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.

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

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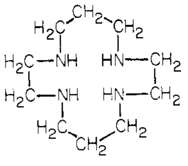
The preparation and characterization of octahedral cyclam (1,4,8,11-tetraazacyclotetradecane) complexes of the first transition series, viz., chromium(III),[1] manganese(III),[2] iron(III),[2] cobalt(III),[3,4] nickel(II),[5] and nickel(III),[2] have been described. With the exception of chromium(III), 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

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Table II. Characteristic Infrared Absorption Bands (2100–2000, 910–790, 870–830, and 400–200 cm^{-1}) for the Differentiation of *cis*- or *trans*-[Cr(cyclam)X_2] X Complexes

	freq of absorption bands, cm^{-1} [a]							
X	C–N[b]	N–H[c]				C–S[b]	CH_2[c]	Cr–X str
trans Cl		890 s	882 s				804 s	338 s
trans NCS	2090 s, 2070 s, 2050 s	885 s	878 m			865 w	802 m	344 s
cis Cl			872 m	862 m sh	854 m		815 w, 805 m	335 s, 316 s
cis NCS	2085 s, 2080 s, 2040 s		870 m	860 m	850 m sh	840 w	818 m, 810 m	340 m, 330 m, 320 m

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [b] Vibrations associated with thiocyanate. [c] Vibrations associated with cyclam.

refluxing time was shortened to 3 h. In acid medium, the isomerization was negligible, and this probably accounts for previous unsuccessful attempts[1] to isomerize the cis complexes. We have not been able to synthesize the trans complexes directly from the free cyclic ligand.

The isomeric purity of the new complexes was confirmed by the observation that the electronic absorption spectra were not affected by repeated recrystallization. Furthermore, when these complexes were absorbed on cation exchanger Dowex 50W-X8 (20-50 mesh) in the H^+ form, only a single band was developed which could be eluted with hydrochloric acid (1 M).

As shown in Table I, the assignment of a geometric configuration to these complexes, based entirely on the comparison of the visible absorption spectra with those of known bis(ethylenediamine) [$(en)_2$] analogues,[1] was not too reliable for the pair of isothiocyanato complexes since their visible absorption spectra are rather similar. The use of infrared spectroscopy for the differentiation of cis and trans isomers of cyclam complexes has been explored extensively.[2,7,8] A consistent variation, being independent of the nature of the central metal ions, other ligands, and counterions present, has been found in the 790–910 cm^{-1} region. Trans complexes invariably showed two groups of bands, a doublet near 890 cm^{-1} arising essentially from the secondary amine vibration and a singlet near 810 cm^{-1} due predominantly to the methylene vibration.[7] The amine vibration of cis complexes showed at least three bands in a lower frequency range (840–890 cm^{-1}) while the methylene vibration split into two bands in the 790–830-cm^{-1} region. As shown in Table II, the infrared spectra of the new complexes are clearly consistent with a trans configuration. The far-infrared spectra (400–200 cm^{-1}) of the four complexes *cis*- and *trans*-[Cr(cyclam)X_2]X ($X^- = Cl^-$ or NCS^-) are remarkably similar except for the strong bands which could be assigned to the ν(Cr–X) vibration. The observation that trans complexes showed only one band whereas cis complexes showed two (for $X^- = Cl^-$) or three bands (for $X^- = NCS^-$) strongly supports the previous assignment of the geometric configuration to these complexes. As for the differentiation of the N- and S-bonding modes of the ambidentate thiocyanate ligand in *cis*- and *trans*-[Cr(cyclam)$(NCS)_2$]NCS, infrared spectroscopy in the ν(C–N) and ν(C–S) regions is not very useful.[9] We have not been able to detect any band assignable to the S-bonded ν(C–S) vibration in the 690–720-cm^{-1} region. In the N-bonded ν(C–S) region although absorptions are found at 865 and 840 cm^{-1} for the trans and cis isomer, respectively, they are rather weak. The assignment of a N-bonding mode is supported by the far-infrared spectra of these complexes. It was pointed out by Forster and Goodgame[10] that for analogous complexes with the same symmetry the following order of metal–ligand vibrations was observed: ν(M–*N*CS) > ν(M–Cl) > ν(M–*S*CN) > ν(M–Br). As shown in Table I, the two thiocyanate complexes can be assumed accordingly to be N bonded.

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Registry No. *trans*-[Cr(cyclam)Cl_2]Cl, 27385-72-4; *trans*-[Cr(cyclam)$(NCS)_2$](NCS), 72173-09-2; *trans*-[Cr(cyclam)$(NCS)_2$](ClO_4), 72151-28-1; *cis*-[Cr(cyclam)Cl_2]Cl, 27435-95-6; *cis*-[Cr(cyclam)$(NCS)_2$](NCS), 27436-02-8.

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Correspondence

The Noncorrelation of *Dq* and $E_{1/2}$ in Metal Complexes. The Importance of the Spherical Ligand Field Term

Sir:

Recently there has been a great deal of interest in the effect of ligands on the redox potentials of transition-metal ions. Several studies in which the metal ion is held constant and the ligands are systematically varied have revealed surprisingly large changes in the redox potentials caused by rather subtle variations in the ligands.[1-7] It is not uncommon to observe 1–2 V changes in the redox potential of a given metal ion as a result of seemingly minor variations in the ligands. These observations have practical application in the molecular design of new electron-transfer reagents and of complexes containing metal ions in unusual oxidation states.

Although it has been demonstrated for several redox couples, e.g., Cr(III)/Cr(II),[5] Fe(III)/Fe(II),[2,3] Co(III)/Co(II),[2,3] Ni(III)/Ni(II)/Ni(I),[1-3] Cu(II)/Cu(O),[6,7] Ru(III)/Ru(II),[4] that the potentials can be predictably varied over a wide range, there is no satisfactory explanation for the observed changes

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