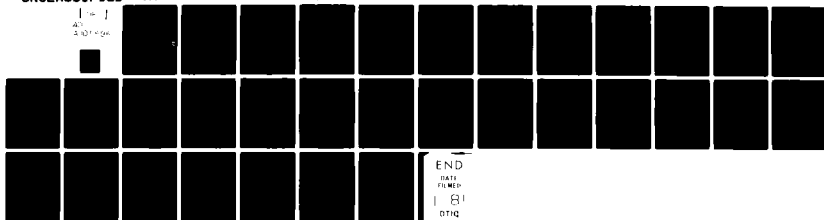


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PREPARATION AND MOLECULAR AND CRYSTAL STRUCTURE OF TRANS-R,S-CR--ETC(U)
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Preparation and Molecular and Crystal Structure of

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by

Helmut R. Mäecke, Bernard F. Mentzen, Jean Pierre Piaux, and Arthur W. Adamson

Prepared for Publication

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University of Southern California
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Los Angeles, California 90007

September 17, 1981

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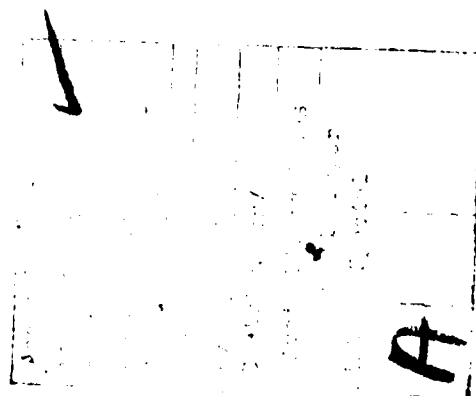
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Preparation and Molecular and Crystal Structure of
trans-R.S-[Cr(2,3,2-tet)(NCS)₂] NCS

Helmut R. Mäecke,^{*1a} Bernard F. Mentzen,^{1b} Jean Pierre Puaux,^{1c} and
Arthur W. Adamson.^{*1d}

Abstract

The complex $[\text{Cr}(2,3,2\text{-tet})(\text{NCS})_2]\text{NCS}$ was prepared by a route expected to yield the cis form, namely by stereoretentive substitution of thiocyanate for chloride in cis- $\text{Cr}(2,3,2\text{-tet})\text{Cl}_2^+$. 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 P_2^1/c space group with $a = 8.153(2)$, $b = 15.556(2)$, and $c = 14.175(2)$ Å, and $\beta = 99.84(2)$. 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 $\text{Cr}(2,3,2\text{-tet})(\text{NCS})_2^+$ was found to be $6.4 \times 10^{-8} \text{ sec}^{-1}$ 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 $\text{CrN}_4(\text{NCS})_2^+$ where N_4 denotes a tetradentate ligand, 2 ethylene diamine, or four ammonia ligands, and desired members of this series were cis and trans-Cr(2,3,2-tet)(NCS)₂⁺.

Since substitution reactions of Cr(III) amines are generally isomer-retentive,^{3,4} it was assumed that replacement of chloride by thiocyanate in authentic cis-Cr(2,3,2-tet)Cl₂⁺ 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 μsec in 20 °C aqueous solution).⁵ The absorption spectrum, (see Fig. 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 isomer determination from spectra has been noted before, in the case of thiocyanate complexes.^{7,8}

Experimental

Materials. - The ligand 2,3,2-tet (1,4,8,11-tetraazaundecane, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$) was obtained from Strem Chemicals, Inc., and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ from Riedel de Haën. Cis-[Cr(2,3,2-tet)Cl₂]Cl $\cdot$ H₂O was synthesized following a literature procedure.⁹ 2.7 g of

of $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ were dissolved in 50 ml of DMSO (dimethyl sulfoxide) and 1.6 g of 2,3,2-tet were added. The mixture was boiled for thirty minutes, 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 Cr(III) ammine, was obtained on evaporation of the washings. This by-product 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 CrO_4^{2-} , following basic peroxide oxidation¹¹ gave $15.25 \pm 0.15 \% \text{ Cr}$, as compared to a calculated value of 15.42%.

$[\text{Cr}(2,3,2\text{-tet})(\text{NCS})_2]\text{NCS}$. - 1.4 g of the cis-dichloro compound above were dissolved in 40 cm^3 of water, and 1.5 g of sodium thiocyanate were added. The mixture was heated, at 90°C for four hours, 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%. Analytical results were as follows: calculated for $[\text{Cr}(2,3,2\text{-tet})(\text{NCS})_2] \text{NCS}$: C, 31.08%; H, 5.22%; N, 25.37%; Cr, 13.45%. Found: C, 31.06%; H, 5.25%; 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-23 with 0.1 M NaClO_4 occurred as a single narrow band. The emission from D_1° fitted a single exponential, not expected if two isomers were present. Finally, repeated recrystallizations did not alter the u.v.-visible absorption spectrum.

Absorption spectra. - The u.v.-visible absorption spectrum of aqueous $\text{Cr}(2,3,2\text{-tet})(\text{NCS})_2^+$ (the trans isomer, to anticipate the structure determination) is shown in Fig. 1. The maxima are (λ , nm;

$\epsilon \text{ M}^{-1} \text{ cm}^{-1}$): (232; 1.92×10^4), (308; 9.58×10^3), (362; 69.5), (485; 92.7).

The spectrum was obtained by means of a Beckman Acta MVI spectrophotometer.

The infrared absorption spectrum was determined on using a Perkin Elmer model 157G instrument (K Br 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 POP 8/A computer, using $\text{MoK}\alpha$ radiation from a highly oriented graphite-crystal monochromator. The orientation matrix was refined by least-square computations using 21 reflections in the reference list. Diffraction data were collected at $291 \pm 1 \text{ K}$ by using the $\omega - 2\theta$ technique for the $1 < \theta < 30^\circ$ range. The scan widths (S_w) were calculated from $S_w = (0.80 + 0.35 \tan \theta)^\circ$. The calculated scan angle was extended at each side by 25% for background determination. The net count was then calculated as $\text{NC} = I - 2 (\text{LB} + \text{RB})$, where I , LB and RB are respectively the integrated peak intensity, the left and the right background. Reflections were considered as unobserved if a rapid prescan was less than 10 counts above the background. In order to detect possible x-ray destruction of the crystal, the (4,4, -2) reflection was periodically checked. Data reduction yielded 2380 unique reflections in the half reflection sphere ($h k l$, $h k \bar{l}$ triplets), which were corrected for standard Lorentz and polarization factors and the absorption was neglected ($\mu_R = .29$).

Structure solution and refinement. - The structure was solved by the usual heavy-atom method. A PATERSON 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 $\omega = (a + b|F_o|)^{21,13}$ was introduced together with the position of all the 20 hydrogen atoms. The final refinement with the hydrogen atoms led to a $R(R_w)$ value of 0.0295 (0.0332).

The refinements were performed by using least-squares full-matrix calculations. The atomic coordinates and the thermal parameters were refined by minimizing $\sum \omega(|F_o| - |F_c|)^2$, the weighting function being $\omega = (2|F_o|_{\min} + |F_o| - 2|F_o|^2/|F_o|_{\max})^{-1}$ 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 Figs. 2 and 3, and clearly defines the complex as being the trans-R,S-isomer, or mesoform contrary to the synthetic expectation. 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).

Referring to Fig. 2 or 3, the four nitrogens of the tetramine 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, gauche conformation, respectively. The two coordinated thiocyanate groups are almost co-linear, completing a slightly distorted octahedron. The coordinated thiocyanate groups are further from linearity than is the

counter anion. 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 $1 \text{ \AA}$. 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 complexes⁷ 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 $800 - 900 \text{ cm}^{-1}$ 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.

Again, isomer designation has 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 (Fig. 1). Moreover, the extinction coefficients are larger for our complex than for cis- $\text{Cr(en)}_2\text{Cl}_2^+$ ($\epsilon_{528} = 71 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{402} = 69 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁵ It certainly appears that for thiocyanate containing Cr(III) amines, the D_{4h} ligand field splitting is smaller than for analogous chloride complexes, and the extinction coefficients, 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 non-stereoretentive substitution of thiocyanate for chloride in the case of cis-Cr(2,3,2-tet)Cl₂⁺. 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. The cis Cr(2,3,2-tet)Cl₂⁺ is prepared in DMSO, 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 DMSO 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)(H₂O)²⁺, with a rate constant of 53 °C of 6.4x10⁻⁸ sec⁻¹ (as determined by the rate of thiocyanate release). The complex is thus far less labile than trans-Cr(en)₂Cl₂²⁺¹⁰ or trans-Cr(en)₂(NCS)₂²⁺¹⁷ (k(55°C) = 6.6x10⁻⁶ sec⁻¹) and less labile even than cis-Cr(cyclam)(NCS)₂⁺ for which k_{53°C} is 1.5x10⁻⁷ sec⁻¹.⁵ We plan to examine separately the possible correlation between thermal robustness and doublet state emission lifetime, suggested from proposed emission rules.

Acknowledgements

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References

- (1) (a) Institut für Anorganische Chemie, der Universität Basel, Spitalstrasse 51, CH-4056, Basel, Switzerland. (b) Laboratoire de chimie Minérale I, bat. 731, Université Claude-Bernard, 69622 Villeurbanne Cedex, France. (c) Laboratoire de Cinétique et Génie Chimiques, Bat. 404, I.N.S.A., 69621 Villeurbanne Cedex, France. (d) Department of Chemistry, University of Southern California, Los Angeles, CA 90007, U.S.A.
- (2) See Walters, R. T.; Adamson, A. W. Acta Chem. Scand. 1979, A33, 53.
- (3) Garner, C. S.; House, D. A. Transition Metal Chem. 1970, 6, 200.
- (4) Couldwell, M. C.; House, D. A. Inorg. Chem. 1972, 11, 2024.
- (5) Macke, H. R.; Adamson, A. W. unpublished work.
- (6) Perumareddi, J. R. Coord. Chem. Rev. 1969, 4, 73.
- (7) Poon, C. K.; Pun, K. C. Inorg. Chem. 1980, 19, 568.
- (8) Zinato, E.; Riccieri, P. Inorg. Chem. 1973, 12, 1451.
- (9) Bosnich, B.; Gillard, R. D.; McKenzie, E. D.; Webb, G. A. J. Chem. Soc. A, 1966, 1331.
- (10) Kutal, C.; Adamson, A. W. Inorg. Chem. 1973, 12, 1990.
- (11) Haupt, G. J. Res. Nat. Bur. Stand. 1952, 48, 414.
- (12) All calculations were performed on the Université de Paris-Sud Orsay, AMDAHL 470-V7 computer through the IRC terminal. In addition to a local program library, we also used slightly modified programs of: Busing, W. R., Martin, K. O., Levy, H. A.. Reports ORNL - TM 305 and 306; Oak Ridge National Laboratory, Oak Ridge, Tenn. For graphical purposes, the Johnson's thermal ellipsoid plot program ORTEP was used.
- (13) Stout, G. H.; Jensen, L. H. "X-Ray Structure Determination"; MacMillan, London, 1968, pp. 454-453.

- (14) See Kirk, A.D.; Moss, K.C.; Valentin, J.G. Can. J. Chem.,
1971, 49, 1524.
- (15) Vitiello, J. D.; Billo, E. J. Inorg. Chem. 1980, 19, 3477.
- (16) Cook, D. F.; McKenzie, E. D. Inorg. Chim. Acta, 1978, 29, 193.
- (17) Holba, V. Z. Phys. Chem. 1964, 226, 408.

Table I

Summary of Crystal Data and Intensity Collection
for trans-[Cr(2,3,-tet)(NCS)₂]NCS

mol wt	386.5
space group	P ₂ 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 dims, mm	0.35 x 0.35 x 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 σ (I)
refined scale factor	.803 (2)

Table II

Selected Bond Lengths (Å) and Angles (degrees) for
trans-[Cr(2,3,2-tet)(NCS)₂]NCS

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

Table III

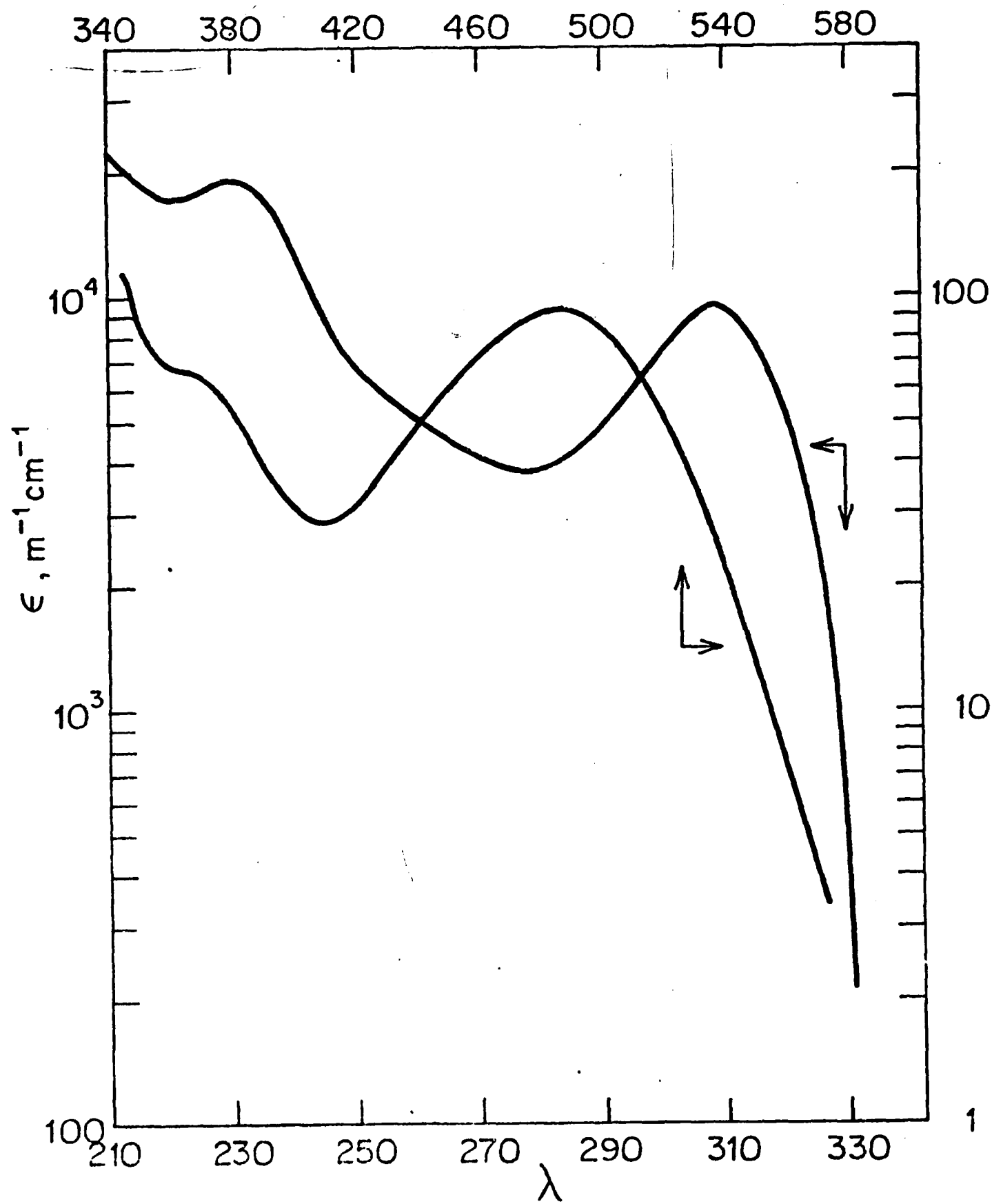
Comparison of Infrared Features for cis and trans Complexes^a

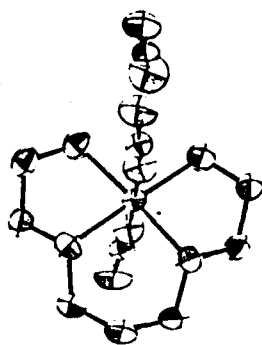
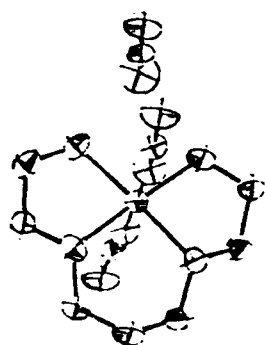
	$\bar{\nu}(\text{C}\equiv\text{N})$	$\rho_r(\text{NH}_2)$	$\nu(\text{C-S})$	$\rho_a(\text{CH}_2)$
<u>trans</u> -Cr(cyclam)Cl ₂ ^{+ b}		890s 882s		804s
<u>cis</u> -Cr(cyclam)Cl ₂ ^{+ b}		872m 862m(sh) 854m		815w 805m
<u>trans</u> -Cr(cyclam)(NCS) ₂ ^{+ b}	2090s 2070s 2050s	885s 878m	865w	802m
<u>cis</u> -Cr(cyclam)(NCS) ₂ ^{+ b}	2085s 2080s 2040s	870m 860m 850(sh)	840w	818m 810m
<u>trans</u> -Cr(2,3,4-tet)(NCS) ₂ ^{+ b}	2055 vs	890s 875m		800s

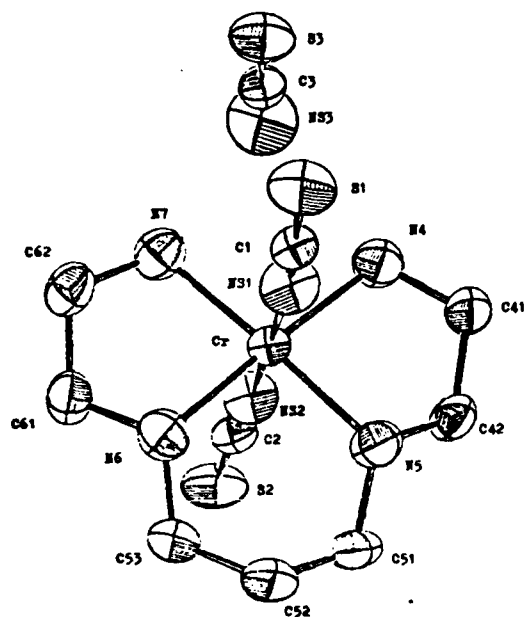
^a Selected features - see text.^b C. K. Poon and K. C. Pun, 1980, 568, 19.

Legends for the Figures.

- Figure 1. Absorption spectrum for aqueous trans-[Cr(2,3,2-tet)(NCS)₂]NCS.
- Figure 2. Stereoview of the trans-[Cr(2,3,2-tet)(NCS)₂]NCS unit.
- Figure 3. The trans-[Cr(2,3,2-tet)(NCS)₂]NCS unit with atom numbering scheme. Atoms are drawn as 50% probability ellipsoids.







Preparation and Molecular and Crystal Structure of

-trans-R.S-[Cr(2,3,2-tet)(NCS)₂] NCS

Helmut R. Mäecke,^{*1a} Bernard F. Mentzen,^{1b} Jean Pierre Piaux,^{1c} and
Arthur W. Adamson.^{*1d}

SUPPLEMENTARY MATERIAL

TABLE I

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS

ATOM	x	y	z	Beq ^b
Cr	0.38521 (5)	0.26183 (2)	0.32885 (2)	2.6
S1	0.6754 (1)	0.39544 (5)	0.10591 (5)	4.3
S2	0.1186 (1)	0.09798 (6)	0.53832 (6)	6.6
S3	0.7751 (1)	0.43280 (5)	0.46696 (5)	5.5
NS1	0.4961 (3)	0.3221 (1)	0.2339 (1)	4.1
NS2	0.2766 (2)	0.2032 (1)	0.4256 (1)	4.0
NS3	0.6009 (4)	0.3742 (2)	0.6047 (2)	6.2
N4	0.3396 (3)	0.3814 (1)	0.3868 (1)	4.9
N5	0.1561 (3)	0.2828 (1)	0.2439 (1)	4.4
N6	0.4207 (3)	0.1462 (1)	0.2650 (1)	4.0
N7	0.6152 (3)	0.2351 (1)	0.4097 (1)	4.1
C1	0.5711 (3)	0.3521 (2)	0.1797 (2)	2.9
C2	0.2120 (3)	0.1594 (2)	0.4744 (2)	3.7
C3	0.6737 (4)	0.3990 (2)	0.5487 (2)	3.9
C41	0.1987 (4)	0.4187 (2)	0.3269 (2)	5.3
C42	0.0684 (4)	0.3477 (2)	0.2938 (2)	4.5
C43	0.1987 (4)	0.2071 (2)	0.2127 (2)	5.6

ATOM	x	y	z	Beq ^b
C52	0.1422 (4)	0.1402 (2)	0.1651 (2)	7.1
C53	0.2729 (4)	0.0918 (2)	0.2320 (2)	5.3
C61	0.5522 (4)	0.0991 (2)	0.3302 (2)	3.2
C62	0.6880 (4)	0.1621 (2)	0.3641 (2)	2.9
H41	0.328 (4)	0.3722 (2)	0.452 (2)	5.5 (8)
H42	0.435 (5)	0.422 (2)	0.387 (3)	7.1 (9)
H411	0.146 (4)	0.465 (2)	0.352 (3)	6.8 (9)
H412	0.236 (5)	0.446 (2)	0.274 (3)	5.7 (9)
H421	0.036 (4)	0.314 (2)	0.345 (3)	5.3 (8)
H422	-0.023 (5)	0.368 (3)	0.251 (3)	7.3(1.0)
H5	0.183 (4)	0.308 (2)	0.182 (2)	4.2 (7)
H511	0.020 (4)	0.161 (2)	0.272 (2)	4.1 (7)
H512	-0.039 (5)	0.227 (3)	0.175 (3)	6.8 (1.0)
H521	0.130 (4)	0.110 (2)	0.116 (2)	5.7 (9)
H522	0.072 (5)	0.110 (2)	0.139 (3)	6.3 (9)
H531	0.223 (4)	0.110 (2)	0.288 (2)	4.7 (8)
H532	0.316 (4)	0.110 (2)	0.200 (2)	5.3 (7)
H5	0.463 (4)	0.104 (2)	0.205 (2)	4.6 (7)

ATOM	x	y	z	Beq ^b
H611	0.579 (4)	0.049 (2)	0.303 (2)	4.8 (7)
H612	0.503 (4)	0.074 (2)	0.385 (2)	4.1 (7)
H621	0.730 (4)	0.181 (2)	0.314 (2)	3.9 (6)
H622	0.769 (4)	0.137 (2)	0.407 (3)	5.6 (8)
H71	0.599 (4)	0.221 (2)	0.474 (2)	5.3 (8)
H72	0.692 (4)	0.284 (2)	0.419 (2)	5.5 (8)

a ESd_s shown in parentheses have been adjusted to the last digit (or digits) of the preceding number (or numbers)

b Calculations for all but the H atoms have been made with anisotropic thermal parameters. These are available as supplementary material. Equivalent isotropic parameters have been calculated from the refined β_{ij} parameters through

$$\text{Beq} = 4/3 \beta_{ij} a_i a_j$$

TABLE II

DISTANCES ($\text{\AA}$) AND ANGLES (Deg)

INTERMOLECULAR DISTANCES AND ANGLES

Cr POLYHEDRON

Cr-NS1	1.981 (2)	N7-N4	3.175 (3)
Cr-NS2	1.978 (2)	NS1-N4	2.848 (3)
Cr-N4	2.092 (2)	NS1-N5	2.866 (3)
Cr-N5	2.068 (2)	NS1-N6	2.855 (3)
Cr-N6	2.057 (2)	NS1-N7	2.856 (3)
Cr-N7	2.067 (2)	NS2-N4	2.889 (3)
N4-N5	2.767 (3)	NS2-N5	2.876 (3)
N5-N6	3.007 (3)	NS2-N6	2.875 (3)
N6-N7	2.743 (3)	NS2-N7	2.851 (3)
NS1-Cr-NS2	178.89 (9)	N5-N4-N7	87.85(8)
NS1-Cr-N4	88.75 (9)	N4-N5-N6	91.71(8)
NS1-Cr-N5	90.07 (9)	N5-N6-N7	91.80(8)
NS1-Cr-N6	90.00 (9)	N6-N7-N4	88.64(8)
NS1-Cr-N7	89.76 (9)	NS1-N4-NS2	87.23(9)
NS2-Cr-N4	90.42 (9)	NS1-N5-NS2	87.16(8)
NS2-Cr-N5	90.86 (9)	NS1-N6-NS2	87.38(8)
NS2-Cr-N6	90.87 (9)	NS1-N7-NS2	87.82(9)
NS2-Cr-N7	89.65 (9)	N4-NS1-N6	93.26(9)
N4-Cr-N5	89.90 (9)	NS-NS1-N7	92.50(9)
N4-Cr-N6	90.50 (9)	N4-NS2-N6	92.01(9)
N6-Cr-N7	89.80 (9)	NS-NS2-N7	92.38(9)
N7-Cr-N4	89.42 (8)		

.../...

...

THIOCYANATE IONS

C1-S1	1.605 (3)	NS1-C1-S1	176.8 (1)
C2-S2	1.596 (3)	NS2-C2-S2	171.9 (2)
C3-S3	1.622 (3)	NS3-C3-S3	178.6 (3)
C1-NS1	1.159 (3)		
C2-NS2	1.160 (3)		
C3-NS3	1.136 (3)		

TETRAAMINE CHAIN

N4-C41	1.488 (4)	N4-C41-C42	108.9 (2)
C41-C42	1.499 (4)	C41-C42-N5	108.0 (2)
C42-N5	1.484 (4)	C42-N5-C51	112.2 (2)
N5-C51	1.483 (4)	N5-C51-C52	111.8 (2)
C51-C52	1.509 (4)	C51-C52-C53	114.7 (3)
C52-C53	1.502 (4)	C52-C53-N6	111.4 (2)
C53-N6	1.480 (4)	C53-N6-C61	112.2 (2)
N6-C61	1.484 (3)	N6-C61-C62	107.1 (2)
C61-C62	1.496 (4)	C61-C62-N7	108.2 (2)
C62-N7	1.480 (4)		

NITROGEN-HYDROGEN BONDS

N4-H41	0.91 (3)	N4-H41-Cr	108.0 (2)
N4-H42	1.00 (4)	N4-H41-Cr	105.7 (2)
		N4-H42-Cr	115.3 (2)

N5-H5	1.02 (3)	N5-C42-Cr	106.9 (2)
		N5-C51-Cr	118.1 (2)
		N5-H5-Cr	110.6 (2)

... / ...

N6-H6	1.01 (3)	C53-N6-H6	106 (2)	Cr-N6-C53	118.1 (2)
		C61-N6-H7	110 (2)	Cr-N6-C61	107.4 (2)
				Cr-N6-H6	100.8 (2)

N7-H71	0.97 (3)	C62-N7-H71	112 (2)	Cr-N7-C62	107.8 (2)
N7-H72	0.98 (3)	C62-N7-H72	111 (2)	Cr-N7-H71	115.0 (2)
		H71-N7-H72	104 (3)	Cr-N7-H72	116.7 (2)

CARBON HYDROGEN BONDS

C41-H411	0.90 (4)	N4-C41-H412	102 (2)
C41-H412	0.99 (4)	C42-C41-H411	116 (2)
		C42-C41-H412	113 (2)
N4-C41-H411	115 (2)	H411-C41-H412	101 (3)

C42-H421	0.98 (4)	N5-C42-C422	108 (3)
C42-H422	0.94 (4)	C41-C42-C421	114 (2)
N5-C42-C421	102 (2)	C41-C42-H422	111 (3)
		H421-C42-H422	113 (3)

C51-H511	1.00 (3)	N5-C51-H512	106 (3)
		C52-C51-H511	108 (2)
C52-H512	0.88 (4)		
N5-C51-H511	107 (2)	C52-C51-H512	113 (2)
		H511-C51-H512	111 (3)

C52-H521	0.98 (4)	C53-C52-H521	108 (2)
C52-H522	0.84 (4)	C53-C52-H55	108 (3)
C51-C52-H522	107 (3)	H521-C52-H522	109 (3)
C51-C52-H521	110 (3)		

...

C53-H531	0.98 (4)	N6-C53-H522	106 (2)
C53-H532	1.02 (3)	C52-C53-H531	111 (2)
N6-C53-H531	108 (2)	C52-C53-H532	112 (2)
		H531-C53-H532	108 (3)

C61-H611	0.91 (3)	N6-C61-H612	109 (2)
C61-H612	1.01 (3)	C62-C61-H611	119 (2)
N6-C61-H611	111 (2)	C62-C61-H612	112 (2)
		H611-C61-H612	99 (3)

C62-H621	0.89 (3)	N7-C62-H622	110 (2)
C62-H622	0.91 (3)	C61-C62-H621	109 (2)
N7-C62-H621	110 (2)	C61-C62-H622	110 (2)
		H621-C62-H622	110 (3)

TABLE III

EQUATION OF LEAST-SQUARES PLANE (a)

N4 - N5 - N6 - N7

$$0.5720 X + 0.4638 Y - 0.6765 Z - 0.1356 = 0$$

ATOM	D, Å ^a	ATOM	D, Å ^b
N4	0.009 (3)	N6	0.010 (2)
N5	- 0.010 (2)	N7	- 0.010 (2)
Cr ^c	- 0.0133(3)	C51 ^c	- 0.713 (3)
NS1 ^c	1.967 (2)	C52 ^c	- 0.250 (3)
NS2 ^c	1.991 (2)	C53 ^c	- 0.136 (3)
C41 ^c	0.222 (3)	C61 ^c	- 0.423 (3)
C42 ^c	- 0.492 (3)	C62 ^c	0.297 (3)

- a Planes are defined as $AX + BY + CZ + D = 0$, X, Y and Z being orthogonalized coordinates .
- b Distance of a given atom from the mean plane
- c Atoms not included in the calculation of the plane .

Table IV. Infrared spectrum of tr- Cr(2,3,2-tet)(NCS)₂⁺NCS⁻

3310	ν	}	ν (N-H)
3220	m_{sh}		
3200	m		
3130	s_{sh}		
3110	s		
2970	ν_{sp}	}	ν (C-H)
2960	m		
2930	m_{sp}		
2880	m_{sp}		
2055	ν		ν (C=N)
1585	s		$\delta_{as}(N-H_2)$
1485	ν	}	δ (CH ₂)
1465	ν_{sh}		
1455	m		
1445	ν_{sp}		
1420	ν		
1380	ν		
1370	ν		
1340	ν_{sp}	}	$\rho_{\nu}(CH_2)$
1330	ν_{sp}		

1313	ν_w	}	$\gamma_s(\text{NH}_2)$
1302	ν_{sp}		
1294	ν_{sh}		
1234	ν_w	}	$\rho_w(\text{NH}_2)$
1153	ν		
1142	ν_{sp}		
1119	ν	}	$\gamma(\text{NH}_2)$
1087	ν_{sh}		
1082	ν_{sp}		
1050	ν	}	$\rho_t(\text{NH}_2)$
1032	ν		
1026	ν		
998	ν_{sp}		
990	ν_{sp}	}	$\rho_r(\text{CH}_2) + \rho_r(\text{NH}_2)$
941	ν_{sp}		
918	ν_w		
888	ν_{sp}		
874	ν	}	$\nu(\text{C-S})$ coordinated
800	ν_{sp}		
744	ν_{sp}		
693	ν_{sp}		
642	ν_{sp}		$\nu(\text{C-S})$ non coordinated

S-12

549	m _{sp}	}	V (Cr-N)
534	w		

516 vw

492	m	}	δ (SCN)
484	m _{sd}		

468 w

445 vw

390	m	}	δ (cycle)
340	m		
336	m _{sd}		
313	vw		

250 vw

m: medium; s: strong; v: very; w: weak; sh: shoulder;
sp: sharp.

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