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A Chromium(III) 2,2′-Bipyrimidine (bipym) Complex, (Et$_4$N)[Cr(NCS)$_4$(bipym)]

María Teresa Garland,[a] Ricardo F. Baggio,[b] Florence Berezovsky,[c] Smaïl Triki[c] and Jean Sala Pala[c]

[a]*Facultad de Ciencias Físicas y Matemáticas, Departamento de Física, Universidad de Chile, Santiago de Chile, Chile,* [b]*Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina, and* [c]*UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique, Université de Bretagne Occidentale, BP 809, 29285 Brest CEDEX, France. E-mail: mtgarlan@cec.uchile.cl*

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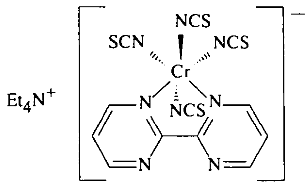
Abstract

The title structure, tetraethylammonium tetrakis(isothiocyanato)(2,2′-bipyrimidine-*N*,*N*′)chromium(III), [(C$_2$H$_5$)$_4$N][Cr(NCS)$_4$(C$_8$H$_6$N$_4$)], consists of discrete [Cr(NCS)$_4$(bipym)]$^-$ and [(C$_2$H$_5$)$_4$N]$^+$ ions. The Cr^{3+} ion lies on a mirror plane and has a regular octahedral coordination polyhedron. The bipym group is planar, with unexceptional bond distances and angles.

Comment

2,2′-Bipyrimidine (bipym) is a versatile ligand able to coordinate in a bidentate mode or in a bis(bidentate) bridging mode to yield mono- or polynuclear complexes (De Munno & Julve, 1996). Structural data for bipym-containing complexes of first-row transition metal ions are essentially limited to the 2+ oxidation state and mainly concern, for their intrinsic magnetic properties, copper (Julve *et al.*, 1993; Decurtins *et al.*, 1996) and manganese derivatives (De Munno *et al.*, 1996; Cortes *et al.*, 1996; Hong *et al.*, 1996). The present work concerns a bipyrimidine complex with a paramagnetic Cr$^{\text{III}}$ cation, (I). As far as we know, the structural data presented here are the first example of an M^{III}–bipym system.



(I)

The structure consists of discrete units of [Cr(NCS)$_4$(bipym)]$^-$ (Fig. 1) and [(C$_2$H$_5$)$_4$N]$^+$ ions. In the anionic complex, the metal coordination geometry can be described as octahedral, bisected by the space-group mirror plane through the metal center and two of the NCS$^-$ groups. The geometry is regular, the main departure being the small N1—Cr—N1 angle [78.5 (2)°] constrained by the bidentate character of the bipym ligand. The two heterocycles in the bipym moiety are planar within experimental error [maximum deviation: 0.006 (4) Å for C3] and so is the resulting bicyclic ligand [rotation around the C4—C4(x, $\frac{1}{2}-y$, z) bond being 0.30 (15)°]. The four Cr—N(CS) bonds average 1.986 (5) Å and are slightly shorter than Cr—N(bipym) bonds [2.072 (3) Å]. The isolated counterion, also bisected by the mirror plane, is unusually well behaved, with reasonable displacement parameters, and bonds and angles within normal ranges. The packing of the structure viewed along the monoclinic axis, shows 'cationic' and 'anionic' planes which are clearly seen evolving perpendicular to the c axis, at c = 0.0 and c = 0.5, respectively. A few long non-bonding contacts connecting both types of planes [C31—H31*A*···N2(x, y, $1+z$) 2.544 (4) and C3—H3*A*···S1*C*($-x$, $1-y$, $1-z$) 2.942 (4) Å], stabilize the crystal structure.

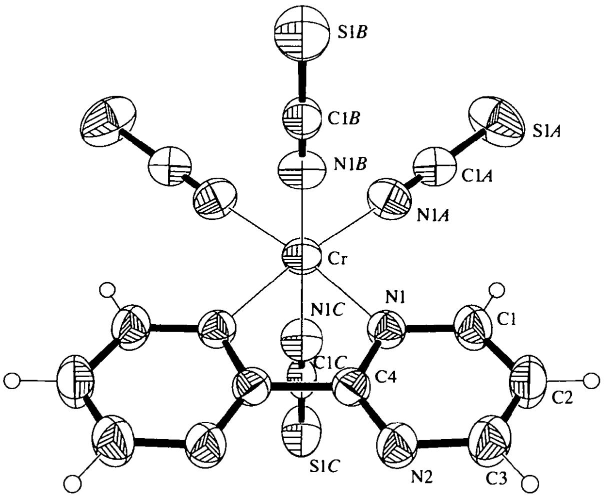


Fig. 1. View of the Cr coordination sphere, showing the labeling scheme used. Displacement ellipsoids are shown at the 50% probability level.

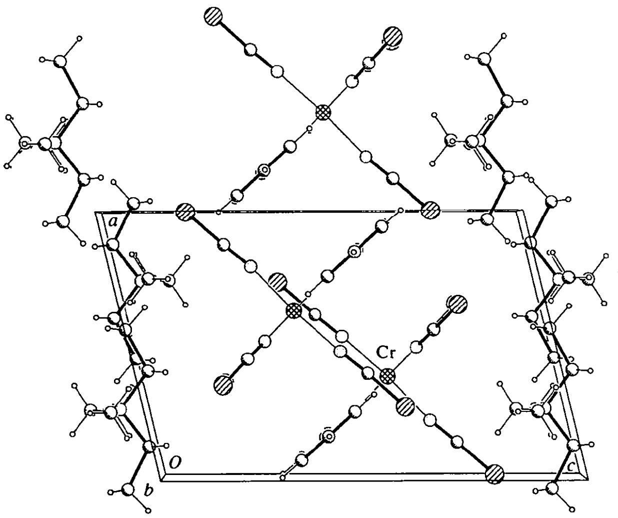


Fig. 2. Packing diagram viewed along the *b* axis showing positively and negatively charged planes building up perpendicular to the *c* axis.

Experimental

2,2'-Bipyrimidine (bipym) (0.316 g, 2 mmol) and $[(C_2H_5)_4N]_3$-$[Cr(NCS)_6]$ (1.582 g, 2 mmol) were dissolved in acetonitrile (20 ml). The resulting solution was then refluxed with continuous stirring for 12 h. Slow evaporation of this solution resulted in red cubic single crystals of the title compound. Analysis calculated (%): C 41.9, H 4.6, N 22.0, S 22.4, Cr 9.1. Found (%): C 42.2, H 4.6, N 22.0, S 21.5, Cr 8.2.

Crystal data

$(C_8H_{20}N)[Cr(NCS)_4$-
$(C_8H_6N_4)]$
$M_r = 572.74$
Monoclinic
$P2_1/m$
$a = 8.870\,(2)$ Å
$b = 11.956\,(3)$ Å
$c = 13.699\,(3)$ Å
$\beta = 103.48\,(2)°$
$V = 1412.7\,(5)$ Å^3
$Z = 2$
$D_x = 1.346$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$12.5°$
$\mu = 0.726$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.30 \times 0.10 \times 0.10$ mm
Deep red

Data collection

Siemens $R3m$ diffractometer
$\theta/2\theta$ scans
Absorption correction:
ψ scan (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
$T_{min} = 0.80$, $T_{max} = 0.95$
2571 measured reflections
2425 independent reflections

1680 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.05°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -11 \rightarrow 15$
2 standard reflections every 98 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.147$
$S = 0.982$
2423 reflections
172 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.9949P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.325$ e Å^{-3}
$\Delta\rho_{min} = -0.247$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	U_{eq}
Cr	0.37350 (9)	1/4	0.59242 (6)	0.0488 (3)
S1*A*	0.6472 (2)	0.53457 (13)	0.79989 (10)	0.1050 (5)
S1*B*	0.7324 (2)	1/4	0.38451 (12)	0.0735 (5)
S1*C*	0.0028 (2)	1/4	0.79165 (14)	0.0816 (5)
N1*A*	0.4857 (4)	0.3717 (3)	0.6777 (2)	0.0656 (9)
N1*B*	0.5259 (5)	1/4	0.5066 (4)	0.0586 (12)
N1*C*	0.2075 (5)	1/4	0.6686 (3)	0.0612 (12)
N	−0.2602 (5)	1/4	1.0582 (3)	0.0538 (11)
C1*A*	0.5518 (4)	0.4389 (4)	0.7279 (3)	0.0579 (10)
C1*B*	0.6082 (6)	1/4	0.4546 (4)	0.0490 (12)
C1*C*	0.1252 (6)	1/4	0.7205 (4)	0.0492 (13)
C11	−0.1222 (7)	1/4	1.0113 (5)	0.085 (2)
C12	0.0354 (7)	1/4	1.0839 (5)	0.118 (3)
C31	−0.2593 (5)	0.3505 (4)	1.1266 (3)	0.0717 (12)
C32	−0.2529 (7)	0.4634 (4)	1.0786 (4)	0.127 (2)
C21	−0.4028 (7)	1/4	0.9713 (4)	0.068 (2)
C22	−0.5574 (7)	1/4	1.0003 (5)	0.085 (2)
N1	0.2407 (3)	0.3598 (2)	0.4902 (2)	0.0466 (7)
C1	0.2435 (4)	0.4717 (3)	0.4931 (3)	0.0604 (10)
C2	0.1535 (5)	0.5339 (3)	0.4176 (3)	0.0705 (12)
C3	0.0617 (5)	0.4778 (3)	0.3392 (3)	0.0683 (11)
N2	0.0552 (3)	0.3659 (3)	0.3341 (2)	0.0561 (8)
C4	0.1455 (4)	0.3122 (3)	0.4099 (2)	0.0441 (8)

Table 2. *Selected bond lengths (Å, °)*

Cr—N1*A*	1.982 (3)	N—C31	1.523 (5)
Cr—N1*B*	1.988 (5)	C11—C12	1.515 (8)
Cr—N1*C*	1.993 (5)	C31—C32	1.508 (6)
Cr—N1	2.074 (3)	C21—C22	1.513 (8)
S1*A*—C1*A*	1.615 (4)	N1—C1	1.339 (5)
S1*B*—C1*B*	1.621 (6)	N1—C4	1.346 (4)
S1*C*—C1*C*	1.619 (6)	C1—C2	1.369 (5)
N1*A*—C1*A*	1.129 (5)	C2—C3	1.363 (5)
N1*B*—C1*B*	1.132 (6)	C3—N2	1.340 (5)
N1*C*—C1*C*	1.132 (6)	N2—C4	1.321 (4)
N—C11	1.510 (7)	C4—C4'	1.488 (7)
N—C21	1.522 (6)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The data were collected using a variable scan speed of 4.19–29.3° min^{-1}. The structure was solved through a combination of direct methods and difference Fourier synthesis. Refinement was performed with *SHELXL*93 (Sheldrick, 1993) on F^2, using the whole data set. H atoms were positioned geometrically, riding both in position as well as in thermal displacement parameter. The final difference Fourier appeared featureless.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93 and *PARST* (Nardelli, 1983).

The authors would like to thank the Fundación Andes for the purchase of the single crystal diffractometer currently operating at the Universidad de Chile.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1039). Services for accessing these data are described at the back of the journal.

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Mononuclear Indium and Gallium Tetrachlorocatecholate Complexes

Yvonne G. Lawson, Nicholas C. Norman, A. Guy Orpen and Michael J. Quayle

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, England. E-mail: guy.orpen@bris.ac.uk

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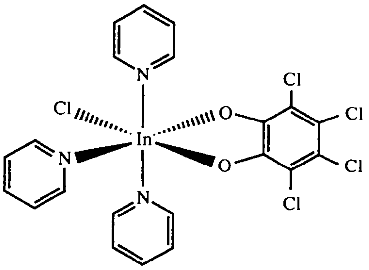
Abstract

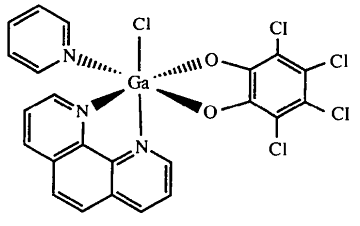
Two mononuclear tetrachlorocatecholate complexes, chlorotri(pyridine-*N*)[3,4,5,6-tetrachloro-1,2-benzenediolato(2−)-*O*,*O*′]indium, $[InCl(1,2\text{-}O_2C_6Cl_4)(py)_3]$, (1), and chloro(1,10-phenanthroline-*N*,*N*′)(pyridine-*N*)[3,4,5,6-tetrachloro-1,2-benzenediolato(2−)-*O*,*O*′]gallium, $[GaCl(1,2\text{-}O_2C_6Cl_4)(py)(phen)]$, (2) (py is pyridine, C_5H_5N, and phen is 1,10-phenanthroline, $C_{12}H_8N_2$), have been structurally characterized as solvates, (1) as its bis(diethyl ether) solvate and (2) as its 3.5-pyridine solvate. Both (1) and (2) contain octahedrally coordinated metals but with the nitrogen donor ligands in a *mer* arrangement in (1) and a *fac* arrangement in (2). Stabilization by intramolecular CH···O and CH···Cl interactions is evident, and, together with steric considerations, is likely to promote the observed configurations. Compound (1) shows an interesting packing arrangement of infinite planar sheets held together by short Cl···Cl contacts.

Comment

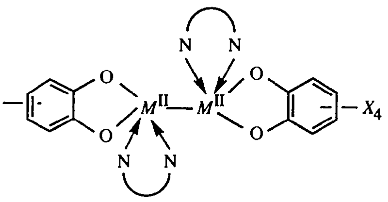
The compounds $[InCl(py)_3(1,2\text{-}O_2C_6Cl_4)].2Et_2O$ and $[GaCl(py)(phen)(1,2\text{-}O_2C_6Cl_4)].3.5py$ were obtained as minor crystalline products from reactions carried out in order to synthesize M^{II}–M^{II} dimer species $[M_2(O_2C_6Cl_4)_2(phen)_2]$ (M = Ga or In) by procedures related to those of Tuck and co-workers (Annan & Tuck, 1989).



(1)



(2)



Compound (1) (Fig. 1) crystallizes as a 1:2 Et_2O solvate in the orthorhombic space group *Pnma* with the catecholate, chloride and one pyridine lying on a mirror plane, and exhibits an octahedral coordination about the indium centre [N1—In1—N1$^{\text{i}}$ 173.7 (2)°]. The structural data are consistent with the complex being an indium(III) catecholate species since the In—O bond

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