

constrained to be 1.2 times the equivalent isotropic parameter of the attached N atoms.

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1994*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994*a*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This work was supported in part by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Missouri Research Board and University of Missouri–St Louis Research Award Fund.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1480). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Aullón, G., Bellamy, D., Brammer, L., Bruton, E. A. & Orpen, A. G. (1998). *Chem. Commun.* pp. 653–654.
- Biradha, K., Desiraju, G. R., Braga, D. & Grepioni, F. (1996). *Organometallics*, **15**, 1284–1295.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Braga, D., Biradha, K., Grepioni, F., Pedireddi, V. R. & Desiraju, G. R. (1995). *J. Am. Chem. Soc.* **117**, 3156–3166.
- Braga, D. & Grepioni, F. (1997). *Acc. Chem. Res.* **30**, 81–87.
- Braga, D., Grepioni, F., Sabatino, P. & Desiraju, G. R. (1994). *Organometallics*, **13**, 3532–3543.
- Braga, D., Grepioni, F., Tedesco, E., Biradha, K. & Desiraju, G. R. (1996). *Organometallics*, **15**, 2692–2699.
- Braga, D., Grepioni, F., Tedesco, E., Biradha, K. & Desiraju, G. R. (1997). *Organometallics*, **16**, 1846–1856.
- Brammer, L., Charnock, J. M., Goggin, P. L., Goodfellow, R. J., Orpen, A. G. & Koetzle, T. F. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1789–1798.
- Brammer, L., McCann, M. C., Bullock, R. M., McMullan, R. K. & Sherwood, P. (1992). *Organometallics*, **11**, 2339–2341.
- Brammer, L. & Zhao, D. (1994). *Organometallics*, **13**, 1545–1547.
- Brammer, L., Zhao, D., Ladipo, F. T. & Braddock-Wilking, J. (1995). *Acta Cryst.* **B51**, 632–640.
- Calderazzo, F., Fachinetti, G., Marchetti, F. & Zanazzi, P. F. (1981). *J. Chem. Soc. Chem. Commun.* pp. 181–183.
- Epstein, L., Shubina, E. S., Krylov, A. N., Kreindlin, A. Z. & Ribinskaya, M. I. (1993). *J. Organomet. Chem.* **447**, 277–280.
- Fairhurst, S. A., Henderson, R. A., Hughes, D. L., Ibrahim, S. K. & Pickett, C. J. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1569–1570.
- Kazarian, S. G., Hamley, P. A. & Poliakov, M. (1993). *J. Am. Chem. Soc.* **115**, 9069–9079.
- Mareque Rivas, J. C. & Brammer, L. (1998*a*). *Acta Cryst.* **C54**, 757–760.
- Mareque Rivas, J. C. & Brammer, L. (1998*b*). *Coord. Chem Rev.* In the press.
- Mareque Rivas, J. C. & Brammer, L. (1998*c*). *Inorg. Chem.* In the press.
- Mareque Rivas, J. C. & Brammer, L. (1998*d*). In preparation.
- Müller, T. E., Mingos, D. M. P. & Williams, D. J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1787–1788.
- Peris, E. & Crabtree, R. H. (1995). *J. Chem. Soc. Chem. Commun.* pp. 2179–2180.
- Sheldrick, G. M. (1995). *SADABS. Program for Empirical Absorption Correction*. Version 2. University of Göttingen, Germany.
- Siemens (1994*a*). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994*b*). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wehman-Ooyevaar, I. C. M., Grove, D. M., Kooijman, H., van der Sluis, P., Spek, A. L. & van Koten, G. (1992). *J. Am. Chem. Soc.* **114**, 9916–9924.
- Zhao, D., Ladipo, F. T., Braddock-Wilking, J., Brammer, L. & Sherwood, P. (1996). *Organometallics*, **15**, 1441–1445.

Acta Cryst. (1998). **C54**, 1802–1804

catena-Poly[[tetrakis(imidazole-*N*³)-copper(II)]- μ -(dichromato-*O*:*O'*)

LONG PAN,^a NENGWU ZHENG,^{a*} XIAOYU ZHOU,^a
YONGGANG WU,^a QINGSHENG WU^a AND XIANGLIN JIN^b

^aDepartment of Chemistry, University of Science & Technology of China, Hefei Anhui 230026, People's Republic of China, and ^bDepartment of Chemistry, University of Beijing, Beijing 100871, People's Republic of China. E-mail: lpan@mail.ach.ustc.edu.cn

(Received 6 May 1997; accepted 7 May 1998)

Abstract

The title compound, $[\{\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_4\}(\text{Cr}_2\text{O}_7)]_n$, containing a $[\text{Cr}(\text{Him})_4]^{2+}$ cation (Him = imidazole) and a dichromate anion, was obtained by hydrothermal synthesis. Each Him ligand coordinates to the Cu atom via one N atom, forming a tetragonally elongated octahedral geometry with a basal plane defined by four coplanar imidazole N atoms, the axial sites being occupied by O atoms from two dichromato ligands. The dichromate anions bridge the Cu ions to form one-dimensional zigzag chains.

Comment

Complexes of Cu^{2+} and Him with halides have been structurally characterized, such as $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$, $[\text{Cu}(\text{Him})_4]\text{I}_2$ and $[\text{Cu}(\text{Him})_4]\text{Br}_2$ (Vreugdenhil *et al.*, 1984; Akhtar *et al.*, 1968; Ballester *et al.*, 1993; Parker & Breneman, 1995). These molecular structures reveal that the bromide and iodide anions are weakly bound in the axial coordination sites, but in $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$, the fluoride ions are not coordinated to the Cu ion, the fifth and sixth octahedral sites above and below the CuN_4 plane being occupied by two water molecules. The structures of some complexes of oxo acid anions with imidazole–copper(II) have also been reported: $[\text{Cu}(\text{Him})_4(\text{SO}_4)]$, $[\text{Cu}(\text{Him})_4(\text{NO}_3)]$ and $[\text{Cu}(\text{Him})_4(\text{ClO}_4)_2]$ (Fransson & Lundberg, 1972;

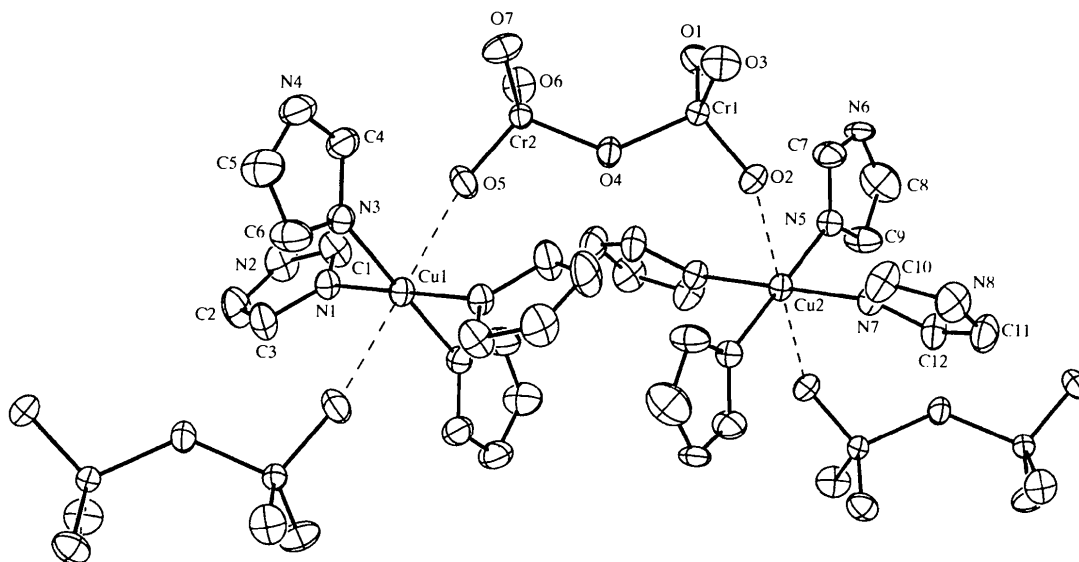
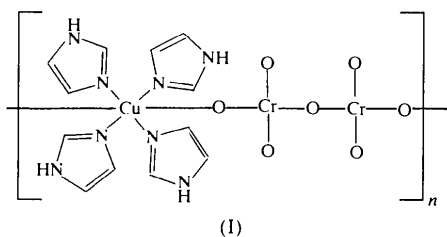


Fig. 1. Part of the polymeric chain structure of (I), with 30% probability ellipsoids and with unique atoms labelled.

McFadden *et al.*, 1976; Ivarsson, 1973). In these compounds, there are two apical bonds to the O atoms of the sulfato, nitrate and perchlorato groups. The Cu...O distances in these complexes are 2.574 (4), 2.566 [average of 2.606 (6) and 2.526 (6) Å] and 2.625 (5) Å, respectively.

We have investigated a related complex with dichromate as the oxo anion, $[\text{Cu}(\text{Him})_4]\text{Cr}_2\text{O}_7$, (I). The asymmetric unit contains two discrete half-cations and one dichromate anion. Each square-planar $[\text{Cu}(\text{Him})_4]^{2+}$ cation has Cu on an inversion centre. The Cu—N distances and angles agree well with the corresponding mean equatorial geometry in many other octahedral Cu^{II} complexes with unidentate or bidentate N-donor ligands (Ivarsson, 1973; de Munno *et al.*, 1993; Su *et al.*, 1993). The axial Cu...O distances to dichromate are similar to those in $[\text{Cu}(\text{Him})_4](\text{SO}_4)$ (Fransson & Lundberg, 1972), but are longer than the Cu...O_{sulfato} distance (2.41 Å) in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Bacon & Curry, 1962), in which the coordination around the Cu atoms is also a distorted octahedron, with two sulfate O atoms in the apical positions. These Cu...O distances fall in the range observed for semi-coordination (Ivarsson, 1973). As usual, the dichromate anion consists of two apex-linked distorted tetrahedra. Bond lengths and angles in the dichromate anion are normal (Jannin *et al.*, 1993).



The Cu^{2+} ions are bridged by dichromate ligands to form one-dimensional zigzag chains (Fig. 1). The shortest Cr...Cu distances are 4.013 (1) and 4.060 (2) Å. Dichromate as a bridging ligand has previously been reported by Dave & Czernuszewicz (1994).

Experimental

A mixture of $\text{Cu}(\text{NO}_3)_2$ (0.24 g, 1 mmol), Him (0.27 g, 4 mmol) and $\text{K}_2\text{Cr}_2\text{O}_7$ (0.295 g, 1 mmol) was dissolved in deionized water (20 ml) and transferred to a Teflon-lined steel bomb, which was sealed, heated at 413 K for 12 h, and then cooled gradually over 8 h to room temperature. The precipitate was filtered off to give an orange solution, from which pale-brown crystals of $[\text{Cu}(\text{Him})_4]\text{Cr}_2\text{O}_7$ were collected after a few days.

Crystal data

$[\text{CuCr}_2\text{O}_7(\text{C}_3\text{H}_4\text{N}_2)_4]$

$M_r = 551.87$

Triclinic

$P\bar{1}$

$a = 9.901$ (2) Å

$b = 13.314$ (3) Å

$c = 9.555$ (2) Å

$\alpha = 100.34$ (3)°

$\beta = 117.81$ (3)°

$\gamma = 69.25$ (3)°

$V = 1041.7$ (4) Å³

$Z = 2$

$D_x = 1.759$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 5\text{--}13^\circ$

$\mu = 2.087$ mm⁻¹

$T = 293$ (2) K

Block

$0.4 \times 0.2 \times 0.2$ mm

Pale brown

Data collection

Rigaku AFC-6S diffractometer

2734 reflections with $F^2 > 2\sigma(F^2)$

$\omega/2\theta$ scans
Absorption correction:
 ψ scan (Coppens *et al.*,
1965)
 $T_{\min} = 0.528$, $T_{\max} = 0.659$
3893 measured reflections
3662 independent reflections

$R_{\text{int}} = 0.023$
 $\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 11$
 $k = -14 \rightarrow 15$
 $l = -11 \rightarrow 10$
3 standard reflections
every 150 reflections
intensity decay: 1%

Refinement

Refinement on F^2
 $R = 0.035$
 $wR = 0.091$
 $S = 1.033$
3662 reflections
275 parameters
H atoms riding, with fixed
 $U_{\text{iso}} = 0.08 \text{ \AA}^2$
 $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.0728P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.006$
 $\Delta\rho_{\max} = 0.442 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.529 \text{ e \AA}^{-3}$
Extinction correction:
SHELXL97
Extinction coefficient:
0.0013 (5)
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cr1—O3	1.600 (3)	Cr2—O4	1.771 (3)
Cr1—O1	1.605 (3)	Cu1—N3	2.000 (3)
Cr1—O2	1.607 (3)	Cu1—N1	2.005 (3)
Cr1—O4	1.777 (3)	Cu1—O5	2.554 (3)
Cr2—O7	1.601 (3)	Cu2—N7	2.000 (3)
Cr2—O5	1.607 (3)	Cu2—N5	2.002 (3)
Cr2—O6	1.607 (3)	Cu2—O2	2.578 (3)
O3—Cr1—O1	108.03 (17)	O6—Cr2—O4	110.13 (16)
O3—Cr1—O2	111.74 (17)	N3—Cu1—N1	91.83 (13)
O1—Cr1—O2	109.85 (17)	N3—Cu1—O5	90.54 (12)
O3—Cr1—O4	110.30 (17)	N1—Cu1—O5	85.49 (12)
O1—Cr1—O4	110.22 (15)	N7—Cu2—N5	91.54 (14)
O2—Cr1—O4	106.72 (15)	N7—Cu2—O2	84.86 (12)
O7—Cr2—O5	110.25 (18)	N5—Cu2—O2	90.44 (12)
O7—Cr2—O6	108.84 (17)	Cr1—O2—Cu2	146.05 (17)
O5—Cr2—O6	112.08 (17)	Cr2—O4—Cr1	131.32 (18)
O7—Cr2—O4	109.12 (16)	Cr2—O5—Cu1	154.00 (18)
O5—Cr2—O4	106.37 (16)		

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *SHELXS97* (Sheldrick, 1997b). Program(s) used to solve structure: *SHELXS97*. Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *SHELXL97*.

We thank the Anhui Provincial Foundation of Natural Science Research and the National Natural Science Foundation of China for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1190). Services for accessing these data are described at the back of the journal.

References

- Akhtar, F., Goodgame, D. M. L., Goodgame, M., Rayner-Canham, G. W. & Skapski, A. C. (1968). *Chem. Commun.* pp. 1389–1390.
Bacon, G. E. & Curry, N. A. (1962). *Proc. R. Soc. London Ser. A*, **266**, 95.

- Ballester, J., Parker, O. J. & Breneman, G. L. (1993). *Acta Cryst.* **C49**, 1421–1424.
Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
Dave, B. C. & Czernuszewicz, R. S. (1994). *Inorg. Chem.* **33**, 847–848.
Fransson, G. & Lundberg, B. K. S. (1972). *Acta Chem. Scand.* **26**, 3969–3979.
Ivarsson, G. (1973). *Acta Chem. Scand.* **27**, 3523–3530.
Jannin, M., Puget, R., de Brauer, C. & Perret, R. (1993). *Acta Cryst.* **C49**, 749–751.
McFadden, D. L., McPhail, A. T., Garner, C. D. & Mabbs, F. E. (1976). *J. Chem. Soc. Dalton Trans.* pp. 47–52.
Molecular Structure Corporation (1994). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Munno, G. de, Julve, M., Nicolo, F., Lloret, F., Gaus, J., Ruiz, R. & Sinn, E. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 613–615.
Parker, O. J. & Breneman, G. L. (1995). *Acta Cryst.* **C51**, 1097–1099.
Sheldrick, G. M. (1997a). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997b). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.2 for MS-DOS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Su, C. C., Liu, Y. L., Liu, S. J. & Chang, T. H. (1993). *Polyhedron*, **12**, 2687–2696.
Vreugdenhil, W., Birker, P. J. M. W. L., Hoedt, R. W. M. ten, Verschoor, G. C. & Reedijk, J. (1984). *J. Chem. Soc. Dalton Trans.* pp. 429–432.

Acta Cryst. (1998), **C54**, 1804–1807

Bis[tris(1,2-ethandiamin)cadmium]-tetraiodocadm- diiodide

CARSTEN WIECZORREK UND KARL-FRIEDRICH TEBBE

*Institut für Anorganische Chemie, Universität zu Köln,
Greinstraße 6, D-50939 Köln, Germany. E-mail:
tebbe@rrz.uni-koeln.de*

(Eingegangen am 26. Februar 1998; angenommen am 23. Juni 1998)

Abstract

The title compound, bis[tris(1,2-ethanediamine-*N,N'*)-cadmium] tetraiodocadm-ate diiodide, [Cd(C₂H₈N₂)₃]₂·[CdI₄]₂, contains the nearly octahedral [Cd(en)₃]²⁺ cation in both enantiomeric forms, the nearly tetrahedral [CdI₄]²⁻ anion and I⁻ anions. The geometries of the complex ions are as expected, *e.g.* $d(\text{Cd—N}) = 2,348(5)$, $2,364(5)$ and $2,418(5)$ Å, and $d(\text{Cd—I}) = 2,7867(4)$ Å.

Kommentar

Wir interessieren uns seit langem für Strukturen von Polyiodiden komplexer Kationen (Tebbe, 1977),