed from cell 1 and rinsed with stock cell electrolyte for cell 2 (which was stored in the wetbox in a squeeze-type plastic wash bottle). The voltage difference $\mathcal{E}_1 - \mathcal{E}_2$ (see Results) was stable to ±0.1 mV from the beginning of the measurements.

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[1] To whom inquiries concerning this paper should be sent.

[2] D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 242.

[3] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp 219–234.

[4] P. A. Rock, *Inorg. Chem.*, **7**, 837 (1968).

[5] J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).

[6] R. C. Murray, Jr., and P. A. Rock, *Electrochim. Acta*, **13**, 969 (1968).

[7] G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 311 (1951).

[8] Both calculations and spectrophotometric experiments showed that $Co(OH)_2)_6{}^{2+}$ and $Co(en)_3{}^{3+}$ do not react with one another in these solutions.

Over the course of a 6-hr period, however, $\mathcal{E}_1 - \mathcal{E}_2$ generally decreased about 1 mV probably owing to oxidation of $\mathrm{Co(en)_3^{2+}}$ by traces of oxygen. For this reason an attempt was made to complete the measurements including the temperature dependence in less than 12 hr. Spectrophotometric measurements on the solution from cell 1 confirmed that less than 1% of the $\mathrm{Co(en)_3^{2+}}$ was oxidized in 4 hr under our conditions. As found previously[6] the value of $\mathcal{E}_1 - \mathcal{E}_2$ at fixed cell concentrations was independent (to within ±0.5 mV) of the particular glass electrode used.

Results

The glass electrodes used have a silver–silver chloride internal element dipping into a 0.10 *M* NaCl(aq) solution; hence, we postulate (using strong electrolyte standard states) for the cell reaction of cell 1

$$\mathrm{Co(en)_3^{2+}}(m_2) = \mathrm{Co(en)_3^{3+}}(m_1) + \mathrm{e^-}$$

$$3\mathrm{Cl^-}(3m_1 + 2m_2 + m_3) = 3\mathrm{Cl^-}(3m_1 + 2m_2 + m_3)$$

$$\mathrm{Na^+}(m_3) = \mathrm{Na^+(glass)}$$

$$\mathrm{Na^+(glass)} = \mathrm{Na^+}(0.1\ M\ \mathrm{NaCl})$$

$$\mathrm{AgCl(s)} + \mathrm{e^-} = \mathrm{Ag(s)} + \mathrm{Cl^-}(0.1\ M\ \mathrm{NaCl})$$

Addition of these equations yields

$$\mathrm{Co(en)_3^{2+}}(m_2) + 3\mathrm{Cl^-}(3m_1 + 2m_2 + m_3) + \mathrm{Na^+}(m_3) + \mathrm{AgCl(s)} = \mathrm{Co(en)_3^{3+}}(m_1) + 3\mathrm{Cl^-}(3m_1 + 2m_2 + m_3) + \mathrm{NaCl}(0.1\ M) + \mathrm{Ag(s)} \qquad (3)$$

For the operation of cell 2 we postulate

$$\mathrm{Hg(l)} + \mathrm{Cl^-}(m_4) = 0.5\mathrm{Hg_2Cl_2(s)} + \mathrm{e^-}$$

$$\mathrm{Na^+}(m_4) = \mathrm{Na^+(glass)}$$

$$\mathrm{Na^+(glass)} = \mathrm{Na^+}(0.1\ M\ \mathrm{NaCl})$$

$$\mathrm{AgCl(s)} + \mathrm{e^-} = \mathrm{Ag(s)} + \mathrm{Cl^-}(0.1\ M\ \mathrm{NaCl})$$

Summing these equations leads to

$$\mathrm{Hg(l)} + \mathrm{Na^+}(m_4) + \mathrm{Cl^-}(m_4) + \mathrm{AgCl(s)} = 0.5\mathrm{Hg_2Cl_2(s)} + \mathrm{Ag(s)} + \mathrm{NaCl}(0.1\ M\ \mathrm{NaCl}) \qquad (4)$$

for the over-all cell reaction. Subtracting eq 4 from eq 3 yields

$$\{\mathrm{Co(en)_3^{2+}}(m_2) + 2\mathrm{Cl^-}(3m_1 + 2m_2 + m_3)\} + \{\mathrm{Na^+}(m_3) + \mathrm{Cl^-}(3m_1 + 2m_2 + m_3)\} + 0.5\mathrm{Hg_2Cl_2(s)} = \{\mathrm{Co(en)_3^{3+}}(m_1) + 3\mathrm{Cl^-}(3m_1 + 2m_2 + m_3)\} + \mathrm{Hg(l)} + \mathrm{Na^+}(m_4) + \mathrm{Cl^-}(m_4) \qquad (5)$$

Equation 5 is the cell reaction of the hypothetical double cell

$$\mathrm{Au(s)}|\mathrm{Co(en)_3Cl_3}(m_1),\ \mathrm{Co(en)_3Cl_2}(m_2),\ \mathrm{NaCl}(m_3),\ \mathrm{en}(M)|\text{glass–glass}|\mathrm{NaCl}(m_4)|\mathrm{Hg_2Cl_2(s)}|\mathrm{Hg(l)} \qquad (6)$$

It is evident from reaction 5 that all of the properties of the particular glass electrode used cancel out in the net cell reaction, and in addition cell 6 has no liquid junctions.

Application of the Nernst equation to reaction 5 yields

$$\mathcal{E} = \mathcal{E}_1 - \mathcal{E}_2 = \mathcal{E}^\circ - \frac{RT}{F}\ln\left\{\frac{a_{\mathrm{Na^+}(2)}a_{\mathrm{Cl^-}(2)}a_{\mathrm{Hg(l)}}a_{\mathrm{Co(III)}}a_{\mathrm{Cl^-}(1)}{}^3}{a_{\mathrm{Hg_2Cl_2(s)}}{}^{1/2}a_{\mathrm{Na^+}(1)}a_{\mathrm{Cl^-}(1)}a_{\mathrm{Co(II)}}a_{\mathrm{Cl^-}(1)}{}^2}\right\} \qquad (7)$$

where $\mathcal{E}_1$ and $\mathcal{E}_2$ are the observed voltages of cells 1 and 2, respectively, which are taken as positive when the left electrode in the cell diagram as written is negative. At 1 atm pressure $a_{\mathrm{Hg_2Cl_2}} = a_{\mathrm{Hg}} = 1.0000$. Introducing $a_i = m_i\gamma_i$ and combining individual ion activity coefficients to obtain mean activity coefficients we have

$$\mathcal{E}_1 - \mathcal{E}_2 = \mathcal{E}^\circ - \frac{RT}{F}\ln\left\{\frac{m_4{}^2m_1\gamma_\pm{}^2(\text{of NaCl at } m_4)\gamma_\pm{}^4(\text{of }\mathrm{Co(en)_3Cl_3}\text{ in mix})}{m_3m_2\gamma_\pm{}^2(\text{of NaCl in mix})\gamma_\pm{}^3(\text{of }\mathrm{Co(en)_3Cl_2}\text{ in mix})}\right\} \qquad (8)$$

Rearranging this equation and introducing the variable $\mathcal{E}'$ we have

$$\mathcal{E}' = \mathcal{E}_1 - \mathcal{E}_2 + \frac{RT}{F}\ln\frac{m_4{}^2m_1}{m_3m_2} + \frac{RT}{F}\ln\gamma_\pm{}^2(\text{of NaCl at } m_4) = \mathcal{E}^\circ - \frac{RT}{F}\ln\left\{\frac{\gamma_\pm{}^4(\text{of }\mathrm{Co(en)_3Cl_3}\text{ in mix})}{\gamma_\pm{}^2(\text{of NaCl in mix})\gamma_\pm{}^3(\text{of }\mathrm{Co(en)_3Cl_2}\text{ in mix})}\right\}$$

Since all of the quantities on the left-hand side of this equation are known and further since

$$\log\gamma_\pm \longrightarrow -A|Z_+Z_-|I^{1/2}/(1 + I^{1/2}) \text{ as } I \longrightarrow 0$$

(where I is the total ionic strength of the mixed electrolyte solution in cell 1), a plot of $\mathcal{E}'$ *vs.* $I^{1/2}/(1 + I^{1/2})$ should show a straight line at low I with intercept of $\mathcal{E}^\circ$. The Debye–Hückel theoretical slope of this line at 25° is $0.059158 \times 0.511[(4 \times 3) - (2 \times 1) - (3 \times 2)] = 0.121$.

The data obtained on cells 1 and 2 are collected in Table I. A standard least-squares analysis of the data in Table I yields a slope of 0.125 and an intercept of $\mathcal{E}^\circ = 447.1$ mV. If we require these data to take exactly the theoretical Debye–Hückel slope of 0.121, then a least-squares treatment of the data yields an intercept of $\mathcal{E}^\circ = 448.0$ mV. Accordingly we take 448 ± 2 mV as the value of the standard cell voltage as 25°. Taking the standard oxidation potential of the $\mathrm{Hg(l)}|\mathrm{Hg_2Cl_2(s)}|\mathrm{Cl^-(aq)}$ electrode at 25° as[7] −268.0 mV, we compute $\mathcal{E}^\circ = 180 \pm 2$ mV for the standard oxidation potential of the $\mathrm{Co(en)_3^{2+,3+}(aq)}$ electrode at 25°.

The fairly close agreement between the observed and theoretical slopes in the extrapolation to obtain $\mathcal{E}^\circ$ confirms our choice of strong electrolyte standard states for $\mathrm{Co(en)_3Cl_3(aq)}$ and $\mathrm{Co(en)_3Cl_2(aq)}$. For this reason it is not necessary to introduce ion-pairing constants in the thermodynamic analysis of the cell data even though it has been shown[9] that ion pairs evidently exist in detectable amounts in such solutions. With strong electrolyte standard states ion pairing is taken into account by the activity coefficients as a deviation from ideality.

The temperature dependence of $\mathcal{E}_1 - \mathcal{E}_2$ for cells I, II, IV, and VI in Table I was also investigated. Owing to the observed slow decrease in voltage with time (*ca.* 1 mV/6 hr) high precision was not possible in the temperature dependence investigations. The best results were obtained for cells II and VI. For these cells it proved possible to complete the measurements in less than 8 hr without any apparatus failures. The data obtained for these cells were as follows. For cell II we found for $\mathcal{E}_1 - \mathcal{E}_2$ (in mV), where the numbers in parentheses are the temperatures in °C: 475.8 (25.00), 473.3 (26.80), 471.8 (28.16), 468.2 (30.21), 464.4 (32.90), and 462.5 (34.39). For cell IV we found: 421.0 (25.40), 415.9 (28.55), and 409.4 (33.90). Values of $\mathcal{E}_1 - \mathcal{E}_2$ at 30 and 35° were interpolated from these

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[9] I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951).

TABLE I

MEASUREMENTS AT 25° ON THE CELLS

$Au(s)|Co(en)_3Cl_3(m_1), Co(en)_3Cl_2(m_2), NaCl(m_3), H_2NCH_2CH_2NH_2(M)|glass$ (1); $Hg(l)|Hg_2Cl_2(s)|NaCl(m_4)|glass$ (2)

Cell[a]	M [en]	m_1 [$Co(en)_3Cl_3$]	m_2 [$Co(en)_3Cl_2$]	m_3 [NaCl]	m_4 [NaCl]	$\mathcal{E}_1 - \mathcal{E}_2$, mV	$\mathcal{E}'$,[b] mV	$I^{1/2}/(1 + I^{1/2})$
I	0.270	0.001001	0.001000	0.09948	0.09952	550.5	478.3	0.2478
II	0.288	0.001000	0.000990	0.009961	0.09952	475.9	463.0	0.1210
III	0.353	0.000583	0.000847	0.006203	0.09951	472.0	461.4	0.09962
IV	0.270	0.000582	0.000850	0.003452	0.09952	452.5	457.0	0.08879
V	0.285	0.000316	0.000457	0.002094	0.09951	438.9	456.5	0.06822
VI	0.276	0.000176	0.000280	0.001072	0.09951	421.4	453.6	0.05167

[a] These numbers refer to the hypothetical double cell (6) [see text]. [b] $\mathcal{E}'$ is defined in eq 9 [see text].

data. The two points in each case fell quite close to a line having the Debye–Hückel theoretical slope (the predicted slopes are 0.124 and 0.127; the observed slopes are 0.120 and 0.125, respectively). The data were therefore used to fix $\mathcal{E}^\circ$ at 30 and 35° using the theoretical slopes. The results obtained for $\mathcal{E}^\circ$ are 448.0 (25.0°), 440.7 (30.0°), and 434.1 mV (35.0°). From these data we obtain a value of $d\mathcal{E}^\circ/dT = -1.39 \pm 0.09$ mV/deg.

From the observed value of $d\mathcal{E}^\circ/dT$ we compute $\Delta S^\circ = -32.1 \pm 1.9$ gibbs at 25° for the reaction

$$Co(en)_3{}^{2+}(aq) + 0.5Hg_2Cl_2(s) = Hg(l) + Cl^-(aq) + Co(en)_3{}^{3+}(aq)$$

From our value of $\mathcal{E}^\circ$ at 25° for this reaction (448 mV) we compute $\Delta G^\circ = -10.3$ kcal at 25° for the reaction. Combination of the above ΔG° and ΔS° yields $\Delta H^\circ = -20.0$ kcal at 25° for this reaction. From the foregoing values of ΔS°, ΔG°, and ΔH° together with other available thermodynamic data[10] for $Hg_2Cl_2(s)$, $Hg(l)$, and $Cl^-(aq)$ we compute at 25°

$$\bar{S}^\circ[Co(en)_3{}^{3+}(aq)] - \bar{S}^\circ[Co(en)_3{}^{2+}(aq)] = -40 \text{ gibbs}$$

$$\Delta\bar{G}_f{}^\circ[Co(en)_3{}^{3+}(aq)] - \Delta\bar{G}_f{}^\circ[Co(en)_3{}^{2+}] = -4.1 \text{ kcal}$$

$$\Delta\bar{H}_f{}^\circ[Co(en)_3{}^{3+}(aq)] - \Delta\bar{H}_f{}^\circ[Co(en)_3{}^{2+}] = -11.7 \text{ kcal}$$

Unfortunately insufficient thermodynamic data are available at present to calculate the values of $\bar{S}^\circ$, $\Delta\bar{G}_f{}^\circ$, and $\Delta\bar{H}_f{}^\circ$ for the individual ions $Co(en)_3{}^{3+}(aq)$ and $Co(en)_3{}^{2+}(aq)$. The entropy difference of -40 gibbs confirms the previously estimated value.[4]

Conclusion

On the basis of potentiometric titration data obtained from cells with liquid junction, Bjerrum computed a standard oxidation potential of +259 mV at 30° in 1 M KCl for the $Co(en)_3{}^{2+,3+}(aq)$ electrode. Our temperature coefficient of -1.39 mV/deg for the $Co(en)_3{}^{2+,3+}$ *vs.* calomel cell together with the reported temperature coefficient of the calomel electrode[11] of +0.320 mV/deg yields -1.07 mV/deg for the temperature coefficient of the standard oxidation potential of the $Co(en)_3{}^{2+,3+}$ electrode at 25°. Using this result to bring Bjerrum's value to 25° yields $\mathcal{E}^\circ[1\ M\ KCl] = +254$ mV. Correcting this value to $I = 0$, assuming $\mathcal{E}'$ *vs.* $I^{1/2}/(1 + I^{1/2})$ is linear[12] up to $I = 1.0$, yields a value of $254 - 60 = 194$ mV compared to our ($I = 0$) value of 180 mV. The agreement is not too bad considering the difficulties associated with working with $Co(en)_3{}^{2+}(aq)$ which is rapidly oxidized by oxygen, together with the possible uncertainties arising from liquid junction potentials and activity coefficient effects at $I = 1.0$. The agreement with the independently estimated value[4] of -0.41 V is very poor. Since the value of ΔS° for the $Co(en)_3{}^{2+,3+}(aq)$ electrode of -40 gibbs agrees quite well with the estimated value[4] of -39 gibbs, this eliminates the possibility that the discrepancy arises from a poor estimate for ΔS°. This discrepancy between measured and estimated $\mathcal{E}^\circ$ casts suspicion on the method of estimating $\mathcal{E}^\circ$ values from entropies and ligand field parameters proposed by Rock.[4] Why this estimation method appears to work for the iron couples and some, but not all, of the cobalt couples remains at present a mystery to us.

It has been reported that $Co(en)_3{}^{3+}(aq)$ is slowly reduced by Ag(s) in the presence of $Cl^-(aq)$, and this observation has been offered[2] as evidence for the reported $Co(en)_3{}^{2+,3+}(aq)$ standard oxidation potential as being too positive. Although our value is significantly lower than the previously reported value, it still yields the result that the reaction

$$Ag(s) + Cl^-(aq) + Co(en)_3{}^{3+}(aq) \rightleftharpoons AgCl(s) + Co(en)_3{}^{2+}$$

is thermodynamically unfavorable since $\mathcal{E}^\circ = -0.222 - 0.180 = -0.402$ V. We have repeated this experiment and found no evidence of the reduction of a 5×10^{-3} M $Co(en)_3Cl_3(aq)$ solution by Ag(s) after 10 days at room temperature, nor after heating the solution to 80° for about 1 hr.

Some preliminary experiments were also carried out on the $Co(NH_3)_6{}^{2+,3+}$ system and it was noted that cells (similar to those for the ethylenediamine complexes) involving this electrode were electrochemically reversible (as had been found previously by Bjerrum). We did not pursue this investigation further, however, because calculations using Bjerrum's stability constant data for the ammine complexes[3] showed that even at $NH_3(aq)$ concentrations as high as 6 M $Co(NH_3)_6{}^{2+}(aq)$ comprises less than 50% of the cobalt(II)–ammine species present.

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[10] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

[11] A. J. de Bethune and N. A. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," C. A. Hampel Publishing Co., Skokie, Ill, 1964, p 11.

[12] This cannot be regarded as a particularly reliable assumption, but it is probably not too bad in this case since our data show that $\mathcal{E}'$ *vs.* $I^{1/2}/(1 + I^{1/2})$ is essentially linear up to about $I = 0.1$.

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New Chromium Chalcogenides Prepared at High Pressure and the Crystal Growth of Chromium Sesquisulfide

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The new chromium chalcogenides Cr_5S_8, Cr_5Se_8, and $Cr_5S_{4.8}Se_{3.2}$ have been prepared at pressures of 65–89 kbars. These phases have higher chalcogen-to-chromium ratios than have previously been reported in these systems. It is shown that they are isostructural with the known V_5S_8 and V_5Se_8 compounds. Their magnetic and electrical properties are reported, as well as the electrical properties of rhombohedral Cr_2S_3, which has been obtained for the first time in single-crystal form.

Introduction

The chromium–sulfur system has been extensively investigated by Jellinek.[1] In his work the phases CrS, Cr_7S_8, Cr_5S_6, Cr_3S_4, and Cr_2S_3 (two forms) were identified and their structures were established. The effect of high pressure upon the magnetic properties of both Cr_5S_6 and Cr_2S_3 through disordering is discussed by Yuzuri and Nakamura.[2] In the chromium–selenium system, the phases CrSe, Cr_7Se_8, Cr_3Se_4, and Cr_2Se_3 have been reported in detail.[3–5] The largest number of phases have been reported in the chromium–tellurium system and comprise CrTe, Cr_7Te_8, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3, and Cr_5Te_8.[6–8]

The purpose of this work was to investigate the preparation of new chromium chalcogenides having high chalcogen-to-chromium ratios by using excess chalcogen at high reaction pressures. Phases of stoichiometry Cr_5X_8 (X = S and/or Se) were obtained, and their structures, as well as electrical and magnetic properties, were determined. In addition, single crystals of the known rhombohedral form of Cr_2S_3 were prepared, and their properties are reported.

Experimental Section

Preparation of Cr_5X_8 Compounds.—Reactions were carried out under pressure in a tetrahedral anvil press of National Bureau of Standards design[9] using a cylindrical boron nitride crucible surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The calibration points used to establish the pressure developed were the transitions Bi(I) → Bi(II) (25.37 ± 0.02 kbars), Bi(II) → Bi(III) (26.96 ± 0.18 kbars), Tl(II) → Tl(III) (36.69 ± 0.11 kbars), and Ba(II) → Ba(III) (59.0 ± 1.0 kbars). All compressions were made on the assembly at room temperature and the charge was then heated to the desired temperature which was measured with a Pt-Rh thermocouple, uncorrected for pressure effects. The thermocouple was adjacent to the center of the graphite heater.

High-purity reactants (>99.99% pure) were ground together and pelleted prior to reaction. Depending upon reactant densities, pellets weighed approximately 0.1–0.8 g.

The chromium sulfide phase was obtained in the form of black microcrystals when a mixture of Cr_2S_3–(1.0–1.5)S was pressured to 89 kbars and heated for 2 hr at 1200° followed by a quench to room temperature. The product was extracted overnight with CS_2 to remove unreacted S.

The chromium selenide and mixed-anion chromium sulfide selenide phases were prepared from a mixture of the elements of composition Cr–2Se or Cr–S–Se that was pressured to 65 kbars and heated for 2 hr at 1200° followed by a 4-hr cool to 400° and a quench to room temperature. Silvery, rod-shaped crystals formed at the sample ends in each case, and unreacted chalcogen was transported to the sample center. Crystals from the end regions only were used for characterization.

Preparation of Cr_2S_3 Single Crystals.—A mixture of 0.260 g of Cr and 0.641 g of S (Cr-4S) sealed in evacuated, heavy-walled silica tubing (8-mm o.d. × 8-cm length) was heated at 1350° under an external argon pressure of 3 kbars for 2 hr. The silica tubing flowed so as to transmit this pressure to the reactants. Following extraction with CS_2 to remove excess S, black platelets of Cr_2S_3 up to about 1 mm in length were isolated.

Chemical Composition.—The compositions of the new chromium sulfide and selenide phases were determined by thermogravimetry. Reaction in an oxygen atmosphere at a temperature up to about 1000° gave Cr_2O_3. With the sulfide and selenide binaries, the compositions $CrS_{1.62}$ and $CrSe_{1.60}$, *i.e.*, Cr_5X_8, were indicated. Assuming this ratio of chromium to chalcogen, a mixed sulfide–selenide $CrS_{0.96}Se_{0.64}$, *i.e.*, $Cr_5S_{4.8}Se_{3.2}$, was indicated. This ratio of S to Se was in good agreement with that calculated from the X-ray unit cell dimensions obtained on this phase as compared to those of the end members Cr_5S_8 and Cr_5Se_8. This use of Vegard's rule indicated the composition $Cr_5S_{4.9}Se_{3.1}$.

Electrical and Magnetic Measurements.—Except for Cr_5S_8, which was obtained only in powder form, electrical resistivity was measured on reasonably well-shaped single crystals using a standard four-probe technique. Activation energy of resistivity, E_a, is defined by the relation $\rho = \rho_0 e^{E_a/kT}$. A Faraday balance

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