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# Structures of Chromium(III) Cyclam Complexes. 5. Structure of *trans*-Dichloro-(1,4,8,11-tetraazacyclotetradecane)-chromium(III) Isothiocyanate

J. Bouckaert,* D. Maes and J. N. Lisgarten

*Department of Ultrastructure, Instituut voor Moleculaire Biologie, Vrije Universiteit Brussel, Paardenstraat 65, B-1640 Sint-Genesius Rode, Belgium*

T. K. Chattopadhyay and R. A. Palmer

*Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England*

M. A. Mazid

*Department of Chemistry, University of Wales College at Cardiff, PO 912, Cardiff CF1 3TB, Wales*

D. M. Gazi

*Department of Chemistry, Birkbeck College, University of London, Malet Street, London WC1E 7HX, England*

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## Abstract

The crystal and molecular structure of *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane-*N*,*N'*,*N''*,*N'''*)chromium(III) isothiocyanate has been determined. The cyclam (1,4,8,11-tetraazacyclotetradecane) moiety exists in a chair conformation located on a crystallographic centre of symmetry. The equatorial nitrogen ligands and the central chromium ion are exactly coplanar. The isothiocyanate counterion exhibits statistical disorder, the ion being straddled across the inversion centre with the C atom close to (0.5, 0, 0).

## Comment

In an attempt to prepare the non-centrosymmetric complex *trans*-[Cr(cyclam)(NCS)Cl]Cl by a substitution method, some dark-red crystals were obtained. Preliminary spectroscopic data suggested that the red compound was the isothiocyanate salt of the complex ion *trans*-[Cr(cyclam)Cl₂]⁺. The crystal structure was determined to confirm this.

The centrosymmetric *trans*-dichloro(cyclam)chromium(III) isothiocyanate can be compared with the enantiomeric *trans*-bromochloro(cyclam)chromium-(III) bromide (Chattopadhyay, Palmer, Lisgarten, Wyns & Gazi, 1992), the centrosymmetric *trans*-dibromo(cyclam)chromium(III) bromide (Lisgarten, Palmer, Hemmings & Gazi, 1990), the centrosymmetric *trans*-dichloro(cyclam)chromium(III) bromide (Dealwis, Janes, Palmer, Lisgarten, Maes & Gazi, 1992) and the *trans*-dicyano(cyclam)chromium(III) perchlorate (Hemmings, Lisgarten, Palmer & Gazi, 1990).

The cyclam assumes a chair conformation. The C1—C2 and N3—C4 bond lengths are unusually long for no obvious reason. All other bond lengths and angles in this moiety are normal.
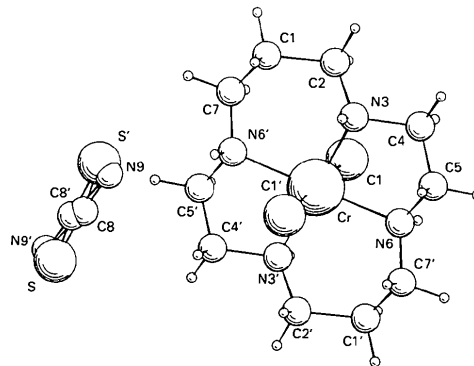


Fig. 1. Minimum overlap view of the molecule. The primed atoms are related by a crystallographic inversion centre *via* the symmetry operation 1 − *x*, 1 − *y*, 1 − *z*.
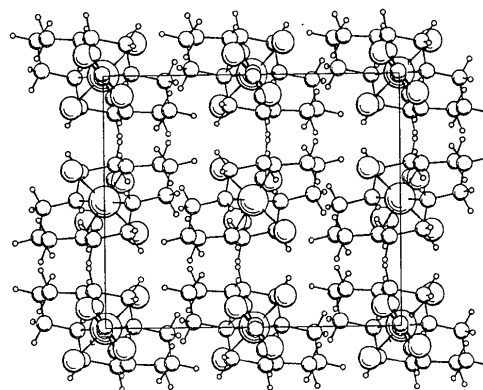


Fig. 2. Crystal packing viewed along **a**.

The mean Cr—N ligand distance of 2.084 (2) Å is consistent with many literature values, *e.g.* for *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (Lisgarten, Palmer, Hemmings & Gazi, 1990), *trans*-amminebis(ethylenediamine)fluorochromium(III) perchlorate (Beveridge, Bushnell & Kirk, 1985), aquadi-$\mu$-methoxy-bis[(7-amino-4-methyl-5-azahept-3-en-2-onato-$O,N,N'$)-chromium(III)] diperchlorate (Clegg, 1985). The equatorial nitrogen ligands and the central chromium ion are exactly coplanar. The Cl—Cr—Cl', N3—Cr—N3' and N6—Cr—N6' angles are exactly linear, due to symmetry requirements.

## Experimental

### Crystal data

[CrCl$_2$(C$_{10}$H$_{24}$N$_4$)][NCS]
$M_r$ = 381.31
Orthorhombic
*Pcab*
$a$ = 11.700 (1) Å
$b$ = 10.878 (1) Å
$c$ = 12.892 (1) Å
$V$ = 1640.8 Å$^3$
$Z$ = 4
$D_x$ = 1.55 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71069 Å

Cell parameters from 25 reflections
$\theta$ = 11.5-14°
$\mu$ = 1.13 mm$^{-1}$
$T$ = 293 K
Prismatic
0.50 × 0.40 × 0.40 mm
Red
Crystal source: aqueous solution

### Data collection

Enraf-Nonius FAST diffractometer
Absorption correction: none
7892 measured reflections
2043 independent reflections
1413 observed reflections
[$I > 3\sigma(I)$]
$R_{int}$ = 0.024

$\theta_{max}$ = 27.0°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 11$
3 standard reflections
monitored every 100 reflections
intensity variation: <5%

### Refinement

Refinement on $F^2$
Final $R$ = 0.036
$wR$ = 0.036
1413 reflections
125 parameters
Only H-atom $U$'s refined
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.878
$\Delta\rho_{max}$ = 0.58 e Å$^{-3}$
$\Delta\rho_{min}$ = -0.68 e Å$^{-3}$
Atomic scattering factors from *SHELX76* and *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å$^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cr † | 0.0000 | 0.0000 | 0.0000 | 0.0168 (1) |
| Cl | −0.1071 (1) | 0.1249 (1) | −0.1078 (1) | 0.0291 (1) |
| C1 | 0.0730 (3) | −0.1385 (3) | −0.2203 (2) | 0.0377 (4) |
| C2 | −0.0611 (3) | −0.1470 (3) | −0.1874 (2) | 0.0318 (4) |
| N3 | −0.0761 (2) | −0.1404 (2) | −0.0732 (2) | 0.0240 (4) |
| C4 | −0.2040 (3) | −0.1480 (3) | −0.0378 (3) | 0.0329 (4) |
| C5 | −0.2097 (3) | −0.1216 (3) | 0.0776 (3) | 0.0336 (4) |
| N6 | −0.1530 (2) | −0.0059 (2) | 0.0943 (2) | 0.0251 (3) |
| C7 | −0.1350 (3) | 0.0220 (3) | 0.2059 (2) | 0.0353 (4) |
| S | 0.5480 (3) | 0.0785 (2) | 0.0613 (2) | 0.0488 (3) |
| C8 | 0.4878 (9) | −0.0196 (8) | 0.0008 (9) | 0.0670 (5) |
| N9 | 0.4361 (8) | −0.0896 (8) | −0.0326 (7) | 0.0568 (5) |

† Atom fixed to define origin.

Table 2. *Geometric parameters* (Å, °)

Primed atoms are related by a centre of symmetry at (0,0,0).

| | | | |
|---|---|---|---|
| Cl—Cr | 2.312 (1) | N6—C7 | 1.485 (4) |
| N3—Cr | 2.004 (2) | C1—C2 | 1.628 (2) |
| N6—Cr | 2.165 (2) | C4—C5 | 1.517 (5) |
| N3—C2 | 1.484 (4) | C7—C1' | 1.472 (5) |
| N3—C4 | 1.566 (4) | S—C8 | 1.498 (10) |
| N6—C5 | 1.438 (4) | N9—C8 | 1.064 (11) |
| N3—Cr—Cl | 85.6 (1) | C2—N3—C4 | 113.5 (2) |
| N6—Cr—Cl | 84.7 (1) | C4—C5—N6 | 107.0 (2) |
| N3—Cr—N6 | 82.8 (1) | N3—C4—C5 | 108.5 (3) |
| C2—N3—Cr | 116.9 (2) | C1—C7—N6 | 111.6 (3) |
| C4—N3—Cr | 109.1 (2) | N9—C8—S | 171.2 (12) |
| C7'—C1—C2—N3 | −69.01 (1) | C4—C5—N6—C7 | −170.50 (6) |
| C1—C2—N3—C4 | 180.00 (8) | C5—N6—C7—C1' | 177.83 (23) |
| C2—N3—C4—C5 | −171.81 (7) | N6—C7—C1'—C2' | −69.42 (1) |
| N3—C4—C5—N6 | 53.85 (1) | | |

The structure was solved by the heavy-atom method. The position of the Cr atom was fixed to define the origin and H-atom positions were fixed geometrically. Refinement was performed by full-matrix least-squares methods using *SHELX76* (Sheldrick, 1976) with anisotropic temperature factors for all the non-H atoms and isotropic temperature factors for the H atoms. The H atom coordinates were not refined. The counterion was refined with an occupancy factor of 0.5 which revealed its two possible positions generated by the inversion centre at (0.5,0,0). Calculations were carried out on a VAX 11/750 computer. Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975). Molecular illustrations were drawn with *PLUTO* (Motherwell & Clegg, 1978).

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# Structure of Dicarbonylbis-(μ-3,5-dimethylpyrazolyl)-bis(4-tolyl diphenylphosphinite)diiridium(I)–Dichloromethane (1/1)

RAMY S. FARID†

*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

LAWRENCE M. HENLING*

*The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA*

HARRY B. GRAY

*Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

## Abstract

In bis(μ-3,5-dimethylpyrazolyl-*N*:*N′*)-bis[carbonyl(4-tolyl diphenylphosphinite-*P*)iridium(I)] dichloromethane solvate, two Ir$^1$ atoms are joined by two 3,5-dimethylpyrazolyl bridges with one carbonyl and one 4-tolyl diphenylphosphinite ligand completing the square-planar geometry about each Ir atom. The Ir···Ir distance of 3.307 (1) Å is greater than the distance of 3.22 Å found in a similar pyrazolyl-bridged iridium(I) dimer [Fox (1989). PhD dissertation, California Institute of Technology, USA].

## Comment

The title compound [Ir(μ-pz*)(CO)(Ph$_2$POC$_6$H$_4$CH$_3$)]$_2$, where pz* is 3,5-dimethylpyrazolyl, was synthesized as a model complex for the study of electron transfer in iridium dimer/pyridinium donor–acceptor complexes (Ir$_2$–

py$^+$). The photophysical and electrochemical data for this compound reveal energetic and kinetic parameters [$E_{00}(S_1)$] = 2.4, $E_{00}(T_1)$ = 1.9 eV, $E_{1/2}$(Ir$_2$/Ir$_2^+$) = 0.4 V versus SSCE (sodium saturated calomel electrode), $\tau_S$ = 125 ps, $\tau_T$ = 1 μs] used in analyzing electron-transfer rates for the series of Ir$_2$–py$^+$ complexes. The synthesis of this compound is reported elsewhere (Farid, Chang, Winkler & Gray, 1993). Slow evaporation of a methylene chloride/acetonitrile solution produced acicular crystals.

The molecule exhibits approximate $C_{2v}$ symmetry. The square-planar Ir atoms are almost identical and are coordinated to two adjacent dimethylpyrazolyl ligands with an average Ir—N distance of 2.077 [10] Å, where square brackets indicate a scatter e.s.d. A carbonyl ligand at 1.804 [9] Å and a tolyl diphenylphosphinite group with an Ir—P bond of 2.224 [0] Å complete the coordination shell about each Ir atom. The N—Ir—N angle is 84.1 [14]° and the other three angles about the Ir atom range from 91.4 [6] to 92.4 [4]°.

The bridging pyrazolyl groups retain the structure of the free ligand. The dihedral angle between the two pyrazolyl groups is 78.8 (6)°. The torsion angles Ir(1)—N(1)—N(2)—Ir(2) and Ir(1)—N(3)—N(4)—Ir(2)
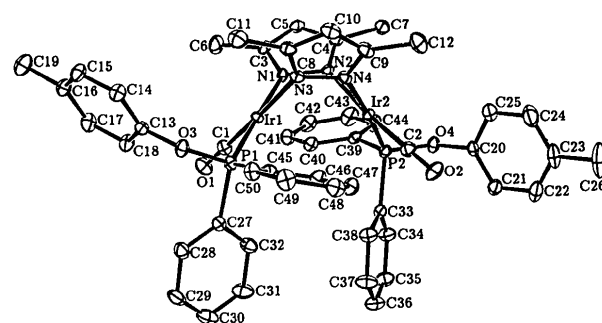


Fig. 1. An *ORTEP* view of the dimer with 15% probability ellipsoids. H atoms are not shown.
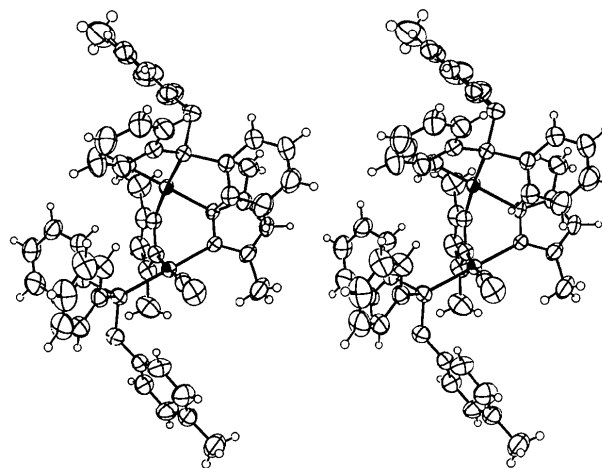


Fig. 2. An *ORTEP* stereoview of the iridium complex; atoms are drawn at the 50% probability level with H atoms at one tenth scale.

† Current address: Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA.