Table 1. *Selected bond lengths (Å)*

Rh3—P1	2.345 (2)	Rh3—B7	2.237 (9)
Rh3—P2	2.276 (2)	Rh3—B8	2.250 (9)
Rh3—C1	2.289 (8)	Br9—B9	1.974 (9)
Rh3—C2	2.241 (8)	Br12—B12	1.980 (9)
Rh3—B4	2.298 (9)	C1—C2	1.631 (11)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*A*···Br9	0.97	2.87	3.838 (17)	178
C7—H7*B*···Br12	0.97	2.88	3.537 (14)	126

In a penultimate $\Delta\rho$ map, the top peak in the peak list was 1.24 Å from Rh3 in a position consistent with it being associated with the H atom bonded to Rh3; this is a relatively short distance (the Rh/H covalent radii sum is 1.68 Å). In the final refinement cycles, this H atom was included at the coordinates from the difference map and not refined. Other H atoms were treated as riding atoms with C—H 0.93–1.10 and B—H 1.10 Å.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976), *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek, 1996*b*). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*93 and *WordPerfect* macro *PREPCIF*97 (Ferguson, 1997).

The generous loan of Rh salts by Johnson Matthey plc is gratefully acknowledged (TRS). GF thanks the Natural Sciences and Engineering Research Council (Canada) for Research Grants and PMcE thanks Forbairt, Ireland, for support. Thanks are also due to Dr B. Štíbr and his colleagues in the Czech Republic for the sample of 1,2-$C_2B_{10}H_{12}$.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1472). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1992). *CAD*-4-*PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1997). *PREPCIF*97. *A WordPerfect*-5.1 *Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL*93 *Programs*. University of Guelph, Canada.

Ferguson, G., Spalding, T. R. & McEneaney, P. A. (1996). *Acta Cryst.* C**52**, 2710–2713.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Hardy, G. E., Callahan, K. P., Strouse, C. E. & Hawthorne, M. F. (1976). *Acta Cryst.* B**32**, 264–266.

Jelinek, T., Baldwin, P., Scheidt, W. R. & Reed, C. A. (1993). *Inorg. Chem.* **32**, 1982–1990.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kirillova, N. I., Zhdanov, A. S., Gusev, A. I., Kirin, V. N., Khyazev, S. P. & Sokolova, T. V. (1989). *Metall. Khim.* **2**, 859–861.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sivý, P., Preisinger, A., Baumgartner, O., Valach, F., Koreň, B. & Matel, L. (1986). *Acta Cryst.* C**42**, 24–27.

Spek, A. L. (1996*a*). *PLATON*. *Molecular Geometry Program*. Version of August 1996. University of Utrecht, The Netherlands.

Spek, A. L. (1996*b*). *PLUTON*. *Molecular Graphics Program*. Version of August 1996. University of Utrecht, The Netherlands.

Zakharkin, L. I. & Kalinin, V. N. (1967). *Izv. Akad. Nauk SSSR Ser. Khim.* **2**, 462–464.

Acta Cryst. (1997). C**53**, 687-691

cis- and *trans*-Diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

Duane A. Friesen, J. Wilson Quail, William L. Waltz and Rodney E. Nashiem

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan, Canada S7N 5C9.
E-mail: quail@sask.usask.ca

(Received 11 October 1996; accepted 10 February 1997)

Abstract

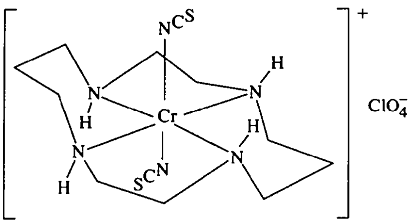
The *cis* isomer of the title compound, $[Cr(NCS)_2(C_{10}H_{24}N_4)](ClO_4)$, is a racemate of the Bosnich type V structure; the *trans* complex is a *meso* substance with a Bosnich type III stereochemistry. There is no appreciable change in the structures of the title compound on cooling, even though there are marked color changes. The Cr—N bond lengths are all in the range 1.983 (2)–1.998 (4) Å for the bonds to the isothiocyanate groups and in the range 2.046 (2)–2.088 (3) Å for the bonds to cyclam N atoms.

Comment

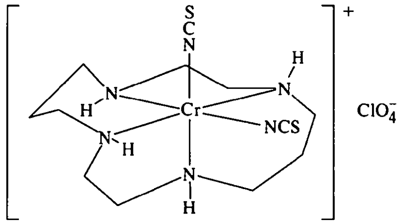
As part of our continuing investigations into the effects of temperature, pressure and solvent on the photobehavior and spectroscopy of octahedral-like Cr^{III} amine complexes (Friesen, Lee, Nashiem, Mezyk & Waltz, 1995; Vincze, Friesen, Mezyk & Waltz, 1992), we have examined the UV–visible spectra as a function of temperature of *trans*-$[Cr(cyclam)(NCS)_2](ClO_4)$, (1*a*) and (1*b*), and *cis*-$[Cr(cyclam)(NCS)_2](ClO_4)$, (2*a*) and (2*b*), where cyclam is 1,4,8,11-tetraazacyclotetradecane, and *a* and *b* denote room- and low-temperature studies, respectively.

A notable feature is that, on cooling powders of each complex to liquid nitrogen temperature, their colors change from orange–red (*cis* isomer) or orange–yellow (*trans* isomer) to bright yellow. The color change is reversible on warming to room temperature. Because

Acta Crystallographica Section C
ISSN 0108-2701 © 1997



(1)



(2)

this thermochromism is also observed for the complex ions dissolved in liquid methanol solutions and cooled to *ca* 180 K, these changes can be attributed at least in part to changes in molecular features. On cooling the methanol solutions, the visible absorption peaks of the first ligand-field band exhibit small blue shifts, indicating an increase in the ligand-field strength. However, the major contributions arise from the behavior of the very intense thiocyanate-to-metal charge transfer (CT) bands with peaks at 324 nm (*cis*) and 318 nm (*trans*) at room temperature. The red side-tails are so intense that they obscure the second ligand-field bands at 288 K, but on cooling, the vibronic envelopes of the CT bands contract to the point where the second ligand-field bands now appear as distinct peaks at 377 nm (*cis*) and 357 nm (*trans*). The behavior of these CT transitions suggested possible major concurrent changes to the thiocyanate ligands. In the extreme, this might involve the occurrence of linkage isomerism; however our results show that, at least in the solid state, the bonding is exclusively Cr—N at both high and low temperatures.

The *cis* isomer (Fig. 1) is a racemate of the Bosnich type V structure, which is the most strain-free of the *cis* conformers. The *trans* complex (Fig. 2) is a *meso* substance with the Cr atom on an inversion center and with Bosnich type III stereochemistry. The Bosnich type III structures are considered to be the most ring-strain-free of the possible *trans* conformers (Bosnich, Poon & Tobe, 1965; House & McKee, 1984). In the *trans* structure, the perchlorate ion is disordered, with the Cl atom located on an inversion center. The *trans* structure joins a growing list of Bosnich type III structures having the composition $[Cr^{III}(cyclam)(X)_2]$ where $X = Cl^-$, Br^-, CN^-, NH_3, $H_2O\text{-}OH^-$ and $Br^-\text{-}Cl^-$ (Palmer *et al.*, 1996, and references therein). All have the six-membered rings in the chair conformation and the Cr—N bond lengths of the CrN_4 moiety in the range 2.05–2.10 Å along with the X—Cr—X angles being at or close to 180°.

For most isothiocyanato systems, the Cr—N—CS bond angle is near 180°, as shown here for the *cis* complex, but some cases exhibit significantly smaller angles as exemplified for the *trans* complex with angles very close to 160° at 173 and 288 K. Several explanations for the bent conformations have been put forward: varying degrees of π-bonding stabilization, *i.e.* —N=C=S *versus* —N≡C—S (Kay, Moore & Glick, 1972; Takeuchi & Saito, 1957); crystal packing (Kay, Moore & Glick, 1972); and interactions with cations or neighboring thiocyanate groups (Jubb, Larkworthy, Leonard, Povey & Tucker, 1989; Zhang, Fan, Zhan, Wang & Han, 1987). Substantially different π-bonding contributions seem improbable in view of the similarity of the *cis* and *trans* complexes in terms of their C—

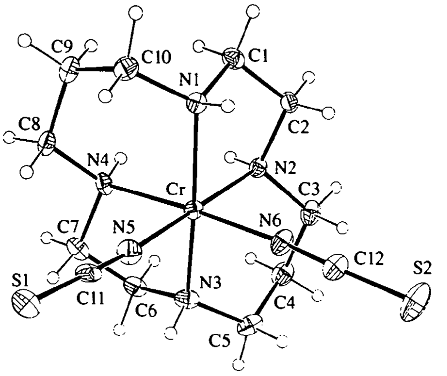


Fig. 1. *ORTEP*II (Johnson, 1976) view of the cation in the *cis* isomer of the title compound at 123 K with displacement ellipsoids drawn at the 30% probability level for the non-H atoms. H atoms are drawn as small spheres of arbitrary size.

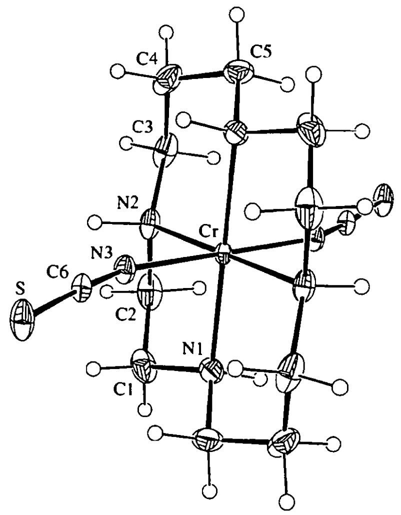


Fig. 2. *ORTEP*II (Johnson, 1976) view of the cation in the *trans* isomer of the title compound at 173 K with displacement ellipsoids drawn at the 30% probability level for the non-H atoms. H atoms are drawn as small spheres of arbitrary size.

N and C—S bond lengths, and also in this context we propose that the thermochromism arises principally from changes in the vibronic spectral envelopes with temperature as described above. In the complex *trans*-(*R*,*S*)-[Cr(2,3,2-tet)(NCS)$_2$](NCS) where tet is 1,4,8,11-tetraazaundecane (an acyclic tetradentate analog to cyclam), the *trans*-NCS groups are nearly collinear (Mäcke, Mentzen, Puaux & Adamson, 1982) and this comparison suggests that the bent Cr—N—C conformation found for *trans*-[Cr(cyclam)(NCS)$_2$](ClO$_4$) arises from steric or packing effects.

Experimental

The *cis* isomer was prepared from *cis*-[Cr(cyclam)Cl$_2$]Cl using an adaptation of existing literature methods (Kane-Maguire, Wallace & Miller, 1985; Ferguson & Tobe, 1970; Friesen, 1994). The *trans* isomer was synthesized from *trans*-[Cr(cyclam)(NO$_3$)$_2$]NO$_3$ hydrate (Kane-Maguire, Wallace & Miller, 1985; Friesen, 1994). The preparation and analysis of these isomers as perchlorate salts using standard procedures has been described elsewhere (Friesen, 1994). Crystals were grown in the dark by slow evaporation of saturated aqueous solutions (0.001 *M* HClO$_4$).

Compound (1*a*)

Crystal data

[Cr(NCS)$_2$(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)
M_r = 467.928
Triclinic
$P\bar{1}$
a = 7.7374 (13) Å
b = 8.5142 (14) Å
c = 9.0238 (9) Å
α = 65.777 (12)°
β = 69.777 (11)°
γ = 83.540 (13)°
V = 508.41 (14) Å^3
Z = 1
D_x = 1.5283 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 11.45–35.40°
μ = 8.031 mm^{-1}
T = 288 (1) K
Plate
0.35 × 0.30 × 0.12 mm
Orange–yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian by integration
$T_{\min}$ = 0.131, $T_{\max}$ = 0.434
4005 measured reflections
2027 independent reflections
1989 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.017
$\theta_{\max}$ = 73°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -9 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.039
$wR(F^2)$ = 0.103
S = 1.047
2027 reflections
140 parameters
H atoms riding (C—H 0.97, N—H 0.91 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.4159P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.005
$\Delta\rho_{\max}$ = 0.834 e Å^{-3}
$\Delta\rho_{\min}$ = −0.612 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0206 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (*1a*)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cr	1/2	1/2	1/2	0.0287 (2)
Cl	0	0	0	0.0729 (4)
S	0.89969 (10)	0.76101 (10)	0.62535 (12)	0.0607 (3)
O1†	−0.1144 (18)	−0.0529 (15)	0.1604 (11)	0.154 (4)
O2†	−0.0044 (15)	0.1856 (9)	−0.0898 (15)	0.155 (4)
O3†	−0.0797 (13)	−0.0680 (14)	−0.0901 (14)	0.149 (4)
O4†	0.1781 (11)	−0.0406 (16)	−0.0372 (19)	0.153 (4)
N1	0.5781 (3)	0.6787 (3)	0.2504 (3)	0.0533 (6)
N2	0.3427 (3)	0.6901 (3)	0.5581 (3)	0.0493 (6)
N3	0.7106 (3)	0.5800 (3)	0.5317 (3)	0.0427 (5)
C1	0.4443 (6)	0.8186 (4)	0.2485 (5)	0.0813 (12)
C2	0.4098 (5)	0.8521 (4)	0.4060 (6)	0.0785 (12)
C3	0.3266 (4)	0.7005 (6)	0.7219 (6)	0.0764 (12)
C4	0.7374 (5)	0.4696 (7)	0.1266 (5)	0.0893 (14)
C5	0.6029 (5)	0.6123 (6)	0.1160 (4)	0.0808 (12)
C6	0.7951 (3)	0.6546 (3)	0.5678 (3)	0.0384 (5)

† Site occupancy = 0.50.

Compound (1*b*)

Crystal data

[Cr(NCS)$_2$(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)
M_r = 467.928
Triclinic
$P\bar{1}$
a = 7.6925 (14) Å
b = 8.471 (2) Å
c = 8.9387 (8) Å
α = 65.930 (15)°
β = 69.870 (12)°
γ = 83.86 (2)°
V = 498.96 (15) Å^3
Z = 1
D_x = 1.557 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 11.53–27.79°
μ = 8.183 mm^{-1}
T = 173 (2) K
Plate
0.35 × 0.30 × 0.12 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: Gaussian by integration
$T_{\min}$ = 0.131, $T_{\max}$ = 0.431
2978 measured reflections
1949 independent reflections
1926 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 73°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = -9 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.030
$wR(F^2)$ = 0.081
S = 1.079
1949 reflections
140 parameters

$(\Delta/\sigma)_{\max}$ < 0.001
$\Delta\rho_{\max}$ = 0.551 e Å^{-3}
$\Delta\rho_{\min}$ = −0.340 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)

H atoms riding (C—H 0.99, N—H 0.93 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.2952P]$
where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient: 0.0198 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1b)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Cr	1/2	1/2	1/2	0.01765 (15)
Cl	0	0	0	0.0437 (2)
S	0.90396 (7)	0.76365 (7)	0.62567 (8)	0.0350 (2)
O1†	−0.1152 (7)	−0.0554 (7)	0.1680 (6)	0.0759 (14)
O2†	−0.0080 (8)	0.1897 (5)	−0.0897 (7)	0.088 (2)
O3†	−0.0834 (7)	−0.0685 (7)	−0.0932 (7)	0.0797 (14)
O4†	0.1806 (6)	−0.0416 (8)	−0.0357 (9)	0.088 (2)
N1	0.5784 (2)	0.6846 (2)	0.2493 (2)	0.0305 (4)
N2	0.3442 (2)	0.6889 (2)	0.5642 (2)	0.0289 (4)
N3	0.7134 (2)	0.5766 (2)	0.5341 (2)	0.0263 (4)
C1	0.4446 (4)	0.8249 (3)	0.2506 (3)	0.0449 (6)
C2	0.4122 (3)	0.8546 (3)	0.4125 (4)	0.0428 (6)
C3	0.3292 (3)	0.6954 (3)	0.7316 (3)	0.0422 (6)
C4	0.2643 (3)	0.5218 (4)	0.8825 (3)	0.0478 (6)
C5	0.4000 (3)	0.3781 (4)	0.8887 (3)	0.0434 (6)
C6	0.7983 (2)	0.6537 (2)	0.5695 (2)	0.0234 (4)

† Site occupancy = 0.50.

Compound (2*a*)

Crystal data

[Cr(NCS)$_2$(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)
$M_r = 467.928$
Monoclinic
$P2_1/c$
$a = 11.0105\ (11)$ Å
$b = 8.6361\ (11)$ Å
$c = 21.645\ (2)$ Å
$\beta = 90.105\ (8)°$
$V = 2058.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.510$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.84–18.66°$
$\mu = 0.918$ mm^{-1}
$T = 288\ (1)$ K
Prism
0.30 × 0.21 × 0.11 mm
Orange–red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: none
3918 measured reflections
3608 independent reflections
2164 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.052$
$wR(F^2) = 0.136$
$S = 1.188$
3600 reflections
235 parameters
H atoms riding (C—H 0.97, N—H 0.91 Å)
$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.672$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.344$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2a)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Cr	0.79235 (6)	0.84712 (8)	0.14360 (3)	0.0437 (2)
Cl	0.55854 (13)	0.31563 (15)	0.10606 (7)	0.0677 (4)
S1	0.80518 (12)	0.4698 (2)	0.30351 (7)	0.0708 (4)
S2	1.1461 (2)	0.6087 (3)	0.06464 (9)	0.1234 (8)
O1	0.6646 (7)	0.3854 (7)	0.1186 (5)	0.228 (5)
O2	0.5376 (9)	0.2333 (9)	0.1599 (4)	0.254 (6)
O3	0.4648 (4)	0.4197 (5)	0.0966 (2)	0.105 (2)
O4	0.5684 (5)	0.1986 (7)	0.0633 (3)	0.148 (3)
N1	0.8851 (3)	1.0030 (4)	0.1991 (2)	0.0528 (10)
N2	0.8058 (3)	1.0224 (5)	0.0785 (2)	0.0511 (9)
N3	0.6780 (3)	0.7268 (5)	0.0844 (2)	0.0598 (11)
N4	0.6291 (3)	0.9232 (4)	0.1811 (2)	0.0506 (10)
N5	0.7920 (4)	0.6788 (5)	0.2070 (2)	0.0613 (11)
N6	0.9446 (4)	0.7598 (5)	0.1096 (2)	0.0635 (12)
C1	0.8926 (5)	1.1542 (6)	0.1671 (2)	0.0620 (13)
C2	0.9063 (4)	1.1267 (6)	0.0999 (2)	0.0618 (13)
C3	0.8258 (5)	0.9755 (8)	0.0127 (2)	0.076 (2)
C4	0.7245 (6)	0.8756 (8)	−0.0120 (3)	0.083 (2)
C5	0.7128 (6)	0.7185 (7)	0.0176 (3)	0.081 (2)
C6	0.5510 (4)	0.7821 (6)	0.0932 (3)	0.0649 (15)
C7	0.5342 (4)	0.8137 (6)	0.1608 (3)	0.068 (2)
C8	0.6265 (4)	0.9471 (6)	0.2494 (2)	0.0646 (14)
C9	0.7164 (5)	1.0629 (7)	0.2728 (2)	0.070 (2)
C10	0.8482 (5)	1.0177 (7)	0.2646 (2)	0.0646 (14)
C11	0.7977 (4)	0.5911 (6)	0.2471 (2)	0.0522 (12)
C12	1.0274 (5)	0.6934 (7)	0.0907 (2)	0.0669 (15)

Compound (2*b*)

Crystal data

[Cr(NCS)$_2$(C$_{10}$H$_{24}$N$_4$)](ClO$_4$)
$M_r = 467.928$
Monoclinic
$P2_1/c$
$a = 10.975\ (2)$ Å
$b = 8.690\ (2)$ Å
$c = 21.144\ (4)$ Å
$\beta = 90.607\ (14)°$
$V = 2016.4\ (7)$ Å^3
$Z = 4$
$D_x = 1.541$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.98–18.65°$
$\mu = 0.937$ mm^{-1}
$T = 123\ (2)$ K
Prism
0.30 × 0.21 × 0.11 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: none
3837 measured reflections
3530 independent reflections
2571 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$
$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.117$
$S = 1.125$
3523 reflections
235 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 1.9572P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.825$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.599$ e Å^{-3}

H atoms riding (C—H 0.99, N—H 0.93 Å)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2b)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr	0.79090 (5)	0.84208 (7)	0.14397 (3)	0.0211 (2)
Cl	0.57355 (9)	0.31502 (11)	0.10763 (5)	0.0314 (3)
S1	0.80522 (9)	0.45855 (12)	0.30540 (5)	0.0324 (3)
S2	1.14716 (12)	0.6151 (2)	0.05818 (6)	0.0513 (4)
O1	0.6906 (3)	0.3872 (4)	0.1027 (2)	0.0696 (13)
O2	0.5704 (4)	0.2481 (5)	0.1699 (2)	0.0778 (14)
O3	0.4784 (3)	0.4250 (3)	0.0989 (2)	0.0427 (8)
O4	0.5680 (3)	0.1954 (4)	0.0620 (2)	0.0566 (10)
N1	0.8868 (3)	0.9939 (4)	0.2026 (2)	0.0246 (7)
N2	0.8061 (3)	1.0196 (4)	0.07827 (15)	0.0232 (7)
N3	0.6751 (3)	0.7262 (4)	0.0823 (2)	0.0304 (8)
N4	0.6288 (3)	0.9197 (4)	0.1826 (2)	0.0258 (7)
N5	0.7891 (3)	0.6739 (4)	0.2080 (2)	0.0297 (8)
N6	0.9427 (3)	0.7538 (4)	0.1090 (2)	0.0312 (8)
C1	0.8940 (3)	1.1471 (5)	0.1709 (2)	0.0277 (9)
C2	0.9079 (3)	1.1206 (5)	0.1007 (2)	0.0275 (9)
C3	0.8257 (4)	0.9735 (6)	0.0113 (2)	0.0347 (10)
C4	0.7228 (4)	0.8761 (6)	−0.0153 (2)	0.0375 (10)
C5	0.7094 (4)	0.7198 (5)	0.0145 (2)	0.0365 (10)
C6	0.5479 (4)	0.7839 (5)	0.0916 (2)	0.0334 (10)
C7	0.5312 (4)	0.8128 (5)	0.1605 (2)	0.0318 (9)
C8	0.6253 (4)	0.9388 (5)	0.2527 (2)	0.0297 (9)
C9	0.7178 (4)	1.0527 (5)	0.2779 (2)	0.0342 (10)
C10	0.8503 (4)	1.0063 (5)	0.2694 (2)	0.0308 (9)
C11	0.7959 (3)	0.5827 (4)	0.2484 (2)	0.0266 (9)
C12	1.0285 (4)	0.6944 (5)	0.0879 (2)	0.0299 (9)

Table 5. *Selected bond distances (Å) and bond angles (°)*

	(1*a*)	(1*b*)	(2*a*)	(2*b*)
Cr—N1	2.051 (2)	2.060 (2)	2.072 (4)	2.088 (3)
Cr—N2	2.046 (2)	2.048 (2)	2.074 (4)	2.084 (3)
Cr—N3			2.075 (4)	2.073 (3)
Cr—N4			2.080 (3)	2.078 (3)
Cr—N5			1.998 (4)	1.992 (3)
Cr—N3	1.983 (2)	1.985 (2)		
Cr—N6			1.981 (4)	1.984 (3)
N5—C11			1.155 (6)	1.167 (5)
N3—C6	1.161 (3)	1.165 (2)		
N6—C12			1.152 (6)	1.167 (5)
C11—S1			1.611 (5)	1.620 (4)
C6—S	1.608 (3)	1.614 (2)		
C12—S2			1.601 (5)	1.607 (4)
Cr—N5—C11			173.5 (4)	174.0 (3)
Cr—N3—C6	160.6 (2)	159.46 (14)		
Cr—N6—C12			172.5 (5)	176.3 (4)
N5—C11—S1			179.6 (5)	178.9 (4)
N3—C6—S	176.3 (2)	176.4 (2)		
N6—C12—S2			177.2 (6)	179.0 (4)

For the *trans* isomer, collected with Cu radiation, the ω-scan width was (1.20 + 0.142tanθ)° with a θ-scan rate of 2.05–10.06° min^{-1} at both room and low temperature. For the *cis* isomer, collected with Mo radiation, the ω-scan width was (1.20 + 0.35tanθ)° with a θ-scan rate of 2.49–6.71° min^{-1} at both room and low temperature. The scan angle was extended 25% on each side of each peak for background measurement. Refinement was by full-matrix least-squares methods.

All H atoms were placed in calculated positions on the corresponding N and C atoms (C—H = 0.97 Å at 288 K and 0.99 Å at 173 and 123 K; N—H = 0.91 Å at 288 K and 0.93 Å at 173 and 123 K). The U_{iso} of each H atom was assigned to be 1.2 times the U_{eq} of an attached C atom and 1.5 times the U_{eq} of an attached N atom.

For all compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 and *CELDIM*, *CAD*-4 *Software*; data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992); program(s) used to refine structure: *NRCVAX*94, *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94, *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *NRCVAX*94, *SHELXL*93, *WordPerfect* macro *PREPCIF*97 (Ferguson, 1997).

We thank the Natural Sciences and Engineering Council of Canada for providing funds for an X-ray diffractometer (to JWQ), research grants (to JWQ and WLW) and a postgraduate scholarship (to DAF). We also thank the University of Saskatchewan for scholarship support (to DAF and REN).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1243). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1997). *PREPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL93 Programs*. University of Guelph, Canada.

Ferguson, J. & Tobe, M. L. (1970). *Inorg. Chim. Acta*, **4**, 109–112.

Friesen, D. A. (1994). PhD thesis, University of Saskatchewan, Canada.

Friesen, D. A., Lee, S. H., Nashiem, R. E., Mezyk, S. P. & Waltz, W. L. (1995). *Inorg. Chem.* **34**, 4026–4031.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

House, D. A. & McKee, V. (1984). *Inorg. Chem.* **23**, 4237–4242.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Jubb, J., Larkworthy, L. F., Leonard, G. A., Povey, D. C. & Tucker, B. J. (1989). *J. Chem. Soc. Dalton Trans.* pp. 1631–1633.

Kane-Maguire, N. A. P., Wallace, K. C. & Miller, D. B. (1985). *Inorg. Chem.* **24**, 597–605.

Kay, J., Moore, J. W. & Glick, M. D. (1972). *Inorg. Chem.* **11**, 2818–2826.

Mäcke, H. R., Mentzen, B. F., Puaux, J. P. & Adamson, A. W. (1982). *Inorg. Chem.* **21**, 3080–3082.

Palmer, R. A., Potter, B. S., Tanriverdi, S., Lisgarten, J. N., Flint, C. D. & Majaha Gazi, D. (1996). *Acta Cryst.* C**52**, 1177–1180.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Takeuchi, Y. & Saito, Y. (1957). *Bull. Chem. Soc. Jpn*, **30**, 319–325.

Vincze, L., Friesen, D. A., Mezyk, S. P. & Waltz, W. L. (1992). *Inorg. Chem.* **31**, 4950–4958.

Zhang, W., Fan, Y., Zhan, S., Wang, X. & Han, W. (1987). *J. Struct. Chem.* **6**, 274–282.