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Structures of Mercury Dichloride–Dipotassium Dichromate (1/1), HgCl₂.K₂Cr₂O₇, and Mercury Dichloride–Diammonium Dichromate (1/1), HgCl₂.(NH₄)₂Cr₂O₇

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Abstract. $HgCl_2.K_2Cr_2O_7$: $M_r = 565.69$, $P2_1/n$, $a = 12.372$ (8), $b = 10.438$ (8), $c = 8.191$ (5) Å, $\beta = 92.32$ (5)°, $V = 1056.9$ Å^3, $Z = 4$, $D_x = 3.555$ Mg m^{-3}, Ag $K\alpha$, $\lambda = 0.5608$ Å, $\mu = 98.76$ cm^{-1}, $F(000) = 1024$, room temperature, $R = 0.042$ for 1470 independent reflexions. $HgCl_2.(NH_4)_2Cr_2O_7$: $M_r = 523.56$, $P2_1/a$, $a = 14.891$ (5), $b = 7.604$ (5), $c = 9.620$ (6) Å, $\beta = 96.02$ (5)°, $V = 1083.2$ Å^3, $Z = 4$, $D_x = 3.210$ Mg m^{-3}, Ag $K\alpha$, $\lambda = 0.5608$ Å, $\mu = 92.64$ cm^{-1}, $F(000) = 960$, room temperature, $R = 0.032$ for 1369 independent reflexions. The structures comprise Cr_2O_7 groups which show no unusual features. Linkages of the mercury polyhedra are quite different in the two structures. In the ammonium salt, finite centrosymmetrical $Hg_2Cl_4O_8$ groups are present, located on the (110) planes, while infinite $HgCl_2O_2$ chains, running along **c**, exist in the potassium salt.

Introduction. These two adduct compounds were described as early as 1859 (Groth) but up to now never investigated from a structural point of view. This work is part of the investigation of condensed chromic anions: $(Cr_nO_{3n+1})^{2-}$ (Durif & Averbuch-Pouchot, 1979; Blum & Tran Qui, 1979; Blum, Averbuch-Pouchot & Guitel, 1979; Blum, 1979).

Crystals of these two compounds are readily prepared by slow evaporation at room temperature of solutions containing mercury chloride and alkali dichromates in an equimolar ratio.

Experimental. $HgCl_2.K_2Cr_2O_7$: Cube-shaped crystal $0.15 \times 0.17 \times 0.17$ mm, Philips PW 1100 diffractometer, graphite-monochromated Ag $K\alpha$ radiation, ω scan, scan width $1.2°$, scan speed $0.02°$ s^{-1}, total background measurement 20 s, 25 reflexions used for measuring lattice parameters, no absorption correction, $2\theta_{max} = 48°$; $h_{max} = 17$, $k_{max} = 15$, $l_{max} = 11$; intensity-reference reflexions ($\overline{9}32$ and $9\overline{3}2$) showed no appreciable variation; 1895 independent reflexions, 1470 with $F_o > 2 \sigma_F$; structure solved using classical methods: study of a three-dimensional Patterson function, followed by successive Fourier syntheses; $\sum w \Delta F^2$ minimized; atomic coordinates, anisotropic thermal parameters and a scale factor refined; final $R = 0.042$, $R_w = 0.047$, $S = 4.248$; unit weights; max. Δ/σ 0.0 except for the scale factor (0.03) for the final refinement cycle; max./min. heights in final difference Fourier map ± 4.8 e Å^{-3}; correction for extinction 0.19×10^{-7}; atomic scattering factors and f' and f'' values from *International Tables for X-ray Crystallography* (1974); Enraf–Nonius Structure Determination Package (Frenz, 1980).

$HgCl_2.(NH_4)_2Cr_2O_7$: Approximately cube-shaped crystal $0.18 \times 0.17 \times 0.15$, Philips PW 1100 diffractometer, graphite-monochromated Ag $K\alpha$ radiation, ω scan, scan width $1.30°$, scan speed $0.02°$ s^{-1}, 18 reflexions used for measuring lattice parameters, no absorption correction, $2\theta_{max} = 50°$, $h_{max} = 22$, $k_{max} = 11$, $l_{max} = 14$; intensity-reference reflexions ($2\overline{4}2$ and $\overline{2}4\overline{2}$) showed no appreciable variation; 2484 independent reflexions, 1369 with $F_o > 3 \sigma_F$; structure solved using classical methods: study of a three-dimensional

Table 1. *Final atomic coordinates for* $HgCl_2.K_2Cr_2O_7$

$$B_{eq} = \tfrac{4}{3}\Sigma\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Hg(1)	0	0	0	2·00 (2)
Hg(2)	0	0	0·5	2·06 (2)
Cr(1)	0·3864 (2)	0·1671 (2)	0·0437 (2)	1·38 (5)
Cr(2)	0·3897 (2)	0·1636 (2)	0·4537 (2)	1·34 (5)
K(1)	0·1586 (2)	0·3249 (3)	0·7485 (4)	1·90 (7)
K(2)	0·1301 (2)	0·3489 (3)	0·2515 (4)	2·19 (8)
Cl(1)	0·1381 (3)	0·0219 (4)	0·2034 (4)	2·19 (9)
Cl(2)	0·1377 (3)	0·0187 (4)	0·7034 (4)	2·19 (9)
O(L)	0·4041 (7)	0·116 (1)	0·249 (1)	2·2 (3)
O(E11)	−0·0046 (10)	0·255 (1)	0·494 (2)	2·9 (3)
O(E12)	0·2832 (9)	0·261 (1)	0·021 (1)	2·4 (3)
O(E13)	0·3720 (12)	0·036 (1)	0·936 (2)	3·7 (4)
O(E21)	0·4958 (12)	0·248 (1)	0·507 (2)	3·4 (3)
O(E22)	0·3891 (10)	0·035 (1)	0·559 (1)	3·0 (3)
O(E23)	0·2809 (9)	0·243 (1)	0·474 (1)	3·5 (3)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *in the* Cr_2O_7 *group of* $HgCl_2.K_2Cr_2O_7$

Cr(1)O₄tetrahedron

Cr(1)	O(L)	O(E11)	O(E12)	O(E13)
O(L)	1·770 (5)	2·765 (9)	2·796 (7)	2·708 (8)
O(E11)	108·3 (3)	1·640 (7)	2·649 (10)	2·692 (9)
O(E12)	111·3 (2)	108·9 (4)	1·617 (6)	2·697 (9)
O(E13)	105·4 (3)	110·7 (4)	112·2 (3)	1·633 (6)

Cr(2)O₄tetrahedron

Cr(2)	O(L)	O(E21)	O(E22)	O(E23)
O(L)	1·766 (5)	2·732 (9)	2·689 (8)	2·778 (8)
O(E21)	107·3 (3)	1·623 (7)	2·623 (9)	2·662 (11)
O(E22)	106·2 (3)	109·3 (4)	1·594 (6)	2·633 (8)
O(E23)	111·2 (3)	111·5 (4)	111·2 (3)	1·598 (6)

Cr(1)–O(L)–Cr(2)	143·4 (3)
Cr(1)–Cr(2)	3·357 (1)

Patterson function, followed by successive Fourier syntheses; $\Sigma w\Delta F^2$ minimized; H atoms not located; atomic coordinates, anisotropic thermal parameters and a scale factor refined; final $R = 0.032$, $R_w = 0.040$, $S = 3.855$; unit weights; 8 $\Delta/\sigma \le 0.02$, others 0·00 for final refinement cycle; max./min. heights in final difference Fourier map ± 1.3 e Å⁻³; correction for secondary extinction 0·76 × 10⁻⁷; atomic scattering factors and f' and f'' values from *International Tables for X-ray Crystallography* (1974); *Enraf–Nonius Structure Determination Package* (Frenz, 1980).

Discussion. HgCl₂.K₂Cr₂O₇. Table 1 gives the final atomic coordinates and equivalent isotropic thermal parameters.* Fig. 1 gives a projection of the atomic arrangement along **b**, and Fig. 2 a description of the cation coordination. In this structure all the Cr₂O₇ groups are approximately parallel to **c**. They do not present any significant particular characteristics and their geometry is described in Table 2.

The Hg atoms located on symmetry centres are surrounded by two oxygen atoms [Hg–O = 2·650 (7) Å] and four chlorine atoms: two at short distances [Hg–Cl = 2·346 (2) Å] and two others at longer ones [Hg–Cl = 3·031 (2) Å]. If one takes into account these long Hg–Cl distances, the Hg co-ordination polyhedra link so as to form (HgCl₂O₂)ₓ chains running along **c**. These chains are alternately at $x \simeq 0.0$ and $x \simeq 0.50$, and connected by the potassium coordination polyhedra. Table 3 gives the interatomic distances for the Hg and K atoms.

HgCl₂.(NH₄)₂Cr₂O₇: Table 4 gives the final atomic coordinates and equivalent isotropic thermal parameters.* Fig. 3 gives a projection of the atomic arrangement along the *b* axis. While nothing unusual is observed in the geometrical configuration of the Cr₂O₇
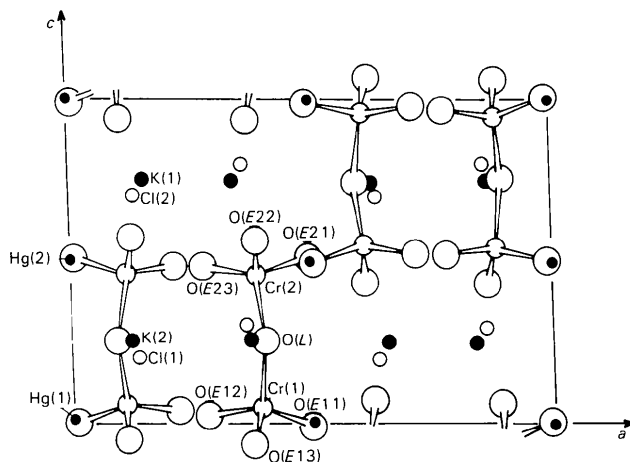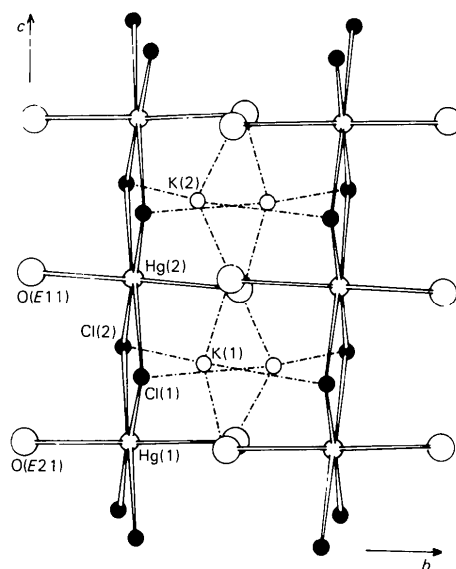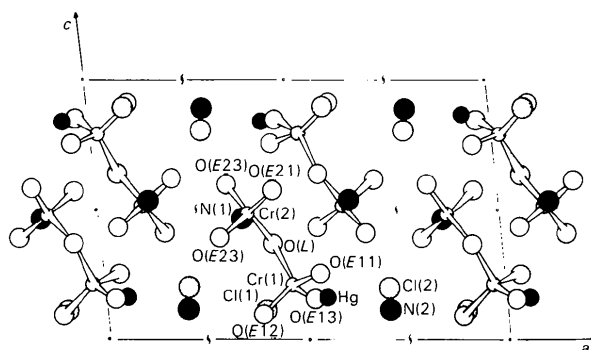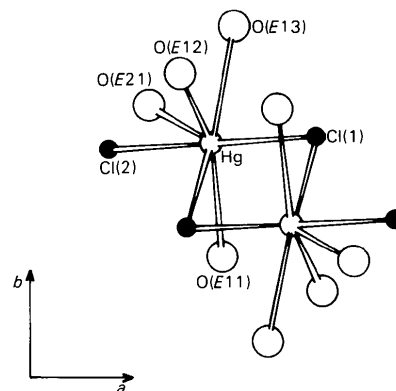
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39195 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Main interatomic distances* (Å) *in the associated cation polyhedra in* $HgCl_2.K_2Cr_2O_7$

Hg(1) coordination		Hg(2) coordination	
Hg(1)–Cl(1)	2·349 (2) (×2)	Hg(2)–Cl(1)	3·034 (2) (×2)
Hg(1)–Cl(2)	3·029 (2) (×2)	Hg(2)–Cl(2)	2·343 (2) (×2)
Hg(1)–O(E21)	2·636 (7) (×2)	Hg(2)–O(E11)	2·663 (7) (×2)

K(1) coordination			
K(1)–O(L)	3·209 (5)	K(1)–O(E21)	3·076 (9)
K(1)–O(E11)	2·935 (8)	K(1)–O(E22)	2·780 (6)
K(1)–O(E12)	2·740 (6)	K(1)–O(E23)	2·891 (6)
K(1)–O(E13)	2·691 (6)	K(1)–Cl(2)	3·227 (3)
		K(1)–Cl(2)	3·243 (3)

K(2) coordination			
K(2)–O(L)	2·817 (6)	K(2)–O(E21)	2·741 (8)
K(2)–O(E11)	2·819 (7)	K(2)–O(E22)	3·203 (7)
K(2)–O(E12)	2·879 (6)	K(2)–O(E23)	2·779 (6)
K(2)–O(E13)	3·222 (7)	K(2)–Cl(1)	3·437 (3)
		K(2)–Cl(1)	3·397 (3)

Table 4. *Final atomic coordinates for* $HgCl_2.(NH_4)_2Cr_2O_7$

$$B_{eq} = \tfrac{4}{3}\Sigma\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Hg	0·06039 (3)	0·11953 (8)	0·16122 (6)	2·23 (1)
Cr(1)	0·0256 (1)	0·3770 (3)	0·7905 (2)	1·78 (4)
Cr(2)	0·1220 (1)	0·3099 (3)	0·5191 (2)	1·77 (5)
Cl(1)	0·4042 (2)	0·3763 (6)	0·1119 (4)	2·87 (8)
Cl(2)	0·2163 (2)	0·1011 (6)	0·1992 (4)	3·09 (9)
O(L)	0·0650 (6)	0·448 (1)	0·6314 (8)	2·3 (2)
O(E11)	0·4555 (7)	0·288 (1)	0·7519 (10)	3·1 (3)
O(E12)	0·1089 (6)	0·325 (1)	0·9009 (10)	2·9 (3)
O(E13)	0·0265 (7)	0·464 (1)	0·1490 (12)	3·4 (3)
O(E21)	0·0513 (6)	0·176 (1)	0·4333 (9)	2·7 (3)
O(E22)	0·1690 (6)	0·435 (1)	0·4145 (10)	3·1 (3)
O(E23)	0·1987 (7)	0·197 (1)	0·6118 (11)	3·4 (3)
N(1)	0·3639 (8)	0·311 (2)	0·467 (1)	3·0 (3)
N(2)	0·2926 (7)	0·102 (2)	0·877 (1)	2·7 (3)

Table 5. *Main interatomic distances (Å) and bond angles (°) in the* Cr_2O_7 *group of* $HgCl_2.(NH_4)_2Cr_2O_7$

$Cr(1)O_4$tetrahedron

Cr(1)	O(L)	O(E11)	O(E12)	O(E13)
O(L)	1·780 (4)	2·757 (7)	2·769 (7)	2·715 (7)
O(E11)	107·1 (3)	1·647 (5)	2·705 (7)	2·641 (8)
O(E12)	110·1 (3)	113·1 (3)	1·596 (5)	2·581 (8)
O(E13)	107·7 (3)	109·9 (3)	108·8 (3)	1·579 (5)

$Cr(2)O_4$tetrahedron

Cr(2)	O(L)	O(E21)	O(E22)	O(E23)
O(L)	1·782 (4)	2·806 (7)	2·727 (6)	2·776 (7)
O(E21)	110·7 (2)	1·628 (5)	2·655 (7)	2·646 (7)
O(E22)	107·5 (3)	110·9 (3)	1·597 (5)	2·623 (8)
O(E23)	109·3 (2)	109·1 (3)	109·3 (3)	1·619 (5)

Cr(1)–O(L)–Cr(2)	124·4 (3)
Cr(1)–Cr(2)	3·151 (1)

Table 6. *Main interatomic distances (Å) in the associated cation polyhedra in* $HgCl_2.(NH_4)_2Cr_2O_7$

Hg coordination

Hg–Cl(1)	3·300 (2)	Hg–O(E11)	2·677 (5)
Hg–Cl(1)	2·325 (2)	Hg–O(E12)	3·100 (5)
Hg–Cl(2)	2·316 (2)	Hg–O(E13)	2·669 (5)
		Hg–O(E21)	2·669 (5)

$N(1)H_4$ coordination

N(1)–O(L)	3·140 (8)	N(1)–O(E22)	3·041 (8)
N(1)–O(E11)	2·938 (8)	N(1)–O(E22)	3·141 (9)
N(1)–O(E21)	3·152 (8)	N(1)–O(E23)	3·077 (9)
N(1)–O(E21)	2·845 (7)	N(1)–O(E23)	3·147 (9)
N(1)–Cl(1)	3·562 (7)	N(1)–Cl(2)	3·580 (7)

$N(2)H_4$ coordination

N(2)–O(E11)	3·153 (8)	N(2)–O(E13)	2·926 (8)
N(2)–O(E12)	3·247 (8)	N(2)–O(E22)	3·187 (8)
N(2)–O(E12)	3·238 (8)	N(2)–O(E23)	2·873 (8)
N(2)–Cl(1)	3·378 (7)	N(2)–Cl(2)	3·409 (6)
N(2)–Cl(1)	3·408 (6)		

Fig. 2. $(HgCl_2O_2)_x$ chains and their linkage by K atoms in projection along the a axis.

Fig. 3. Projection of $HgCl_2.(NH_4)_2Cr_2O_7$ along the b axis.

Fig. 1. Projection of $HgCl_2.K_2Cr_2O_7$ along the b axis.

Fig. 4. Projection of an $Hg_2Cl_4O_8$ group along the c axis.

groups (Table 5) the behaviour of the mercury-atom linkage is to be noted. Each mercury atom is surrounded by four oxygen and three chlorine atoms. These polyhedra are grouped in pairs so as to form finite centrosymmetrical $Hg_2Cl_4O_8$ groups located in the (110) planes. The common edge between these two polyhedra is made by two Cl(1) atoms. Fig. 4 reports the configuration of one of these groups in the projection along the c axis while Table 6 gives the main interatomic distances in the associated cation polyhedra.

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Structure du Triphosphate de Cuivre(II) et de Trisodium Dodécahydraté, CuNa₃P₃O₁₀.12H₂O

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Abstract. $M_r = 601.6$, monoclinic, $P2_1/n$, $a = 15.052$ (8), $b = 9.234$ (3), $c = 14.767$ (8) Å, $\beta = 90.03$ (5)°, $V = 2052.5$ Å³, $Z = 4$, $D_x = 1.947$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu = 1.508$ mm⁻¹, $F(000) = 1228$, $T = 293$ K. Final $R = 0.045$ for 2351 observed independent reflexions. Linear P_3O_{10} groups are linked by a three-dimensional network of copper and sodium polyhedra. The condensed anion has a pseudo m symmetry. These anions twist around 2_1 axes to form two kinds of channels parallel to the b axis. In these channels are located the CuO_6 octahedra and the sodium polyhedra. The copper coordination is a distorted octahedron built up by three oxygen atoms and three water molecules.

Introduction. La série des tripolyphosphates du type $M^{II}Na_3P_3O_{10}.12H_2O$ a été caractérisée du point de vue cristallographique par Rakotomahanina, Averbuch-Pouchot & Durif (1972) pour M^{II} = Ni, Co, Mn, Mg, Zn et Cd. Le sel de cuivre correspondant n'a jamais pu être préparé en utilisant la méthode décrite par les auteurs pour les sels cités plus haut. Récemment des cristaux de ce sel: $CuNa_3P_3O_{10}.12H_2O$, ont pu être préparés en utilisant une méthode originale (Jouini & Durif, 1983). Une étude préliminaire par la méthode de Weissenberg de l'un de ces cristaux montre que ce sel a

mêmes paramètres réticulaires et même groupe spatial que les autres composés de la série.

Du point de vue structural la seule étude connue est une communication de congrès (Herceg, 1974) dans laquelle l'auteur proposait un modèle de structure pour le composé du manganèse. Ces résultats n'ont malheureusement jamais été publiés. Dans le présent travail nous décrivons la structure cristalline de cette série de sels en utilisant pour ce faire le composé du cuivre: $CuNa_3P_3O_{10}.12H_2O$.

Partie expérimentale. Prisme bipyramidal de section presque carrée, 0,16 × 0,16 × 0,24 mm: appareillage: Philips PW 1100; monochromateur: graphite; paramètres cristallins obtenus avec 25 réflexions d'angle haut: domaine des mesures: 4 à 25° (θ); type de balayage: ω; domaine de balayage: 1,20° (θ); vitesse de balayage: 0,02°s⁻¹; réflexions de référence: $35\overline{7}$ et $\overline{3}5\overline{7}$, variation négligeable; temps de mesure du fond continu: 20 s; nombre de réflexions mesurées: 3559 (h −22→22, k 0→16, l 0→22), 3168 réflexions indépendantes ont été extraites; correction de Lorentz–polarisation, aucune correction d'absorption. Aucune donnée technique ne figurant dans la communication de Herceg (1974) la structure a été redéterminée par des méthodes classiques: exploitation de la fonction de Patterson et