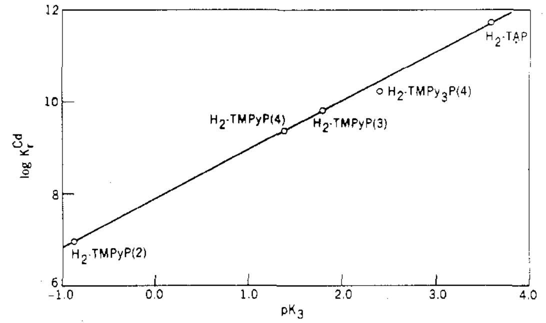


Figure 1. Plot of the log of the cadmium porphyrin dissociation rate constants, k_r^{Cd}, vs. the porphyrin protonation parameter, pK_3.

therefore primarily determine the trend in the K_e^{Cd} values. k_r^{Cd} ranges from 5×10^{11} M^{-2} s^{-1} for CdTAP to 9×10^{6} M^{-2} s^{-1} for CdTMpyP(2), a factor of 58 000. The zinc porphyrins basically follow the same trend.[1]

Aside from H$_2$TMpyP(2) which shows atypical behavior,[2] it is becoming clear that metal–porphyrin formation rates for similarly charged porphyrins are relatively independent or increase slightly with an increase in porphyrin basicity. This is found for the cadmium porphyrins in this study and for both the Cu^{2+}/meso-substituted tetraphenylporphyrins[11] and the Zn^{2+}/3,8-disubstituted deuteroporphyrin ester[12] metalation reactions. The metalloporphyrin acid-catalyzed dissociation reactions usually depend on porphyrin basicity. A linear relationship was noted between log k_r^{Zn} and pK_3 for the H$^+$/3,8-disubstituted deuteroporphyrin ester zinc complex reactions in methanol.[13] Figure 1 shows that a similar relationship of the form

$$\log k_r^{Dd} = 1.05\mathrm{p}K_3 + 7.85 \qquad (4)$$

holds for these meso-substituted CdP reactions in aqueous solution. log K_e^{Cd} is also linearly related to pK_3 in the same fashion.

For H$_2$TMpyP(4),[1] the ratio k_f^{Cd}/k_f^{Zn} is 10^3, while the dissociation rate ratio k_r^{Cd}/k_r^{Zn} is 10^{11}. The zinc porphyrins are thus 10^8 times more stable than their corresponding cadmium porphyrin counterparts. The greater lability of aquo Cd^{2+} as compared to Zn^{2+} partially explains the formation rate differences. The smaller charge/radius ratio of Cd^{2+} as opposed to that of Zn^{2+} and the fact that cadmium probably lies further out of the mean porphyrin plane than does zinc both suggest weaker metal to porphyrin bonding in cadmium porphyrins. This in turn might favor a higher (than with zinc) equilibrium concentration of porphyrins where the cadmium ion is bonded to three (rather than four) central porphyrin nitrogen atoms, producing intermediates having vacant coordination positions for proton attack. The higher equilibrium concentration of such reactive entities in cadmium–porphyrin systems would lead to faster acid-solvolysis rates.

The kinetics of the electrophilic substitution of Zn^{2+} for Cd^{2+} in cadmium porphyrins has been studied,[14] and as with the H$^+$/CdP reactions, the Zn^{2+}/CdP rates depend strongly on porphyrin basicity. At ambient temperatures, cadmium coordinated to the more basic porphyrin is displaced faster by Zn^{2+}. Such displacement rates parallel[15,16] the relative porphyrin basicity parameter, $E_{1/2}^{r}(1)$, the reduction potential of the free base porphyrin forming the radical anion H$_2$P$^{-}\cdot$.

A number of studies are appearing on the uses of water-soluble porphyrins for the analytical determination of low concentrations of metal ions.[17,18] Our present results indicate what porphyrin factors lead to maximal complexation in aqueous solutions.

Acknowledgment. We thank Howard University NIH Biomedical Research Support Grant RR 7117 for financial support.

---

(11) F. Longo, E. Brown, D. Quimby, A. Adler, and M. Meot-Ner, *Ann. N.Y. Acad. Sci.*, **206**, 420 (1973).

(12) J. James and P. Hambright, *Inorg. Chem.*, **12**, 474 (1973).

(13) B. Shears, B. Shah, and P. Hambright, *J. Am. Chem. Soc.*, **93**, 776 (1971).

(14) J. Reid and P. Hambright, *Inorg. Chim. Acta.*, **33**, L135, (1979).

(15) P. Worthington, P. Hambright, R. F. X. Williams, J. Reid, A. Shamim, J. Turay, C. Burnham, D. Bell, R. G. Little, N. Datta-Gupta, and U. Eisner, *J. Inorg. Biochem.*, in press.

(16) R. F. X. Williams and P. Hambright, *Bioinorg. Chem.*, **9**, 537 (1978).

(17) J. Itoh, T. Yotsuyanagi, and K. Aomura, *Anal. Chim. Acta.*, **74**, 53 (1975).

(18) H. Koh, K. Kawamura, and H. Ishii, *Nippon Kagaku Kaishi*, 591 (1979).

Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

Synthesis and Characterization of a Hydroxycarbonyl Complex of Platinum: *trans*-[PtCl(COOH)(PEt$_3$)$_2$]

Marta Catellani and Jack Halpern*

Received July 25, 1979

(Hydroxycarbonyl)metal complexes, [L$_n$M–COOH], have been postulated as intermediates in the oxidation of (free or coordinated) CO by metal ions,[1-3] in the isotopic oxygen exchange of metal carbonyls with H$_2$O,[4,5] in the homogeneous catalysis of the water-gas shift reaction,[6] and in reactions (exemplified by eq 1) of metal carbonyls with water to form the corresponding hydrides.[7,8] Notwithstanding the widespread roles attributed to such species as transient intermediates in a variety of important reactions, only a few hydroxycarbonyl complexes have actually been isolated and even partially characterized.[9-12] We now wish to report the synthesis, isolation, and direct characterization of the (hydroxycarbonyl)platinum complex, *trans*-[PtCl(COOH)(PEt$_3$)$_2$] (**2**). We also present evidence for the previously postulated role of **2** as an intermediate in the reaction of *trans*-[PtCl(CO)(PEt$_3$)$_2$]$^+$ (**1**) with water (eq 1).[8] In addition we describe the first characterization of a hydroxycarbonyl complex, *trans*-[PtCl(^{13}COOH)(PEt$_3$)$_2$], by ^{13}C NMR.

$$\underset{\mathbf{1}}{trans\text{-}[\mathrm{PtCl(CO)(PEt_3)_2}]^+} \xrightarrow[-\mathrm{H}^+]{\mathrm{H_2O}} \underset{\mathbf{2}}{trans\text{-}[\mathrm{PtCl(COOH)(PEt_3)_2}]} \xrightarrow{-\mathrm{CO_2}} trans\text{-}[\mathrm{PtHCl(PEt_3)_2}] \qquad (1)$$

---

(1) Harkness, A. C.; Halpern, J. *J. Am. Chem. Soc.* **1961**, *83*, 1258.

(2) Nakamura, S.; Halpern, J. *J. Am. Chem. Soc.* **1961**, *83*, 4102.

(3) Bercaw, J. E.; Goh, L. Y.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *94*, 6534.

(4) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5940.

(5) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300.

(6) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941.

(7) Kruck, T.; Noack, M. *Chem. Ber.* **1964**, *97*, 1693.

(8) Clark, H. C.; Jacobs, W. J. *Inorg. Chem.* **1970**, *9*, 1229.

(9) Deeming, A. J., Shaw, B. L. *J. Chem. Soc. A* **1969**, 443.

(10) Appleton, T. G.; Bennett, M. A. *J. Organomet. Chem.* **1973**, *55*, C88.

(11) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741.

(12) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

0020-1669/80/1319-0566$01.00/0

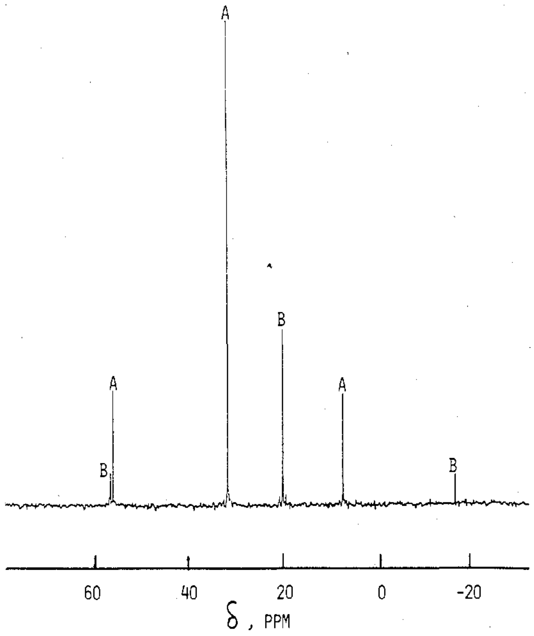


Figure 1. ^{31}P NMR spectrum (broad band proton decoupled) of a 12.5:1 (v/v) acetone/water solution containing 0.025 M $[PtCl(CO)(PEt_3)_2]BF_4$ at −35 °C: A, $[PtCl(CO)(PEt_3)_2]^+$; B, $[PtCl(COOH)(PEt_3)_2]$.

Results and Discussion

$[PtCl(COOH)(PEt_3)_2]$ was prepared by the reaction of $[PtCl(CO)(PEt_3)_2]^+$ (dissolved in acetone) with water (see Experimental Section) and was characterized analytically and by IR and NMR spectroscopy. Anal. Calcd for $C_{13}H_{31}O_2ClP_2Pt$: C, 30.50; H, 6.10; Cl, 6.92; P, 12.10; Pt, 38.11. Found: C, 30.68; H, 6.17, Cl, 6.93; P, 11.95; Pt, 37.98.

The infrared spectrum of **2** (Nujol and HCBD mulls) exhibited an –OH band at 3140 (w) cm^{-1} and –COO bands at 1595 (vs) and 1150 (s) cm^{-1}. Correspondingly, $[PtCl(COOD)(PEt_3)_2]$ exhibited an isotopically shifted OD band at 2240 cm^{-1} as well as a new band at 2040 cm^{-1} (whose OH counterpart at 2885 cm^{-1} is presumably obscured by the phosphine CH stretching region).

NMR: ^{31}P (36.4 MHz, acetone-d_6) δ 21.3, accompanied by ^{195}Pt satellites (s, 2 P, $J_{Pt-P} = 2748$ Hz); ^1H (270 MHz, acetone-d_6) δ 1.96 (m, 6 CH_2), δ 1.16 (m, 6 CH_3). The ^1H NMR signal due to the COOH group was not detected in acetone but could be observed in other solvents, i.e., toluene-d_8 (δ 11.0), acetonitrile-d_3 (δ 8.5), and benzene-d_6 (δ 8.8).

$[PtCl(COOH)(PEt_3)_2]$ was air stable for several hours but decomposed on prolonged standing at room temperature under N_2 or vacuum to give a residue whose infrared spectrum contained a strong band in the Pt–H stretching region (2230 cm^{-1}). On warming of solid **2** at 170 °C for 15 min under vacuum, CO_2 was evolved (identified mass spectrometrically), leaving a pale yellow residue identified by infrared spectra as being mainly $[PtHCl(PEt_3)_2]$ (ν_{Pt-H} 2230 cm^{-1}). Decomposition of $[PtCl(COOD)(PEt_3)_2]$ yielded a residue whose infrared spectrum exhibited the corresponding Pt–D band at ca. 1600 cm^{-1}. Both residues also contained a broad impurity band at ca. 1800 cm^{-1} which was not identified. Slow decomposition of $[PtCl(COOH)(PEt_3)_2]$ to yield $[PtHCl(PEt_3)_2]$ also was observed in several solvents including acetone and benzene. It is planned to examine the kinetics of this reaction.

The addition of small amounts (ca. 10–20%) of water to an acetone solution of $[PtCl(CO)(PEt_3)_2]BF_4$ resulted in slow reaction to form $[PtHCl(PEt_3)]_2$. Only traces of a species identifiable as **2** could be detected by NMR at *room temperature*. However, lowering the temperature to −35 °C resulted in suppression of the formation of $[PtHCl(PEt_3)_2]$ and accumulation of the intermediate **2**. Under these conditions the well-defined equilibrium corresponding to eq 2 was established and could be monitored by ^{31}P NMR[13] ($[PtCl(CO)(PEt_3)_2]^+$, δ 32.7, $J_{Pt-P} = 1816$ Hz), as depicted in Figure 1.

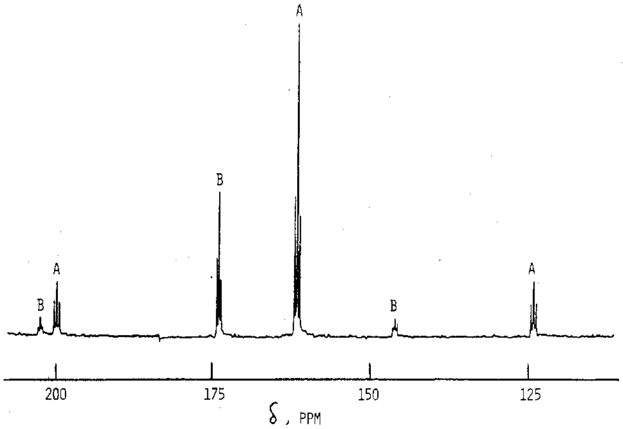


Figure 2. ^{13}C NMR spectrum (broad band proton decoupled) of a 5:1 (v/v) acetone/water solution containing ca. 0.1 M $[PtCl(^{13}CO)(PEt_3)_2]BF_4$ (90% ^{13}C enriched) at −35 °C: A, $[PtCl(^{13}CO)(PEt_3)_2]^+$; B, $[PtCl(^{13}COOH)(PEt_3)_2]$.

$$trans\text{-}[PtCl(CO)(PEt_3)_2]^+ + H_2O \rightleftarrows trans\text{-}[PtCl(COOH)(PEt_3)_2] + H^+ \quad (2)$$

The synthesis of $[PtCl(^{13}CO)(PEt_3)_2]$ also permitted the characterization of **1** and **2**, and the monitoring of equilibrium 2, by ^{13}C NMR. ^{13}C NMR (22.63 MHz, 5:1 acetone-d_6/water, v/v): $[PtCl(^{13}CO)(PEt_3)]^+$ δ 161.0, accompanied by ^{195}Pt satellites (t, 1 CO, $J_{Pt-C} = 1797$ Hz, $J_{P-C} = 9$ Hz); $[PtCl(^{13}COOH)(PEt_3)_2]$ δ 173.4 (t, 1 COOH, $J_{Pt-C} = 1337$ Hz, $J_{P-C} = 8$ Hz). The ^{13}C NMR spectrum of an equilibrium mixture of **1** and **2** in acetone/water (5:1 v/v) is depicted in Figure 2.

The position of equilibrium 2 at −35 °C was found to depend upon the medium composition, the ratio [**1**]:[**2**] (estimated from the intensities of the ^{31}P NMR signals) decreasing with increasing water concentration. Thus, [**1**]:[**2**] ≈ 2.5 in 12.5:1 (v/v) acetone/water and ≈1.5 in 5:1 (v/v) acetone/water. Furthermore, as expected, the addition of acid (0.1 M $HClO_4$) shifted equilibrium 2 completely to the left, whereas addition of base (ca. 0.04 M 2,4,6-tri-*tert*-butylpyridine or KOH) shifted it almost completely to the right.

Finally, some comment about the NMR coupling constants of **1** and **2** would seem to be in order. The transformation of **1** to **2** is accompanied by a *decrease* in J_{Pt-C} (1797–1337 Hz) and an *increase* in J_{Pt-P} (1816–2748 Hz). Both these trends are consistent with greater π back-bonding in Pt–CO relative to Pt–COOH, resulting in stronger Pt–C bonding and weaker Pt–P bonding in **1** compared with **2**.

Experimental Section

$[PtCl(COOH)(PEt_3)_2]$. $[PtCl(CO)(PEt_3)_2]BF_4$ (0.1 g), prepared as described elsewhere,[14] was dissolved in acetone (2 mL) under nitrogen, followed by addition of water (10 mL). Ether extraction, followed by evaporation of the solvent under reduced pressure, yielded a white microcrystalline solid (**2**) which was dried under vacuum for 8 h (yield 0.08 g, 90%).

Spectral Measurements. Infrared spectra were recorded with a Perkin-Elmer 283 spectrometer. ^1H NMR spectra were recorded with a Bruker HS-270 spectrometer interfaced with a Nicolet 1080 com-

---

[13] The ^{31}P NMR parameters of **2** varied slightly with the solvent composition, e.g., δ 20.7, $J_{Pt-P} = 2726$ Hz, in 12.5:1 (v/v) acetone/water and δ 20.5, $J_{Pt-P} = 2702$ Hz, in 5:1 (v/v) acetone/water.

[14] Clark, H. C.; Dixon, K. R.; Jacobs, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 2259.

puter; ^{13}C and ^{31}P NMR spectra (FT) were recorded with a Bruker HFX-90E spectrometer, interfaced with a Nicolet 1080 computer. Elemental analyses were performed by Galbraith Laboratories.

Acknowledgment. Support of this research through grants from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Engelhard Minerals and Chemicals Corp. for a generous loan of platinum. The NMR facilities used in this research were supported in part through the University of Chicago Cancer Center, Grant No. NIH-CA-14599.

Registry No. **2**, 72121-30-3; *trans*-$[PtCl(CO)(PEt_3)_2]BF_4$, 16743-82-1; *trans*-$[PtHCl(PEt_3)_2]$, 16842-17-4.

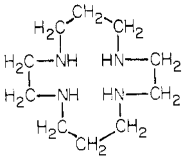
Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

Improved Syntheses of Trans Isomers of Chromium(III) Complexes with 1,4,8,11-Tetraazacyclotetradecane

C.-K. Poon* and K. C. Pun

Received March 29, 1979

The preparation and characterization of octahedral cyclam (1,4,8,11-tetraazacyclotetradecane) complexes of the first transition series, viz., chromium(III),[1] manganese(III),[2] iron(III),[2] cobalt(III),[3,4] nickel(II),[5] and nickel(III),[2] have been described. With the exception of chromium(III), all the metal ions form stable complexes with a trans configuration. In the case of cobalt(III)[4] and iron(III)[2] some thermodynamically less stable cis complexes have also been described. For chromium(III), however, difficulties were encountered[1] in the preparation of trans complexes, e.g., to quote Ferguson and Tobe[1] "attempts to prepare this isomer (*trans*-$[Cr(cyclam)Cl_2]^+$) in good yield were unsuccessful and, in every case, only the cis isomer was obtained" and "the trans isomer rarely comprised more than 10% of the total product and occasionally was not present at all". Our desire to study the electrochemical, photochemical, and thermal substitution reactions of trans cyclam complexes of chromium(III) has prompted us to examine a new synthetic route, which we wish to report, for a large-scale preparation of *trans*-$[Cr(cyclam)Cl_2]^+$ and hence other trans derivatives.



cyclam

Experimental Section

trans-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride, *trans*-$[Cr(cyclam)Cl_2]Cl$, was prepared by refluxing an aqueous solution of *cis*-$[Cr(cyclam)Cl_2]Cl$[1] (2 g in 100 mL), the pH of which had been adjusted to about 7 with 2,4,6-trimethylpyridine (about 2–3 drops), for about 8 h. The resulting solution was acidified with concentrated hydrochloric acid and was then evaporated to dryness. Upon concentration, the dark red solution gradually turned to dark purple. The residue was extracted three times with *cold* absolute methanol (2 × 50 mL and 15 mL). The combined methanolic extract was evaporated to dryness, and the residue was further extracted three times with *cold* methanol (3 × 25 mL). The residue remaining became pinkish red which was the unisomerized cis isomer. The final combined methanolic extract was evaporated to dryness, and the dark purple powder was recrystallized from hydrochloric acid (1 M). The needle crystals were washed with acetone and diethyl ether and dried under vacuum at 78 °C; yield 1.1 g. Anal. Calcd for $C_{10}H_{24}N_4Cl_3Cr$: C, 33.5; H, 6.7; N, 15.6; Cl, 29.7. Found: C, 33.4; H, 6.6; N, 15.4; Cl, 29.8.

Table I. Electronic Absorption Spectra of Some *cis*- and *trans*-$[CrLX_2]^+$ [L = cyclam or $(en)_2$] Complexes

complexes	λ_{max},[a] nm
trans-$[Cr(en)_2Cl_2]^+$ [b]	578 (24.5), 453 (23), 396 (34)
trans-$[Cr(cyclam)Cl_2]^+$ [c]	567 (19.9), ~404 sh (29.9), 364 (33.5)
trans-$[Cr(cyclam)Cl_2]^+$ [d]	568 (22), ~407 sh (33), 366 (37)
trans-$[Cr(cyclam)Cl_2]^+$ [e]	572 (19.9), ~407 sh (35), 365 (41)
cis-$[Cr(en)_2Cl_2]^+$ [b]	528 (71), 402 (69)
Cis-$[Cr(cyclam)Cl_2]^+$ [e]	529 (111), 404 (106)
trans-$[Cr(en)_2(NCS)_2]^+$ [f]	486 (95), ~365 sh (67)
trans-$[Cr(cyclam)(NCS)_2]^+$ [c]	483 (139), ~364 sh (117)
cis-$[Cr(en)_2(NCS)_2]^+$ [f]	490 (148), 370 (91)
cis-$[Cr(cyclam)(NCS)_2]^+$ [e]	486 (189), 368 (101)

[a] Molar absorptivities in cm^{-1} L mol^{-1} are given in parentheses; sh = shoulder. [b] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, 83, 4152 (1961). [c] This work. [d] C. Kutal and A. W. Adamson, *J. Am. Chem. Soc.*, 93, 5581 (1971). [e] J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, 4, 109 (1970). [f] D. A. House and C. S. Garner, *J. Am. Chem. Soc.*, 88, 2156 (1966).

trans-Diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III) thiocyanate hemihydrate, *trans*-$[Cr(cyclam)(NCS)_2](NCS)\cdot{}^1/_2H_2O$, was prepared by refluxing an aqueous solution (pH about 7 with 2–3 drops of 2,4,6-trimethylpyridine) of *trans*-$[Cr(cyclam)Cl_2]Cl$ (0.2 g in 20 mL) for about 2 h. NaNCS (0.3 g) was added to the resulting solution which was then acidified with concentrated nitric acid. The solution was evaporated to dryness during which it turned to orange in color. The complex was recrystallized by suspending the residue in a boiling 0.5 M NaNCS solution (10 mL) under reflux for about 15 min. The hot solution was filtered, and upon cooling of the solution orange crystals were slowly separated, which were filtered off, washed with alcohol and diethyl ether, and dried under vacuum at 78 °C; yield 0.1 g. Anal. Calcd for $C_{13}H_{35}N_7O_{1/2}S_3Cr$: C, 35.9; H, 5.8; N, 22.5. Found: C, 36.0; H, 5.6; N, 22.3.

The *perchlorate* salt, *trans*-$[Cr(cyclam)(NCS)_2]ClO_4$, was prepared by a dropwise addition of concentrated $HClO_4$ to an aqueous solution of *trans*-$[Cr(cyclam)(NCS)_2](NCS)\cdot{}^1/_2H_2O$ (0.1 g in 5 mL) until an orange powder appeared, which was filtered off, washed with alcohol and diethyl ether, and dried under vacuum at 78 °C. Anal. Calcd for $C_{12}H_{24}N_6ClO_4S_2Cr$: C, 30.8; H, 5.2; N, 18.0; Cl, 7.6. Found: C, 30.7; H, 5.3; N, 17.7; Cl, 7.5.

cis-$[Cr(cyclam)X_2]X$ ($X = Cl^-$ or NCS^-) complexes were prepared by the literature methods.[1]

Physical Measurements. Visible and ultraviolet absorption spectra of freshly prepared aqueous solution were measured with a Beckman Acta CIII spectrophotometer. Infrared spectra were measured in Nujol mulls on a Perkin-Elmer 577 spectrophotometer.

Results and Discussion

The isomerization of *cis*-$[Cr(cyclam)Cl_2]^+$ to the trans isomer is pH dependent, being most efficient at a pH of about 7. At this pH the starting material was essentially hydrolyzed to *cis*-$[Cr(cyclam)(OH)(H_2O)]^{2+}$[1] which then underwent isomerization. It was known that the isomerization of the corresponding cobalt(III) complex also went by way of *cis*-$[Co(cyclam)OH)(H_2O)]^{2+}$.[6] In any case, the isomerization was slow, the yield being reduced to only about 14% if the

---

(1) J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, **4**, 109 (1970).
(2) P. K. Chan and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 858 (1976).
(3) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
(4) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1549 (1968).
(5) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **5**, 1514 (1966).
(6) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).

0020-1669/80/1319-0568$01.00/0