

(2,2'-Bipyridine- κ^2N,N')(dichromato- κO)copper(II)Paul A. Maggard, Amy L. Kopf, Charlotte L. Stern and
Kenneth R. Poeppelmeier*Department of Chemistry, Northwestern University, Evanston, IL 60208, USA
Correspondence e-mail: krp@nwu.eduReceived 24 September 2001
Accepted 19 December 2001
Online 12 March 2002

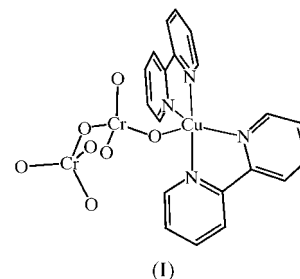
The title compound, $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$, a new mixed-metal molecular compound, contains isolated molecular units, each comprised of one Cu^{II} atom coordinated to two 2,2'-bipyridine ligands and also to an oxygen vertex of a dichromate anion. The Cu^{II} atom has an approximate trigonal-bipyramidal geometry, which is consistent with previous studies. Both enantiomers of the chiral complex molecule are present and are related by inversion centers. In a reported pyridine analogue, achiral $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$ chains pack in the non-centrosymmetric space group $Pna2_1$. Differences in the organic ligands influence the chirality and dimensionality of the $\text{Cu}-\text{Cr}_2\text{O}_7$ bonding.

Comment

Non-centrosymmetric molecular units, such as those with tetrahedral or distorted octahedral geometries, have been cited for their roles in the synthesis of non-centrosymmetric (NCS) solids (Halasyamani & Poeppelmeier, 1998). Recently, $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$ (Norquist *et al.*, 2001) was reported in an NCS space group, with chains comprising alternating octahedral CuN_4O_2 and tetrahedral Cr_2O_7 polyhedra, which are connected through shared oxygen vertices. The chains are reported to exhibit similarities to the helical $\text{TiO}_{4/2}\text{O}_{2/2}$ chain (4/2 refers to four oxygen vertices each shared between two titanium polyhedra) found in non-centrosymmetric KTiOPO_4 (Tordjman *et al.*, 1974). In separate research, prior physicochemical and reactivity studies of the title compound, (I), have focused on the importance of weak Cr_2O_7 coordination to Cu for either selective oxidation or mutagenic activity (Cieslak-Golonka *et al.*, 1991; Szyba *et al.*, 1992). In light of the above interests, a complete crystallographic study of (2,2'-bipyridine)(dichromato)copper(II), (I), seemed justified.

Crystals of (I) were hydrothermally synthesized from Cu and Cr oxides and 2,2'-bipyridine inside an autoclave. A view of the resulting mixed-metal (Cu/Cr) molecule is shown in Fig. 1. The inversion symmetry occurs between separate left-

and right-handed molecules of (I). The crystal structures of (I) and $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$ (Norquist *et al.*, 2001) exhibit similar Cr—O and Cu—N bond lengths. The shared oxygen vertex (O4) between the chromium centers is approximately 0.12 Å further from the chromium centers than are the unshared oxygen vertices, as in $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$. The dihydrate of (I) also exhibits similar molecular units spaced by water molecules (Ii *et al.*, 1996).



Two dramatic differences between the non-centrosymmetric structure of $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$ and (I) are caused by the ligand change. The first is that in (I), the copper coordination is approximately trigonal bipyramidal (CuON_4), as in the dihydrate (Ii *et al.*, 1996), while in $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$, it is octahedral (CuN_4O_2). The distortion of the Cu atom from regular octahedral geometry has been associated with the predicted d_{z^2} ground state of (I) from electron-spin resonance (ESR) data (Cieslak-Golonka *et al.*, 1991). Both a trigonal bipyramidal and octahedral copper coordination is consistent with a +2 oxidation state, which balances the 2− charge on the $[\text{Cr}_2\text{O}_7]^{2-}$ anion. Structurally, the approximate bipyramidal coordination in (I) occurs because a second Cr_2O_7 group does not bind (*trans*) to copper, likely related to the greater steric

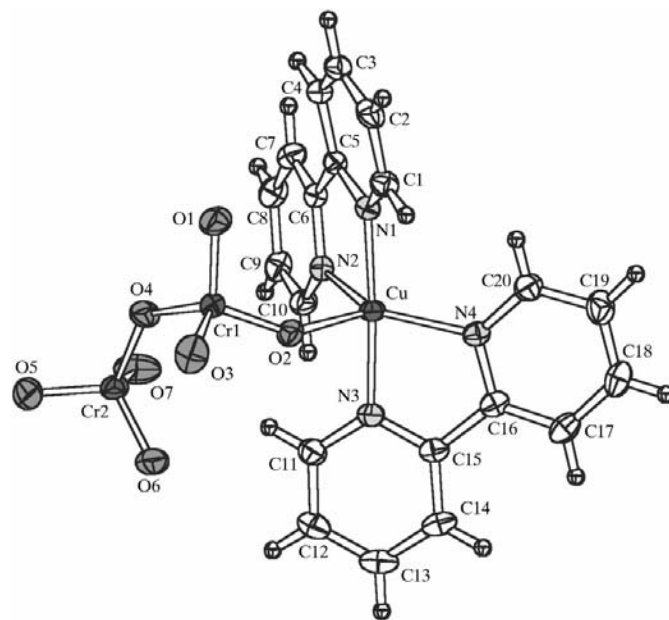


Figure 1
Displacement ellipsoid plot (50% probability) of the mixed-metal title molecule.

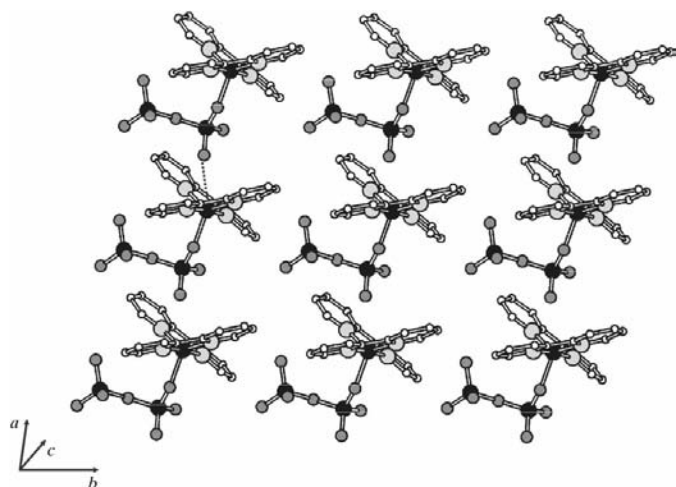


Figure 2
The molecular packing of one layer of (I). Each layer stacks on top of the next, with an inversion and shift in $a/2$.

effects of 2,2'-dipyridine compared with pyridine. The second difference is that (I) contains isolated molecular units rather than the infinite chains seen in the pyridine analogue. Again, this is a result of the monodentate coordination of Cr_2O_7 , which eliminates extended $\text{Cu}-\text{O}-\text{Cr}-\text{O}-\text{Cr}-\text{O}-\text{Cu}$ bonding. The next closest $\text{Cu}-\text{Cr}_2\text{O}_7$ contact between neighboring molecules in (I) is 3.250 (3) Å (drawn with a dotted line in Fig. 2), much longer than the shorter $\text{Cu}-\text{Cr}_2\text{O}_7$ distance of 2.116 (2) Å. Similar arguments also apply to the dihydrate structure of (I) (Ii *et al.*, 1996), where internal water molecules probably do not influence the $\text{Cu}-\text{Cr}_2\text{O}_7$ bonding.

Non-coordinated O atoms at the end of the dichromate anion (O5, O6 and O7) have more lone pairs of electrons available and are compensated by additional short $\text{O}\cdots\text{H}$ distances to the 2,2'-bipyridine ligand. Both O2 and O4 are coordinated to two cations, one Cu and one Cr, and each has only one short distance to hydrogen (2.4–2.5 Å). The remaining O atoms (O1 and O3 on the coordinated CrO_4 tetrahedron) also have few short $\text{O}\cdots\text{H}$ contacts; $\text{H}\cdots\text{O}1$ 2.66 and 2.59 Å, and $\text{H}\cdots\text{O}3$ 2.62 Å. The non-coordinated CrO_4 tetrahedron has relatively more $\text{O}\cdots\text{H}$ contacts: O5 2.41, 2.43 and 2.55 Å; O6 2.48, 2.52 and 2.60 Å; O7 2.36, 2.50, 2.67, 2.76 and 2.81 Å.

The crystal packing of one layer of molecules of (I) is shown in Fig. 2. In contrast to the non-centrosymmetric structure of $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$, which contains infinite chains, the full crystal packing of (I) contains an inversion center between the successive layers. When considering if a solid will crystallize in a centrosymmetric or non-centrosymmetric space group, it is required that a solid is restricted to non-centrosymmetric space groups when a single enantiomer of a chiral unit, such as a helix, is present. However, the chiral title molecules are racemically mixed, and the three-dimensional structure is non-centrosymmetric. In contrast, the individual $\text{Cu}-\text{Cr}_2\text{O}_7$ chains in $[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{pyridine})_4]$ are achiral, so that enantiomer formation does not influence its (non)centricity.

Experimental

The title compound was synthesized by placing CuO (89.4 mg), $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (157.5 mg) and 2,2'-bipyridine (195.2 mg) in a Teflon pouch (Harrison *et al.*, 1993). To the pouch were added NH_4HF_2 (178.2 mg) and deionized H_2O (1125 mg). The pouch was heat-sealed and placed in a 125 ml autoclave, which was back-filled with H_2O (45 ml). The autoclave was heated inside an oven for 24 h at 423 K and cooled to room temperature at a rate of 6 K h^{-1} . The pouch was opened in air and (I) was recovered in 85% yield based on CuO by filtration.

Crystal data

$[\text{Cu}(\text{Cr}_2\text{O}_7)(\text{C}_{10}\text{H}_8\text{N}_2)_2]$
 $M_r = 591.91$
 Triclinic, $P\bar{1}$
 $a = 7.7958$ (11) Å
 $b = 9.9319$ (14) Å
 $c = 14.849$ (2) Å
 $\alpha = 74.673$ (2)°
 $\beta = 81.960$ (2)°
 $\gamma = 79.617$ (2)°
 $V = 1085.5$ (3) Å³
 $Z = 2$
 $D_x = 1.811$ Mg m^{-3}

$D_m = 1.840$ (3) Mg m^{-3}
 D_m measured by flotation pycnometry
 Mo $K\alpha$ radiation
 Cell parameters from 5015 reflections
 $\theta = 4\text{--}28^\circ$
 $\mu = 2.01$ mm^{-1}
 $T = 153$ (2) K
 Block, translucent dark green
 0.16 × 0.12 × 0.09 mm

Data collection

Bruker SMART 1000 diffractometer
 ω scans
 Absorption correction: empirical (SADABS; Blessing, 1995)
 $T_{\min} = 0.649$, $T_{\max} = 0.838$
 10 019 measured reflections

5015 independent reflections
 4227 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 28.3^\circ$
 $h = -10 \rightarrow 10$
 $k = -13 \rightarrow 12$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.109$
 $S = 1.06$
 5015 reflections
 307 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.4903P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.71$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—N3	1.977 (2)	Cr1—O2	1.6429 (18)
Cu—N1	1.990 (2)	Cr1—O4	1.7720 (19)
Cu—N4	2.030 (2)	Cr2—O6	1.610 (2)
Cu—N2	2.054 (2)	Cr2—O5	1.615 (2)
Cu—O2	2.1161 (18)	Cr2—O7	1.626 (2)
Cr1—O3	1.609 (2)	Cr2—O4	1.7880 (18)
Cr1—O1	1.612 (2)		
N3—Cu—N1	174.48 (8)	O3—Cr1—O4	109.53 (10)
N3—Cu—N4	81.16 (9)	O1—Cr1—O4	106.18 (10)
N1—Cu—N4	100.63 (8)	O2—Cr1—O4	110.14 (10)
N3—Cu—N2	101.57 (9)	O6—Cr2—O5	110.62 (11)
N1—Cu—N2	81.06 (8)	O6—Cr2—O7	109.43 (13)
N4—Cu—N2	133.32 (8)	O5—Cr2—O7	110.13 (13)
O3—Cr1—O1	111.36 (12)	O6—Cr2—O4	110.88 (10)
O3—Cr1—O2	108.68 (10)	O5—Cr2—O4	108.99 (10)
O1—Cr1—O2	110.93 (10)	O7—Cr2—O4	106.71 (10)

H atoms of the 2,2'-bipyridine ligand were constrained to ride at distances of 0.93 Å, with an isotropic displacement parameter 1.5 times that of the associated C atom. The largest residual electron-density peak was 0.85 Å from atom Cr2.

Data collection: *SMART-NT* (Siemens, 1996); cell refinement: *SAINT-Plus* (Siemens, 1996); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999).

The authors acknowledge support from the National Science Foundation, Solid State Chemistry (award No. DMR-9727516), and made use of the Central Facilities supported by the MRSEC program, National Science Foundation, at the Materials Research Center of Northwestern University (award No. DMR-0076097).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1351). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst. A* **51**, 33–38.
- Cieslak-Golonka, M., Bartecki, A. & Jezierska, J. (1991). *Polyhedron*, **10**, 2179–2184.
- Dowty, E. (1999). *ATOMS*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
- Halasyamani, P. S. & Poeppelmeier, K. R. (1998). *Chem. Mater.* **10**, 2753–2769.
- Harrison, W. T. A., Nenoff, T. M., Gier, T. E. & Stucky, G. D. (1993). *Inorg. Chem.* **32**, 2437–2441.
- Ii, J., Ke, Y., Wang, Q. & Wu, X. (1996). *Cryst. Res. Technol.* **31**, 453–458.
- Norquist, A. J., Heier, K. R., Halasyamani, P. S., Stern, C. L. & Poeppelmeier, K. R. (2001). *Inorg. Chem.* **40**, 2015–2019.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *SMART-NT* and *SAINT-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Szyba, K., Cieslak-Golonka, M., Gasiorowski, K. & Urban, J. (1992). *Bio-metals*, **5**, 157–161.
- Tordjman, P. I., Masse, R. & Guitel, J. C. (1974). *Z. Kristallogr.* **139**, 103–115.