

Fig. 3. Stereoscopic ORTEP (Johnson, 1971) drawing of the packing of $[\text{Rh}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_{11})][\text{BF}_4]$ with the split positions of the BF_4 groups.

layer being on the face of the unit cell and the other at the center (Fig. 3).

In conclusion, it can be said that the X-ray structure of $[(\text{RhC}_5\text{Me}_5)(\text{C}_6\text{H}_{11})][\text{BF}_4]$ fully confirms the structural assignment based on spectroscopic measurements and that the complex constitutes a typical example of a compound with an 'agostic' hydrogen bridge.

References

- ASHWORTH, T. V., CHALMERS, A. A., MEINTJIES, E., OOSTHUIZEN, H. & SINGLETON, E. (1985). *J. Organomet. Chem.* **286**, 237–246.
- ASHWORTH, T. V., SINGLETON, E., LAING, M. & POPE, L. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1032–1036.
- BOOTH, B. L., HASZELDINE, R. N. & HILL, M. (1969). *J. Chem. Soc. A*, pp. 1299–1303.
- BROOKHART, M. & GREEN, M. L. H. (1983). *J. Organomet. Chem.* **250**, 395–408.
- BROOKHART, M., LAMANNA, W. & HUMPHREY, M. B. (1982). *J. Am. Chem. Soc.* **104**, 2117–2126.
- BROWN, R. K., WILLIAMS, J. M., SCHULTZ, A. J., STUCKY, G. D., ITTEL, S. D. & HARLOW, R. L. (1980). *J. Am. Chem. Soc.* **102**, 981–987.
- BUCHMANN, B., PIANTINI, U., VON PHILIPSBORN, W. & SALZER, A. (1987). *Helv. Chim. Acta*, **70**, 1487–1506.
- ELSCHENBROICH, CH. & SALZER, A. (1989). *Organometallics*, pp. 267–268.
- GREEN, M., NORMAN, N. C. & ORPEN, A. G. (1981). *J. Am. Chem. Soc.* **103**, 1269–1271.
- HURSTHOUSE, M. B., MALIK, K. M. A., MINGOS, D. M. P. & WILLOUGHBY, S. D. (1980). *J. Organomet. Chem.* **192**, 235–251.
- JOHNSON, C. K. (1971). ORTEP. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- LEE, H. & MAITLIS, P. M. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2316–2321.
- MICHAEL, G., KAUB, J. & KREITER, C. G. (1985a). *Angew. Chem.* **97**, 503–505; *Angew. Chem. Int. Ed. Engl.* **24**, 502–504.
- MICHAEL, G., KAUB, J. & KREITER, C. G. (1985b). *Chem. Ber.* **118**, 3944–3958.
- SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
- SHELDRICK, G. M. (1985). SHELXS86. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.

Acta Cryst. (1991). **C47**, 279–282

Structure of Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Di- μ -iodo-bis[diiodocadmate(II)], (BEDT-TTF) $_2$ [Cd $_2$ I $_6$]

BY XIANHUI BU, ZHENGWEI SU AND PHILIP COPPENS

Chemistry Department, State University of New York at Buffalo, Buffalo, NY 14214, USA

(Received 20 March 1990; accepted 3 July 1990)

Abstract. $(\text{C}_{10}\text{H}_8\text{S}_8)_2[\text{Cd}_2\text{I}_6]$, $M_r = 1755.60$, triclinic, $P\bar{1}$, $a = 9.067$ (2), $b = 10.515$ (1), $c = 12.441$ (2) Å, $\alpha = 97.12$ (1), $\beta = 103.43$ (1), $\gamma = 106.13$ (1)°, $V = 1085$ (1) Å 3 , $Z = 1$, $D_x = 2.69$ g cm $^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 59.6$ cm $^{-1}$, $F(000) = 806$, room temperature, $R(F) = 0.051$, $wR = 0.061$ for 2761 unique reflections. The structure consists of pairs of BEDT-TTF cations [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] with an interplanar separation of 3.53 Å and Cd $_2$ I $_6^{2-}$ anions formed by two CdI $_4^{2-}$ tetrahedra sharing one common edge. π - π molecular overlap exists within each pair of BEDT-TTF molecules, while different pairs are linked via S \cdots S contacts, which are as short as 3.339 (3) Å.

Introduction. Organic salts based on BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] and related molecules are among the most interesting solid-state materials. A salt of BEDT-TTF, (BEDT-TTF) $_2$ [Cu(NCS) $_2$] (Urayama *et al.*, 1988), has the highest T_c value of the known organic superconductors, while other highly conducting salts are based on the related cation BEDO-TTF [bis(ethylenedioxy)tetrathiafulvalene] (Suzuki, Yamochi, Srdanov, Hinkelman & Wudl, 1989; Wudl *et al.*, 1990; Beno *et al.*, 1990). The salts of these cations show enormous variety, as illustrated in a recent survey (Williams *et al.*, 1987). The present study is part of a program of synthesis of new organic salts by electrocrystal-

lization techniques, and the correlation of their structures with physical properties. The structure analysis of $(BEDT-TTF)_2[HgBr_4]$.trichloroethane (Bu, Coppens & Naughton, 1990) is the previous report in this series.

Experimental. Crystals of $(BEDT-TTF)_2[Cd_2I_6]$ were prepared by electrocrystallization (Pt electrodes) with a home-made dc source. A current of $5.0 \mu A$ was applied to a $0.3mM$ BEDT-TTF 1,2,2-trichloroethane solution saturated with $(Et_4N)_2[CdI_4]$. $(Et_4N)_2[CdI_4]$ was prepared by mixing Et_4NI with CdI_2 (molar ratio 2:1) in absolute ethanol. Black shiny thin plates were found on the anode after one week. An initial attempt to grow crystals in a mixture of 60 ml tetrahydrofuran and 25 ml acetonitrile produced crystals of a BEDT-TTF iodide according to the results of the electron fluorescence microprobe analysis (EDX).

A single crystal of $(BEDT-TTF)_2[Cd_2I_6]$, $0.16 \times 0.15 \times 0.025$ mm, was mounted on top of a glass fiber. Oscillation and Weissenberg photographs indicated the crystal to be triclinic. Unit-cell dimensions were determined from a least-squares refinement of the setting angles of 25 reflections ($25 < 2\theta < 36^\circ$). Room-temperature data were collected on a MicroVAX-controlled CAD-4 diffractometer with the $\theta/2\theta$ scan technique and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Three standard reflections monitored throughout the data collection showed very small changes in intensity (less than 3%). 4076 reflections with $1.5 < \theta < 25^\circ$ were measured ($h = 0, 10, k = -12, 12, l = -14, 14$) and averaged to give 3841 unique reflections, the internal agreement factor $R(F) = 0.023$. Data were reduced using a set of programs written by Blessing (1987) and numerical absorption corrections were applied. The transmission factors ranged from 0.41 to 0.87. The centrosymmetric space group $P\bar{1}$ was suggested by the intensity statistics and confirmed by the successful structure solution and refinement. The original Cd and I atomic positions were obtained by direct methods using *MULTAN11/82* from the Enraf-Nonius (1979) VAX *SDP* package. Additional atoms were located in difference Fourier maps. Scattering factors (including anomalous contributions) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final full-matrix refinement was carried out with the program *LINEX84* (1984). 2761 unique reflections with $I > 2\sigma(I)$ were used in the refinement with anisotropic thermal parameters for all non-H atoms. H atoms were not included. A total of 199 variables were refined, minimizing the function $\sum[w(|F_{obs}| - k|F_{cal}|)^2]$, where $w = 1/\sigma^2(F)$; $\sigma(F) = \sigma(F^2)/2F$; $\sigma(F^2) = [\sigma^2_{counting} + (0.02|F|^2)]^{1/2}$. Parameter shifts in the final least-squares cycles were smaller than

Table 1. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	U_{eq}^*
I1	0.4110 (1)	0.31566 (9)	0.13676 (8)	0.0578 (4)
I2	0.0974 (1)	0.09120 (9)	0.34989 (8)	0.0518 (4)
I3	0.1162 (1)	-0.14213 (9)	0.01068 (8)	0.0527 (4)
Cd	0.1540 (1)	0.11237 (9)	0.14681 (8)	0.0476 (4)
S1	-0.3962 (5)	0.3885 (3)	0.6676 (3)	0.051 (1)
S2	-0.3521 (4)	0.1417 (3)	0.5684 (3)	0.040 (1)
S3	-0.2599 (4)	0.5412 (3)	0.4890 (3)	0.049 (1)
S4	-0.1992 (4)	0.3010 (3)	0.3927 (3)	0.043 (1)
S5	-0.5072 (5)	0.2793 (3)	0.8531 (3)	0.053 (1)
S6	-0.4708 (4)	-0.0205 (3)	0.7241 (3)	0.040 (1)
S7	-0.1098 (5)	0.7163 (3)	0.3519 (3)	0.062 (2)
S8	-0.0471 (6)	0.4293 (4)	0.2318 (4)	0.071 (2)
C1	-0.334 (1)	0.309 (1)	0.5664 (9)	0.035 (4)
C2	-0.270 (1)	0.376 (1)	0.4928 (10)	0.038 (5)
C3	-0.443 (1)	0.254 (1)	0.7342 (10)	0.037 (4)
C4	-0.424 (1)	0.138 (1)	0.6858 (10)	0.036 (4)
C5	-0.162 (1)	0.556 (1)	0.385 (1)	0.038 (5)
C6	-0.133 (1)	0.445 (1)	0.341 (1)	0.044 (5)
C7	-0.641 (2)	0.111 (2)	0.840 (2)	0.10 (1)
C8	-0.574 (2)	0.002 (2)	0.828 (2)	0.077 (9)
C9	-0.074 (3)	0.684 (2)	0.217 (2)	0.09 (1)
C10	-0.120 (3)	0.552 (2)	0.156 (1)	0.12 (1)

*Temperature factor defined as: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klib^*c^*)]$ and $U_{eq} = 1/3\sum_i U_{ij}a_i^*a_j^*a_i \cdot a_j$; all atoms were refined anisotropically.

0.01 σ . For 2761 reflections, $R(F) = 0.051$, $wR = 0.061$, GOF = 2.19.

Final atomic coordinates and thermal parameters are listed in Table 1,* while bond lengths and angles are given in Table 2. Fig. 1 shows the atomic labeling scheme for the BEDT-TTF molecule and Fig. 2 is a packing diagram of the unit cell. The geometry of the $Cd_2I_6^{2-}$ anion and the labeling of Cd and I are shown in Fig. 3, while the intermolecular contacts are illustrated in Fig. 4.

Discussion. The unit cell contains two crystallographically equivalent BEDT-TTF cations and one $Cd_2I_6^{2-}$ anion. The $Cd_2I_6^{2-}$ anion is formed by two CdI_4^{2-} tetrahedra sharing one common edge (Fig. 3). This complex anion has a crystallographic center of symmetry relating the two CdI_3 moieties. The Cd—Cd distance is 4.022 \AA . Orioli & Ciampolini (1972) first reported the X-ray evidence of the existence of $Cd_2I_6^{2-}$ with a Cd—Cd distance of 3.71 \AA .

BEDT-TTF molecules form pairs of closely spaced parallel molecules. There is a significant offset (approximately 5.9 \AA) along the long molecular axis within each pair of BEDT-TTF molecules. The separation between least-squares planes of two BEDT-TTF molecules within the pair is 3.53 \AA , while the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53387 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

I1—Cd	2.729 (1)	S5—C3	1.73 (1)
I2—Cd	2.716 (2)	S5—C7	1.81 (2)
I3—Cd	2.871 (1)	S6—C4	1.76 (1)
I3'—Cd	2.879 (1)	S6—C8	1.79 (2)
Cd'—Cd	4.022 (1)	S7—C5	1.75 (1)
S1—C1	1.72 (1)	S7—C9	1.80 (2)
S1—C3	1.73 (1)	S8—C6	1.73 (2)
S2—C1	1.72 (1)	S8—C10	1.87 (2)
S2—C4	1.73 (1)	C1—C2	1.36 (2)
S3—C2	1.73 (1)	C3—C4	1.36 (2)
S3—C5	1.73 (1)	C5—C6	1.34 (2)
S4—C2	1.73 (1)	C7—C8	1.44 (3)
S4—C6	1.73 (1)	C9—C10	1.40 (3)
I1—Cd—I2	119.01 (4)	S3—C2—C1	122 (1)
I1—Cd—I3	112.97 (5)	S4—C2—C1	123 (1)
I1—Cd—I3'	104.97 (4)	S1—C3—S5	117.4 (7)
I2—Cd—I3'	111.12 (5)	S1—C3—C4	115 (1)
I2—Cd—I3	113.58 (4)	S5—C3—C4	127 (1)
I3—Cd—I3'	91.22 (3)	S2—C4—C6	114.1 (7)
Cd—I3—Cd'	88.78 (4)	S2—C4—C3	118 (1)
C1—S1—C3	96.5 (6)	S6—C4—C3	128 (1)
C2—S2—C4	95.1 (6)	S3—C5—S7	115.1 (7)
C2—S3—C5	95.7 (6)	S3—C5—C6	117 (1)
C2—S4—C6	95.7 (6)	S7—C5—C6	128 (1)
C3—S5—C7	99.3 (9)	S4—C6—S8	116.4 (7)
C4—S6—C8	102.9 (7)	S4—C6—C5	117 (1)
C5—S7—C9	103.3 (9)	S8—C6—C5	126 (1)
C6—S8—C10	97.0 (1)	S5—C7—C8	116 (2)
S1—C1—S2	115.2 (7)	S6—C8—C7	122 (2)
S1—C1—C2	122 (1)	S7—C9—C10	120 (2)
S2—C1—C2	123 (1)	S8—C10—C9	116 (1)
S3—C2—S4	114.5 (7)		

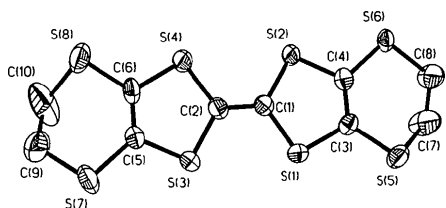


Fig. 1. Molecular diagram of the BEDT-TTF moiety showing the labeling of the atoms. Ellipsoids are 50% probability surfaces.

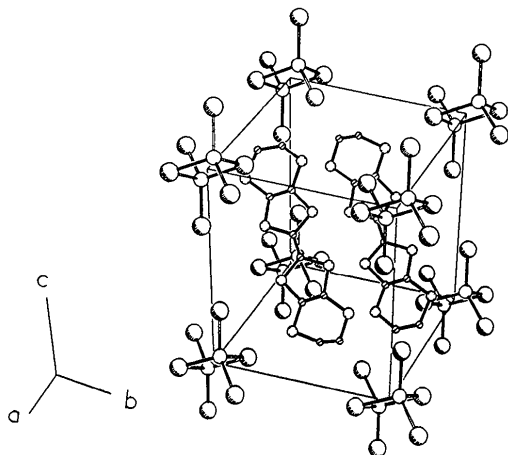


Fig. 2. The packing diagram of the unit cell.

shortest S...S distances are 3.77 Å (Table 3), a distance larger than the van der Waals radii sum of 3.6 Å. However, short lateral S...S distances are found between different pairs, the shortest being only 3.34 Å, which is equal to the shortest S...S distance at room temperature reported by Williams *et al.* (1987). Cd₂I₆²⁻ anions are situated at cavities formed by pairs of BEDT-TTF molecules. This packing arrangement prevents the formation of uniform BEDT-TTF layers which occur in many BEDT-TTF salts. The unit charge of the BEDT-TTF molecules explains the extremely high resistance of the crystals (> 100 MΩ) as measured by a four-probe contact method at room temperature.

The two ethylene groups of the BEDT-TTF molecule are disordered as indicated by the large thermal parameters of the C7—C10 atoms (Fig. 1 and Table 1). This can be attributed to the interactions between the disordered ethylene groups and the adjacent Cd₂I₆²⁻ anions (Fig. 2). Disorder

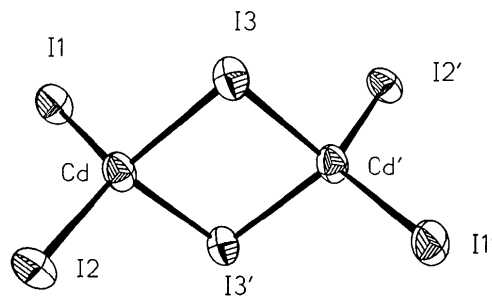
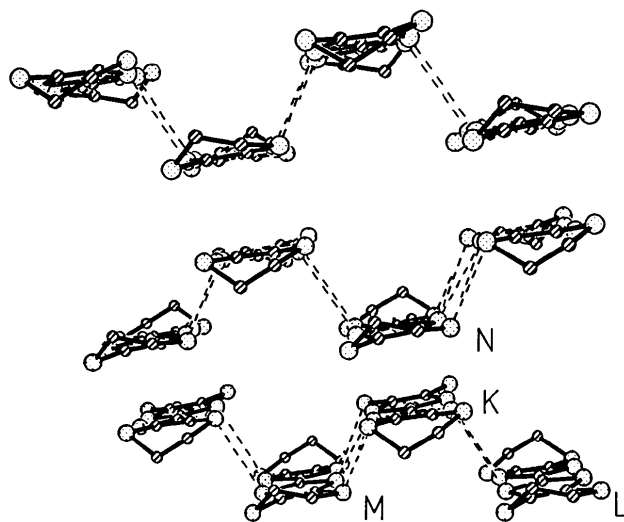
Fig. 3. The Cd₂I₆²⁻ ion. Ellipsoids are 50% probability surfaces.Fig. 4. Arrangement of the BEDT-TTF molecules. Intermolecular S...S distances less than 3.6 Å are shown by dashed lines. Symmetry codes are: (K) x, y, z ; (L) $-1-x, -1-y, 1-z$; (M) $-1-x, -y, 1-z$; (N) $-x, 1-y, 1-z$.

Table 3. Intermolecular S...S distances (\AA) less than 3.9 \AA

S1K—S8N	3.766 (6)	S1K—S3L	3.589 (6)
S3K—S8N	3.830 (5)	S5K—S7L	3.817 (6)
S2K—S7N	3.870 (5)	S6K—S2M	3.527 (4)
S4K—S7N	3.777 (5)	S2K—S2M	3.339 (3)
S3K—S4N	3.868 (5)	S6K—S4M	3.432 (4)

K, L, M and N refer to the BEDT-TTF molecules in Fig. 4.

of at least one of the ethylene groups has been found among other BEDT-TTF salts, including β -(BEDT-TTF) $_2$ I $_3$ (Leung *et al.*, 1985) and (BEDT-TTF) $_2$ [Cu(NCS) $_2$] (Urayama *et al.*, 1988). Short H...X (X = Br, I, NCS) contacts less than the van der Waals radii sums are believed to be the dominating factor for the disorder of the ethylene group. For the present structure, accurate hydrogen positions are not available. From the calculated positions of H atoms, the shortest H...I contacts are estimated to be of the order of 3.1 \AA .

A number of BEDT-TTF salts containing Hg have been reported including a low-temperature superconducting phase (BEDT-TTF) $_4$ [Hg $_{2.8}$ Br $_8$], but the present report is the first structural study of a Cd-containing salt.

Support of this work by the Petroleum Research Fund of the American Chemical Society (PRF21392-AC6-C) and the National Science Foundation

(CHE8711736) is gratefully acknowledged. We thank Dr M. Naughton for conductivity measurements.

References

- BENO, M. A., WANG, H. H., CARLSON, K. D., KINI, A. M., FRANKENBACH, G. M., FERRARO, J. R., LARSON, N., MCGABE, G. D., THOMPSON, J., PURNAMA, C., VASHON, M., WILLIAMS, J. M., JUNG, D. & WHANGBO, M.-H. (1990). *Mol. Cryst. Liq. Cryst.* **181**, 145–159.
- BLESSING, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
- BU, X., COPPENS, P. & NAUGHTON, M. (1990). *Acta Cryst.* **C46**, 1609–1612.
- Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- LEUNG, P. C. W., EMGE, T. J., BENO, M. A., WANG, H. H., WILLIAMS, J. M., PETRICEK, V. & COPPENS, P. (1985). *J. Am. Chem. Soc.* **107**, 6184–6191.
- LINEX84 (1984). Chemistry Department, State Univ. of New York at Buffalo, New York, USA.
- ORIOLE, P. L. & CIAMPOLINI, M. (1972). *J. Chem. Soc. Chem. Commun.* pp. 1280–1281.
- SUZUKI, T., YAMACHI, H., SRDANOV, G., HINKELMAN, K. & WUDL, F. (1989). *J. Am. Chem. Soc.* **111**, 3108–3109.
- URAYAMA, H., YAMACHI, H., SAITO, G., SATO, S., KAWAMOTO, A., TANAKA, J., MORI, T., MARUYAMA, Y. & INOKUCHI, H. (1988). *Chem. Lett.* pp. 463–466.
- WILLIAMS, J. M., WANG, H. H., EMGE, T. J., GEISER, U., BENO, M. A., LEUNG, P. C. W., CARLSON, K. D., THORN, R. J., SCULTZ, A. J. & WHANGBO, M. H. (1987). *Prog. Inorg. Chem.* **35**, 51–218.
- WUDL, F., YAMACHI, H., SUZUKI, T., ISOTALO, H., FITE, C., KASMAI, H., LIU, K., SRDANOV, G., MALY, K., FROST-JENSEN, A. & COPPENS, P. (1990). *J. Am. Chem. Soc.* **112**, 2461–2462.

Acta Cryst. (1991). **C47**, 282–286

Structure of Tetraaquacobalt(II) Bromide Dihydrate (Cobalt Bromide Hexahydrate)

BY ANTHONY C. BLACKBURN, JUDITH C. GALLUCCI AND ROGER E. GERKIN*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

(Received 20 March 1990; accepted 4 July 1990)

Abstract. Tetraaquacobalt(II) bromide dihydrate, $[Co(H_2O)_4]Br_2 \cdot 2H_2O$, $M_r = 326.83$, monoclinic, $C2/m$, $a = 11.0158$ (12), $b = 7.1694$ (10), $c = 6.9111$ (10) \AA , $\beta = 124.761$ (7) $^\circ$, $V = 448.4$ (1) \AA^3 , $Z = 2$, $F(000) = 314$, $D_x = 2.420$ g cm^{-3} , $\lambda(\text{Mo } K\alpha) = 0.71069$ \AA , $T = 296$ K, $\mu = 107.13$ cm^{-1} , $R = 0.022$ for 532 unique reflections having $I > 0$. The single type of Co ion is octahedrally coordinated by four equivalent water-molecule O atoms at the observed distance 2.081 (2) \AA and two equivalent Br ions at the observed distance 2.6048 (5) \AA in an array which, with respect to its angles, departs only slightly from regular octahedral geometry. The cobalt–oxygen–

bromine complex was found to manifest rigid-body behavior. The cobalt–oxygen distance corrected for rigid-body motion was found to be 2.088 \AA ; the corrected cobalt–bromine distance, 2.6081 \AA . Associated with each complex are two water molecules of hydration. Assignment and refinement of the coordinates of the four non-equivalent H atoms permitted detailed analysis of the hydrogen bonding, which involves each of the four non-equivalent H atoms significantly. The structure as determined in this study differs markedly from that presented in the sole published single-crystal study [Stroganov, Andreev, Kožina & Solov'ev (1961). *Vestn. Leningr. Univ. Ser. Mat. Fiz. Khim.* **16**, 114–119]. In particular, the space-group assignment differs and the pat-

* Author to whom correspondence should be addressed.