of the higher oxidation states of early transition metals and of the second- and third-row transition metals, as compared in this case to the reductions found with later first-row metals (Cr to Cu). Thermogravimetric analysis (Figure 4, curves B–D) showed these dissolved oxides in a sulfur dioxide/nitrogen atmosphere gave similar "stabilization of sulfur trioxide as pyrosulfate", as was found in nitrogen atmospheres.[1] In each case the experimentally determined weight of evolved sulfur trioxide (indicated by arrows in Figure 4) agreed well with the observed weight loss, showing that no sulfur trioxide had been formed by reduction reactions analogous to eq 18. All the observed sulfur trioxide could be accounted for by pyrosulfate decomposition (eq 5), but the slower weight loss when these transition-metal oxides were present suggested that the latter had dissolved to give cationic species, probably polymeric, which, though more thermally stable than pyrosulfate, ultimately decomposed to the same product. Similar stabilization had been observed when sulfur dioxide was not present.[1] This behavior is to be contrasted with that reported earlier in this paper, when iron(II) and manganese(II) caused more rapid decomposition of pyrosulfate, probably because the latter transition metals existed as nonpolymerized cations whose Lux–Flood acidity would be the most important factor in promoting decomposition.

**Acknowledgment.** Grateful thanks are expressed to SERC and ISC Chemicals, Avonmouth, U.K., for CASE Scholarships to R.I.D. and to D.J.R.

**Registry No.** SO$_2$, 7446-09-5; CuSO$_4$, 7758-98-7; Li$_2$SO$_4$, 10377-48-7; K$_2$SO$_4$, 7778-80-5; Na$_2$SO$_4$, 7757-82-6; Cu$_2$SO$_4$, 17599-81-4; Fe$_2$(SO$_4$)$_3$, 10028-22-5; K$_2$S$_2$O$_7$, 7790-62-7; FeSO$_4$, 7720-78-7; MnO$_2$, 1313-13-9; Na$_2$CO$_3$, 497-19-8; K$_2$Cr$_2$O$_7$, 7778-50-9; K$_2$CrO$_4$, 7789-00-6; TiO$_2$, 13463-67-7; MoO$_3$, 1313-27-5; WO$_3$, 1314-35-8; Cu, 7440-50-8.

---

# Notes

Contribution from the Department of Chemistry,
University of Northern Iowa, Cedar Falls, Iowa 50614

## Tetraamine Complexes of Chromium(III). 5. Preparation of Bis(carboxylato)bis(1,2-ethanediamine)chromium(III) Complexes

James C. Chang

*Received September 24, 1985*

In 1970 Vaughn et al.[1] reported the preparation of *trans*-bis(acetato)bis(1,2-propanediamine)chromium(III) chloride monohydrate. Green et al.[2] used this method to prepare *trans*-bis(nicotinato-*O*)bis(1,3-propanediamine)chromium(III) chloride tetrahydrate. This method is now used to prepare some bis(carboxylato)bis(1,2-ethanediamine)chromium(III) complexes reported here.

### Experimental Section

**Preparation of Compounds.** In a typical preparation, 15 g (0.056 mol) of commercial CrCl$_3$·6H$_2$O (Baker Analyzed) and 0.30 mol of a carboxylic acid were mixed in 50 mL of distilled water. If the acid (such as benzoic acid and nicotinic acid) did not completely dissolve in water, a slurry was made by stirring with a magnetic stirrer. Then 50 mL (0.75 mol) of 1,2-ethanediamine was added dropwise to the mixture over a period of 45–60 min, the mixture being stirred constantly. After the addition of the amine, the mixture was heated to ca. 60 °C for 1 h and then evaporated on a steam bath in an evaporating dish until a solid crust formed on top of the liquid. After the mixture cooled to room temperature, any solid formed was filtered out and washed with a little absolute ethanol, followed by washing with acetone and drying in air. The propionic acid, isobutyric acid, 2,2-dimethylpropionic (pivalic) acid, benzoic acid, and nicotinic acid complexes were prepared; and the analytical results are summarized in Table I.

**Analytical Methods.** Chromium was determined as previously described,[3] and ionic chloride was determined by the method of Clarke[4] after ion-exchange chromatography, also as previously described.[5] Benzoate and nicotinate were determined by their UV spectra after chromatographing samples of the compounds on Na$^+$-form Dowex 50W-X8 columns and eluting the carboxylates with water. Carbon, nitrogen, and hydrogen were determined by H-M-W Laboratories, Phoenix, AZ.

**Physical Measurements.** The visible and UV spectra were measured by a Cary 14 or a Varian DMS 90 spectrophotometer, and the IR spectra were measured by a Perkin-Elmer Model 1500 FT-IR spectrophotometer, using KBr pellets of the compounds. Electrical conductances were measured by a Yellow Springs YSI Model 32 conductance meter.

### Results and Discussion

In this work several aliphatic carboxylic acids were used in an attempt to prepare a variety of compounds, but only the complexes of propionic, isobutyric, and pivalic acids were successfully prepared. In the preparation of acetic, butyric, valeric, and isovaleric acid complexes, the reaction mixtures had colors (red-orange) similar to those of the other preparations; but no solid product was obtained.

The formulas of the compounds prepared are listed in Table I, based upon the elemental analyses. In contrast to the 1,3-propanediamine complexes,[1,2] the counterions of four of the five compounds prepared in this work were not chloride but the carboxylate anions. Molar conductance values (see Table II) indicated that all the compounds are 1:1 electrolytes, and the benzoate and nicotinate complexes have chromium to free carboxylate ratios of nearly 1 (1.07 and 1.04, respectively).

The IR spectra of the five compounds prepared showed shifts of the COO$^-$ frequencies and the absence of the C=O stretching frequency characteristic of the carboxylic acids. For the propionate, isobutyrate, and pivalate complexes, $\nu_a$(COO$^-$) of the carboxylate anion at ca. 1560 cm$^{-1}$ was shifted to 1600–1620 cm$^{-1}$ and $\nu_s$(COO$^-$) at ca. 1450 and 1420 cm$^{-1}$ were shifted to 1380–1395 and 1345–1360 cm$^{-1}$. For the benzoate complex, $\nu_a$(COO$^-$) at 1595 cm$^{-1}$ and $\nu_s$(COO$^-$) at 1545 and 1410 cm$^{-1}$ were shifted to 1605 cm$^{-1}$ and to 1380 and 1353 cm$^{-1}$, respectively. These observations all indicate that the carboxylates are monodentate ligands.[6] For the nicotinate complex, however, $\nu_a$(COO$^-$) was shifted from 1620 to 1612 cm$^{-1}$ although the shift of $\nu_s$(COO$^-$) from 1420 and 1324 cm$^{-1}$ to 1380 and 1355 cm$^{-1}$ was similar to those of the other complexes and the nicotinate complexes previously prepared.[7] Although the shift of $\nu_a$(COO$^-$) to lower energy suggested bidentate ligation of the nicotinate anion, the analysis of the compound corresponds to three nicotinate anions per chromium atom, and the only formula that fits this analysis is a complex including two monodentate nicotinate anions and a third nicotinate as a counterion. The nicotinate counterion is confirmed by the chromium to free nicotinate ratio of 1.07.

The visible and UV spectra of the compounds in aqueous solutions are summarized in Table II. The spectra of *cis*- and *trans*-bis(acetato)bis(1,2-ethanediamine)chromium(III), reported by Nakahara,[8] are included for comparison. It can be seen that

---

(1) Vaughn, J. W.; Seiler, G. J.; Johnson, M. W.; Traister, G. L. *Inorg. Chem.* **1970**, *9*, 2786.

(2) Green, C. A.; Bianchini, R. J.; Legg, J. I. *Inorg. Chem.* **1984**, *23*, 2713.

(3) Chang, J. C. *J. Inorg. Nucl. Chem.* **1969**, *30*, 945.

(4) Clarke, F. E. *Anal. Chem.* **1950**, *22*, 553.

(5) Chang, J. C. *J. Inorg. Nucl. Chem.* **1975**, *37*, 855.

(6) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 232.

(7) Chang, J. C.; Gerdom, L. E.; Baenziger, N. C.; Goff, H. M. *Inorg. Chem.* **1983**, *22*, 1739.

**Table I.** Analytical Results for the Complexes of the Type $[Cr(OA)_2(en)_2]^+$

| OA$^{-a}$ | | % Cr | % C | % N | % H | % Cl | proposed formula |
|---|---|---|---|---|---|---|---|
| OPr$^-$ | found | 13.62 | 39.79 | 14.52 | 7.91 | | $[Cr(OPr)_2(en)_2](OPr)$ |
| | calcd$^b$ | 13.28 | 39.89 | 14.31 | 7.98 | | |
| OiBu$^-$ | found | 10.76 | 42.56 | 13.64 | 8.61 | | $[Cr(OiBu)_2(en)_2](OiBu)\cdot H_2O$ |
| | calcd$^b$ | 11.52 | 42.56 | 12.41 | 8.71 | | |
| OPiv$^-$ | found | 12.77 | 40.92 | 13.70 | 8.26 | 8.64 | $[Cr(OPiv)_2(en)_2]Cl$ |
| | calcd$^b$ | 12.69 | 41.02 | 13.67 | 8.36 | 8.65 | |
| OBz$^-$ | found | 9.75 | 55.18 | 10.89 | 6.03 | | $[Cr(OBz)_2(en)_2](OBz)$ |
| | calcd$^b$ | 9.71 | 56.07 | 10.46 | 5.83 | | |
| ONic$^-$ | found | 9.46 | 47.12 | 18.20 | 5.46 | | $[Cr(ONic)_2(en)_2](ONic)\cdot H_2O$ |
| | calcd$^b$ | 9.34 | 47.48 | 17.62 | 5.43 | | |

$^a$OPr$^-$ = propionate, OiBu$^-$ = isobutyrate, OPiv = pivalate (2,2-dimethylpropionate), OBz$^-$ = benzoate, ONic$^-$ = nicotinate-*O*.

**Table II.** UV–Visible Spectra and Molar Conductances of Complexes of the Type $[Cr(OA)_2(en)_2]^+$ in Water at 25 °C

| | λ, nm (ε, L mol$^{-1}$ cm$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| OA$^-$ | $\lambda_{max}$ | $\lambda_{min}$ | $\lambda_{max}$ | $\lambda_{min}$ | $\lambda_{max}$ | 10*Dq*, cm$^{-1}$ × 10$^3$ | $\Lambda_M$, S cm$^2$ mol$^{-1}$ | ref |
| OAc$^{-a}$ (cis) | | | 373 (44)$^b$ | 422 (8)$^b$ | 503 (83)$^b$ | 19.9 | | 6 |
| OAc$^-$ (trans) | | | 373 (46)$^b$ | 465 (18)$^b$<br>420 sh (25)$^b$ | 530 (40)$^b$ | 18.9 | | 6 |
| OPr$^-$ | | | 372 (61.8) | 422 (17.9) | 497 (110) | 20.1 | 65.3 | this work |
| OiBu$^-$ | | | 372 (59.6) | 422 (19.0) | 497 (99.4) | 20.1 | 131 | this work |
| OPiv$^-$ | | | 372 (61.6) | 423 (18.4) | 498 (106) | 20.1 | 96.6 | this work |
| OBz$^-$ | 231 (35 000) | 308 (43.3) | 355 (68.6) | 423 (29.1)<br>460 sh (40) | 498 (55.3) | 20.1 | 60.2 | this work |
| ONic$^-$ (cis) | 261 (11 500) | 331 (29.3) | 370 (67.1) | 418 (24.5) | 490 (107) | 20.4 | | 7 |
| ONic$^-$ | 262 (11 200) | 315 (131) | 342 (141) | 430 (46.9)<br>470 sh (50) | 493 (57.0) | 20.3 | 93.5 | this work |

$^a$OAc = acetate. $^b$Estimated from the spectral curves in the cited literature.

the spectra of the propionate, isobutyrate, and pivalate complexes all resemble the spectrum of *cis*-$[Cr(OAc)_2(en)_2]^+$, suggesting the cis configuration for these complexes. This is in contrast to the finding of Vaughn et al.[1] for the configuration of the bis(acetato)bis(1,3-propanediamine)chromium(III). The spectra of the benzoate and the nicotinate complexes exhibit a slight shoulder at 460–470 nm, suggesting the trans configuration for these two complexes. The spectrum of the nicotinate complex reported here is different from that of *cis*-$[Cr(ONic)_2(en)_2]^+$ reported earlier.[7] Actually, the spectrum of *cis*-$[Cr(ONic)_2(en)_2]^+$ is very similar to the spectra of the aliphatic carboxylate complexes; this spectrum is also included in Table II for comparison.

In order to ascertain the lability of these complexes qualitatively, the visible spectra of the aqueous solutions of these complexes were scanned over a period of 30 min at ca. 25 °C. For the three aliphatic carboxylate complexes the $\lambda_{max}$ were shifted to longer wavelengths slowly and three isosbestic points were observed as follows: OPr$^-$ 545, 435, 396 nm; OiBu$^-$ 548, 436, 400 nm; OPiv$^-$ 553, 434, 403 nm. The percentage decrease in the absorbance at the low-energy maximum, over a period of 20 min, was ca. 21%, 15%, and 12% for the propionate, isobutyrate, and pivalate complexes, respectively, suggesting that the most branched aliphatic carboxylate ligand (pivalate) reacts the slowest.

The visible spectra of the benzoate and the nicotinate complexes changed very little over a 60-min period. For the nicotinate complex, the absorbance at 495 nm showed less than 3% decrease in 2.5 h and ca. 17% decrease after 24 h.

In 0.1 M $HClO_4$ solutions, these complexes showed much faster decrease in the absorbances and shifts of $\lambda_{max}$ to longer wavelengths. For the three aliphatic carboxylate complexes, only one isosbestic point at ca. 527 nm was observed. Two more isosbestic points were near $\lambda_{min}$ and could not be accurately determined. For the benzoate complex, also only one isosbestic point at 522 nm was observed while the other two near $\lambda_{min}$ could not be determined. The differences in the isosbestic points in aqueous solutions and in $HClO_4$ solutions suggested different reaction paths in water and in acid. This is not surprising because of the tendency of both the carboxylate and the diamine to protonate in acidic solutions. Also, the Cr–N rupture path was observed in other Cr(III)–amine complexes.[9–13] More detailed studies of the reactions of these complexes are under way.

The visible spectrum of the nicotinate complex in 0.1 M $HClO_4$ also changed very little with time. The absorbance at 342 nm showed only a 7% decrease over a 24-h period at ca. 25 °C. the biological activity of this complex has not been tested.

**Registry No.** $[Cr(OPr)_2(en)_2](OPr)$, 101652-58-8; $[Cr(OiBu)_2(en)_2](OiBu)$, 101652-60-2; $[Cr(OPiv)_2(en)_2](OPiv)$, 101670-92-2; $[Cr(OBz)_2(en)_2](OBz)$, 101652-62-4; $[Cr(ONic)_2(en)_2](ONic)$, 101758-89-8.

---

(8) Nakahara, M. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 901.

(9) Zinato, E.; Lindholm, R.; Adamson, A. W. *J. Inorg. Nucl. Chem.* **1969**, *31*, 449.

(10) Couldwell, M. C.; House, D. A. *Inorg. Chem.* **1972**, *11*, 2024.

(11) Guastalla, G.; Swaddle, T. W. *Inorg. Chem.* **1974**, *13*, 61.

(12) Ramasami, T.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 359.

(13) Williamson, R. L. M.A. Thesis, University of Northern Iowa, 1984.

Contribution from the Department of Chemistry,
North Carolina State University,
Raleigh, North Carolina 27695-8204

# The Unusual Structural Feature of Binuclear Platinum Chains $[Pt_2(L\text{-}L)_4X]^{n-}_{\infty}$

Myung-Hwan Whangbo*[†] and Enric Canadell[‡]

*Received September 11, 1985*

Binuclear platinum chains $[Pt_2(L\text{-}L)_4X]^{n-}_{\infty}$, **1** (L-L = $CH_3CS_2^-$, X = I, *n* = 0; L-L = $(HO_2P\text{–}O\text{–}PO_2H)^{2-}$, X = Br, *n* = 4),[1] contain platinum atoms of formal oxidation state +2.5 and have a symmetrical $Pt^{2.5+}$–X–$Pt^{2.5+}$ bridge.[2] These binuclear chains are closely related to mixed-valence, mononuclear platinum analogues

---

[†] Camille and Henry Dreyfus Teacher-Scholar (1980–1985).

[‡] Present address: Laboratoire de Chimie Theorique, Universite de Paris-Sud, 91405 Orsay Cedex, France.

0020-1669/86/1325-1726$01.50/0 © 1986 American Chemical Society