of Table V suggests that this is probably an oversimplification, and ongoing studies of a more extended series of compounds are required before more definite conclusions can be reached.[53]

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Registry No. **2a**, 81554-46-3; **2b**, 81554-48-5; **2c**, 81554-49-6; **3a**, 81554-51-0; **3b**, 81600-77-3; **4a**, 81554-52-1; **4b**, 81554-53-2; **4c**, 81554-54-3; **5**, 81554-29-2; **6**, 81554-30-5; **7**, 81554-32-7; **8**, 81554-33-8; 1,5-bis(salicylideneamino)pentan-3-ol, 81555-05-7; 1,5-diaminopentan-3-ol, 81555-06-8; pyridine-2-carboxaldehyde, 1121-60-4; 1,3-diaminopropan-2-ol, 616-29-5; pyrrole-2-carboxaldehyde, 1003-29-8; salicylaldehyde, 69-72-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen atom parameters, least-squares planes, observed and calculated structure factors, and magnetic properties (24 pages). Ordering information is given on any current masthead page.

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Preparation and Molecular and Crystal Structure of *trans*-(*R*,*S*)-[Cr(2,3,2-tet)(NCS)$_2$]NCS

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The complex [Cr(2,3,2-tet)(NCS)$_2$]NCS was prepared by a route expected to yield the cis form, namely, by stereoretentive substitution of thiocyanate for chloride in *cis*-Cr(2,3,2-tet)Cl$_2^+$. Crystal structure determination shows, however, that it is the trans isomer that actually is obtained. The structure determination was by X-ray single-crystal analysis. The thiocyanate complex crystallizes in the monoclinic $P2_1/c$ space group with a = 8.153 (2) Å, b = 15.556 (2) Å, c = 14.175 (2) Å, and β = 99.84 (2)°. There are four formula units per unit cell. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement led to a final value of the R (R_w) index of 0.0295 (0.0332) based on 2380 unique reflections. The chromium atom is hexacoordinated, and the six nitrogen atoms form a slightly distorted octahedron with a nearly planar CrN$_4$ unit. The use of visible and infrared spectroscopy for isomer identification is discussed for the case of thiocyanate-containing metal ammine complexes. Finally, the rate constant for thermal aquation of thiocyanate by aqueous Cr(2,3,2-tet)(NCS)$_2^+$ was found to be 6.4×10^{-8} s^{-1} at 53 °C.

Introduction

The crystal structure determination reported here was undertaken as the final resolution of an isomeric ambiguity that developed in the course of another investigation. We have been interested in the emission lifetimes from the first doublet thexi state, D$_1^0$, of Cr(III) complexes in aqueous solution.[2] Certain emission rules were proposed, as well as a possible correlation of lifetime, τ, with ground-state reactivity. The specific current study is one of the series CrN$_4$(NCS)$_2^+$ where N$_4$ denotes a tetradentate ligand, 2-ethylenediamine, or four ammonia ligands, and desired members of this series were *cis*- and *trans*-Cr(2,3,2-tet)(NCS)$_2^+$.

Since substitution reactins of chromium(III) ammines are generally isomer retentive,[3,4] it was assumed that replacement of chloride by thiocyanate in authentic *cis*-Cr(2,3,2-tet)Cl$_2^+$ would lead to the cis thiocyanato complex. The reaction proceeded cleanly; the product chromatographed as a single isomer, yet its emission lifetime was much longer than expected (26.4 μs in 20 °C aqueous solution).[5] The absorption spectrum (see Figure 1) showed resemblances to those of both *cis*- and *trans*-Cr(en)$_2$(NCS)$_2^+$. There is no splitting of the first ligand field or L$_1$ band, as often occurs with trans complexes, however.[6] The problem of siomer determination from spectra has been noted before in the case of thiocyanate complexes.[7,8]

Experimental Section

Materials. The ligand 2,3,2-tet (1,4,8,11-tetraazaundecane, H$_2$NCH$_2$CH$_2$NHCH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$) was obtained from Strem Chemicals, Inc., and CrCl$_3$·6H$_2$O from Riedel de Häen. *cis*-[Cr(2,3,2-tet)Cl$_2$]Cl·H$_2$O was synthesized following a literature procedure.[9] A 2.7-g sample of CrCl$_3$·6H$_2$O was dissolved in 50 mL of Me$_2$SO (dimethyl sulfoxide) and 1.6 g of 2,3,2-tet were added. The mixture was boiled for 30 min, followed by the addition of 150 cm^3 of acetone, which resulted in the precipitation of 2.5 g of a pink-violet solid. The product was washed with about 10 cm^3 of ice-cold methanol. About 150 mg of a light green solid, the color typical of a *trans*-dichloro chromium(III) ammine, was obtained on evaporation of the washings. This byproduct exhibited a three-band absorption spectrum and has been described earlier.[10] The spectrum of the main pink-violet product agreed as well with that in the literature,[9] and the analysis for chromium as CrO$_4^{2-}$, following basic perioxide oxidation,[11] gave 15.25 ± 0.15% of Cr, as compared to a calculated value of 15.42%.

[Cr(2,3,2-tet)(NCS)$_2$]NCS. A 1.4-g sample of the *cis*-dichloro compound above was dissolved in 40 cm^3 of water, and 1.5 g of sodium thiocyanate was added. The mixture was heated, at 90 °C for 4 h, with stirring. On cooling to room temperature a clean appearing crop of orange-red crystals was obtained, which was washed with 10 cm^3 of cold water to give a yield of 1.45 g or 85%. Anal. Calcd for

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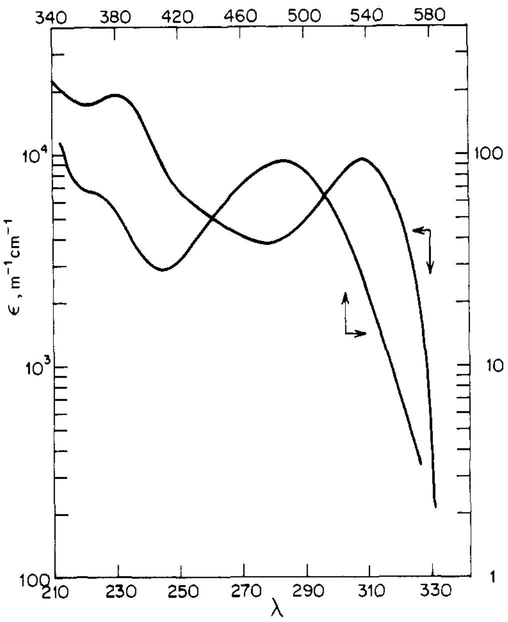

Figure 1. Absorption spectrum for aqueous *trans*-[Cr(2,3,2-tet)(NCS)$_2$]NCS.

[Cr(2,3,2-tet)(NCS)$_2$]NCS: C, 31.08; H, 5.22; N, 25.37; Cr, 13.45. Found: C, 31.06; H, 5.26; N, 25.36; Cr, 13.40. The product appeared to be isomerically pure. The crystals were uniform in color and shape. Elution from Sephadex SP-25 with 0.1 M NaClO$_4$ occurred as a single narrow band. The emission from $D_1{}^0$ fitted a single exponential, not expected if two isomers were present. Finally, repeated recrystallizations did not alter the UV–visible absorption spectrum.

Absorption Spectra. The UV–visible absorption spectrum of aqueous Cr(2,3,2-tet)(NCS)$_2{}^+$ (the trans isomer, to anticipate the structure determination) is shown in Figure 1. The maxima are (λ, nm (ε, M^{-1} cm^{-1})): 232 (1.92 × 10^4), 308 (9.58 × 10^3), 362 (69.5), 485 (92.7).

The infrared absorption spectrum was determined with a Beckman IR 4240 instrument (KBr pellet). The detailed listing of features is available as supplementary material.

Collection and Reduction of the X-Ray Data. A single crystal was mounted on an ENRAF-NONIUS four-circle CAD-4 diffractometer, controlled by a PDP 8/A computer, using Mo K$\bar{\alpha}$ radiation from a highly oriented graphite-crystal monochromator. The orientation matrix was refined by least-squares computations using 21 reflections in the reference list. Diffraction data were collected at 291 ± 1 K by using the ω–2θ techique for the $1° < \theta < 30°$ range. The scan widths (SW) were calculated from SW = $(0.80 + 0.35 \tan\theta)°$. The calculated scan angle was extended at each side by 25% for background determination. The net count was then calculated as NC = $I - 2(\mathrm{LB} + \mathrm{RB})$, where I, LB, and RB are respectively the integrated peak intensity and the left and the right background counts. Reflections were considered as unobserved if a rapid prescan was less than 10 counts above the background. So that possible X-ray destruction of the crystal could be detected, the (4,4,–2) reflection was periodically checked. Data reduction yielded 2380 unique reflections in the half-reflection sphere (hkl, $hk\bar{l}$ triplets), which were corrected for standard Lorentz and polarization factors, and the absorption was neglected ($\mu R = 0.29$).

Structure Solution and Refinement. The structure was solved by the usual heavy-atom method.[12] A Patterson map revealed the position of the chromium atom. After the positional and thermal parameters of the chromium atom were refined, a Fourier transform revealed the sulfur, nitrogen, and carbon atoms of the thiocyanate groups and the four nitrogen atoms of the tetradentate tetramine ligand. After refinement of the positions, a subsequent Fourier transform revealed the missing nine carbon atoms of the tetramine chain. At this stage of the refinement, the weighting function $w = (a + b|F_o|)$[12,13] was introduced together with the position of all the 20 hydrogen atoms. The final refinement with the hydrogen atoms led to a R (Rw) value of 0.0295 (0.0332).

Table I. Summary of Crystal Data and Intensity Collection for *trans*-[Cr(2,3,-tet)(NCS)$_2$]NCS

mol wt	386.5
space group	$P2_1/c$
a, Å	8.153 (2)
b, Å	15.556 (2)
c, Å	14.175 (2)
β, deg	99.84 (2)
V, Å^3	1771.21
cell content	4 (CrS$_2$N$_6$C$_{10}$H$_2$, SCN)
ρ(calcd), g cm^{-3}	1.43
cryst dimens, mm	0.35 × 0.35 × 0.4
μ, cm^{-1}	9.73
scan speed, deg min^{-1}	10.06–1.68
measd reflctns	4254
obsd reflctns used	2380, $I > 2\sigma(I)$
refined scale factor	0.803 (2)

Table II. Selected Bond Lengths (A) and Angles (Deg) for *trans*-[Cr(2,3,2-tet)(NCS)$_2$]NCS

Cr–NS1	1.981 (2)	N6–N7	2.743 (3)
Cr–NS2	1.978 (2)	N7–N4	3.175 (3)
Cr–N4	2.092 (2)	C1–S1	1.605 (3)
Cr–N5	2.068 (2)	C2–S2	1.596 (3)
Cr–N6	2.057 (2)	C3–S3	1.622 (3)
Cr–N7	2.067 (2)	C1–NS1	1.159 (3)
N4–N5	2.767 (3)	C2–NS2	1.160 (3)
N5–N6	3.007 (3)	C3–NS3	1.136 (3)
NS1–Cr–NS2	178.89 (9)	NS2–C2–S2	177.9 (2)
NS1–Cr–N4	88.75 (9)	NS3–C3–S3	178.6 (3)
NS1–Cr–N5	90.07 (9)	N4–C41–C42	108.9 (2)
NS1–Cr–N6	90.00 (9)	C41–C42–N5	108.0 (2)
NS1–Cr–N7	89.76 (9)	C42–N5–C51	112.2 (2)
NS1–C1–S1	176.8 (1)	N5–C51–C52	111.8 (2)

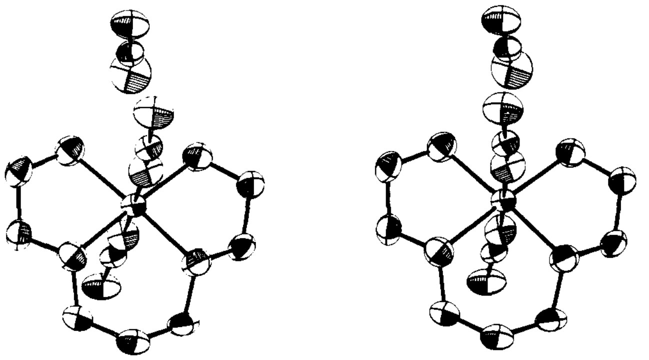

Figure 2. Stereoview of the *trans*-[Cr(2,3,2-tet)(NCS)$_2$]NCS unit.

The refinement was performed by using full-matrix least-squares calculations. The atomic coordinates and the thermal parameters were refined by minimizing $\sum w(|F_o| - |F_c|)^2$, the weighting function being $w = (2|F_o|_{\min} + |F_o| - 2|F_o|^2/|F_o|_{\max})^{-1}$ in the last stage. Listings of the observed and calculated structure amplitudes and of the anisotropic U_{ij} parameters of all but the hydrogen atoms are available as supplementary material.

Results and Discussion

Structural Results. The crystal structure data and experimental conditions are summarized in Table I. Of principal interest to us, the molecular structure is as shown in Figures 2 and 3 and clearly defines the complex as being the trans *RS* isomer, or meso form, contrary to the synthetic expectation.

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[12] All calculations were performed on the Université de Paris-Sud, Orsay, France, AMDAHL 470-V7 computer through the IRC terminal. In addition to a local program library, we also used slightly modified programs: Busing, W. R.; Martin, K. O.; Levy, H. A. Reports ORNL TM 305 and 306; Oak Ridge National Laboratory: Oak Ridge, TN. For graphical purposes, the Johnson's thermal ellipsoid plot program ORTEP was used.

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Table III. Comparison of Infrared Features (cm^{-1}) for Cis and Trans Complexes[a]

	$\bar{\nu}(C{\equiv}N)$	$\rho_r(NH_2)$	$\nu(C-S)$	$\rho_a(CH_2)$	Cr–X str
trans-Cr(cyclam)Cl_2^+ [b]		890 s, 882 s		804 s	
cis-Cr(cyclam)Cl_2^+ [b]		872 m, 862 m (sh), 854 m		815 w, 805 m	
trans-Cr(cyclam)$(NCS)_2^+$ [b]	2090 s, 2070 s, 2050 s	885 s, 878 m	865 w	802 m	344 s
cis-Cr(cyclam)$(NCS)_2^+$ [b]	2085 s, 2080 s, 2040 s	870 m, 860 m, 850 (sh)	840 w	818 m, 810 m	340 m, 330 m, 320 m
trans-Cr(2,3,2-tet)$(NCS)_2^+$	2060 br vs, 2020 s	890 s, 875 m		800 s	348 s, 340 m (sh), 320 m

[a] Selected features—see text. [b] Reference 7.

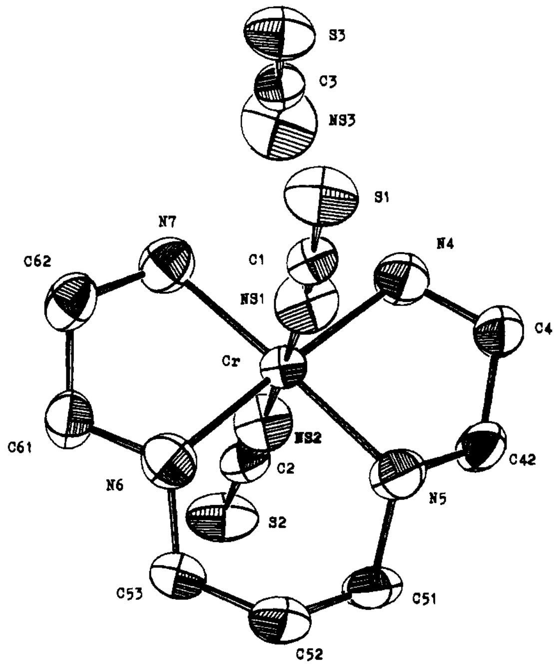

Figure 3. The *trans*-[Cr(2,3,2-tet)$(NCS)_2$]NCS unit with atom numbering scheme. Atoms are drawn as 50% probability ellipsoids.

Some representative bond distances and angles are given in Table II (a detailed listing, including ones involving hydrogen atoms is available as part of the supplementary material).

With reference to Figure 2 or 3, the four nitrogens of the tetraamine ligand form an almost perfect plane, the chromium atom being located at 0.0133 (3) Å above it, which allows an almost perfect Cr(III)–ligand overlap. The three rings are in the gauche, chair, and gauche conformations, respectively. The two coordinated thiocyanate groups are almost collinear, completing a slightly distorted octahedron. The coordinated thiocyanate groups are further form linearity than is the counteranion. The nitrogen atoms of the amine as well as the carbon atoms of the tetramine chain are at the center of slightly distorted tetrahedra, the bond angles being close to the theoretical value of 109.6°. The average nitrogen–hydrogen and carbon–hydrogen bond distances, not included in Table II, are close to 1 Å. Other distances such as between the various nitrogens are about as expected.

Use of Absorption Spectra for Isomer Designation. Infrared spectroscopy has on occasion been invoked in assigning isomers in octahedral complexes,[7] and the present case provides a test of the reliability of the criterion. The more relevant frequencies are given in Table III for several complexes. The most consistent variations are in the 800–900-cm^{-1} region. One criterion has been that the presence of a doublet near 890 cm^{-1} and a singlet near 800 cm^{-1} indicates a trans configuration. The cis complexes show at least three bands around 860 cm^{-1} and a doublet around 810 cm^{-1}. It would have been satisfactory to use these criteria here in that the assignment of trans configuration would have been correctly made.

Isomer designation has also been concluded from the appearance of the first and second ligand field absorption bands. The L_1 band tends to show a shoulder in the case of the trans form, and both bands tend to be less intense than for the cis isomer. Yet in the present case, no shoulder is apparent (Figure 1). Moreover, the extinction coefficients are larger for our complex than for *cis*-Cr$(en)_2Cl_2^+$ (ϵ_{528} 71 M^{-1} cm^{-1} and ϵ_{402} 69 M^{-1} cm^{-1}).[15] It certainly appears that for thiocyanate-containing chromium(III) ammines, the D_{4h} ligand field splitting is smaller than for analogous chloride complexes, and the extinction coefficients are higher. The relatively large extinction coefficients may result from intensity stealing from the thiocyanate charge-transfer transition at 308 nm.

Stereochemical Aspects. We can speculate about the reason for the nonstereoretentive substitution of thiocyanate for chloride in the case of *cis*-Cr(2,3,2-tet)Cl_2^+. It does appear that the 2,3,2-tet ligand favors a trans configuration; this has been demonstrated in cases involving Co(III), Rh(III), and Ni(II) complexes.[9] Only with Cr(III) was a cis configuration obtained. The stereochemistry could be determined as a matter either of kinetics or of thermodynamic preference. For example, on mixing aqueous Ni(II) and 2,3,2-tet, the less stable cis isomer first obtains, followed by a slow isomerization to the trans form.[15] Solvent may play a role. *cis*-Cr(2,3,2-tet)Cl_2^+ is prepared in Me_2SO, while our preparation of the thiocyanato complex was in aqueous solution, a medium in which protonation of the ligand may be of importance. Again, results on Ni(2,3,2-tet)$^{2+}$ are of interest; the cis complex is the most stable isomer in Me_2SO whereas the trans form is the more stable in water.[16]

The thermal aquation reaction of the *trans*-Cr(2,3,2-tet)$(NCS)_2^+$ gives a single product, most likely *trans*-Cr(2,3,2-tet)(NCS)$(H_2O)^{2+}$, with a rate constant at 53 °C of 6.4×10^{-8} s^{-1} (as determined by the rate of thiocyanate release). The complex is thus far less labile than *trans*-Cr$(en)_2Cl_2^{2+}$ [10] or *trans*-Cr$(en)_2(NCS)_2^{2+}$ [17] (k(55 °C) = 6.6×10^{-6} s^{-1}) and less labile even than *cis*-Cr(cyclam)$(NCS)_2^+$ for which k(53 °C) is 1.5×10^{-7} s^{-1}.[5] We plan to examine separately the possible correlation between thermal robustness and doublet-state emission lifetime, suggested from proposed emission rules.

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Registry No. *trans*-[Cr(2,3,2-tet)$(NCS)_2$]NCS, 81603-14-7; *cis*-[Cr(2,3,2-tet)Cl_2]Cl, 40813-71-6.

Supplementary Material Available: Listings of positional and anisotropic thermal parameters (Table SI), distances and angles (Table SII), least-squares planes (Table SIII), and infrared data (Table SIV) (11 pages). Ordering information is given on any current masthead page.

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