Les longueurs et angles de liaison des coordinats oxalato sont dans le Tableau 2. La liaison C—O est longue (moyenne: 1,29 Å) lorsqu'il y a coordination avec le ruthénium alors qu'elle n'est que de 1,21 Å dans le cas contraire. L'angle O—C—C vaut en moyenne 120,1° lorsque l'oxygène n'est pas coordiné, alors qu'il mesure seulement 114,8° lorsque l'oxygène coordine le ruthénium par formation de cycles de chélation. En conséquence, l'angle O—C—O est grand: 125,1°.

Concernant l'entourage des atomes de potassium, les plus courtes distances entre atomes de potassium et d'oxygène, sont voisines de la somme des rayons ioniques (2,73 Å) (Tableau 2).

Les molécules d'eau sont groupées dans des tunnels parallèles à l'axe [100].

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μ-Dichromato(VI)-*O,O′*-bis(ethylenediamine)copper(II): Structure, Thermochemistry and Magnetic Susceptibility

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Abstract. $[Cu\{Cr_2O_7\}(C_2H_8N_2)_2]$, $M_r = 399{\cdot}73$, monoclinic, $C2/c$, $a = 16{\cdot}166\ (2)$, $b = 5{\cdot}6830\ (9)$, $c = 15{\cdot}106\ (2)$ Å, $\beta = 109{\cdot}45\ (1)°$, $V = 1309$ Å^3, $D_m = 2{\cdot}032\ (3)$, $D_x = 2{\cdot}028$ g cm^{-3}, $Z = 4$ (Cu at $\bar{1}$, O on 2), λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 32·38 cm^{-1}, $F(000) = 804$, $T = 291$ K, final refinement on F [1321 data with $F_o^2 > 3\sigma(F_o^2)$, $2\theta_{\max} = 60{\cdot}0°$]: $R = 0{\cdot}036$, $wR = 0{\cdot}040$. The copper is tetragonally coordinated, ethylenediamine forming the square plane [Cu—N 2·015 (4), 2·008 (4) Å] and $Cr_2O_7^{2-}$ occupying the axial sites [Cu—O 2·525 (3) Å] giving rise to infinite —Cu—O—Cr—O—Cr—O—Cu— chains parallel to **c**. Magnetic-susceptibility data in the range 1·7 to 80 K are well fit by the Curie–Weiss expression $\chi_m = 0{\cdot}4122/(T+0{\cdot}198)$, indicating little coupling of electron spins. On heating, the compound loses ethylenediamine and oxygen in three well defined steps to yield polycrystalline $CuCr_2O_4$ and Cr_2O_3. The intermediates, empirical formulae $Cu(en)Cr_2O_7$ and $CuCr_2O_5$, are X-ray amorphous.

Introduction. As part of our study of the thermal decomposition of different copper–chromium coordination compounds we have prepared crystals of the title compound, (μ-Cr_2O_7-*O,O′*)Cu(en)$_2$, (I), and examined their magnetic and thermal decomposition behaviour. This complex was first obtained by Parravano & Pasta (1907).

Experimental. After saturation of a chromic acid solution with copper hydroxide carbonate, $Cu_2(OH)_2CO_3$, a stoichiometric amount of ethylenediamine was added. The precipitation starts slowly with formation of dirty-yellow to browish very thin lamellae with a metallic, gold-like lustre. By recrystallization from hot water larger, more prismatic crystals of identical colour and texture could be grown for structure determination. They were washed with cold water, alcohol and ether, and dried in air.

Preliminary precession and Weissenberg photographs established symmetry and systematic absences consistent with the monoclinic space groups *Cc* or *C*2/*c*. Data collection: Picker FACS-I diffractometer

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using the Lenhert (1975) system; unit-cell constants and crystal orientation from least-squares refinement of 16 automatically centred reflections in the range $32\cdot32 < 2\theta < 36\cdot37°$ with graphite-monochromated Mo $K\alpha_1$ radiation ($\lambda = 0\cdot70926$ Å); scan parameters: θ–2θ scans from 1·0° below $K\alpha_1$ to 0·85° above $K\alpha_2$, 2° min^{-1} in 2θ with rescan option; h (–22 to 18), k (–7 to 0), l (0 to 21); 2149 data ($h+k = 2n+1$ not measured); no significant variation of six standard reflections; Lorentz, polarization and absorption corrections: crystal 0·19 × 0·16 × 0·06 mm, transmission coefficients 0·599–0·827; all calculations with a local IBM3033 modification of the Northwestern University Crystallographic Computing Library (Waters & Ibers, 1977); neutral-atom scattering factors and anomalous-dispersion corrections for Cu and Cr taken from *International Tables for X-ray Crystallography* (1974). The structure was solved using *MULTAN*78 in space group *Cc*. Twofold symmetry of the $Cr_2O_7^{2-}$ ion and an inversion centre at the $Cu(en)_2^{2+}$ group became apparent and remaining calculations were carried out in *C*2/*c*. All hydrogen atoms were located and assigned a temperature factor of $B = 2\cdot5$ Å^2, and in subsequent cycles their positional parameters were varied. All other atoms were refined anisotropically. A parameter for secondary extinction was refined [final value $9\cdot3\,(5) \times 10^{-7}$], giving a total of 109 variable parameters. At convergence (max. shift/e.s.d. < 0·5) the values for R and wR (on F) were 0·036 and 0·040. The weighting scheme, $1/\sigma^2$ where $\sigma^2 = \sigma^2(\text{counting}) + (0\cdot04F_o^2)^2$, showed no dependency of the minimized function upon $|F_o|$ or $(\sin\theta)/\lambda$. The final difference Fourier map was flat and featureless with a highest peak of 0·52 e Å^{-3} (*cf.* H atoms 0·70–0·49 e Å^{-3}) in the vicinity of the atom with the greatest thermal motion, O(3).*

Magnetic-susceptibility data in the range 1·7 to 300 K were measured using a vibrating-sample susceptometer, and corrected for diamagnetism. Differential thermal analyses and thermogravimetric analyses were made using a Stanton–Redcroft STA-780 and a Perkin–Elmer TGA-7, using small samples (< 5 mg), as with larger samples crystals had a propensity to leap out of the pan. A Guinier–Lenné camera recorded diffraction patterns as a function of temperature and time.

Discussion. Final atomic coordinates are given in Table 1, and bond distances and angles appear in Table 2. The copper complex and the atom labelling scheme are illustrated in Fig. 1 and the unit-cell diagram is in Fig. 2.

Table 1. *Final positional parameters for* $Cu(en)_2Cr_2O_7$

Estimated standard deviations in the least significant figures are given in parentheses in this and subsequent tables. The isotropic temperature factors for non-hydrogen atoms are from the last cycle of isotropic refinement made after the absorption correction.

	x	*y*	*z*	*B*(Å^2)
Cu	0	½	½	1·87 (3)
Cr	0·08481 (4)	0·19086 (11)	0·34290 (4)	2·22 (3)
O(1)	0	0·3313 (7)	¼	2·6 (2)
O(2)	0·04716 (19)	0·1442 (5)	0·42872 (18)	2·8 (1)
O(3)	0·1125 (2)	–0·0524 (6)	0·3077 (2)	4·3 (2)
O(4)	0·16583 (19)	0·3717 (6)	0·3754 (2)	3·8 (1)
N(1)	0·1131 (2)	0·6717 (7)	0·5159 (2)	2·6 (1)
N(2)	0·0657 (2)	0·3546 (6)	0·6248 (2)	2·5 (1)
C(1)	0·1680 (3)	0·6528 (9)	0·6161 (3)	3·4 (2)
C(2)	0·1601 (3)	0·4060 (10)	0·6475 (3)	3·3 (2)
H(1*A*)	0·104 (4)	0·807 (9)	0·495 (4)	2·5
H(1*B*)	0·134 (3)	0·615 (10)	0·479 (4)	2·5
H(2*A*)	0·052 (3)	0·411 (9)	0·670 (4)	2·5
H(2*B*)	0·055 (4)	0·228 (9)	0·627 (4)	2·5
H(3*A*)	0·149 (3)	0·761 (9)	0·653 (4)	2·5
H(3*B*)	0·224 (4)	0·685 (9)	0·619 (4)	2·5
H(4*A*)	0·189 (3)	0·417 (9)	0·708 (4)	2·5
H(4*B*)	0·183 (3)	0·285 (9)	0·612 (4)	2·5

Table 2. *Bond distances* (Å) *and angles* (°)

Cu–N(1)	2·015 (4)	Cr–O(1)	1·790 (2)
Cu–N(2)	2·008 (4)	Cr–O(2)	1·627 (3)
Cu–O(2)	2·525 (3)	Cr–O(3)	1·597 (3)
N(1)–C(1)	1·482 (5)	Cr–O(4)	1·608 (3)
N(2)–C(2)	1·479 (6)		
C(1)–C(2)	1·499 (7)		
N(1)–Cu–N(1′)	180	O(2)–Cr–O(3)	110·2 (2)
N(1)–Cu–N(2)	85·0 (1)	O(2)–Cr–O(4)	110·1 (1)
N(1)–Cu–N(2′)	95·0 (1)	O(3)–Cr–O(4)	111·4 (2)
O(2)–Cu–N(1)	92·7 (1)	Cr–O(1)–Cr′	127·0 (2)
O(2)–Cu–N(2)	86·0 (1)	Cu–O(2)–Cr	117·1 (1)
O(2)–Cu–O(2′)	180	Cu–N(1)–C(1)	107·3 (3)
O(1)–Cr–O(2)	107·8 (1)	Cu–N(2)–C(2)	108·6 (3)
O(1)–Cr–O(3)	110·6 (2)	N(1)–C(1)–C(2)	107·9 (4)
O(1)–Cr–O(4)	106·7 (2)	N(2)–C(2)–C(1)	107·5 (4)

The crystal structure is generally similar to that of bis(1,2-propanediamine)copper(II) dichromate (Uggla, Visti, Klinga & Näsäkkälä, 1970) with square-planar copper ions bridged by dichromate ions to form infinite –Cu–O–Cr–O–Cr–O–Cu– chains. In complex (I) the oxygen atom bridging the two chromium atoms sits on the twofold axis, whereas in the 1,2-propanediamine species it sits on a centre of inversion leading to an unprecedented linear Cr–O–Cr group with an anomalously short Cr–O separation of 1·57 (1) Å. In the former complex O–Cr–O bond angles lie in the range 90 to 117 (2)°. In our complex and other dichromate salts (*e.g.* $K_2Cr_2O_7$, Brandon & Brown, 1968) the CrO_4 moieties form nearly regular tetrahedra. In view of the imprecision ($R = 0\cdot136$) and the limited data available on the 1,2-propanediamine complex we believe that quantitative metrical details on this structure should be treated with caution.

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* Tables of structure factor amplitudes $10|F_o|$ *vs* $10|F_c|$, anisotropic thermal parameters and Fig. 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42819 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The only other copper(II) dichromate(VI) complex of which we are aware is the diaquacopper(II) dichromate(VI) complex (Blum & Guitel, 1980). No symmetry is imposed and bond parameters for the dichromate ion are closely similar to (I). The crystal structure, by contrast, is a three-dimensional network.

The conformation of the chains in (I) is to some extent dictated by hydrogen bonds within the chains [N(1)···O(4) 3·056 (5), H(1*B*)···O(4) 2·27 (5) Å, N(1)–H(1*B*)···O(4) 164 (5)°; N(2)···O(1) 3·038 (4), H(2*A*)···O(1) 2·24 (5) Å, N(2)–H(2*A*)···O(1) 159 (5)°]. The chains themselves are linked by one hydrogen bond [N(1)···O(2) 3·025 (5), H(1*A*)···O(2) 2·21 (5) Å, N(1)–H(1*A*)···O(2) 167 (5)°]. There are in addition two weak interchain interactions between methylene hydrogen atoms and oxygen atoms [*e.g.* C(1)···O(3) 3·395 (6), H(3*B*)···O(3) 2·61 (5) Å, C(1)–H(3*B*)···O(3) 143 (5)°; C(2)···O(4) 3·342 (6), H(4*B*)···O(4) 2·56 (5) Å, C(2)–H(4*B*)···O(4) 135 (5)°]. Otherwise the chains are well isolated.

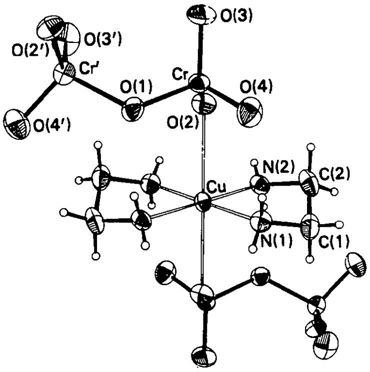

Fig. 1. *ORTEP* diagram (Johnson, 1965) of the copper ion and its ligands. Thermal ellipsoids are drawn at the 50% probability level, with hydrogen atoms shown artificially small.

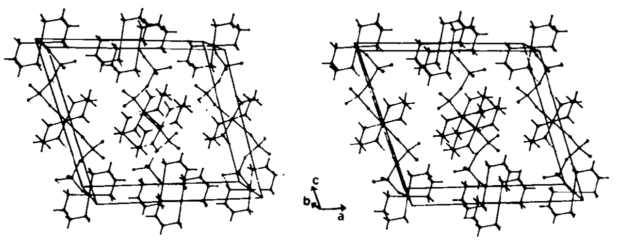

Fig. 2. Unit-cell stereodiagram showing the linking of the $\mathrm{Cu(en)_2^{2+}}$ ions with the $\mathrm{Cr_2O_7^{2-}}$ ions to form infinite chains. Hydrogen bonds between H(N) and O atoms are shown with dotted lines. For clarity, intrachain links are shown only on the outer two chains, interchain links on the inner chains. Intrachain hydrogen bonds on the inner chains may be envisaged by application of the centring operation to the outer chains.

In view of the distinctive colour of the material the magnetic susceptibility was measured. The copper centres are effectively uncoupled, either antiferro- or ferromagnetically. The data and Curie–Weiss-law fit are shown in Fig. 3. The value of θ in the low-temperature region (1·7–80 K) is suggestive of very weak antiferromagnetic coupling. The value of g derived (2·096) is reasonable for $\mathrm{Cu^{2+}}$.

The combined differential thermal analysis and thermogravimetric measurements are illustrated in Fig. 4 (deposited). The following sequence of steps is consistent with the observed weights of the intermediate materials, expressed as a percentage of the original weight (the calculated percentages are in parentheses):

$$\begin{array}{ccc} \mathrm{Cu(en)_2Cr_2O_7} \xrightarrow[-\mathrm{en}]{483\ \mathrm{K}} & \mathrm{Cu(en)Cr_2O_7} & \xrightarrow[-(\mathrm{en}+\mathrm{O_2})]{588\ \mathrm{K}} \\ 100\% & 83{\cdot}3\ (85{\cdot}0) & \end{array}$$

$$\begin{array}{cc} \text{‘}\mathrm{CuCr_2O_5}\text{’} \xrightarrow[-\frac{1}{2}\mathrm{O_2}]{728\ \mathrm{K}} & \mathrm{CuCr_2O_4} \\ 62{\cdot}1\ (61{\cdot}9) & 57{\cdot}0\ (57{\cdot}9) \end{array}$$

Note that the egress of ethylenediamine could not be observed by mass spectrometry, presumably owing to decomposition. The two intermediate materials are

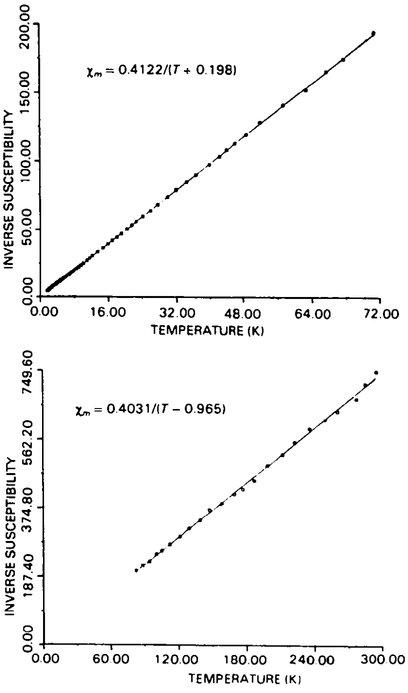

Fig. 3. Magnetic-susceptibility data for $\mathrm{Cu(en)_2Cr_2O_7}$. The solid line is the calculated fit to the experimental data.

amorphous to X-rays. For the final material, empirical formula $CuCr_2O_4$, the entire diffraction pattern could be interpreted in terms of diffraction from cubic $CuCr_2O_4$ (ASTM 26–509) plus Cr_2O_3 (minor component). The CuO needed to complement the Cr_2O_3 could not be identified in the X-ray powder diffraction pattern.

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Etude Structurale de l'(Hexaméthylphosphoramide)dioxobis(trifluoro-1 phényl-4 butanedionato-2,4)uranium(VI)

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Abstract. $[UO_2(C_{10}H_6F_3O_2)_2(C_6H_{18}N_3OP)]$, $M_r =$ 879·53, monoclinic, $P2_1/n$, $a = 9{\cdot}330\,(3)$, $b = 29{\cdot}332\,(10)$, $c = 12{\cdot}125\,(2)$ Å, $\beta = 99{\cdot}76\,(2)°$, $V = 3270$ Å^3, $Z = 4$, $D_x = 1{\cdot}786$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 4{\cdot}830$ mm^{-1}, $F(000) = 1696$, $T = 295$ K, $R = 0{\cdot}047$ for 2700 independent reflections. The molecular structure consists of a linear UO_2^{2+} ion [U—O 1·760 (12), 1·778 (13) Å; O—U—O 177·4 (6)°] surrounded in its equatorial plane by five oxygen atoms from two bidentate β diketones [U—O 2·396 (11), 2·362 (13), 2·403 (14), 2·384 (12) Å] and one monodentate oxophosphine ligand [U—O 2·309 (13) Å].

Introduction. Les structures d'un bon nombre de complexes de β dicétones et d'uranyle sont connues, un troisième ligande donneur d'oxygène ou d'azote venant compléter la coordinence cinq de l'uranyle. Ces structures permettent de déterminer l'influence de la nature et de l'encombrement stérique du troisième ligande sur la déformation du pentagone autour de l'uranyle, ainsi que sur la linéarité de l'ion UO_2. En effet, l'adduit peut être une molécule simple comme H_2O (Frasson, Bombieri & Panattoni, 1966) et NO_3 (Graziani, Marangoni, Paolucci & Forsellini, 1978), un amide, par exemple le diméthylformamide (Charpin, Lance, Nierlich & Vigner, 1985), une molécule cyclique comme la pyridine (Alcock, Flanders & Brown, 1984), une cétoamine présentant des liaisons hydrogène intramoléculaires (Rodgers, Nassimbeni, Pauptit, Orpen & Haigh, 1977). Nous décrivons la structure d'un complexe d'uranyle avec la β dicétone substituée dite tfba (trifluorobenzoylacétone) et l'hexaméthylphosphoramide (hmpa).

Partie expérimentale. Cristal de couleur jaune et de dimensions 400 × 300 × 200 µm; diffractomètre automatique Enraf–Nonius CAD-4; monochromateur de graphite; paramètres de maille affinés à partir de 25 réflexions indépendantes; correction d'absorption empirique selon Walker & Stuart (1983); $-12 < h < 12$, $0 < k < 34$, $0 < l < 14$; $2° < \theta < 25°$; trois réflexions de contrôle d'intensité mesurées toutes les heures avec une perte moyenne de 1% en 52 h; intensités corrigées des facteurs de Lorentz et de polarisation; 6009 réflexions mesurées dont 2700 indépendantes avec $I > 3\sigma(I)$; structure résolue par la méthode de l'atome lourd; affinements basés sur F en utilisant une matrice totale; facteurs de diffusion des atomes neutres des *International Tables for X-ray Crystallography* (1974) corrigés de f' et f'' ($f'_U = -10{,}673$, $f''_U = 9{,}654$); agitation thermique anisotrope pour U, F, P et O; atomes d'H introduits en position calculée (C—H = 0,95 Å, $B = 5$ Å^2) non affinés mais contraints de suivre leurs atomes de carbone; $R_F = 0{,}047$; wR