

“Symmetric or unsymmetric?” Interpretazioni e dispute cristallografiche su sistemi molecolari contenenti legami metallo-metallo

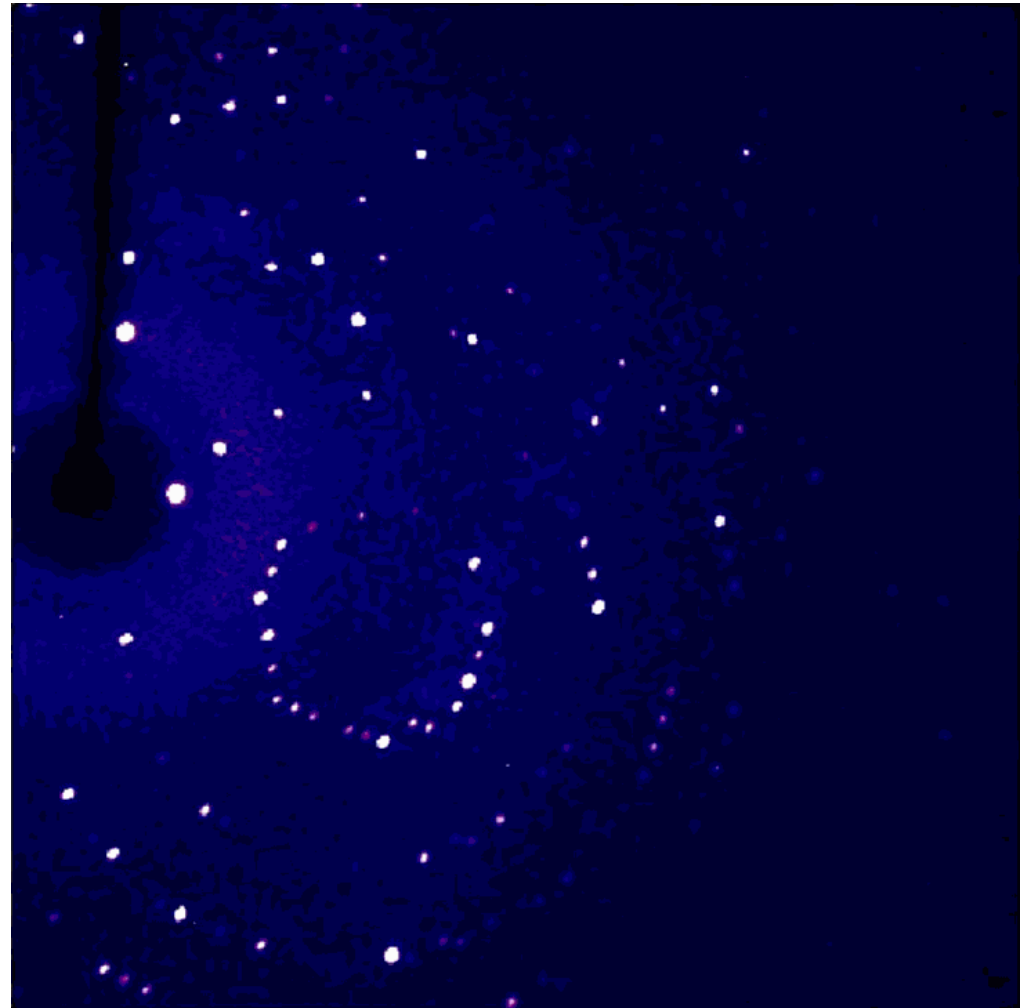
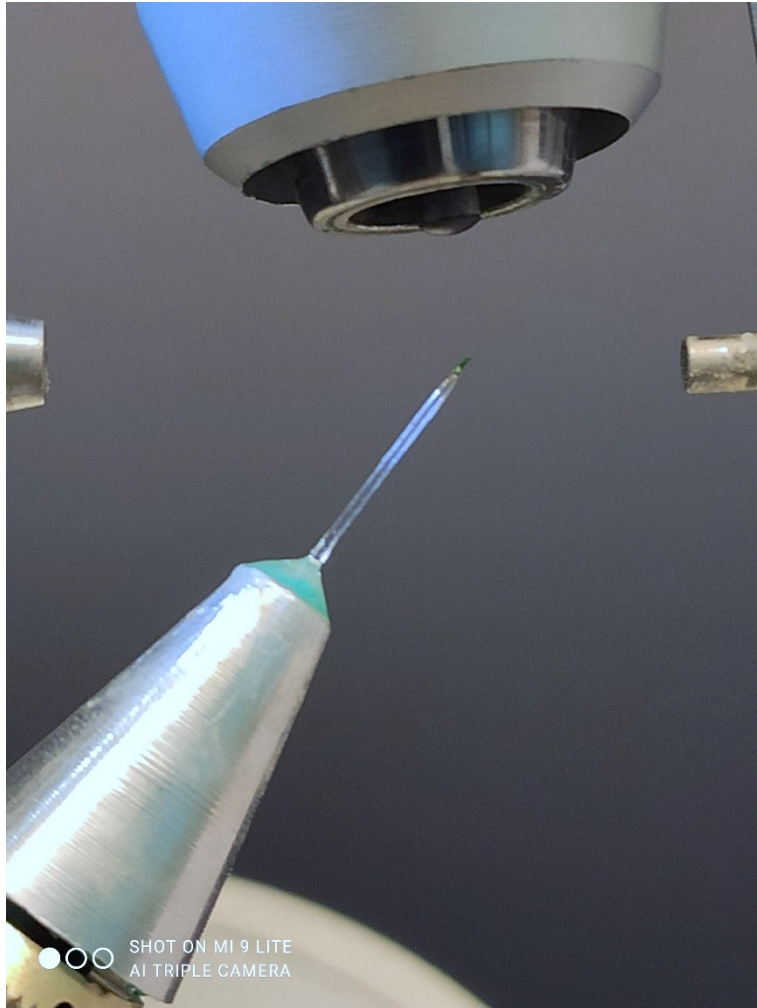


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Workshop Diffrazione Raggi X, Centro Interdipartimentale Grandi Strumenti
CINQUANTA, 7 novembre 2024

Diffrazione dei raggi-X su cristallo singolo



Diffrazione dei raggi-X su cristallo singolo

The History of Molecular Structure Determination Viewed through the Nobel Prizes

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<http://www.iucr.org/people/nobel-prize>

Diffrazione dei raggi-X su cristallo singolo

Acta Cryst. (1995). B51, 897–907

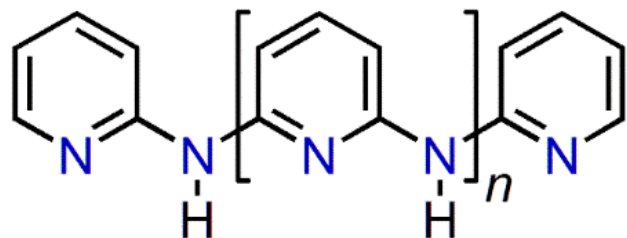
Some Thoughts on Choosing the Correct Space Group

BY RICHARD E. MARSH

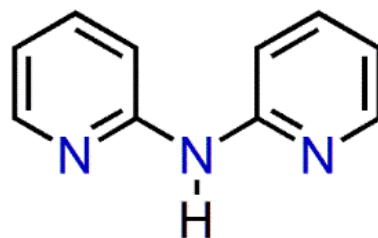
The Beckman Institute, California Institute of Technology, Pasadena, CA 91125, USA*

The determination of a ‘small molecule’ crystal structure by means of single-crystal X-ray diffraction is one of the relatively few techniques in the physical sciences where, in most cases, the number of observations greatly exceeds the number of quantities being measured, and hence might be described as an ‘exact’ science.

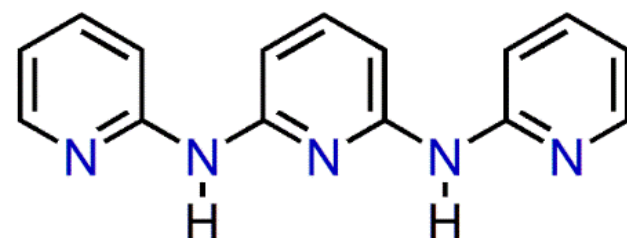
Extended Metal Atom Chains (EMACs)



oligo- α -pyridylamine

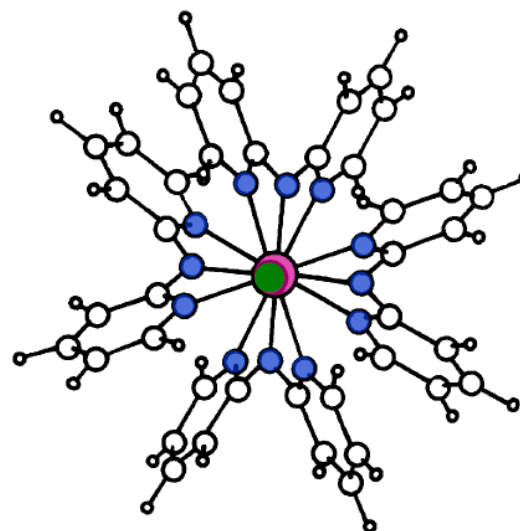
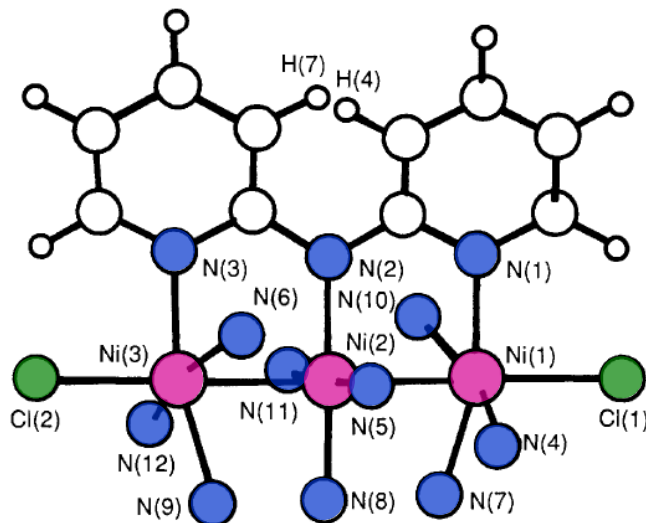


Hdpa ($n = 0$)



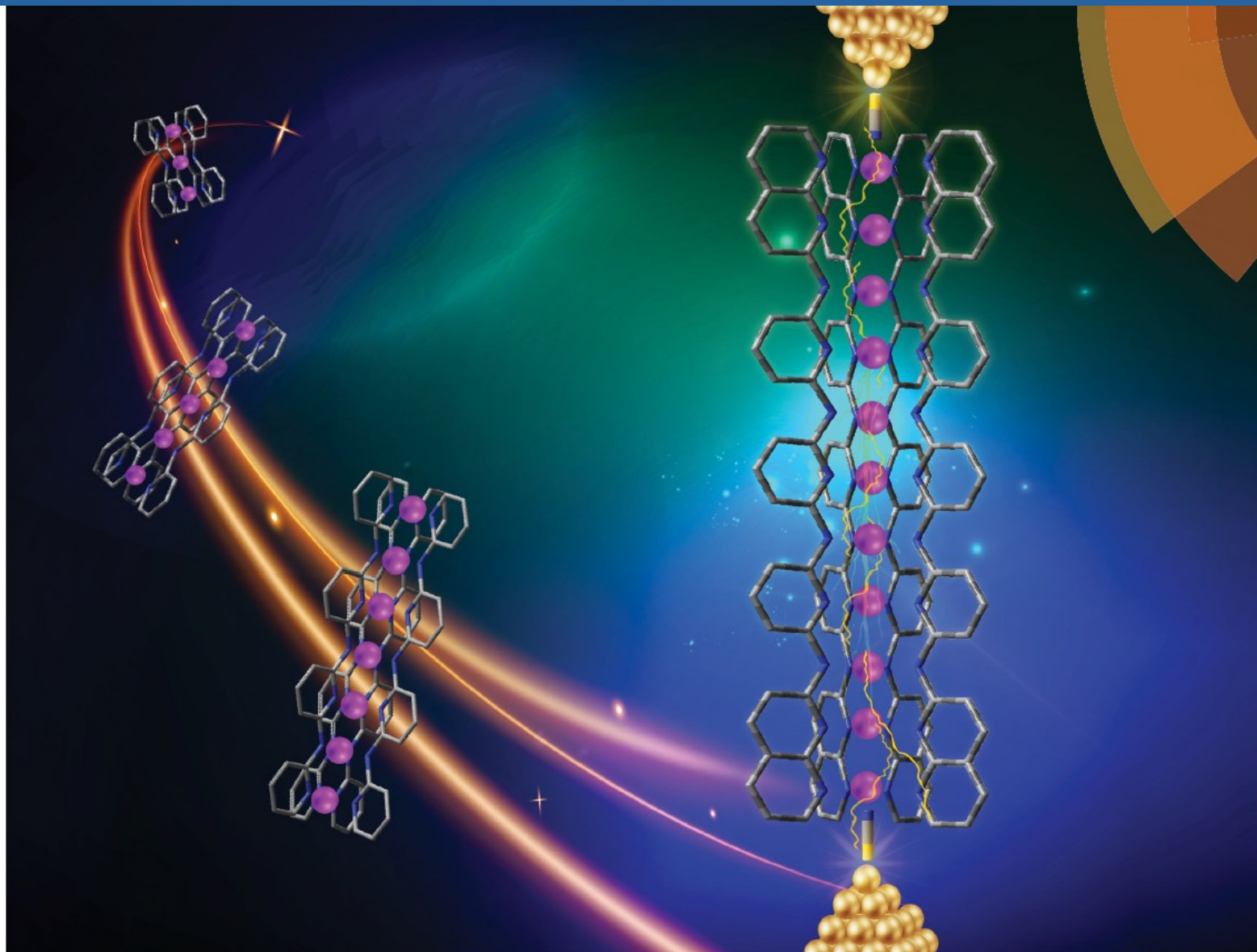
H₂tpda ($n = 1$)

T. J. Hurley, M. A. Robinson, *Inorg. Chem.* 1968, 7, 33

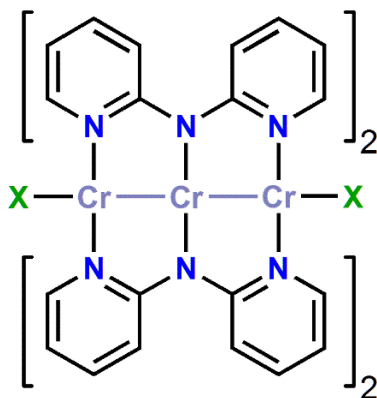


S. Aduldecha, B. Hathaway, *J. Chem. Soc. Dalton Trans.* 1991, 993

Molecular wires

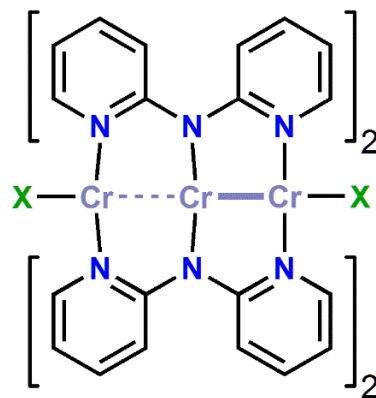


The structural dispute

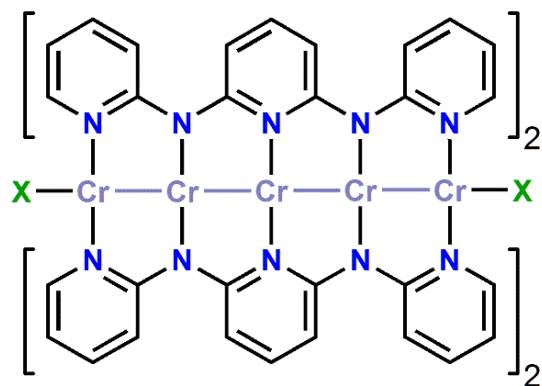
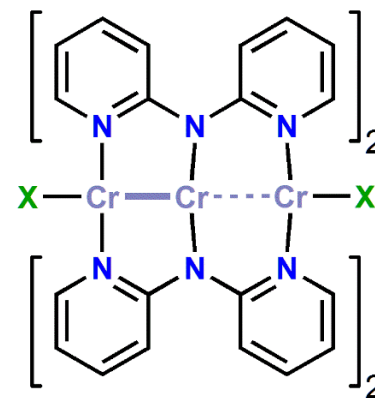


sym (D_4)

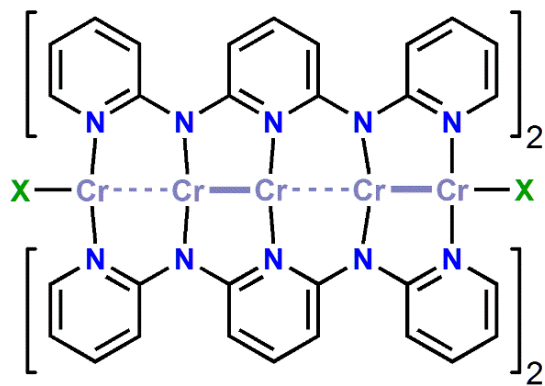
X = Cl, SCN



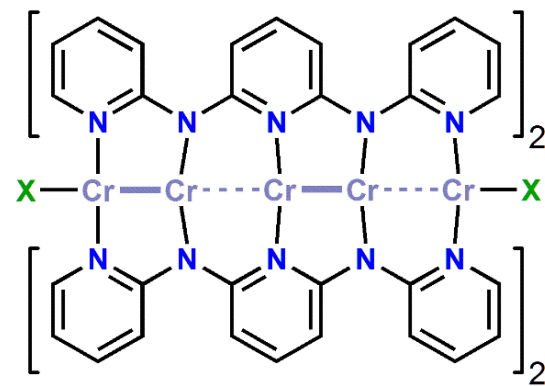
unsym (C_4)



sym (D_4)



unsym (C_4)

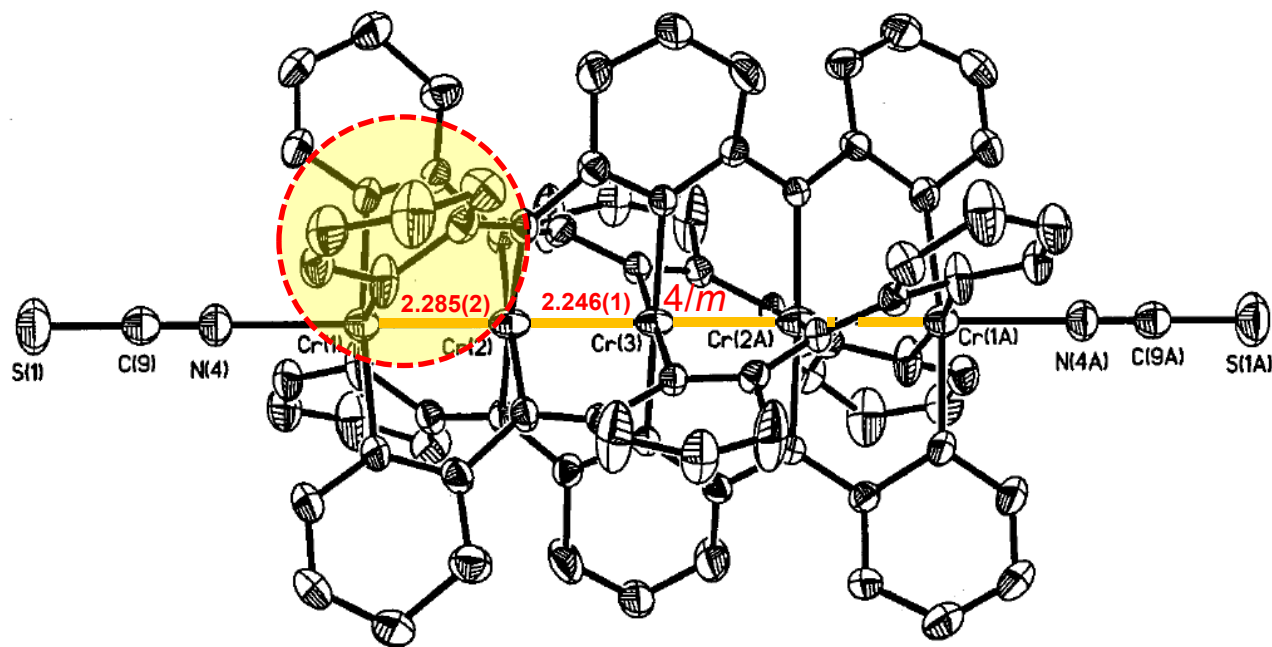


S.-M. Peng's group on $[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$

Linear Five-Centred Chromium Multiple Bonds Bridged by Four tpda^{2-} Ligands [tpda^{2-} = tripyridyldiamido dianion] – Synthesis and Structural Studies

Hsiao-Chi Chang,^[a] Jia-Tzung Li,^[a] Chih-Chieh Wang,^[a] Tzu-Wei Lin,^[a] Hsiao-Ching Lee,^[a] Gene-Hsiang Lee,^[a] and Shie-Ming Peng*^[a]

^[a] Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC



RT, $I4/m$, $R1 = 5.43\%$

"...a delocalized $\text{Cr}^{\text{II}}\text{-Cr}^{\text{II}}\text{-Cr}^{\text{II}}\text{-Cr}^{\text{II}}\text{-Cr}^{\text{II}}$ five-centred metal-metal bond..."

"...the right-turn and left-turn helical complexes are seriously disordered in the crystal..."

received: Jan 12, 1999

Figure 2. Crystal structure of $[\text{Cr}_5(\mu_5\text{-tpda})_4(\text{NCS})_2]$ 2. Atoms are shown as 20% vibrational thermal ellipsoids

F. A. Cotton's group on $[\text{Cr}_5(\text{tpda})_4\text{Cl}_2]\cdot\text{solv}$

A chain of five chromium(II) atoms: a desired compound with an undesired, unsurprising, but important structure

F. Albert Cotton,^{*a} Lee M. Daniels,^a Tongbu Lu,^a Carlos A. Murillo^{*a,b} and Xiaoping Wang^a

^a *The Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA.
E-mail: cotton@tamu.edu; murillo@tamu.edu*

^b *Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica*

DALTON
COMMUNICATION

(Feb 1999)

Getting the right answer to a key question concerning molecular wires

F. Albert Cotton,^{*a} Lee M. Daniels,^a Carlos A. Murillo^{*a,b} and Xiaoping Wang^a

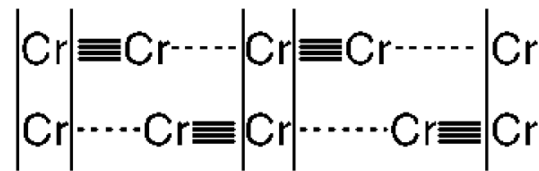
^a *Laboratory for Molecular Structure and Bonding and Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA. E-mail: cotton@TAMU.edu*

^b *Department of Chemistry, Universidad de Costa Rica, Ciudad Universitaria, Costa Rica.
E-mail: murillo@TAMU.edu*

ChemComm

(Dec 1999)

It is shown that the $\text{Cr}_5(\text{tpda})_4\text{Cl}_2$ molecule has alternating long and short ($\text{Cr}\cdots\text{Cr}$) contacts in three compounds, including one in which an evenly spaced chain was recently claimed.



F. A. Cotton et al., *J. Chem. Soc. Dalton Trans.* 1999, 517
F. A. Cotton et al., *Chem. Commun.* 1999, 2416

More on $[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2] \cdot 2.5\text{CH}_2\text{Cl}_2$

Extended metal atom chains (EMACs) of five chromium or cobalt atoms: Symmetrical or unsymmetrical?

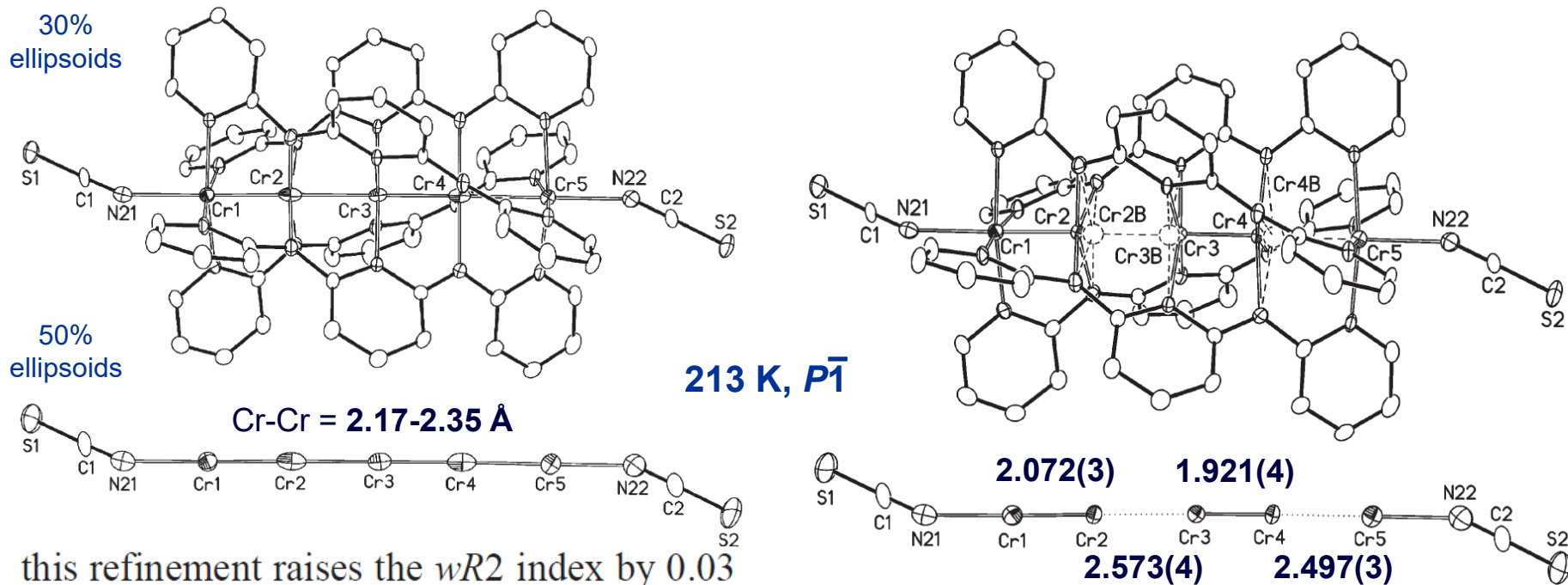
John F. Berry,^a F. Albert Cotton,^{*a} Christopher S. Fewox,^a Tongbu Lu,^{a,b} Carlos A. Murillo^{*a} and Xiaoping Wang^a

^a Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012

^b School of Chemistry & Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China

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Dalton



More on $[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2] \cdot 2.5\text{CH}_2\text{Cl}_2$

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Dalton
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Thus, we have shown for the *third* time that Cr_5^{10+} complexes are *unsymmetrical* and exist with alternating short (quadruply bonded) and long interatomic distances with an isolated terminal high spin Cr^{II} ion responsible for the four unpaired electrons of the compound.

$[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$: Cotton's conjecture proven



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DOI: 10.1039/d2dt03103e

XIPHOS
diffraction
facility

The structure of a pentachromium(II) extended metal atom chain at 3 K: Cotton's conjecture proven†

Andrea Cornia, ^{*a} Alessio Nicolini, ^a Charles J. McMonagle^{‡b} and Michael R. Probert ^{*b}

^a*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia & INSTM, I-41125 Modena, Italy. E-mail: acornia@unimore.it*

^b*Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK. E-mail: Michael.Probert@newcastle.ac.uk*



[Cr₅(tpda)₄(NCS)₂]: Cotton's conjecture proven



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^a*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia & INSTM, I-41125 Modena, Italy. E-mail: acornia@unimore.it*

^b*Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK. E-mail: Michael.Probert@newcastle.ac.uk*

- structural determination from 292 to 3 K
- monoclinic *C2/c*
- $a = 15.0605(4) \text{ \AA} \sim c = 14.9728(4) \text{ \AA}$, $b = 26.1672(7) \text{ \AA}$, $\beta = 90.023(2)^\circ \sim 90^\circ$ (at 3 K)
- two domains of similar size *pseudo-merohedrally twinned* by 90° rotation around *y* to *emulate tetragonal* (unnoticed by Peng's group)

$[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$: Cotton's conjecture proven



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^bChemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK. E-mail: Michael.Probert@newcastle.ac.uk

False tetragonal cell

(unique axis z)

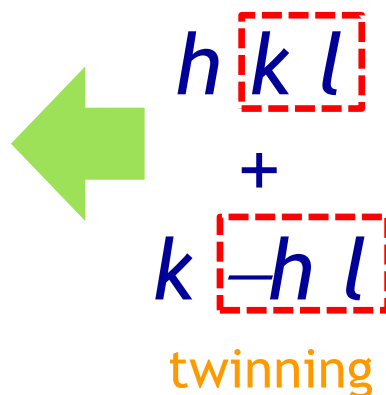
exp. limiting conditions:

hkl : $h+l$ and $k+l$ not both odd

$hk0$: h and k even

$00l$: l even

(impossible in tetragonal
space groups)



$A2/a$ (unique axis z)

limiting conditions:

hkl : $k+l$ even

$hk0$: h and k even

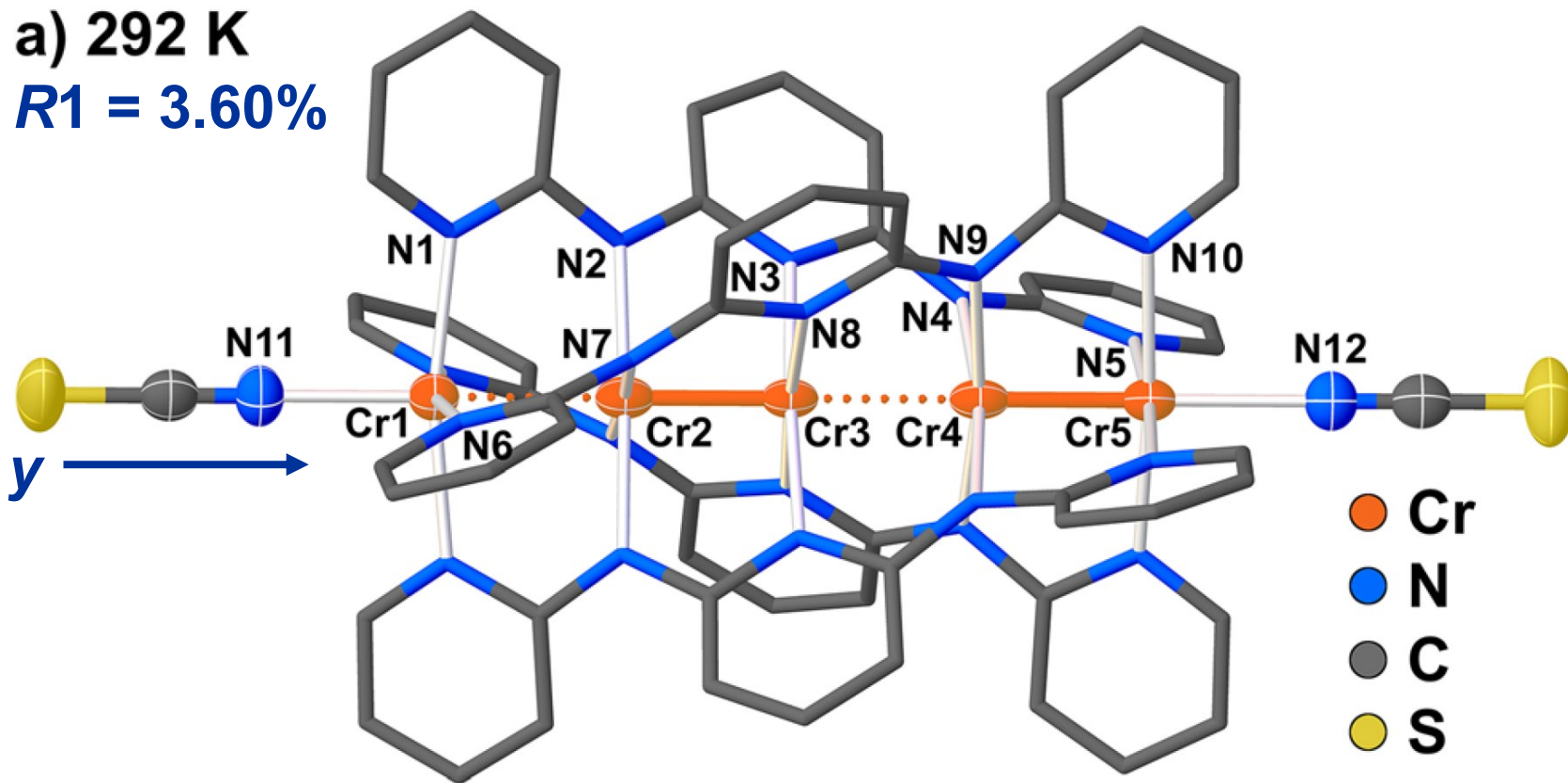
$00l$: l even

relabelling

$C2/c$ (unique axis y)

$[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$: Cotton's conjecture proven

a) 292 K
 $R1 = 3.60\%$



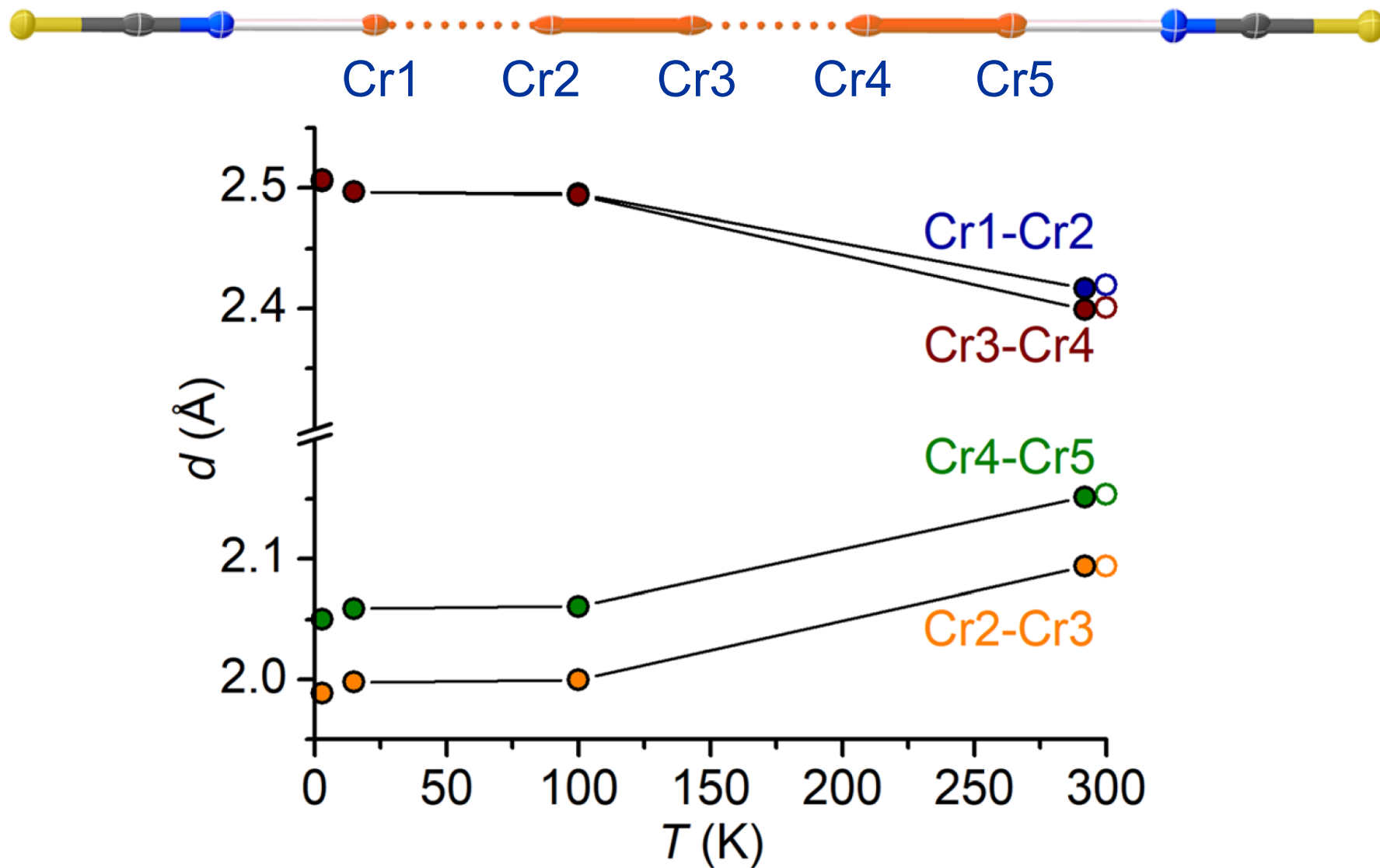
b) 3 K

$R1 = 3.43\%$

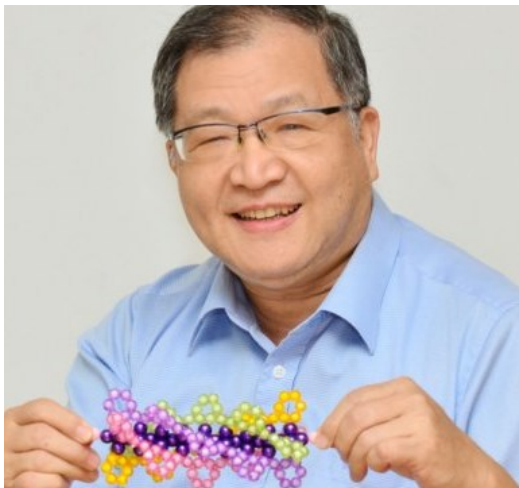
50% ellipsoids



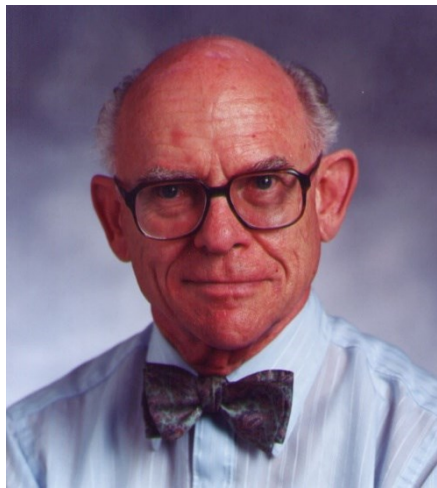
$[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$: Cotton's conjecture proven



Acknowledgments



Shie-Ming Peng



**Frank Albert Cotton
(1930-2007)**



Michael R. Probert

A. Nicolini (chemistry)

*Dipartimento di Scienze Chimiche e Geologiche e
UdR INSTM (UniMORE), Modena*

C. McMonagle (low- T X-ray diffraction)

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