

In these rare-earth systems studied here and previously, the soft mode which causes the phase transition to occur is electronic, and arises because there is an effective quadrupolar coupling between the rare-earth ions. This quadrupolar coupling has already been postulated in an earlier investigation (Will & Schäfer, 1971) and treated theoretically by Sivardière & Blume (1972).

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Organometallic Compounds Containing a Guanidinium Group. Crystal and Molecular Structure of (Creatinine)phenylmercury(II) Nitrate Monohydrate

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Abstract

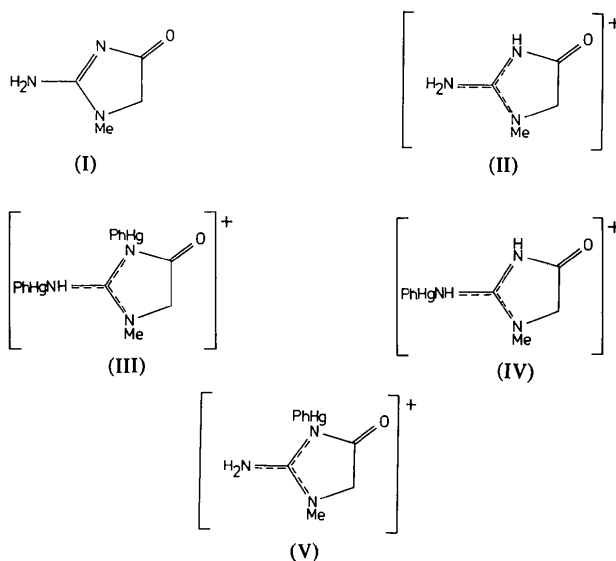
[Hg(C₆H₅)(C₄H₇N₃O)].NO₃.H₂O, C₁₀H₁₂HgN₄O₄.H₂O is monoclinic with $a = 10.255(5)$, $b = 19.838(9)$, $c = 6.859(3)$ Å, $\beta = 97.81(10)^\circ$, $Z = 4$, space group $P2_1/n$. The structure was refined to $R = 0.071$. The complex has a PhHg^{II} group bonded to a ring N atom of creatinine to form the cation [PhHgNC(NH₂)N(Me)CH₂CO]⁺. The C–Hg–N group is non-linear, $174(1)^\circ$, and there is a weak interaction between Hg and a nitrate O atom. The creatinine and phenyl rings are almost coplanar, and the cations are stacked approximately along [001] with phenyl and creatinine rings of adjacent ions almost parallel and 3.372 Å apart.

Introduction

Basic phenylmercuric nitrate, PhHg(OH.NO₃)_{1/2}, reacts with creatinine (I) in aqueous ethanol to form a 2:1 complex [(PhHg)₂C₄H₆N₃O][NO₃] which exists in two crystalline forms, and in the presence of nitric acid a 1:1 complex containing the cation [PhHg(C₄H₇N₃O)]⁺ is formed (Canty, Fyfe & Gatehouse, 1978). ¹H NMR spectra of the complexes and creatinine hydronitrate (II), and a crystal structure determination of one crystalline form of the 2:1 complex (III), indicate that they contain a planar guanidinium group based on [CN₃]⁺.

Infrared spectra of the complexes and their deuterated analogues are consistent with bonding of PhHg^{II} to the exocyclic N atom in the 1:1 complex (IV), although the alternative structure (V) could not be eliminated. In order to determine whether (IV) or (V) exists in the solid state we have determined the structure of [PhHg(C₄H₇N₃O)][NO₃].H₂O.

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Experimental

Suitable crystals were available from the initial preparations used for microanalysis and spectroscopic studies (Canty, Fyfe & Gatehouse, 1978). Microanalytical data suggested formulation of this complex as a hemihydrate, but it is denoted a monohydrate on the basis of agreement between measured and calculated densities and subsequent successful refinement as a monohydrate, including refinement of the O atom site occupation factor.

Crystal data

$\text{C}_{10}\text{H}_{12}\text{HgN}_4\text{O}_4 \cdot \text{H}_2\text{O}$, $M_r = 470.83$, monoclinic, $a = 10.255$ (5), $b = 19.838$ (9), $c = 6.859$ (3) Å, $\beta = 97.81$ (10)°, $U = 1382.37$ Å³, $D_m = 2.25$ (7) (by flotation in methyl iodide/bromoform), $Z = 4$, $D_c = 2.26$ Mg m⁻³, $F(000) = 887.85$. Data were collected at 293 K, Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), $\mu(\text{Mo } K\alpha) = 10.74$ mm⁻¹. Space group $P2_1/n$ from systematic absences: $h0l$, $h + l$ odd, $0k0$, k odd. Cell parameters were determined with a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator (Gatehouse & Miskin, 1974).

Intensity measurements

Intensities were collected on the diffractometer from a colourless to white crystal $0.03 \times 0.03 \times 0.13$ mm (optimum size 0.18) that had been checked for cracking or twinning with a polarizing microscope. The crystal was mounted on a silica capillary with Resiweld epoxy cement and centred on the goniometer with high-angle reflections selected from an initial rapid data collection. Three standard reflections monitored at 90

min intervals showed no significant variation in intensity. Data were collected by the ω -scan technique with a symmetric scan width of $\pm 0.6^\circ$ in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of $0.03^\circ \text{ s}^{-1}$. The Mo $K\alpha$ radiation was monochromatized with a flat graphite crystal and no reflection was sufficiently intense to warrant the insertion of an attenuation filter. The data were processed with a program written for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). The background-corrected intensities were assigned e.s.d.'s, $\sigma(I) = [\text{CT} + (t_c/t_b)^2(B_1 + B_2)]^{1/2}$, where CT is the total integrated peak count obtained in scan time t_c , B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = \text{CT} - (t_c/t_b)(B_1 + B_2)$. Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects. An absorption correction was applied based on the indexed crystal faces (100), ($\bar{1}00$), (010), (0 $\bar{1}0$), (001), and (00 $\bar{1}$), and direction cosines were calculated for the PW 1100 data. Maximum and minimum values of the transmission factors were 0.7864 and 0.7416 respectively. The total number of reflections measured to $2\theta(\text{Mo } K\alpha) = 60^\circ$ was 4448; of these, 126 were rejected as being systematically absent or having zero F or I and 298 were multiple observations [the measure of agreement was

$$\left(\frac{\sum \{N \sum [w(F_{\text{av}} - F)^2]\}}{\sum [(N-1) \sum (wF^2)]} \right)^{1/2} = 0.046.$$

[The inner summations are over the N equivalent reflections averaged to give F_{av} , and the outer summations are over all unique reflections (Sheldrick, 1976).] This left 4024 unique reflections of which 1092 obeyed the condition $I \geq 3\sigma(I)$ and were used in the subsequent refinement.

Structure determination and refinement

The structure was solved by Patterson and Fourier techniques; the Hg atom position was refined and all non-hydrogen atoms were located in the subsequent difference synthesis. The function minimized in the full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. With the Hg atom refined anisotropically and other non-hydrogen atoms refined isotropically, $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.072$. As microanalysis suggested the complex to be a hemihydrate (Canty, Fyfe & Gatehouse, 1978) the site occupation factor for the O atom of the water molecule was refined and indicated the complex to be a monohydrate [site occupation factor 1.02 (4)]. Although a difference synthesis revealed some H atom positions the coordinates of all H atoms bonded to C were calculated with C—H = 1.08 Å; coordinates of H atoms bonded to N and O were not calculated. Finally, full-matrix least-squares refinement with anisotropic thermal

parameters for Hg and isotropic thermal parameters for other non-hydrogen atoms with the H atoms riding on their respective C atoms gave $R = 0.071$ and $R^1 = 0.056$ (for observed reflections),* where $R^1 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The final difference synthesis had no major characteristic $> 1.19 \text{ e } \text{\AA}^{-3}$, this being in the vicinity of the Hg atom. The largest shift to e.s.d. ratio for the non-hydrogen atoms in the final cycle was 0.010 for the C(10) y parameter.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34078 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and thermal parameters ($\times 10^4$) for non-hydrogen atoms, with e.s.d.'s in parentheses

Mercury refined anisotropically, $U_{22} = 424$ (7), $U_{33} = 493$ (8), $U_{12} = 29$ (10), $U_{13} = 78$ (5), $U_{23} = -28$ (13). Thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{11}/U_{iso}
Hg	10362 (1)	-209 (1)	2546 (2)	317 (6)
C(1)	13267 (27)	-411 (15)	3049 (41)	466 (69)
C(2)	14408 (23)	-921 (12)	3228 (39)	369 (62)
C(3)	14233 (24)	-2204 (13)	2916 (43)	567 (69)
C(4)	12328 (34)	-1456 (18)	2656 (50)	741 (73)
C(5)	8756 (26)	410 (13)	2309 (37)	319 (60)
C(6)	9072 (28)	1116 (15)	2597 (44)	589 (68)
C(7)	8006 (29)	1547 (17)	2448 (44)	632 (71)
C(8)	6724 (25)	1324 (14)	2275 (38)	345 (61)
C(9)	6454 (26)	665 (15)	1953 (40)	493 (65)
C(10)	7481 (24)	181 (16)	2085 (36)	415 (60)
N(1)	13642 (21)	-1553 (11)	2826 (33)	367 (54)
N(2)	11428 (21)	-1910 (12)	2467 (36)	482 (57)
N(3)	12069 (21)	-741 (12)	2800 (34)	484 (58)
N(4)	8263 (36)	-1493 (20)	1950 (53)	1167 (78)
O(1)	13359 (16)	188 (12)	3106 (24)	522 (48)
O(2)	8721 (23)	-1291 (13)	567 (37)	1063 (67)
O(3)	6965 (26)	-1599 (13)	1246 (39)	1140 (69)
O(4)	8490 (30)	-1478 (17)	3558 (47)	1514 (77)
O(5)	16816 (19)	-1687 (11)	-3297 (32)	753 (59)

Table 2. Final fractional coordinates and thermal parameters ($\times 10^4$) for H atoms, numbered according to the C atoms to which they are attached

	x	y	z	U_{iso}
H(21)	14966	-919	4682	655
H(22)	15062	-831	2147	647
H(31)	15290	-2153	3050	790
H(32)	13884	-2480	1589	686
H(33)	13972	-2473	4175	683
H(6)	10074	1294	2906	641
H(7)	8185	2084	2469	853
H(8)	5937	1677	2396	845
H(9)	5444	503	1590	893
H(10)	7266	-352	2011	867

Final fractional coordinates, thermal parameters, interatomic distances and angles, and equations of mean planes are given in Tables 1, 2, 3 and 4 respectively. Scattering factors were taken from Cromer & Mann (1968) and corrections for anomalous dispersion from Cromer & Liberman (1970).

All calculations were carried out on the Monash University B 6700 computer; the major programs used were *SHELX 76* (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964), *MEANPL* (Blow, 1960) and *ORTEP* (Johnson, 1965).

Discussion of the structure

The crystal is made up of $[\text{PhHgNC}(\text{NH}_2)\text{N}(\text{Me})\text{CH}_2\text{CO}]^+$ cations containing the PhHg^{II} group bonded to the ring N atom, nitrate ions, and water molecules (V, Figs. 1, 2). The creatinine ring is essentially planar (Table 4), and coplanar with the phenyl ring as the angle between the planes is only 0.77° . Bond lengths within the creatinine ring indicate delocalization of the carbonyl C(1)O with the guanidinium moiety as the C(1)-N(3) distance, 1.38 (4) \AA , is appropriate for multiple-bond character.

Table 3. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

(a) The mercury environment			
Hg-C(5)	2.04 (2)	Hg...O(2)	2.94 (2)
Hg-N(3)	2.03 (2)		
C(5)-Hg-N(3)	174 (1)	C(5)-Hg...O(2)	90 (1)
		N(3)-Hg...O(2)	95 (1)
(b) The creatinine ring			
C(1)-C(2)	1.54 (4)	C(4)-N(1)	1.35 (4)
C(1)-O(1)	1.19 (4)	C(4)-N(2)	1.28 (4)
C(1)-N(3)	1.38 (4)	C(4)-N(3)	1.45 (4)
C(2)-N(1)	1.49 (3)		
C(3)-N(1)	1.42 (3)		
C(2)-C(1)-N(3)	111 (2)	N(2)-C(4)-N(3)	124 (3)
C(2)-C(1)-O(1)	127 (2)	C(2)-N(1)-C(3)	123 (2)
N(3)-C(1)-O(1)	123 (3)	C(3)-N(1)-C(4)	123 (2)
C(1)-C(2)-N(1)	99 (2)	C(1)-N(3)-C(4)	108 (2)
N(1)-C(4)-N(2)	127 (3)	C(1)-N(3)-Hg	120 (2)
N(1)-C(4)-N(3)	109 (3)	C(4)-N(3)-Hg	132 (2)
(c) The phenyl ring			
C(5)-C(6)	1.44 (4)	C(8)-C(9)	1.35 (4)
C(6)-C(7)	1.38 (4)	C(9)-C(10)	1.42 (4)
C(7)-C(8)	1.38 (4)	C(5)-C(10)	1.37 (3)
Hg-C(5)-C(6)	114 (2)	C(6)-C(7)-C(8)	123 (3)
Hg-C(5)-C(10)	124 (2)	C(7)-C(8)-C(9)	120 (3)
C(6)-C(5)-C(10)	122 (2)	C(8)-C(9)-C(10)	121 (3)
C(5)-C(6)-C(7)	115 (3)	C(5)-C(10)-C(9)	118 (3)
(d) The nitrate ion			
N(4)-O(2)	1.18 (5)	N(4)-O(4)	1.10 (5)
N(4)-O(3)	1.37 (4)		
O(2)-N(4)-O(3)	104 (3)	O(3)-N(4)-O(4)	115 (4)
O(2)-N(4)-O(4)	138 (4)		

Hg—C and Hg—N lengths, 2.04 (2) and 2.03 (2) Å respectively, are similar to those found in $[(\text{PhHg})_2\text{C}_4\text{H}_6\text{N}_3\text{O}][\text{NO}_3]$ (III), 2.02 (2), 2.03 (2) and 2.00 (3), 2.06 (3) Å respectively (Canty, Fyfe & Gatehouse, 1978). The nearest atom to Hg, except for C(5) and N(3), is the nitrate O(2) at 2.94 (2) Å, *ca* 0–0.3 Å less than the sum of the van der Waals radii, 2.9 Å [Hg 1.5 (Grdenić, 1965), O 1.4 Å (Pauling, 1960)], or 3.13 Å using Grdenić's upper limit of 1.73 Å for the radius of Hg. Consistent with the presence of an Hg...O(2) interaction the angle C(5)—Hg—N(3) is 174 (1)° with C(5) and N(3) bent away from O(2) and coplanar with Hg and O(2) [sum of angles at Hg 359 (1)°, Hg is –0.039 Å out of the C(5), O(2), N(3) plane]. Other O atoms are at distances >3.13 Å.

The packing diagram indicates that the cations are stacked approximately along [001] (Fig. 2). There is a centre of symmetry between each cation so that positively charged creatinine rings have two phenyl rings as near neighbours. The distance between these planes, 3.372 Å, indicates the presence of weak interactions when compared with Pauling's (1960) van der Waals radii for aromatic rings (1.85 Å) and methyl groups (2.0 Å). Nitrate ions and water molecules occur between parallel chains of stacked cations. H atoms of the exocyclic NH₂ group and water molecules are assumed to form a complex hydrogen-bonding network, as there are several distances between non-hydrogen atoms of *ca* 3 Å, *viz* O(5)...N(2) 2.87 (3),

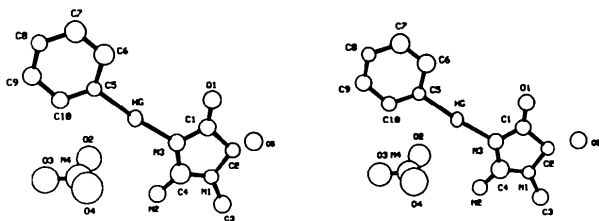


Fig. 1. Structure of the cation $[\text{PhHg}(\text{C}_4\text{H}_7\text{N}_3\text{O})]^+$ and nitrate ion in $[\text{PhHg}(\text{C}_4\text{H}_7\text{N}_3\text{O})][\text{NO}_3] \cdot \text{H}_2\text{O}$.

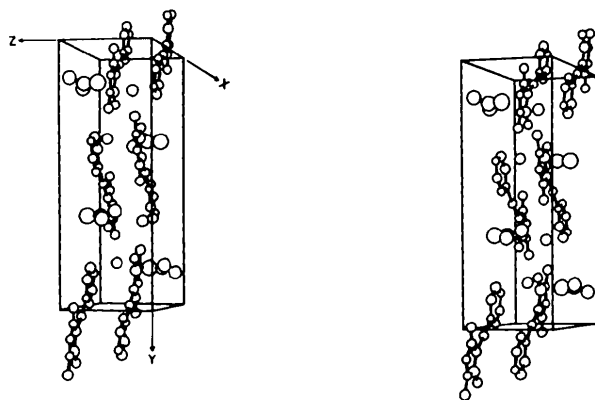


Fig. 2. Packing diagram showing the contents of the unit cell and illustrating the stacking of cations approximately along [001].

Table 4. Equations of mean planes and deviations (Å) of individual atoms from planes

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z in the crystal system by the equation:

$$\begin{pmatrix} 10.255000 & 0.000000 & -0.932059 \\ 0.000000 & 19.838000 & 0.000000 \\ 0.000000 & 0.000000 & 6.795377 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix}$$

Plane I: Mean plane through N(3), C(1), C(2), N(1), and C(4)

$$0.1277X + 0.0896Y - 0.9878Z + 3.2963 = 0$$

N(3)	–0.015 (23)	N(2)	–0.079 (24)
C(1)	–0.030 (28)	C(3)	–0.071 (29)
C(2)	–0.033 (26)	O(1)	0.110 (19)
N(1)	0.028 (22)	Hg	0.029 (2)
C(4)	–0.010 (34)		

Coordinates (orthogonal) of centre of gravity of the plane
(–3.8834, 21.8540, 4.8168)

Plane II: Mean plane through C(5), C(6), C(7), C(8), C(9) and C(10)

$$0.1145X + 0.0886Y - 0.9865Z - 0.0918 = 0$$

C(5)	0.015 (25)	C(9)	0.033 (27)
C(6)	–0.020 (30)	C(10)	–0.022 (24)
C(7)	0.032 (30)	Hg	–0.067 (2)
C(8)	–0.039 (26)		

Coordinates (orthogonal) of centre of gravity of the plane
(–2.5210, 21.5714, 1.5476)

Plane III: Mean plane through N(4), O(2), O(3), and O(4)

$$0.2803X - 0.9541Y - 0.1054Z - 4.9256 = 0$$

N(4)	0.085 (39)	O(3)	–0.019 (25)
O(2)	–0.031 (26)	O(4)	–0.036 (34)

Angles between normals to the planes

Plane	Direction cosines		
I	0.1145	0.0886	–0.9895
II	0.1277	0.0896	–0.9878
III	0.2803	–0.9541	–0.1054

Angles (°)

Planes I/II	0.77
Planes I/III	87.03
Planes II/III	86.88

O(5)...O(4) 2.96 (4), O(1)...O(5) 2.98 (3), O(3)...O(5) 3.10 (3), and O(2)...O(5) 3.17 (3) Å where O(5) belongs to water, O(1) to the carbonyl group, O(2), O(3), O(4) to the nitrate ion, and N(2) to the exocyclic NH₂ group. The nitrate ions and water molecules may be regarded as occupying channels between chains of stacked cations, consistent with dehydration of the complex at atmospheric pressure with phosphorus pentoxide and rapid formation of the hydrate on exposure to air (Canty, Fyfe & Gatehouse, 1978).

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The Crystal Structure of Δ, Δ - μ -Hydroxo- μ -sulfato-bis[bis(ethylenediamine)chromium(III)] Dithionate Hydrate

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Abstract

$[(\text{en})_2\text{Cr}(\text{OH})(\text{SO}_4)\text{Cr}(\text{en})_2]_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $[\text{Cr}_2(\text{C}_2\text{H}_8\text{N}_4)_4(\text{OH})(\text{SO}_4)_2(\text{S}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $2(\text{C}_8\text{H}_{33}\text{Cr}_2\text{N}_8\text{O}_5\text{S})^3+3(\text{S}_2\text{O}_6)^{2-} \cdot 2\text{H}_2\text{O}$, crystallizes in space group $P2_1/c$, with $a = 9.206(2)$, $b = 26.931(8)$, $c = 12.012(3)$ Å, $\beta = 110.40(2)^\circ$, $Z = 2$. The structure was refined to $R = 0.069$ for 4227 diffractometric intensities. The complex ion contains a non-crystallographic mirror plane and the conformation of the chelate rings is ${}^{\lambda}_8\Delta A_1^{\delta}$. The bridging six-membered ring has a distorted chair conformation. The Cr–Cr separation is $3.706(2)$ Å. The crystal structure is intensively hydrogen-bonded.

Introduction

The present investigation was undertaken in order to establish the configuration of the compound formed by the novel reaction between the *meso* diol Δ, Δ - $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ and sulfuric acid. The resulting sulfato-bridged cation Δ, Δ - $[(\text{en})_2\text{Cr}(\text{OH})(\text{SO}_4)\text{Cr}(\text{en})_2]^{4+}$ is the first sulfato-bridged binuclear Cr^{III} complex isolated as a salt. It is very robust in acid solution. In basic solution the hydroxo bridge is first deprotonated ($\text{pK} \approx 12$) and then the sulfato bridge is cleaved giving the mono-ol Δ, Δ - $[(\text{OH})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})]^{3+}$ (Springborg, 1978). The present compound may serve as a model for the poorly characterized

sulfato-bridged species involved in the chemistry of Cr tanning processes.

Experimental

The red prismatic crystal used for data collection was prepared as described by Springborg (1978). Photographs showed that $h0l$ were absent for $l \neq 2n$ and $0k0$ for $k \neq 2n$, so the space group is $P2_1/c$. The cell dimensions are $a = 9.206(2)$, $b = 26.931(8)$, $c = 12.012(3)$ Å, $\beta = 110.40(2)^\circ$, $V = 2791$ Å³. They were obtained by least-squares refinement of 98 θ angles (Mo $K\alpha$, $\lambda = 0.71069$ Å) measured on a Nonius three-circle automatic diffractometer with a graphite monochromator. The formula weight is 1431.4 ($\text{C}_{16}\text{H}_{70}\text{Cr}_4\text{N}_{16}\text{O}_{30}\text{S}_8$); D_o measured by flotation at 295 K = 1.71, $D_c = 1.71$ Mg m⁻³ for $Z = 2$, corresponding to half a formula unit (*i.e.* one complex ion, one and a half dithionate ions and one water molecule) per asymmetric unit. $\mu(\text{Mo } K\alpha) = 1.18$ mm⁻¹.

A crystal with average diameter 0.2 mm was mounted along a and intensities were measured out to $\theta = 28.6^\circ$ with a computer-controlled Supper diffractometer (Kryger, 1975). Monochromatic Mo $K\alpha$ radiation was used with a scintillation counter and pulse-height analyzer. About 14 000 reflections within a hemisphere were measured by the background-peak-background method. 4227 independent reflections with structure factors greater than 2.5 times their e.s.d.'s

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